

Study of correlations between microstructure and piezoelectric properties of PZT thin films

Veronika Kovacova

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Veronika Kovacova. Study of correlations between microstructure and piezoelectric properties of PZT thin films. Electronics. Université Grenoble Alpes, 2015. English. NNT: 2015GREAT113. tel-01267372

HAL Id: tel-01267372 https://theses.hal.science/tel-01267372

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UNIVERSITÉ GRENOBLE ALPES

THÈSE

Pour obtenir le grade de

DOCTEUR DE L'UNIVERSITÉ GRENOBLE ALPES

Spécialité : Nano Electronique et Nano Technologies Arrêté ministériel : 7 août 2006

Présentée par

Veronika KOVACOVA

Thèse dirigée par Emmanuel DEFAY

préparée au sein du Laboratoire d'Electronique et des Technologies de l'Information dans l'École Doctorale Electronique, Electrotechnique, Automatique et Traitement du Signal

Etude des corrélations entre la microstructure et les propriétés piézoélectriques des films minces de Pb(Zr,Ti)O₃

Thèse soutenue publiquement le **20 novembre 2015** devant le jury composé de :

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Remerciements

Je tiens tout d'abord à remercier mes rapporteurs Maryline Guilloux-Viry et Daniel Chateigner d'avoir évalué ce travail de thèse ainsi que les autres membres du jury Rose-Marie Sauvage, Skandar Basrour, Emmanuel Defaÿ, Gwenaël Le Rhun, Patrice Gergaud et Nicolas Vaxelaire. Je vous remercie pour vos remarques et pour les discussions intéressantes que nous avons eues le jour de la soutenance.

Je voudrais remercier en particulier à mon directeur de thèse Emmanuel Defaÿ. C'est surtout grâce a lui, son expertise scientifique, son enthousiasme et son soutient que ma thèse c'est aussi bien passé. Un grand merci également à mon encadrant Gwenaël Le Rhun pour son aide au quotidien, ses encouragements et sa bonne humeur. Merci a Nicolas et Patrice pour leur expertise sur les rayons x et pour la possibilité de faire des mesures dans leur laboratoire ainsi qu'a l'ESRF. C'était un plaisir de collaborer avec eux. Je remercie également à Philippe Robert et Stéphane Fanget de m'avoir accueillie dans leur laboratoire et de m'avoir donné accès à des moyens exceptionnels pour mener à bien mon projet.

Je voudrais remercier à Christel, Marjolaine pour leur temps et leur patience lors de la constitution de nombreux carnets de lot pour moi. Je remercie également à toutes les personnes avec qui j'ai collaboré au BHT, en particulier Laurence Andreutti et Mathieu Delcroix en gravure chimique. Merci également à Aurélien Suhm, Josiane Peyron et a Jean Guerrero.

Je tiens à remercier Thierry Chevolleau, Marlène Terrier et d'autres personnes de la PTA pour leurs conseilles à différents moments de ma thèse.

Je voudrais remercier à la plateforme de caractérisations électriques, en particulier à Denis Blachier, Patrick Grosgeorges et Marcel Audouin parmi d'autres pour leur aide et leurs conseils.

Merci à Nadine Davide et Irène Pheng pour le temps qu'elles ont consacré à la préparation des échantillons PZT pour l'ESRF.

Merci à Guillaume Audouin, Nicolas Bernier et David Cooper et la plateforme de nanocaractérisation pour leur aide et dévouement à la problématique PZT.

Merci à Christine et à Béa qui m'ont beaucoup aidé et facilité la vie tout au long de ces trois années.

Je voudrais remercier à tous mes colocataires de bureau Christel, Gwen, Bruno, Henri, Aurélien, Yin, Julie, Thibaut, PH, Ossama et Habib. Merci pour votre bonne humeur, pour les discussions intéressantes qu'on a eu ensemble et pour vos encouragements. C'était un plaisir de partager le bureau avec vous !

Merci à tous mes collègues du labo Sylvain, Warda, Hélène, Elena, Boris, Vanessa, Valentin, Cécile, Clémence, Bertrand, Marie Claire, Catherine, Hervé et Patrick. C'était toujours un plaisir de partager le café et un gâteau avec vous.

Un grand merci à Aurélien et Marie qui m'ont fait découvrir la région grenobloise, surtout ses montagnes et ses lacs.

Je remercie à mes amis Elvira, Veronica, Carine, Marion, Bérénice, Dom, Danielka, Darinka et Peto. Je vous suis infiniment reconnaissante d'avoir été là pendant les moments difficiles ainsi que pendant les moments de joie.

Je voudrais remercier de tout mon cœur à ma famille, mes parents et mon frère Jozko. Merci de m'encourager pendant toutes ces années et de m'avoir donné la possibilité de réaliser mes rêves.

Et finalement un grand merci à Roman qui m'a toujours soutenu pendant ces trois années.

Introduction

"There is plenty of room at the bottom" was the name of Feynman's 1959 lecture, where he considered the possibility of manipulating objects at micro and nano-scale [1]. He presented the concept of building one-quarter scale machine tools analogous to those that could be found in any machine shop. His ideas about what we today call MEMS (Micro Electro Mechanical System) went unnoticed at that time. It wasn't until the 1980's that we saw the appearance of the first MEMS devices, which were essentially pressure sensors and accelerometers. It took ten more years to make MEMS compatible with integrated circuits. Nowadays, the MEMS sector represents a \$11.1 B business and it should double by 2020 [2]. According to the type of use, MEMS can be categorized as sensors, whose purpose is to detect some characteristics of their environment and actuators, whose purpose is to produce motion and basically act upon an environment. The typical MEMS sensor applications are pressure sensor, gyroscope, accelerometer, IR imaging and energy harvesting devices. The typical MEMS actuators are ink-jet heads for large format printers, autofocus lenses, digital speakers, micro-mirrors for scanning, small-scale drones, hard-disc reading heads and micro-pumps.

Several technologies coexist in the domain of MEMS actuators, namely electrostatic, thermal and technology based on piezoelectric or magnetic active layers. The latter is very interesting in terms of response time and the ratio deformation versus applied voltage. The main drawbacks are the complexity of the material and its integration into devices.

Here we focus our attention on one of the most used piezoelectric active layers, morphotropic lead titanate zirconate (PZT) thin films. PZT films are one of the most performant piezoelectric films. However, our aim is to further enhance PZT properties. Our strategy for reaching this goal is to understand microstructural mechanisms behind piezoelectricity in these films. For this purpose, this PhD thesis addresses the study of correlations between piezoelectric effect and microstructure in PZT thin films. The main characterization technique used to investigate PZT microstructure is X-ray diffraction (XRD). We not only describe PZT texture, crystal size and strain condition, but we also take advantage of the non-destructive nature of this characterization technique in order to observe PZT behavior under electric field so called in-situ XRD.

This work was carried out at CEA LETI (CEA: Commissariat à l'Energie Atomique et aux Energies Alternatives, LETI: Laboratoire d'électronique et de technologie de l'information) in Grenoble. Our laboratory LCMA (Laboratoire des Composants Micro-actionneurs) is focused on research and development of micro-actuators. LCMA has extensive experience in sol-gel PZT thin film fabrication. Our films are one of the most performant piezoelectric films worldwide. These films are then integrated into devices for actuation purposes developed inside the laboratory or in collaboration projects. LCMA is also involved in the transfer of sol-gel PZT film fabrication process to industry.

This manuscript consists of three chapters. Chapter I aims to introduce the background related to this thesis. First piezoelectric materials and applications are presented, followed by the definition of the piezoelectric effect. Then, we focus on the main subject of this thesis, the lead zirconate titanate (PbZrTiO₃) material, bulk ceramics and thin films. A brief review of PZT thin films applications and market situation will be given. PZT exhibits its best piezoelectric properties at the composition corresponding to the morphotropic phase boundary (MPB). We will take a closer view of MPB PZT microstructure. After PZT bulk ceramics microstructure has been described, we will present recent

review of theories explaining the microstructural origin of piezoelectricity in PZT ceramics. We will then turn our attention to PZT thin films fabricated by the sol-gel method. We will summarize recent literature about microstructure and PZT behaviour under an electric field, culminating in the definition of the objectives of this thesis.

The beginning of Chapter II is dedicated to the PZT material elaboration and sample fabrication. We also present the main characterization techniques, in particular XRD as well as explaining all potential contributions of this characterization method in order to reach our objectives, especially texture, crystal size and strain evaluation. The Rietveld and Combined Analysis approach for data treatment are also presented. In-situ XRD and the sample preparation for this experiment are then given. This is followed by a description and illustration of both diffraction setups used for XRD experiments. Then, we briefly present Precession Electron Diffraction (ED) and Secondary Ion Mass Spectrometry (SIMS). The end of this chapter is dedicated to electric and piezoelectric measurement principles and the equipment used.

Chapter III shows the main experiments achieved in order to reach goals fixed in this thesis, the major results and related discussions. This chapter is divided into three parts. First, we explore local correlations between Zr and Ti composition gradient and PZT microstructure. This study was possible thanks to the Nano-pencil beam available at ESRF. This beam enabled us to perform vertical scans of one µm-thick PZT thin films. This experiment showed very high sensibility of PZT microstructure in its composition. Then, we study microstructural modifications correlated to piezoelectricity by observing the effect of an electric field on PZT microstructure using in-situ XRD. Profile refinements showed us microstructural modifications that can be explained as phase transition. The end of the chapter is dedicated to analyzing the effect of Zr/Ti composition homogeneity on the phase transition under electric field. Samples with different gradients are characterized by in-situ XRD. Correlations between composition homogeneity, piezoelectric performances and phase transition are drawn and discussed.

This manuscript ends with the general conclusion followed by perspectives for future work and experiments interesting for studying PZT thin films, especially in-situ characterizations.

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Chapter I: Piezoelectricity versus microstructure

Introduction

The main objective of this first chapter is to define the background and the context related to the elaboration of this manuscript. Thus, the beginning is dedicated to piezoelectric materials, in particular piezoelectric thin films and their application. Then we introduce the piezoelectric effect, using thermodynamics and mechanical approach.

The second part deals with the main subject studied in this thesis, the lead zirconate titanate (PZT for $Pb(Zr,Ti)O_3$) material. After a general presentation of PZT, we briefly describe PZT bulk ceramics and PZT thin films. Examples of applications and the current marked situation of the latter are then reported.

The last part of the first chapter is devoted to the microstructure of morphotropic PZT. After studies on bulk PZT ceramics have been described, the typical microstructural imprint and microstructural modifications related to piezoelectric effect are presented. Following this, typical microstructural features of sol-gel fabricated PZT thin films and some recent studies and issues about PZT thin films are introduced. At the end of this chapter, we present the main goals of this work and our research strategy.

1. Piezoelectricity and applications

The first part of Chapter I briefly introduces piezoelectric materials, focusing on thin films. Today's leading and emerging thin films as well as their applications are given. The piezoelectric effect is the main phenomenon studied in this manuscript. Thus, this part is also dedicated to piezoelectricity, explained through crystallographic, thermodynamic and mechanical approach. Piezoelectricity in thin films is also explained.

1.1. Piezoelectric materials and applications

Just a few decades after the discovery of piezoelectric effect at the end of 19th century, 20 natural crystallographic classes had been identified, in which the piezoelectric effect occurred. The first serious application of piezoelectricity was the ultrasonic submarine detector invented by Paul Langevin in 1917 and tested during World War I. The detector was made of thin quartz crystals glued between two plates of steel. After this success, conceptual ideas for other piezoelectric devices like microphones, accelerometers, ultrasonic transducers, bender element actuators and signal filters were developed. However, their performances were low and the materials availability for production was limited as they were natural crystals. Fabrication of metallic oxide powders by sintering method begun during World War II. These new materials showed better overall performances, especially regarding piezoelectric properties. Their piezoelectric coefficients were 100 times greater than the coefficients of the natural crystals. This breakthrough allowed development of material sciences around piezoelectric ceramics like BaSrTiO₃ and later on the PbZrTiO₃. The main research topics were the doping effect with other elements and study of correlations between crystal structure and electro-mechanical properties. The discovery of metallic oxide powders enabled a spectacular increase of piezoelectric and ferroelectric application fields, as well as an enormous increase of patent deposition. We can highlight some devices such as powerful sonars, ceramic phono cartridge, piezo ignition systems, sonobuoy, small sensitive microphones and ceramic audio tone transducers. Another technological bond was registered in 1980s with synthesis of PbZrNiO₃-PbTiO₃ and PbMnNbO₃-PbTiO₃ crystals. These materials are called relaxors and they have extremely high electrostrictive coefficients that overtake their piezoelectricity.

From the beginning of 1980's, piezoelectric materials appeared in the form of thin films of several microns. These new fabrication directions responded to the request coming from microelectronic industry. Thin film technology allows thicknesses far lower than those attainable by grinding or tooling bulk ceramics to be obtained. New applications coupling microelectronics with miniaturized systems involving piezoelectric and ferroelectric materials were imagined, among them: FeRAM, integrated passive devices, acoustic resonators, microsensors and microactuators. Thus, from this moment, materials fabricated in the form of bulk ceramics have been developed in the form of thin films.

1.1.1. Leading thin films

Besides miniaturization, thin films are interesting for their fast response and low working voltage. The most used piezoelectric thin films are zirconium oxide (ZnO), aluminum nitride (AIN) and lead

zirconate titanate (PZT). Table I. 1 shows their dielectric and piezoelectric performances in comparison to Quartz and bulk PZT performances.

Physical parameter	Coefficients/figures of merit	Quartz X-axis [1]	Bulk 52/48 PZT [2]	ZnO [3]	AIN [3]	PZT 52/48 [3, 4]
Deflection force, piezoelectric charge of deflected piezoelectric laminated structure	e _{31,eff} (C/m ²)	-	-12.2*	-1.0	-1.05	-821
Out-of-plain strain due to electric field applied in the out-of-plain direction	d33,eff (pm/V)	2.31*	564*	5.9	3.9	60 150
Relative permittivity	E 33	4.6	3332	10.9	10.5	300 1600
Piezoelectric voltage in deflected piezoelectric laminated structure	e _{31,eff} / ε ₀ ε ₃₃ (GV/m)	-	-4.1x10 ^{-4*}	-10.3	-11.3	-0.71.8
Coupling coefficient for plate wave	$e^{2}_{31,eff} / \epsilon_{0}\epsilon_{33}$ (GPa)	-	0.005	10.3	11.9	6 18
Dielectric losses	tanδ (@ 1 to 10 kHz, 10 ⁵ V/m)	-	0.004 0.04	0.01 0.1	0.003	0.01 0.03
Signal-to-noise ratio	e _{31,eff} /√(ε₀ ε₃₃ tanδ) (10 ⁵ Pa ½)	-	-3.511.3	-310	-20	-48
Stiffness coefficient	c ^E 33 (GPa)	107	141	208	395	98
Coupling coefficient for thickness wave	$k^2 = d^2_{33,eff}$. $c^{E_{33}} / \epsilon_0 \epsilon_{33}$	1%	152%	7.4%	6.5%	7% 15%

 Table I. 1 : Table summarizing piezoelectric and dielectric coefficients and figures of merit for ZnO, AlN and

 PZT thin films * not an effective value

AlN is a III-V compound semiconductor material with large direct gap (6 eV). Thus, it is used in optics, namely as UV Light-Emitting Diodes (LEDs). AlN is also attractive for its good piezoelectric properties, coupling factor and stable acoustic wave propagation. It is for this reason that this material is very interesting for acoustic filters. The phenomenon exploited in these applications is the generation of bulk or surface acoustic waves within piezoelectric material. When reflected and incident waves are in phase, material admittance reaches maximum. Otherwise, when waves are in phase opposition, material impedance reaches its maximum. This corresponds to material resonance and antiresonance respectively. Note that the corresponding frequencies depend on the resonator thickness. The first Thin-Film Bulk Acoustic Resonators (FBAR) were fabricated with ZnO. This material has a better coupling coefficient than AlN but its acoustic properties vary with temperature. Moreover, AlN has better break down voltage than ZnO. Thus, AlN progressively replaced ZnO. Nowadays, both AlN and ZnO are subjects of interesting R&D studies. Performances of Scandium doped AlN are implemented in acoustic filters [5]. ZnO fabricated in form of nanowires is used for many exciting applications, for example fingerprint scanning and gas sensors [6].

PZT is known for its excellent piezoelectric properties at its morphotropic composition. These properties are sought namely for actuator applications. Two actuator modes are essentially exploited; the mode involving material deflection and the mode using longitudinal actuation. The reference coefficients change depending on the actuation mode: $e_{31,eff}$ and d_{31} are important for the deflection actuation mode and $d_{33,eff}$ for the longitudinal mode (see Chapter I 1.2.3 for effective coefficient). PZT thin films are the research subject of this thesis. Electromechanical and microstructural properties and applications of this material are further exploited in the second and the last sections of this chapter.

1.1.2. Resonators, sensors and actuators applications

Thin-film acoustic resonators (FBARs) are used as Radio-Frequency (RF) cell-phones and other wireless applications. These filters are mounted immediately after antennas aiming to remove unwanted frequencies from being transmitted into devices, while allowing other frequencies to be received and transmitted. FBARs can be found in cell phone duplexers too. A duplexer is a device that isolates a receiver from the transmitter in radar and radio communication systems, allowing bidirectional communication using only one path [7].

Other FBARs applications are oscillators giving very precise time references. The advantage of FBAR in comparison to traditional Quartz oscillators is the possibility of integration into silicon. This opportunity opens perspectives of complete RF system integration.

FBARs can be used as sensors too. Piezoelectric resonators are very sensitive to external disturbances like mass deposition. Even micro-mass deposition causes resonance frequency shifting. This property is exploited in mass spectrometers in medical or military domains [8]. Another application of resonators are pressure sensors. Here, resonance disturbance is caused by pressure variations [9].

The resonant effect of piezoelectrics is also used for capturing vibrations from the environment. The mechanical energy of vibrations is transformed into electric charges through the direct piezoelectric effect. This principle is exploited in energy harvesting devices [10].

Another sensor like applications of piezoelectrics is in accelerometers, which measure the linear acceleration of an object. Here, both direct and inverse piezoelectric effect can be exploited.

Piezoelectric actuators is a large family of devices exploring the inverse piezoelectric effect. Their main advantages are fast reactivity and weak actuation voltages. The most known examples of actuators using piezoelectric thin films are micro-mirrors [11, 12] integrated in laser printers, barcode readers and DLP video-projectors, as well as RF piezoelectric micro-switches [13, 14], ink-jet printing heads [15] and digital speakers [16]. Piezoelectric actuators are also used for positioning requiring high precision, for example in hard-disc reading heads [17].

1.1.3. Emerging materials

Research and development on PZT awakened interest in artificial materials containing morphotropic phase boundary. Thus, many other materials, based on perovskite structure and containing lead were studied, among which were relaxors. These materials are paraelectric, so they do not have polarization hysteresis. They exhibit great deformations due to electrostriction. PbZn_{1/3}Nb_{2/3}O₃-PbTiO₃ (PZN-PT), (Pb,La)(Zr,Ti)O₃ (PLZT) and PbMg_{1/3}Nb_{2/3}O₃-PbTiO₃ (PMN-PT) at their morphotropic composition are examples of relaxor materials. These materials are direct concurrent to PZT.

Lead-free materials are another example of emerging materials. Lead is considered toxic, thus it is subject to legislation restrictions. However, in terms of piezoelectric properties, there is no lead-free material equivalent to PZT or relaxors so far. The most promising materials without lead are based on $BaTiO_3$ and (K,Na)NbO₃[18].

Lithium niobate (LiNbO₃) belongs to another interesting piezoelectric thin film category, notably for its piezoelectric coupling coefficients [19]. They have six times better coupling than AlN. The most important issue for this material is its thin film deposition technique. There is no other technique

than grinding and layer transfer. $LiNbO_3$ nanowires deposition is an interesting alternative for nanoscale structures deposition.

Coefficients/figure s of merit	PMN-PT (100) oriented [20, 21, 22]	(K,Na)NbO [23, 24, 18]	Ba(Ti _{0.89} Sn _{0.11})O ₃ [25]	(Bi _{0.5} ,Na _{0.5})₀.9₄Ba₀. ₀₅TiO₃ [26]	LiNbO₃ [19, 27, 28]
e _{31,eff} (C/m²)	-27	-5.5	-	-	1.77
d _{33,eff} (pm/V)	30	53.5	135	26	7.1
ε ₃₃	2500	600	2000	-	20
tanδ	0.15	0.03	0.04	-	-
e _{31,eff} ² /ε ₀ ε ₃₃ (GPa)	50	5.6	-	-	-

Table I. 2 summarizes piezoelectric properties for some examples of emerging materials.

Table I. 2 : Table summarizing piezoelectric properties of some emergent piezoelectric materials

We can see how large, diverse and dynamic the family of piezoelectric materials is. The next section turns our attention to the piezoelectric effect and introduces principles of piezoelectricity through crystallography, thermodynamics and mechanical approach. The case of thin films is also covered.

1.2. Piezoelectricity

With regard to crystalline materials, their properties related to polarization changes, such as piezoelectricity, pyroelectricity or ferroelectricity can be predicted from the symmetry of their elementary components. By knowing the exact position and charge of each ion constituting the crystal cell, one can tell where the barycenters of positive and negative charges are and how they will evolve under non-hydrostatic pressure or in unidirectional electric field.

Crystalline materials can be divided into 32 crystal classes. In order to be **piezoelectric**, the crystal has to gain an electric polarization during mechanical solicitation. Therefore, centrosymmetric crystals, as well as class 432, are not piezoelectric. However, these 11 centrosymmetric classes can still change their dimensions along the direction of an applied electric field because of electrostatic attraction between electric field-induced dipoles. This phenomenon is called **electrostriction** and occurs in all dielectrics. Strain induced by electrostriction is proportional to the square of induced polarization. Note that the piezoelectric effect has a linear link to polarization. In addition, electrostriction is not reversible. No stress can induce polarization by electrostriction, though it infers the variation of dielectric constant. Finally, electrostrictive strain amplitude is usually much weaker in comparison to the strain induced by piezoelectric. However, the best electrostrictive materials exhibit a higher strain than the best piezoelectrics. Materials with the highest electrostrictive constants are relaxor ferroelectrics, for example lead magnesium niobate (PMN) or lead magnesium niobate-lead titanate (PMNPT).

Out of the 20 piezoelectric crystal classes, ten are polarized even if no stress is applied to them. This spontaneous polarization is related to specific crystallographic directions and it is sensitive to change in temperature. Thus, these materials are called pyroelectric. Aluminum nitride (AIN) and zinc oxide (ZnO) are examples of pyroelectric materials.

Among the pyroelectric crystals, those whose polarization is mobile in their crystal lattice while electric field is applied, reversible if the voltage is sufficiently high and describes a hysteresis loop with electric field, are called ferroelectric. Materials of perovskite crystal structure like BaSrTiO₃ and PbZrTiO₃ and ilmenite structures like lithium niobate (LiNbO₃) are ferroelectric when the temperature is lower than the Curie temperature. The summary of these crystal classes splitting is presented in Figure I. 1.



Figure I. 1: 32 crystalline classes categorized by their electric properties

Note that piezoelectricity is also observable in some polymers like polyvinylidene fluorive (PVDF) with no crystalline structure. In PVDF, piezoelectric effect depends on the conformation of long-chain molecules. The inter-twined chains attract or repel each other under an electric field.

The piezoelectric effect describes the property that converts mechanical energy into electrical energy by modification of the crystal electric polarization due to the mechanical stress [7]. This conversion is linear and reversible. It was discovered by Pierre and Jacques Curie at the end of the 19th century. Their experiment resulted in conclusive measurements of electric charges on the surface of several crystals including tourmaline, quartz, topaz, sugar cane and Rochelle salt when applying a mechanical pressure. It was published in 1880 [29]. They concluded that materials generate an electrical charge as a result of applying mechanical force. This was the first demonstration of a direct piezoelectric effect (Figure I. 2 a). Immediately, the term piezoelectricity appeared which is derived from the greek piezo, which means to squeeze or press, and *electric*, which means amber. Along with lightning, the electrostatic force of amber when rubbed with fur was humanity's first experience of electricity. The converse piezoelectric effect was theoretically predicted by Gabriel Lippmann in 1881 [30] and subsequently demonstrated by the Curie brothers [31]. The converse effect refers to the mechanical strain generated by materials when submitted to electric field (Figure I. 2 b). Note that the deformation is proportional to the applied voltage.



Figure I. 2: Direct (a) and converse (b) piezoelectric effect

1.2.1. Thermodynamic approach

Direct and converse piezoelectric effects are correlated to energetic properties of materials. The thermodynamic approach is usually adopted in order to explain electromechanical couplings related to the piezoelectric effect [7, 32].

The strategy of the thermodynamic approach lies in the decomposition of the internal energy system in different contributions. In the case of ferroelectrics, the contributions are mechanical, electrical and thermal. Writing the expression of internal energy U of the system enables the determination of the state of the system as a function of independent macroscopic variables. Note that U is a state function, thus in order to describe the energy transfer in the system, initial and final states of the transforming system are needed.

The considered conjugated variables for mechanical contribution are strain *S* and stress *T*, for electric contribution there is electric field *E* and electric displacement *D* and for thermal contribution there is temperature ϑ and entropy σ . In the case of a quasi-static transformation, the equation system is:

$$dU = \vartheta d\sigma + T dS + E dD$$

Here, ϑ , *T* and *E* are intensive parameters related to bulk material properties. They do not depend on samples' dimensions. Parameters σ , *S* and *D* are called extensive variables because they depend on the amount of material. Here, they are considered as variables. We can use the internal energy equation in order to characterize the equilibrium of the system (*dU=0*), which corresponds to *do*, *dS* and *dD* equal to zero and ϑ , *T* and *E* constants and we can find the thermodynamic potential of the considered transformation.

In practice, parameters ϑ , *T* and *E* are more likely to be manipulated than σ , *S* and *D*. Thanks to the Legendre transformations of internal energy, the variable set can be changed. This operation enables us to define the Gibbs free energy.

$$G = U - \vartheta \sigma - TS - ED \text{ which becomes after derivation } dG = -\sigma d\vartheta - SdT - DdE$$
with
$$\begin{cases}
\sigma = -(\frac{\partial G}{\partial \vartheta})_{T,E} \\
S = -(\frac{\partial G}{\partial T})_{E,\vartheta} \\
D = -(\frac{\partial G}{\partial E})_{\vartheta,T}
\end{cases}$$

The thermodynamic equilibrium is characterized by temperature, stress and electric field. The derivatives of σ , *S* and *D* with respect to T, ϑ and E are written below:

$$\begin{pmatrix} d\sigma \\ dS \\ dD \end{pmatrix} = \begin{pmatrix} \left(\frac{\partial\sigma}{\partial\vartheta}\right)_{T,E} & \left(\frac{\partial\sigma}{\partial T}\right)_{E,\vartheta} & \left(\frac{\partial\sigma}{\partial E}\right)_{\vartheta,T} \\ \left(\frac{\partial S}{\partial\vartheta}\right)_{T,E} & \left(\frac{\partial S}{\partial T}\right)_{E,\vartheta} & \left(\frac{\partial S}{\partial E}\right)_{\vartheta,T} \\ \left(\frac{\partial D}{\partial\vartheta}\right)_{T,E} & \left(\frac{\partial D}{\partial T}\right)_{E,\vartheta} & \left(\frac{\partial D}{\partial E}\right)_{\vartheta,T} \end{pmatrix} \begin{pmatrix} d\vartheta \\ dT \\ dE \end{pmatrix}$$

Each partial derivative of the equation above stands for a coefficient related to one physical effect. Note that the coefficients are tensors of various ranks from 0 to 4. The diagonal terms correspond to direct properties linking two parameters of the same nature. **Heat capacity** connects entropy and temperature, elastic compliance joins strain and stress and dielectric permittivity links electric displacement to electric field. The coupling coefficients link variables of different natures. They correspond to physical quantities such as **thermal dilatation** and its converse effect called **piezocaloric effect**, then **pyroelectric effect** and its converse **electrocaloric effect** and finally **direct** and **converse piezoelectric effect**. Moreover, the second derivatives of these coefficients are continuous, thus there is equality of the cross derivatives. Therefore, coefficients of direct and significant, especially in the case of ferroelectric materials.

The thermodynamic approach enables to describe notably direct and inverse piezoelectric effect.

1.2.2. Piezoelectric formalism

The mechanical approach developed in this section is inspired by the document "Standards on Piezoelectricity" and its revision [33, 34]. We saw that piezoelectricity appears naturally from energy examination. However, in practice, piezoelectric equations do not take into account heat terms, assuming isentropic and isothermal conditions. Considering mechanical and electrical effects as well as associated couplings, we can rewrite the equation describing thermodynamic equilibrium. One has to bear in mind that state functions are defined by the choice of independent variables, namely mechanical *S* and *T* and electrical *E* and *D* variables. In this manner, the thermodynamic behaviour of a system can be described by four equivalent couples of electro-mechanical equations. These four equivalent equation couples, each of them describing both direct and converse piezoelectric effect, are written below:

$$\begin{cases} S_{ij} = s_{ijkl}^E T_{kl} + d_{kij} E_k \\ D_i = d_{ikl} T_{kl} + \varepsilon_{ik}^T E_k \end{cases}$$
$$\begin{cases} S_{ij} = s_{ijkl}^D T_{kl} + g_{kij} D_k \\ E_i = -g_{ikl} T_{kl} + \beta_{ik}^T D_k \end{cases}$$
$$\begin{cases} T_{ij} = c_{ijkl}^D S_{kl} - h_{kij} D_k \\ E_i = -h_{ikl} S_{kl} + \beta_{ik}^S D_k \end{cases}$$

$$\begin{cases} T_{ij} = c_{ijkl}^E S_{kl} - e_{kij} E_k \\ D_i = e_{ikl} S_{kl} + \varepsilon_{ik}^S E_k \end{cases}$$

These equation couples use fourth rank tensors s^{E} , s^{D} , c^{E} , c^{D} , which describe material stiffness and elasticity under constant electric field or electric displacement. The second rank tensors ε^{T} , ε^{S} , β^{T} , β^{S} stand for dielectric permittivity and impermittivity under constant stress and strain. Finally, there are four third rank piezoelectric tensors g, d, h and e. Note that these four equivalent formalisms contain relationships between all their terms. All of them are listed in the Standards of Piezoelectricity [33]. Considering the first pair of equations, relation expressing material deformation *S* as a linear function of stress *T* (corresponding to the Hooke's law) and as a linear function of electric field *E*, describes

the direct piezoelectric effect. The coupled equation expressing electric displacement D in function of stress T and electric field E, describes the inverse piezoelectric effect. Taking another pair of equations, one can describe the direct and the inverse piezoelectric effect in function of other variables.

In order to use the matrices of mechanical, piezoelectric and electric tensors in practice, one has to use their reduced notation [33]. As the piezoelectric tensors featured in this manuscript are *e* and *d*, the corresponding coupled equations are rewritten below in reduced notation.

$$\begin{cases} S_p = s_{pq}^E T_q + \boldsymbol{d}_{\boldsymbol{k}\boldsymbol{p}} E_k \\ D_i = \boldsymbol{d}_{\boldsymbol{i}\boldsymbol{q}} T_q + \varepsilon_{\boldsymbol{i}\boldsymbol{k}}^T E_k \end{cases} \\ \begin{cases} T_p = c_{pq}^E S_q - \boldsymbol{e}_{\boldsymbol{k}\boldsymbol{p}} E_k \\ D_i = \boldsymbol{e}_{\boldsymbol{i}\boldsymbol{q}} S_q + \varepsilon_{\boldsymbol{i}\boldsymbol{k}}^S E_k \end{cases} \end{cases}$$

The conversion rules are summarized in the table below (Table I. 3).

ij or kl	p or q
11	1
22	2
33	3
23 or 32	4
31 or 13	5
12 or 21	6

Table I. 3: Conversion rules for the reduced notation

The matrix below corresponds to the direct piezoelectric effect tensor *e*, written in reduced notation.

$$e = \begin{pmatrix} e_{11} & e_{12} & e_{13} & e_{14} & e_{15} & e_{14} \\ e_{21} & e_{22} & e_{23} & e_{24} & e_{25} & e_{24} \\ e_{31} & e_{32} & e_{33} & e_{34} & e_{35} & e_{34} \end{pmatrix}$$

1.2.3. The case of clamped thin films

Piezoelectric thin films are deposited on substrates that are usually much thicker than films themselves. For example, 200 mm in diameter Silicon wafer is 725 μ m-thick. In comparison, thin film is usually from several 100 nm to 2 μ m-thick. If film remains clamped (no membrane or cantilever technology) one can apply some mechanical assumptions that simplify piezoelectric equations.

As the substrate is a lot thicker than the thin film, it is the former, which imposes the strain. Thus, if there is no substrate motion, in-plane film strains are equal to zero. Moreover, the film surface is free of stress in the direction perpendicular to the substrate. Figure I. 3 outlines these clamped thin film assumptions.



Figure I. 3 : Scheme of a thin film clamped by substrate with reference axes on the left hand side and the summary of thin film assumptions on the right hand size.

If we put these conditions to the first of the piezoelectric equations presented above and consider the symmetry of the strain tensor and equivalence of d_{31} and d_{32} , we arrive to these three following expressions:

$$S_{1} = 0 = s_{11}^{E}T_{1} + s_{12}^{E}T_{2} + d_{31}E_{3} \quad (1)$$

$$S_{2} = 0 = s_{12}^{E}T_{1} + s_{11}^{E}T_{2} + d_{31}E_{3} \quad (2)$$

$$S_{3} = s_{13}^{E}T_{1} + s_{13}^{E}T_{2} + d_{33}E_{3} \quad (3)$$

Subtracting the first (1) and the second (2) equation, one can find the expression proving that $T_1=T_2$.

$$s_{11}^E T_1 - s_{12}^E T_1 + s_{12}^E T_2 - s_{11}^E T_2 = 0$$

In adding the first equation (1) to the second (2), one obtains:

$$(s_{11}^E + s_{12}^E)T_1 = -d_{31}E_3$$

Expressing the term T_1 thanks to the latter equation and putting the expression to the third equation (3), knowing that $T_1=T_2$ gives:

$$S_3 = d_{33}E_3 - 2\frac{s_{13}^E}{s_{11}^E + s_{12}^E}d_{31}E_3$$

It is difficult to distinguish transverse coefficients contributions from longitudinal coefficients contributions when measuring d_{33} piezoelectric coefficients. In order to overcome this problem, effective coefficient $d_{33,eff}$ was established [35].

$$S_3 = \left(d_{33} - 2\frac{s_{13}^E}{s_{11}^E + s_{12}^E}d_{31}\right)E_3 = d_{33,eff}E_3$$

The same situation happens with e_{31} coefficient. In order to take into account substrate clamping effect, effective coefficient $e_{31,eff}$ was set [35, 36]. With the same reasoning as for $d_{33,eff}$, we can find the following expression of $e_{31,eff}$.

$$T_1 = \left(\frac{c_{13}^E}{c_{33}^E}e_{33} - e_{31}\right)E_3 = -e_{31,eff}E_3$$

Longitudinal effective coefficient $d_{33,eff}$ and transverse effective coefficient $e_{31,eff}$ are the references for evaluation of piezoelectric performances of substrate clamped thin films. These coefficients measurement is detailed in Chapter II. 3.2.

The physical principles of piezoelectricity as well as examples of well-known piezoelectric materials and their applications are given and new emerging materials are presented. There is unceasing research into new efficient materials, new applications and improvements of existing materials and their applications, which proves the dynamism of piezoelectric community.

Now, let us draw our attention to the main subject of this thesis, which is one of the piezoelectric community materials, the PZT. After general presentation of PZT, we will focus on one particular composition, which corresponds to the morphotropic phase boundary (MPB). PZT is known to exhibit its best properties at this composition.

2. Lead titanate zirconate Pb(Zr,Ti)O₃

Lead titanate zirconate (PZT) is a solid solution of $PbTiO_3$ and $PbZrO_3$ with chemical formula $Pb(Zr_x,Ti_{1-x})O_3$. PZT crystallizes in perovskite configuration, ABO₃. The corresponding unit cell in the tetragonal crystallographic phase is illustrated in Figure I. 4.



Figure I. 4: Representation of PZT unit cell in perovskite ABO₃ structure. Note that A sites represented in red are occupied by lead atoms and B sites illustrated in yellow are occupied by Zr or Ti atoms. In addition, B site displacement under an electric field is shown.

Figure I. 5 a shows the complete phase diagram of bulk PZT for T>0°C. Note that a zoom to the MPB region is provided in Figure I. 5 b. In terms of composition and temperature, PZT can be paraelectric, ferroelectric or antiferroelectric. At temperatures higher than 500°C, PZT crystallizes in cubic Pc phase. This phase is centrosymmetric, thus the barycenter of positive and negative charges coexist, making PZT paraelectric. Curie temperature (CT) is the temperature, where ferroelectric materials undergo crystal symmetry changes resulting in loss or gain of their spontaneous polarisation (Figure I. 5). Materials are only ferroelectric below the CT, where their structure is noncentrosymmetric and allows spontaneous polarisation. Above the CT, materials become centrosymmetric and lose their spontaneous electric polarisation. Thus below the Curie temperature, PZT cubic phase changes into non-centrosymmetric phases, namely tetragonal P_{T} , rhombohedral P_{R} , orthorhombic A_0 or monoclinic F_M (Figure I. 5 b), depending on composition. Barycenters of positive and negative charges are no longer intermingled, which gives PZT a spontaneous polarization. Moreover, positions of Zr/Ti cations modify with electric field and change the value of polarization. Figure I. 4 shows central atom displacement under voltage in the tetragonal PZT phase. Thus, at low temperature PZT becomes ferroelectric. Note that ferroelectricity implies piezoelectricity (Chapter I. 1), so PZT is piezoelectric.



Figure I. 5: Complete bulk PZT phase diagram (a) [37]. Pc stands for cubic phase, $F_{R(HT)}$ and $F_{R(LT)}$ are rhombohedral high temperature and low temperature phases, F_T means tetragonal phase and A_0 stands for orthorhombic phase. Spontaneous polarisation axis direction and their number for tetragonal and rhombohedral phases are indicated. Note that Curie temperature is illustrated in red, Morphotropic Phase Boundary (MPB) in green. Zoom to the MPB composition of PZT bulk phase diagram (b) [38]. F_M stands for the monoclinic phase.

The nature of ferroelectric PZT phase depends on Zr/Ti ratio. PZT with amount of Ti superior than 48% is tetragonal, whereas PZT with Zr ratio superior than 52% crystallizes in rhombohedral phase. Near the morphotropic phase boundary and at low temperature, PZT crystallizes in monoclinic phase [39]. For 0 to 2% of Ti, PZT crystallizes in orthorhombic phase, which is antiferroelectric.

PZT spontaneous polarization vector orientation depends on PZT crystallographic phase. In the tetragonal phase, spontaneous polarization occurs naturally along the <100> direction. As the tetragonal phase contains six equivalent <100> directions, polarization vector can be oriented in six different directions, which defines six domain configurations (Figure I. 6 a). In the rhombohedral phase, spontaneous polarization occurs along <111> direction. The rhombohedral phase contains eight equivalent <111> directions, each of them defining one domain configuration (Figure I. 6 b). The monoclinic phase related polarization vector lies in (110) crystallographic plane (Figure I. 6 c). Thus, the monoclinic phase possesses the most domain configurations.



Figure I. 6: Scheme of polarisation directions in tetragonal (a), rhombohedral (b) and monoclinic (c) phase [40]

From the ferroelectric point of view, homogeneous areas of material with the same polarization orientation are referred to as domains. There can be several domains in one single crystal or one grain [7]. This point is in disagreement with the crystallographic point of view [41]. Indeed, in crystallography one refers to a single crystal or crystallite, when talking about domains diffracting in a coherent way. Thus, there cannot be multiple domains in one crystal. A grain from the crystallographic point of view can be made up of one or several crystallites. A polycrystal is composed of many grains, separated by grain boundaries. For the sake of clarity, in this manuscript we will refer to domain or crystallite when talking about ferroelectric domain or coherent diffracting domain. An aggregate of domains will be called a grain.

Domain walls are boundaries that exist between areas of unlike polarization orientation or domains. In the tetragonal phase, 90° domains are strain-producing and 180° domains are non-strain-producing. In the rhombohedral phase 71° and 109° domains are strain-producing. 180° domains remain as non-strain-producing. Note that macroscopic changes occur when strain-producing domains are switched. When many adjacent domains switch in a like manner, it is referred to the domain reorientation or switching.

The morphotropic phase boundary (MPB) is the transition region situated at the interface between two crystallographic phases. PZT MPB is very abrupt, so it can be associated with a specific chemical composition: 52% Zirconium and 48% Titanium in the case of bulk PZT. The main feature of interest

of MPB is that this composition corresponds to the maximum in dielectric and piezoelectric properties.

Following this general description of PZT material, we will now focus on morphotropic bulk and thin films. In particular, applications and the market situation of PZT thin films will be reported.

2.1. PZT Bulk Ceramics

Pure morphotropic PZT of perovskite crystallographic structure exhibits outstanding piezoelectric performances. High d_{33} , d_{31} and d_{15} piezoelectric coefficients, high electromechanical coupling, low dielectric losses and high permittivity make PZT a very popular material for actuation. PZT bulk ceramic performances have already been reported in Table I. 1.

Note that PZT bulk ceramics are very often used with a dopant (<3%) to improve and optimize their basic properties for specific applications [42]. Donor dopants create metal (cation) vacancies, which facilitates the mobility of domain walls and hence the polarization change in the material. Typically, they have large piezoelectric constants, high coupling factors, moderate permittivity and higher dielectric loss. They are at the origin of **soft PZT** used in **high sensitivity** applications. Acceptor dopants create oxygen (anion) vacancies and give rise to PZT with lower piezoelectric constants, but are very stable under electrical or mechanical stresses and with low dielectric loss. It is called **hard PZT**. Hard PZT is usually found in applications requiring **high power**. Table I. 4 gives a relative comparison between soft and hard PZT.

Characteristic	Soft Ceramic PZT	Hard Ceramic PZT
Piezoelectric Constants	larger	smaller
Permittivity	higher lower	
Dielectric losses	higher	lower
Electromechanical Coupling Factors	larger	smaller
Electrical Resistance	very high	lower
Mechanical Quality Factors	low	high
Coercive Field	low higher	
Linearity	poor	better
Polarization/Depolarization	easier	more difficult

Table I. 4: Comparison of soft versus hard PZT performances [43]

Soft PZT is interesting when high coupling and charge sensitivity is important such as ultrasonic nondestructive testing and the evaluation of flow measurements and object monitoring (Figure I. 7), actuators for micro and nanopositioning, vibration detectors and electro-acoustic applications as sound transducers and microphones [44].



Figure I. 7: PZT ultrasound transducer [45]

Hard PZT is used for the generation of high-power acoustic applications. Typical examples of such devices are ultrasonic cleaners (kHz frequency range) (Figure I. 8), machining of materials (ultrasonic welding, bonding and drilling), ultrasonic processors (liquids dispersion), sonar devices.



Figure I. 8: PZT transducer for ultrasonic cleaning [46]

2.2. PZT Thin films

Although there will be always requests for bulk devices, it is obvious that industry continues to turn toward thin film devices [42]. The main reasons include lower operating voltages, size and weight compatibility with integration trends, better processing compatibility with silicon technology, ease of manufacture, and lower costs through integration. Note that the Table I. 1 enables comparison of piezoelectric and dielectric properties of PZT bulk and thin films. This part aims at presenting morphotropic PZT thin films elaboration techniques, their application and actual market situation.

2.2.1. Main fabrication techniques

Currently, there are various techniques for PZT thin film manufacture. Note that denomination **thin films** gather film thicknesses from 0.1 to 5 μ m. Films from 5 to 20 μ m are called thick films. Table I. 5 summarizes the major deposition methods presently used for PZT thin films. There are two predominant categories of PZT film deposition: physical vapour deposition (PVD) and chemical processes involving chemical vapour deposition (CVD) and chemical solution deposition [42]. The former requires a vacuum in order to perform atom or ion deposition whereas the latter does not. Thus, one could classify them as vacuum techniques and non-vacuum techniques.

Physical vapour deposition	Chemical vapour deposition	Chemical solution deposition
Sputtering Laser ablation	MOCVD (metal-organic CVD)	Sol-gel

Table I. 5: Main PZT film deposition techniques

Advantages of the vacuum technique are dry processing, high purity of the final material, compatibility with semiconductor integrated-circuit processing and possible epitaxial growth. On the other hand, these techniques have often a small deposition rate, high temperature post deposition annealing for crystallization and also high equipment and maintenance costs. The non-vacuum deposition advantages are a high deposition rate, large deposition area and low equipment and maintenance costs. The only drawback is high toxicity of solution precursors. For all these reasons, plus deposition versatility (spin-on/spray-on/dip-coating and ink-jet printing) and composition flexibility, the most successful deposition techniques are the wet chemical solution deposition, namely the sol-gel technique. Even if sol-gel and PVD show similar performances [47], sol-gel technique is advanced in terms of integration.

Figure I. 9 shows the most used deposition techniques in 6" equivalent wafers shipped. The chart displays that more than 90% wafers are fabricated by the sol-gel deposition technique. Moreover, the forecast based on the maturity of other deposition techniques in comparison to sol-gel, claims that sol-gel will most probably remain the major deposition method for another decade.



Figure I. 9: PZT thin films deposition technology state and future tendencies expressed in 6" equivalent wafers [3].

All in all the fact that sol-gel PZT is well established, has low cost fabrication and excellent performance are relevant arguments to continue the research on sol-gel deposited PZT thin films.

2.2.2. Applications

The first mass production of PZT thin films started in the 1980's thanks to the computer data storage market. PZT replaced the dielectric layer of D-RAMs, which enabled non-volatility, that is to say it retains data in memory without power supply. The new device called Ferroelectric RAM (FeRAM) uses domain polarity change under voltage in order to create a binary switch. Note that nowadays, PZT films for FeRAM application are mainly fabricated by PVD Sputtering and MOCVD method.

The application of PZT thin films that followed was Integrated Passive Devices (IPDs). Their mass production began in the 1990's. IPDs represent a collection of dedicated process technologies that allow the integration of several passive components on a single piece. They offer high integration ratio and improved performance. IPDs are used in RF, High brightness LEDs and for electrostatic discharge (ESD) and electromagnetic interference (EMI) protection. PZT films for IPDs are fabricated by PVD sputtering and Sol-gel method.

The latest to be introduced were Sensors and Actuators Micro-electromechanical Systems (MEMS). Their production begun in late 2000's with Ink Jet heads for Large Format Printers from Panasonic and EPSON and Panasonic gyros for automotive industry. PZT is very attractive for MEMS applications because of its high piezoelectric and pyroelectric performances. Besides Ink Jet heads and Inertial MEMS, piezoelectricity is used in autofocus, piezoelectric switches (Figure I. 10 a) [13, 14], micro-mirrors (Figure I. 10 b), energy harvesting, MEMS speakers (Figure I. 10 c) [16], drones (Figure I. 10 d), hard-disc reading heads and ultrasound sensors and transducers. The pyroelectric effect of PZT is employed in IR detection. Note that PZT films for MEMS are mainly fabricated by Solgel and PVD sputtering method.

c.



d.

b.



Figure I. 10: Lower half of ohmic piezoelectric switch (a), micro-mirror (b), digital loud speaker with the zoom on one speaklet (c) fabricated in CEA Leti and Robobee drone developed in MIT [48] (d).

Figure I. 11 summarizes PZT thin film applications in terms of PZT physical properties, namely piezoelectricity, high permittivity and pyroelectricity.



Figure I. 11: PZT thin films applications correlated to the PZT material properties [3]

The enhancement of piezoelectric coupling is the major concern for majority of sensor and actuator applications. Figure I. 12 shows research and development laboratories as a function of the three main PZT-application domains.



Figure I. 12: Main research and development laboratories classified according to PZT applications [3].

R&D is closely linked to market demand, thus the next paragraph is dedicated to a brief overview of the market situation of PZT thin films.

2.2.3. Market

According to the Yole report, the PZT thin film market is relatively small, but stable and growing. Today, in terms of market value PZT thin films applications represent about \$650M. Figure I. 13 shows the PZT market situation and its evolution over the next three years. One can see that MEMS represent more than 50% of total market value and the tendency is the same for 2018. The remaining part of the market is equally divided between IPDs and FeRAMs. By 2018, it is estimated that the FeRAMs market will increase by about \$70M, while IPDs market will decrease by \$20M.





Table I. 6 summarizes the key PZT thin films market players according to the PZT application domain.

FeRAM	IPDs	MEMS
Rohm	ST Microelectronics	EPSON
Cypress	NXP	Panasonics
Fujitsu	ON	Pyreos
Ramtron		Philips
IBM		Mitsumi
Texas Instrument		ST Microelectronics
		TDK
		EPCOS
		VTT
		Infineon
		Polight
		XAAR
		IBM
		Chirp
		Texas Instrument
		Silmach
		Wavelens
		Dimatix
		Océ
		Bosch
		Siemens
		Noviomems
		СНІ
		Silex
		FAB
		Silicon Sensing
		Global Foundries

Table I. 6: Major players in PZT thin film industry [3]

Now, we turn our focus to MEMS applications. Figure I. 14 presents today's situation and the tendencies of the MEMS market. Yole estimates that the thin film PZT MEMS market is mostly driven by Panasonic gyro with \$264M and by Ink Jet heads by \$69M. Even if market evaluations predict a decrease of Panasonic gyro and Ink Jet, new applications such as Autofocus are believed to compensate this market drop. Thus, the MEMS market value should remain stable.



Figure I. 14: PZT MEMS market and trends [3]

This part was dedicated to introducing the object of research described in this manuscript, namely MPB PZT material. Following a general description of the material at the beginning, we focused on PZT bulk ceramics and their applications. Then, our attention was drawn to PZT thin films: the major elaboration techniques were compared and their main applications were listed, namely FeRAM, IPDs

and MEMS. An overview of R&D laboratories as a function of PZT thin films application was given. PZT thin films' market, its current situation and the major market players were presented.

The major concern of R&D on PZT films is enhancing its overall properties. There are several strategies to reaching this goal: studies of PZT doping with other elements, studies of interfaces between electrodes and PZT and studies of PZT microstructure in order to draw correlations with piezoelectricity. In this thesis, we try to develop the third strategy. We believe that in order to be able to enhance performances of existing materials, one has to understand the microstructure basics of physical effects driving these remarkable macroscopic properties. Thus, the following part is a review of microstructural features typical of MPB PZT and its modifications under voltage related to the piezoelectric effect.

3. MPB PZT microstructure

The following part of this chapter is dedicated to the morphotropic PZT microstructure studies and observations. Firstly, we introduce the morphotropic phase boundary, trying to explain what it is and why material properties are raised up at this composition. Then we focus on MPB in PZT with bulk ceramics, their microstructure and in-situ observations, following on with the research studies about sol-gel PZT thin films microstructure, in particular texture, gradient and residual stress. This chapter ends with some recent in-situ microstructure characterizations of PZT thin films and announcement of the main goals of this thesis.

3.1. What is MPB?

The morphotropic phase boundary (MPB) is the transition region situated at the interface between two ferroelectric crystallographic phases. Nowadays, it is used when talking about the phase transition between tetragonal and rhombohedral ferroelectric phases resulting from composition variation or mechanical pressure. The main feature of interest of MPB is that this composition corresponds to the maximum of dielectric and piezoelectric properties for the given material. Modern engineered piezoelectric materials have more and more complex microstructure, which obscures the microstructural origins of piezoelectric effect. However, one point remains the same, the best properties are correlated to the MPB. This sub-section is a review dedicated to MPB. It will try to answer questions regarding **the nature of MPB**, **why MPB exalts piezoelectric properties** and **how we can manage to obtain it**.

In 2008 Ahart et al published an interesting article in Nature about the origin of MPB [49]. In his study, Ahart shows that an MPB like microstructure can be mechanically induced in materials that naturally do not possess any MPB. The experiment was performed on bulk PbTiO₃ (PTO) using cryogenic, high-pressure, in-situ Raman spectroscopy and synchrotron X-ray diffraction. Observations revealed that with the pressure increase, PTO undergoes two phase transitions, namely from tetragonal to monoclinic at 10 GPa and from monoclinic to rhombohedral at 18 GPa. Moreover, large electromechanical coupling is predicted for the transiting PTO. The pressure dependent PTO phase diagram driven by experimental results is similar to the composition dependent phase diagram of PbZrTiO₃ (PZT) near room temperature. Indeed, PZT transforms from tetragonal phase to the rhombohedral phase, passing through the monoclinic phase [38], while Zr amount in PZT increases. Here, one can see a parallel between the mechanically induced microstructure states of PTO and chemically induced microstructural states of PZT stable at the constant temperature and at atmospheric pressure. This experiment might show that solid solutions containing PTO with high electromechanical coupling are a result of tuning of the high-pressure strained form of PTO into ambient pressure via strains generated by substituting atoms. This theory implies that the intern chemical pressure in complex piezoelectric solid solutions is responsible for the MPB and the high electromechanical coupling in this region. Following this theory, Ahart proposes Pb_{0.5}Sn_{0.5}TiO₃ as a new promising material with high electromechanical coupling. It is worth repeating that MPB results from both mechanical stress and chemical stress. This explains why the MPB composition varies between bulk and thin films, which have different stress conditions.

The intermediate monoclinic state of MPB was further studied by Jin et al on the example of PMN-PT [50]. The study demonstrates that at the **MPB the domains composing piezoelectric material are**

miniaturized. It is claimed that the previously determined monoclinic phase is in fact a macroscopic imprint of an adaptive mixed state with microdomain-averaged adjustable topological parameters and polarization. The study then verifies several invariance conditions related to the cell parameter changes under temperature, composition and electric field. All these conditions seem to be rigorously fulfilled. Interestingly enough, they are related to the martensitic like transformations. Note, that martensitic transformations are named after the displacive transformation between austenite and martensite phase in steels. Now, it regroups all diffusionless transformations, that is to say transformations involving coordinate movements of atoms relative to their neighbours.

Rossetti at al adopts a more thermodynamic approach of MPB in 2007 [51]. The study demonstrates, through Landau, simplified equation that crystallographic anisotropy of polarization vanishes at the MPB. Since the domain wall energy is determined from the energy cost of polarization rotation, the domain wall energy also disappears. According to the classical theory of domains, the domain size D is related to domain wall energy γ through D ~ $\sqrt{\gamma}$ [52]. Thus, a **decrease of the domain wall energy** leads to domain miniaturization and consequently to an increase in the number of domain walls. Moreover, bulk MPB PZT microstructure investigations were performed by neutron and synchrotron X-ray diffraction as well as TEM imaging. These observations confirmed unusually small dimensions of domains. According to Rosetti, the observed PZT microstructures are not necessarily resulting from any specific monoclinic phase. They might be tetragonal and rhombohedral nanodomains that only mimic the monoclinic phase, because of diffraction artefacts due to nanometric dimensions. However, the presence of monoclinic phase cannot be completely excluded. To conclude, the MPB PZT might be seen as a ferroelectric glass because of polarization direction and crystallographic lattice decoupling. High polarization mobility makes the material highly sensitive to an electric field and defects. It also enables the explanation of dielectric permittivity and polarization peaking at MPB. Schonau et al also defend this theory. By investigating PZT ceramics with high resolution XRD, TEM and paramagnetic resonance, she has found the presence of tetragonal and rhombohedral nanodomains [53].

The study of Ahluwalia et al form 2005 concerning the influence of the domain size and the piezoelectric coefficients, namely d_{33} coefficients, shows that **smaller domain sizes induce higher piezoelectric coefficients** [54]. The reason for enhanced properties is thought to be domain miniaturisation, which induces higher density of domain walls and **diminishes the shear stress** between domains. Note that pre-existing shear strain also limits the total shear experienced by the crystals. The study is based on the Ginzburg-Landau equations resolution in function of domain dimensions of multi-domain systems.

This theory was experimentally confirmed with piezoelectric measurements on domain-size engineered $BaTiO_3$ crystals, performed by Wada et al [55]. d_{31} and coupling coefficients show that the smaller the domain size, the greater the piezoelectric performances.

To conclude, MPB in piezoelectrics has a complex microstructure. It is probably composed of a mixture of small and unstable domains of different crystallographic phases. Their low polarisation rotation energy and low shear stress are thought to produce one of the highest electromechanical properties.

PZT material has been known since the 1950's. Firstly, it was developed uniquely in the form of bulk ceramics. It is only since the 1980's that PZT has appeared in the form of thin films. Thus, the research on PZT bulk ceramics is far more advanced than on PZT thin films. Even if this manuscript essentially describes the study of PZT thin films, it is important to summarize knowledge about PZT

bulk ceramics. This preliminary work will enable us to lay a firm foundation for the discussion of thin films.

3.2. Bulk PZT

The following subsection is dedicated to PZT bulk ceramics microstructure observations at the morphotropic composition.

3.2.1. Microstructure

PZT bulk ceramics are often prepared by conventional solid-state reaction techniques (mixed-oxide process) using high purity (> than 99.9%) reagent grade powders of lead carbonate, zirconium oxide, and titanium [56, 39, 53]. Firstly, these powders undergo a series of calcinations at 900°C for at least 6 hours. Then they are milled and sieved in order to obtain grains of the right size. Afterwards, these grains are mixed with an organic binder and shaped into pellets by uniaxial cold pressing. After burnout of the binder, pellets are sintered at 1250°C in a covered crucible for 2 hours, and furnace cooled. In order to minimize the volatilization of lead, PbZrO₃ is used as a lead source in the crucible. If additional grinding and polishing of samples is needed, they undergo another annealing in air at 550°C for 5 hours and then cooled down slowly to eliminate created strains.

Bulk PZT microstructure results directly from the fabrication technique. It is characterized by uniform grains bonded tightly together. Even if small porosities exist, the material aspect is rather compact. Grains are constituted of randomly oriented crystallites. Thus, bulk PZT is very close to a perfect powder. The grain sizes of PZT range from 22 μ m (Schonau et al [53]) to about 2 to 6 mm (as reported by Haertling et al [42]). Grains are composed of lamellas or so-called 'twinned' domains. The domains width is about 50 to 200 nm at MPB [53] and they are separated by domain walls, which are one or two unit cells wide. As the domain wall seems to be an invariant plane, it is in coherence with the martensitic theory [53].

Moreover, high resolution TEM imaging, performed by Schonau et al, shows another microscopic feature that appears within these lamella domains. Indeed, one can find smaller domains inside of the lamellas. These 'nanodomains' are from 3 to 30 nm thick (Figure I. 15) [53]. Local Electron Paramagnetic Resonance (EPR) characterization shows that the nanodomains are of the very same phase as the Zr rich PZT, that is to say the rhombohedral phase.


Figure I. 15: TEM image of bulk PZT at the morphotropic composition [53]. One can see lamellas corresponding to twinned 90° tetragonal domains and nanoscopic features inside lamellas that correspond to rhombohedral nanodomains.

The synchrotron XRD pattern shows the presence of peaks corresponding to the tetragonal and monoclinic phases at MPB. Note that diffraction peaks are more broadened at the MPB, which is characteristic of the presence of small crystallites. Schonau et al pointed out that the XRD pattern is strongly influenced by the nanoscopic size of domains observed in TEM experiments. In fact, tetragonal, rhombohedral or monoclinic nanodomains would result in the same monoclinic-like XRD pattern because of the coherence effects between nanostructures. Thus, considering both local (TEM, EPR) and statistic (XRD) characterisations, martensitic theory and simulations of XRD pattern in function of domain sizes, they conclude that the observed microdomains correspond to the tetragonal phase, while nanodomains are likely to be of rhombohedral internal symmetry. This MPB like microstructure is typical for PZT with Zr compositional range from 52 to 56%. Rossetti at al confirmed, by thermodynamic stability studies, that phase coexistence at MPB is likely to occur at nanoscale level [57].

It is worth saying that the final PZT sample is unstressed and randomly oriented. The summary of the bulk PZT microstructural characteristics is presented in the Table I. 7.

Grain size	22 μm 6 mm	
Domain size	50200 nm	
Nanodomains	330 nm	
Crystallographic phases	Tetragonal, rhombohedral, monoclinic	
Orientation	Random	
Stress	Unstressed	

Table I. 7: Summary of PZT bulk ceramic microstructural characteristics [42, 53]

Having described the microstructure of bulk PZT, some piezoelectric effect theories explaining high performances of PZT at MPB will now be presented and discussed.

3.2.2. Microstructure and piezoelectricity

Piezoelectric effect is, basically, the macroscopic result of atomic or ionic displacement on microstructural level due to external electric field. These microstructural modifications are divided into two groups, namely **intrinsic** and **extrinsic** contributions to the piezoelectric effect [58]. Intrinsic contributions are related to the lattice changes in crystallites or domains with the exact same crystallographic phase and orientation. Extrinsic contributions result from interactions between domains. Domain switching (or domain wall displacement), phase boundary displacement are the most typical examples of extrinsic contributions. In this section, we firstly present intrinsic contributions to the piezoelectric effect in MPB ferroelectrics, followed by a discussion of theories about extrinsic contributions.

As previously explained, intrinsic contribution is characteristic to the material itself. Thus, it is logical to treat this approach with regard to single crystallites. Damjanovic et al in the study published in 2005 investigated intrinsic PZT properties near MPB using thermodynamic phenomenological approach, namely the Landau–Ginzburg–Devonshire model [58]. The author was considering tetragonal and rhombohedral PZT lattice close to the MPB. Note that monoclinic phase was not included in the model. Damjanovic demonstrates that as the composition approaches the MPB, the Gibbs Free energy (ΔG) flattens, that is to say less energy is needed for atoms to shift from their stable position. The ΔG decrease also means higher susceptibility of the system to **atom displacement and polarization rotation**, which could explain the increase of dielectric susceptibility and piezoelectric coefficients of MPB single crystals. Polarization rotation and atomic displacement are not the only contributors to the intrinsic piezoelectric effect. As pointed out by the article, crystals with dense domain structure but fixed domain walls exhibit enhanced piezoelectric properties, which demonstrates that electric field and stress-induced effects might be involved.

However, ferroelectrics are more often used in the form of polycrystalline ceramics or thin films. In this case, crystallites are not alone and intrinsic contributions are not sufficient to describe material behaviour. Extrinsic contributions originate in the interaction between crystals. Crystals are no longer free to move but they evolve depending on the state of their neighbours. Typical extrinsic contributions are **movement of domain walls** and **displacement of interphase boundaries**. These phenomena are responsible for nonlinearity (field dependence of the piezoelectric coefficient), weak-field hysteresis, frequency dispersion of the properties, creep, and aging. In some materials, more than 50% of the response is due to the extrinsic contribution [58].

There are several theories about high performances of PZT ceramics found at the MPB region. Here, we try to summarize the most important ones.

Among the first published experiments on PZT was the paper of Berlincourt et al in 1959 [59]. Electric poling and compressive stress effect on PZT domains were tested. 90° and 180° domains (equivalent to 71° and 109° for rhombohedral symmetry) reorientation was observed and determined by mechanical strains measured by strain gauges.

Li et al studied the domain switching ability of polycrystalline ferroelectrics in an article published in Nature, in 2005 [60]. This article develops a coarse-grained theory derived from the Devonshire-

Ginzburg-Landau theory and tries to implement it to the bulk MPB PZT. The main idea is that the domain switching is dependent upon the orientation, polarization and strain of its neighbouring crystals constituting the grain. The theory describes domain switching as a highly correlated and collective process, which is facilitated in polyoriented multiphased materials. In particular, it is shown that equiaxed polycrystals, which are either tetragonal or rhombohedral are unable to switch, while polycrystals with these two coexisting symmetries can switch. This theory could explain the high polarization of MPB piezoelectrics.

Tetragonal and rhombohedral domain response to an electric field was studied by Guo et al [56]. Insitu high-resolution powder diffraction of close to MPB PZT, showed that both tetragonal and rhombohedral domains tend to elongate along directions characteristic of the monoclinic distortion rather than along the polarization direction of the electric field. Based on this observation, Guo et al suggest that the monoclinic phase is the bridge between the tetragonal and rhombohedral phases located at the MPB of PZT. Figure I. 16 shows the schematic view of lead shifting related to rhombohedral (a), monoclinic (b) and tetragonal (c) crystal cell. The monoclinic phase can be viewed as either a condensation along one of the <110> directions of the local displacement present in the tetragonal phase or as a condensation of the local displacement along one of the <100> directions present in the rhombohedral plane. Moreover, the monoclinic phase is known to have a polarization axis in the (110) crystallographic plane, which increases the number of possible polarization directions in comparison to tetragonal or rhombohedral phases. Thus according to Guo et al, the striking performances of MPB PZT are explained by the presence of the monoclinic phase. The same thesis is supported by Noheda et al [39].



Figure I. 16: Schemes of projections of rhombohedral (a), monoclinic (b) and tetragonal (c) unit cell on the pseudocubic (110) plane. The solid circles are positions of Pb atom. Black circles correspond to the Pb

position in the cubic structure and grey circles stand for the Pb shifts related to the tetragonal and rhombohedral phase. The heavy and dashed arrows are pointing to Pb positions in monoclinic phase [56].

In 2003, Rogan et al performed in-situ neutron diffraction experiments based on the direct piezoelectric effect. MPB PZT samples were characterized while they were submitted to compressive load. Collected data was analysed with tetragonal and rhombohedral phases. Results show the tetragonal and rhombohedral domains switching (Figure I. 17). The rhombohedral phase is observed to be more reactive than the tetragonal phase. Thus, Rogan et al believe that this phase plays a significant role in the macroscopic electromechanical behavior of PZT.



Figure I. 17: Fraction of switched domains under compressive stress with respect to perfect powder. Experiment performed by Rogan et al [61]

Figure I. 18 shows the results of synchrotron in-situ XRD experiment on MPB PZT performed by Schonau et al [62]. Note that according to the previous TEM (Figure I. 15) and EPR observations, the tetragonal phase is related to the microdomain lamellas and the monoclinic phase stands for the rhombohedral nanodomains. In addition, the monoclinic phase used in the Rietveld fit of MPB PZT is in better coherence with PZT diffraction patterns than the rhombohedral phase even for Zr rich PZT.



Figure I. 18: Phase fraction evolution under electric field for MPB PZT [62]

The tetragonal-to-monoclinic phase transition, clearly seen in the Figure I. 18, is interpreted as related to the nanodomains rearrangement under an electric field. The first theory developed by

Schonau says that nanodomains rearrange to form rhombohedral-like microdomains, while tetragonal microdomains reorient out of diffraction conditions, that is to say tetragonal texture modifies under an electric field. The theory claims that macroscopic rotation of polarization is due to the redistribution of nanodomain orientation, which is possible thanks to the low domain wall energy, enabling high mobility of domain walls. The second interpretation proposed by Schonau is tetragonal-to-rhombohedral phase transition.

In-situ XRD on MPB PZT bulk ceramic was performed by Hinterstein et al too [63, 64]. In order to get rid of the texture effect, Hinterstein used 45°-scattering geometry. In this manner, reliable phase analysis in function of voltage could be achieved. Note that Schonau et al admitted to having difficulties in arriving at one final theory because of the texture effect of tetragonal phase.



Figure I. 19: Monoclinic and tetragonal phase ratio variation observed with in-situ XRD by Hintersteirn et al [63].

In order to perform the Rietveld analysis, Hinterstein et al used tetragonal and monoclinic PZT phases, because they enabled them to perform the fit with better reliability factors. Figure I. 19 shows the phase ratio variation of PZT under an electric field. One can see clearly that a tetragonal-to-monoclinic phase transition occurs under the electric field. Based on these observations, Hinterstein et al believe that high piezoelectric response is explained by the polarization rotation mechanism, in the contrast to Schonau et al, who proposes the martensitic transition theory.

Ahluwalia et al studied phase transition extrinsic contribution to the piezoelectric effect. The continuum Ginzburg-Landau model used in theoretical study of MPB predicts that piezoelectric material undergoes a phase transition while exposing the polarisation along non-polar direction [54]. The theory supposes an initial rectangular symmetry, which changes into rhombohedral symmetry under an electric field. Note that this symmetry modification occurs at smaller voltages as domain size decreases. For Ahluwalia, smaller domains require less shearing stress to transit. As MPB is widely believed to contain small domain sizes, this theory could explain why electromechanical properties are enhanced in MPB.

Table I. 8 summarizes all these observations based on piezoelectric theories.

Piezoelectric theories	References	
Tetragonal and rhombohedral domain switching	Berlincourt et al 1959 Li et al 2005 Rogan et al 2003	
Monoclinic phase	Guo et al 2000 Noheda et al 2000	
Adaptable "monoclinic" nanodomains	Rossetti et al 1999 Schonau et al 2007	
Tetragonal-to- monoclinic phase transition	Hinterstein et al 2011	
Rectangular-to- rhombohedral symmetry change	Ahluwalia et al 2005 (Schonau et al 2007)	

Table I. 8: Summary of piezoelectric effect theories in bulk PZT

3.3. PZT thin films

Reviewing PZT bulk ceramics microstructure at the morphotropic composition and its modifications related to the piezoelectric effect gave us a good basis for beginning with the microstructure of PZT thin films, in particular sol-gel fabricated films. We will focus on microstructural features pointing out differences between PZT bulk and thin films, namely texture, chemical gradient and stress. Finally, we will summarize in-situ experiments performed on PZT thin films, which will directly lead us to formulation of the main objectives of this thesis.

3.3.1. Microstructure

The microstructural difference between PZT bulk ceramic and sol-gel thin film microstructure obviously originates in the method of fabrication. Bulk ceramics are manufactured by the mechanical adhesion of crystals by sintering at 1250°C for 2 hours, while thin films crystals form during the crystallization annealing at 700°C in 1 minute. This process is performed each time the desired thickness of layer is coated on the wafer. Thus, the first difference is that sol-gel PZT crystals have to nucleate, whereas bulk ceramics already have crystals.

3.3.1.1. Texture of the layer

The preferred orientation also called texture happens because these thin films are fabricated by a process involving crystal growth. The PZT crystallization is controlled by the nucleation phenomenon. The initiation of crystallite nucleation needs more energy than continuing crystal growth [65, 66]. Therefore the texture of the whole film is determined by the orientation of the first layer.

The nature of the texture is defined essentially by two phenomena, thermodynamics and kinetics of the crystal growth [67, 68]. While thermodynamics privileges (100) orientation because of the smaller surface energy which gives higher stability to the (100) textured crystals, the crystal-growth kinetics privileges the (111) texture. The final film texture is influenced by nucleation. The creation of lots of nucleation sites enables (111) texture, whereas few nucleation sites give (100) texture. The nucleation decreases the energy interface and so privileges (111) orientation. Therefore all mechanisms enhance nucleation as the formation of intermetallic compounds on the surface of the Pt bottom electrode; Ti diffusion and Pt residual stress are mechanisms that enhance (111) orientation [67].

In order to get rid of the thermodynamics vs kinetics competition, one can use very thin seed layers in order to define a particular crystal orientation in PZT layers. To give some examples, $PbTiO_3$ and PbO are used to enhance (100) texture [69, 65], Ti and TiO_2 for (111) texture [70, 71] and $SrTiO_3$ for the (110) texture [72].

Texture turned out to be a crucial parameter for engineering PZT thin films for MEMS actuators where the transverse piezoelectric coefficient is of high importance. Ledermann et al. in 2003 pointed out that (100)-textured PZT films exhibit better transverse piezoelectric properties than (111)-textured films, independently of the film thickness up to 4 μ m. Conversely, (111)-textured films have a better relative dielectric permittivity, ε_r (Figure I. 20) [69]. Note that for $e_{31,eff}$, the peaking properties of both textures are not located at the same position in the PZT phase diagram. The $e_{31,eff}$ peak for (111) texture is at 45% of Zr and the peak for (100) texture is located at 53% of Zr, which is in the MPB. ε_r peaks at the MPB.



Figure I. 20: Transverse piezoelectric coefficient e31,eff and dielectric permittivity as a function of PZT thin film composition [69]

These observations were confirmed by Cueff in CEA Leti. The film orientation was controlled by Pt residual tensile stress. Wafers with greater Pt tensile stress were more likely to produce (111)-oriented PZT whereas wafers with smaller Pt tensile stress were more likely to produce (100)-oriented PZT. Note that measurements of $e_{31,eff}$ and $d_{31,eff}$ piezoelectric coefficients showed that (100)-textured MPB PZT films are more efficient than (111)-textured films [73].

A large dielectric permittivity is required for integrated capacitors, thus (111) PZT films are interesting for the microelectronic industry. (100)-textured PZT is known for its piezoelectric properties, therefore it is suitable for MEMS applications.

Nowadays, the CEA Leti sol-gel PZT thin films for MEMS applications all have (100) texture. This preferred orientation is set by the orientation of the first deposited PZT layer. This fabrication method was used to produce all samples studied in the present thesis.

3.3.1.2. Zr/Ti chemical gradient

The Zr/Ti chemical gradient across sol-gel PZT films (Figure I. 21), was first evidenced by Amanuma et al. in 1994 [74]. With Auger Electron Spectroscopy (AES), the authors observed that as the film crystallizes, less Ti and more Zr is contained in the PZT crystals. Moreover, the number of oscillations of Zr and Ti concentration within PZT films matches with the number of crystallizations. Transmission Electron Microscopy (TEM) enabled them to see the columnar shape of PZT crystals and the continuous epitaxial growth of the layer on its underlying layer. They concluded that the PZT crystallization begins with Ti-rich crystals at the surface of the underlying layer and that the crystallization proceeds from the bottom to the top. The authors were right. As explained by Peng et al on example of MOD PZT in 1992, when PZT crystallizes, the PbTiO₃ forms before PbZrO₃ because the activation energy for nucleation is smaller and the free energy is more exothermic for Ti rich compounds [75, 69].



Figure I. 21 : Zr/Ti composition gradient within the PZT sol-gel thin film fabricated in CEA Leti. Scanning Electron Microscopy image of a chemically etched PZT film on the left-hand side, and Secondary Ion Mass Spectrometry in depth profile of Zr and Ti on the right-hand side.

As the final Zr/Ti ratio in the PZT films shows in-depth inhomogeneity, the films might not be morphotropic through their entire thickness. Ledermann et al estimates the composition variation of Zr/Ti as high as +-20% [6]. Note that his 53/47 MPB PZT thin films were up to 4 μ m thick and the

crystallization took place every time 4 layers had been deposited. This PZT film already had very good properties and could compete with its undoped ceramic counterparts. To illustrate (100)-textured 2 μ m-thick PZT thin films properties: the transverse effective piezoelectric coefficient $e_{31,eff}$ reaches -12 C/m², the longitudinal effective piezoelectric coefficient $d_{33,eff}$ is equal to 85pm/V and the dielectric permittivity is as high as 935[6].

However, one could say that if the film compositional homogeneity was resolved, the PZT film would exhibit even better performances. Calame et al followed the same reasoning. In his article published in 2007, he succeeded in overcoming the Zr/Ti gradient by using four different compositions of PZT precursor solutions with Zr part varying from 43 to 63 %. The crystallization was done after 4 layers with decreasing amount of Zr. The process was repeated until 2 μ m-thickness was reached. This improved sol-gel method gave only 2.5% of Zr/Ti compositional variation through the film. Note that the film was (100)-oriented with e_{31,eff} equal to 17.7 C/m² and with dielectric permittivity reaching 1620 (Figure I. 22) [4].



Figure I. 22 : Transverse piezoelectric coefficient $e_{31,eff}$ as a function of PZT thin film composition, orientation and Zr/Ti gradient elimination [76].

This upgraded sol-gel technique eliminating Zr/Ti chemical gradient was further exploited by Abergel et al in CEA Leti [77]. With three different compositions of PZT precursors, first Zr rich of composition 59/41, second of MPB composition 52/48 and third Ti rich of composition 43/57, the crystallization occurred every time 3 layers were deposited. With this technique the performances of PZT films were as high as -27 C/m² for $e_{31,eff}$ and -200 pm/V for $d_{31,eff}$. Note that these coefficients were obtained while fields higher than the coercive field were applied to the film. Note that the values of $e_{31,eff}$ are very close to the maximum theoretical values for PZT according to Setter et al [78].

3.3.1.3. Crystal size

Crystal and domain sizes are dependent on duration and temperature of the annealing process. Thus, it is not surprising that bulk ceramics have larger crystals and domains. Figure I. 23 (a) shows a SEM image of the PZT film surface. One can see grains 50 to 500 nm in size. However, in vertical direction (perpendicular to the substrate), the grains cross through the entire film thickness as shown on the Figure I. 23 (b). The reported domain size is 100 nm and smaller [79].



Figure I. 23: SEM image of the PZT sol-gel surface (a) [69] and TEM image of the film cross section (b) [80].

3.3.1.4. Residual stress

Another particularity of thin films is the presence of **residual stress**. It is unavoidable and highly dependent on the fabrication technique. In 2011 Zhang et al studied the influence of the thin film's stress condition on its microstructure [81]. Note that film stress is dependent on the film's thickness too. Thus, a set of films with different thicknesses were manufactured in order to simulate different stress states. The films were then investigated using XRD and Raman spectroscopy. XRD phase analysis was performed using tetragonal and monoclinic phases. Zhang et al demonstrated that the stress condition of PZT thin films modifies the phase ratio in PZT and shifts the position of MPB. The more the film is stressed, the more the MPB shifts to the Ti-rich region.

Table I. 9 summarizes the main microstructural differences between bulk and sol-gel thin film PZT.

	Bulk PZT	Sol-gel thin film PZT
Grain size	22 µm 6 mm	50 500 nm [79, 69]
Domain size	50200 nm	<100 nm [79]
Nanodomains	330 nm	Not observed
Stress	Unstressed	Stressed by substrate
Crystal orientation	Random oriented	Textured
Crystal growth orientation	Poly-oriented	From the substrate
Crystallographic phases	ystallographic phases Tetragonal, rhombohedral, monoclinic	

Table I. 9: Summary of the main microstructural differences between bulk ceramics and thin film PZT

From the XRD point of view, the sol-gel thin film's microstructure, namely small domains, stress and texture, make the experiment more complicated. In order to obtain texture-unbiased data, one has to make the cartography of the sample reciprocal space by collecting diffraction data at many different sample positions. Moreover, small domains are at the origin of the diffraction peaks recovery, which makes the phase analysis difficult. The goal of this thesis work is the close analysis of the microstructure of sol-gel MPB PZT thin films fabricated at CEA Leti. In particular, the crystallographic phases, the thin film stress state and the influence of the Zr/Ti chemical gradient will be investigated.

After the presentation of basic microstructural differences between bulk and thin film PZT, we will focus our attention on correlations between the microstructure and the piezoelectric effect.

3.3.2. Microstructure and piezoelectricity

In the previous part, we saw microstructural characteristics of sol-gel PZT thin films. It was pointed out that in contrast to bulk PZT, thin films microstructure is more complex and needs many more parameters to be described. Thus, one can expect slight differences in piezoelectric behaviour as well. For instance, the preferred orientation of thin films induces texture dependence of electro-mechanical performances [82]. Moreover, the presence of residual stress corrupts the phase ratio and domain distribution in thin films [81, 83]. Then, according to thermodynamic studies, small grains and small domain size increase the mobility of domain walls [60]. Finally, the Zr/Ti chemical gradient in sol-gel thin films is responsible for the drop in dielectric and piezoelectric performances [69].

Therefore, sol-gel MPB PZT microstructure is very delicate and difficult to interpret. This is the reason why most of the electric poling effect and in-situ under voltage microstructure observations were performed out of MPB, most often in tetragonal PZT. Here, we give some interesting observations from the literature about intrinsic and extrinsic contributions to the piezoelectric effect, poling induced electric and microstructural changes and high-voltage-induced crack formation in PZT thin films.

Thin film PZT were thought to have only a very small extrinsic contribution to piezoelectric effect because of substrate clamping. The change came with the studies of Osone et al and Nakajima et al [84, 85]. They investigated tetragonal PZT thin film microstructure by in-situ XRD and Raman analysis. Figure I. 24 a shows XRD pattern of PZT film and its variation under voltage from Osone et al. The collected data revealed a lattice deformation under voltage belonging to intrinsic contributions and a

clear a-to-c domain switching (Figure I. 24 b), which is classified among extrinsic contributions to piezoelectric effect. Moreover, the strain resulting from domain switching was estimated and compared with the total strain measured by AFM. It turned out that 60 - 100% of film strain comes from domain switching. Note that his value is in agreement with bulk PZT characterization.



Figure I. 24: XRD pattern from 20° to 50° with a zoom to 002/200 peaks (a) and c-domain ratio variation versus voltage (b) [84].

It is worth noticing, that Lee et al observed the same phenomena on epitaxial tetragonal thin films [86].

The electric poling effect on tetragonal PZT thin films was studied by Kohli et al and Nakajima et al [87, 85]. They both showed a correlation between polarization and PZT microstructure. The polarization hysteresis measurements in the Figure I. 25 a. show that high voltage pulse-poling and hot dc-poling enhance the value of remnant polarization. The XRD pattern around 100/001 tetragonal PZT peaks in Figure I. 25 b. is evidence that pulse-poling causes irreversible a-t-c domain switching. Note that hot-dc poling exhibits the same impact on PZT microstructure.

These results demonstrate that an irreversible 90° domain reorientation is the microstructural origin of the polarization enhancement in pulse-poling or hot dc-poling in tetragonal PZT films. Note that hot dc-poling has better polarization retention and less back-switching than pulse-poled treatment.



Figure I. 25: Hysteresis loop of unpoled and pulse-poled tetragonal PZT film (a) and XRD of (100) and (001) tetragonal peaks of unpoled and pulse-poled sample (b) [87].

Tetragonal PZT thin films were investigated by Kobayashi et al too [88]. Interestingly enough, SEM images of high-voltage poled (>60V) PZT cantilevers show crack formation (Figure I. 26). These cracks are believed to be the result of stress generated by a-to-c domain switching.



Figure I. 26: SEM image of PZT thin film after 50V poling (a,b) and 90V poling (c,d) [88]

According to the author's knowledge, no MPB PZT thin film in-situ observations have been published until now. Thus, the second goal of this thesis is to perform an in-situ observation of MPB PZT thin film under an electric field, in order to find the microstructural phenomenon behind piezoelectricity in these films.

3.4. Objectives of this thesis

This small section aims to repeat the main goals of this thesis.

- 1. Close analysis of the microstructure of sol-gel MPB PZT thin films fabricated at CEA Leti: investigation of crystallographic phases, thin film stress state and Zr/Ti chemical gradient influence on the PZT microstructure
- 2. In-situ observation of MPB PZT thin film microstructure under an electric field
- 3. Drawing correlations between microstructure and microstructural changes under an electric field with piezoelectric effect in sol-gel morphotropic PZT thin films

Conclusion

This introductory chapter began with the presentation of piezoelectric materials, in particular thin films and their applications. The piezoelectric effect was also explained through thermodynamic and mechanical approach. Special attention to piezoelectricity phenomenon in thin films was given.

The second part of this chapter was dedicated to the main subject of this thesis, the PZT material. Firstly, we briefly presented PZT bulk ceramics, following with PZT thin films, their applications, namely FeRAM, IPDs and MEMS, and the current market situation.

The morphotropic phase boundary of PZT is particularly interesting because at this composition the material exhibits its best electromechanical properties. The third part of this chapter discussed microstructural aspect of morphotropic PZT. The microstructure of PZT bulk ceramics was reviewed and the most important piezoelectric effect explaining theories were presented. Then, our attention was driven to the sol-gel PZT films and their microstructure. Recent observations of PZT thin film microstructural changes under an electric field were given. However, no direct in-situ experiments on morphotropic sol-gel fabricated PZT thin films were reported. Thus, the major contribution of this thesis is the microstructural study of sol-gel morphotropic PZT and in-situ under voltage observations. The main objective of this thesis is to come up with correlations between microstructure and piezoelectric effect of MPB PZT thin films fabricated by sol-gel method.

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Chapter II: Film elaboration and characterization technologies

Introduction

The second chapter of this manuscript begins with a detailed description of PZT thin films elaboration by sol-gel deposition technique. The fabrication process and deposition particularities like film texture and Zr/Ti chemical gradient related to this method are covered. Then, the main microstructure characterization method, the X-ray diffraction (XRD), is introduced. The bases of Xrays and XRD are recalled and main diffraction pattern analysis techniques are presented. The potential of XRD contribution to the PZT microstructure description is pointed out. Afterwards, different XRD characterization setups used for PZT observations are described and compared. The third part of this chapter is dedicated to electric and piezoelectric characterization techniques employed in order to compare electromechanical performances of PZT capacitors.

1. Elaboration of PZT capacitors

Fabrication of PZT thin film requires different specific steps. Here, we present the fabrication process of the most used design of PZT capacitors, where PZT is found within a metal-insulator-metal (MIM) capacitor. The top-down approach is adopted in the manufacture process. MIM design exploits the transverse piezoelectric coefficient of PZT, d_{31} , which is mostly used in MEMS actuators [1]. Note that in applications taking advantage of the longitudinal piezoelectric coefficient d_{33} , like MEMS sensors, the design of interdigitated electrodes is usually preferred [2]. Prior to the device manufacture, a PZT film has to be elaborated.

1.1. PZT films elaboration

Figure II. 27 summarizes deposited layers necessary for PZT MIM fabrication process. In CEA Leti, PZT is currently fabricated on 200 mm substrates. Firstly, a thermal oxide layer is grown on Silicon (Si) substrate for passivation. Then, a very thin layer of titanium oxide (TiO_2) is needed to ensure a good adhesion for Platinum (Pt) bottom electrode and for preventing the lead diffusion. Once Pt is deposited, one can proceed to the PZT deposition.

- a. Silicon substrate
- c. TiO₂ layer deposition





Figure II. 27: PZT thin film fabrication steps



b. Thermal SiO₂

d. Pt bottom electrode deposition



1.1.1. Steps prior to the PZT deposition

The starting point is 200 mm in diameter and 725 μ m-thick single crystal Si substrate (Figure II. 27 a). Usually, the substrate is (100)-oriented and undoped, with low resistivity commonly between 1 and 50 Ω .m. The wafer has to be cleaned from all organic contaminants, native oxide layer, which naturally creates on the Si surface, and any ionic contaminants, before any manipulation. The RCA clean is a standard set of wafer cleaning steps prior to the high temperature processing.

Once the wafer is clean, 500 nm SiO_2 diffusion barrier is thermally grown on the Si surface (Figure II. 27 b). The processing takes place under 1100°C in presence of oxygen and steam, in dedicated furnaces. The temperature rise and drop are handled under neutral atmosphere.

Afterwards, a very thin, 10 nm-thick Titanium (Ti) layer is deposited by Physical Vapor Deposition sputtering (PVD). The principle of PVD sputtering is a glow plasma discharge, which is accelerated by electric or magnetic field. Then, the plasma particles hit the material target sputtering away some as a vapor for subsequent deposition on the wafer surface. The PVD deposition of Ti is followed by a thermal annealing at 700°C in oxygen in order to obtain 20 nm of TiO₂ (Figure II. 27 *c*).

Pt layer is deposited by sputtering at 450°C. This temperature promotes the (111) Pt orientation and tensile stress in the Pt film. In case of lower deposition temperature, for example 25°C, both (111) and (100) orientations occur. According to Cueff et al, Pt deposited at 25°C undergoes a small compressive stress and as the deposition temperature rises, Pt stress becomes more tensile [3]. The Pt orientation used to be a crucial point, because it defined the orientation of PZT [4]. Nowadays, this issue has been overcome with the first PZT layer deposited with sol-gel method acting like a seed layer. The latter guarantees the (100) orientation of the entire PZT film fabricated in CEA Leti clean rooms.

1.1.2. PZT sol-gel deposition

The raw material for the PZT sol-gel deposition technique is a mixture of partially hydrolyzed metallic precursors, called *sol*, in a solution containing solvents. This metal-organic solution has a very specific composition in order to give the desired morphotropic composition of the PZT which is 52% of Zr and 48% of Ti (see Chapter I for details). The Table II 10 shows the general chemical composition of the sol-gel solution. Note that lead acetate is usually present in solution with an excess of about 10%, in order to level the amount of lead evaporated during the thin film annealings and the amount of lead diffused and concentrated under the Pt bottom electrode.

Chemical compounds	Chemical formula	Wt%
Lead acetate	Pb(CH ₃ CO ₂) ₃ H ₂ O	12%
Zirconium tetra-butoxide	Zr(n-OC ₄ H ₉) ₄	6%
Titanium tetra-iso-propoxide	so-propoxide Ti(i-OC ₃ H ₇) ₄	
1-Butanol	C₄H₃OH	68%
Propylene Glycol	CH₃CH(OH)CH₂OH	10%
Acetylacetone	CH ₃ C(O)CH ₂ C(O)CH ₃ 109	

Table II 10: General chemical composition of PZT precursor used for PZT sol-gel deposition, given by our supplier, Mitsubishi Materials Corporation. The precursor contains three metallic compounds, one for each metal within the PZT, and three solvents.

When the volume fraction of sol increases, the viscosity of the solution increases until forming a *gel*. Gel is a diphasic system containing liquid locked in a solid phase network.

1.1.2.1. Four-step deposition process

Firstly, a small amount of PZT solution is taken with a transfer pipet and split on the 200mm preprocessed substrate wafer containing Pt bottom electrode. The wafer is then immediately spun on a spinner in order to make the deposition uniform. In contact with water contained in air, the sol hydrolyses completely and becomes gel.

The thickness of the PZT layer and its orientation is controlled by the rotation speed of the spin coating (Table II. 11). The higher the rotation speed, the thinner the PZT layer. Moreover, PZT is (100)-oriented for rotation speeds smaller than 1200 rpm and changes the orientation to (110) for rotation speed above 1200 rpm.

Rotation speed (rpm)	Film thickness after crystallization (nm)	PZT crystals orientation
800	65	100
1000	55	100
1200	42,2	110
1400	36,8	110
1600	31,6	110

Table II. 11 : Influence of the spin-coating speed rotation on the thickness and the orientation of PZT layer.The film thickness was determined by X-ray Reflectometry and the crystal orientation was determined by X-ray diffraction.

The typical spin coating parameters are set to 1000 rpm for rotation speed, 1500 rpm/s for acceleration and 20s for the spin duration.

After **the coating step**, the wafer is dried on a hot plate (HP) at 130°C for 5 min. **The drying step** enables the residual solvents locked within the gel to evaporate. **Calcination** is performed at 360°C for 6 min, on another HP. This step is used to eliminate solvents and organic compounds present initially in the solution which did not evaporate during drying. Spin-coating, drying and calcination of PZT are performed under extraction as PZT solution is known to be toxic and carcinogenic, mutagenic and reprotoxic (CMR) substance. After calcination, another layer of PZT can be spun until 6 layers are deposited. The first layer is an exception, the crystallization is done right after its calcination in order to induce (100) orientation. This layer acts then as the seed layer for the next deposited layers.

After calcination, the PZT is still in amorphous state. So as to make the PZT crystallize in perovskite phase, the wafer has to reach at least 500°C [1]. The **crystallization** occurs in Rapid Thermal Annealing (RTA) furnace where PZT is exposed to the oxygen flux at 700°C for 1 min. During crystallization, oxygen in RTA annealing chamber is at atmospheric pressure. The rise of the temperature has to be finely controlled in order to prevent the film from cracking. Heat is delivered by infra-red lamps and the temperature of the wafer is controlled by calibrated pyrometers.

Once the layers are crystallized, the whole procedure can be repeated until the desired thickness is reached. The sol-gel deposition process is summarized in the figure below.



Repeated until desired thickness is reached

Figure II. 28 : Layout of the sol-gel deposition process.

1.1.2.2. Thin film microstructure

Sol-gel PZT microstructure derives directly from the fabrication method. Unlike bulk PZT, which results from mechanical adhesion of crystals, sol-gel PZT has to nucleate. Nucleation is an important process, because it determines the crystallographic phase and crystal orientation. Thus, this particularity gives to thin film crystals the property of being **oriented in space**, on the contrary of bulk ceramics, which are random-oriented. Crystal orientation of sol-gel films is determined by the crystal growth orientation (from the substrate to the free surface of the sample), and the orientation and the stress-state of the layers underneath [5]. The crystal orientation phenomenon and its control are explained in more details in Chapter I. 3.2.2.1. Once the first layer of PZT is crystallized, next deposited layers continue crystallizing in the same direction, because PZT has a **nucleation-limited growth**, which means that nucleation is more energetic than crystal growth. Thus, the first layer determines the PZT film orientation. Nowadays, the CEA Leti sol-gel PZT thin films for MEMS applications have all (100) texture. This preferred orientation is set by the orientation of the first deposited PZT layer. This fabrication method is used to produce all samples studied in the present thesis.

Another difference between bulk and sol-gel films arises from the thermodynamics of the crystal growth of $PbTiO_3$ and $PbZrO_3$. $PbTiO_3$ possesses smaller crystallization enthalpy, thus it needs less energy to form than $PbZrO_3$. This is not a problem in bulk ceramics, where global homogeneity is obtained by sintering at 1250°C during 2h. In case of sol-gel thin films, the diffusivity of elements in amorphous phase of PZT is higher than the propagation speed of the crystallization frontier [5]. The

result of this phenomenon is the **Zr/Ti chemical gradient** occurring in sol-gel thin films. The chemical gradient details and control are described in Chapter I. 3.2.2.2.

In this study, three PZT thin films containing different compositional gradients were fabricated. The first without compensation of Zr/Ti gradient, the second with gradient compensation called gradient-free and the third with an amplified gradient, where the order of solutions was reversed in comparison to gradient-free PZT. The crystallization occurred every time 6 layers were deposited which means that the deposition of each layer was doubled in comparison to Abergel's study. Figure II. 29 details the composition of the PZT solutions used in the fabrication of these three types of PZT films. The six-layer deposition and crystallization process pursued until 1 μ m-thickness was achieved.



Figure II. 29 : Composition of PZT solutions used in the fabrication of a. Standard Gradient, b. Gradient Free and c. Amplified gradient PZT thin films.

1.2. Device fabrication

In order to create a MIM stack, a **top electrode** material needs to be deposited. Generally, the top electrode is made of 100 nm Ruthenium (Ru) or Platinum (Pt) layer. The deposition is made by PVD sputtering at room temperature. In this study, only Ru top electrode has been used.

The Ru and the PZT layers are then patterned with a specific design to obtain the desired devices. For electric and piezoelectric measurements and standard XRD measurements, only Ru patterning is needed. The patterning is performed by depositing a positive photosensitive chemical resist on the wafer surface. The wafer is then insulated by UV light through a mask containing the desired pattern. This pattern transfer from the mask to the resist is called **photolithography**. The resist is then developed. Parts of the resist protected by the pattern of the mask and therefore preserved from the light, stay on the wafer after development and continue to protect Ru underneath. Parts exposed to the UV are disintegrated. Ru becomes unprotected. Then the wafer undergoes **Ru wet-etching** with sodium hypochloride (NaOCI). In this manner, the pattern from the resist transfers to the Ru layer.

Finally the resist is removed with acetone and isopropyl alcohol (IPA). After wafer dicing, the process of device fabrication is finished and devices are ready for testing.

Sometimes, in order to have a better access to the bottom electrode, or so as to eliminate the matter that does not participate to the piezoelectric effect for in-situ XRD (explained later in this chapter), **PZT etching** is needed too. The whole etching process is then done in three steps. Firstly the Ru is etched with the mask corresponding to the pattern of PZT. Resist is then removed and Ru acts as hard mask to the PZT wet-etching. PZT is etched with a solution containing a mixture of hydrochloric acid (HCl) and water. Once PZT is etched, Ru can be patterned and etched again in order to obtain a more proper design. Afterwards the device is cut from the wafer.

In case of a very small device dimensions (<300 µm) and the necessity of wire bonding, **the ultrasonic bonding machine** (USBM) is used thanks to its precision. The USBM uses high-frequency ultrasonic vibrations and pressure between gold (Au) or aluminum (AI) wire and the device top electrode, to bond them together with a solid-state weld. However, this welding does not work very well on Ru. 150 nm Au layer is therefore deposited on the top of Ru electrodes via **lift-off process**. In the lift-off process, contrary to the deposition-lithography-etching process, photolithography precedes layer deposition. Firstly photoresist is deposited and patterned. Note that regions covered by the resist will be preserved from the metal deposition. Afterwards, Au is deposited on the patterned resist. Finally, the wafer is dipped in acetone for 30 min in order to eliminate the resist and lift off the excess of metal on the wafer surface. Note that 10 nm of Ti is used as a bonding layer between Ru and Au layer.

The next part of this chapter exposes the microstructure characterization techniques used to study the PZT films.

2. Microstructure characterization

The PZT thin film constituting the active layer in MIM capacitors is polycrystalline, textured, stressed and contains a Zr/Ti chemical gradient across the thickness (Chapter II.1.1.2.1). Naturally X-ray diffraction (XRD) and electron diffraction (ED) comes to mind as potential methods to characterize PZT microstructure. Note that neutron diffraction needs greater material volumes than thin films can offer, thus this characterization method is abandoned. The strength of XRD is the diversity of information this technique can give, averaged to the volume seen by the X-ray beam. On the other hand, ED is suitable for very local microstructural studies which are interesting because they are complementary to the X-rays. The disadvantage of ED is that samples have to be thin lamella-shaped for the observation. This step alters samples properties in comparison to their natural state of functioning. Unlike electrons which have lower penetration depth, with the X-rays even buried layers can be characterized.

XRD technique seems to be the method of choice for PZT microstructure characterization. Therefore, this method will be described in details focusing on its contribution to the PZT study. Precession ED in Transmission Electron microscope (TEM) will be mentioned too. Finally, the Secondary Ion Mass Spectrometry (SIMS) used to characterize the PZT chemical gradient will be shortly presented.

2.1. X-ray diffraction

The XRD section is divided in three subsections. The first summarizes the potential contributions of the technique for PZT thin film microstructure study. The second part treats the analyzing techniques used to inspect the diffraction patterns. The principle of Combined Analysis is presented. Finally, the third section describes and compares the diffraction setups used in PZT characterization. Note that Appendix A 1 briefly reports the history and basis of X-rays, covering the X-ray interaction with matter and the principle of X-ray diffraction.

2.1.1. XRD contribution to the PZT microstructure study

As discussed in Chapter I., the morphotropic phase of PZT lays on the boundary (MPB) between tetragonal and rhombohedral phases where the Zr/Ti ratio is close to 52/48 [6]. In 2000, Joseph et al showed by XRD on a PZT ceramic that the MPB is indeed composed of a mixture of these two phases [7]. He estimated the tetragonal-to-rhombohedra phase ratio close to 54/46 in the MPB. At the same time, Noheda et al. demonstrates the presence of a monoclinic phase rather than rhombohedral within the MPB PZT [8]. In her paper, she observed that the MPB is composed with tetragonal and monoclinic crystals (Figure II. 30) and she proposes that the monoclinic distortion is at the origin of the high piezoelectric performances of MPB PZT because of high polarization mobility in the monoclinic unit cell. The monoclinic phase is also presented as the bridge between tetragonal and rhombohedral phases. This theory well corresponds to the observation of local monoclinic displacement in crystals of rhombohedral PZT phase published by Corker et al in 1998 [9].



Figure II. 30 : The PZT bulk phase diagram merging Jaffe's and Noheda's contributions [8].

Note that these previous studies were performed on PZT ceramic pellets fabricated by sintering of reagent-grade powders of PZT undergoing several long thermal treatments, in order to obtain a perfectly homogeneous, stress-free and almost perfect powder-like PZT with big crystals. The pellets were then characterized in synchrotron and the data were analyzed with classic Rietveld analysis programs such as FullProf or Jana. The powder crystals dimensions went from 0.2 to 1 μ m, which produces thin and high peaks and avoids peak recovery. The dataset is then clearer and easier to interpret. Another advantage of powder diffraction is that crystals are randomly oriented. This allows recording the positions of all the crystallographic planes with one simple 20 measurement in a classical laboratory diffractometer or in one beam shot in synchrotron without any particular sample alignment.

Unlike ceramics, PZT thin films possess several special structural features that do not exist in bulk ceramics and that complexify the material microstructure (see Chapter I. for details). These features are due to the thin film fabrication techniques involving nucleation and crystal growth on an underlying metallic or ceramic layer. First of all, the thin films crystals grow in a preferential crystallographic direction, which means that one crystallographic plane does not have the same statistic representation in all directions. This loss of random crystal orientation in comparison to bulk ceramics is called **texture**. The influence of the texture on the dielectric and piezoelectric properties is discussed in Chapter II. 3. 3. 1. 1.

As a result of the rapid thermal annealing at 700°C serving for PZT crystallization and different thermal expansion constants of PZT (9 ppm) and substrate layers (2.6 ppm for Si), after cooling down to the room temperature, the PZT sol-gel film undergoes an **in-plane tensile stress** of several hundreds of MPa.

Another PZT thin film feature is small **crystal dimensions**. Due to this particularity, PZT diffraction peaks are small and wide, which promotes peak overlapping with other materials present in the stack and hinders identifying and quantifying PZT phases.

The **Zr/Ti chemical gradient** is characteristic of the sol-gel PZT. Due to the thermodynamics, PbTiO₃ crystallizes earlier than PbZrO₃, which creates the gradient within the layer even if the morphotropic composition sol-gel precursor is used for spin-coating.

The XRD characterization technique is able to give statistic information about all these features specific to the PZT films. Therefore, XRD is a powerful tool that enables a very fine microstructural comparison between PZT films. Moreover, the in-situ XRD can characterize the variations of these features while an electric field is applied to the device. Therefore, XRD could clarify the mechanism of piezoelectric response of PZT thin films.

Piezoelectric effect is composed with intrinsic and extrinsic contributions (see Chapter I.3 for more details). To simplify, intrinsic contribution are related to the domain lattice deformation, while extrinsic contributions result from the interactions between domains, like domain switching or phase transition.

Several theories explaining the piezoelectric effect in bulk and thin film MPB PZT exist. The first one is the theory of the a-to-c domain switching in tetragonal [10, 11, 12, 13] and rhombohedral phase [14] under electric field. According to this theory both phases exhibit a domain switching but rhombohedral phase is more reactive. The domain switching phenomenon is observable by the texture evolution of both tetragonal and rhombohedral phases under electric field. Typically, in order to confirm the a-to-c domain switching for the tetragonal phase, one looks for the (100)-to-(001) texture switching of the tetragonal phase crystals.

Second theory claims, that MPB PZT possesses its great piezoelectric properties thanks to the monoclinic phase, which enables a great mobility of the polarization axis in the monoclinic (110) plane [8]. In order to verify this theory, a quantitative phase analysis with tetragonal, rhombohedral and monoclinic phase could be performed on PZT under electric field. The theory would be confirmed if the presence of monoclinic phase was clearly detected.

In 2003, Jin et al published a theory of an adaptive monoclinic phase, very reactive to the electric field, made of tetragonal and rhombohedral microdomains, with low domain wall energy, which would be the reason of the enhanced properties near the MPB [15]. Since small crystals of similar phases are difficult to identify and discern with XRD, this theory would be challenging to prove with only XRD characterization.

In 2011, Hinterstein et al showed an electric field induced tetragonal-to-monoclinic phase transition in a MPB PZT ceramic. He claims that the piezoelectric effect is based on the ability of the tetragonal phase to transform to the monoclinic phase [16]. The phase identification and the phase ratio variation under electric field could help in stating whether this theory applies to the PZT thin films as well.

Note that piezoelectric theories are explained in more details in Chapter I.3. By quantifying the tetragonal-to-rhombohedral or monoclinic phase ratio evolution under electric field, the texture evolution, Zr/Ti gradient changes and in-plain stress evolution with voltage, in-situ XRD could contribute to the understanding of piezoelectric and ferroelectric effects in PZT sol-gel thin films.

2.1.1. Diffraction data analysis

Remember that PZT thin film is a 1 μ m-thick layer, which is polycrystalline, textured and stressed with potentially small crystallites. The data analysis of such a material depends on the amount and quality of collected data. This is dependent on the time budget and on the diffraction apparatus. Thus, two options exist. One can focus on one particular material property, for example texture analysis, and do the most suitable data acquisition for quantifying this property separately. In case of texture, it happens to be the pole figure acquisition (see section 2.1.4. for details). The second option is to consider the material as an entity with a system of properties, which can influence one another.

This option involves exhaustive data collection for cartographying all crystallographic planes of the material and then structure resolution with a system of interdependent equations describing each of them a particular property. This approach is called the Combined Analysis (CA) [17].

The CA is derived from the Rietveld Analysis elaborated in the 1970's for powder diffraction data investigation [18]. It was used to ease the phase dissociation in case of important peak recovery. Nowadays, it is the method of choice for refining the crystallographic structure of powders, namely cell parameters, phase quantification, crystallite dimensions and micro-deformations, which stand for the local deformation fluctuations within crystallites. Fullprof and Jana are examples of programs using Rietveld method for structure refinement. However, sometimes it is impossible to grind the material so as to obtain a perfect powder and perform the Rietveld analysis. Besides that it would damage the material itself; it would destroy valuable information about the material state of functioning. Moreover, it is hard to imagine how to scrape off 1 μ m-thick layer of PZT from the substrate stack and reduce it to powder. The CA is the Rietveld analysis but adapted to layered, textured and stressed materials such as thin films. Maud is an example of program using CA approach for structure refinement [19].

The CA enables a very complete view of material microstructure analysis. Therefore this approach is here adopted in order to explain how valuable information can be extracted from XRD datasets. Note that presented methods and equations can be taken separately and used outside of the CA frame. The following sections describing Rietveld analysis and Combined analysis are inspired by book written by Daniel Chateigner, called Combined Analysis [17].

In order to explain the CA, the Rietveld approach will be explained firstly and then other formalism will be added in order to satisfy textured and strained structures.

2.1.1.1. Rietveld Analysis

Collected data are the result of three major contributors: the *crystallographic phases of material*, namely crystal structure, microstructure, quantity, cell volume, texture, stress and chemistry, then the *instrument geometry characteristics*, so as the beam intensity, Lorentz-Polarization, background, resolution, aberrations and radiation and finally the *sample characteristics* like its position, shape, dimensions and orientation. Each contribution can be written in terms of parameters that can be refined or optimized. The equation resuming all parameters contribution is presented below.

$$y_{ic} = y_{ib} + \sum_{\Phi=1}^{N_{\Phi}} S_{\Phi} \sum_{k=K_1}^{K} j_{\Phi k} L p_{\Phi k} P_{\Phi k} |F_{\Phi k}|^2 \Omega_{i\Phi k} A_i$$

Visually, one can associate the above equation to the pattern determined by its background and the reflection peaks, which can be determined by their intensity, shape, number and positions. Using this classification, the equation could be divided in four sections. See the color distribution of the equation above.

Now, let's explain the terms of the equation in more details. y_{ic} stands for calculated intensity at the ith point, y_{ib} is the corresponding background, S_{Φ} is the scale factor proportional to the volume fraction of each refined phase Φ , $j_{\Phi k}$ is the multiplicity factor of the peak k for phase Φ , $Lp_{\Phi k}$ is the Lorentz-polarisation factor, $P_{\Phi k}$ is the correction factor describing preffered orientation of phase Φ ,

 $F_{\Phi k}$ is the structure factor of the phase including thermal vibrations, $\Omega_{i\Phi k}$ describes the profile function of the peaks of phase Φ , which presents instrumental and potential sample broadenings and finally A_i representing the absorption factor which takes into account the experimental and sample geometries. In the following section, the modeling of these terms will be explained.

The background y_{ib} at the ith point can be described using two main different approaches empirical or physical approach. The empirical approach sees the background as an array of points that can be simulated by an Mst order polynomial function:

$$y_{ib} = \sum_{g=1}^{G} G_{ig} + \sum_{m=0}^{M} B \left[\left(\frac{2\theta_i}{Bkpos} \right) - 1 \right]^m$$

G and B are the total number of Gaussians and the order of the polynomia respectively, Bkpos is the origin in degrees.

The y_{ib} can be expressed also by the Fourier series analytical function, where BK_j with j=[0;11] are refinable parameters :

$$B(i) = BK_0 + BK_1 \cos 2\theta_i + \dots + BK_{11} \cos 11 * 2\theta_i$$

The last non-phenomenological model is the point-to-point smoothing by using interpolation procedures. The goal is to replace the ith intensity of the background by the average over its 2N neighbors. This approach was firstly proposed by Brukner [20].

$$\langle y_i \rangle = \frac{1}{2N} \sum_{j=-N}^{N} y_{i+j} \text{ with } j \neq 0$$

Physical approach uses phenomenological approach and tries to explain the observed background by description of the physical reality like presence of amorphous phase, crystal local imperfections and thermal scattering. Riello et all. proposed some solutions describing background contributors independently [21].

The scale factor S_{Φ} is defined as follows:

$$S_{\Phi} = \left(\frac{\rho' v}{\rho V_c^2}\right)_{\Phi} C \text{ with } C = \frac{\Phi_0 \lambda^3 h w t}{8 r^2}$$

where ρ' represents the effective density of the phase Φ in the sample, ρ is the theoretical density of the phase, v is the volume of the phase, V_c is the volume of the unit cell, Φ_0 is the incident flux, h and w stand for height and width of the detecting slit and *t* is the counting time.

The Lorentz-polarization function $Lp_{\Phi k}$ is dependent on the diffraction instrument parameters, namely the geometry, the detector, the beam size and the sample volume, the sample angular positioning and from monochromator (α angle), if any. For the classical Bragg-Brentano diffraction instrument, involving specular diffraction in reflection mode, the $Lp_{\Phi k}$ can be defined as follows:

$$L_p = \frac{1 + \cos^2(2theta_m)\cos^2(2theta)}{2\sin^2 theta\cos theta}$$

theta_m is the respective monochromator *m* and *theta* is the Bragg angle on the pattern. For unpolarized incident beam on the sample which is the case of the setup used for the PZT film characterization (see the section 2.1.4.), the term $\cos^2(2theta_m) = 1$. See the Figure II 31 for the *Lp* factor evolution vs Bragg angle for an unpolarized beam. For synchrotron radiation when the beam is vertically polarized, $\cos^2(2theta_m) = 0$.



Figure II 31 : Lorentz-polarization factor evolution for an unpolarized beam in function of 20 Bragg angle.

The Texture correction $P_{\Phi k}$ in Rietveld approach is expressed usually by March-Dollase formula:

$$P_{\phi,k} = \frac{1}{m_k} \sum_{n=1}^{m_k} \left(P_{MD}^2 \cos^2 \alpha_n + \frac{\sin^2 \alpha_n}{P_{MD}} \right)^{\frac{-3}{2}}$$

 P_{MD} is the March-Dollase parameter, α_n is the angle between the preferred orientation vector and the crystallographic plane hkl (in the crystallographic cell coordinate system). The summation is done over all equivalent hkl reflections m_k . This texture modeling is used for cylindrical texture symmetry.

The Structure factor $F_{\Phi k}$ (see Appendix A.3) relative to a phase Φ and a crystallographic plane k, which can be defined by its Miller indices, is defined as follows:

$$F_{hkl} = \sum_{j} N_j f_j e^{2\pi i (hx_j + ky_j + lz_j)} e^{-M_j}$$

The terms *h*, *k*, *l* are Miller indices and x_{j} , y_{j} , z_{j} are atomic positions of the atom *j* in the unit cell, f_{j} is the atomic scattering factor for atom *j*, N_{j} is the site occupation factor of site *j* and the M_j is the thermal vibration parameter. The thermal vibration is seen as atomic displacement and it is modeled as Debye-Waller phenomenon.

The X-ray scattering factor f_j is usually written as:

$$f_j(h,\lambda) = f_{j,0}(h) + f'_j(\lambda) + if''_j(\lambda)$$

where $f_{j,0}(h)$ is the normal atomic scattering factor, and $f'_j(l) + if''_j(l)$ are due to anomalous scattering and strongly vary close to absorption edges of elements (photoelectric effect) while they are nearly constant at some distance from them. Globally, the atomic scattering factor decreases with the diffraction angle and is proportional to the number of electrons.

The Absorption factor A_i is an additional correction that compensates the volume and the absorption variations while rotating the sample by ω and χ . Using a point detector, the observed intensities of the top layer can be corrected as follows:

$$y_i(0) = y_i(\chi) \frac{1 - e^{\frac{-2\mu T}{\sin \theta_i}}}{1 - e^{\frac{-2\mu T}{\sin \theta_i \cos \chi}}}$$

 $y_i(0)$ is the corrected profile intensity like if no χ angle was applied, $y_i(\chi)$ stands for the profile intensity measured in the χ orientation at the i^{th} point of the profile, μ is the linear absorption coefficient of the film and T is the film thickness.

For the multilayer, the absorption factor becomes the equation below, with μ_j the linear absorption coefficient and T_j the thickness of the covering layers.

$$y_{i}(0) = y_{i}(\chi) \frac{(1 - e^{\frac{-2\mu T}{\sin \theta_{i}}})e^{\frac{-2\sum_{j=0}^{l-1}\mu_{j}T_{j}}{\sin \theta_{i}}}}{(1 - e^{\frac{-2\mu T}{\sin \theta_{i} \cos \chi}})e^{\frac{-2\sum_{j=0}^{l-1}\mu_{j}T_{j}}{\sin \theta_{i} \cos \chi}}}$$

The profile shape function $\Omega_{i\Phi k}$ defines the function that will be used in order to simulate the shape of the peeks. It can be for example Gaussian, Cauchy, Voigt, Pseudo-Voigt or Pearson VII. Here, the Pseudo-Voigt function is described as it is widely used in refinement programs.

$$\Omega_{i\Phi k} = I_n \left[\eta_k \frac{1}{1 + S_{i,k}^2} + (1 - \eta_k) e^{-S_{i,k}^2 \ln 2} \right] \text{ with } S_{i,k} = \frac{2\theta_i - 2\theta_k}{\omega_k}$$

 ω stands for the Caglioti formula and η for the Gaussianity and they are expressed as follows :

$$\omega^{2} = W + V tan\theta + U tan^{2}\theta$$
$$\eta = \sum_{n=0}^{N_{g}} c_{n} (2\theta)^{n}$$

The final goal of refining code for Rietveld is to minimize the following function by the method of least squares for example.

$$M = \sum_{i} w_{io} (y_{io} - y_{ic})^2$$

Here the w_{io} stands for $\frac{1}{\sigma_{io}^2}$ which is the statistical weight associated with the observed intensity y_{io} at the ith measured point and σ_{io} is the variance of the observed y_{io} . y_{ic} represents the calculated intensity at the point i.
The least squares is the standard approach to approximate an overdetermined system. However, there are also genetic or evolutionary algorithms, derivative difference minimization and simulated annealing or Monte Carlo approximation method.

The Rietveld approach is powerful tool for powder structure resolution. Layered sample structures needing absorption and volume corrections with cylindrical texture can be analyses as well. However, the texture modeling is only valid for axially-distributed, single component textures. The models serve for the texture correction in comparison to perfect powders, but not for a complex texture resolution. The latter needs the texture description in terms of distribution densities and orientation distribution function (ODF) refinement. Moreover, the PZT thin film is known to be strained and to have anisotropic crystallite dimensions and Rietveld method neither cover the strain-stress problem, nor the anisotropic crystallite sizes. Therefore, in CA the Rietveld refinement works side by side with programs analyzing the texture, residual strains, crystalline size (other formalisms are not treated here because they were not used in PZT characterization). Programs contained in CA are running automatically and they interact between each other. For example, when the Rietveld refinement finishes extracting intensities of profiles corresponding to different sample orientations, they are entered to the texture analysis. The result of the texture analysis is then re-injected to the Rietveld analysis to correct it. Meanwhile, residual stress characterization is run. All these operations running together, lead to a set of refined parameters, which describes the best the real sample.

2.1.1.2. Combined Analysis

In the frame of CA, the sample is characterized from different angles. Thus, the Rietveld analysis equation has to be re-written in order to consider all these sample orientations y in order to resolve properly the texture:

$$y_{ic}(\mathbf{y}) = y_{ib}(\mathbf{y}) + \sum_{\Phi=1}^{N_{\Phi}} S_{\Phi} \sum_{k=K_1}^{K} j_{\Phi k} L p_{\Phi k} P_{\Phi k} |F_{\Phi k}|^2 \Omega_{i\Phi k} A_i(\mathbf{y})$$

y orientations are defined by χ , φ and ω angle positions (Figure II 32). Each rotation axis is a potential reason of misalignment and defocusing. The defocusing concerns namely χ and ω angles. Note, that it occurs at low angles for ω and high angles for χ , when the beam is spread over more flat sample surface and the diffracted beam is not entirely seen by the detector. Moreover, the diffracted peaks might shift a little due to the angular misalignments of diffractometer. These reasons imply the necessity of an instrument calibration (IC). The IC consists in characterizing a well-known sample for instance LaB₆ or W. Since the sample structure and geometry are known, the collected data are used to characterize the third component of XRD profile, the instrument contribution via the IC parameters.



Figure II 32 : Crystallographic angles in the rotation system of the diffractometer.

The IC parameters are χ and ω broadening, peak asymmetry, peak 20 shifting, Caglioti parameters W, V and U and Gaussianity (η) parameters describing the peak profile function, $\Omega_{i\Phi k}$. Then, the IC can be stored and reused for the real sample structure refinement.

Besides Rietveld analysis, the texture, stress-strain and crystal size formalisms are needed in order to characterize PZT thin films. The following sections will focus on each one of these formalisms.

2.1.1.3. Texture formalism

The best representation of texture are pole figures (PF). A PF represents the localization of orientation distribution densities for one particular {hkl} diffracting plane, relative to one crystallographic phase, in sample space. Two different manners of position representation by plane projection exist, namely the stereographic and Lambert-Schmidt or equal area projections. See the projection principle below (Figure II. 33).



Figure II. 33 : Illustration of stereographic (a) and equal area (b) projections principle.

Firstly, a direct PF relative to one h=<hkl>, $I_h(y)$, based on the diffracted intensities, is built. This PF is then normalized using the random texture intensities of powder corresponding to the analyzed phase. The PF is then expressed in terms of distribution densities $P_h(y)$. Note, that the density unit is the "multiple of a random distribution", or "m.r.d.".

$$P_{h}(y) = \frac{I_{h}(y)}{I_{h}^{random}}$$

with $I_{h}^{random} = \frac{I_{h}^{total}}{\int_{\varphi_{y}=0}^{2\pi} \int_{\theta_{y}=0}^{2\pi} \sin\theta_{y} d\theta_{y} d\varphi_{y}}$ and I_{h}^{total}

$$= \int_{\varphi_y=0}^{2\pi} \int_{\theta_y=0}^{\frac{\pi}{2}} I_h(\theta_y, \varphi_y) \sin\theta_y d\theta_y d\varphi_y$$

Thus, the normalization is valid only for complete PF, I_h^{total} . However, the correction factors for absorption and diffracting volume integrated in AC programs like Maud, take care of completeness of the PF. The normalized PF expression is now:

$$\frac{dV(y)}{dV} = \frac{1}{4\pi} P_h(y) dy$$

It represents the volume density of crystallites oriented in ϑ_{y} , ϕ_{y} . *V* is the irradiated volume of the sample and dV(y) is the volume of crystallites with *h* orientations between *y* and *y*+*dy*. The factor $\frac{1}{4\pi}$ stands for normalization of the PF into distribution densities.

Another angle needs to be added in order to orient the crystal plane within the sample. PF need to be transformed in ODF or orientation distribution function. The ODF represents statistical distribution of crystallites orientations. The scheme of transformation is illustrated on the figure below (Figure II. 34).



Figure II. 34 : The principle of PF to orientation transformation. Note that one more direction is fixed in ODF in comparison to the PF.

The expression of ODF, f(g), is :

$$\frac{dV(g)}{dV} = \frac{1}{8\pi^2} f(g) dg$$

Finally, the fundamental equation of quantitative texture analysis (QTA) is written as:

$$P_h(y) = \frac{1}{2\pi} \int_{h/\!\!/ y} f(y) d\tilde{\varphi}$$

There are several models used to simulate texture, f(g): Williams-Imhof-Matthies-Vinel (WIMW), Entropy-WIMW, Entropy maximization, Exponential harmonics, Generalized spherical harmonics and Standard function. The texture of PZT thin film is sharp and well defined, thus Standard function is the most convenient model. In Standard function one has to define all textures present in the sample relative to sample phases and the software refines χ and ϕ angle of the *hkl* relatively to the crystal space and to the sample space.

The texture strength can be estimated by ODF texture index, F^2 expressed in m.r.d.². For powder texture, the $F^2=1$ and for the single crystal F^2 tends to infinity.

$$F^2 = \frac{1}{8\pi^2} \sum_i f^{2(g_i)} \Delta g_i$$

The quality and the physical meaning of the fit are well estimated by visual inspection. One has to compare the recalculated pole figure from OD and the experimental pole figure.

2.1.1.4. Stress-strain formalism

The widely used classical stress-strain analysis uses $sin^2\psi$ method. Note that ψ stands for χ in the previous parts of this manuscript. The method consists in tracking the 2ϑ position of a particular *hkl* peak in function of χ . One can calculate the deformation $\varepsilon_{\psi,\varphi}$ as follows:

$$\varepsilon_{\psi,\varphi} = \frac{d_{\psi,\varphi} - d_0}{d_0}$$

 $d_{\psi,\varphi}$ stands for the interatomic distance of *hkl* peak, calculated with the Braggs law from the 2ϑ position and d_0 is unstrained interatomic distance taken at ψ =45°. d spacing and $\sin^2\psi$ are linked by a linear relationship. The general formula to compute strain in isotropic materials along scattering vector $\varepsilon_{\psi,\varphi}$ is:

$$\varepsilon_{\psi,\varphi} = \frac{1+v}{E} \left[\left(\sigma_{\varphi} - \sigma_{33} \right) \sin^2 \psi + \left(\sigma_{13} \cos \varphi + \sigma_{23} \sin \varphi \right) \sin 2\psi \right] - \frac{v}{E} \left(\sigma_{11} + \sigma_{22} + \sigma_{33} \right) \\ \sigma_{\varphi} = \sigma_{11} \cos^2 \varphi + \sigma_{12} \sin 2\varphi + \sigma_{22} \sin^2 \varphi$$

Here, σ_{φ} stands for the stress in the φ direction. Assuming that the sample surface is free of stress (small penetration depth approximation), *d*-spacing and $sin^2\psi$ are linked by the following equation:

$$\varepsilon_{\psi,\varphi} = \frac{v+1}{E}\sigma_{\varphi}sin^{2}\psi - \frac{v}{E}(\sigma_{11} + \sigma_{22})$$

The 'triaxial stress with isotropic E' Maud model corresponds to the $sin^2\psi$ method. This model was used for the stress-strain estimation in PZT thin films.

2.1.1.5. Phase quantification

The intensity of the diffracted peak k relative to the phase j is directly proportional to the phase volume fraction.

$$I_j^k = I \frac{f_j}{V_j^2} L_k \left| F_{k,j} \right|^2 P_{k,j} A_j$$

Note that *I* is the incident beam intensity, f_j stands for the phase volume fraction, V_j is the cell volume, L_k the Lorentz-polarization factor, $F_{k,j}$ the structure factor, $P_{k,j}$ for the texture and A_j is absorption correction factor.

Traditional methods like Internal standard, Polymorph method or Reference intensity ration (RIR), quantify phase ratio by comparison to a known phase, use peak intensity instead of the peak surface, use few peaks and do not take into account the texture.

The quantitative phase analysis can be determined by Rietveld method, too. In fact, the scale factor S_{Φ} , of the general Rietveld formula includes already phase volume v, cell volume V_c , effective and theoretical density of phases ρ' and ρ , as well as incident beam intensity C.

$$S_{\Phi} = \left(\frac{\rho'\nu}{\rho V_c^2}\right)_{\Phi} C$$

Thus, the volume fraction f_i and the weighted fractions w_i , can be written as:

$$f_j = \frac{S_j}{\sum_{i=1}^{N \text{ phases}} S_i} \text{ and } w_j = \frac{S_j \rho_j}{\sum_{i=1}^{N \text{ phases}} S_i \rho_i}$$

The Rietveld approach is the method used for phase quantification in Maud software and used for the PZT thin film phase evolution quantification in in-situ XRD.

2.1.1.6. Crystal size and micro-distortions

The peak broadening can be seen as convolution of several microstructure effects like small size of coherently diffracting domains (crystallites) or micro-strains. Here, micro-strains are considered as small fluctuations of macroscopic strain (section 2.1.3.2) within crystallites. In general, the contribution of crystallite size to the peak shape is considered Lorentzian-like, whereas the contribution of micro-strain is more Gaussian-like.

The traditional way of quantifying crystal size involves isotropy assumption on crystal dimensions. It is called the Scherrer formula, proposed by Scherrer in 1918 [22]. This method exploits the influence of small crystal size to diffraction peak broadening. The crystal size is related to the FWHM (Full Width Half Maximum) component of the Lorentzian peak modelization:

$$R = \frac{K\lambda}{H_L \cos \theta}$$

Here, R stands for mean crystallite apparent size, K is the Scherrer constant depending of the crystallite geometry (K=1 for sphere like crystallites), λ is the wavelength and H_L stands for the

FWHM of the peak at 2θ . The Gaussian FWHM component of the peak shape in Scherrer's approach is directly relative to the micro-distortion.

The Williamson-Hall technique requires FWHM determination of each diffracted peak (*h*). The crystal size and micro-strains in Lorentz-like broadening equation are as follows:

$$\frac{\beta_h \cos \theta}{\lambda} = \frac{1}{R_h} + 4\varepsilon_h \frac{\sin \theta}{\lambda}$$

 β_h stands for the integral breadth of the peak in Lorentz model and is defined as equal to the surface of the peak divided by the peak maximum intensity. R_h stands for the mean crystallite size and ε_h is the micro-distortion in one particular direction of the sample. If the broadening contributions can be considered Gaussian-like, the equation below is used:

$$\left(\frac{\beta_h \cos \theta}{\lambda}\right)^2 = \frac{1}{R_h^2} + 16\varepsilon_h^2 \left(\frac{\sin \theta}{\lambda}\right)^2$$

For anisotropic crystal sizes and micro-strains, this should be done for every direction of the sample. For poly-phased materials, when the peaks overlap, Rietveld method is preferred. The Popa analysis by spherical harmonics approximation is used for the PZT analysis, thus this method will be briefly described.

The peak shape $\Omega_{i\Phi k}$ is approached by Pseudo-Voigt model which is composed by Gaussian and Lorentzian contributions. These contributions expressed in function of the peak internal breadth are:

$$G_{h}(k) = \beta_{Gh}^{-1} e^{\left(\frac{-\pi(2\theta_{h})^{2}}{\beta_{Gh}^{2}}\right)} \quad and \quad L_{h}(k) = \beta_{Lh}^{-1} \left(\frac{1}{1 + \frac{\pi^{2}(2\theta_{h})^{2}}{\beta_{Lh}^{2}}}\right)$$

with $\beta_{Gh} = 2 \tan \theta_{h} \sqrt{2\pi\varepsilon_{h}^{2}} \quad and \quad \beta_{Lh} = \frac{2\lambda}{3R_{h}\cos\theta_{h}}$

Considering R_h as a mean crystallite size in h direction, R_h can be developed in a convergent series of spherical harmonics, which coefficients are refinable parameters.

$$R_h = \sum_{l=0}^{L} \sum_{m=0}^{l} R_l^m K_l^m(\varphi, \chi)$$

In the same manner, the micro-strains are developed into series with coefficients that can be refined in CA software.

2.1.1.7. Refining strategy and reliability factors

Refining strategy in CA approach:

Refining the structure by CA approach involves following a particular strategy going from the most influencing parameters to the least influencing parameters:

- Scale factor + background 2 θ , ϕ and χ dependent
- Basic structural parameters : unit cell, atomic positions
- Texture
- Phase fractions
- Strains
- Microstructure parameters : mean crystallite size, macrostrains, defects
- Atomic occupations, thermal vibrations

Reliability factors:

In order to evaluate the refinement quality, several factors allow statistical comparison between measured profile and calculated model:

Reliability factor of the pattern: $R_p = \frac{\sum_i |y_{i0} - y_{ic}|}{\sum_i y_{i0}}$

Reliability factor of the weighted profile: $R_{wp} = \left[\frac{\sum_{i} w_{i0}(y_{i0} - y_{ic})^2}{\sum_{i} w_{i0} y_{i0}^2}\right]^{\frac{1}{2}}$

Here, y_{i0} stands for measured intensity, y_{ic} for calculated intensity and w_{i0} is weight, usually expressed as $\frac{1}{y_{i0}}$ assuming a counting variance $\sigma_i^2 = y_{i0}$.

The **Goodness of fit** χ is dissociated from the influence of the number of parameters to fit, the way they are linked and the number of observations.

$$\chi^{2} = \frac{\sum_{i} w_{i0} (y_{i0} - y_{ic} - y_{ib})^{2}}{(N - P + C)} = \left(\frac{R_{wp}}{R_{exp}}\right)^{2} \text{ with Expected reliability factor: } R_{exp} = \frac{R_{wp}}{\sqrt{\chi^{2}}} = \left[\frac{(N - P + C)}{\sum_{i} w_{i0} y_{i0}^{2}}\right]^{\frac{1}{2}}$$

The *N* and *P* stand for the amount of information used and the number of refined parameters and *C* is the number of applied constraints between the parameters. *X* should approach 1 for the exact fitting. In reality this value is larger. In Maud χ^2 is defined as σ .

After this detailed presentation of diffraction analysis tools, XRD experimental setups used in sample characterization will be described and compared.

2.1.2. XRD experimental setups

This section is dedicated to the description of two different setups used in XRD characterization of PZT films, namely *laboratory diffractometer reflection mode* and *ESRF transmission mode*. For both setups, X-ray generation techniques are explained and setup particularities from PZT thin film characterization perspective are pointed out.

2.1.2.1. Copper anode and reflection mode

In the laboratory diffractometer, the beam is produced inside of an X-ray tube. Its principle of functioning is illustrated in Figure II 35. The vacuum tube is composed of a positively charged Tungsten filament, which generates electrons and a negatively charged anticathode, usually made of Copper or Molybdenum. Here, we use a Copper anticathode. Electrons are emitted from the filament towards the anticathode thanks to the high potential difference between them.



Figure II 35 : Illustration of X-ray tube [23]

During collision with the target, kinetic energy of high-velocity electron beam is mostly dissipated as heat. Only about 1% of the total energy is at the origin of X-rays emissions, namely **Bremsstrahlung** and **Characteristic X-ray emission** of the target material (Figure II. 36).





Bremsstrahlung emission is created during the hard braking of electrons, when striking with the atoms of the target. The kinetic energy of electrons eV, is transformed to the radiant energy of X photons hv, such as hv is strictly inferior to eV. The continuous spectrum of emitted photons is a distribution of wavelengths λ strictly superior to λ_m . Note that λ_m is the maximum wavelength and it

is defined as equal to $\frac{hc}{eV}$. The spectrum shape is always the same. It is initiated at λ_m with the maximum at approximately 1.5 λ_m .

Characteristic X-ray emission is produced when electrons have enough energy to knock an orbital electron out of the inner electron shell of the atom from the target. Electron from higher energy level then fills up the vacancy and X-ray photon is emitted. This process results in emission of few discrete rays, which are characteristic of the target element. These rays are corresponding to the allowed high energetic electron transitions. Thus, the M_{III} -K, M_{II} -K, L_{III} -K and L_{II} -K shell transitions are corresponding respectively to K β 1, K β 2, K α 1 and K α 2 rays.

The next part will be focused on diffraction set-up description and its advantages and disadvantages regarding PZT thin film characterization.

XRD setup



Figure II. 37 : XRD characterization setup in laboratory diffractometer

The diffraction measurements are achieved with a four circle X-Pert Panalytical diffractometer, in reflection geometry (Figure II. 37). A series of aperture slits are installed in the path of incident X-ray beam to define divergence angle and width of the incident beam, namely the polycapillary lens as primary optics and a crossed slit collimator with an aperture of $2 \times 2 \text{ mm}^2$. On the path of diffracted X-ray beam, aperture slits determine angular resolution. In addition to the parallel plate collimator, the secondary optics was composed with a flat-graphite monochromator in order to avoid K β rays and a proportional point detector. During characterization, intensity of diffracted X-ray beam is measured with detector while sample and detector are changing angles in the rotational system, according to the specific XRD mode. Finally, intensity is recorded as a function of those angles. The figure below (Figure II. 38) illustrates the angles related to the sample that are likely to be changed during alignment and characterization. Note that 2θ angle is relative to the detector position.

The most used XRD modes for PZT thin films characterization are: ω scan called "the rocking curve", χ and ϕ scans used for pole figures acquisition and $2\theta/\omega$ symmetrical mode used for in-plane and out-of-plane structural characterization.



Figure II. 38 : Crystallographic angles in the rotation system of the diffractometer.

 ω scan is the mode where incident and diffracted beams rotate simultaneously in the same direction. Referring to Figure II. 38, ω scan implies changes in ω angle, while 20 remains constant. This mode is primarily used to analyze crystalline quality of the film in terms of mosaicity, misorientation and inhomogeneity.

Pole figure can be regarded as a series of φ scans with χ angle varying from 0 to 90° and covering a semi-spherical surface. Meanwhile, 2 θ and ω angles are set to see one particular crystallographic plane. Thus, the pole figure might be associated to the cartography of specific crystallographic planes in space. Results can be visualized in a 2D image as illustrated in the figure below (Figure II 39).



Figure II 39 : Pole figure of (100) oriented, fiber-textured PZT thin film

20/ ω is the mode that simultaneously rotates 20 and ω angles while keeping $\theta = \omega$. If χ is kept equal to 0 during scanning, the scattering vector Δk is always along the normal direction of the film surface. In this manner, the reciprocal vector and the lattice constant in the out-of-plane direction are analyzed. If χ is nonzero, the scattering vector Δk is no more along the normal direction of the film surface but it can take all directions between 0 and 90° depending on χ . This allows characterizing the

crystallographic planes between out-of plane direction, corresponding to $\chi=0^{\circ}$ and in-plane direction, corresponding to $\chi=90^{\circ}$. It is very useful for measuring stress and verifying the sample texture. Moreover, it gives an idea of the in-plane dimensions of crystallites.

 $2\theta/\omega$ acquisitions for χ and φ varying respectively from 0 to 90° and from 0 to 360° are necessary to perform a fine Combined Analysis (CA) of crystalline structure, especially if one does not have any clue of the material structure. Typically, with 2.5° angular step for χ and φ and with $2\theta/\omega$ acquisition going from 20° to 105° at each point taking about one hour, the complete data acquisition would take over 200 days in the laboratory diffractometer. This is practically impossible. Thus, to collect CA like data, one has to have some basic knowledge about the sample structure and texture in order to decrease the quantity of required data. For example, the studied PZT thin films have (100) fiber texture, thus once aligned to the fiber axis, the structure is symmetrical with respect to φ axis and data can be collected with φ constant. As for χ axis, other phenomena occur, which shorten the χ angle acquisition range, namely the beam defocusing effect.

The defocusing effect is due to the sample flatness. As χ increases, the beam is more and more spread over the sample surface, which causes peak broadening (Figure II 40). Note that for bulk samples, the increase of irradiated area is compensated by greater beam absorption. The diffracted volume is just the same. Thus, the surface of the peak is equal and independent of χ . In order to have unbiased intensity, one has to integrate the broaden peak. Note that peak broadening effect can be partially decreased by using analyzer or parallel plate collimator placed in front of the detector.



Figure II 40 : Defocusing effect in the reflection geometry illustrated for the $2\theta/\omega$ acquisition mode for two sample positions corresponding to $\chi=0$ and $\chi>0$. Z_A stands for the sample surface normal [17]

As the peak broadens, the maximum intensity goes down and depending on the slit aperture, only a part of the peak might be seen by detector. Consequently, the peak intensity is lower than it theoretically should be. Even if one integrates the full broaden peak, the compensation cannot reach χ =90° because the beam goes partly out of the sample at this angle. As a matter of fact, the defocusing phenomenon prevents the compete measurements. The measurable zone is typically above χ =60°. This shortens the AC measurement time to only 24 hours. Note that as χ does not go below 60°, the in plane peaks are impossible to visualize.

There is another phenomenon that is worth mentioning, when analyzing flat and thin materials such as PZT films in reflection geometry, which does not occur in bulk samples. The diffracted volume of thin film is not constant in function of χ and ω . While irradiated area changes in function of χ and ω , the penetration depth remains the same since the beam crosses the whole film thickness. Note that the absorption length a_1 of K α 1 Copper ray vertically arriving on the surface of PbZrTiO₃ is 4.9 µm. a_1 stands for the depth into material, measured along the surface normal, where intensity of X-rays falls to $\frac{1}{e}$ of its value from the surface. The figure below (Figure II 41) shows the variation of the penetration depth in function of χ and ω angles.



Figure II 41 : Penetration depth of the X-rays in function of ω and χ rotation of the sample

Another phenomenon that biases recorded intensities of diffracted peaks is the layered structure of PZT capacitor. In reflection geometry the beam firstly hits the top electrode, where it diffracts and is partially absorbed. Then it continues diffracting and being absorbed in PZT layer and finally in Pt layer and Si substrate. Moreover, absorption of superior layers varies in function of incident angle of the beam, because their thicknesses seen by the beam are different. Thus, relative intensities between collected diffracted peaks are incorrect.

In many programs diffraction volume and absorption corrections are handled for various experimental geometries and in function of sample dimensions and position (see the section 2.1.3. about Absorption correction factor). For instance, MAUD diffraction analyzing program takes care of these effects, if of course the input parameters relative to the sample geometry are correctly informed.

2.1.2.2. ESRF beam and transmission mode

Another set of XRD experiences on PZT thin films were run upon proposal in European Synchrotron Radiation Facility (ESRF). Synchrotron is a powerful source of X-rays, which uses the principle of

energy emission from accelerated electrons. Electrons are emitted from an electron gun and preliminary accelerated in the linear accelerator and in the synchrotron booster, until they reach 6 GeV. Then they are injected to the storage ring. Note that booster refills the storage ring several time per day. As the electrons travel around the ring, they pass through some auxiliary components such as bending magnets (BM) and undulators, called also insertion devices (ID). They are illustrated on the figure below (Figure II 42). These components change electron beam direction, which generates X-rays. The beam is then directed to the beam-lines carrying the name of their supplying component.



Figure II 42 : Schemes of Insertion Device on the left and Bending Magnet on the right, bending electron beam and producing X-rays [24].

The first role of the beam-line is to adapt the beam coming from the storage ring. Specialized mirrors and crystal optics may be used to focus the beam and to select the desired radiation energy. ESRF scientists are working with monochromatic and white beams going from 10 to 120 keV. Diffraction experiences take place in the experimental hutch, where the beam arrives and samples and detectors are mounted. The experimental hutch is externally controlled from the control cabin.

XRD setup

Diffraction measurements on PZT samples were performed on ID11 beam-line in transmission geometry. For our experiment, high energy X-ray nano-pencil beam was used with high z-axis resolution. In this manner PZT in plane microstructure and chemical Zr/Ti gradient can be observed. These particular beam properties could be achieved thanks to 100 m-long focusing line with two vertical focusing lenses as illustrated in Figure II 43. The first is placed 60 m from the source and the second about 20 cm before the sample stage. Thereby, the beam vertical size could achieve 100 nm, while the horizontal size was about 50 microns. Greater horizontal size enables to have a good crystalline statistics.



Figure II 43 : ID11 beam line focusing setup with two refractive lenses

This beam-line characteristics and this particular setup are needed for measurements involving a vertical scanning of the thin film cross-section. The main goal of this experiment is to reveal the Zr/Ti chemical gradient impact on the crystallographic structure of the sample. Since the expected chemical gradient is 300 nm wide, the nano-pencil beam is needed. Hard X-ray beam of cca 50 keV is chosen in order to collect high order diffraction lines on the CCD camera. The used camera is a 14 bit

dynamic FReLoN CCD camera with a 2048 per 2048 pixel chip, with 14 μ m-wide pixels. A fluorescence detector is used to ease sample alignment and to collect the chemical profile from the sample cross-section. In order to properly align the PZT capacitor with the nano-pencil beam, a piezo-stage is mounted above the sample holder, allowing a nanometric control of sample z position. This experiment could not be achieved using only laboratory diffractometer. All elements of diffraction measurement setup are summarized on the figure below (Figure II 44).



Figure II 44 : Scheme of the main components of the diffraction setup on ID11 beam-line

2.1.3. Setup comparisons

The following section will focus on main differences between ESRF and laboratory diffractometer setup. Advantages and disadvantages from PZT film characterization point of view will be discussed.

2.1.3.1. ESRF vs X-ray tube

Brilliance is an important gauge of X-ray source quality. It accounts the number of photons produced per second, angular divergence of photons, beam cross sectional area and photons falling within a bandwidth of 0.1 % of the central wavelength of frequency. In practice, the greater the brilliance, the more photons are concentrated on a spot. Brilliance of ESRF beams is 10^{20} photons/s/mm²/mr²/0.1%bw, whereas the X-ray tube beam brilliance is only 10^7 (Figure II 45).



Figure II 45 : Comparison of X-ray source average brilliance [25]

High brilliance and CCD camera of ESRF beam-line enables huge time saving. Experiences that would take hundreds of days in diffractometer laboratory, take several minutes in ESRF.

2.1.3.2. Transmission mode vs reflection mode

Another advantage of ID11 beam-line is transmission experimental setup. As explained in the previous section, reflection XRD mode does not allow seeing in plane crystallographic structure because of beam defocalisation on the flat sample surface and because of sample shadowing on the detector, for χ close to 90°. However, in-plane data provides valuable information about the microstructure by completing the film texture and enabling verification and better quantification of crystallographic phases composing complex samples such as PZT thin film. Transmission mode allows seeing crystallographic structure in 360° according to χ angle and thus analyzing texture, strain and crystallite dimensions of our PZT layer (Figure II 46). After image de-texturation by simple χ -integration of the image, we can lower the texture effect on the diffracted data and perform quantitative phase analysis.



Figure II 46 : CCD image of PZT taken in sample cross-section from ID11 (a) and image of the diffraction setup (b). Note that ψ =0° corresponds to the out-of-plane axis and ψ =90° corresponds to the in-plane axis.

Table II. 12 provides a summary of transmission and reflection mode comparison.

Transmission mode ESRF	+	Fast acquisition Easy handling of diffracting volume No parasitic peaks from electrode layers Small instrumental function
	-	Smaller precision on d-spacing
Reflection mode	+	Better precision on d-spacing
Laboratory	-	More complex
		Longer acquisitions

Table II. 12 : Summary of advantages and disadvantages of both transmission and reflection modes.

2.1.4. In-situ XRD

Both ESRF and laboratory diffractometer setups were used for in-situ XRD characterization of PZT capacitors under electric field. These experiments required specially prepared PZT capacitors (Figure II 47) wired to a DC voltage source able to deliver continuous voltage between -30 to 30 V.

The sample for in-situ XRD in reflection mode performed in laboratory was a 7x7 mm² cleaved chip carrying 5x5 mm² PZT capacitor. The access to the bottom electrode was provided with a Silver paste, deposited on the chip border. Wiring was performed using deported contacts. Figure II 47 a shows golden 38 μ m-thick wires connecting capacitor electrodes to the PCB (printed circuit board) support, which holds the capacitor. Then thicker, isolated wires connect the PCB to the voltage source with a pair of crocodile clips.

a.





Figure II 47 : Prototype samples for in-situ XRD: laboratory diffractometer sample (a) and ESRF sample (b)

b.

In-situ XRD in transmission mode performed in ESRF requires the X-ray beam to cross the sample, thus the prototype is more innovative (Figure II 47 b). The capacitor is L-shaped and entirely fabricated by clean room technique, in order to avoid short-circuits that are likely to occur by cleaving or grinding the wafer. The capacitor is from 200 to 400 μ m-large and 1 cm-long. In addition to Ru top electrode, a golden electrode was deposited on the sample surface, so as to promote adhesion of golden wires. Microscopic wires were connected via ultrasound bonding machine as described in the Chapter II part 1, dedicated to the sample preparation techniques. The connection to the voltage source was made with thicker, isolated wires.

2.2. TEM precession and SIMS characterization

Although X-ray diffraction is the main technique used to characterize PZT films, other characterization techniques of valuable contribution to PZT microstructure study should not be forgotten. Here, precession electron diffraction for local structure determination and secondary ion mass spectrometry for the composition profile verification, are shortly presented.

2.2.1. *Precession electron microscopy*

Electron diffraction (ED) is used to study crystal microstructure in a very similar way than X-ray diffraction. Its limitation in comparison to X-rays is the resolution. The precision on the unit cell dimension for ED is about 5*10⁻³ nm, while it is about 10⁻⁴ nm in case of XRD. The main advantages of ED in comparison to X-rays are stronger scattering and possibility to study very small crystals. Note that it is difficult to solve the structure with ED data from bulk crystals because of multiple scattering due to dynamic diffraction of electrons. There are algorithms, which enable to solve the atomic structure reliably, but high quality intensities are required. This is usually very challenging. Precession technique is a powerful method of improving the quality of electron diffraction data making them look kinematic like. Note that kinematic diffraction means that the diffracted beam is not intense enough to re-diffract once more. This is typical for the majority of X-ray diffraction cases.

Precession means motion of rotation axis of a rigid body describing a cone. During beam precession, the beam is tilted and it precesses at high frequency though the optical axis on a conical surface (Figure II. 48).



Figure II. 48: Precession electronic diffraction scheme [26]

The crystal is not moving, but Ewald sphere is precessing around the optical axis. Therefore many (hkl) intensities far away in reciprocal space appear with intensities integrated over the excitation error and the data look similar to kinematic diffraction data (Figure II. 49). Note that precession ED is usually installed in Transmission Electron Microscopes (TEM).



Figure II. 49: Scheme of the beam and Ewald sphere tilt resulting in (hkl) peak integration and therefore better resolution [27].

The main advantages of precession over classic ED are reduction of slight misorientations of the sample, more completely recorded reflections, more spots intercepted by Ewald sphere and easier structure solving thanks to the kinematic-like diffraction.

Advantages regarding PZT thin films are related to the local aspect of the analysis, which is complementary to the statistic-like analysis of X-rays. Precession ED is able to give information about crystal orientation, texture and distinguish crystallographic phases.

PZT has 100 nm-high columnar grains, containing crystallites of about 20 nm. In order to avoid the grain superposition, a 60nm-thin lamella was cut from the wafer (Figure II. 50). The lamella was then used for the precession ED on Jeol 2010 FEF microscope. Note that in case of grain superposition, indexation of crystallographic planes is not reliable unless one grain contributes much more than the others.



Figure II. 50: SEM images of PZT lamella prepared by Focused Ion Beam (FIB) for precession observation. Lamella is 1 μ m long and from 60 to 80 nm thin.

2.2.2. SIMS characterization

Secondary Ion Mass Spectrometry (SIMS) is the characterization technique that enables to establish the chemical composition variation in function of the layer thickness. The sample to analyze is locally abraded with Cesium ions. Then sputtered atoms and molecules from the layer are progressively ionized, accelerated and analyzed in a mass spectrometer, where their composition is defined. PZT sol-gel is known to possess a Zr/Ti composition gradient through the film thickness (Chapter II. 1.1.2.2.). Thus we use SIMS in order to characterize this gradient.

To summarize, the second part of Chapter II presents microstructure and chemical characterization techniques employed to study PZT thin film. X-ray diffraction is very rich in information that is averaged to the millions of crystallites of the PZT layer. It gives a global view of the material texture, stress, crystallite size and involved crystallographic phases. Precession electron diffraction gives a more confined point of view of the material, which completes XRD results. Finally, SIMS characterization provides information about chemical composition of PZT film.

Microscopic structural and chemical characterizations are interesting because they allow seeing the inside of the material and they help to understand the essence of material functioning. Now we will complete these microstructural characterizations with electric and piezoelectric characterizations of different MPB PZT thin films.

3. Electric and piezoelectric characterization

From industrial point of view, the most important matter is material performances for real applications. In case of piezo-MEMS industry, it is the material capacity to polarize, to resist to the voltage and to transform electric energy to deformation and vice versa. In order to compare MPB PZT properties, a set of electric and piezoelectric measurements were run on all our samples. AixACCT society, based in Aachen in Germany, is specialized in conception and production of electric and piezoelectric thin films. They propose efficient modules enabling characterization of PZT films. These modules will be detailed in following parts of this chapter.

3.1. Electric characterizations

In this section, electric parameters describing PZT performances and the corresponding measurement set-ups are presented. The first parameter characterizing a dielectric material is the relative dielectric permittivity, ε_r . Therefore, the beginning of this section is dedicated to ε_r and to its dispersion dependency. Then polarization measurements and voltage stress measurements are presented.

3.1.1. Dielectric permittivity measurements

PZT is a dielectric material composed with small crystallites. Dielectric means that when submitted to electric field PZT will polarize rather than conduct electricity. Unlike perfect dielectrics, PZT has a spontaneous polarization, which means that it is polarized even if no electric field is applied. This polarization results from misalignment of barycenters of positive and negative charges in PZT unit cell. Thus PZT crystals can be associated to electric dipoles carrying the spontaneous polarization. When an external electric field is applied, dipoles try to align with the direction of the field so as to decrease the free energy [28]. Unlike pyroelectric materials, where spontaneous polarization value is unchangeable, in ferroelectrics like PZT, polarization changes in function of applied electric field. The polarization value in one direction can be associated to the number of dipoles heading in that direction per unit of volume.

The parameter that reports the ability of material to polarize is the dielectric permittivity ε , or the relative dielectric permittivity ε_r . The following equations express the relationship between dielectric polarization density **P**, applied electric field **E**, dielectric permittivity ε , relative permittivity of the material ε_r , electric permittivity of the free space constant ε_0 which is equal to 8,854.10⁻¹² F/m and electric susceptibility χ , in an isotropic medium.

$$P = \varepsilon_0 \chi E$$

with $\chi = \varepsilon_r - 1$ and $\varepsilon = \varepsilon_0 \varepsilon_r$

If the medium is anisotropic, polarization, electric field and relative permittivity become a second rank tensor. In case of MIM capacitors, ε_r corresponds to ε_{r33} because the permittivity is measured between two electrodes along the perpendicular axis to the capacitor plane. Practical way to determine ε_r is the capacitance measurement with an impedance meter. Permittivity is related to

capacitance **C** through geometry of the MIM capacitor, which is equivalent to a simple parallel-plate capacitor:

$$C = \varepsilon_0 \varepsilon_r \frac{A}{d}$$

Note, that **A** stands for capacitor surface and **d** for the distance between two capacitor electrodes.

3.1.1.1. LRC meter vs AixACCT Systems

Dielectric characterizations were performed firstly on LCR meter HP 4194 and then on AixACCT apparatus. For the sake of clarity, the characterization method is explained on example of LRC meter. LRC meter applies to the capacitor a signal composed with dc bias V_{DC} and ac voltage V_{AC} with frequency f as follows:

$$V_{TOT} = V_{DC} + V_{AC} \sin(2\pi f t)$$

Then LRC meter measures complex voltage \tilde{V} and complex current \tilde{I} passing through the testing capacitor. The complex impedance is determined from the ratio of these two values:

$$\tilde{Z} = \frac{V}{\tilde{I}}$$

LRC meter is the test equipment used to measure capacitance or inductance and resistance. One or the other, results depend on assumptions made on the circuit model (Figure II. 51). Depending on measurement frequency and hypothesis on device losses, one can choose series circuit model (Cs-Rs) or parallel circuit model (Cp-G). In series circuit model, real and imaginary parts of impedance \tilde{Z} are represented respectively by resistance **R** and reactance **X**. In parallel circuit model, admittance \tilde{Y} is usually represented and its real and imaginary parts are respectively conductance **G** and susceptance **B**. Note that admittance is the inverse of impedance. Equations below give real and imaginary parts of \tilde{Z} and \tilde{Y} for capacitors:

$$\begin{split} \widetilde{Z} &= \frac{\widetilde{U}}{\widetilde{I}} = R + jX = R_s - \frac{1}{2\pi f C_s} j \\ \widetilde{Y} &= \frac{\widetilde{I}}{\widetilde{U}} = G + jB = G - 2\pi f C_p j \end{split}$$

Small capacitance and large measurement frequencies result in large reactance X. In this case series resistance **Rs** (Figure II. 51) might be negligible and therefore parallel model (Cp-G) should be applied. This is the case of PZT films. Otherwise, for large capacitance and small measurement frequencies, the series model (Cs-Rs) should be chosen.

Logically, for the inductance measurements, this reasoning gives reverse conclusions.



Figure II. 51 : LRC circuit and the choice of circuit models in capacitor reasoning.

RLC meter gives also the values of dissipation factor D, called loss tangent $tan(\delta)$. It is defined as tangent of the difference between phase angle of perfect and real capacitor. Usually it is multiplied by 100 to be expressed in percentage.



Figure II. 52 : Graphical representation of complex impedance [29]

Using graphical representation of complex impedance (Figure II. 52) and knowing that the perfect impedance is associated to the pure reactance, D is also defined as follows:

$$D = \frac{R}{|X|} = \frac{G}{|B|}$$

Note that LCR measures the quality factor Q, too. It is defined, as the reverse of the dissipation factor.

The functioning of the **AixACCT Measurement System** is represented on the Figure II. 53. The Graphical User Interface (GUI) pilots the Measurement Service (MS). The MS controls the Measurement Hardware, interprets all responses and informs the GUI of the results. MS runs on a variety of different configurations in order to give access to different type of measurements. Its measuring method is similar to the method of LRC meter but more automatic.

AixACCT Measurement Systems



Figure II. 53 : Structure of AixACCT measurement system

CVM mode is one of the small signal response measurement modes on AixACCT Systems. It gives capacitance and loss tangent in function of applied voltage in the same way as LCR meter. The input parameters are basically the same as for LCR meter, namely dc bias, ac voltage and frequency. One can choose between continuous triangular or sinusoidal, or non-continuous staircase dc bias modes. In the staircase mode, voltage is applied in consecutive unipolar excitation signal pulses. These pulses are biased dc voltage pulses with a sine wave of ac small signal. Consequently the whole hysteresis loop can be described. The capacitance and loss tangent are then calculated from AC small signal current response of the sample.

Usually capacitance versus voltage measurements for our 1 μ m-thick PZT capacitors are performed from -25 V to 25 V with ac sine signal frequency from 1 to 5 kHz and amplitude going from 50 to 100 mV. Figure II. 54 shows a typical ϵ_r vs voltage response of PZT thin film capacitor.



Figure II. 54 : Relative dielectric permittivity of PZT ferroelectric film in CVM mode.

3.1.1.2. Permittivity dispersion dependency

Sources of positive and negative charges within dielectric material such as PZT are miscellaneous, going from the ferroelectric domain walls movement, dipolar and trapped charges' vibrations, to the atomic displacement and relative movements between electrons and nuclei (Figure II. 55). These various sources have different response times to electric field. Therefore, material polarization is not instantaneous and it is **frequency dependent**. As reported before, the parameter that describes the ability to polarize is dielectric permittivity ε . Debye model is commonly used to describe dielectric relaxation of ideal, non-interacting dipoles to an *ac* electric field. It is expressed as follows:

$$\hat{}(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{1 + j\omega\tau}$$

 $\hat{\varepsilon}$ is a complex dielectric permittivity, ε_{∞} stands for the permittivity at high frequency, $\Delta \varepsilon = \varepsilon_s - \varepsilon_{\infty}$, where ε_s is low frequency permittivity, ω is angular frequency of electric field and τ is the characterization relaxation time of the dielectric.

$$\hat{\varepsilon} = \varepsilon' + j\varepsilon''$$

The equation above shows that dielectric permittivity is a complex value with a real part ε' , which is related to the stored energy within the medium and an imaginary part ε'' relative to the dissipated energy.



Figure II. 55 : Dielectric permittivity evolution in function of frequency in a dielectric [30]

3.1.2. Polarization measurements

There are three methods for polarization measurement of ferroelectric capacitors by current response, namely Sawyer Tower [31], Shunt and Virtual ground method. The forth method applies an excitation current and measures the voltage drop. It is called Current step method. Each of these methods is shortly described in next paragraphs.

The principle of **Sawyer Tower method** (Figure II. 56) is charge measurement across a reference capacitor C_{ref} , mounted in series with the test capacitor C_{test} . An oscilloscope measures applied ac voltage with one channel (V1) and the voltage drop in the reference capacitor with the second channel (V2). V2 is proportional to the accumulated charge on the test capacitor through the charge conservation on an isolated conducer.



Figure II. 56 : Illustration of a Sawyer Tower circuit [32]

Then polarization of the reference capacitor is calculated as follows:

$$P = \frac{Q}{A} = \frac{C_{test}V_{test}}{A_{Ctest}} = \frac{C_{ref}V_2}{A_{Ctest}} \qquad \qquad E = \frac{V_1 - V_2}{t_{Ctest}}$$

Note that Q stands for charge, A for area and t for thickness of the tested capacitor. The reference capacitor has to be 20 to 30 times greater than the tested capacitor, in order to be negligible when connected in series.

Shunt method is very similar to Sawyer Tower, but instead of a reference capacitor, one uses a reference resistor, called shunt resistor. The voltage drop across the shunt is proportional to the current flowing through it and since the value of resistance is known, current is easily calculable. Finally, polarization charge is obtained through current integration.

$$Q = \int i dt$$

Virtual ground method is using a current-to-voltage convertor build on an operational amplifier with a feedback resistor on a virtually ground level. Similarly to Shunt method, it requires a current integration over time, too. However, no reference elements are needed.

Unlike previous methods, **Current step method** uses an applied current as excitation signal. This current induces a voltage drop over the sample. Therefore, in order to perform the measurement, no additional reference elements are required. AixACCT uses this method too.

Sawyer Tower method and DHM module on AixACCT System were used for polarization characterization on PZT thin films. Measurements were performed with sine and triangular excitation signal of -25 V to 25 V with frequency of 1 kHz. Ferroelectric materials such as PZT, have a very typical polarization curve shape called ferroelectric hysteresis loop Figure II. 57.



Figure II. 57 : Polarization ferroelectric loop vs voltage in PZT thin film capacitors

From polarization hysteresis loop, one can read three important components characterizing the polarization abilities of a ferroelectric, namely coercive voltage **Vc**, remnant polarization **Pr** and saturated polarization **Ps**. Coercive voltage is the voltage at zero polarization. Remnant polarization is the remaining polarization at zero voltage and saturated polarization is the polarization maximum or minimum.

3.1.3. LRVS

Linear ramp voltage stress (LRVS) test is the reference measurement evaluating capacity of a device to resist to an applied voltage. Electric field ramp used to qualify PZT samples was 0.1 MV/(m.s). For 1 μ m-thick sample the voltage ramp is 100 mV/s. All samples were tested in voltage range from 0 to 100 V and their Break Down (BD) voltage was identified. PZT capacitors surface was 500x500 μ m² large. Measurements were performed on a Cascade probe station connected to Agilent 4156C semiconductor parameter analyzer. Agilent is performing a variety of electric measurements among which I-V characteristics.

3.2. Piezoelectric characterizations

This section is dedicated to direct and inverse piezoelectric effect characterizations. Transverse effective piezoelectric coefficient relative to the direct effect, $e_{31,eff}$, and longitudinal effective piezoelectric coefficient relative to the inverse piezoelectric effect, $d_{33,eff}$, are the reference coefficients to compare piezoelectric performances of clamped thin films. Hereafter, we present measurement techniques for $e_{31,eff}$ coefficient extraction, namely Four-Point Bending modulus (4PB) [33] and $d_{33,eff}$ coefficient measurement using Double Beam Laser Interferometer modulus (DBLI) [34]. Both testing units are provided by AixACCT Systems Company. Note, that $d_{33,eff}$ allows comparison with XRD in-situ results because in both characterizations techniques the same converse piezoelectric effect is observed.

3.2.1. Direct piezoelectric effect

Transverse effective piezoelectric coefficient of direct piezoelectric effect, e_{31} is linearly linking applied mechanical stress to electric response of piezoelectric material. This relationship is shown in equation below (see Chapter I. 1.2 for more details about piezoelectricity).

$$T_{ij} = c_{ijkl}^E S_{kl} - \boldsymbol{e_{kij}} E_k$$

Here, **T** refers to mechanical stress, **c** is elastic stiffness at constant electric field, **S** stands for applied mechanical strain and **E** is electric field. The difference between e_{31} and $e_{31, eff}$ coefficients is that $e_{31, eff}$ applies to clamped films, where we cannot distinguish e_{33} coefficient contribution. $e_{31, eff}$ equals to $e_{31} - e_{33*}(c_{33}^{e_{13}}/c_{33}^{e_{33}})$ [35, 36].

In order to determine e_{31, eff}, we collect electric charges generated when material deforms. The measurement principle is a classical 4-point bending test adapted to thin films deposited on stiff substrates, usually Si. Figure II. 58 illustrates the measurement apparatus. A well-known mechanical force is applied to the sample through the outer two supports. This induces a homogeneous longitudinal stress and strain distribution between the inner two supports. The sample displacement is recorded by a single beam laser interferometer. Electric charges produced by sample deflection are harvested by the outer two supports.



Figure II. 58 : Outline of Aixacct 4PB tool [33]

The bending sample is a particularly designed cantilever containing substrate and PZT thin film , which is placed between two electrodes. Figure II. 59 shows the cantilever design and its specifications. Details of the sample fabrication are described in Chapter II. 1.



Figure II. 59 : Cantilever design and specifications for e_{31,eff} testing [33]

4PB system is controlled by TF Analyser. This software is sending orders to mechanically load the sample, it records samples response and calculates $e_{31,eff}$ coefficient according the following equation:

$$e_{31,eff} = \frac{Q}{A} \frac{\left(\frac{l}{2}\right)^2 + u^2}{hu(1 - v_{Si})}$$

Q refers to collected charges, **I** is bending distance, **A** is electrode area, **h** stands for cantilever thickness, **u** is cantilever imposed displacement and v_{si} is Poisson ration of the substrate. In our case substrate is made of Silicon. As cantilever displacement is much smaller than bending distance, $e_{31,eff}$ can be simplified to following expression:

$$e_{31,eff} \simeq \frac{Ql^2}{4Ahu(1-\nu_{Si})}$$

Note that when using Silicon monocrystalline wafer, Poisson ration is strongly anisotropic and varies in function of crystallographic direction. v_{Si} is equal to 0.28 in <100> direction, whereas it is equal to 0.06 in <110> direction, which is the natural cleavage direction of Si. Therefore, one has to pay

attention and choose v_{Si} corresponding to the crystallographic orientation of cantilever substrate, after being cut from the wafer. Otherwise, a misestimation of 30% might occur.

3.2.2. Converse piezoelectric effect

Longitudinal effective piezoelectric coefficient related to converse piezoelectric effect, $d_{33,eff}$, linearly links applied voltage to the generated mechanical strain by equation below:

$$S_{ij} = s_{ijkl}^E T_{kl} + \frac{d_{kij}}{E_k} E_k$$

S stands for mechanical strain, **s** is elastic compliance at constant electric field, **T** refers to mechanical induced stress and **E** is electric field applied to the material. Note that $d_{33,eff}$ applies to clamped samples, where it is difficult to isolate d_{33} contribution alone. $d_{33,eff}$ is defined as $d_{33} - 2$ $s_{13}^{E}/(s_{11}^{E}+s_{12}^{E})*d_{31}$ [35].

AixACCT also developed an apparatus for $d_{33,eff}$ extraction, the Double Beam Laser Interferometry (DBLI) unit. In order to determine $d_{33,eff}$ coefficient, one has to measure the sample deformation in the direction of applied electric field. Note that DBLI unit performs differential measurements, which are provided by two laser beams. One is watching the sample from the top and the other from the bottom. Thus, theoretically only piezoelectric layer strain is considered. Substrate bending contribution and noise are absent from the measurement. Figure II. 60 summarizes DBLI measurement setup.



Figure II. 60 : DBMI measurement setup

However, it was experimentally observed that $d_{33,eff}$ varies with electrode size. In 2013, Sivaramakrishnan et al explained that intrinsic $d_{33,eff}$ is independent from electrode size, but substrate contribution is dependent on the relative size of electrode versus substrate thickness [34]. When this ratio becomes greater than 1, $d_{33,eff}$ is constantly overestimated, whereas ratio smaller than 1 leads to underestimation of $d_{33,eff}$. Substrate contribution vanishes when electrode size is about the same thickness as substrate. Note that these observations are related to Si substrate.

Conclusion

To conclude, the beginning of this chapter focuses on PZT fabrication technique. Sol-gel PZT fabrication is detailed and microstructural features resulting from this deposition method are presented and linked to material performances. Then we present the main PZT microstructure characterization technique, namely XRD. Its potential contributions to microstructural studies of PZT are listed. Afterwards, XRD analyzing methods are described and compared. The main diffraction setups used in PZT characterization, namely laboratory and ESRF setup, are illustrated and compared. Finally, electric and piezoelectric characterization methods and their principles are presented.

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Chapter III: Correlations between PZT thin film microstructure and piezoelectric properties

Introduction

The third chapter of this manuscript is dedicated to the detailed description of correlations between the microstructure of morphotropic sol-gel PZT and its macroscopic properties, namely piezoelectric. Firstly, we study the Zr/Ti chemical gradient effect on PZT microstructure across the thin film. Note that the cross-sectional microstructural observations were made possible thanks to the state-of-art nano-pencil beam from ID11 in ESRF. Special shaped samples were prepared for this occasion. This experiment is described and observation results are reported and discussed in the first section of this chapter.

We then focus on microstructural changes in PZT films under an electric field using in-situ X-ray diffraction (XRD). X-rays characterize PZT capacitor while it receives a continuous electric field. The experimental setup and acquisition programs are presented. The collected pattern is then analysed and microstructural modifications are quantified with the Maud program, assuming (001) texture for both tetragonal and rhombohedral crystals at 0V. Afterwards, piezoelectric measurements are performed on the probing sample, more specifically, the longitudinal piezoelectric coefficient $d_{33,eff}$ is determined. The measured value of $d_{33,eff}$ is then compared to $d_{33,eff}$ estimated by in-situ XRD results.

The influence of Zr/Ti chemical gradient across PZT films on dielectric and piezoelectric properties is already known [1]. The more the sample is homogeneous and morphotropic, the better performances it manifests. Then the in-situ XRD shows a phase transition in PZT under voltage. Thus, the final part of this chapter is dedicated to the study of Zr/Ti chemical gradient's influence on the phase transition in sol-gel PZT thin films. Morphotropic PZT capacitors with different Zr/Ti gradients are prepared and examined by in-situ XRD and collected patterns are analysed by Maud. Then the XRD results are associated with the samples homogeneity and electro-mechanical performances. Correlations between microstructure and piezoelectric properties of PZT thin films are drawn.
1. Effect of the chemical gradient on the microstructure of PZT thin films

The Zr/Ti chemical gradient through the film thickness is the typical signature of sol-gel deposition method [2]. This gradient originates from the final thermal annealing of the deposited layer, enabling its crystallisation. As $PbTiO_3$ is more thermodynamically favourable than $PbZrO_3$ [3], it is the first to crystallize. Thus, the first crystals to be formed are Ti-rich. As the crystallisation occurs in the direction substrate-free surface, the part of the layer close to the substrate is Ti-rich [2]. Consequently, the last crystals to be formed are Zr-rich and they are located at the layer surface. Therefore, even if the initial precursor solution is of morphotropic composition, the PZT layer after crystallisation is likely not morphotropic through its entire thickness [1]. The detailed description of the Zr-Ti gradient phenomenon is described in Chapter II. 1.1.2.3.

In 2007, Calame et al. succeeded in overcoming the composition homogeneity problem using four different precursor solutions [1]. Moreover, the new homogeneous PZT film was more performant than its previous version. For example the dielectric permittivity of the PZT increased from 1400 to 1600 and the effective transverse piezoelectric coefficient $e_{31,eff}$ improved of about 45%.

Previously, it has been observed that performances of PZT films are closely linked to its microstructure. In particular, dielectric and piezoelectric performances are closely linked to PZT texture [4, 5]. Now, we see that PZT properties changes with Zr/Ti homogeneity, while layer texture remains the same. One could ask whether, or not, there is any microstructural involvement.

The best solution for statistical study of PZT microstructure is X-ray diffraction. However, the classical diffractometer setup involves a Cu anode, a mm-thick beam and a reflection diffraction mode, which averages information from the entire 1 μ m-thick PZT layer. This is not suitable for Zr/Ti gradient characterization. The best conditions to observe this gradient are cross-sectional film scan in transmission diffraction geometry and adapted beam dimensions. Logically, the probe has to be smaller than the characterized effect. Considering that the Zr/Ti gradient repeats every 360 nm, the beam should be no more than 120 nm-wide. In this way, at least three points may be collected in the thickness of one PZT layer during the vertical scan. In order to have the beam crossing the sample and a good focal depth, a hard X-ray beam is necessary.

Thanks to recent progress in X-ray optics, ESRF have developed a technology of a highly energetic, nano-focused, strongly asymmetric beam, thin film vertical profiling is now possible [6]. This technology is called the nano-pencil beam. The X-ray beam is vertically confined into about 100 nm allowing sufficiently small characterization probe for in-depth scanning. Horizontally, the beam is 50 μ m wide, which guarantees diffraction of enough grains to obtain satisfactory statistics. This beam is available on ID11 beamline.

We managed to have 9 shifts of beamtime at ID11 in the ESRF synchrotron. The main objective of the experiment was to characterize the Zr/Ti gradient effect on PZT microstructure. For this purpose, three special-shaped samples of different gradient amplitudes were prepared, namely the sample with gradient issued from standard sol-gel preparation called Standard Gradient, the sample with attenuated gradient called Gradient Free fabricated with three precursor solutions of different Zr/Ti composition and finally the sample with strengthened gradient called Amplified Gradient. The latter

is obtained using the same set of precursor solutions as for Gradient Free fabrication but inversely applied. The Amplified Gradient sample is studied purely to magnify the effect of gradient. The expected outcome from this experiment is mainly PZT phase analysis for each measured point in the PZT layer, in order to extract the phase variation versus film depth. In addition, this experiment enables us to locally confirm the (100) PZT texture and to determine the eventual stress and crystallite size distribution in the space.

For the sake of clarity, the first part of Chapter III, dedicated to the study of Zr/Ti chemical gradient effect on the PZT microstructure, keeps the following structure. Firstly, we present the samples and their elaboration. Then, preliminary SIMS characterization results are given, followed by dielectric and piezoelectric characterization of the three samples. Afterwards, the X-ray diffraction experiment is described, namely the XRD setup used and the data analysis. The final section of this part is dedicated to discussion.

1.1. Sample elaboration

The PZT layer elaboration by sol-gel technique has already been reported in detail in Chapter II 1.1. Note in particular Chapter II 1.1.2.3, which presents the three precursor solutions used in the fabrication of the three different PZT gradients characterized in this experiment. The Standard Gradient sample is made of the standard morphotropic composition solution, composed by 52% of Zr and 48% of Ti. The Gradient Free sample is made of three different solutions: the Zr-rich solution for the deposition of the first two layers, which is composed of 59% Zr and 41% Ti; the standard solution with a composition of 52/48 for the two middle layers and the Ti-rich solution consisting of 43% Zr and 57% Ti for the deposition of the final two layers of the six-layer period, followed by thermal annealing. Finally, the Amplified Gradient is composed of the same three precursor solutions as the Gradient Free, but their order of deposition is reversed. Note that the crystallization annealing is performed each time 6 layers have been deposited. This enables the enlarging of the Zr/Ti gradient up to about 360 nm.

In order to permit dielectric, piezoelectric and XRD characterizations of PZT, the full-sheet PZT wafers have been processed into devices. Chapter II 1.2 describes the device fabrication procedure. For dielectric and piezoelectric measurements, only the Ru top electrode needs to be patterned. PZT can remain full-sheet. The mask for Ru patterning is shown in Figure III. 61. Square-shaped electrodes are employed to characterize capacitance and polarization, whereas cantilevers are shaped for the transverse effective piezoelectric coefficient measurement $e_{31,eff}$ on the 4PB AixACCT apparatus (see Chapter II 3.2.1 for details). Note that the bottom electrode contact is provided by silver paste, gently spread on the sample's edge, short-circuiting the large top electrode on the right side of the cantilever represented in Figure III. 61.



Figure III. 61: The pattern of the photolithography mask for Ru patterning. The red dotted lines show how the chip is going to be cut.

In order to have better control of the PZT capacitor width for XRD characterization, PZT patterning is needed in addition to Ru patterning. Note that for this XRD experiment, the sample width is set to 200 μ m. This parameter happens to be a compromise between the beam absorption length in PZT, the nano-beam depth of field at the chosen beam energy and the substrate-induced stress release of the film, caused by PZT patterning.

With regard to a particular material, the beam absorption decreases while the beam energy increases. Thus, in order to get rid of the absorption problem, high energy X-rays are a good choice. However, a high-energy beam results in smaller depth of focus and it also involves large beam size, which is not suitable for this experiment. Thus, selecting a smaller sample width could enable the use of a less energetic beam and allow a small beam spot with reasonable focal depth. Nevertheless, samples with small dimensions cannot perfectly represent PZT thin film because of stress relaxation. Hereafter, some indications for resolving the problem are given.

Table III. 13 reports the beam focal parameters variation versus beam energy. The most suitable beam energy is 50 keV or lower due to the focal spot size and the focal depth.

Energy (keV)	Focal distance (mm)	Focal depth (mm)	Focal spot (nm)	
30	100.5	0.65	80	
40	99.7	0.45	100	
50	100.1	0.34	150	
60	124.0	0.30	250	

Table III. 13: Lens parameters versus beam energy [7]

PZT is quite a good X-ray absorbing material thanks to the presence of Pb. Figure III. 62 plots the X-ray absorption versus the beam energy for the 200 μ m-wide PZT sample. The 42 keV beam visualized by the vertical black line suits this sample condition perfectly.



Figure III. 62: The X-ray absorption versus the beam energy for 200 μ m-wide PZT [8]. The blue dotted line indicates the μ R value equal to 1. In transmission geometry, the ideal value of μ R is 1 or below, because the sample absorption is minimal and no corrections are usually needed. The red dotted line stands for μ R equal of 5. For μ R equal and higher than 5, the measurement is not possible in transmission geometry because of severe beam absorption by the sample. The black vertical line indicates the 42 keV beam energy. The corresponding μ R is equal to 0.94.

Note that for wider samples, the absorption curve is shifted to the right. Table III.14 shows the maximum sample width for optimal beam transmission through the sample versus beam energy. One can notice that the sample width rapidly decreases with the decrease of the beam energy. In order to use 30 keV beam, the sample should be less than 100 μ m-wide.

Beam Energy (keV)	Sample width (µm)		
30	80		
40	180		
50	360		

Table III.14: Beam energy versus maximum sample thickness for optimal X-ray transmission [8].

The stress release is estimated with a simplified model assuming isotropic elasticity and independence of the vertical position in the sample, z [9]. According to this model, the film stress $\sigma_{f,x}$ at the distance x from the sample edge, is correlated with Young's modulus E, and Poisson's ratio u of substrate s and film f through the coefficient K.

$$K = \frac{E_s (1 - v_f^2)}{E_f (1 - v_s^2)}$$

Given that samples were cut in <110> direction of Si, the elastic constants taken for the calculation are $E_s = 170$ GPa and $u_s = 0.06$ [10]. PZT elastic constants are considered isotropic in-plane with $E_f = 82$ GPa and $u_f = 0.39$ [11]. Therefore, K is equal to 1.75. The equation linking $\sigma_{f,x}$ to the distance from the sample edge has the following expression [9].

$$\sigma_{f,x(x)} = \sigma_0 - \frac{2h}{\pi K} \int_0^\infty \frac{\partial \sigma_{f,x}(u)}{\partial u} \frac{du}{x-u}$$

Here σ_0 stands for the stress of a fully clamped film and h is the film width. The equation can be solved using the method of finite difference and transformed to matrix form for the resolution [9]. Figure III. 63 shows the distribution of stress in function of the distance from the sample edge. Note that 30 µm from the sample edge, the PZT film stress is equal to 90% of the stress of a perfectly clamped film.



Figure III. 63: Distribution of the film stress σ_f versus distance *x* from the film edge. h stands for the PZT film width, here h is equal to 1µm.

As the sample width should be much higher than 60 μ m, the beam energies from 30 to 40 keV involving sample width from 80 to 180 μ m, were abandoned. The decisive parameter for the choice of the beam energy among the remaining energies, going from 40 to 50 keV, was the beam spot size. Finally, the beam energy was chosen to be 42 keV, having large depth of focus and about 100 nm-small beam size. This energy allows working with 200 μ m-wide samples, which is enough to ignore stress relaxation. The final sample pattern is shown in Figure III. 64.



Figure III. 64: SEM image of the PZT capacitor made for ESRF experience. The entire sample is 1500 µm-large and 540 µm-wide. There is a Focused Ion Beam (FIB) etched basin in front of the PZT capacitor. It is made to decrease the probability of the beam reflection from Pt layer.

The sample is then cut and glued with a UV glue to the edge of a bigger holder so that it can easily be manipulated during experiment.

1.2. Preliminary characterizations

Firstly, some preliminary measurements were run on all three PZT samples. The Zr/Ti gradient was verified by SIMS characterisation. Then, electric and piezoelectric characterisations were performed in order to check Calame's observation about the link between Zr/Ti gradient and PZT performances on our samples too [1]. The expected result is better dielectric and piezoelectric performances for smaller composition gradient.

1.2.1. SIMS characterization

The SIMS characterisation technique was described shortly in Chapter II. 2.2.2. This measurement was used to check the presence of Zr/Ti gradient through the film thickness.



a. Standard Gradient



Figure III. 65: SIMS profiles of Standard Gradient (a), Gradient Free (b) and Amplified Gradient (c) PZT films. For each concentration profile, the free surface of the sample is located on the left hand side and the substrate is on the right hand side.

SIMS profiles in Figure III. 65 show Zr, Ti and Pt concentration variations (except Figure III. 65 c). As expected, three Zr/Ti gradients are present in PZT films, corresponding to three crystallisation annealings. Note that Zr and Ti amounts vary inversely in these gradients. As explained before, this phenomenon is due to thermodynamics. The Ti peak located right after Pt (Figure III. 65 a and b) is due to the TiO_2 layer, which was deposited to enhance Pt adhesion.

1.2.2. Electric characterization

Capacitance versus voltage (CV) characterisation is often the first measurement verifying good functionality of the fabricated PZT. It enables us to determine relative dielectric permittivity ε_r , which represents the ability of a material to polarize. The three films were characterised using square surface capacitors of 1 mm². The characterization parameters were 1 kHz frequency, 50mV AC sine signal and ±25V DC bias. Measurements were performed on both HP 4194 and AixACCT apparatus as described in Chapter II. 3.1.1. Results of these measurements are reported in the table below (Table III. 15).

Then, the polarisation hysteresis (PE) characterization was carried out. PE enables the description of the polarization loop through three parameters, namely coercive field, saturated polarisation and remnant polarization. The three PZT capacitors were stimulated with a sine signal of $\pm 25V$ at the frequency of 1 kHz. These measurements were performed on AixACCT apparatus. Characterization details are described in Chapter II. 3.1.2. PE results are exposed in Table III. 15 too.

Finally, the LRVS (Linear Ramp Voltage Stress) measurements were performed, characterizing material capacity to resist the voltage. The experimental voltage ramp was 0.1 MV/(m.s). See Chapter II. 3.1.3 for more details about this characterization technique. Corresponding results are reported in Table III. 15.

Sample	C (nF)	Dielectric loss (%)	Dielectric permittivity	Coercive field (kV/cm)	Saturated polarisation (µC/cm²)	Remnant polarization (μC/cm²)	LRVS (BD) (kV/cm)
Standard Gradient	10.8	4.5	1235	36.6	34.9	15.4	760
Gradient Free	13.9	6.2	1568	37	37.1	18.1	400
Amplified Gradient	10.1	5.7	1143	38	34	15.3	490

Table III. 15: Table summarising electric characterisation results of PZT samples. Note that each given value is the mean value of three measurements, resulting from three different capacitors.

As expected, electric measurement results show that Gradient Free PZT has better dielectric permittivity and polarisation parameters. However, in terms of dielectric losses and break down voltage, Standard Gradient sample is more performant. Results from Gradient Free and Standard Gradient seem to confirm the McPherson law about dielectric permittivity and breakdown voltage dependence, based on thermochemical model [12]. According to the model, the predicted breakdown shows ~ $(\epsilon)^{-1/2}$ dependence. Here, Gradient Free PZT has higher dielectric permittivity than Standard Gradient. As for breakdown, Standard Gradient is more efficient than Gradient Free.

1.2.3. Piezoelectric characterization

Then piezoelectric characterization was performed on the three PZT compositional gradients. In particular, the effective transverse piezoelectric coefficient $e_{31,eff}$ was evaluated. These measurements were accomplished on dedicated cantilevers (Figure III. 61) using the 4PB modulus of AixACCT apparatus. This characterisation is described in more detail in Chapter II. 3.2.1. After the first series of $e_{31,eff}$ measurements, PZT cantilevers were polarised at 20 V during 30 min at room temperature. Then, measurements were repeated again and compared to previous results. No significant differences were observed. Afterwards, PZT cantilevers were polarized at higher temperature. They were rapidly heated to 200°C, left at this temperature for 30 min and then slowly cooled down at the rate of 1°C/min. During the whole operation a 20 V voltage was applied to samples. Then, the $e_{31,eff}$ coefficient was measured again. Table III. 16 sums up piezoelectric results for the three PZT composition gradients.

Sample	e _{31,eff} (C/m ²)	e _{31,eff} (C/m ²) 20V, 30min, room T	e _{31,eff} (C/m²) 20V, 30min, 200°C	
Standard Gradient	-8.3	-8.5	-14.2	
Gradient Free	-10.9	-11.0	-16.2	
Amplified Gradient	-6.7	-6.8	-7	

Table III. 16: The table summarizes the results of effective transverse piezoelectric coefficient measurement for three PZT gradients.

 $e_{31,eff}$ measurements show that Gradient Free sample possesses the best properties. Thus, it confirms that higher compositional homogeneity leads to better piezoelectric performances.

The preliminary measurements were performed in order to verify the presence of Zr/Ti chemical gradient in the probed samples, to check the samples functionality and to compare their electric and piezoelectric performances. As previously reported, the morphotropic phase PZT sample with the best compositional homogeneity exhibits the best electric and dielectric properties in terms of ε_r and $e_{31,eff}$ coefficient. The next section shows XRD measurements performed to characterize the local cross-sectional microstructure in PZT layer and to investigate microstructural inhomogeneity due to the presence of Zr/Ti compositional gradient.

1.3. XRD measurements

The three PZT compositional gradients were characterized by transmission X-ray diffraction through their thickness. The following section begins with the description of the setup of the experiment and the data acquisition strategy. Then, the data treatment and finally the experiment's results are presented.

1.3.1. Setup description

ID11 is a state of the art beamline in ESRF, included in its recent upgrade program. This beamline is 100 m-long, with two X-ray condensers used for beam focusing. The first is placed one third of the way along the line and the second several tens of cm before the sample. The first condenser leads to a significant increase in flux and suppresses harmonics, thanks to the chromatic aspects of focusing. The second condenser is nano-focusing the beam, giving its final shape. It is based on refractive optics [13].

The experimental parameters were 42 keV beam energy and approximately 100 nm-high and a 50 μ m-wide beam spot. Moreover, the beam focal distance was 10 cm and its depth of field was around 400 μ m. XRD characterizations take place in the experimental hutch, located at the end of the beamline. Our measurement setup was composed of a piezo-stage enabling very fine sample positioning, especially its vertical translation, an energy dispersive fluorescence camera for the sample alignment and chemical composition characterisation and a Frelon ESRF CCD camera for the diffraction data collection. This setup is illustrated in Figure III. 66.



Figure III. 66: The setup of the experiment at ID11. The setup contains the fluorescence detector, the CCD camera and the translation piezo-stage where the sample is placed. Note that the beam is arriving from the left-hand side.

The sample is finely aligned with the beam thanks to the piezo-stage and the fluorescence camera. Knowing the sample stack, namely the thickness of Pt and Ru layer, the precision of alignment is related to the real beam size on the sample. The latter is estimated by the deconvolution of the real thickness of the layer from the thickness seen by the fluorescence camera. The challenge is to find the smallest Pt and Ru layer dimensions seen by the camera. This setup position would correspond to the sample horizontally aligned to the beam and centred in the beam focus. Note that the best beam height obtained during our experiment was close to 140 nm.

Once the sample is aligned, it is vertically scanned with the X-ray beam, with 100 nm step size. Each image is collected using from 2 s to 10 s X-ray exposure, depending on the dataset number. Our recording strategy was firstly to collect sets of rapid shots and then eventually, if we had some spare time, to collect lengthier shots in order to have finer, clearer images. Thus the first images were recorded with short exposure and the latest with long exposures.

The 2D images were collected on the CCD camera, which was positioned in order to see the entire 360° Debye ring, until at least four ranges of (100) PZT diffraction peaks were clearly observed. Note that higher angle peaks enable an easier identification of tetragonal and rhombohedral PZT crystallographic phases, due to the more distant positions of peaks at high 20 angles. At the same time as XRD measurements were done, the fluorescence camera collects the fluorescence photons from the PZT cross-section for the chemical composition analysis.

1.3.2. Data exploitation

After collection, the data has to be corrected and transformed into a suitable form to be analysed by Maud refinement program. Here, the aim of data analysis is mainly quantitative phase analysis (QPA). PZT at morphotropic composition is theoretically composed of tetragonal, rhombohedral and monoclinic phase. The objective of the QPA is to determine the percentage of phases constituting the PZT layer. Then, the phase quantity evolution versus the depth of the layer is extracted.

Firstly, the detector calibration was performed in order to determine the direct beam position and to correct the non-orthogonality of the detector. The data correction, also called data reduction, was achieved with the newly available pyFAI python package [14]. This package takes into account the detector corrections and the used geometry to rectify the data.

Then, each XRD image was azimuthally integrated to transform the Debye rings into peaks as a function of 2 ϑ . In this manner, the intensity versus 2 ϑ can be plotted for each z position. Note that azimuthal integration of the Debye rings lowers the texture effect in the data. Thus, one can try to perform quantitative phase analysis in the similar way as polycrystalline samples. Indeed, it is easier to refine phases without dealing with the texture effect related to each phase.

Following this, the intensity versus 20 profile was analysed using Maud refinement program [15]. The input parameters for this study were tetragonal P4mm [16], rhombohedral R3m [17] and monoclinic Cm [16] PZT phases. However, as the monoclinic phase was not needed in order to explain the XRD pattern, it was not used for the refinement. Caglioti parameters related to the instrumental function were set to zero because we did not have the data for calculation of the instrumental function corresponding to this set-up. The only refined variables were the background, the beam intensity, the unit cell dimensions, the PZT phase proportion and the peak broadening parameters, in particular crystal size. The refinement strategy was the same as the one described at the end of Chapter II 2.1.1.

Figure III. 67 shows refinement figures for the Amplified gradient sample. Three different PZT layer depths under the top electrode are shown, namely 100 nm, 200 nm and 300 nm.



Figure III. 67: XRD profile refinements for phase analysis at 100, 200 and 300 nm from the free surface for Amplified gradient sample. Note that the red line corresponds to the tetragonal P4mm phase, the green line to the rhombohedral phase R3m, the black line is the sum of both refined phases and the blue dots stand for the experimental data. The blue arrow is pointing to the (103), (301) and (310) peaks of PZT because the phase variation is the most visible there. Close to the surface (at 100nm), PZT is more rhombohedral and as the beam progresses into the sample (at 300nm), more tetragonal phase is detected.

1.3.3. Results

Figure III. 68 shows the results of fluorescence analysis of PZT samples. Only Zr, Ru and Au/Pt fluorescence lines were recorded because of the energy range of the detector. The Zr composition variations can be clearly seen in the Standard gradient (a) profile. Note that the Zr amount changes in the same way as in the SIMS analysis (Figure III. 65). More Zr is found at the interface PZT/Ru top electrode and each 360 nm within the PZT film, which corresponds to the crystallisation annealing period. The Zr composition variation in Gradient Free sample (b) is smoother. However, we could not

extract any reliable fluorescence profile from Amplified gradient sample. Thus, to confirm the gradient amplitude, we only provide SIMS characterization results.



Figure III. 68: Fluorescence analysis results for Standard gradient (a), and Gradient Free (b) samples. Ru, Zr and Au/Pt fluorescence lines were collected at each z-position and integrated to obtain the final intensity of each element.

Moreover, the diffraction experimental data shows the crystallographic phase ratio variation versus PZT layer depth. Figure III. 69 represents the tetragonal and the rhombohedral phase quantity variation in function of z-position for Gradient Free (a) and Amplified gradient (b) samples. The variation is larger in the sample with Amplified gradient, where it reaches nearly 9.7%. There is 4.9% of phase variation in the Gradient Free sample. The average structure of Gradient Free sample is 47.6% of tetragonal phase and 52.5% of rhombohedral phase. The average structure of Amplified gradient sample is 37.2% of tetragonal phase and 62.8% of rhombohedral phase. Data from Standard gradient were not conclusive enough to extract any crystallographic phase versus depth variation. However, as we know the composition of precursor solutions and SIMS profile, one can predict that Standard gradient average structure will be situated between Gradient Free and Amplified gradient. Thus, Standard gradient should contain in average 42.4% of tetragonal phase and 57.6% of rhombohedral phase. The phase variation through the Standard gradient film should be 7.3%.







Figure III. 69: Tetragonal P4mm and rhombohedral R3m crystallographic phase percentage variation versus the PZT layer depth for Gradient Free (a) and Amplified gradient sample (b). Here, z=0 corresponds to the interface PZT/top electrode. Black dashed lines represent RTA interfaces.

1.4. Zr/Ti gradient effect on the PZT microstructure

The XRD results in the PZT cross-section show that the Zr/Ti chemical gradient seen by SIMS is at the origin of a crystallographic phase gradient. Ti-rich zones of the PZT layer crystallise preferentially in tetragonal phase whereas Zr-rich zones contain more rhombohedral phase. This is in line with the PZT phase diagram. Ti-rich PZT with Ti composition >48% crystallizes in tetragonal form and Zr-rich PZT with Zr composition >52% crystallizes in rhombohedral form. Thus from the crystallographic point of view, the fabricated PZT film is not entirely morphotropic even if produced with the morphotropic precursor solution. In reality, the film composition and microstructure alternate between tetragonal and rhombohedral phases. According to our analysis, GF sample contains in average 47.6% of tetragonal crystals and 52.4% of rhombohedral crystals. Note that the phase composition of Gradient Free sample agrees with the MPB composition, that is to say 48% of Ti and 52% of Zr. However, we would like to remind that there is no absolute accuracy on the results as the refinement was not performed in standard conditions.

The electric and piezoelectric measurements showed that GF sample has better dielectric permittivity, polarisation and piezoelectric properties. This observation corresponds to Calame's one in 2007. The more the sample is homogenous, the better it performs.

The phase gradient is logically the lowest in the sample with the highest composition homogeneity, that is to say the GF sample. Indeed, the observed phase composition variation through the film

thickness is about 5%. This observation reveals the possibility of material performance improvement by exploiting the material homogeneity improvement. The increase of compositional homogeneity could be achieved by using better-adjusted precursor solutions. In order to avoid the chemical gradient, the first deposited Zr-rich solution should contain more than 59% of Zr and the final Ti-rich solution should contain more than 57% of Ti. Another possibility might be the change of deposition technique. Sputtering or Pulsed Laser Deposition (PLD) are known to produce composition homogeneous films.

1.5. Conclusion

To conclude, this part shows that the Zr/Ti chemical gradient due to sol-gel deposition method directly influences PZT microstructure. Thanks to the nano-pencil beam XRD experience in ESRF, we were able to follow the evolution of PZT phases with 120 nm-steps and correlate them with the chemical profile of the layer. Moreover, electric and piezoelectric measurements were performed on the same layers. The results confirm that the more homogeneous the MPB PZT samples are, the better the dielectric and the piezoelectric properties are. The XRD observations show that better chemical homogeneity induces better microstructural homogeneity in terms of phase variation. Thus, one can correlate the crystallographic phase homogeneity to better electric and piezoelectric performances. As the Gradient Free sample contains 5% phase variation through the film, the composition adjustments to eliminate phase variation may still be achieved thanks to the modification of precursor solutions for sol-gel deposition or the choice of different deposition techniques like sputtering or PLD, though they exhibit some drawbacks that should be addressed.

PZT crystallographic phase, chemical composition and electric and dielectric properties correlations manifest the sensibility of PZT microstructure and performances upon the Zr/Ti composition at the MPB.

2. Phase transition under electric field

The second section of Chapter III is dedicated to the study of the piezoelectric effect of PZT in MPB from the microstructural point of view. There are several theories explaining the principle of the piezoelectric effect in PZT. They are mainly based on bulk PZT observation. The first is the theory of the a-to-c domain switching in tetragonal [18, 19, 20, 21] and rhombohedral phase [22] under an electric field. According to this theory both phases exhibit domain switching but the rhombohedral phase is more reactive to the electric and mechanical stimulation [22]. The second theory claims that MPB PZT exhibits excellent piezoelectric properties thanks to the monoclinic phase, which enables a large mobility of the polarization axis in the monoclinic (110) plane [23]. In 2003, Jin et al. published a theory of an adaptive monoclinic phase, which was very reactive to the electric field, composed of tetragonal and rhombohedral microdomains, with low domain wall energy. He proposed that it could be the reason for enhanced properties near the MPB [24]. In 2011, Hinterstein et al. came up with another theory. They observed an electric field induced tetragonal-to-monoclinic phase transition in MPB PZT ceramic via in-situ X-ray diffraction (XRD) [25]. They claim that MPB PZT piezoelectric effect is based on the ability of the tetragonal phase to transform to the monoclinic phase.

Here, we propose a study of the piezoelectric effect of morphotropic PZT thin films, fabricated by solgel method, from the crystallographic point of view. This study aims to identify the microstructural modifications responsible for PZT piezoelectric effect and to correlate these modifications with the piezoelectric performances of PZT. In order to clarify this phenomenon, the converse piezoelectric effect is characterized by direct observation of PZT microstructure under electric field using in-situ Xray diffraction. Note that the sample used for characterisations was PZT Gradient Free (GF) from the previous section (Chapter III. 1.2.1.). The main difference of this sample in comparison with standard sol-gel morphotropic PZT is the attenuation of Zr/Ti gradient.

To summarize this part, first XRD and TEM observations will be described in order to acquire a better knowledge of PZT microstructure. These measurements are followed by in-situ XRD on PZT capacitors. The collected peak profiles are analysed and the results are used to calculate the longitudinal piezoelectric coefficient d_{33} . Then, the calculated coefficient is compared to the measured d_{33} on the same PZT by the DBLI method. Finally, a discussion closes this part of the chapter.

2.1. Preliminary characterisations

The main goal of this section is to present detailed information about morphotropic PZT GF thin film microstructure. No voltage is applied during these measurements. First, XRD on full sheet deposited 1 μ m-thick PZT was performed, more precisely Pole Figures, sin²psi analysis and Combined Analysis, giving global characteristics of the film. Information like film texture, strains, phase quantification, crystallite sizes and micro-stress with the refinement reliability factors are given. Note that all measurements were performed on an XPert Panalytical diffractometer. One can refer to Chapter II. 2.1.2.1 and Figure II. 21. for details. Then, the PZT film microstructure was characterized locally using electron microscopy with High Resolution TEM (RHTEM) and electron diffraction with TEM precession.

The GF sample has already been characterized electrically and piezoelectrically in the previous section (Chapter III. 1.2). Here, in addition to these results, we characterize the sample by DBLI method in order to evaluate the $d_{33,eff}$ coefficient. This result will be compared to the calculated d_{33} resulting from the following in-situ XRD analysis.

2.1.1. XRD analysis

Figure III. 70 shows two preliminary XRD characterisations. The first is the classical $2\vartheta/\omega$ acquisition (see Chapter II. 2.1.2.1 for further details) with the incident and diffracted beam plan perpendicular to the sample surface. The collected profile depicts PZT, Ru and Pt peaks corresponding to crystallographic planes that are parallel to the sample surface. This measurement shows that perovskite is the only visible phase, without traces of pyrochlore and it gives the initial idea about the sample texture through the area of the visible peaks. Note that this measurement alone is not sufficient to determine the sample's texture. It only says that the sample is textured and that there is a population of [100] crystals oriented perpendicularly to the sample surface.

The second preliminary XRD characterisation is the acquisition of Pole Figures (PF) of the principal PZT planes, (namely {100}, {110} and {111}) in order to map their positions and to verify the PZT texture. Details about PF characterisation and representation are given in Chapter II. 2.1.2.1. Note that, there is no differentiation between tetragonal and rhombohedral phases. Pole figures are collected using the angle corresponding to the peak position from the $2\vartheta/\omega$ profile. Figure III. 70 shows the collected PF. The {100} PF presents the main location of {100} plans, which peaks at $\psi=0^{\circ}$ and $\phi=0^{\circ}$, with a mosaïcity of 12°. Thus, it means that the sample exhibits (100)-fiber texture. Moreover, {110} and {111} planes with their position at 45.3° and 55° respectively confirm the (100) fiber texture.



Figure III. 70: $\vartheta/2\vartheta$ profile and pole figures corresponding to {100}, {110} and {111} crystallographic planes of PZT [26]

The following characterisation was the $\sin^2\psi$ analysis for PZT and Pt film strain and stress determination. See Chapter III. 2.1.1.2 for details about $\sin^2\psi$ analysis. Calculations were performed on 111 PZT and 111 Pt peaks. Their 2 ϑ positions were followed as a function of ψ from ψ =0° to ψ =65°. Figure III. 71 shows the strain evolution versus $\sin^2\psi$ for PZT. Note that the d₀ dimension corresponding to the unstrained cell is extracted at ψ =45°.



Figure III. 71: Strain versus sin²ψ for 111 PZT peak

PZT stress is then extracted from the equation on Figure III. 71. Using PZT elastic constants E=82 GPa and ν =0.39, and assuming isotropic elastic properties of the film, σ_{PZT} is equal to 72 MPa.

Figure III. 72 shows strain versus $\sin^2\psi$ evolution for Pt. Using the elastic constants E=168 GPa and υ =0.3, the calculated σ_{Pt} is equal to 900 MPa.



Figure III. 72: Strain versus sin²ψ for 111 Pt peak

 $\sin^2 \psi$ characterisations show that both PZT and Pt are under tensile stress. This result is coherent with the fabrication process. Si substrate, Pt and PZT are all heated at 700°C for PZT crystallisation. At this temperature, substrate and all films are unstressed. Stress is created as the sample returns to room temperature, because of the difference between thermal expansion coefficients *a* of each

element. Note that $a_{Si} = 2.6$ ppm/K, $a_{Pt} = 8.8$ ppm/K and $a_{PZT} = 9$ ppm/K. Thus, as the temperature drops, Pt and PZT layers shrink much more than Si substrate. Finally, at room temperature, Si applies tensile stress to both Pt and PZT layers.

The last preliminary XRD characterisation is Combined Analysis (CA), performed with the Maud refinement program [15]. CA needs a very complete dataset including $2\vartheta/\omega$ diffraction profiles for ψ going from 0° to 65° and ϕ from 0° to 360°, with a step size of about 2.5° for both angles. However, this is very time consuming, especially when the data collection is performed with a point detector. Thanks to the preliminary XRD characterisations, we know that PZT has (100) fiber texture. This information enables us to neglect all data resulting from ϕ sample rotation. It is sufficient to find the [100] fiber axis and to perform $2\vartheta/\omega$ acquisition for ψ from 0° to 65°. Note that for ψ higher than 65°, the data suffers from severe beam defocusing and diffracting volume incoherencies (see Chapter III.2.1.2.1.). More details about the data collection and analysis can be found in Chapter III. 2.1.1. and 2.1.2.

Prior to the sample refinement, the instrumental function has to be determined and de-correlated from the sample data (see Chapter II. 2.1.1 part related to the CA for more details). For this purpose, a LaB₆ calibration powder was characterized in the exact same geometry as the real sample. The dimensions and microstructure of LaB₆ are well known, so they can be fixed, while the instrumental parameters for diffractometer calibration are refined. The instrumental parameters to be refined are ψ (equivalent to χ) and ω broadening, peak asymmetry, peak 20 shifting, Caglioti parameters W, V and U and Gaussianity (η) parameters. After refinement, all these parameters can be extracted in a *.mdb* file and stored (Appendix B). Later on, they can be easily uploaded into real sample refinement Maud files.

Maud files contain several tabs enabling the acquisition of all known information about the sample before parameters refinement. Dataset tab is used to upload the dataset and the instrumental calibration file (.mdb) and to determine the background modelling strategy. For this refinement, polynomial background and interpolated background models were chosen. The Phases tab gathers all information related to sample crystallographic phases. Each phase Cif file is loaded there (Appendix C present cif files related to tetragonal and rhombohedral PZT phases). A set of properties is defined for each phase including texture, strain, crystallite size and microstress among others. Several models describe each phase property. Here the user chooses the most adapted model to the particular phase property and defines the initial parameters. To give an example, steep textures are often modelled with a Standard function texture model. This model enables the definition of the fiber texture axis. When stress modelling for in-plane isotropic samples, one can choose the Triaxial stress isotropic E model with isotropic elastic parameters and a condition of equality for in-plane stresses σ_{11} = σ_{22} . The model Popa rules are often chosen for anisotropic crystallite size and r.m.s. microstrain refinement. Finally, the Sample tab is used for definition of sample parameters. It specifies the samples geometry, namely the layer stack and thicknesses of various layers that compose the sample. In order to begin refinement, one has to choose the parameters to refine and press the refinement button (refer to Chapter II. 2.1.1 Combined Analysis for more details).

PZT was refined using two phases, namely the tetragonal P4mm and the rhombohedral R3m phase. The monoclinic Cm phase was removed from the fit, because it did not improve the fit. P4mm and

R3m phases enable to explain the dataset better. The corresponding reliability factors are Rwp = 19.4% and Rexp = 9.5%, leaving the goodness of fit σ equal to 2.04, which is rather satisfactory [27]. Figure III. 73 shows the raw data versus refined data. According to the visual inspection, texture and stress seem to be fitted well enough too.



Figure III. 73: Data vs fit performed with Maud program on GF PZT sample. For each dataset, $2\vartheta/\omega$ profiles are plotted in function of ψ .

Figure III. 74 shows the sum of $2\vartheta/\omega$ according to ψ angle. This representation enables to see the phase refinement quality without the interference of texture. Pink and blue lines plot the fitted P4mm and R3m PZT phases respectively. Positions of diffraction planes in the collected 2ϑ range for both phases are represented underneath the refined $2\vartheta/\omega$ profile.



Figure III. 74: Sum of all $2\vartheta/\omega$ profiles according to angle ψ . Blue dots stand for experimental data, blue line represents fitted R3m PZT phase, pink line is for P4mm PZT phase and black line represents the sum of all fitted phases, namely Pt, Ru and both PZT phases. Positions of diffraction planes in the collected 2ϑ range for all four fitted phases are shown underneath the refined $2\vartheta/\omega$ profile. Note that bottom rectangle represents the difference between experimental data and fit.

PZT phase composition corresponding to the refinement shown in Figure III. 73 and Figure III. 74 is 61% of tetragonal and 39% of rhombohedral phase. Corresponding crystallite dimensions refinement is reported in Figure III. 15. Here crystallite refers to the smallest coherently diffracting domain.

a.



b.



Figure III. 75: The crystal size and form refinement results for PZT P4mm (a) and R3m (b). The diameter for P4mm is about 50 nm and the out-of-plane vs diagonal dimensions for R3m are 35nm/67nm.

For Maud texture modelization rhombohedral R3m in not a standard setting, thus it was subsequently modified in order to enable the modelization and refinement. Rhombohedral R3m space group was changed into triclinic P1 group. Unit cell parameters and atom positions were modified so as to respect the P3m space group (Appendix D). The reconstructed pole figures issued from the profile refinement are plotted in Figure III. 76. They show the orientation distribution of major crystallographic planes of PZT, Pt and Ru in m.r.d. units (multiple of random distribution, please refer to Chapter II. 2.1.1 Texture for more details). They confirm (100) orientation of PZT, (111) orientation of Pt and (002) orientation of Ru crystals.











Figure III. 76: Reconstructed pole figures for Pt (a), PZT P4mm (b), PZT R3m (c) and for Ru (d). Orientation distribution probabilities are expressed in m.r.d. units. F² the texture index is equal to 1 for all phases.

The stress-strain analysis of PZT and Pt layers were refined as well. However, the final values stayed around the values found by preliminary $\sin^2 \psi$ analysis, namely 70 MPa for PZT and 890 MPa for Pt. The quantitative phase analysis converged to 46.6% of rhombohedral phase and 53.4% of tetragonal phase. However, one has to have in mind that phase quantification is particularly difficult in this case because of the high resemblance of both refined PZT phases coupled with peak broadening due to small crystals.

The phase discernibility problem when small crystals are involved is illustrated in Figure III. 77. The smaller the crystals are, the more difficult the discernibility of phases is. In the case of PZT crystallites, we are in the situation between 50 and 10 nm.





Figure III. 77: Example of tetragonal P4mm and monoclinic Cm PZT diffraction pattern in function of crystallite size: 200 nm (a), 50 nm (b) and 10 nm (c). This modelization is based on Scherrer's equation.

The whole refinement parameter list is given in Appendix D.

2.1.2. STEM and TEM precession

Transmission electron imaging on the Titan Ultimate Microscope and precession electron diffraction on Jeol 2010 FEF were performed in order to obtain information about the local microstructure of PZT. Note that this approach is complementary to the statistical vision of XRD.

Figure III. 78 shows BF (a) and DF (b) images of the PZT lamella. Note that the contrast is due to different orientations of grains. One can observe several uniform grains, which are homogeneous in orientation, striated grains, which resembles to crystal twins and some grains with a more complex internal structure, which are close to grains observed in bulk morphotropic PZT observed by Schönau et al denominated nanodomains [28].

a.BF Striated grains



Homogeneous grains

c. HAADF



Grains with complex structure - nanodomain structures

Figure III. 78: The STEM images taken with three detectors: bright field (a), dark field (b) and high-angle annular dark-field (c). White circles depict features we can observe in PZT: uniform grains, striated grains and complex nanodomains-like grains. Note that the substrate is on the left-hand side and the sample surface in on the right-hand side.

b. DF

TEM images show clear interfaces between PZT layers corresponding to the crystallisation annealing. However, the grain boundaries are continuous from one layer to another and PZT grains seem to keep the same orientation after crystallisation annealing, as seen by Amanuma et al in 1994 [29]. The HAADF imaging (c) is less sensitive to crystal orientation and more sensitive to density difference. However, as PZT has very similar densities in its tetragonal and in its rhombohedral phase, no clear phase differences are visible.

In order to analyse local microstructure, precession electron diffraction was performed on the PZT lamella. You can refer to Chapter II. 2.2.1 for more details about precession electron diffraction.

The precession mapping was recorded on the surface of $1.95*1.5 \ \mu\text{m}^2$, using 7.5 nm steps between diffraction images. These parameters give the resulting image of 260 by 200 pixels. The probe size was about 7 nm and the precession angle cca 0.96°. The acquisition speed was 0.1 s per image.

The precession technique is very sensitive to crystal orientation. Figure III. 79 (a-c) present in-plane and out-of-plane orientations of PZT grains. Each image illustrates orientation distribution according to one direction (x, y or z-axis). The corresponding inverse pole figures are shown underneath. The in-plane distribution of orientations seems random, while the out-of-plane orientation is mostly (100). This confirms the (100)-fiber texture of PZT. Note that this observation also confirms that grains keep the same orientation after crystallisation annealing.

a. X-axis



c. Z-axis





Figure III. 79: The orientation analysis of grains in PZT lamella in in-plane x and y axis (a, b) and out-of-plane z-axis (c). The corresponding inverse pole figures are underneath. Note, that the [001] orientation corresponds here to the *a* domains because of the manner the lattice constants were declared in the refinement software.

b. Y-axis



Then, the PZT lamella was used for phase analysis. Figure III. 80 shows results of indexation and the virtual bright field image, which is a reconstructed bright field image of the observed area. Grains seem to be monophasic and roughly 2/3 of the grains are tetragonal and 1/3 of the grains correspond to the rhombohedral phase on this part of the lamella.





Figure III. 80: Result of phase analysis of PZT lamella on the left hand side. Tetragonal phase is illustrated by red color, while rhombohedral phase is presented by green color. The image on the right hand side is the virtual bright field image corresponding to the analyzed area. Note that the virtual bright field is the reconstructed image from all precession diffraction profiles. It is very similar to the STEM bright field.

Striated zones of the lamella were analysed with HRTEM in order to confirm the presence of crystal twins. Figure III. 81 shows the image and the FFT from the striated zone. The images confirm the presence of two crystal twins in the direction of electron beam. However, HRTEM measurements show that the majority of striated zones result from superposition of random oriented grains causing Moiré's interferences. Thus, even if twin crystals exist in the lamella, there are very few. Note that PZT crystal twins in crystallography are likely to correspond to PZT domains in microelectromechanics. This observation means that in this particular PZT area, there are very few PZT domains.



Figure III. 81: TEM image on the left hand side and reduced Fast Fourier Transform (FFT) on the right hand side.

To summarize, local TEM and electron diffraction characterization confirmed PZT (100)-fiber texture and the presence of tetragonal and rhombohedral phases in the PZT layer. Furthermore, TEM analysis revealed a rather complex grain microstructure with nm-size domains. The presence of several twinned crystals was confirmed but they remain rare. This information gives an idea about the presence of domains in PZT. Finally, the local analysis by TEM precession does not confirm the phase gradient through the thin film seen by XRD. Note that the XRD technique shows 5% of phase variation for GF thin film. This disagreement is certainly due to the local nature of TEM ED analysis. On the other hand, XRD gives information from much larger area, which erases local fluctuations.

2.1.3. Piezoelectric characterisation

The longitudinal piezoelectric coefficient $d_{33,eff}$ was characterized by DBLI apparatus from AixACCT. One can refer to Chapter II. 3.2.2. for details about this measurement technique. Note that the characterisation was performed on a 1 mm² PZT capacitor in order to easily de-correlate the piezoelectric effect coming from PZT induced Si substrate bending. The measured $d_{33,eff}$ is equal to $125\pm5pm/V$. This value is in line with the best values obtained for gradient free PZT as reported in Calame's thesis [30].

2.2. In-situ XRD

GF PZT was then characterised by an in-situ, under electric field XRD. This characterisation was possible thanks to the preliminary studies of PZT. Indeed, they gave us very complete information about PZT microstructure and enabled us to diminish the time of in-situ XRD measurements by focusing only to the parts of diffraction profile of major interest. This section presents the sample preparation and the in-situ XRD setup, followed by the profile analysis and the refinement results.

2.2.1. Sample preparation

Capacitors were prepared as described in Chapter II. 1.2 with one level of lithography. Only Ru top electrode was patterned, leaving PZT full sheet. After wafer cutting, 7*7 mm² samples containing each 5*5 mm² capacitors were fabricated as detailed in Chapter II. 2.1.4.

2.2.2. Experimental setup

The XRD setup used for characterisation is a laboratory diffractometer and data collection was made in reflection diffraction mode. One can see Chapter II. 2.1.2.1 for details. Figure III. 82 presents the outline of in-situ XRD setup with the PZT capacitor under voltage placed in the X-ray beam path.



b.



Figure III. 82: XRD setup for in-situ characterisation (a) with the zoom on the sample (b).

The strategy for in-situ data collection results from the preliminary characterisation results, as well as the rocking curve characterisation of (200) PZT peak under an electric field (see Chapter II. 2.1.2.1 for details). As the PZT manifests a strong (100) texture, which does not change its mosaïcity with an electric field, the voltage impact was studied in the region of {100} crystallographic planes of the tetragonal and rhombohedral phases, going to their fourth reflection order. Thus, $2\vartheta/\omega$ datasets were collected for three 2ϑ ranges, namely [20.3, 23.3]°, [43, 46]°, and [95, 101]° for the first, second, and fourth order of (100) reflection, respectively. The fourth order reflection is of high importance because of easier peak separation. Due to Bragg's law, peaks, which nearly superpose at low 2ϑ angles are distinguishable at higher 2ϑ angles. 2ϑ step width and duration were respectively 0.02° and 2 s for {100} and {200} planes. The time per step for {400} planes was 4 s. The successive voltages applied to the sample were 20, 10, 0, -10, -20, -10, 0, 10, 20, and 30 V. Note that no prepoling had been performed prior to this experiment.

This strategy for data collection was used rather than complete dataset collection for Combined Analysis mainly because of the time necessary for such data acquisition. Assuming one day of collection per voltage, it would take at least 11 days to acquire necessary data. Moreover, the PZT

microstructure may evolve in time while constant voltage is applied. Finally, there is always the risk of breakdown.

Figure III. 83 shows the $2\vartheta/\omega$ profile evolution near (400) peak in function of voltage range from 0 to 30 V. The position of (400) peaks for P4mm and R3m phases are reported as stated in the Inorganic Crystal Structure Database (ICSD), namely 92059 for P4mm and 24562 for R3m (refer to Appendix C for corresponding cif files). The portion of collected data corresponding to the (400) PZT peak is chosen because the profile change versus voltage is the most visible there. Even if one was to expect three diffraction peaks in this range, we only observe one experimental peak with contributions coming from P4mm and R3m phases. This peak shifts slightly towards the lower 2ϑ angles and its intensity decreases when the voltage is applied. The tetragonal c-domains are not clearly visible here and their amount does not change with voltage. Finally, the peak evolution versus electric field is perfectly reversible. Data for all applied voltages are reported in Appendix E.



Figure III. 83: $2\vartheta/\omega$ profile evolution near (400) PZT peak versus applied voltage. Positions of {400} diffraction peaks of P4mm and R3m phases are indicated. The arrow represents the peak evolution versus voltage. The peak shifts to the lower 2ϑ angle and its intensity decreases.

2.2.3. Profile analysis

The PZT XRD profiles were analyzed using two crystallographic space groups, namely tetragonal P4mm and rhombohedral R3m as well as Ruthenium hexagonal P63/mmc. MAUD software was used to fit the experimental results. Assuming (100) fiber texture for both P4mm and R3m structures, the structure refinement enables us to quantify the phase percentage. The crystallographic models used in the simulation were "polynomial" for background modeling, "standard function" for P4mm and R3m texture, and "isotropic size - strain" for crystallite size and microstrain.

Figure III. 84 shows the peak profile refinement of the $2\vartheta/\omega$ scans with MAUD near (400) PZT peak at 0 V and 30 V. The (400) peak was selected because the microstructure change with voltage is the most visible. Note that the PZT peak area remains constant for all applied fields. P4mm and R3m phases were fitted for all applied voltages. The (202) Ru peak is also reported, as it appears in the area of interest. The (004) PZT P4mm peak is not visible whatever the voltage. In consequence, the

tetragonal c-domains are not included in the refinement process. The Ru peak and the background were fitted at 0 V and then kept constant for all refinements. These limitations enabled a satisfactory fit to be obtained as showed in Figure III. 84. At 0 V, both P4mm and R3m PZT phases are clearly identified. At 30 V, the amount of R3m phase drastically increases and cancels out P4mm occurrence. Note, that there is no need to implement strain in the model to fit the experiment.



Figure III. 84: Refinement of $2\vartheta/\omega$ scans near {400} peaks of PZT at 0V and 30V. (400) PZT rhombohedral R3m (blue line) and tetragonal P4mm (green line) phases and (202) Ru reflections (red line) are identified and fitted. Blue dots are experimental data and black solid lines correspond to the sum of the three fitted peaks.

2.2.4. Refinement results

Figure III. 85 shows the relative volume proportion of P4mm and R3m PZT phases versus voltage, as determined by MAUD software. The amount of rhombohedral phase is 40% at 0 V and it reaches 100% at 30 V. This effect seems to be symmetric when applying negative voltage. Note that the phase quantity evolution versus voltage diagram shows no or very little hysteresis.

As the volume of rhombohedral phase increases, the magnitude of tetragonal phase decreases. These observations suggest a voltage-induced phase transition under electric field in PZT morphotropic thin film.



Figure III. 85: Phase variation versus applied voltage of PZT tetragonal P4mm and rhombohedral R3m phases. Solid points are results of the profile refinement. There are two points for all voltages except -20 and 30 V. Solid lines are guides for the eyes, based on the solid points' average value. Solid vertical lines are the error bars.

Note that the phase composition found with the nano-pencil beam experiment in Gradient Free sample, which was 47.6 % of PZT tetragonal phase and 52.4% of PZT rhombohedral phase (Chapter III. 1.3.3) is in agreement with the phase composition found with in-situ XRD experiment at 0V.

2.3. PZT phase transition under electric field

The in-situ XRD characterisation results bring to mind electric field-induced phase transition in PZT sol-gel thin films at morphotropic composition. More precisely, as we observed no visible *c*-domain presence, **the transition occurs from** *a***-oriented domains of tetragonal phase to the rhombohedral phase.** The transition between two phases of morphotropic PZT induced by an electric field was reported by Hinterstein et al. in 2011 [25] in the case of bulk ceramic PZT. In this paper, the transition from tetragonal P4mm to monoclinic Cm phase was identified. In our study, R3m phase fits the collected data better than Cm phase. Note that Cm phase is a subgroup of both tetragonal P4mm and rhombohedral R3m symmetries.

Another interesting remark is that the area of (400) PZT peak in not changing with voltage. This means that **no domain switching** occurs. At the initial state at 0V, the film is mostly composed of a-domains. This may result from the film's tensile stress due to Si substrate. Then, with the increase in voltage, the *a*-domain crystals seem to shear into rhombohedral crystals. Their z-cell dimension elongates and their x(or y)-cell dimension shrinks as the electric field is applied.

One could ask whether the peak displacement versus voltage could be simply strained tetragonal cells. The argument against this theory is the intensity variation of the PZT peak and the stress magnitude induced in PZT film. Firstly, cell deformation is seen as peak position displacement while peak intensity remains the same. Secondly, the stress corresponding to the peak displacement would be of several GPa, which is extremely high and could damage PZT structure. Note that PZT was

still functional after in-situ XRD experiment. Thus, the phase transition is likely to be the explanation of the observed phenomenon.

Our XRD studies showed that sol-gel morphotropic PZT thin films fabricated in CEA Leti are composed of nanometer-size crystallites. One could make a connection with Schonau et al XRD and TEM observations performed on bulk MPB PZT [28]. In her article from 2007, she reported that PZT is composed with tetragonal microdomains and rhombohedral nanodomains. Rossetti et al have demonstrated using a low-ordered Landau expression satisfying the Gibbs rule that, in the range of the MPB the phase coexistence of rhombohedral and tetragonal phase is likely to occur on nanoscale level [31]. Schonau et al also performed in-situ XRD experiments and observed microstructural changes involving monoclinic and tetragonal phase variation [32]. The monoclinic phase was used in XRD refinement because it interpreted better the diffraction pattern of nanoscopic features identified later on as rhombohedral phase nanocrystallites. This observation was interpreted either as rhombohedral nanodomains rearrangement with tetragonal texture variation with voltage, or as tetragonal to rhombohedral phase transition. In the article from 2007 she believes that "small domains are able to react with more flexibility to the applied electric field due to smaller domain-wall energy" [32]. Indeed domain size D is correlated to the domain wall energy y through $D \sim \sqrt{\gamma}$ [33]. Thus, the domain or crystallite miniaturization is connected to the domain wall energy decrease. In 2005, Ahluwalia et al studied the influence of the domain size and the piezoelectric coefficients, namely d_{33} coefficients [34]. They showed that smaller domain sizes induce higher piezoelectric coefficients. The explanation of enhanced piezoelectric properties is thought to be the domain miniaturization: it induces higher density of domain walls and diminishes the shear stress between domains. Note that pre-existing shear strain also limits the total shear experienced by the crystallites. Thus, small domain size might be one of the necessary features of high performant MPB PZT.

Moreover, the ΔG was calculated for the polarization axis rotations of the tetragonal and rhombohedral PZT phase [35]. It seems that tetragonal [100] to rhombohedral [111] polarization axis transformation occurs through monoclinic distortion, that is to say by polarization axis rotation through (1-10) pseudocubic crystallographic plane. As the composition of PZT approaches MPB, ΔG flattens anisotropically in anticipation of appearance of polarization axis in different crystallographic direction. This is an interesting remark. One could ask if an external polarization of piezoelectric material at MPB could rotate the polarization axis and take advantage of low ΔG for initiation of a phase transition. Interestingly enough, the article makes a link between composition, temperature, stress and electric field effect on the ΔG . Indeed, they all induce flattening of ΔG near the MPB in very similar ways.

The XRD profile refinement gives the opportunity to roughly extract $d_{33,eff}$ independently from the DBLI method. Indeed, we know that the amount of volume phase transited from P4mm to R3m (60% at 30 V) and the PZT cell dimensions for both phases.

$$d_{33,eff} = \frac{s_{33}}{E_3}$$

$$s_{33} = \frac{a_{30V} - a_0}{a_0} \text{ and } E_3 = \frac{V}{t}$$

$$e_{10} = a_{10} + a_{10} + a_{10} + a_{10}$$

with $a_{30V} = \varphi_{R3m \ 30V} * a_{R3m} + \varphi_{P4mm \ 30V} * a_{P4mm}$ and $a_0 = \varphi_{R3m \ 0V} * a_{R3m} + \varphi_{P4mm \ 0V} * a_{P4mm}$ Note that s_{33} stands for the mean PZT cell value deformation in 33 direction, originating from the piezoelectric effect, E stands for the electric field in 3 direction, V is the applied voltage, t is the sample thickness, a_{30V} stands for the average PZT cell value at 30 V and a_0 stands for the average PZT cell value at 0V. $\varphi_{R3m \ 30V}$ is the phase ratio of the rhombohedral phase at 30 V, a_{R3m} is the dimension of rhombohedral cell, $\varphi_{P4mm \ 30V}$ is is the phase ratio of the tetragonal phase at 30 V, a_{R3m} is the a-cell dimension of the tetragonal phase, $\varphi_{3m \ 0V}$ is the phase ratio of the rhombohedral phase at 0 V. This method gives a d_{33,eff} equal to 120±25 pm/V at 30 V, which is in the range of what has been measured with the DBLI method, which was 120-130 pm/V. Therefore, it proves that the **piezoelectric effect of this MPB GF PZT film is mostly due to the voltage-induced transition** from tetragonal to rhombohedral phases.

One can also compare this result with the Landau-Ginzburg-Devonshire (LGD) theory prediction. Du et al [5] deduced from LGD that the most favourable phase and orientation for single crystallite / single domain PZT in order to maximize piezoelectricity is [100]-oriented rhombohedral in the morphotropic area. Here, our result suggests that for polycrystalline [100]-oriented 52/48 PZT, it is better to work with PZT in the tetragonal phase, but still very close to the morphotropic in order to have the propensity to transit easily to the rhombohedral phase, when an electric field is applied. We suggest that $d_{33,eff}$ could be improved even further by fine tuning PZT composition in order to exhibit 100% P4mm phase at 0 V, without losing the capability to induce its complete transition to 100% rhombohedral phase. The whole transition from 100% P4mm to 100% R3m should induce $d_{33,eff}$ as high as 200 pm/V according to the peak positions method detailed in the previous section. This represents a 67%-increase compared with our experimental $d_{33,eff}$. Consequently, one should gently increase the amount of Ti in PZT, in order to be slightly more tetragonal.

Finally, one could think that using a pure tetragonal PZT and transiting from 100% *a*-domains to 100% *c*-domains by applying voltage could give much more strain than morphotropic PZT. However, Kobayashi et al. have recently observed that this complete *a* to *c*-domains transition in pure tetragonal PZT with Zr/Ti ratio equal to 30/70, requires a large electric field (0.4 MV/cm) and induces fatal cracks within PZT films [36]. These results suggest that only morphotropic PZT provides sufficient polarization mobility to take advantage of the phase transition in order to enhance the piezoelectric properties.

2.4. Conclusion

To conclude, we observed by in-situ X-Ray diffraction that a tetragonal-to-rhombohedral phase transition occurs in morphotropic 52/48 PZT thin films when an external electric field is applied. In addition, the field-induced domain switching in the tetragonal phase appeared to be negligible in these films. Moreover, the piezoelectric coefficient $d_{33,eff}$ of PZT, determined by both piezoelectric measurements with DBLI and calculations from X-ray peaks displacements versus applied field, appear very similar. This proves that there is a strong correlation between the piezoelectric properties and the field-induced phase transition in morphotropic PZT films. This result suggests that

one could probably even further improve $d_{33,eff}$ by favouring the field-induced phase transition especially by fine tuning PZT films composition.

3. Effect of chemical gradient on the phase transition

In order to introduce the third part of the Chapter III, it is worth reviewing the context and main conclusions of the previous parts.

Although physical vapour deposition and metal organic chemical vapour deposition are existing methods for PZT thin film fabrication, spin coating of metalorganic precursor called also sol-gel deposition method, is the most spread industrial method of PZT wafer production. This method is interesting by its technological maturity, low cost and versatility. As already reported, the sol-gel method particularity is the presence of Zr/Ti composition gradient across the thin film thickness after thermal annealing due to thermodynamics. This gradient can be attenuated using precursors of different chemical composition, as demonstrated by Calame et al [1]. The first part of Chapter III was about the very fine correlation between chemical homogeneity of sol-gel PZT and its microstructure. We observed that a slightly different Zr/Ti chemical composition induces phase variations through the PZT thin film. Moreover, these chemical and microstructural inhomogeneities lower material electric and piezoelectric performances. Results of this study are submitted in APL.

The second part of Chapter III deals with microstructural changes in sol-gel morphotropic PZT correlated with the piezoelectric effect. Several theories explaining the essence of the piezoelectric effect in MPB PZT exist, in particular the domain switching in tetragonal and rhombohedral phases, the rotation of polarization axis of monoclinic phase, the adaptive monoclinic phase composed by tetragonal and rhombohedral nanodomains with low domain wall energy and the electric field induced phase transition. All these theories are described in more details in Chapter I. The second part of Chapter III is dedicated to the study of PZT microstructure in operation in order to verify these theories on a sol-gel morphotropic PZT. In-situ XRD characterization was performed while an external electric field was applied to the PZT capacitor. Subsequent diffraction profile analyses show microstructural changes under voltage, which suggests a phase transition from tetragonal-to-rhombohedral phase. In addition, XRD refinement results were used to estimate the longitudinal piezoelectric coefficient d₃₃. A dedicated apparatus then measured this coefficient. After comparison, the calculated d₃₃ was found to be perfectly coherent with the measured d₃₃. This argument confirms that the phase transition might play a significant role in the microstructural origin of the macroscopic phenomenon called the piezoelectric effect. This study was published in 2014 [26].

The third part of Chapter III is the logical continuation of the first two. It is dedicated to the study of the thin film chemical homogeneity effect on the phase transition occurring while an electric field is applied. Our strategy is to compare the microstructural to voltage response of two PZT samples fabricated by the sol-gel method, which have different Zr/Ti gradients. Here, we claim to demonstrate how the composition gradient specific to sol-gel PZT films, affects the amount of phase transition within these films. This correlation could help in understanding the basis of the piezoelectric effect in morphotropic PZT thin films and in the improvement of film properties.
3.1. PZT samples

Two capacitors containing 1 μ m-thick morphotropic PZT thin films, one with Zr/Ti gradient (G) and the other with attenuated Zr/Ti gradient (GF), were prepared by sol-gel method. Refer to Chapter II.1 for the fabrication details.

3.2. Preliminary characterizations

Both capacitors were subjected to a set of preliminary tests. This section records all characterization results related to the PZT samples, namely microstructural characterizations including SIMS and XRD and electric and piezoelectric characterizations.

3.2.1. Microstructural characterizations

The composition gradient was first identified by SIMS measurements. Figure III. 65 shows composition profiles for both G (a) and GF (b) samples. The Zr/Ti composition gradient repeats every 360 nm, which corresponds to the period of crystallization annealings. The use of three different precursor solutions for fabrication of GF sample successfully attenuates Zr/Ti gradient.

Moreover, the nano-pencil beam XRD characterizations performed in ESRF demonstrated that the Zr/Ti composition gradient is at the origin of a crystallographic phase gradient across PZT films. The film zones richer in Ti contain more tetragonal phase, whereas zones richer in Zr are more rhombohedral like. The phase amount variation estimated by Maud refinement software is about 7.3% for G sample and 5% for GF sample. Refer to Chapter III. 1.3 for more details.

Furthermore, XRD characterizations were performed in our laboratory. The Pole Figure analysis reveals (100) fiber texture for both samples. $Sin^2\psi$ analysis shows that both PZT films undergo a tensile stress that originates from the Si substrate. However, the stress amplitude is more than two times greater in G sample. Results related to GF sample have already been presented in Chapter III. 2.1.1. Those related to G sample are detailed in Appendix F. Table III. 17 summarizes XRD preliminary characterization for both G and GF samples.

Sample nature	Texture	PZT stress (MPa)	Pt stress (MPa)
Gradient	100	162	1092
Gradient Free	100	72	900

Table III. 17: XRD characterisation summary for G and GF samples.

3.2.2. Electric and piezoelectric results

Both samples were characterized electrically and piezoelectrically. Measurement results are presented in Chapter III. 1.2.2. and 1.2.3. They reveal that the GF sample has higher dielectric permittivity, higher saturated and remnant polarization as well as better piezoelectric performances than the G sample. However, in terms of dielectric losses and break down voltage resistance the G sample is more efficient.

Preliminary characterisations are of high importance because they give background information about the sample microstructure and properties and enable time to be saved for a more interesting characterisation, which is in-situ XRD.

3.3. In-situ XRD

Both PZT samples were characterized by in-situ, under electric field XRD. The experiment's setup and the sample preparation relative to this characterization method are the same as described in Chapter III. 2.2. Thus, this section is focused mainly on data refinement strategy and interpretation of obtained results.

3.3.1. Data analysis

Figure III. 86 shows the $2\vartheta/\omega$ profile evolution near (400) peak as a function of voltage from 0 to 30 V for G (a) and GF (b) sample. Orange lines represent the initial 0 V peak and dark blue lines represent the peak at 30 V. We can observe a shift of the peak position to the left side when the voltage is applied, accompanied by peak shape modifications in both samples. Note, that even if three diffraction peaks would be expected in this 2ϑ range, we only observe one experimental peak. However, this peak contains contributions coming from P4mm and R3m phases. The tetragonal c-domains are not clearly visible here and their amount is constant with voltage.



Figure III. 86: $2\vartheta/\omega$ profile evolution near (400) PZT peak versus applied voltage for G (a) and GF (b) sample. Positions of {400} diffraction peaks of P4mm and R3m phases are indicated. Black arrows represent the global peak evolution versus voltage.

The collected diffraction profiles were analyzed with the MAUD program in a very similar manner to that in Chapter III. 2. Tetragonal P4mm and rhombohedral R3m crystallographic space group for PZT and hexagonal P63/mmc space group for Ruthenium peak were used for the profile fitting. Assuming the (100)-fiber texture for both P4mm and R3m structures, the profile refinement allows a quantitative phase analysis of PZT. For the Gradient sample, we enabled the rhombohedral phase stress refinement, because the peak position shifts with voltage below the theoretical (400) peak position. The crystallographic models used in the simulation were *polynomial* for the background modeling, *standard function* for the PZT texture, *triaxial stress isotropic E* for R3m stress modeling and *isotropic size-strain* for the crystallite size and strain.

Figure III. 87 shows the peak profile refinement with MAUD near (400) PZT peak at 0 V and 30 V for G (a) and GF (b) films. P4mm and R3m PZT phases were fitted for all applied voltages. The (202) Ru peak also appears in the area of interest. However, it was not fitted for all voltages. Ru peak as well as the background were refined for 0 V and then kept constant for all other voltages. The (004) P4mm PZT peak is not visible at 0 V and remains absent under voltage. In consequence, the tetragonal c-domains are not included in refinement process. These limitations enabled us to obtain a satisfactory fit as Figure III. 87 shows. At 0 V, both P4mm and R3m PZT phases are clearly identified for both G and GF samples. At 30 V, the amount of R3m phase increases while the amount of P4mm phase decreases for both phases. Note that at 30 V the amount of tetragonal phase seems to disappear completely in the case of GF, whereas it is still visible in the G sample.



Figure III. 87: Refinement of $2\vartheta/\omega$ scans near {400} peak, at 0 V and 30 V, of PZT G (a) and GF (b) films. (400) PZT rhombohedral R3m (blue lines) and tetragonal P4mm (green lines) phases and (202) Ru reflections (red lines) are identified and fitted. Blue dots are experimental data and black solid lines correspond to the sum of the three fitted peaks.

3.3.2. Refinement results

Figure III. 88 shows the relative tetragonal P4mm and rhombohedral R3m phase ratio variation versus voltage for G (a) and GF (b) samples refined by MAUD software. The amount of tetragonal phase decreases and the amount of rhombohedral phase increases with voltage for both samples. These observations suggest that there is a tetragonal-to-rhombohedral phase transition induced by an electric field in both PZT samples. However, the phase ratio variation appears about four times greater for the GF sample than for the G. More precisely, there is only 15% phase variation in G whereas about 60% in GF. Note that the effect for positive and negative voltage seems symmetric. In addition, the phase transition conveys the impression of reversibility in both samples. Even if GF phase ratio variation produces slight hysteresis, G sample shows no hysteresis in phase evolution vs electric field.

It is worth saying that the G sample (400) peak undergoes enormous shifting to the left-hand side under voltage. The peak position corresponding to 30 V does not correspond to any peaks of tetragonal, rhombohedral or monoclinic PZT phase. Thus in the case of the G sample, we suppose a deformation of the rhombohedral unit cell under voltage. Thus, additionally to the phase transition, the G sample exhibits a unit cell deformation while an electric field is applied. This voltage generated in-plane stress, has been estimated by MAUD refinement assuming isotropic elastic properties. Figure III. 89 shows in-plane stress induced in rhombohedral unit cell under voltage. The stress has a compressive character going from 0 to -440 MPa as the absolute value of voltage increases. The electric field is applied to the sample in the out-of-plane direction. Consequently, the sample is elongated in this direction and tends to shrink in the in-plane direction. Therefore, the compressive character of the generated stress seems perfectly logical. In addition, effects of positive and negative

voltages seem to be symmetric and the observed phenomenon is reversible. Note that the voltageinduced stress is one out of three components of the total stress experienced by the film, namely residual stress, ferroelectric stress from the initial domain pattern and voltage induced stress [37].



Figure III. 88: Tetragonal P4mm and rhombohedral R3m phase ratio variation versus voltage for G (a) and GF (b) samples. Solid points are results of the profile refinement. There are two points for all voltages except -20 and 30 V. Solid lines are guides for the eyes, based on the solid points' average value. Solid vertical lines are error bars.



Figure III. 89: Stress evolution versus voltage in rhombohedral phase of PZT Gradient sample. As for the previous diagram, the blue solid points are results of the profile refinement. There are at least two points for all voltages except -20 and 30 V. Solid lines are guides for the eyes, based on the solid point's average value. Solid vertical lines are error bars.

3.4. Phase transition versus Zr/Ti chemical gradient

Both morphotropic PZT samples independently of Zr/Ti gradient exhibit **microstructural modifications that can be attributed to tetragonal-to-rhombohedral phase transitions**. In both

samples no tetragonal *c*-domains are clearly visible in the out-of-plane direction. Thus, the phase transition occurs more precisely from the tetragonal *a*-domain to the rhombohedral phase. This observation is in agreement with Hinterstein's theory of phase transition as the microscopic origin of the piezoelectric effect in PZT. Note, that his theory is based on experiments with bulk PZT.

The **amount of phase transition is greater in GF than in G sample**. Thus, the phase transition is correlated to the Zr/Ti chemical homogeneity at the MPB. The more the sample composition is homogeneous, the more the phase transition occurs. Moreover, the first part of Chapter III showed that the composition gradient induces a phase gradient across PZT films. Thus, the phase transition is correlated to the microstructure homogeneity of PZT films. In particular, better microstructure homogeneity leads to higher phase transition.

A correlation can be drawn between the amount of phase transition and the phase homogeneity demonstrated by nano-pencil beam characterisation (Chapter III.1). As the GF sample has more morphotropic phase (52/48) and it exhibits more phase transition under voltage, one could say that the amount of morphotropic composition is correlated to the amount of phase transition. Moreover, it could be said that the phase transition induced by an electric field is located in the PZT of the exact morphotropic composition.

Moreover, PZT at morphotropic composition exhibits better properties in terms of dielectric permittivity, polarisation and piezoelectric coefficients in comparison to pure tetragonal or pure rhombohedral PZT. This argument confirms the previous hypothesis about the amount of morphotropic PZT in our probe samples. The G sample expresses slightly lower performances than the GF because it possesses less morphotropic phase. Its properties can be seen as "diluted" in comparison to GF. From a microstructural point of view, the **decrease of electric and piezoelectric performances might be explained as the direct consequence of phase heterogeneities and thus more microstrains between crystals [1]**.

In order to fit the diffraction pattern of G film, the lattice strain has to be allowed in the profile refinement, whereas this is not needed for the GF sample. The explanation of this phenomenon could be that the voltage-induced phase transition is not enough to dissipate the elastic energy of an applied electric field in the G sample, because the amount of transition is too low in comparison to the GF. Thus, the G rhombohedral lattice deforms to compensate for this strong electric field.

It should be said that according to $\sin^2 \psi$ analysis **GF experiences more than two times lower stress than G sample**. Indeed, sol-gel GF approaches to the stress condition of PVD-fabricated MPB PZT [37]. Note that PVD PZT is deposited on the same stack and is exposed during fabrication to similar temperatures as sol-gel PZT. However, unlike sol-gel, PVD films are known for their composition homogeneity. This is the argument in favour of the idea that the residual stress in sol-gel fabricated films comes from the non-uniform crystallisation shrinkage due to the composition inhomogeneity rather than from the Si substrate.

In the second part of Chapter III, it was remarked upon that XRD refinement results can be used to estimate the value of the longitudinal piezoelectric coefficient $d_{33,eff}$. In particular, it was shown that for the GF sample, the calculated and the measured d_{33} values match quite well. If we repeat this d_{33}

estimation for the G sample by adding contributions of both phase transition and rhombohedral cell deformation, we obtain 105±20 pm/V at 30 V. This calculation differs slightly from the one for GF, thus it is detailed below.

$$d_{33,eff} = \frac{s_{33}}{E_3}$$

$$s_{33} = \frac{a_{30V} - a_0}{a_0} \text{ and } E_3 = \frac{V}{t}$$
with $a_{30V} = (\varphi_{R3m \ 30V} \ * \ a_{R3m}) \ * \ s_{R3m \ 30V} + \varphi_{P4mm \ 30V} \ * \ a_{P4mm}$
and $a_0 = \varphi_{R3m \ 0V} \ * \ a_{R3m} \ + \varphi_{P4mm \ 0V} \ * \ a_{P4mm}$

Note that s_{33} stands for the mean PZT cell value deformation in 33 direction due to the piezoelectric effect, E stands for the electric field in 3 direction, V is the applied voltage, t is the sample thickness, a_{30V} stands for the average PZT cell value at 30V and a_0 stands for the average PZT cell value at 0V. $\varphi_{R3m 30V}$ is the phase ratio of the rhombohedral phase at 30V, a_{R3m} is the dimension of rhombohedral cell, $s_{R3m 30V}$ stands for the deformation of the rhombohedral cell under 30V, $\varphi_{P4mm 30V}$ is the phase ratio of the tetragonal phase at 30V, a_{P4mm} is the a-cell dimension of the tetragonal phase ratio of the rhombohedral phase at 0V and finally $\varphi_{P4mm 0V}$ is the phase ratio of the tetragonal phase at 0V.

This result appears to be in agreement with the mean $d_{33,eff}$ values found for standard morphotropic sol-gel fabricated PZT, which is about 100 pm/V [38]. Thus, once more, microstructure modifications under an electric field, namely the phase transition and the cell deformation in the case of G sample, enable an explanation of the macroscopic film deformation under voltage known as the piezoelectric effect.

Finally, it is worth pointing out that $d_{33,eff}$ of GF is greater than the $d_{33,eff}$ of G sample. Thus, the piezoelectric effect resulting from the pure phase transition has a better outcome than the piezoelectric effect resulting from both phase transition and cell deformation. Hence, it seems reasonable to assume that perfectly homogeneous morphotropic PZT film, with 100% tetragonal phase transiting to rhombohedral phase, would lead to the best piezoelectric properties. We can see that the most important ingredients in PZT thin films engineering are composition homogeneity, low residual stress and small crystallite size (seen in Chapter III 2). Note that crystal orientation is another crucial point but it is not included here because its effects are already well known.

3.5. Conclusion

To conclude, the in-situ under electric field XRD brought us new elements in understanding the piezoelectric effect in morphotropic PZT sol-gel thin films. Both tested samples, differing in Zr/Ti compositional gradient, exhibit *a*-domain tetragonal-to-rhombohedral phase transition while an electric field is applied. The field-induced domain switching in the tetragonal phase appears to be negligible in these films. The main outcome of this experiment is the correlation between the film compositional and microstructural homogeneity and the nature and amount of microstructural changes occurring in films while an electric field is applied. In the G sample, the quantity of phase transition is about four times lower than in GF sample. Nevertheless, the G sample undergoes

rhombohedral cell deformation in addition to the phase transition. Note that the phase transition seems to take place in PZT of the exact morphotropic composition. As the G sample is more heterogeneous, it contains less morphotropic phase and thus it exhibits less phase transition. The smaller quantity of phase transition seems to be compensated by rhombohedral cell deformation. On the other side, a smaller amount of morphotropic phase might be the reason for lower electric and piezoelectric performances of the G sample. This observation suggests that perfectly homogeneous morphotropic PZT film, with 100% of tetragonal phase transiting to rhombohedral phase, could lead to the most efficient PZT thin film.

Finally, the in-situ under electric field XRD was performed with the nano-pencil beam at ID11 beamline in ESRF on the G and GF samples. As the diffraction was in transmission mode, this measurement enabled the cross-sectional scanning of 1 μ m-thick PZT film with about 140 nm resolution. This measurement would permit to localise the morphotropic phase in the PZT layer and to validate the hypothesis of phase transition under an electric field in MPB PZT. It allows the observation of the local composition inhomogeneity and microstructure gradient impact on this phase transition. However, at the moment of writing, the data is still under treatment.

Conclusion

Chapter III presents the main experiments conceived in searching for correlations between microstructure and piezoelectric properties and it exposes the related results. The subject of the present study are sol-gel fabricated PZT thin films of morphotropic composition.

Nowadays, the sol-gel deposition technique is widely used for PZT production. Thanks to the maturity and flexibility of this fabrication technique and the performances of PZT, this technique has persisted in being the leading technique for at least a decade. Sol-gel is known to induce Zr/Ti chemical gradient through the film thickness due to different thermodynamics of crystal formation for PTO and PZO. Thus, the composition gradient forms each time the crystallization annealing of newly deposited PZT layers occurs. The solution to overcoming the gradient is the use of different precursor solutions compensating for the composition variations. In addition, the Zr/Ti gradient is also known to lower most PZT electric and piezoelectric performances, namely dielectric permittivity, polarization, longitudinal and transverse piezoelectric coefficients. Therefore, this chemical gradient was studied closely in the first part of this chapter. The nano-pencil beam XRD in ESRF was performed in the transmission geometry on PZT samples with different Zr/Ti gradient. 140 nm-beam allowed the 1 μ m PZT cross-sectional scan and demonstrated the presence of phase gradient in the layer, following the composition gradient. Zones with a Zr excess were more rhombohedral and zones with a Ti excess were more tetragonal like. This observation shows very high sensibility of the microstructure upon the chemical composition of morphotropic PZT.

There are several theories explaining the piezoelectric effect in morphotropic PZT bulk ceramic and thin films on microstructural level. To cite the main theories, there is the domain switching in tetragonal and rhombohedral phase, the rotation of polarization axis of monoclinic phase, the adaptive monoclinic phase composed of tetragonal and rhombohedral nanodomains with low domain wall energy or an electric field induced phase transition. Our objective was to find what theory best fit our material's behaviour under voltage. Thus, we performed in-situ under electric field XRD with our best PZT film. In other words, we put a PZT capacitor under voltage in the X-ray beam. XRD profile refinements show microstructural modifications under voltage, which can be interpreted as *a*-domain tetragonal-to-rhombohedral phase transition. No a-to-*c*-domain switching was detected. Note that monoclinic PZT phase was not used in refinement, as it did not fit our diffraction pattern. Moreover, the longitudinal piezoelectric coefficient $d_{33,eff}$ that was estimated by XRD refinement results, is in accordance with the measured $d_{33,eff}$ by AixACCT apparatus.

Finally, the effect of Zr/Ti chemical gradient on the phase transition was studied. Two samples with different gradients were observed by in-situ XRD. The refinement results showed about four times more phase transition in the sample with attenuated gradient in comparison to the sample with standard Zr/Ti gradient. Thus, the more homogeneous morphotropic sample exhibits more phase transition. In addition to the phase transition, the profile fitting of PZT with gradient evidenced the appearance of a tensile strain in the out-of-plane direction in the rhombohedral PZT cell. d_{33,eff} coefficient estimation for this sample taking into account both microstructural contributions was found to be in the same range as the average d_{33,eff} of this type of PZT samples. The piezoelectric properties of the sample with attenuated Zr/Ti gradient are better than the properties of the sample with gradient. This means that the voltage induced phase transition is more efficient than the voltage induced strain in rhombohedral PZT cells. The most efficient phenomenon in terms of cell dimensions change under voltage is in theory the a-to-*c*-domain switching. Nonetheless, it was proven experimentally that in tetragonal PZT this domain switching is not sustainable, because the stress

generated during switching damages the PZT. To conclude, the best option would be PZT with 100% tetragonal phase transiting completely to rhombohedral under voltage.

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General conclusion

Sol-gel morphotropic PZT thin films composed of active layers are currently one of the most used materials in piezo MEMS applications. They are widely exploited for their outstanding piezoelectric properties. Despite their intensive use, the microstructure of these PZT films is not very well known. Scientific articles often discuss the microstructure of PZT bulk ceramics or PZT films with their composition shifted to the pure tetragonal or to the pure rhombohedral phases, making its analysis simpler. However, microstructure is the physical basis of the piezoelectric effect in materials. We believe that the understanding of microstructural origins of piezoelectric effect is one of the keys to piezoelectric property enhancement. Thus, the main objective of this thesis work was to search for and study correlations between microstructure and piezoelectric effect in sol-gel fabricated morphotropic PZT thin films. Our strategy for reaching this goal was to analyze closely the microstructure of these films, using overall and statistical characterization methods like X-ray diffraction (XRD) and local characterization methods, namely Transmission Electron Microscopy (TEM), Electron diffraction (ED) and Secondary Ion Mass Spectrometry (SIMS). In particular, crystallographic phases, thin film stress state and the influence of the Zr/Ti chemical gradient were investigated. We also took advantage of the non-intruding character of XRD and we performed insitu XRD on PZT capacitors while an electric field was applied. Thanks to this characterization, we could observe voltage induced microstructural changes occurring within PZT. Results of these analyses were then associated to electric and piezoelectric characterizations of PZT films. Thanks to this study, interesting microstructure and piezoelectricity correlations could be drawn for sol-gel morphotropic PZT thin films.

This work began with the introductory chapter (Chapter I), aiming to present the background related to the thesis. Firstly, we presented typical examples of piezoelectric materials, especially thin films, and their piezoelectric properties and applications. The piezoelectric effect was then described using thermodynamic and mechanical approach. The chapter continued by focusing on the main subject studied in this thesis, the Pb(Zr,TiO)₃ (PZT). After the general description of the material, we briefly presented PZT bulk ceramics and PZT thin films, namely their applications and actual market situation. PZT exhibit its best properties at the composition corresponding to the morphotropic phase boundary (MPB). Believing that the understanding of connections between microstructure and piezoelectricity would enable us to enhance PZT piezoelectric properties, we then summarized microstructural studies performed on MPB PZT. The research on bulk ceramics is more advanced because it started earlier. Thus, first we presented an overview about theories explaining the piezoelectric effect in these materials, namely a-to-c domain switching, polarization axis rotation, rhombohedral nanodomains reorientation and tetragonal-to-monoclinic phase transition. The final part was dedicated to the sol-gel morphotropic PZT thin films. The most particular microstructural features associated to the sol-gel PZT are presented, namely texture, stress and Zr/Ti composition gradient. Then, we introduced some recent in-situ studies of microstructural changes in PZT thin films provoked by an electric field. However, we realized that only PZT films with their composition shifted from the MPB are studied in in-situ experiments in literature. Thus, we defined the main objective of the thesis. Our major goal was to analyze PZT microstructure and to draw correlations between microstructure and the piezoelectric effect of MPB PZT thin films fabricated by sol-gel method. We aimed to reach this goal with microstructural study of sol-gel MPB PZT and in-situ under voltage observations.

Material fabrication and characterization methods were described in Chapter II. All through the thesis one can refer to this part for details about the sol-gel deposition method, fabrication of PZT samples and microstructural, electric and piezoelectric characterization techniques. The beginning of the chapter focuses on the sol-gel PZT deposition technique. Microstructural features resulting from this deposition method are detailed and linked to the material's performances. Then, we present the fabrication process of PZT capacitors used in our experiments. Each step from PZT film deposition until the achievement of final capacitor samples is explained. Afterwards, we focus on characterization techniques used in order to achieve the main goals of this work. The main microstructural characterization technique is X-ray diffraction (XRD). Firstly, the main contributions of XRD to our study are given. We then describe the data analysis techniques namely Rietveld and Combines Analysis. Two diffraction setups, laboratory and ESRF setup, are described and compared in relation to PZT thin films study. This is followed by a brief presentation of local microstructure and composition characterization methods, which are respectively Precession Electron Diffraction and Secondary Ion Mass Spectrometry. Finally, we turn our attention to electric and piezoelectric characterization methods. Basic electric characterizations are presented, namely capacitance, relative dielectric permittivity and polarization measurements. Then, piezoelectric measurements techniques relative to the direct and the inverse effects were described.

Chapter III is dedicated to the description of the main experiments aiming to research of correlations between microstructure and the piezoelectric effect and to the presentation of the major results. The first part is focused on the sol-gel deposition technique microstructure particularities and their effect on piezoelectric properties. In today's world sol-gel is widely used and has a well established deposition technique. Moreover sol-gel PZT is among the most performant PZT thin films worldwide. The typical signature of sol-gel deposition is Zr/Ti chemical gradient across the film thickness. The appearance of the gradient is related to thermodynamics. The enthalpy of formation of $PbTiO_3$ crystals is lower than the enthalpy of crystallization of PbZrO₃. For this reason the composition gradient forms every time the crystallization annealing of a newly deposited PZT layer takes place. Note that this Zr/Ti gradient may be compensated using precursor solutions of different compositions. The gradient is also known to lower most PZT electric and piezoelectric performances, namely dielectric permittivity, polarization, longitudinal and transverse piezoelectric coefficients. Thus, the first experiment presented in this manuscript was dedicated to the investigation of the composition gradient effect on the PZT microstructure. Three samples with a morphotropic PZT active layer with three different compositions gradients were characterized using the Nano-pencil beam transmission XRD in ESRF. The 140 nm-wide beam enabled the cross-sectional scan of 1 µmthick PZT layers and evidenced the tetragonal and rhombohedral phase gradient that followed exactly the Zr/Ti composition gradient. Zones with Zr excess were more rhombohedral and zones with Ti excess were more tetragonal like. Moreover, samples with higher compositional gradient evidenced also higher microstructural phase gradient. Note that samples with higher composition gradient, possess poorer dielectric and piezoelectric performances. Thus our first correlation concerns the Zr/Ti composition gradient, the microstructural gradient and the film performances. The more the chemical composition of the sample is homogeneous, the more the sample's microstructure is homogeneous and the better the dielectric and the piezoelectric performances are. Also these observations show very high sensibility of PZT microstructure on the chemical composition. The PZT with the lowest composition gradient still possesses 5% of phase gradient according to XRD.

The second part focused on theories explaining the piezoelectric effect in morphotropic PZT on microstructural level. There are several theories based mostly on PZT bulk ceramics observation. To give some examples, there is domain switching in tetragonal and rhombohedral phase, polarization axis rotation in monoclinic phase, reorganization of rhombohedral nanodomains with low domain wall energy and voltage induced phase transition. Our ambition was to perform is-situ under electric field experiments in order to find, which theory fits the best for our thin films. Thus, we performed in-situ XRD with our best PZT film. The profile refinements showed microstructural modifications under voltage. At 0V, we identified that PZT is composed with 60% of tetragonal phase and 40% of rhombohedral phase. Then as the voltage increased, the amount of tetragonal phase decreased and the amount of rhombohedral phase increased reaching 100% at 30 V. These microstructural modifications can be interpreted as *a*-domain tetragonal-to-rhombohedral phase transition. Note that neither tetragonal c-domains were detected, nor *a*-to-*c* domain switching under voltage was identified. The morphotropic phase was not used in refinement as it did not fit our diffraction pattern. Thus, our second correlation is related to the mechanism driving the piezoelectric effect in our PZT thin film, which seems to be the electric-induced phase transition. This observation enabled estimation of the longitudinal piezoelectric coefficient $d_{33,eff}$, which appears to be in accordance with the measured $d_{33,eff}$ by AixACCT apparatus.

The third part is a logical progression from the first two. We studied the effect of the Zr/Ti composition gradient on the phase transition. In-situ XRD under voltage was performed on two PZT capacitors, one with standard Zr/Ti gradient and one with attenuated Zr/Ti gradient. Note that both samples had the same thickness and the same major crystal orientation but the sample with attenuated gradient had better dielectric and piezoelectric performances. The XRD pattern refinement showed that the tetragonal-to-rhombohedral phase transition under voltage occurs in both PZT samples. After quantification, we determined that the transition was about four times greater in the sample with attenuated Zr/Ti gradient. Thus, it seems that the more the sample composition is homogeneous, the more phase transition the sample manifests. Note that the profile refinement brought out the appearance of a tensile stress in the out-of-plane direction of the rhombohedral cell. Thus, in addition to the phase transition, the sample with standard Zr/Ti gradient experiences the rhombohedral cell deformation. The estimation of $d_{33,eff}$ piezoelectric coefficient was performed too. d_{33,eff} was calculated taking into account that both phase transition and cell deformation was in the same range as the average d_{33,eff} for this kind of PZT samples. Thus, our third correlation is that PZT films that have homogeneous composition and microstructure exhibit high dielectric and piezoelectric performance and also experience more phase transition. As the samples with attenuated Zr/Ti gradient in theory contain more pure morphotropic composition PZT, one can think that the phase transition is located within the pure morphotropic PZT. Another conclusion is that the voltage induced phase transition provides higher deformation than the voltage induced strain in rhombohedral PZT cell. Alternatively, one can say that the most performant phenomenon in terms of cell deformation under voltage is in theory the a-to-c-domain switching. However, it was proven experimentally, that in tetragonal PZT this domain switching is not sustainable, because the stress generated during switching damages PZT. This observation led us to the conclusion that the best performant PZT would be the one showing 100% tetragonal-to-rhombohedral phase transition under voltage. This means that the initial PZT composition should be more homogeneous and slightly more tetragonal.

To conclude, the main outcome of this work is the study of morphotropic PZT thin films microstructure in correlation with its dielectric and piezoelectric properties in order to enhance them. Here we demonstrated by XRD the presence of microstructural gradient due to the Zr/Ti composition gradient in PZT films. This observation shows extreme sensibility of microstructure on composition. Moreover, the Zr/Ti gradient lowers PZT performances. Thanks to in-situ under electric field XRD, we confirmed that PZT experiences the tetragonal-to-rhombohedral phase transition while voltage is applied. Moreover, this phase transition is higher in PZT with attenuated Zr/Ti gradient, which also shows a higher piezoelectric coefficient. Thus, the best performant PZT has to be homogeneous with morphotropic composition in order to promote the phase transition.

The work on in-situ characterization continues beyond this thesis. In-situ TEM is a characterization method under development in CEA. Experiments with PZT films are currently in progress. We would like to fabricate and analyse by in-situ XRD the new optimized PZT proposed by this work, which would be more homogeneous and slightly more tetragonal. As reported in this thesis, e_{31.eff} is enhanced by hot dc poling. Therefore, it would be interesting to analyse the microstructural changes due to this poling effect. We are also looking forward to see results from in-situ Laue diffraction of PZT grains. This characterization enables to see behaviour of one PZT grain under voltage. Other interesting experiments are under consideration, namely in-situ XRD with Nano-pencil beam using stroboscopic mode at ESRF. PZT samples should receive AC voltage, synchronized with the beam shutter, which would enable observation of PZT microstructure at low frequency [Hinterstein, PRB n°90, 2014]. Inspired by the success of doped PZT bulk ceramics, we would like to investigate the influence of dopants on the microstructure of PZT thin films. Therefore, we plan to perform in-situ XRD on doped PZT films. Finally, in-situ XRD characterization could be applied to other materials having MPB, for example BCTZ or PMN-PT. We could observe and identify microstructural changes under voltage and verify if there is a phase transition induced by an electric field. Perovskite Scandium doped AIN would be another interesting material to characterize by in-situ XRD.

Appendices

Appendix A :

What is XRD ?

This sub-section explains the very basis of X-rays, covering their discovery, interaction with matter and the principles of X-ray diffraction. The diffraction conditions are reminded, mentioning Bragg's equation, Laue's conditions and Ewald's sphere.

1. X-rays

X-rays is a type of electromagnetic waves, which were discovered at the end of XIXst century by Röntgen. They are of the same kind than the visible light or the Herzian radio waves but their frequency is much greater (Figure A.90). It goes from 3.10^{16} to 3.10^{19} Hz, which corresponds, to the energies from 100 eV to 100 keV. Note that the X-rays of higher energies than 5-10 keV, are called hard X-rays and those of lower energies are called soft X-rays.



Figure A.90 : Electromagnetic spectrum [1]

This high frequency nature of X-rays was discovered by German physicists Max Von Laue, his associate Walter Friedrich and their student Paul Knipping in 1912, who performed the first X-ray diffraction by a crystal. It was the crystal of copper sulphate. This discovery earned Laue the Nobel Prize in Physics in 1914 [2] and had a double contribution. Firstly, this diffraction experiment allowed the subsequent

investigation of x-radiation by means of wavelength determination, and secondly it provided the means for the Braggs' structural analysis of crystals for which they received the Nobel Prize in 1915. X-ray analysis of crystals, as initially developed by Sir Lawrence Bragg, became the most widely used technique for the investigation of crystal structure, leading to incalculable advances in both inorganic and organic chemistry, as well as molecular biology.

The general public knows the X-rays mostly for its medical applications like radiography, tomography and radiotherapy. In order to understand different X-ray applications, the next section will explain the basis of interactions between X-rays and matter.

2. Interactions between X-rays and matter

X-rays can be either absorbed or diffused by matter. The **photoelectric effect** is the interaction involving total absorption of the X-rays. The **Compton**, **Rayleigh and Thomson scattering** are interactions resulting in X-ray diffusion. The relative importance and efficiency of each process is strongly dependent upon the energy of the photons and upon the density and atomic number of the absorbing medium. The Rayleigh diffusion and photoelectric absorption are interaction mechanisms in the soft X-ray regime and for the lower hard X-ray energies. At higher energies, Compton scattering dominates.

Moreover, the X-ray vs matter interactions can be classified as **elastic** or **inelastic**. When the interaction does not apply any energy transfer or very few, it is called elastic interaction. The radiation then keeps its coherence and the diffusion can lead to the interference phenomenon, which is at the origin of diffraction in the crystalline matter and serves to study the structure of crystals. The inelastic interaction energetically modifies the intern structure of one or more atoms. The energy transfer is non-negligible and the radiation loses its coherence. Note that the elastic and inelastic diffusions are at the origin of physicochemical analysis of matter.

The **photoelectric effect** belongs to the inelastic interactions because the arriving photon uses all its energy to interact with a strongly bonded electron from the inner atomic shell. The electron will escape its orbit with a kinetic energy equal to the difference between the photon energy and its own binding energy. The expelled electron is called the photoelectron. An outer electron of the ionized atom will fill its vacant place. The energy excess created by the electron transfer from the outer to the inner shell will produce most of the time a characteristic photon (Figure A. 91).



Figure A. 91: Illustration of Photoelectric effect resulting in characteristic photon production and Rayleigh and Compton scattering [3]

The released energy can be also transferred to another electron, which is ejected, from the atom, resulting in the Auger electron emission (Figure A. 92). Note that these effects are used for the elemental detection through X-ray spectroscopy and Auger electron spectroscopy.



Auger electron emission

Figure A. 92: Illustration of Auger electron emission resulting atomic deexcitation [4]

Compton scattering is the predominant interaction between X-rays and soft tissue in medical imaging. In this process the photon interacts inelastically with an outer shell electron sufficiently to eject it from orbit (Figure A. 91). As a result of the interaction, the photon decreases its energy and continues moving in a new direction. Thus, the Compton effect has an absorption component and a scattering component. The amount of energy lost by the photon is proportional to the angle between the original and the scattered photon direction.

Rayleigh scattering is an elastic interaction between X-rays and matter, where the X-ray interacts with polarizable entities and is scattered under a very low angle with no energy loss (Figure A. 91). This type of scattering is dependent on particle size, its refractive index and the wave frequency. High frequency radiation is scattered far more effectively than low frequency radiation. The most common example of

Rayleigh scattering is the scattering of visible light from the Sun by the atoms of nitrogen and oxygen in atmosphere. Blue light has higher frequency, so it is scattered more than the other colours out of the solar light-rays. Therefore, the sky appears blue during the most of the day. At the sunset as the light passes through more atmosphere, even more blue light is scattered, leaving an excess of red light. Thus, sunsets appear redder.

Thomson scattering is an elastic interaction between X-rays and charged particles of the atoms, which are protons and electrons. Whether an electromagnetic wave arrives on a system of charged particles, the electric and the magnetic component of the wave exert a force on the particles. This causes the particles to oscillate with the same frequency as the incident wave. The oscillating charges then act like scatterers and they radiate in the same frequency as the incident wave but in all directions. Thus, the energy of the incident wave is absorbed by the particle and then reemitted in form of a spherical wave. This phenomenon is the basis of the X-ray diffraction characterization. This interaction will be explained in more details in the following section.

3. X-ray diffraction : From one electron to crystals

Let's begin with the scattering by a free electron (Figure A. 93). The electromagnetic plane linearly polarized wave $\vec{E_0}$ is traveling along Ox. In the point O, the wave hits an electron, which then undergoes an acceleration \vec{a} , equal to $\frac{e}{m}\vec{E_0}$ where e stands for the electric charge and m for the mass of the electron. The accelerated electron then in its turn radiates an electromagnetic wave given by Maxwell equations, which in a random point P is described as:

$$E = am \frac{r_e}{e} \frac{\sin \alpha}{r}$$

Here, r_e stands for the electron radius $=\frac{e^2}{mc^2}=2.82 \ 10^{-15}m$; r is the distance OP and α represents the angle between OP and the acceleration vector \vec{a} .



Figure A. 93: Scattering by one electron

If P is situated in the plane yOx, E is perpendicular to this plane and is given by $E_{\perp} = E_0 \frac{r_e}{r}$. If P is situated in zOx plane, E is parallel to this plane and is equal to $E_{\parallel} = E_0 r_e \frac{\cos(2\theta)}{r}$. Thus, a non-polarized incident beam will deliver a scattered coherent intensity of $\frac{1}{2}(I_{\perp} + I_{\parallel}) = I_0 r_e^2 \frac{(1+\cos^2 2\theta)}{2r^2}$. Expressed in solid angle units, this equation is **the Thomson's formula**:

$$I_{e-} = I_0 r_e^2 \frac{(1 + \cos^2 2\theta)}{2}$$

The term r_e is proportional to the inverse of the particle mass. Hence, replacing the electron by a single proton would give a negligible scattered intensity. It would be 1840^2 times smaller. Thus, only the electrons are considered in the X-ray diffraction by the matter.

The binding forces between atom and electron are not considered in the Thomson's model. The factor containing θ is called the **Polarization factor P(20)** and express that the beam after diffraction becomes partially polarized. P(20) is defined as equal to $\frac{(1+\cos^2 2\theta)}{2}$.

Now, let's consider **the scattering produced by an atom**. This time the electromagnetic wave hits Z electrons, which are no more free but bonded to the atomic nucleus. The binding energy is stronger with the higher Z. The strength of the bondage increases also when considering deeper shells.

In order to solve the problem, the spotty attribute of electron has to be replaced by the notion of charge repartition represented by an electric charge density p(r) which stands for the probability of the presence of an electron at the distance r.

We give the name **Atomic scattering factor** to the ratio between the amplitude scattered by an atom and a single electron. The Atomic scattering factor is:

$$f = \int_{r} \rho(r) e^{(2\pi i r * S)} dr$$

Note that S stand for the difference between the incident beam wave vector v_0 and the diffracted beam wave vector v.

Suppose a unit cell that has n atom at the position r_j with j = [1;n] with respect to the origin of the unit cell. Alone, they diffract according to their Atomic scattering factor. If the origin is transferred from their nucleus to the origin of the unit cell, the phase angle change by $2\pi r_j^*S$. The sum of scattering by separate atoms in the unit cell is called the **Structure factor** and is expressed as follows:

$$F(S) = \sum_{j=1}^{n} f_j e^{2\pi i r_j * S}$$

Now, let's suppose that the crystal has translation vectors a, b and c and contains a large number of unit cells, n_1 in the a direction, n_2 in the b direction and n_3 in the c direction. To obtain **the scattering by the crystal**, one has to add the scattering by all unit cells with respect to a single origin O. Consider the own origin of a unit cell at position ta+ub+vc with t, u and v whole numbers. Then, the sum of all unit cell gives the total wave **K(S)** scattered by the crystal:



Form factor

The form factor corresponds to the multiplication of the unit cell in space in order to form the entire crystal.

4. Diffraction conditions

For formulation of diffraction conditions, let's consider an infinitely large crystal. Because of huge number of unit cells and because their scattering vectors are pointing in different directions, the scattering by a crystal is in general zero. However, in the case a*S, b*S and c*S are integers, the vectors interfere constructively and the crystal scattering can be of appreciable intensity. This is the **Laue condition**:

$$a * S = h$$
$$b * S = k$$
$$c * S = l$$

Here, a,b and c stand for the translation vectors and hkl are the Miller indices. In these conditions, all unit cells scatter in phase.

The second diffraction condition is called the Bragg's law. The law explains that there are constructive interferences between two diffracted waves, if the path difference between them is the multiple of the wavelength. The

Figure A. 94 illustrates this principle.



Figure A. 94: Illustration of Bragg's law [5]

Thus, the well-known Bragg's equation emerges:

$$\frac{2d\sin\theta}{\lambda} = 1$$

The Ewald's condition can be geometrically explained using the reciprocal lattice and the Ewald's sphere (

Figure A. 95). The Ewald's sphere is a sphere of radius $\frac{1}{\lambda}$ centered at C. The condition enabling the plane (hkl) to diffract is that the corresponding reciprocal node is located on the Ewald's sphere.



Figure A. 95: Illustration of the Ewald's sphere and Ewald's condition [6]

These three diffraction conditions are equivalent and their use depends on the experimental circumstances.

Appendix B:

Instrumental function X-Pert Panalytical

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_riet_par_2-theta_offset
_0.032827515
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#end_subordinateObject_none cal

#subordinateObject Instrument disalignment

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#end_subordinateObject_Instrument disalignment

#subordinateObject Bragg-Brentano

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_pd_instr_monochr_pre_spec none
_pd_instr_2theta_monochr_pre 0
_pd_instr_divg_ax_src/samp 0.27
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#subordinateObject Theta-2Theta

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#subordinateObject_Ka2

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#subordinateObject_Kb

diffrn radiation wavelength id 'Kb'

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#end_subordinateObject_Kb

#end_subordinateObject_X-ray

#subordinateObject_Scintillation

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_riet_asymmetry_tan dep true
_riet_omega/chi_broadening_convoluted true
_riet_par_asymmetry_truncation 0.4
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_riet_par_asymmetry_value
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  0
loop_
_riet_par_caglioti_value
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  0.042373955
  0.0068384507
loop_
_riet_par_gaussian_value
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 0.0028461183
loop_
_riet_par_broadening_chi
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#subordinateObject none abs
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#end_subordinateObject_none abs

Appendix C :

1. CIF file for tetragonal PZT: 92059-ICSD

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#©2012 by Fachinformationszentrum Karlsruhe, and the U.S. Secretary of
#Commerce on behalf of the United States. All rights reserved.
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_audit_creation_date
                            2002/10/01
_chemical_name_systematic
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                                'Pb ((Zr0.52 Ti0.48) 03)'
_chemical_formula_sum
                              '03 Pb1 Ti0.48 Zr0.52'
_publ_section_title
Tetragonal-to-monoclinic phase transition in a ferroelectric
perovskite: the structure of Pb Zr0.52 Ti0.48 O3
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_citation_journal_abbrev
_citation_year
citation journal volume
_citation_journal_issue
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_citation_page_last
_citation_journal_id_ASTM
primary 'Physical Review, Serie 3. B - Condensed Matter (18,1978-)'
2000 61 13 8687 8695 PRBMDO
_publ_author_name
Noheda, B.;Gonzalo, J.A.;Cross, L.E.;Guo, R.;Park, S.-E.;Cox,
D.E.; Shirane, G.
_cell_length_a
                        4.0460(1)
_cell_length_b
                        4.0460(1)
_cell_length_c
                        4.1394(1)
_cell_angle_alpha
                          90.
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_atom_site_aniso_label _atom_site_aniso_type_symbol _atom_site_aniso_U_11

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_atom_site_aniso_U_23
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2. CIF file for rhombohedral PZT: 24562-ICSD*

*Note that this phase in not a standard setting, thus it was subsequently modified in order to enable Maud texture modelization. Rhombohedral R3m space group was changed into monoclinic P1 group. Unit cell parameters and atom positions were modified so as to respect the P3m space group. data_24562-ICSD #©2012 by Fachinformationszentrum Karlsruhe, and the U.S. Secretary of #Commerce on behalf of the United States. All rights reserved. database code ICSD 24562 _audit_creation_date 1980/01/01 _audit_update_record 2012/08/01 _chemical_name_systematic Lead Zirconium Titanium Oxide (1/0.58/0.42/3) _chemical_formula_structural 'Pb (Zr0.58 Ti0.42) 03' chemical formula sum '03 Pb1 Ti0.42 Zr0.58' _publ_section_title Atomic structures of two rhombohedral ferroelectric phases in the Pb (Zr Ti) 03 solid solution series loop_ _citation_id _citation_journal_abbrev _citation_year _citation_journal_volume _citation_page_first _citation_page_last _citation_journal_id_ASTM primary 'Solid State Communications' 1969 7 865 868 SSCOA4 2 'Journal of the Physical Society of Japan' 1953 8 615 629 JUPSAU _publ_author_name Michel, C.; Moreau, J.M.; Achenbach, G.D.; Gerson, R.; James, W.J.

; _cell_length_a 4.07 _cell_length_b 4.07 _cell_length_c 4.07 _cell_angle_alpha 89.65 _cell_angle_beta 89.65 _cell_angle_gamma 89.65 _cell_volume 67.42 _cell_formula_units_Z 1 _symmetry_space_group_name_H-M 'R 3 m R' _symmetry_Int_Tables_number 160 _refine_ls_R_factor_all 0.038 loop_ _symmetry_equiv_pos_site_id _symmetry_equiv_pos_as_xyz 1 'z, y, x' 2 'z, x, y' 3 'x, z, y' 4 'y, z, x' 5 'y, x, z' 6 'x, y, z' loop_ _atom_type_symbol _atom_type_oxidation_number 02--2 Pb2+ 2 Ti4+ 4 Zr4+ 4 loop_ _atom_site_label _atom_site_type_symbol _atom_site_symmetry_multiplicity _atom_site_Wyckoff_symbol _atom_site_fract_x _atom_site_fract_y _atom_site_fract_z _atom_site_occupancy _atom_site_attached_hydrogens Pb1 Pb2+1 a 0.552 0.552 0.552 1.0 Zr1 Zr4+ 1 a 0.038 0.038 0.038 0.58 0 Ti1 Ti4+1 a 0.038 0.038 0.038 0.42 0 01 02-3 b 0.558 0 0 1.0

#End of data_24562-ICSD

Appendix D:

Refined parameters: PZT Gradient Free sample

p17 00v 00S -40	-	-	-	-	****	false
Sample_x	-	-	-	-	****	false
_pd_spec_orientation_omega	0	0.0	0.0	0.0	Fixed	false
_pd_spec_orientation_chi	0	0.0	0.0	0.0	Fixed	false
_pd_spec_orientation_phi	0	0.0	0.0	0.0	Fixed	false
_riet_par_spec_displac_x	0	0.0	0.0	0.0	Fixed	false
_riet_par_spec_displac_y	0	0.0	0.0	0.0	Fixed	false
_riet_par_spec_displac_z	0	0.0	0.0	0.0	Fixed	false
_pd_spec_size_axial	7	0.0	100.0	0.0	Fixed	false
_pd_spec_size_equat	6	0.0	100.0	0.0	Fixed	false
_pd_spec_size_thick	0.000002	0.0	100.0	0.0	Fixed	false
_pd_spec_size_radius	0	0.0	100.0	0.0	Fixed	false
_pd_spec_size_radius_y	0	0.0	100.0	0.0	Fixed	false
Ru	-	-	-	-	****	false
_riet_par_spec_layer_thickness	1050.2983	0.1	1.0E8	0.0	Fixed	false
_reflectivity_layer_critical_qc	0.04	0.0010	0.5	0.0	Fixed	false
_reflectivity_layer_absorption	2.0E-7	1.0E-8	1.0E-5	0.0	Fixed	false
_reflectivity_layer_roughness	2.0	0.01	100.0	0.0	Fixed	false
_pd_phase_atom_%0	0	0.0	1.0	0.0	Fixed	false
_pd_phase_atom_%1	1.0	0.0	1.0	0.0	Fixed	false
_pd_phase_atom_%2	0	0.0	1.0	0.0	Fixed	false
_pd_phase_atom_%3	0	0.0	1.0	0.0	Fixed	false
PZT	-	-	-	-	****	false
_riet_par_spec_layer_thickness	11715.449	0.1	1.0E8	0.0	Fixed	false
_reflectivity_layer_critical_qc	0.04	0.001	0.5	0.0	Fixed	false
_reflectivity_layer_absorption	2.0E-7	1.0E-8	1.0E-5	0.0	Fixed	false
_reflectivity_layer_roughness	2.0	0.01	100.0	0.0	Fixed	false
_pd_phase_atom_%0	0	0.0	1.0	0.0	Fixed	false
_pd_phase_atom_%1	0	0.0	1.0	0.0	Fixed	false
_pd_phase_atom_%2	0.465977	0.0	319.0	0.012911369	Refined	false
_pd_phase_atom_%3	0.534023	0.0	1.0	0.0	Equal to	false
Pt	-	-	-	-	****	false
_riet_par_spec_layer_thickness	1000	0.1	1.0E8	0.0	Fixed	false
_reflectivity_layer_critical_qc	0.04	0.001	0.5	0.0	Fixed	false
_reflectivity_layer_absorption	2.0E-7	1.0E-8	1.0E-5	0.0	Fixed	false
_reflectivity_layer_roughness	2.0	0.01	100.0	0.0	Fixed	false
_pd_phase_atom_%0	1.0	0.0	1.0	0.0	Fixed	false
_pd_phase_atom_%1	0	0.0	1.0	0.0	Fixed	false
_pd_phase_atom_%2	0	0.0	1.0	0.0	Fixed	false
_pd_phase_atom_%3	0	0.0	1.0	0.0	Fixed	false
DataFileSet_x	-	-	-	-	****	false
_riet_par_background_exp_shift	0	0.0	0.0	0.0	Fixed	false
_riet_par_background_exp_thermal_shift	0	0.0	0.0	0.0	Fixed	false

_pd_spec_orientation_omega	0	0.0	0.0	0.0	Fixed	false
_pd_spec_orientation_chi	0	0.0	0.0	0.0	Fixed	false
_pd_spec_orientation_phi	0	0.0	0.0	0.0	Fixed	false
_riet_par_background_pol0	253.94798	-7176.7773	8771.617	0.0	Fixed	false
_riet_par_background_pol1	-5.1382375	-77.26483	0.0	0.0	Fixed	false
_riet_par_background_pol2	0.02963356	-77.26483	4.6889005	0.0	Fixed	false
_riet_par_background_chi0	-0.67886883	-7.7608953	70.81745	0.0	Fixed	false
_riet_par_background_chi1	0.027329285	-0.30797815	0.37641773	0.0	Fixed	false
_riet_par_background_chi2	-2.4177111E-4	-0.30797815	0.37641773	0.0	Fixed	false
XPert Pro	-	-	-	-	****	false
_pd_proc_intensity_incident	8.426755	0.0	10000.0	0.017204542	Refined	false
riet par 2-theta offset0	-0.087602995	-1387.6238	0.29544765	0.0	Fixed	false
Bragg-Brentano	-	-	-	-	****	false
diffrn radiation polarisn norm	0	0.0	360.0	0.0	Fixed	false
diffrn radiation polarisn ratio	0	0.0	1.0	0.0	Fixed	false
X-rav	-	-	-	-	****	false
Ka1	-	-	-	-	****	false
diffrn radiation wavelength	1.5405980	0.1	10.0	0.0	Fixed	false
diffrn radiation wavelength wt	1	0.0	1 01	0.0	Fixed	false
Ka2	-	-	-	-	****	false
diffrn radiation wavelength	1 5444260	0.1	10.0	0.0	Fixed	false
diffrn radiation wavelength wt	0.5005	0.0	1.01	0.0	Fixed	falso
_unini_radiation_wavelengtii_wt	-	-	-	-	*****	falso
diffra radiation wavelength	1 3022500	0.1	10.0	0.0	Fived	falso
diffra radiation wavelength wt	0.3043367	0.1	10.0	0.0	Fixed	falso
Carlioti DV	0.3943307	0.0	1.01	0.0	*****	falso
riet par asymmetry value0	-	-	-	-	Fived	falco
_net_par_asymmetry_value0	0	0.0	1000.0	0.0	Fixed	false
_net_par_asymmetry_value1	0	0.0	0.0	0.0	Fixed	false
_net_par_cagnoti_value0	0.06131076	-0.1	0.1	0.0	Fixed	false
_riet_par_cagnoti_value1	0.042373955	-0.3813656	0.4661135	0.0	Fixed	faise
_riet_par_cagnoti_value2	0.0068384507	-0.3813656	0.4661135	0.0	Fixed	faise
_riet_par_gaussian_value0	0.027112907	-1.0	2.0	0.0	Fixed	faise
_riet_par_gaussian_value1	0.0028461183	-0.025615064	0.031307302	0.0	Fixed	faise
_riet_par_broadening_chi0	0	0.0	0.0	0.0	Fixed	false
_riet_par_broadening_chi1	0.009925562	-0.089330055	0.10918118	0.0	Fixed	false
_riet_par_broadening_chi2	-0.005506634	-0.089330055	0.10918118	0.0	Fixed	false
Vero_PZT_tdt_8oct13_P17_C1_1.xrdml(0)	-	-	-	-	****	false
_pd_meas_counts_monitor	1.0	0.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_x_2R	0	-10.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
Vero_PZT_tdt_8oct13_P17_C2_2.xrdml(0)	-	-	-	-	****	false
_pd_meas_counts_monitor	1.0	0.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_x_2R	0	-10.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
Vero_PZT_tdt_8oct13_P17_C3_3.xrdml(0)	-	-	-	-	****	false
_pd_meas_counts_monitor	1.0	0.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_x_2R	0	-10.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
Vero_PZT_tdt_8oct13_P17_C4_4.xrdml(0)	-	-	-	-	****	false
_pd_meas_counts_monitor	1.0	0.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_x_2R	0	-10.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
Vero_PZT_tdt_8oct13_P17_C5_5.xrdml(0)	-	-	-	-	****	false
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_pd_meas_counts_monitor	1.0	0.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_x_2R	0	-10.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
Vero_PZT_tdt_8oct13_P17_C6_6.xrdml(0)	-	-	-	-	****	false
_pd_meas_counts_monitor	1.0	0.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_x_2R	0	-10.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
Vero_PZT_tdt_8oct13_P17_C7_7.xrdml(0)	-	-	-	-	****	false
_pd_meas_counts_monitor	1.0	0.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_x_2R	0	-10.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
Vero_PZT_tdt_8oct13_P17_C8_8.xrdml(0)	-	-	-	-	****	false
_pd_meas_counts_monitor	1.0	0.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_x_2R	0	-10.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
Vero PZT tdt 8oct13 P17 C9 9.xrdml(0)	-	-	-	-	****	false
_pd_meas_counts_monitor	1.0	0.0	10.0	0.0	Fixed	false
riet par spec displac x 2R	0	-10.0	10.0	0.0	Fixed	false
riet par spec displac z 2R	0	-10.0	10.0	0.0	Fixed	false
Vero PZT tdt 8oct13 P17 C10 10.xrdml(0)	-	-	-	-	****	false
pd meas counts monitor	1.0	0.0	10.0	0.0	Fixed	false
riet par spec displac x 2R	0	-10.0	10.0	0.0	Fixed	false
riet par spec displac z 2R	0	-10.0	10.0	0.0	Fixed	false
Vero PZT tdt 8oct13 P17 C11 11.xrdml(0)	-		-	-	****	false
pd meas counts monitor	1.0	0.0	10.0	0.0	Fixed	false
riet par spec displac x 2R	0	-10.0	10.0	0.0	Fixed	false
riet par spec displac z 2R	0	-10.0	10.0	0.0	Fixed	false
Vero PZT tdt 8oct13 P17 C12 12.xrdml(0)	-		-	-	****	false
pd meas counts monitor	1.0	0.0	10.0	0.0	Fixed	false
riet par spec displac x 2R	0	-10.0	10.0	0.0	Fixed	false
riet par spec displac z 2R	0	-10.0	10.0	0.0	Fixed	false
Vero PZT tdt 8oct13 P17 C13 13.xrdml(0)	-		-	-	****	false
nd meas counts monitor	1.0	0.0	10.0	0.0	Fixed	false
riet par spec displac x 2R	0	-10.0	10.0	0.0	Fixed	false
riet par spec displac z 2R	0	-10.0	10.0	0.0	Fixed	false
Vero PZT tdt 8oct13 P17 C14 14.xrdml(0)	-	-	-	-	****	false
pd meas counts monitor	1.0	0.0	10.0	0.0	Fixed	false
riet par spec displac x 2R	0	-10.0	10.0	0.0	Fixed	false
riet par spec displac z 2R	0	-10.0	10.0	0.0	Fixed	false
Vero PZT tdt 8oct13 P17 C15 15.xrdml(0)	-		-	-	****	false
nd meas counts monitor	1.0	0.0	10.0	0.0	Fixed	false
riet par spec displac x 2R	0	-10.0	10.0	0.0	Fixed	false
riet par spec displac z 2R	0	-10.0	10.0	0.0	Fixed	false
Vero PZT tdt 8oct13 P17 C16 16 xrdml(0)	-	-	-	-	****	false
nd meas counts monitor	1.0	0.0	10.0	0.0	Fixed	false
riet nar snec displac y 2R	0	-10.0	10.0	0.0	Fixed	false
riet par spec displac z 2R	0	-10.0	10.0	0.0	Fixed	false
Vero PZT tdt 80ct13 P17 C17 17 xrdml(0)	-	-	-	-	****	false
pd meas counts monitor	1.0	0.0	10.0	0.0	Fixed	false
riet par spec displac x 2R	0	-10.0	10.0	0.0	Fixed	false
riet par spec displac z 2R	0	-10.0	10.0	0.0	Fixed	false
				-		

Vero_PZT_tdt_8oct13_P17_C18_18.xrdml(0)	-	-	-	-	****	false
_pd_meas_counts_monitor	1.0	0.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_x_2R	0	-10.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
Vero_PZT_tdt_8oct13_P17_C19_19.xrdml(0)	-	-	-	-	****	false
_pd_meas_counts_monitor	1.0	0.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_x_2R	0	-10.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
Vero_PZT_tdt_8oct13_P17_C20_20.xrdml(0)	-	-	-	-	****	false
_pd_meas_counts_monitor	1.0	0.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_x_2R	0	-10.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
Vero_PZT_tdt_8oct13_P17_C21_21.xrdml(0)	-	-	-	-	****	false
_pd_meas_counts_monitor	1.0	0.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_x_2R	0	-10.0	10.0	0.0	Fixed	false
riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
Vero PZT tdt 8oct13 P17 C22 22.xrdml(0)	-	-	-	-	****	false
pd meas counts monitor	1.0	0.0	10.0	0.0	Fixed	false
riet par spec displac x 2R	0	-10.0	10.0	0.0	Fixed	false
riet par spec displac z 2R	0	-10.0	10.0	0.0	Fixed	false
Vero PZT tdt 8oct13 P17 C23 23.xrdml(0)	-	-	-	-	****	false
nd meas counts monitor	1.0	0.0	10.0	0.0	Fixed	false
riet nar spec displac x 2R	0	-10.0	10.0	0.0	Fixed	false
riet par spec_displac_z 2R	0	-10.0	10.0	0.0	Fixed	false
Vero PZT tdt 8oct13 P17 C24 24 xrdml(0)	-	-	-	-	****	false
nd meas counts monitor	10	0.0	10.0	0.0	Fixed	false
riet nar spec displac x 2R	0	-10.0	10.0	0.0	Fixed	false
riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
Vero P7T tdt 8oct13 P17 (25 25 xrdml(0)	-	-	-	-	****	false
nd meas counts monitor	10	0.0	10.0	0.0	Fixed	false
riet nar snec displac y 2R	0	-10.0	10.0	0.0	Fixed	false
riet par spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
P+ 1011109	-	-10.0	-	-	*****	false
call length a	3 9199934	5.0	30.0	5 2582942F-5	Refined	falso
riot par strain thormal	0	-0.1	0.1	0.0	Fived	falso
aventl absorpt cryst size	0	-0.1	100.0	0.0	Fixed	false
riot par phase scale factor	10	0.001	100.0	0.0	Fixed	false
Standard Eurotions	1.0	0.0	100.0	0.0	*****	false
rita odf background	-	-	- 10	-	Fired	false
111	0.001	0.0	1.0	0.0	****	false
111 tautura fibar component intensity	-	-	-	-	Fired	false
_texture_liber_component_intensity	1	0.0	1.0	0.0	Pixeu	false
_texture_liber_component_theta	-0.028893834	0.0	90.0	0.030014997	Renneu	false
_texture_liber_component_pnix		0.0	360.0	0.0	Fixed	faise
_texture_liber_component_thetaH	54.00054	0.0	90.0	13.820964	Renned	faise
_texture_nber_component_pnih	45.290276	0.0	360.0	11.790444	Refined	faise
_texture_fiber_component_fwhm	10.23889	0.0	360.0	0.36155993	Refined	false
_texture_hber_component_gauss_content	0.747952	0.0	1.0	0.0	Fixed	false
Popa rules	-	-	-	-	TTTTT	false
_riet_par_anisocryst_size0	2231.2048	5.0	10000.0	158.07777	Kefined	raise
_riet_par_anisocryst_size1	0204472	-18855.904	1000.0	0.0	rixed	raise
_riet_par_anisocryst_size2	-930.1173	-18855.904	1000.0	262.2402	Refined	false
_riet_par_anisocryst_size3	0	-1000.0	1000.0	0.0	Fixed	false

_riet_par_aniso_microstrain0	0.0014747246	-0.1	0.1	0.0	Fixed	false
_riet_par_aniso_microstrain1	-8.49071E-4	-0.1	0.1	0.0	Fixed	false
Triaxial Stress Isotropic E	-	-	-	-	****	false
_rista_elastic_modulus_E	168	1.0	900.0	0.0	Fixed	false
_rista_poisson_ratio_v	0.3	-0.1	0.5	0.0	Fixed	false
_rista_macrostress_11	0.900	-500.0	500.0	0.0	Fixed	false
_rista_macrostress_22	0.9	-500.0	500.0	0.0	Equal to	false
rista macrostress 33	0	-500.0	500.0	0.0	Fixed	false
rista_macrostress_23	0	-500.0	500.0	0.0	Fixed	false
rista macrostress 13	0	-500.0	500.0	0.0	Fixed	false
rista_macrostress_12	0	-500.0	500.0	0.0	Fixed	false
Atomic Structure	-	-	-	-	****	false
Pt1	-	-	-	-	****	false
atom site occupancy	1.	0.0	1.0	0.0	Fixed	false
atom site fract x	0	0.0	1.0	0.0	Fixed	false
atom site fract v	0	0.0	1.0	0.0	Fixed	false
atom site fract z	0	0.0	1.0	0.0	Fixed	false
atom site B iso or equiv	1.1029571	-1.0	10.0	0.0	Fixed	false
atom site aniso B 11	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 22	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 33	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 23	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 13	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 12	0	-1.0	10.0	0.0	Fixed	false
Bu 9008513	-	-	-	-	****	false
cell length a	2,7079813	5.0	30.0	2.504754E-4	Refined	false
cell length c	4.285157	5.0	30.0	1.8110029E-4	Refined	false
riet par strain thermal	0	-0.1	0.1	0.0	Fixed	false
exptl absorpt cryst size	0	0.001	100.0	0.0	Fixed	false
riet par phase scale factor	1.0	0.0	100.0	0.0	Fixed	false
Standard Functions	-	-	-	-	****	false
rita odf background	0.001	0.0	1.0	0.0	Fixed	false
002	-	-	-	-	****	false
texture fiber component intensity	1	0.0	10	0.0	Fixed	false
texture fiber component thetaY	4.6246295	0.0	90.0	0.09636736	Refined	false
texture fiber component phiY	0	0.0	360.0	0.0	Fixed	false
texture fiber component thetaH	0	0.0	90.0	0.0	Fixed	false
texture fiber component phiH	0	0.0	360.0	0.0	Fixed	false
texture fiber component fwhm	14.329416	0.0	360.0	0.1192068	Refined	false
texture fiber component gauss content	0.026825886	0.0	1.0	0.0	Fixed	false
Pona rules	-	-	-	-	****	false
riet par anisocryst size()	673.3349	5.0	10000.0	24.089277	Refined	false
riet par anisocryst size1	-798 2228	-33000.0	12241 131	93 57528	Refined	false
riet par anisocryst size?	423.92	-18855.904	1000.0	54.601627	Refined	false
riet par aniso microstrain()	0.0026990799	-0.1	0.1	0.0	Fixed	false
riet par aniso microstrain1	0.0010799746	-0.1	0.1	0.0	Fixed	false
riet par aniso microstrain?	0	-0.1	0.1	0.0	Fixed	false
Triaxial Stress Isotropic F	-	-	-	-	****	false
rista elastic modulus E	447	1.0	900.0	0.0	Fixed	false
rista poisson ratio v	0.3	-0.1	0.5	0.0	Fixed	false
rista macrostress 11	-0.023167167	-500.0	500.0	0.0	Fixed	false
rista macrostress 22	-0.023167167	-500.0	500.0	0.0	Equal to	false

_rista_macrostress_33	0	-500.0	500.0	0.0	Fixed	false
_rista_macrostress_23	0	-500.0	500.0	0.0	Fixed	false
_rista_macrostress_13	0	-500.0	500.0	0.0	Fixed	false
_rista_macrostress_12	0	-500.0	500.0	0.0	Fixed	false
Atomic Structure	-	-	-	-	****	false
Ru	-	-	-	-	****	false
_atom_site_occupancy	1.0	0.0	1.0	0.0	Fixed	false
_atom_site_fract_x	0.33333	0.0	1.0	0.0	Fixed	false
_atom_site_fract_y	0.66667	0.0	1.0	0.0	Fixed	false
_atom_site_fract_z	0.25000	0.0	1.0	0.0	Fixed	false
_atom_site_B_iso_or_equiv	1.1029571	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_11	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_22	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_33	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_23	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_13	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_12	0	-1.0	10.0	0.0	Fixed	false
R3mR-P1	-	-	-	-	****	false
_cell_length_a	4.080077	5.0	30.0	3.3182852E-4	Refined	false
_cell_length_b	4.080077	5.0	30.0	0.0	Equal to	false
_cell_length_c	4.080077	5.0	30.0	0.0	Equal to	false
_cell_angle_alpha	90.049484	90.0	120.0	0.014744201	Refined	false
_cell_angle_beta	90.049484	90.0	120.0	0.0	Equal to	false
_cell_angle_gamma	90.049484	90.0	120.0	0.0	Equal to	false
_riet_par_strain_thermal	0	-0.1	0.1	0.0	Fixed	false
_exptl_absorpt_cryst_size	0	0.001	100.0	0.0	Fixed	false
_riet_par_phase_scale_factor	1.0	0.0	100.0	0.0	Fixed	false
Standard Functions	-	-	-	-	****	false
_rita_odf_background	0.01	0.0	1.0	0.0	Fixed	false
100	-	-	-	-	****	false
_texture_fiber_component_intensity	1	0.0	1.0	0.0	Fixed	false
_texture_fiber_component_thetaY	0	0.0	90.0	0.0	Fixed	false
_texture_fiber_component_phiY	0	0.0	360.0	0.0	Fixed	false
_texture_fiber_component_thetaH	90	0.0	90.0	0.0	Fixed	false
_texture_fiber_component_phiH	0	0.0	360.0	0.0	Fixed	false
_texture_fiber_component_fwhm	22.293371	0.0	360.0	0.24876776	Refined	false
_texture_fiber_component_gauss_content	0.5	0.0	1.0	0.0	Fixed	false
Popa rules	-	-	-	-	****	false
_riet_par_anisocryst_size0	476.2413	-4482.9575	5479.1704	10.428997	Refined	false
_riet_par_anisocryst_size1	0	-33000.0	16506.537	0.0	Fixed	false
_riet_par_anisocryst_size2	1001.23413	-33000.0	16506.537	30.48347	Refined	false
_riet_par_anisocryst_size3	0	-33000.0	16506.537	0.0	Fixed	false
_riet_par_anisocryst_size4	0	-1000.0	1000.0	0.0	Fixed	false
_riet_par_anisocryst_size5	0	-1000.0	1000.0	0.0	Fixed	false
_riet_par_anisocryst_size6	0	-1000.0	1000.0	0.0	Fixed	false
_riet_par_anisocryst_size7	0	-1000.0	1000.0	0.0	Fixed	false
_riet_par_anisocryst_size8	0	-1000.0	1000.0	0.0	Fixed	false
_riet_par_anisocryst_size9	0	-1000.0	1000.0	0.0	Fixed	false
_riet_par_anisocryst_size10	0	-1000.0	1000.0	0.0	Fixed	false
_riet_par_anisocryst_size11	0	-1000.0	1000.0	0.0	Fixed	false
_riet_par_anisocryst_size12	0	-1000.0	1000.0	0.0	Fixed	false
_riet_par_anisocryst_size13	0	-1000.0	1000.0	0.0	Fixed	false

_riet_par_anisocryst_size14	0	-1000.0	1000.0	0.0	Fixed	false
_riet_par_aniso_microstrain0	0.002572371	-0.014465252	0.017679753	0.0	Fixed	false
_riet_par_aniso_microstrain1	0.0028757493	-0.025881743	0.031633243	0.0	Fixed	false
_riet_par_aniso_microstrain2	0	-0.025881743	0.031633243	0.0	Fixed	false
_riet_par_aniso_microstrain3	0	-0.025881743	0.031633243	0.0	Fixed	false
_riet_par_aniso_microstrain4	0	-0.1	0.1	0.0	Fixed	false
_riet_par_aniso_microstrain5	0	-0.1	0.1	0.0	Fixed	false
_riet_par_aniso_microstrain6	0	-0.1	0.1	0.0	Fixed	false
riet_par_aniso_microstrain7	0	-0.1	0.1	0.0	Fixed	false
riet par aniso microstrain8	0	-0.1	0.1	0.0	Fixed	false
riet_par_aniso_microstrain9	0	-0.1	0.1	0.0	Fixed	false
riet par aniso microstrain10	0	-0.1	0.1	0.0	Fixed	false
riet_par_aniso_microstrain11	0	-0.1	0.1	0.0	Fixed	false
riet par aniso microstrain12	0	-0.1	0.1	0.0	Fixed	false
riet par aniso microstrain13	0	-0.1	0.1	0.0	Fixed	false
riet par aniso microstrain14	0	-0.1	0.1	0.0	Fixed	false
Triaxial Stress Isotronic E	-	-	-	-	****	false
rista elastic modulus E	82.1	1.0	900.0	0.0	Fixed	false
rista poisson ratio v	0.39	-0.1	0.5	0.0	Fixed	false
rista macrostress 11	0.070	-500.0	500.0	0.0	Fixed	false
rista macrostress 22	0.07	-500.0	500.0	0.0	Fixed	false
rista macrostress 33	0	-500.0	500.0	0.0	Fixed	false
rista macrostress 23	0	-500.0	500.0	0.0	Fixed	false
rista macrostress 13	0	-500.0	500.0	0.0	Fixed	false
rista macrostross 12	0	-500.0	500.0	0.0	Fixed	false
Atomic Structure	0	-300.0	500.0	0.0	*****	false
Ph1	_	_		_	****	false
rbi	-	-	- 1.0	-	Fived	false
_atom_site_occupancy	1.	0.0	1.0	0.0	Fixed	false
_atom_site_fract_x	0	0.0	1.0	0.0	Fixed	false
_atom_site_nact_y	0	0.0	1.0	0.0	Fixed	false
_atom_site_iract_z	0	0.0	1.0	0.0	Fixed	false
_atom_site_B_iso_or_equiv	0.5	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_11	0	-1.0	10.0	0.0	Fixed	faise
_atom_site_aniso_B_22	0	-1.0	10.0	0.0	Fixed	faise
_atom_site_aniso_B_33	0	-1.0	10.0	0.0	Fixed	faise
_atom_site_aniso_B_23	0	-1.0	10.0	0.0	Fixed	faise
_atom_site_aniso_B_13	0	-1.0	10.0	0.0	Fixed	faise
_atom_site_aniso_B_12	0	-1.0	10.0	0.0	Fixed	false
Zr1	-	-	-	-	*****	false
_atom_site_occupancy	0.58	0.0	1.0	0.0	Fixed	false
_atom_site_fract_x	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_fract_y	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_fract_z	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_B_iso_or_equiv	0.5	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_11	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_22	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_33	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_23	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_13	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_12	0	-1.0	10.0	0.0	Fixed	false
Ti1	-	-	-	-	****	false
_atom_site_occupancy	0.42	0.0	1.0	0.0	Fixed	false

_atom_site_fract_x	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_fract_y	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_fract_z	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_B_iso_or_equiv	0.5	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_11	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_22	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_33	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_23	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_13	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_12	0	-1.0	10.0	0.0	Fixed	false
01	-	-	-	-	****	false
_atom_site_occupancy	1.	0.0	1.0	0.0	Fixed	false
_atom_site_fract_x	0	0.0	1.0	0.0	Fixed	false
_atom_site_fract_y	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_fract_z	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_B_iso_or_equiv	0.5	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_11	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_22	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_33	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_23	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_13	0	-1.0	10.0	0.0	Fixed	false
atom_site_aniso_B_12	0	-1.0	10.0	0.0	Fixed	false
02	-	-	-	-	****	false
_atom_site_occupancy	1.	0.0	1.0	0.0	Fixed	false
_atom_site_fract_x	0.5	0.0	1.0	0.0	Fixed	false
atom_site_fract_y	0	0.0	1.0	0.0	Fixed	false
_atom_site_fract_z	0.5	0.0	1.0	0.0	Fixed	false
atom_site_B_iso_or_equiv	0.5	-1.0	10.0	0.0	Fixed	false
atom_site_aniso_B_11	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 22	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 33	0	-1.0	10.0	0.0	Fixed	false
atom_site_aniso_B_23	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_13	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_12	0	-1.0	10.0	0.0	Fixed	false
03	-	-	-	-	****	false
_atom_site_occupancy	1.	0.0	1.0	0.0	Fixed	false
_atom_site_fract_x	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_fract_y	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_fract_z	0	0.0	1.0	0.0	Fixed	false
_atom_site_B_iso_or_equiv	0.5	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_11	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_22	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_33	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_23	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_13	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 12	0	-1.0	10.0	0.0	Fixed	false
P4mm	-	-	-	-	****	false
_cell_length_a	4.0565805	5.0	30.0	3.2487008E-4	Refined	false
cell_length_c	4.111643	5.0	30.0	8.433906E-4	Refined	false
_riet_par_strain_thermal	0	-0.1	0.1	0.0	Fixed	false
_exptl_absorpt_cryst_size	0	0.001	100.0	0.0	Fixed	false
_riet_par_phase_scale_factor	1.0	0.0	100.0	0.0	Fixed	false

Standard Functions	-	-	-	-	****	false
_rita_odf_background	0.01	0.0	1.0	0.0	Fixed	false
100	-	-	-	-	****	false
_texture_fiber_component_intensity	1	0.0	1.0	0.0	Fixed	false
_texture_fiber_component_thetaY	0	0.0	90.0	0.0	Fixed	false
_texture_fiber_component_phiY	0	0.0	360.0	0.0	Fixed	false
_texture_fiber_component_thetaH	90	0.0	90.0	0.0	Fixed	false
_texture_fiber_component_phiH	0	0.0	360.0	0.0	Fixed	false
_texture_fiber_component_fwhm	22.245054	0.0	360.0	0.19549547	Refined	false
_texture_fiber_component_gauss_content	0.5	0.0	1.0	0.0	Fixed	false
Popa rules	-	-	-	-	****	false
_riet_par_anisocryst_size0	565.185	-4482.9575	5479.1704	13.088317	Refined	false
_riet_par_anisocryst_size1	0	-1000.0	1000.0	0.0	Fixed	false
_riet_par_anisocryst_size2	-6.920066	-33000.0	1000.0	0.35957414	Refined	false
_riet_par_anisocryst_size3	0	-1000.0	1000.0	0.0	Fixed	false
riet_par_aniso_microstrain0	0.0023886801	-0.014465252	0.017679753	0.0	Fixed	false
riet par aniso microstrain1	0	-0.1	0.1	0.0	Fixed	false
riet_par_aniso_microstrain2	0	-0.1	0.1	0.0	Fixed	false
riet par aniso microstrain3	0	-0.1	0.1	0.0	Fixed	false
Triaxial Stress Isotropic E	-	-	-	-	****	false
rista elastic modulus E	81	1.0	900.0	0.0	Fixed	false
rista poisson ratio v	0.39	-0.1	0.5	0.0	Fixed	false
rista macrostress 11	0.07	-500.0	500.0	0.0	Fixed	false
rista macrostress 22	0.07	-500.0	500.0	0.0	Fixed	false
rista macrostress 33	0	-500.0	500.0	0.0	Fixed	false
rista macrostress 23	0	-500.0	500.0	0.0	Fixed	false
rista macrostress 13	0	-500.0	500.0	0.0	Fixed	false
rista macrostress 12	0	-500.0	500.0	0.0	Fixed	false
Atomic Structure	-	-	-	-	****	false
Ph1	-	_	_	-	****	false
atom site occupancy	1	0.0	10	0.0	Fixed	false
atom site fract x	0	0.0	1.0	0.0	Fixed	false
atom_site_fract_x	0	0.0	1.0	0.0	Fixed	false
atom_site_fract_z	0	0.0	1.0	0.0	Fixed	false
atom_site B iso or equiv	0	-1.0	10.0	0.0	Fixed	false
atom_site_niso_B_11	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 22	0	-1.0	10.0	0.0	Fixed	falso
atom_site_aniso_B_22	0	-1.0	10.0	0.0	Fixed	false
atom_site_aniso_B_33	0	-1.0	10.0	0.0	Fixed	false
atom_site_aniso_B_23	0	-1.0	10.0	0.0	Fixed	false
atom site anise B 12	0	-1.0	10.0	0.0	Fixed	falso
_atom_site_ams0_D_12	0	-1.0	10.0	0.0	*****	false
atom site occupancy	0.52	0.0	1.0	0.0	Fived	falso
atom_site_occupancy	0.52	0.0	1.0	0.0	Fixed	false
_atom_site_fract_x	0.5	0.0	1.0	0.0	Fixed	falco
atom_site_fract_y	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_fiact_z	0.4317	1.0	1.0	0.0	Fixed	falco
atom site anise R 11	0.4105/554	-1.0	10.0	0.0	Fixed	false
atom site aniso B 22	0	-1.0	10.0	0.0	Fixed	false
atom_site_aniso_B_22	0	-1.0	10.0	0.0	Fixed	falso
atom site aniso B 23	0	-1.0	10.0	0.0	Fixed	false
atom site aniso R 13	0	-1.0	10.0	0.0	Fixed	falso
_acom_sicc_ams0_D_13	0	1.0	10.0	0.0	IIACU	iaise

_atom_site_aniso_B_12	0	-1.0	10.0	0.0	Fixed	false
Ti1	-	-	-	-	****	false
_atom_site_occupancy	0.48	0.0	1.0	0.0	Fixed	false
_atom_site_fract_x	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_fract_y	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_fract_z	0.4517	0.0	1.0	0.0	Fixed	false
_atom_site_B_iso_or_equiv	0.41057554	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_11	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_22	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_33	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_23	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_13	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_12	0	-1.0	10.0	0.0	Fixed	false
01	-	-	-	-	****	false
_atom_site_occupancy	1.	0.0	1.0	0.0	Fixed	false
_atom_site_fract_x	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_fract_y	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_fract_z	0.8973	0.0	1.0	0.0	Fixed	false
_atom_site_B_iso_or_equiv	0.4816367	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_11	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_22	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_33	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_23	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_13	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_12	0	-1.0	10.0	0.0	Fixed	false
02	-	-	-	-	****	false
_atom_site_occupancy	1.	0.0	1.0	0.0	Fixed	false
_atom_site_fract_x	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_fract_y	0	0.0	1.0	0.0	Fixed	false
_atom_site_fract_z	0.3785	0.0	1.0	0.0	Fixed	false
_atom_site_B_iso_or_equiv	1.5633453	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_11	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_22	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_33	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_23	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_13	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_12	0	-1.0	10.0	0.0	Fixed	false

Appendix E:

Profile evolution versus electric field for Gradient Free PZT



Appendix F:



1. $2\vartheta/\omega$ profile for Standard gradient and Gradient Free samples

2. Pole Figures for Standard gradient sample





3. Strain versus $sin^2\psi$ for 111 PZT peak





4. Strain versus $sin^2\psi$ for 111 Pt peak

5. Combined Analysis:



5.1. Data vs fit performed with Maud program on Standard Gradient PZT sample

5.2. Sum of all $2\vartheta/\omega$ profiles according to angle ψ



Blue dots stand for experimental data, blue line represents fitted R3m PZT phase, pink line is for P4mm PZT phase and black line represents the sum of all fitted phases, namely Pt, Ru and both PZT phases. Positions of diffraction planes in the collected 2ϑ range for all four fitted phases are shown underneath the refined $2\vartheta/\omega$ profile. Note that bottom rectangle represents the difference between experimental data and fit. Our best fit corresponds to 54.5% rhombohedral and 45.4% tetragonal phase.

Reliability factors:

```
5, iterations - pause
sig= 5.9031587
Rwp (%) = 32.4887
Rwpnb (%, no bkg) = 39.88403
Rwpnb1 (%, no bkg rescaled) = 36.796368
Rwpnb2 (%, no bkg rescaled^2) = 34.764668
Rb (%) = 23.484207
Rexp (%) = 5.5036125
# iterations = 5
Pt 1011109 , weight %: 100.0 +- 0.0
Ru 9008513 , weight %: 100.0 +- 0.0
R3mR-P1 , weight %: 54.544502 +- 0.96496886
P4mm , weight %: 45.455498 +- 0.0
```

5.3. Refinement parameters for Standard Gradient sample

P14_01	-	-	-	-	****	false
Sample_x	-	-	-	-	****	false
_pd_spec_orientation_omega	0	0.0	0.0	0.0	Fixed	false
_pd_spec_orientation_chi	0	0.0	0.0	0.0	Fixed	false
_pd_spec_orientation_phi	0	0.0	0.0	0.0	Fixed	false
riet_par_spec_displac_x	0	0.0	0.0	0.0	Fixed	false
_riet_par_spec_displac_y	0	0.0	0.0	0.0	Fixed	false
riet par spec displac z	0	0.0	0.0	0.0	Fixed	false
pd spec size axial	7	0.0	100.0	0.0	Fixed	false
pd spec size equat	6	0.0	100.0	0.0	Fixed	false
pd spec size thick	0.000002	0.0	100.0	0.0	Fixed	false
pd spec size radius	0	0.0	100.0	0.0	Fixed	false
pd spec size radius y	0	0.0	100.0	0.0	Fixed	false
Ru	-	-	-	-	****	false
riet par spec layer thickness	227.84406	0.1	1.0E8	9.241379	Refined	false
reflectivity layer critical gc	0.04	0.0010	0.5	0.0	Fixed	false
reflectivity layer absorption	2.0E-7	1.0E-8	1.0E-5	0.0	Fixed	false
reflectivity layer roughness	2.0	0.01	100.0	0.0	Fixed	false
pd phase atom %0	0	0.0	1.0	0.0	Fixed	false
pd phase atom %1	1.0	0.0	1.0	0.0	Fixed	false
pd phase atom %2	0	0.0	1.0	0.0	Fixed	false
pd phase atom %3	0	0.0	1.0	0.0	Fixed	false
PZT	-	-	-	-	****	false
riet par spec layer thickness	11715.449	0.1	1.0E8	0.0	Fixed	false
reflectivity layer critical ac	0.04	0.001	0.5	0.0	Fixed	false
reflectivity layer absorption	2.0E-7	1 0E-8	1.0E-5	0.0	Fixed	false
reflectivity layer roughness	2.0	0.01	100.0	0.0	Fixed	false
nd phase atom %0	0	0.0	10	0.0	Fixed	false
nd nhase atom %1	0	0.0	1.0	0.0	Fixed	false
nd phase atom %?	0 5444767	0.0	319.0	0.009632558	Fixed	false
nd phase atom %3	0.4555233	0.0	10	0.0	Equal to	false
pu_pnuse_utom/05	-	-	-	-	****	false
riet par spec laver thickness	1000	0.1	1.0E8	0.0	Fived	false
reflectivity layer critical ac	0.04	0.001	0.5	0.0	Fixed	false
reflectivity layer absorption	2.0F-7	1.0F-8	1.0F-5	0.0	Fixed	false
reflectivity_layer_roughness	2.01-7	0.01	100.0	0.0	Fixed	false
nd phase atom %0	2.0	0.01	100.0	0.0	Fixed	false
nd phase atom %1	0	0.0	1.0	0.0	Fixed	false
nd phase atom %2	0	0.0	1.0	0.0	Fixed	false
_pu_phase_atom_/62	0	0.0	1.0	0.0	Fixed	false
_pu_pnase_atom_765	0	0.0	1.0	0.0	rixeu *****	false
DataFileSet_x	-	-	-	-	Eined	false
	0	0.0	0.0	0.0	Fixed	false
_net_par_background_exp_inermai_snift	0	0.0	0.0	0.0	Fixed	false
_pd_spec_orientation_omega	0	0.0	0.0	0.0	Fixed	raise
_pd_spec_orientation_chi	0	0.0	0.0	0.0	Fixed	false
_pd_spec_orientation_phi	0	0.0	0.0	0.0	Fixed	false
_riet_par_background_pol0	138.05623	-/1/6.7773	8//1.617	0.0	Fixed	talse
_riet_par_background_poll	0.459099	-//.26483	0.0	0.0	Fixed	talse
_riet_par_background_pol2	-0.0066944472	-//.26483	4.6889005	0.0	Fixed	talse
_riet_par_background_chi0	-0.76211596	-7.7608953	70.81745	0.0	Fixed	false

_riet_par_background_chi1	0.011045209	-0.30797815	0.37641773	0.0	Fixed	false
_riet_par_background_chi2	-1.7822359E-4	-0.30797815	0.37641773	0.0	Fixed	false
XPert Pro	-	-	-	-	****	false
_pd_proc_intensity_incident	48.538376	0.0	10000.0	0.1338388	Refined	false
_riet_par_2-theta_offset0	-0.032827515	0.0	0.0	0.0	Fixed	false
riet par 2-theta offset1	0	0.0	0.0	0.0	Fixed	false
Bragg-Brentano	-	-	-	-	****	false
diffrn radiation polarisn norm	0	0.0	360.0	0.0	Fixed	false
diffrn radiation polarisn ratio	0	0.0	1.0	0.0	Fixed	false
X-ray	-	-	-	-	****	false
Kal	-	-	-	-	****	false
diffrn radiation wavelength	1.5405980	0.1	10.0	0.0	Fixed	false
diffrn radiation wavelength wt	1	0.0	1.01	0.0	Fixed	false
Ka2	-	-	-	-	****	false
diffrn radiation wavelength	1.5444260	0.1	10.0	0.0	Fixed	false
diffrn radiation wavelength wt	0.5	0.0	1.01	0.0	Fixed	false
Kb	-	-	-	-	****	false
diffrn radiation wavelength	1 3922500	0.1	10.0	0.0	Fixed	false
diffrn radiation wavelength wt	0.0022960515	0.0	1.01	0.0	Fixed	false
Caglioti PV	-	-	-	-	****	false
riet par asymmetry value0	0	0.0	1000.0	0.0	Fixed	false
riet par asymmetry value1	0	0.0	0.0	0.0	Fixed	false
riet_par_caglioti_value0	0.08131076	-0.1	0.1	0.0	Fixed	false
riet_par_caglioti_value1	0.042373955	-0.1	0.1	0.0	Fixed	false
riet_par_caglioti_value?	0.0068384507	-0.3813656	0.4661135	0.0	Fixed	false
riet_par_caussian_value0	0.027112907	-0.5815050	0.4001155	0.0	Fixed	false
riet_par_gaussian_value0	0.0027112907	0.025615064	0.021207202	0.0	Fixed	false
riet_par_gaussian_value1	0	-0.023013004	0.051507502	0.0	Fixed	false
riet_par_broadening_chil	0 000025562	0.080220055	0.0	0.0	Fixed	false
	0.009923302	-0.089330033	0.10910110	0.0	Fixed	false
net_par_oroadening_cni2	-0.003306634	-0.089330033	0.10918118	0.0	гіхец *****	false
//////C:/Users/vk23342//Desktop/AC/	-	-	-	-	Eined	false
_pd_meas_counts_monitor	1.0	10.0	10.0	0.0	Fixed	raise
net_par_spec_displac_x_2R	0	-10.0	10.0	0.0	Fixed	raise
_riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	F1xed	false
//////C/Users/vk23342//Desktop/AC/	-	-	-	-	F. 1	raise
_pd_meas_counts_monitor	1.0	0.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_x_2R	0	-10.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
//////C:/Users/vk23342//Desktop/AC/	-	-	-	-	*****	false
_pd_meas_counts_monitor	1.0	0.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_x_2R	0	-10.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
//////C:/Users/vk233427/Desktop/AC/	-	-	-	-	****	false
_pd_meas_counts_monitor	1.0	0.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_x_2R	0	-10.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
//////C:/Users/vk233427/Desktop/AC/	-	-	-	-	****	false
_pd_meas_counts_monitor	1.0	0.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_x_2R	0	-10.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
//////C:/Users/vk233427/Desktop/AC/	-	-	-	-	****	false
_pd_meas_counts_monitor	1.0	0.0	10.0	0.0	Fixed	false
_riet_par_spec_displac_x_2R	0	-10.0	10.0	0.0	Fixed	false

_riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
//////C:/Users/vk233427/Desktop/AC/	-	-	-	-	****	false
_pd_meas_counts_monitor	1.0	0.0	10.0	0.0	Fixed	false
riet_par_spec_displac_x_2R	0	-10.0	10.0	0.0	Fixed	false
riet par spec displac z 2R	0	-10.0	10.0	0.0	Fixed	false
//////C:/Users/vk233427/Desktop/AC/	-	-	-	-	****	false
pd meas counts monitor	1.0	0.0	10.0	0.0	Fixed	false
riet par spec displac x 2R	0	-10.0	10.0	0.0	Fixed	false
riet par spec displac z 2R	0	-10.0	10.0	0.0	Fixed	false
///////C:/Users/vk233427/Desktop/AC/	-	-	-	-	****	false
pd meas counts monitor	1.0	0.0	10.0	0.0	Fixed	false
riet par spec displac x 2R	0	-10.0	10.0	0.0	Fixed	false
riet par spec displac z 2R	0	-10.0	10.0	0.0	Fixed	false
rururu	_	_	-	_	****	false
pd meas counts monitor	1.0	0.0	10.0	0.0	Fixed	false
riet par spec displac x 2R	0	-10.0	10.0	0.0	Fixed	false
riet par spec displac z 2R	0	-10.0	10.0	0.0	Fixed	false
//////////////////////////////////////	-	-	-	-	****	false
nd meas counts monitor	1.0	0.0	10.0	0.0	Fixed	false
riet par spec displac x 2R	0	-10.0	10.0	0.0	Fixed	false
riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
	-	-	-	-	****	false
nd meas counts monitor	1.0	0.0	10.0	0.0	Fixed	false
riet par spec displac x 2R	0	-10.0	10.0	0.0	Fixed	false
riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
	-	-	-	-	****	false
nd meas counts monitor	1.0	0.0	10.0	0.0	Fixed	false
riet par spec displac x 2R	0	-10.0	10.0	0.0	Fixed	false
riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
//////////////////////////////////////	-	-10.0	-	-	****	false
nd meas counts monitor	1.0	0.0	10.0	0.0	Fixed	false
riet par spec displac x 2R	0	-10.0	10.0	0.0	Fixed	false
riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
	-	- 10.0	-	-	****	false
nd meas counts monitor	1.0	0.0	10.0	0.0	Fixed	false
riet par spec displac y 2R	0	-10.0	10.0	0.0	Fixed	false
riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
	-	- 10.0	-	-	****	false
nd meas counts monitor	1.0	0.0	10.0	0.0	Fixed	false
riet par spec displac y 2P	0	10.0	10.0	0.0	Fixed	false
riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	false
	0	-10.0	10.0	0.0	****	false
nd mass sounts monitor	-	-	-	-	Fixed	false
_pu_meas_counts_monitor	1.0	10.0	10.0	0.0	Fixed	false
riet_par_spec_displac_x_2R	0	-10.0	10.0	0.0	Fixed	false
	0	-10.0	10.0	0.0	****	false
	-	-	-	-	Eine 4	false
_pd_meas_counts_monitor	1.0	10.0	10.0	0.0	Fixed	false
riet_par_spec_uisplac_x_2K	0	-10.0	10.0	0.0	Fixed	folce
nct_pat_spec_utsplac_Z_ZK	U	-10.0	10.0	0.0	r 1XCU *****	folge
	-	-	-	-	Eine 4	false
_pu_meas_counts_monitor	1.0	10.0	10.0	0.0	rixed	false
_net_par_spec_uisplac_x_2k	U	-10.0	10.0	0.0	rixed	raise
_riet_par_spec_displac_z_2R	0	-10.0	10.0	0.0	Fixed	talse

Pt 1011109	-	-	-	-	****	false
_cell_length_a	3.9181757	5.0	30.0	8.532138E-5	Refined	false
_riet_par_strain_thermal	0	-0.1	0.1	0.0	Fixed	false
_exptl_absorpt_cryst_size	0	0.001	100.0	0.0	Fixed	false
_riet_par_phase_scale_factor	1.0	0.0	100.0	0.0	Fixed	false
Standard Functions	-	-	-	-	****	false
_rita_odf_background	0.001	0.0	1.0	0.0	Fixed	false
111	-	-	-	-	****	false
_texture_fiber_component_intensity	1	0.0	1.0	0.0	Fixed	false
texture fiber component thetaY	0	0.0	90.0	0.0	Fixed	false
texturefibercomponent_phiY	0	0.0	360.0	0.0	Fixed	false
texture fiber component thetaH	56.118355	0.0	90.0	4.2523656	Refined	false
texture fiber component phiH	47.726826	0.0	360.0	3.1761305	Refined	false
texture fiber component fwhm	6.2539077	0.0	360.0	0.13499075	Refined	false
texture fiber component gauss content	0.747952	0.0	1.0	0.0	Fixed	false
Popa rules	-	-	-	-	*****	false
riet par anisocryst size0	2204.084	5.0	10000.0	410.83582	Refined	false
riet par anisocryst size1	0	-18855.904	1000.0	0.0	Fixed	false
riet par anisocryst size2	-146.8741	-18855.904	1000.0	675.57166	Refined	false
riet par anisocryst size3	0	-1000.0	1000.0	0.0	Fixed	false
riet par aniso microstrain0	0.0014747246	-0.1	0.1	0.0	Fixed	false
riet par aniso microstrain1	-8 49071E-4	-0.1	0.1	0.0	Fixed	false
Triaxial Stress Isotronic E	-	-	-	-	****	false
rista elastic modulus E	168	1.0	900.0	0.0	Fixed	false
rista poisson ratio v	0.3	-0.1	0.5	0.0	Fixed	false
rista macrostress 11	1	-500.0	500.0	0.0	Fixed	false
rista macrostress 22	1 0	-500.0	500.0	0.0	Equal to	false
rista macrostress 33	0	-500.0	500.0	0.0	Fixed	false
rista_macrostress_23	0	500.0	500.0	0.0	Fixed	false
rista_macrostross_13	0	-500.0	500.0	0.0	Fixed	false
_lista_macrostress_13	0	-300.0	500.0	0.0	Fixed	false
_IIsta_IIIacrostress_12	0	-300.0	300.0	0.0	гіхец *****	false
Atomic Suucture	-	-	-	-	****	false
	-	-	-	-	Eined	false
_atom_site_occupancy	1.	0.0	1.0	0.0	Fixed	Taise
_atom_site_fract_x	0	0.0	1.0	0.0	Fixed	faise
_atom_site_fract_y	0	0.0	1.0	0.0	Fixed	Taise
_atom_site_fract_z	0	0.0	1.0	0.0	Fixed	Taise
_atom_site_B_iso_or_equiv	1.1029571	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_11	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_22	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_33	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_23	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_13	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_12	0	-1.0	10.0	0.0	Fixed	false
Ru 9008513	-	-	-	-	****	false
_cell_length_a	2.7060578	5.0	30.0	8.5300003E-4	Refined	false
_cell_length_c	4.2810163	5.0	30.0	0.0010697823	Refined	false
_riet_par_strain_thermal	0	-0.1	0.1	0.0	Fixed	false
_exptl_absorpt_cryst_size	0	0.001	100.0	0.0	Fixed	false
_riet_par_phase_scale_factor	1.0	0.0	100.0	0.0	Fixed	false
Standard Functions	-	-	-	-	****	false
_rita_odf_background	0.001	0.0	1.0	0.0	Fixed	false
002	-	-	-	-	****	false

_texture_fiber_component_intensity	1	0.0	1.0	0.0	Fixed	false
_texture_fiber_component_thetaY	0	0.0	90.0	0.0	Fixed	false
_texture_fiber_component_phiY	0	0.0	360.0	0.0	Fixed	false
texturefibercomponent_thetaH	0	0.0	90.0	0.0	Fixed	false
texture fiber component phiH	0	0.0	360.0	0.0	Fixed	false
texture fiber component fwhm	22.75477	0.0	360.0	0.9761576	Refined	false
texture fiber component gauss content	0.026825886	0.0	1.0	0.0	Fixed	false
Popa rules	_	_	-	_	****	false
riet par anisocryst size0	750.47003	5.0	10000.0	0.0	Fixed	false
riet_par_anisocryst_size1	-1023 8669	-33000.0	12241 131	0.0	Fixed	false
riet_par_anisocryst_size?	625 47095	-18855 904	1000.0	0.0	Fixed	false
riet par aniso microstrain()	0.0026990799	-0.1	0.1	0.0	Fixed	false
riet_par_aniso_microstrain1	0.0020990799	-0.1	0.1	0.0	Fixed	false
	0.0010/99/40	-0.1	0.1	0.0	Fixed	false
_net_par_aniso_inicrostrain2	0	-0.1	0.1	0.0	rixeu *****	false
Thaxial Stress Isotropic E	-	-	-	-	T. 1	raise
_rista_elastic_modulus_E	44/	1.0	900.0	0.0	Fixed	false
_rista_poisson_ratio_v	0.3	-0.1	0.5	0.0	Fixed	false
_rista_macrostress_11	-0.023167167	-500.0	500.0	0.0	Fixed	false
_rista_macrostress_22	-0.023167167	-500.0	500.0	0.0	Equal to	false
_rista_macrostress_33	0	-500.0	500.0	0.0	Fixed	false
_rista_macrostress_23	0	-500.0	500.0	0.0	Fixed	false
_rista_macrostress_13	0	-500.0	500.0	0.0	Fixed	false
_rista_macrostress_12	0	-500.0	500.0	0.0	Fixed	false
Atomic Structure	-	-	-	-	****	false
Ru	-	-	-	-	****	false
_atom_site_occupancy	1.0	0.0	1.0	0.0	Fixed	false
_atom_site_fract_x	0.33333	0.0	1.0	0.0	Fixed	false
_atom_site_fract_y	0.66667	0.0	1.0	0.0	Fixed	false
_atom_site_fract_z	0.25000	0.0	1.0	0.0	Fixed	false
atom site B iso or equiv	1.1029571	-1.0	10.0	0.0	Fixed	false
atom site aniso B 11	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 22	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 33	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 23	0	-1.0	10.0	0.0	Fixed	false
atom_site_aniso_B_13	0	-1.0	10.0	0.0	Fixed	false
atom_site_aniso_B_12	0	-1.0	10.0	0.0	Fixed	false
R3mR_P1	-	- 1.0	-	0.0	****	false
cell length a	4 079444	5.0	30.0	2 6521028E A	Pafinad	false
_cell_length_b	4.079444	5.0	30.0	2.0321928E-4	Equal to	false
_cell_length_s	4.079444	5.0	20.0	0.0	Equal to	false
_cell_length_c	4.079444	5.0	30.0 120.0	0.0	Equal to	false
_cell_angle_alpha	90.29953	90.0	120.0	0.011/35949	Renned E-mail to	false
	90.29953	90.0	120.0	0.0	Equal to	raise
_cell_angle_gamma	90.29953	90.0	120.0	0.0	Equal to	false
_riet_par_strain_thermal	0	-0.1	0.1	0.0	Fixed	false
_exptl_absorpt_cryst_size	0	0.001	100.0	0.0	Fixed	false
_riet_par_phase_scale_factor	1.0	0.0	100.0	0.0	Fixed	false
Standard Functions	-	-	-	-	****	false
_rita_odf_background	0.01	0.0	1.0	0.0	Fixed	false
100	-	-	-	-	****	false
_texture_fiber_component_intensity	1	0.0	1.0	0.0	Fixed	false
_texture_fiber_component_thetaY	0	0.0	90.0	0.0	Fixed	false
_texture_fiber_component_phiY	0	0.0	360.0	0.0	Fixed	false
_texture_fiber_component_thetaH	90	0.0	90.0	0.0	Fixed	false

_texture_fiber_component_phiH	0	0.0	360.0	0.0	Fixed	false
_texture_fiber_component_fwhm	17.442173	0.0	360.0	0.18699174	Refined	false
_texture_fiber_component_gauss_content	0.5	0.0	1.0	0.0	Fixed	false
Popa rules	-	-	-	-	****	false
_riet_par_anisocryst_size0	668.4825	-4482.9575	5479.1704	9.299826	Refined	false
_riet_par_anisocryst_size1	0	-33000.0	16506.537	0.0	Fixed	false
_riet_par_anisocryst_size2	149.15123	-33000.0	16506.537	156.06825	Refined	false
_riet_par_anisocryst_size3	0	-33000.0	16506.537	0.0	Fixed	false
_riet_par_anisocryst_size4	0	-1000.0	1000.0	0.0	Fixed	false
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riet par anisocryst size13	0	-1000.0	1000.0	0.0	Fixed	false
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riet par aniso microstrain2	0	-0.025881743	0.031633243	0.0	Fixed	false
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riet par aniso microstrain4	0	-0.1	0.1	0.0	Fixed	false
riet par aniso microstrain5	0	-0.1	0.1	0.0	Fixed	false
riet par aniso microstrain6	0	-0.1	0.1	0.0	Fixed	false
riet par aniso microstrain7	0	-0.1	0.1	0.0	Fixed	false
riet par aniso microstrain8	0	-0.1	0.1	0.0	Fixed	false
riet par aniso microstrain9	0	-0.1	0.1	0.0	Fixed	false
riet par aniso microstrain10	0	-0.1	0.1	0.0	Fixed	false
riet par aniso microstrain11	0	-0.1	0.1	0.0	Fixed	false
riet par aniso microstrain12	0	-0.1	0.1	0.0	Fixed	false
riet par aniso microstrain13	0	-0.1	0.1	0.0	Fixed	false
riet par aniso microstrain14	0	-0.1	0.1	0.0	Fixed	false
Triaxial Stress Isotronic F	-	-0.1	-	-	****	false
rista elastic modulus E	82.1	1.0	900.0	0.0	Fixed	false
rista poisson ratio y	0.39	-0.1	0.5	0.0	Fixed	false
rista macrostress 11	0.130	500.0	500.0	0.0	Fixed	false
rista_macrostress_22	0.130	-500.0	500.0	0.0	Fixed	false
rista_macrostress_22	0.150	-500.0	500.0	0.0	Fixed	folco
rista_macrostress_22	0	-500.0	500.0	0.0	Fixed	false
rista_macrostress_25	0	-500.0	500.0	0.0	Fixed	false
rista_macrostress_13	0	-500.0	500.0	0.0	Fixed	false
	0	-300.0	300.0	0.0	rixeu *****	false
Atomic Structure	-	-	-	-	*****	false
	-	-	-	-	T 1	faise
_atom_site_occupancy	1.	0.0	1.0	0.0	Fixed	false
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_atom_site_tract_y	0	0.0	1.0	0.0	Fixed	taise
_atom_site_tract_z	0	0.0	1.0	0.0	Fixed	talse
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Zrl	-	-	-	-	****	false
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_atom_site_fract_z	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_B_iso_or_equiv	0.5	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_11	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_22	0	-1.0	10.0	0.0	Fixed	false
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atom_site_aniso_B_23	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 13	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 12	0	-1.0	10.0	0.0	Fixed	false
Til	-	-	-	-	****	false
atom site occupancy	0.42	0.0	1.0	0.0	Fixed	false
atom site fract x	0.5	0.0	1.0	0.0	Fixed	false
atom site fract y	0.5	0.0	1.0	0.0	Fixed	false
atom site fract z	0.5	0.0	1.0	0.0	Fixed	false
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atom site aniso B 11	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 22	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 33	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 23	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 13	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 12	0	-1.0	10.0	0.0	Fixed	false
01	-	-	-	-	****	false
atom site occupancy	1.	0.0	1.0	0.0	Fixed	false
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atom site fract z	0.5	0.0	1.0	0.0	Fixed	false
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atom_site_niso_B_11	0	-1.0	10.0	0.0	Fixed	false
atom_site_aniso_B_??	0	-1.0	10.0	0.0	Fixed	false
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atom_site_aniso_B_33	0	-1.0	10.0	0.0	Fixed	false
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atom site aniso B 12	0	-1.0	10.0	0.0	Fixed	false
	0	-1.0	10.0	0.0	****	folco
otem site ecoupeney	-	-	-	-	Fixed	false
_atom_site_freet_v	1.	0.0	1.0	0.0	Fixed	false
_atom_site_fract_x	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_iract_y	0	0.0	1.0	0.0	Fixed	false
_atom_site_fract_z	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_B_iso_or_equiv	0.5	-1.0	10.0	0.0	Fixed	faise
_atom_site_aniso_B_11	0	-1.0	10.0	0.0	Fixed	faise
_atom_site_aniso_B_22	0	-1.0	10.0	0.0	F1xed	
_atom_site_aniso_B_33	0	-1.0	10.0	0.0	Fixed	Talse
_atom_site_aniso_B_23	0	-1.0	10.0	0.0	r1xed	raise
_atom_site_aniso_B_13	0	-1.0	10.0	0.0	Fixed	talse
_atom_site_aniso_B_12	0	-1.0	10.0	0.0	Fixed	talse
03	-	-	-	-	****	talse
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_atom_site_fract_x	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_fract_y	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_fract_z	0	0.0	1.0	0.0	Fixed	false
_atom_site_B_iso_or_equiv	0.5	-1.0	10.0	0.0	Fixed	false
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_atom_site_aniso_B_33	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_23	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_13	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_12	0	-1.0	10.0	0.0	Fixed	false
P4mm	-	-	-	-	****	false
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cell_length_c	4.113002	5.0	30.0	7.44192E-4	Refined	false
riet_par_strain_thermal	0	-0.1	0.1	0.0	Fixed	false
exptl_absorpt_cryst_size	0	0.001	100.0	0.0	Fixed	false
riet par phase scale factor	1.0	0.0	100.0	0.0	Fixed	false
Standard Functions	-	-	-	-	****	false
rita odf background	0.01	0.0	1.0	0.0	Fixed	false
 100	-	_	-	-	****	false
texture fiber component intensity	1	0.0	1.0	0.0	Fixed	false
texture fiber component thetaY	0	0.0	90.0	0.0	Fixed	false
texture fiber component phiY	0	0.0	360.0	0.0	Fixed	false
texture fiber component thetaH	90	0.0	90.0	0.0	Fixed	false
texture fiber component phiH	0	0.0	360.0	0.0	Fixed	false
texture fiber component fwhm	17.30661	0.0	360.0	0.26583806	Refined	false
texture fiber component gauss content	0.5	0.0	1.0	0.0	Fixed	false
Popa rules	-	-	-	-	****	false
riet par anisocryst size0	718.2765	-4482,9575	5479.1704	24.850943	Refined	false
riet par anisocryst size1	0	-1000.0	1000.0	0.0	Fixed	false
riet par anisocryst size?	-56 859043	-33000.0	1000.0	78 58201	Refined	false
riet_par_anisocryst_size3	0	-1000.0	1000.0	0.0	Fixed	false
riet par aniso microstrain0	0 0023886801	-0.014465252	0.017679753	0.0	Fixed	false
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riet_par_aniso_microstrain?	0	-0.1	0.1	0.0	Fixed	false
riet_par_aniso_microstrain3	0	-0.1	0.1	0.0	Fixed	false
Triavial Stress Isotronic F	-	-0.1	-	0.0	****	false
rista elastic modulus E	- 81	- 1.0	900.0	- 0.0	Fixed	false
rista poisson ratio y	0.30	0.1	0.5	0.0	Fixed	false
_ista_poissoii_iauo_v	0.39	-0.1 500.0	500.0	0.0	Fixed	false
rista_macrostress_11	0.130	-500.0	500.0	0.0	Fixed	false
rista_macrostress_22	0.150	-500.0	500.0	0.0	Fixed	false
rista_macrostress_33	0	-500.0	500.0	0.0	Fixed	false
	0	-500.0	500.0	0.0	Fixed	false
_lista_macrostress_13	0	-300.0	500.0	0.0	Fixed	false
_fista_macrostress_12	0	-500.0	500.0	0.0	F1xea	false
Atomic Structure	-	-	-	-	****	Taise
PDI	-	-	-	-	····	Taise
_atom_site_occupancy	1.	0.0	1.0	0.0	Fixed	talse
_atom_site_tract_x	0	0.0				talce
oroma cuto troot vi	0	0.0	1.0	0.0	Fixed	1415C
_atom_site_fract_y	0 0	0.0 0.0	1.0 1.0	0.0	Fixed	false
_atom_site_fract_z	0 0 0	0.0 0.0 0.0	1.0 1.0 1.0	0.0 0.0 0.0	Fixed Fixed	false false
_atom_site_fract_z _atom_site_B_iso_or_equiv	0 0 0 0	0.0 0.0 0.0 -1.0	1.0 1.0 1.0 10.0	0.0 0.0 0.0 0.0	Fixed Fixed Fixed Fixed	false false false
_atom_site_fract_z _atom_site_B_iso_or_equiv _atom_site_aniso_B_11	0 0 0 0 0	0.0 0.0 -1.0 -1.0	1.0 1.0 1.0 10.0	0.0 0.0 0.0 0.0 0.0	Fixed Fixed Fixed Fixed	false false false false

atom site aniso B 33	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 23	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 13	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 12	0	-1.0	10.0	0.0	Fixed	false
Zr1	_	-	_	_	*****	false
atom site occupancy	0.52	0.0	1.0	0.0	Fixed	false
atom site fract x	0.5	0.0	1.0	0.0	Fixed	false
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atom site fract z	0.4517	0.0	1.0	0.0	Fixed	false
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_atom_site_aniso_B_23	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_13	0	-1.0	10.0	0.0	Fixed	raise
_atom_site_aniso_B_12	0	-1.0	10.0	0.0	Fixed	false
111	-	-	-	-	*****	false
_atom_site_occupancy	0.48	0.0	1.0	0.0	Fixed	false
_atom_site_fract_x	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_fract_y	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_fract_z	0.4517	0.0	1.0	0.0	Fixed	false
_atom_site_B_iso_or_equiv	0.41057554	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_11	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_22	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_33	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_23	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_13	0	-1.0	10.0	0.0	Fixed	false
_atom_site_aniso_B_12	0	-1.0	10.0	0.0	Fixed	false
01	-	-	-	-	*****	false
_atom_site_occupancy	1.	0.0	1.0	0.0	Fixed	false
_atom_site_fract_x	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_fract_y	0.5	0.0	1.0	0.0	Fixed	false
_atom_site_fract_z	0.8973	0.0	1.0	0.0	Fixed	false
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atom site aniso B 11	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 22	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 33	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 23	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 13	0	-1.0	10.0	0.0	Fixed	false
atom site aniso B 12	0	-1.0	10.0	0.0	Fixed	false
02	-	-	-	-	****	false
atom site occupancy	1	0.0	1.0	0.0	Fixed	false
atom site fract x	0.5	0.0	1.0	0.0	Fixed	false
atom site fract v	0.5	0.0	1.0	0.0	Fixed	false
atom site fract z	0 3785	0.0	1.0	0.0	Fixed	false
_atom_site_fract_z	1 5622452	1.0	10.0	0.0	Fixed	false
_atom_site_B_iso_oi_equiv	1.5055455	-1.0	10.0	0.0	Fixed	false
_atom_site_anise_B_22	0	-1.0	10.0	0.0	Fixed	folac
_atom_site_aniso_B_22	0	-1.0	10.0	0.0	Fixed	fal-
_atom_site_aniso_B_33	0	-1.0	10.0	0.0	r ixea	raise
_atom_site_aniso_B_23	0	-1.0	10.0	0.0	Fixed	Talse
_atom_site_aniso_B_13	0	-1.0	10.0	0.0	Fixed	talse
_atom_site_aniso_B_12	0	-1.0	10.0	0.0	Fixed	false

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Thesis summary in English

MEMS have been developed since 1980, when they appeared as derivatives from the microelectronic industry. They were first used in accelerometers and car airbags. They have diversified since then and expanded. One of the main contributors to this expansion are piezoelectric materials. Among them, PbZrTiO₃ (PZT) is widely used for its outstanding piezoelectric performances. Sol-gel PZT thin films fabricated at CEA are worldwide state of the art. In order to stay competitive, several R&D strategies have been developed. One of them is a detailed study of PZT microstructure in order to draw correlations with the piezoelectric effect in PZT films. The goal of this study is to optimize PZT microstructure aiming to reach its best piezoelectric properties. For this purpose, this thesis takes advantage of numerous studies performed on PZT bulk ceramics in order to analyze PZT thin films microstructure and its modifications with voltage.

PZT bulk ceramics of morphotropic composition are now well known from the piezoelectric and microstructural point of view. There are several theories explaining the piezoelectric effect at the microscopic level, namely tetragonal and rhombohedral domain switching, rhombohedral nanodomains rearrangement, polarization axis rotation in the monoclinic phase and the phase transition.

Morphotropic PZT thin films have emerged more recently. Their microstructure is very different from the bulk PZT. Indeed, sol-gel PZT films studied in this manuscript are stressed and contain preferred oriented nanoscale crystals and Ti/Zr composition gradient through the film thickness. Our goal is to study links between the complex microstructure of these films and their piezoelectric properties using X-ray diffraction (XRD).

Thanks to the nano-beam at ESRF, we were able to study the influence of the Zr/Ti chemical gradient on the PZT microstructure. Our observations showed that the composition gradient gives rise to a variation of the tetragonal and rhombohedral phase ratio in the layer thickness. This variation follows Zr/Ti composition oscillations evidenced by SIMS. This experiment shows the sensitivity of PZT microstructure to the PZT chemical composition. At the same time, it suggests the possibility of improving the composition homogeneity of PZT and its performances. The more the PZT composition is homogeneous, the better the piezoelectric coefficients are.

Then, we performed in-situ XRD under electric field experiments on a capacitor containing the PZT active layer with an attenuated Zr/Ti gradient. The PZT diffraction pattern was refined using the tetragonal and the rhombohedral PZT phases. At 0V PZT contains 40% of rhombohedral phase and 60% of tetragonal phase. At 30V, no tetragonal phase is observed any more. Results show an electric field induced phase transition from the tetragonal to the rhombohedral phase.

Finally, we used in-situ XRD to study the influence of Zr/Ti composition gradient on the amplitude of the phase transition of two PZT samples with different Zr/Ti gradient. We showed that the more the sample is homogeneous in composition, the more phase transition it exhibits and the more it is performant.

Finally, to improve the piezoelectric performances of PZT films, we propose to improve PZT compositional homogeneity and slightly increase the Ti content to promote the tetragonal phase in order to amplify the phase transition under voltage.

Résume de thèse en français

Les microsystèmes électromécaniques (MEMS) ont été développés dès le début des années 1980 en s'appuyant sur la technologie de l'industrie microélectronique. Ils ont d'abord été utilisés dans les accéléromètres et les airbags des automobiles. Depuis lors ils se diversifient et connaissent un important essor, notamment grâce à la rapidité De la réponse des matériaux piézoélectriques. La technologie des couches minces piézoélectriques a permis la miniaturisation et les déformations sous tensions d'actionnement plus faibles. Parmi les matériaux piézoélectriques, les films minces de PbZrTiO₃ (PZT) morphotropique sont fréquemment utilisés pour leurs propriétés électromécaniques remarquables. Le PZT fabriqué par la voie sol-gel au CEA Leti est à l'état de l'art mondial. Dans le souci de continuer à être compétitif, plusieurs stratégies de R&D sont envisagées, notamment des études approfondies de la microstructure des films PZT pour l'optimiser, afin d'atteindre les propriétés ultimes du PZT. Dans ce but, cette thèse recherche les corrélations entre la microstructure et l'effet piézoélectrique du PZT.

Le PZT morphotropique massif, apparu dans les années 1950, est un matériau bien étudié du point de vue microstructurale et piézoélectrique. Il existe plusieurs théories expliquant ses performances piézoélectriques au niveau microscopique. Pour citer les plus connues, le basculement de domaine des phases tétragonale et rhomboédrique, le réarrangement des nano-domaines rhomboédriques, la rotation de l'axe de polarisation dans la phase monoclinique et la transition de phase.

Les films minces de PZT morphotropique sont apparus dans les années 1990. Leur microstructure diffère radicalement du PZT massif. Le PZT sol-gel étudié dans ce manuscrit, est contraint et possède une orientation préférentielle des cristaux, des domaines nanométriques et un gradient chimique de Zr et Ti dans l'épaisseur. Notre but est d'étudier les liens entre la microstructure complexe de ces films et leurs propriétés piézoélectriques en utilisant la caractérisation par diffraction des rayons X (DRX).

Grace à l'accès au nano-faisceau à l'ESRF, nous avons pu étudier l'influence du gradient chimique de Zr/Ti sur la microstructure de PZT. Les résultats ont montré que la variation de concentration de Zr et Ti engendre une variation du rapport des phases tétragonale et rhomboédrique dans l'épaisseur de la couche. Cette variation suit les oscillations de Zr/Ti dans les films observées par SIMS. Cette observation montre la sensibilité de la microstructure sur la composition chimique. De même, il en résulte la possibilité d'améliorer l'homogénéité de composition du PZT et de ses performances. Car plus le PZT est homogène en composition, meilleurs sont ses coefficients piézoélectriques (d₃₃, e₃₁).

Par la suite nous avons effectués des expériences in-situ sous champ électrique sur des capacités contenant le PZT avec le gradient de composition atténué. La microstructure de PZT a été affinée en utilisant la phase tétragonale et rhomboédrique. A OV, on estime que le PZT contient 40% de phase rhomboédrique et 60% de phase tétragonale. A 30V, on n'observe plus que la présence de la phase rhomboédrique. Les résultats montrent une diminution de la proportion de phase tétragonale au profit de la phase rhomboédrique sous champ électrique.

Pour finir nous avons étudié l'influence du gradient de concentration sur l'amplitude du changement de phase en analysant deux échantillons de gradient Zr/Ti différents par DRX in-situ. Nous avons pu montrer que plus l'échantillon est homogène chimiquement, plus il est sujet à la transition de phase sous champ électrique et plus il est performant piézoélectriquement.

Finalement, afin d'améliorer les performances piézoélectriques des films PZT, nous proposons de fabriquer des films plus homogènes et plus riches en Ti pour amplifier la transition de phase dans les films.

