



Development of acoustic sensors for the extension of measurements to high temperature in the experimental reactors

Oleksandr Gatsa

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THÈSE POUR OBTENIR LE GRADE DE DOCTEUR DE L'UNIVERSITÉ DE MONTPELLIER

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École doctorale Information, Structures et Systèmes

Unité de recherche UMR5214 Institute d'Électronique et Systèmes

Development of acoustic sensors for the extension of measurements to high temperature in the experimental reactors

Présentée par Oleksandr GATSA

Le 30 Novembre 2018

Sous la direction de Jean-Yves FERRANDIS
et Philippe COMBETTE

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Introduction and Objectives

Optimizing the lifetime of nuclear fuel rods without reducing safety margins (e.g., minimizing clad corrosion or excessive increase of the internal pressure) requires better control of helium and fission gas release within the fuel rod's free volumes. The presence of released fission gas directly influences the thermos-physical behavior of nuclear fuel. High-performance experimental programs and innovative instrumentation for Material Testing Reactors (MTR) allows a good understanding of the mechanics and thermo-physics of nuclear fuel.

These works have been carried out in the frame of a partnership with CEA and are devoted to the development of a new generation of acoustic sensors for characterization of fission gas in the harsh conditions of technological irradiation reactors.

Material Testing Reactors (MTR)

Experimental reactors are nuclear facilities in which a chain reaction is created and maintained to obtain a neutron flux for use in the experiment. The energy produced by the fission reactions is generally not recovered.

The performance of an experimental reactor is characterized by:

- the "spectrum" of the neutrons produced, that is to say the energy distribution of these neutrons, which, according to the selected core, will be representative of a neutron spectrum of low energy, then called thermal energy of the neutron spectrum (energy < 0.625 eV) or a spectrum of high energy neutrons (energy > ~ 0.9 MeV), then called "fast" neutron spectrum;
- the neutron flux produced (from 10^5 neutrons / cm² to more than 10^{15} neutrons / cm²).

The design of each experimental reactor is made regarding its future applications and both the neutron spectrum produced and its intensity is adapted accordingly. In fact, precisely

specialized experimental reactors have highly specific flow characteristics; Multipurpose experimental reactors are able to perform different types of activities. They are designed to produce both fast neutrons and intermediate thermal or neutron spectra with less precise characteristics. The neutrons created in experimental reactors are used primarily to carry out experiments related to the development of nuclear power reactors through an understanding of phenomena involved and validation and qualification of chosen solutions.

It exists three main categories of experimental reactors:

- reactors intended to validate the neutron calculations of power reactors also called "critical models",
- reactors dedicated to studying of accident situations, or "safety reactors",
- reactors designed to study and qualification of structural materials and fuels irradiation behavior, also known as "technological irradiation reactors" or “**material testing reactors**”

Let's look at these last reactors; they hold a major role to play, that of qualifying, under the effect of the irradiation encountered in the reactors, the main components of the latter, namely materials and fuels, sensors, etc.

In essence, an experimental reactor includes more instrumentation in comparison with a power reactor. Indeed, a research reactor is generally used either for neutron studies requiring fine measurements or as an intense source of neutrons for irradiation. To do this, it must be able to accommodate devices that are inserted inside or at the periphery of its heart and that allow performing experiments each of which requires appropriate instrumentation.



Figure 1 – OSIRIS POOL (Saclay, France), CEA MTR devoted to material and fuel irradiation.

OSIRIS reactor has been closed since 2016; Future JHR reactor [1] in CEA Cadarache will provide irradiation facilities for next years.

A number of measuring instruments for exploitation support, and others developed for the purposes of the R&D or irradiation programs, will be found in a research reactor. Each device inserted into a dedicated channel will include its own diagnostics related to the physical parameters that one wishes to evaluate under neutron bombardment. The majority of these measurements are neutronic (activation, capture, fission, delayed neutrons), thermal (temperature, released power, conductivity), mechanical (elongation, swelling, creep, rupture) or chemical (release of gas, corrosion, impurities, radiolysis). The experimental conditions, under which these measurements are carried out, must be correctly described. Hence, detectors capable of carrying out measurements in-situ of local neutron or gamma fluxes, heating and flow rates (since these quantities are, most often, disturbed by the very presence of the device) are required.

In addition to the needs related to the normal operation of the reactor, the operator must be able (likewise in the power reactor) to respond the Safety Authority requests, including neutron aspects such as the critical level, margins of responsiveness or the effectiveness of safety bars. It requires one or more neutron measurement chains that must be precisely calibrated. The associated uncertainties to be included in the calculation of the corresponding margins will have a direct impact on reactor design and operation. In addition, specific instrumentation (dosimeters, detectors, thermocouples, sensors) will be also installed, mostly on site for the specific needs of the operation. It will provide valuable assistance in devices dimensioning and optimization of their locations, thus enabling better management of the search tool.

The instrumentation placed outside the core (known as "ex-core") is distinguished from that placed inside ("in-core"). The particularity of the "in-core" instrumentation is that it must be able to perform its primary function of measurement while withstanding an intense bombardment of neutrons and gamma rays.

Specific constraints must be taken into account during in-core measurement systems design and integration. In particular, this instrumentation must be:

- miniaturized, due to small useful sections of the experimental devices. The detectors placed in the reactor must be installed within a space of a few millimeters;
- reliable. The maintenance or repair of irradiated objects is difficult, in most cases, impossible;
- accurate, due to constantly increasing scientific requirements. For example, dimensional measurements made on samples inside a reactor must be able to detect micrometric variations;
- resistant to nuclear radiation that causes damage (degradation of electrical insulators, breakage of connecting wires, changes in the properties of the materials constituting probes), changes in composition by transmutation, parasitic currents and heating of the detectors;
- resistant to high temperatures (operating temperatures may be higher than 300 ° C),
- Corrosion resistant, reactor experiments are usually conducted in pressurized water or liquid metal (NaK).

To meet these specifications, precautions are taken with regard to the choice of materials (use of metals and ceramics with adequate nuclear properties) and the measurement methods used (comparative methods or online calibrations are preferred). Whenever is possible, the measurement systems are deported out of the neutron flux.

Fission gas release measurements

Measurement of the composition and pressure of noble gases released into the fuel rod (helium, krypton, and xenon) was of a great interest during many years [2], [3]. But a better insight has still to be reached.

In a real gas, the speed of sound depends not only on the gas thermodynamic parameters (temperature, pressure) but also on the gas molar mass. Therefore, the measurement of the speed of sound represents an ideal way of determining both the molar mass of a gas and its composition (in a case of binary mixture).

Nowadays, accurate measurements of the speed of sound in a gas are performed by means of stationary acoustic waves generated in acoustic resonators (cylindrical or spherical) [4], [5].

For more than 20 years, our group, in partnership with EDF has been working on the development of acoustic sensors devoted to the characterization of fission gas in a light-water reactor (LWR) fuel rod. We developed an acoustic sensor to measure the pressure and the composition of gas inside the fuel rod out of the reactor, in a hot cell, where the rod itself act as a cylindrical acoustic interferometer [6], [7]. A full-scale hot cell test of the internal gas pressure and composition measurement by an acoustic sensor was successfully carried out between 2008 and 2010 on irradiated fuel rods in the LECA-STAR facility in the CEA CADARACHE Research Center.

To easily carry out non-destructive measurement of the internal gas pressure and its composition inside the LWR nuclear fuel rod, the acoustic sensor has been specially designed (Figure 2). This sensor has been made in 2007 and is now covered by an international patent [8]. In 2015, a generation of acoustic sensors devoted to the characterization of fission gas was presented. The gas composition and pressure can be defined with an uncertainty of approximately 1% and 10 bars (for around 50 bars and a gas mixture containing 20% Xe/Kr) respectively. This measurement is possible in a hot laboratory facility using a viscous liquid to couple the sensor with the rod.

Since 2015, we have been working out on a new acoustic sensor for an application in a spent fuel pool. This application consists in determining the default rod in a fuel assembly, which

has been declared ‘no leakproof’ during the fuel discharging of the reactor. We develop a new method based on the detection of gas pressure drop into the fuel rod. This method could replace the current one, which is based on the detection of water inside the fuel rod. Currently, the new generation of the transducer and the associated methodology are operational in laboratory conditions for underwater non-destructive measurement and enable the detection of the gas pressure drop inside the fuel rod. The development of sensor application inside a storage pool is studied.

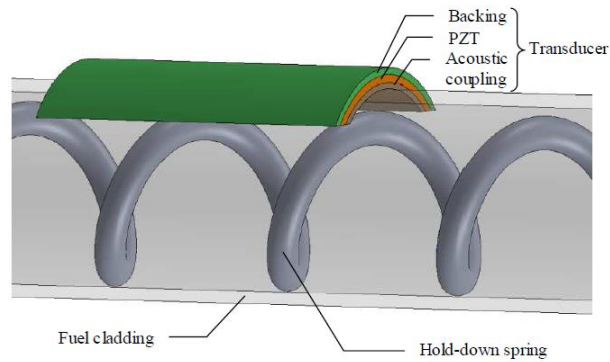


Figure 2 – Schematic representation of the measurement process.

Cladding tube inner diameter $d = 8.36$ mm and cladding tube thickness $l = 57$ μ m.

Traditionally, the evaluation of the released fission gases, in the fuel rod of an experimental reactor, has been content with a simultaneous measurement of the internal pressure of the rod and the temperature of the fuel. However, the simple measurement of the pressure does not provide information on the nature of the released gases, information necessary for the understanding of the modifications undergone in the fuel, during the irradiation. Therefore, in collaboration with the CEA, IES has developed and patented an acoustic measurement system allowing the real-time irradiation monitoring of the molar mass of the gas contained in experimental fuel rods [9]. This acoustic sensor was designed to operate under transient conditions and is able to measure the composition in fuel rods during irradiation. Hence, a better understanding of the high burn-up fuel behavior has been achieved. However, at this stage, it is not possible to give an estimation of the internal pressure because acoustic signals amplitude under neutron and gamma fluencies cannot be predicted.

The device was tested on a high Burn-Up fuel MOX (Mixed OXides) rodlet extracted from

a French PWR (Pressurized Water Reactor) fuel rod irradiated for five cycles. Afterward, the rodlet was irradiated one more time (REMORA 3 experiment) in a rig specifically adapted to be used in the MTR (OSIRIS reactor, Saclay 2010). The REMORA 3 irradiation experiment focused on fission gas release kinetics by on-line measurements of the gas mixture molar mass, and the molar fractions [10].

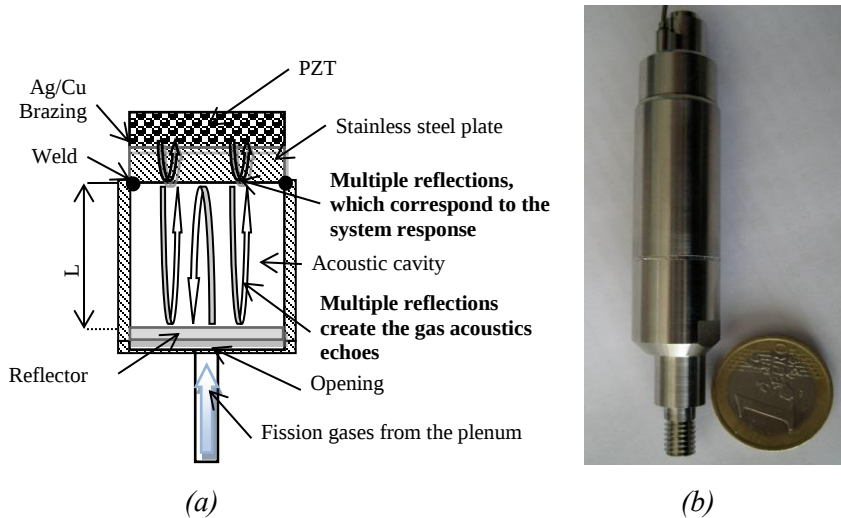


Figure 3 – REMORA acoustic gas sensor.

(a) Schematic representation. (b) Sensor overview.

In practice, the difficulties in brazing and ensuring of parallelism within the active element (Pz27 Ferroperm), stainless steel plate and reflector caused difficulties in signal registration. Transducer limitation in the operating temperature renders it impossible for the application in a new type material testing reactor (MTR). Based on this limitation and the need to operate at higher temperatures, a second approach (which reduces the influence of the parallelism problem) is to apply a screen-printing process in the production of the active element. From 2012 to 2015, F. Very [11] worked with lead zirconate titanate (PZT); the possibility of active element fabrication, characterization, and ultrasonic measurements was investigated.

New generation of acoustic sensors

This thesis work is dedicated to the development of a new generation of ultrasonic sensors for application to a new sensor device operating at high temperature (up to 400°C). In order to establish sensor production methods and properties, the screen-printing technique was used for Sodium Bismuth Titanate (NBT) thick film fabrication. The key results of this study are demonstrated and discussed through material properties characterization (morphology, chemical, electric, dielectric, piezoelectric and electromechanical parameters) and test as a function of temperature.

The main objectives of this study are the integration of the active material (NBT) into a substrate for sensor manufacture, acoustic measurement implementation, and final device prototype release.

The specific objectives of the thesis work are defined as follows:

1. Ceramic material development

- It exists a large range of piezoelectric materials capable of reliable operation within a high-temperature range exceeding PZT capability. Hence, the properties of the selected NBT material shall be fully understood.
- For reliability purpose, the production of ceramics with the **screen-printing** method has to be studied and optimized. Therefore, multiple versions of ceramic material will be fabricated.
- To conclude this part, the evolution of microstructure and the effect of raw materials and dopants on ceramic properties will be examined.

2. Fabrication and characterization of piezoelectric material

- By focusing on the fabrication and characterization of NBT ceramics, the properties of the new sensor device can be estimated. The measurements of material resistivity, dielectric, piezoelectric properties and determination of electromechanical parameters at room temperature provide an insight to the material in accordance with the previous study and allow making a choice of the material version for sensor fabrication.
- The measurement as a function of temperature gives knowledge about piezoelectric

material properties behavior under high temperatures. Indeed, the studies of its properties as a function of temperature is necessary for the ultrasonic sensor dedicated to harsh environment operation.

3. Ultrasonic sensor manufacture and test

- Multiple problems are arising in transducer development: an adaptation of impedance, coefficient of thermal expansion and coupling are just a few to mention. Hence before sensor fabrication, its configuration shall be validated. In this work, the choice of parts of the sensor was based on previous experiments with PZT material. In addition, the theoretical model, based on electrodynamic and impedance matching equations, was applied for the evaluation of the sensor response.
- The measurement of sensor's properties can be seen as a characterization of integrated on substrate piezoelectric material. Besides the material characterization protocol, to envisage sensor's acoustic response at high temperatures, an evolution of its impedance as a function of temperature is required.
- The functionality of the screen-printed NBT sensor shall be confirmed through **acoustic measurements**. For the first evaluation, the sensor device will be put in contact with the liquid medium and the echograms will be recorded. The acoustic measurements in a liquid is an important step which provides information about sensor sensitivity. The measurement of the gas under pressure values corresponding to experimental reactor conditions will show the possibility of instrumentation deployment for fission release measurement in experimental reactors. The applicability of transducers for high-temperature acoustic measurements (up to 400 °C) cannot be tested in the scope of this work. Therefore, the theoretical model validating transducer operability at these temperatures shall be proposed.
- The aspect of dealing with the use of the transducer under irradiation are not treated in this document. However, bibliographic studies are presented.

Chapter 1. Acoustic sensor for harsh environment application

In this chapter, the state of the art on acoustic sensors (transducers) development for harsh environment applications is reviewed. After the description of a basic acoustic transducer concept, a bibliographic study of sensor development is presented from three perspectives. Section 1.1 contains a review on acoustic nuclear instrumentation. In section 1.2 the transducers for measurements under high-temperature environment are presented. The studies of transducer component materials in radiation environment are introduced in section 1.3.

Acoustic sensor or transducer is a device operating by the piezoelectric principle. The active element, which exhibits piezoelectric properties, is the main part of the sensor. By application of the mechanical stress, the electric charge is produced (so-called direct piezoelectric effect). At the same time, the inverse piezoelectric effect appears when the electrical field is applied, whereby mechanical displacement is created.

Transducer characteristics are influenced by numerous factors such as material properties, mechanical and electrical construction, external mechanical and electrical conditions. It is difficult to produce ultrasonic transducers with the exact same characteristics.

The standard piezoelectric transducer consists of three main parts (Figure 1.1): a piezoelectric active element, a front face (placed in contact with the device under test and protects the active element) and a backing (affects sensor resolution).

Hence, the active element and the front face are significant for the acoustic signal transduction, in this Ph.D. thesis, we are regarding both the active element development and its integration into a substrate (front face).

The role of backing is to optimize the emission of acoustic energy towards the front face and to modify the bandwidth of a transducer depending on desired responses. The studies of a backing

development were performed by our colleague R. Boubenia and already presented in his thesis work [12]. However, backing integration with a new type of sensor does not match the scope of this work and might be studied in the future.

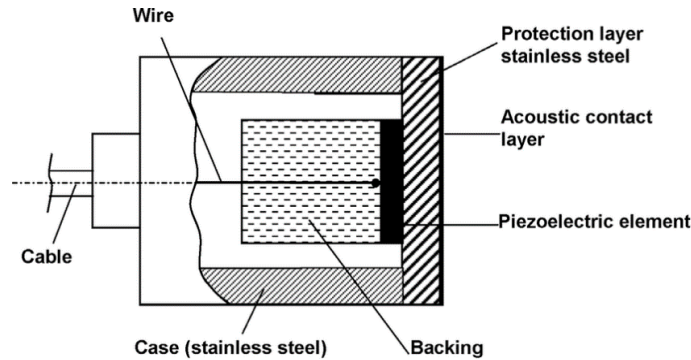


Figure 1.1 – A ‘classic’ schematic of piezoelectric transducer.

To enhance the acoustic impedance matching, the front face can also be covered by an acoustic contact layer. The protection layer is sometimes nothing else then this matching layer.

The acoustic transducers are widely used, for example, in the field of communications, electronics, NDT (nondestructive testing). However, the transducer operation is limited by the Curie temperature of the active element. Above the Curie temperature, the ferroelectric-paraelectric phase transition occurs and the material loses its piezoelectric properties [13]. For the Lead Zirconate Titanate (PZT) material with a high piezoelectric coefficient, this temperature is in the range of 300 °C – 400 °C. Nevertheless, maximum operating temperature is about 2/3 of Curie temperature [14], while higher temperatures lead to the degradation of the material properties.

There are many piezoelectric materials with high Curie temperature, but these materials have a lower piezoelectric coefficient in comparison with standard PZT ceramics. Besides, the serious barrier in the transducer development, for high-temperature measurements, is the difference in thermal expansion of the sensor elements [15]. However, the long-term measurements above the high temperatures (from 200 °C) are relevant, for instance, for nuclear, automotive and aerospace industries. The development of new devices is then of great interest.

1.1 Acoustic nuclear instrumentation

Acoustic methods are widely used in the nuclear plant industry for non-destructive inspection of the internal state of materials in the laboratory and industrial facilities. High temperature, radiative and corrosive environments impose the constraints to acoustic sensors, in particular, to active material elaboration, coupling, and casing.

By reason of recently published detailed review of C. Lhuillier [16] in the specific domain of instrumentation for MTR (Material Testing Reactor), a truly comprehensive review is impossible in the scope of this thesis and will duplicate the existing one. The following brief review presents the main existing problems and solutions proposed.

With the development of Generation IV reactors, the safety constraints and operational temperatures will be increased. French Generation IV reactors will be an advanced version of sodium fast reactors with increased efficiency, lifetime and reliability of the system [17].

The online monitoring inside liquid metal reactors is used for sodium flow measurements, stainless steel internal structure, and vessel inspection as well as for in vessel visualization (liquid sodium is not transparent). Recently, CEA (DEN and DRT/LIST) and AREVA NDT Solutions ® developed two types of high temperature ultrasonic transducers (TUSHT and TUCCS) and an Electro Magnetic Acoustic Transducer (EMAT) [18] – [20] where the lithium niobate (LiNbO_3) crystal with a Curie temperature of about 1150 °C was proposed as piezoelectric material. Indeed, the resistance to neutron damages is improved by Li^{+7} enrichment; therefore, it can withstand a fast neutron fluence of 20^{21} and a 10^6 Gy/h dose rate. The hard-soldering technique is used to bond crystal with stainless steel casing and electrode. The details of experiments performed and the difference between each of the transducer type for the immersion detection in liquid sodium can be found in the review of C. Lhuillier (pp. 20-23) [16].

With ongoing development of new experimental reactor, MYRRHA (IV Generation fast flux research reactor) by the Belgium Nuclear Research Center SCK•CEN, numerous researches dedicated to new ultrasonic instrumentation are in process [21]. MYRRHA is conceptualized as an accelerator-driven system cooled with lead-bismuth eutectic mixture (LBE). In the frame of this

project, the ultrasonic transducer for flow measurement in the plenum was designed. The Bismuth Titanate commercial element Pz46 was used as an active element. All parts that come into contact with the liquid metal (lens, encasing, cabling) are made of 316L stainless steel for optimal compatibility with LBE. The measurements in LBE confirmed the bismuth titanate to be an optimal choice for immerse measurements up to 400 °C.

Researches conducted by Reactor Concepts Research Development and Demonstration Department of the Iowa University are dedicated to the development of the NDT system which is capable to operate in high-temperature liquid media (water, liquid metals or molten salt) for inspection in advanced Small Modular Generation IV reactors [22].

Prior to transducer assembly, its properties were modeled by finite element method. Dimensions, casing, electrode choice, adhesion properties were simulated to determine optimal parameters for transducer fabrication. The BS-PT $[(1-x) \text{BiScO}_3\text{-}x\text{PbTiO}_3]$ piezoelectric material with an operational temperature of approximately 300 °C was used as an active element. It was bonded with nickel faceplate using two-part epoxy (Epotek 353®). The assembly of nickel, BS-PT, and the lead wire was attached to the casing at the final stage (Figure 1.2). The BS-PT transducer with a frequency operation of 2.25 MHz was tested for immersion measurements in silicon oil from 22 °C to 142 °C.

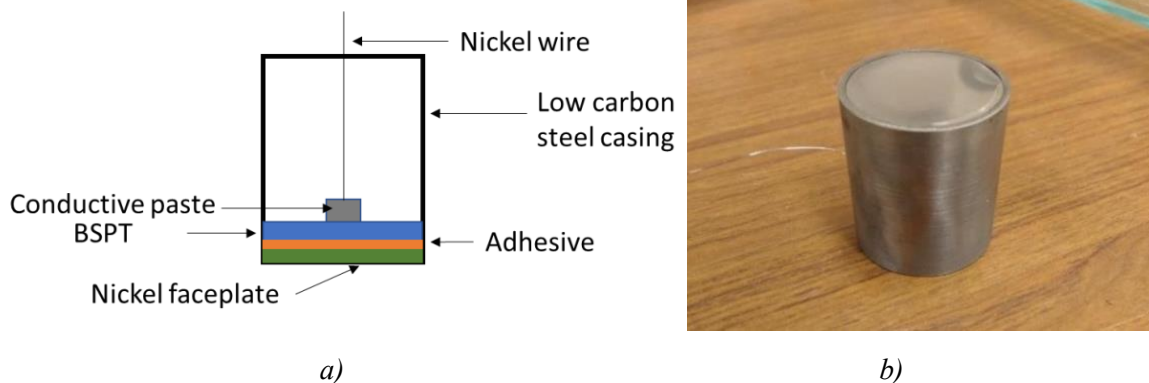


Figure 1.2 – Transducer designed for an immersion test in Small Modular reactors [22].

a) Schematic of transducer design; the BS-PT active element was coupled to Nickel faceplate using two-part epoxy and integrated inside a low carbon steel casing. (b) Photography of final transducer development. The dimension of the transducer is in the centimetric range. Casing walls are 2 mm in thickness.

The critical technology gap existing in the field of online monitoring of nuclear plant pipelines was reduced with the research conducted in the Department of Engineering Science and Mechanics at Pennsylvania State University [23]. The transducers from Bismuth Titanate ($\text{Bi}_3\text{Ti}_4\text{O}_{12}$), Bismuth - Lithium Niobate (BT/LN) and Bismuth - Lead Zirconate Titanate (PZ/BT) ferroelectric ceramics, Lithium Niobate (LiNbO_3), ZnO, $\text{YCa}_4\text{O}(\text{BO}_3)_3$, AlN crystals were fabricated and tested under high temperature and radiation conditions.

Spray and sol-gel technique deposition were used for fabrication of ferroelectric ceramic transducers. The sol-gel method was used to form a slurry that after was air-spray deposited on a substrate to form a transducer. After the deposition, subsequent processing included pyrolyzation, densification, electrode application, lead wire connection, and poling. Due to the porosity of the air-spray deposited piezoelectric material surface, the cracking during sintering occurs. This problem was studied and some solutions, discussed in [23] – [26], were implemented in transducer fabrication. The transducer functionality was tested through the deposition of electrodes by sputtering and painting methods. It was shown that painted electrodes under high temperature (400 °C) degrade which decreases piezoelectric properties of samples. After testing of the transducer in longitudinal mode operation, the comb transducer composed of ring elements on a stainless-steel pipe was fabricated and guided wave modes were successfully generated and received. The acoustic measurements were carried out up to 400 °C, 680 °C and 1000 °C for PZT/BT, Bismuth Titanate and BT/LN (Figure 1.3) transducers correspondingly. The results show that interface reflection is detectable and suggest that transducers have sufficient penetration power. Non-linear methods of defect detection with higher harmonics in Rayleigh and Lamb modes were studied. It was suggested that the sensitivity of crack defect detection can be enhanced by increasing the density of the air-sprayed samples [23].

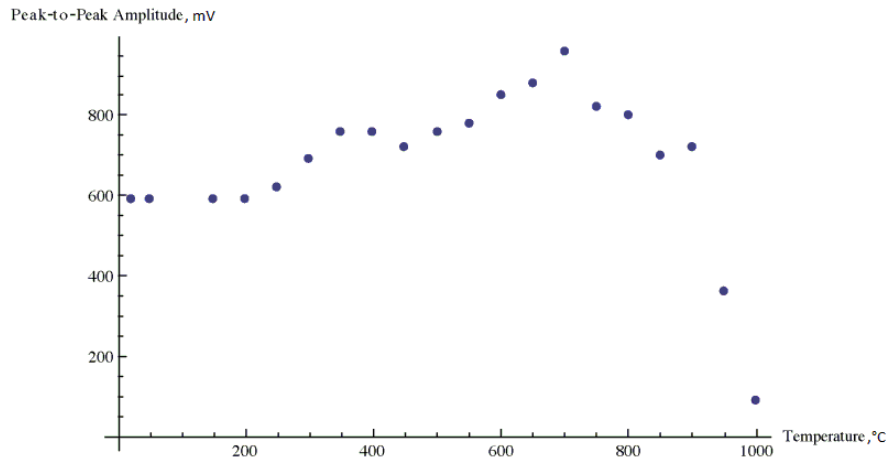


Figure 1.3 – Peak to peak amplitude (mV) as a function of temperature (°C) for BT/LN transducer on Alloy 617 substrate [23].

The experiment shows that non-destructive evaluation with BT/LN transducer (fabricated by the air-spray technique) can be performed up to 950°C.

The significant contribution to high-temperature methodology evaluation of structural/material integrity in nuclear plants was made with the article of D. Parks, S. Zhang and R. Tittmann [27]. The studies on high-temperature piezoelectric crystals ($\text{YCa}_4\text{O}(\text{BO}_3)_3$, LiNbO_3 , and AlN) for use in ultrasonic transducers under continuous operation for 55 h at 550 °C were reported. The coupling problem between transducer elements: a waveguide, a backing, a piezoelectric element, a front face was resolved by insertion of wave spring (UNS S66286) thus the mechanical pressure provided piezoelectric material onto the ultrasonic propagation medium. The experimental fixture of the ultrasonic transducer is shown in Figure 1.4. Tested piezoelectric materials had a surface of approximately 10 mm² with a resonance frequency of 10 MHz. The recorded echo-amplitudes showed that $\text{YCa}_4\text{O}(\text{BO}_3)_3$, LiNbO_3 , and AlN single crystal-based transducer withstand continuous operation without a significant change in signal. Data from the thermal ratcheting testing of piezoelectric materials show that after 48 hours of exposure to 1000 °C the efficiency of ultrasonic transduction for three types of crystals remains in the acceptable range of signal detection (Figure 1.5). Nevertheless, the method of the mechanical assembly of the transducer element with spring showed good coupling properties, the disadvantage was found in coupling materials that were used for acoustic impedance matching. It was found, that the high-

temperature couplant has a relatively short lifetime at 500 °C, which limits the transducer operation. The alternative coupling material shall be implemented for continuous transducer operation.

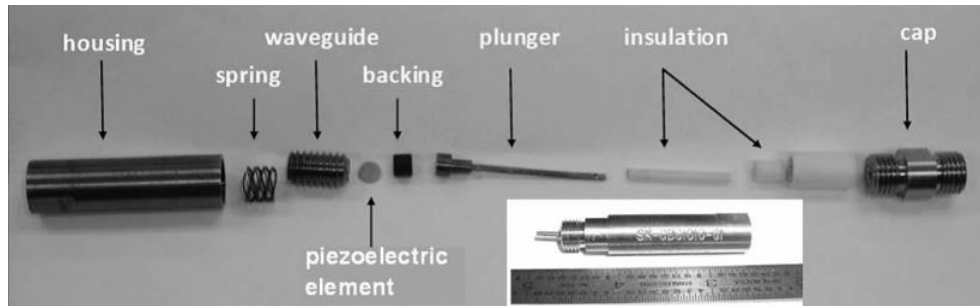


Figure 1.4 – Experimental fixture and the fabricated high-temperature ultrasonic transducer [27].

Active piezoelectric materials were machined in form of a disk with approximately 10 MHz in resonance frequency. The casing was designed to allow further integration and test inside a nuclear reactor.

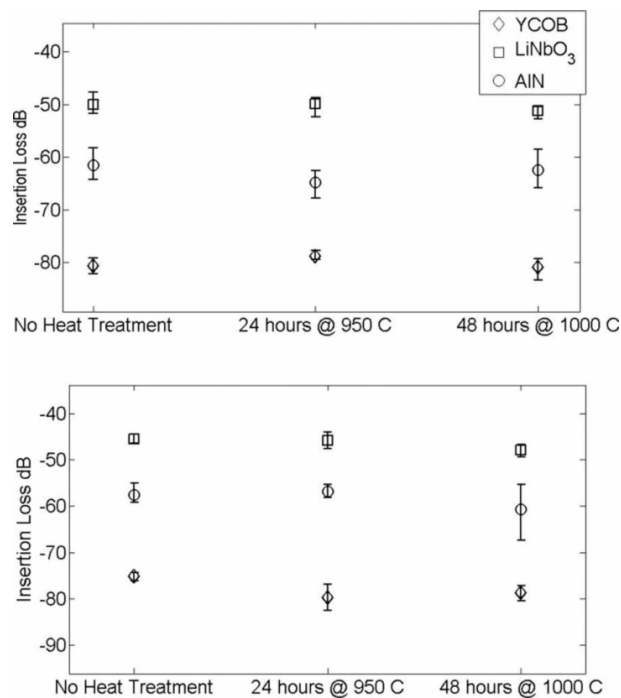


Figure 1.5 – Data from the thermal ratcheting testing of piezoelectric crystals [27].

Significant changes in the dielectric properties with slight changes in the ultrasonic performance of lithium niobate was observed. It is expected that dielectric properties will evolve with time having an impact on ultrasonic properties.

Conclusions

An acoustic technique being non-invasive, flexible and reliable method is in great demand by nuclear industry. The increase in operating temperature and the new requirements on continuous monitoring in-situ for IV Generation reactors impose new challenges in sensor development.

In the presented section, we discussed the most significant findings, which are relevant for this work, and the conclusions on some tendencies are as follows:

- The experiments reported showed promising results for in-situ detection. However, all the authors reported problems met in the coupling phase of transducer fabrication thus the question of transducer amelioration are still open.
- For the temperature range from 200 °C to 400 °C, bismuth-based piezoelectric materials are the preferable choices in terms of its piezoelectric/temperature-endurance response.

In the next section, sensor development will be discussed in the scope of high-temperature environment, overlapping in some instance the studies presented in this section.

1.2 High temperature environment

High-temperature ultrasonic transducers are widely used in the nuclear plant industry for non-destructive testing (NDT). For instance, ultrasonic NDT of steel components in industrial plants is performed at temperatures up to 400°C [15]. However, the measurements with such devices can be performed only for short periods which increase the inspection cost. The problem in the difference of thermal expansion between a piezoelectric material, a front face and a device under test establishes poor performance of commercial sensors.

To increase the operation temperature of the standard piezoelectric transducers based on PZT, various materials have been studied for sensing applications. Among them, Bismuth Titanate $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [25], [26], Lithium Niobate LiNbO_3 [27], [28], Lead Metaniobate PbNbO_6 [29], Yttrium Calcium Oxoborate (YCOB) $\text{YCa}_4\text{O}(\text{BO}_3)_3$ [27], [30], Gallium Orthophosphate GaPO_4 [31], [32],

Aluminium Nitride AlN [27], [33] transducers were designed and tested under harsh environment conditions.

Complete reviews of high-temperature piezoelectric transducers can be found in [15], [34], [35].

Table 1.1 – Properties of high-temperature piezoelectric materials.

	Structure	T _c	ϵ_r	d_{33} , pC/N	k
PZT [36]	Perovskite	~365 °C	1700	370-420	0.7-0.73
PbNbO ₆ [37]	Tungsten-bronze	400 °C	300	85	0.3
PbTiO ₃ [37]	Perovskite	470 °C	190	56	0.45
Bi ₄ Ti ₃ O ₁₂ (BiT) [38]	Aurivillius	600-670 °C	140	16-25	0.15
Na _{0.5} Bi _{4.5} Ti ₄ O ₁₅ (NBT) [39]	Aurivillius	~680 °C	150	16	0.15
K _{0.5} Bi _{4.5} Ti ₄ O ₁₅ (KBT) [40]	Aurivillius	555 °C	212	20	0.09
CaBi ₄ Ti ₄ O ₁₅ [41]	Aurivillius	790 °C	55	8	0.03
La ₂ Ti ₂ O ₇ [42]	Pyrochlore	Operation temperature < 800 °C	25-15	16	0.21-0.25
LiNbO ₃ [37]	Corundum	1150 °C	25		
Quartz [37]		Phase transition at 573 °C	2.3	4.5	0.10
GaPO ₄ [43]		970 °C	7	5	0.11

The choice of active material for high-temperature transducer reported above is based on Curie temperature (T_c, °C), dielectric permittivity (ϵ_r), charge piezoelectric coefficient (d_{33} , pC/N) and electromechanical coupling coefficient (k) (more details on these parameters can be found in Chapter 3). In the Table 1.1 some properties of high temperature piezoelectric materials are presented.

The choice of active material for high-temperature environment becomes the compromise between the aforementioned parameters. Furthermore, chosen piezoelectric material shall withstand high neutron and gamma fluence (Table 1.2; for more details, refer section 1.3).

Table 1.2 – Performance of high-temperature piezoelectric materials.

	Operation temperature, °C	Piezoelectric performance	Resistance on radiation
PZT	< 250	*****	***
Bismuth Titanate	< 600	***	**
AlN	n.a	*	***
LiNbO ₃	< 1000	*	**

The compromise between high Curie temperature and the piezoelectric response is a choice which will be discussed. However, the problematic with piezoelectric element adhesion to the casing is a factor which limits the lifetime of ultrasonic transducers. R. Kažys et al report that 60% of existing high-temperature transducers have a coupling problem [15]. The research of our group, in the frame of REMORA sensor development, shows that the poor coupling of the piezoelectric element is a parameter which degrades transducer properties and complicates registration of the signal [44]. Piezoelectric ceramics have an advantage compared to the single crystal piezoelectric element as it can be directly deposited onto a substrate (front face of the transducer) [45] – [47], thus, the adhesion can be enhanced.

High-temperature ceramic is presented by Aurivillius phase, so-called Bismuth Layer Structure Ferroelectric (BLSF) ceramic. Hence, the following brief review presents the studies on transducer development with BLSF ceramics.

The sol-gel spray technique for high-temperature transducer was first reported in 2000 by Dr. Kobayashi et al. [48]. Lately, the BiT/PZT and Bismuth Titanate transducers were fabricated on a stainless steel substrate [49]. These transducers were able to operate up to 440 °C with a 2 dB loss in signal strength at elevated temperatures and was reported to be successfully used for industrial application as polymer injection molding [50].

Using the same method reported by Kobayashi et al., Dr. Searfass, in his thesis work developed high-temperature Bismuth Titanate ultrasonic transducers [25]. Transducers were tested for operation in longitudinal, Lamb and Rayleigh mode. The sol-gel and air-spray methods were used for material deposition on stainless steel and titanium substrates. The adhesion and transduction efficiencies were improved by microwave sintering and high-intensity ultrasonic mixing during the fabrication process.

Longitudinal and Lamb wave transducers were clamped into the holder and put inside a tube furnace. The temperature was gradually increased up to 680 °C. It was shown that Bismuth Titanate transducer fabricated by air-spray method deposition can generate ultrasonic signals up to 625°C for 3 hours. The sample depoling occurs rapidly at a temperature of 650°C approaching Curie temperature of BiT ceramics. The piezoelectric charge coefficient was found to be in the range of 13-16 pC/N.

In another experiment, the bismuth titanate powder was mixed with lithium niobate crystal powder and added to the sol-gel solution [23]. The transducers of BT-LN type were sprayed on Alloy 617 and the acoustic signal amplitude was registered up to 1000 °C. The delamination of the samples was observed after the temperature cycle, which is probably associated with the oxidation of the stainless steel. Thus, it was suggested that the protective coating is required for this type of environment.

Conclusions

Nevertheless, it exists a great number of reviews on high-temperature piezoelectric sensors, to be mentioned [15], [34], [35], the review was focused on the state of the art concerning the development of BLSF-based sensors. It was found that the common approach by deposition with air-spray method gives promising results in the area of high-temperature measurements (up to 625 °C in some cases). It confirms the assumption, that this type of ceramics can be deposited into a substrate for transducer fabrication which is relevant for our studies (the piezoelectric material in this work was produced to be deposit by screen-printing method). In section 1.3, results presented on transducer response to the radiative environment will complete the state of the art.

1.3 Radiative environment

There is a great demand for acoustic sensors meeting the needs of non-destructive characterization in environments subjected to a large amount of radiation. These sensors are indispensable for periodic inspections of nuclear reactor components, or for an acoustic topography of potential cracks in structures that can lead to radiation leakage. However, the effect of radiation can lead to degradation or even complete destruction of the transducer.

Before quantifying the impact of radiation on sensors, it is important to have some knowledge about radiation and radioactive environment. Radiation occurs when energy is emitted by a source and travels through the medium. It is divided into two groups: non-ionizing and ionizing radiation. Non-ionizing radiation does not carry enough energy to ionize atoms and molecules. The ionizing radiation is a type of radiation by which the electrons can be liberated from atoms and molecules thus represent a hazard to the environment. It is represented by charged particles (alpha, beta and

ions) and non-charged particles (gamma and neutron). The latter interacts with matter generating charges particles ejected from the nucleus (neutron mainly) and from electron cloud. Due to their high power of interaction, charged particles are stopped in the first microns or mm depending on their energy. Accordingly, it is a long-established practice to speak about the radiation environment in terms of gamma radiation and neutron fluence. In Table 1.3, an approximation data of gamma dose quantities found in nuclear reactors are represented [51].

1.3.1 Effect of gamma irradiation

Some articles deal with the effect of gamma rays, combined or not with a flux of neutrons, on the materials used in the manufacture of transducers [51]. However, there is much less about the effect of these same radiations on the complete assembly.

Table 1.3 – Approximation of the Gamma Dose Rate and Cumulative Dose according to the environment [51].

Source of gamma radiation	Dose rate (Gy/h)	Cumulative dose over one year (Gy)
Inside a nuclear power reactor, at full power	10^7	10^{11}
Inside a nuclear power reactor, during shutdown	0.5	4000
Next to used nuclear fuel storage compartment	10^3	10^7
Short-term dose yielding 50% death probability		2.5 – 5

* The gray (Gy) is radiation absorbed dose expressed in one joule of radiation per kilogram of matter.

Many studies have been done to evaluate the effect of radiation on the piezoelectric elements [51] – [59]. It has been shown that the main impact of gamma rays on piezoelectric elements comes from the phenomenon of ionization, that is to say, the creation of electron-hole pairs [60]. In general, it is assumed that the esterification of the transducers is caused by the accumulation of doses.

Indeed, the dose of radiation will interfere according to the following mechanisms:

1. The degradation due to the phenomenon of heating within the material caused by the accumulation of dose. This can be reduced by using materials with high Curie temperatures.

2. Dose accumulation within materials can cause progressive increasing of dielectric losses within the piezoelectric crystal and thus an effective reduction of the piezoelectric effect.
3. The charges due to radiation can be trapped under the electrodes. A high concentration of these charges can potentially create a phenomenon of partial polarization of some dipoles. Indeed, these accumulated charges on each side of the material create a partial magnetic field that can influence its dipoles.

Table 1.4 - Gamma resistance of common piezoelectric materials at moderate temperatures [51].

Piezoelectric material	Curie temperature (°C)	Reported behavior
PZT (several types)	250-360	Reliable operation after a dose of 1.5 MGy [52] Ionization damage threshold of 400 MGy of gamma, but only if temperature and neutron fluence are kept low [61] Gradually increasing damage to PZT sol-gel films in the range 0.05–1 MGy of gamma, but damage is recoverable via post-irradiation bias cycling [62]
Lithium niobate	1142–1210	No significant performance degradation at 100 MGy [55] Slight degradation in the range of 35–88 MGy [61] Some decrease in d_{33} , but no serious performance degradation at a dose of 40 MGy [56]
Aluminum nitride	>1100	No significant performance degradation at a dose of 27 MGy gamma (in combination with neutron fluence) [59] No significant performance degradation at 18.7 MGy [63]
Bismuth titanate	670	Slight reduction of the piezoelectric coefficient at 22.7 MGy [64]
Lead metaniobate	400	A moderate decrease in piezoelectric voltage coefficient g_{33} at 1 MGy absorbed gamma dose [54]

The choice of piezoelectric material for nuclear applications has to be considered regarding the previous studies on materials irradiation. The synthesis, performed by A.N. Sinclair and A.M. Chertov [51], provides detailed information about the state of the art (Table 1.4). In a reactor environment, the gamma could also induce the parasitic current in the connection wires. A variety of radiation-hardened RF coaxial cables are available for which deterioration in cable performance with radiation exposure is minimized [65] – [67].

1.3.2 Effect of neutron fluence

The neutron, which was assumed to be with the proton, one of the constituents of the atomic nucleus, was highlighted by British researcher James Chadwick in 1932. Neutron radiation, as well

as gamma, is a type of indirect ionizing radiation, which presents by neutrons and their interactions with atomic nuclei. The neutron fluence defined as a number of neutrons accumulated during a radiation period within a unit area. As the uncharged particles, neutrons, does not induce direct ionization after interaction with matter (by the emission of an electron). However, neutrons interact with the atom nucleus in several possible ways. It could be captured given either an isotope of the initial element or a change of the nature of the element (transmutation). It could also have an (elastic or inelastic) diffusion reaction with the nucleus. For all the previous reaction, the nucleus is excited after interaction and give back energy to get back to equilibrium state through X-rays photon emission. The latter interacts with electrons leading to the ionization of the matter. There is also a mechanical effect due to the scattering reactions leading to possible displacement of the atoms inside the lattice making damages inside the matter.

Table 1.5 – Neutron fluence damage.

Piezoelectric material	Gamma dose (MGy)	Time-integrated neutron fluence (n/cm2)	Damage description
PZT	n.a.	2.5e1020 thermal + 1.5e1020 fast	Drop in pulse-echo signal magnitude, but only slight damage at 1/10 of the fluence [58]
	0.5 (estimated)	1.6e1017 thermal + 1.6e1016 fast	Measurable drop in response amplitude, but piezoelectric element was still operable [52]
	n.a.	3.5e1019 thermal + 1.4e1019 fast	Measurable drop in electromechanical coupling [57]
	Low	3.6e1018	Permanent damage threshold for a pressure transducer [68]
	0.6	1.7e1019 thermal + 1.6e1018 fast	Complete transducer breakdown, with sharp drop in electrical resistance [69]
Lithium niobate	4	3e1018	No significant damage [68]
	n.a.	2e1021	Disintegration due to neutron capture of Li-6 [58]
	n.a.	2.8e1018 fast	No discernible effect on entire accelerometer [70]
Aluminum nitride	26.8	5.8e1018 thermal + 1.85e1018 fast	No change in d33 [52], [71]
	n.a.	1. 94e1022 fast	Damage is dependent on extent of isotope enrichment between N14 (high neutron capture cross section) and N15 (low cross section) [72]
Bismuth titanate	n.a.	1e1020 fast	Lost 60% of one-way piezoelectric response [65]
Lead metaniobate	n.a.	1e1011 to 2.4e1012	Frequency response degradation ranged from 16% to 92% for entire acoustic emission transducer assembly [73]

A resume of experiment results as a function of neutron fluence to piezoelectric materials and assembled transducers is presented according with the review of Sinclair et Chertov [51] (Table 1.5).

1.3.3 Conclusions

It is important to consider that during irradiations the effect of radiation is mixed, due to the simultaneous presence of gamma rays and neutron flux. In addition, some tests have been carried out with periods of irradiation parallel to continuous exposures. Finally, the sources rarely provide documentation of the temperature conditions and possible variations generated during the experiments. This large amount of influence parameters makes it impossible at this stage to make any conclusions about the exact impact of neutron fluxes on transducer damage.

However, the combination of different published results and data from the expertise of the nuclear industry makes possible to issue a certain number of hypotheses for the development of new sensors [51]:

- It is assumed that the degradation caused by gamma rays on acoustic transducers depends only on the cumulative dose, and not the dose rate provided that there is no significant change in temperature.
- In traditional immersed acoustic transducers, organic elements are the most likely to be damaged. In addition, the creation of gases in the plastic components, can, due to the increase in mechanical stresses, cause damage to the assembly and the piezoelectric element.
- Radiation damage results in a drop in the performance but does not immediately lead to failure of the measurement.
- It is necessary to choose a piezoelectric element at a time adapted to the conditions of radiation and temperature. The use of PZT is recommended in cases where the temperature exposure is below $\sim 200^{\circ}\text{C}$. However, it should be remembered that radiation can cause localized temperature to rise above room temperature. For higher temperatures, lead metaborate is less sensitive but more stable. Finally, above 300°C , titanate bismuth, aluminum nitride and lithium niobate are more suitable. Other

piezoelectric composites can also be alternatives, but it is remained to determine their evolution in the radiative media.

1.4 Conclusions

The multiple research attempts in transducer development for the harsh environment do not give a unified answer to the existing problem. This thesis work is a continuation of previous research in the field of in-situ fission gas detection. Regarding the new requirements for operation temperatures (300 - 400°C) for the new device, the concept of sensor development has to be reconsidered. The ferroelectric ceramics of the Aurivillius phase proved to be a valuable solution in the temperature range of up to 500 °C [61] – [68]. Ceramic from this family (Pz46 commercial element) was used in SCK equipment under an in-situ condition in liquid sodium [21]. Its piezoelectric properties are relatively lower in comparison with low Curie temperature piezoelectric ceramics (ex. PZT) and higher if there are compared to single crystal piezoelectric (ex. Lithium Niobate, AIN). It is expected that Aurivillius type ceramic can be used for fission gas monitoring. In the next chapter, we will focus on the Aurivillius phase ceramic structure and the question related to the enhancement of its properties through doping.

Chapter 2. Aurivillius type ferroelectric ceramics. Sodium Bismuth Titanate*

The recent research in bismuth layer-structured ferroelectrics (BLSF) ceramics have been related to their application for nonvolatile ferroelectric random-access memory [74], [75] and high-temperature piezoelectric transducers [34], [76]. These materials possess a high Curie temperature (T_c), which makes them be a promising solution for automotive, aerospace, nuclear power industry applications. To obtain a relatively high piezoelectric coefficient with the low dielectric loss for BLSF ceramics, the multiple approaches in material development were proposed [77].

Based on the difficulties with the polarization of Bismuth Titanate [11], $\text{Bi}_3\text{Ti}_4\text{O}_{12}$, Aurivillius phase ceramics, the Sodium Bismuth Titanate, $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$, was chosen as an alternative piezoelectric material.

The following chapter provides the basis on ferroelectric ceramic, and Aurivillius type group. In order to improve the piezoelectric properties of Sodium Bismuth Titanate, $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$, a bibliographic study of the substitutions and their impacts on these properties were carried out. The proposed doping mechanism will be presented in conclusions to this chapter.

2.1 Perovskites

Perovskite is both a mineral composed of calcium oxide and titanium of formula, CaTiO_3 , but has also the name of a generic ABO_3 crystal with the same parent structure. This mineral was discovered in 1839 by Gustav Rose in the Ural Mountains and named perovskite after the Russian mineralogist Lev Alekseyevich Perovsky (1792-1856). Many functional oxides crystallize in the perovskite structure.

*Note: The bibliographic transition, presented in this chapter, were carried out in collaboration with chemists. The author appreciates their help.

Perovskites are of great interest because of the great variety of physical properties (ferroelectricity, magnetism, superconductivity...) accordingly to elements in A and B cations. The arrangement of the atoms is as follows: the cation B is located at the center of the cube, inside an octahedral cubic cavity formed by twelve O^{2-} anions, the A cations are placed at the vertices of the cube, the O^{2-} anions are found in the middle of the edges of the cube, and form an octahedron around B. A three-dimensional network of BO_6 octahedral connected by their vertices is formed around the A cation (Figure 2.1). It is important to emphasize that the perovskite structure can accept almost all elements of the periodic table. The cation A is generally a broad low charge ion, such as Ba^{2+} or La^{3+} (ionic radius $> 110 \text{ pm}$) and the cation B is a small high charge ion, such as Ti^{4+} , Nb^{5+} or Fe^{3+} (ionic radius $< 100 \text{ pm}$). The perovskite structure is closely related to materials with interesting electrical properties such as piezoelectricity, ferroelectricity and high-temperature superconductivity [78].

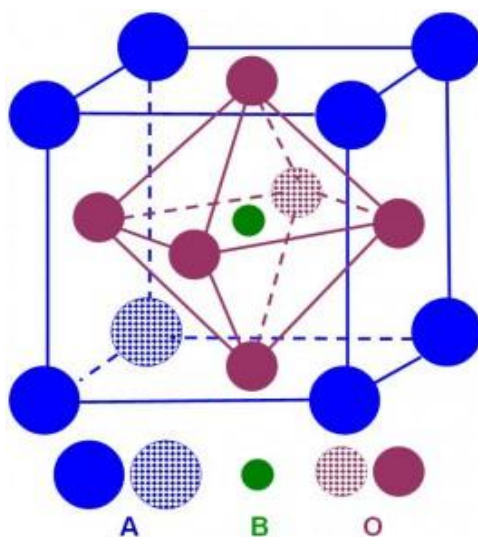


Figure 2.1 – Representation of an ideal perovskite structure of cubic symmetry $Pm3m$ [78].

The most studied example of this family of materials is barium titanate, $BaTiO_3$. At a temperature above 120°C , this compound has a perfect cubic perovskite structure. At room temperature, it adopts a lower symmetry, quadratic mesh in which the various ions can be considered to have been displaced from their sites of high symmetry (Figure 2.2). This displacement results in a spontaneous polarization of the material.

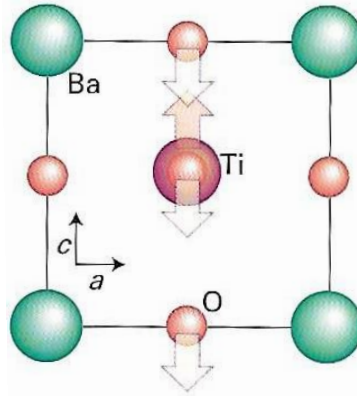


Figure 2.2 – Quadratic structure of BaTiO₃ showing the local displacements of ions, which leads to the ferroelectric behavior of the material [79].

There are 20 classes of defined crystals that can have piezoelectric properties. The pyroelectric and ferroelectric properties are respectively classes and subgroups of piezoelectricity, so any ferroelectric material is also piezoelectric (Figure 2.3), while the opposite statement is false.

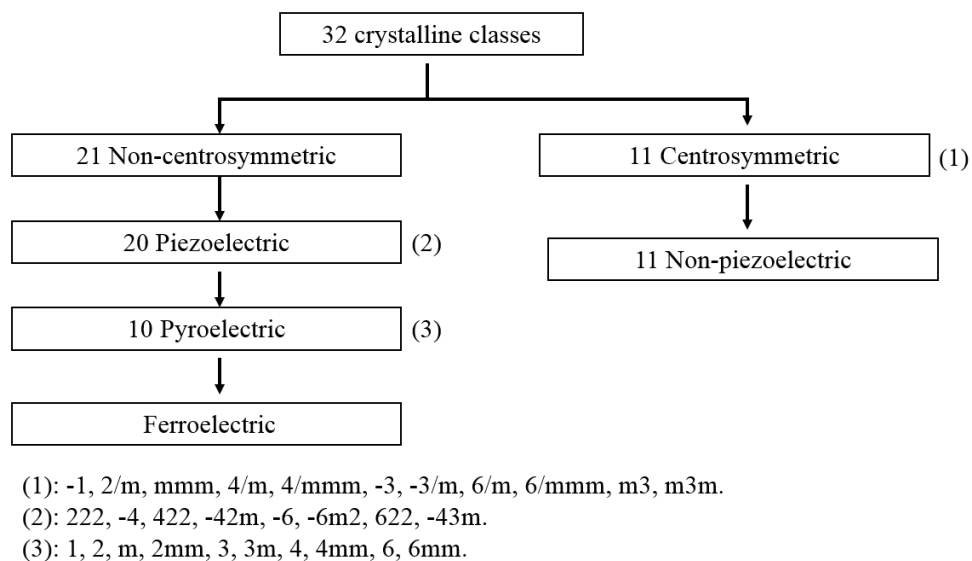


Figure 2.3 – Crystalline classes and electrical properties.

The piezoelectricity defines by the non-centrosymmetric crystalline structure. Ferroelectrics is a group of piezoelectric crystals or polycrystalline solids which possess reversible spontaneous polarization.

2.2 Aurivillius Phases

This crystalline structure, which is a form of perovskite, was first described in 1949 by B. Aurivillius [80] who discovered $\text{PbBi}_2\text{Nb}_2\text{O}_9$, the first member of a large family. The best known so far is Bismuth Titanate, chemical formula $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Since their discovery, the Aurivillius phases have been studied, in particular, for their ferroelectric properties. Their piezoelectric constants, as well as their endurance to stress, make these materials likely possible candidates for the replacement of lead-based perovskites, such as lead zirconate titanate (PZT) and lead magnesium niobate (PMN).

However, the Aurivillius phases generally have lower piezoelectric coefficients than lead-based piezoelectric ceramics, due in part to lower values of electrical permittivity and greater anisotropy [80]. In the case of thickness mode operation, it can be expressed by equation [81]:

$$d_{33} = 2Q_{33}\varepsilon_{33}^T P_r, \quad (\text{C/N}) \quad (2.1)$$

where, d_{33} (C/N) is the piezoelectric charge coefficient in direction 3, Q_{33} is an electrostriction constant for poled ceramics, ε_{33}^T is the permittivity for the dielectric displacement and electric field under conditions of constant stress and P_r is the remanent polarization.

The Aurivillius phases are represented by the general formula $(\text{Bi}_2\text{O}_2)^{2+} (\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$, where A is a cation with the coordination number of 12; B is cation with a small coordination number of 6 and m, an integer between 1 and 5. The classic description "in layers" was the first given by crystallographers and is commonly adopted by scientists. It is based on the principle of an ordered intergrowth of fluorine $(\text{Bi}_2\text{O}_2)^{2+}$ sheets and layers of perovskite $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ blocks, along with the c axis. Their internal growth is realized by the reason of similar oxygen planes co-existence in the two structures called "anionic planes of coincidence". The perovskite blocks of Aurivillius phases can contain many cations and host a large number of heterovalent substitutions (Figure 2.1 and Figure 2.4). In the formulation $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$:

- A represents a combination of cations likely to occupy sites with cubic octahedral [82] coordination (Figure 2.1). These actions may be monovalent, bivalent and trivalent or a mixture of the three such as Na^+ , K^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} , Y^{3+} , Ln^{3+} , Bi^{3+} etc... In

Figure 2.4, the cations in green are those that can occupy the site A. The green writing corresponds to the cations most frequently found in the literature and the boxes in green represent elements that could occupy the site A but not present in the literature.

- **B** represents a combination of cations capable of occupying sites with octahedral [83] coordination (Figure 2.4, violet). These cations can be trivalent, tetravalent pentavalent or hexavalent or a mixture of four such as Fe^{3+} , Cr^{3+} , Ti^{4+} , Zr^{4+} , Nb^{5+} , Ta^{5+} , Mo^{6+} , W^{6+} etc...

+1	+2	+3	+2 à +4	+2 à +5	+2 à +6	+2 à +7	+2 à +8	+2 à +5	+1 à +5	+1 à +5	+1/+2	+1/+3	+2/+4	3/+3/+5	2/+4/+6	-1/+7	+1/+8	
			+4	+5	+3	+2/+3/+4	+3	+3	+3	+1	+2	+3	+4	+3				
H																	He	
Li	Be												B	C	N	O	F	Ne
Na	Mg												Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn		Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd		In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg		Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn		Uut	Fl	Uup	Lv	Uus	Uuo
+2/+3/+4	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
+2 à +7	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				

Figure 2.4 – Periodic table showing the elements likely to occupy site A (green) and site B (violet).

*where numbers from +1 to +8 indicate oxidation state.

The three variables (**A**, **B**, **m**) thus allow a wide variety of chemical compositions. These compounds are orthorhombic at room temperature or more precisely pseudo-quadratic with slight orthorhombic distortion. Each orthorhombic mesh contains two sequences "Bi₂O₂ sheet + perovskite block" offset relative to each other according to a vector ($\frac{1}{2}a + \frac{1}{2}b$) (Figure 2.5).

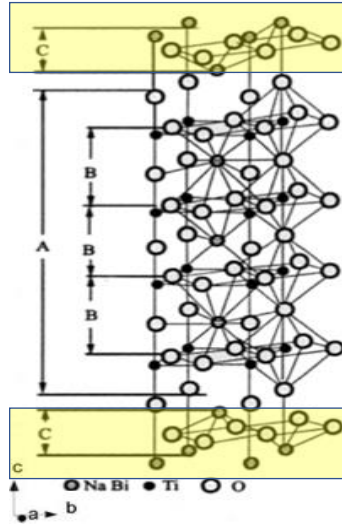


Figure 2.5 – Representation of the half of a pseudo-quadratic unit cell of $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$. (A) Perovskite layer $(\text{Na}_{0.5}\text{Bi}_{2.5}\text{Ti}_4\text{O}_{13})^{2-}$, (B) Structure of hypothetical perovskite $(\text{NaBi})\text{TiO}_3$ and (C) layer of $(\text{Bi}_2\text{O}_2)^{2+}$.

2.3 Sodium Bismuth Titanate, $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$

The BLSF ceramics are characterized by a strongly anisotropic crystal structure, high Curie temperature (T_c), high spontaneous polarization (P_s), and strong endurance to aging and fatigue phenomena. The main contribution to the ferroelectric polarization of these Bi-based structures is the displacement of the cations from site A in the perovskite units, along the axis a , accompanied by rotations of the octahedral around the c axes [84].

$\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$ comprises 4 ferroelectric perovskite layers between the 2 layers of oxides with a Curie temperature of 655°C . Its structure is orthorhombic with cell parameters of: $a = 0.5427$ nm, $b/a = 1.006$ and $c = 4.065$ nm [85]. Above the Curie temperature, the crystal structure becomes tetragonal with space group $I4 / mmm$ [85]. Newnham showed that sodium randomly substitutes bismuth in the perovskite layer by means of XRD [86]. Half of the cell unit of this structure is shown in Figure 2.5.

The configuration of Bi^{3+} is $[\text{Xe}] 4f^{14}5d^{10}6s^2$, where the pair $6s^2$ is responsible for the high polarizability of this cation and its stereochemical activity, which will influence the geometry of

the $(\text{Bi}_2\text{O}_2)^{2+}$ [83] sheets. Moreover, the main distortions existing in this structure result from the displacement of the Bi^{3+} (103 pm) asymmetric ions along the axis a [85].

2.4 Substitution

It is possible to add one or more foreign cations to perovskites. These cations will either substitute the site **A** (Bi) and/or the site **B** (Ti). These substitutions will modify the behavior and characteristics of the powders obtained. These substituents, also called dopants, may be isovalents, acceptors or donors.

The isovalent dopants have a valence equal to that of the substituted ion, such as lanthanides for site **A** (in place of Bismuth) and Cr^{4+} (55 pm) or Ge^{4+} (53 pm) for site **B** (in place of the Ti^{4+} 61 pm). These dopants increase the ionic character of the cell, which results in a decrease of the Curie point and an increase in the dielectric permittivity in the case of PZT at room temperature [87].

The acceptor dopants have a valence lower than that of the substituted ion:

for **A** site: the alkalis (Li^+ 76 pm, Na^+ 102 pm, K^+ 138 pm, Rb^+ 148 pm), Alkaline earth metal (Ca^+ 100 pm, Sr^{2+} 118 pm, Ba^{2+} 135 pm), transition metals (Cu^+ 77 pm, Ag^+ 115 pm, Cd^{2+} 95 pm) and post-transition metals (In^{3+} 80 pm, Tl^+ 150 pm, Pb^{2+} 119 pm),

for **B** site: transition metals (Cr^{3+} 62pm, Mn^{3+} 65pm, Fe^{3+} 55 pm, Co^{2+} 65 pm / Co^{3+} 55 pm) and one post-transition metal (Ga^{3+} 62 pm).

Generally, the acceptor dopants lead to the aging of the material properties and therefore the presence of an internal field. They cause an increase in the mechanical quality factor, the coercive field, and the conductivity, but a decrease in the permittivity, the dielectric losses, the coupling coefficients and the grain size of the ceramic. Materials doped with acceptors are said to be "hard" because they are difficult to depolarize under stress [88].

The donor dopants have a higher valence than the substituted ion: for site **A**, Ce^{4+} (87 pm) and Th^{4+} (94 pm) and for site **B**, the transition metals: V^{5+} (54 pm), Nb^{5+} (64pm), Ta^{5+} (64pm) et W^{6+} (60pm). They generally lead to an increase in the permittivity, the dielectric losses, the coupling coefficients, and the elastic compliance but a decrease in the mechanical quality factor,

the coercive field, the conductivity and Curie temperature. Materials doped with donors are not or only slightly affected by aging. They are said to be "soft" because they can be easily depolarized, and they have opposite effects to those induced by the acceptor dopants [88].

It is possible to dope a ceramic with several donors and/or acceptor substituents. The overall influence of doping on the properties of the material then depends on the concentration and the valence of each dopant [88].

The substitutions present in the literature concerning sodium bismuth titanate, $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$, are concentrated on 4 families of elements: alkalis, alkaline earths, lanthanides, and transition metals. The addition of these latest results in the substitution of the **B** sites, whereas that of the first 3 families tends to substitute the **A** site.

Lanthanides are a good source of stable, broad and trivalent cations with a reasonable range of ionic radius. They can, therefore, take one or more cation positions in ternary or more complex oxides. For example, perovskites of the ABO_3 type can be prepared with lanthanum at the cationic site A, LaFeO_3 . Their ability to change the size of the ion changes the properties of the material. The small lanthanide dopants are intended to substitute the **B** site (with the necessary oxygen deficiency compensation for proton incorporation), while the larger ones substitute the A site. Hence, in the case of perovskite $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$, it seems that these elements substitute both the site **A** and site **B**.

The various doping elements for $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$ reported in the literature are presented in Table 2.1.

2.4.1 Substitution of site A

Concerning the substitution of the site **A** of the perovskite $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$, the 3 types of dopants were tested: the isovalents (lanthanides), the acceptors (Li^+ (76 pm) in co-doping with cerium and Ba^{2+} (135pm)) and donors (Ce^{4+} (87 pm)).

Various difficulties were encountered during the study of the various publications concerning the data on the sizes of the ions. Shannon's publication in 1976 [87] presents the ionic radii of the elements, only according to the articles, the authors do not always use the same ionic radius for the same element, for example, the Bi^{3+} (103pm) is given with sizes ranging from 103 pm to 145 pm,

which makes the synthesis of publications somewhat complicated. In addition, cerium is the element presenting in these publications the most disparities: size of the ion greater than that of Bi [89] or lower [90], [91], and isovalent role [82], [89], [92] or donor [90], [91], [93].

Table 2.1 – Ionic rays of elements presented in the literature (in black the site A; in blue the site B).

Elements	Ionic radius (CN=6) in pm	Elements	Ionic radius (CN=6) in pm	Elements	Ionic radius (CN=6) in pm	Elements	Ionic radius (CN=6) in pm
Li ⁺	76	Ga ³⁺	62	Ce ⁴⁺ Ce ³⁺	87 101	Tm ³⁺ (Tm ²⁺)	88 103
Na ⁺	102	Ge ⁴⁺ (Ge ²⁺)	53 73	(Pr ⁴⁺) Pr ³⁺	(85) 99	Yb ³⁺ (Yb ²⁺)	87 102
K ⁺	138	Rb ⁺	148	Nd ³⁺	98	Lu ³⁺	86
Ca ²⁺	100	Sr ²⁺	118	Pm ³⁺	97	Hf ⁴⁺	71
Ti ⁴⁺ (Ti ³⁺) (Ti ²⁺)	61 67 86	Zr ⁴⁺	72	Sm ³⁺	96	Ta ⁵⁺ (Ta ⁴⁺) (Ta ³⁺)	64 68 72
V ⁵⁺ (V ⁴⁺) (V ³⁺) (V ²⁺)	54 58 64 79	Nb ⁵⁺ (Nb ⁴⁺) (Nb ³⁺)	64 68 72	Eu ³⁺ (Eu ²⁺)	95 (117)	W ⁶⁺ (W ⁵⁺) (W ⁴⁺)	60 62 66
(Cr ⁶⁺) (Cr ⁵⁺) Cr ⁴⁺ Cr ³⁺ (Cr ²⁺)	44 49 55 62 73	(Ag ³⁺) (Ag ²⁺) Ag ⁺	75 94 115	Gd ³⁺	94	(Tl ³⁺) Tl ⁺	89 150
(Mn ⁷⁺) (Mn ⁶⁺) (Mn ⁵⁺) (Mn ⁴⁺) Mn ³⁺ (Mn ²⁺)	46 26 63 53 65 67	Cd ²⁺	95	(Tb ⁴⁺) Tb ³⁺	(76) 92	(Pb ⁴⁺) Pb ²⁺	78 119
(Fe ⁴⁺) Fe ³⁺ (Fe ²⁺)	58 55 61	In ³⁺	80	Dy ³⁺ (Dy ²⁺)	91 (107)	(Bi ⁵⁺) Bi ³⁺	76 103
(Co ⁴⁺) Co ³⁺ Co ²⁺	53 55 65	Ba ²⁺	135	Ho ³⁺	90	Th ⁴⁺	94
(Cu ³⁺) (Cu ²⁺) Cu ⁺	54 73 77	La ³⁺	103	Er ³⁺	89		

Cations with a larger size than bismuth are barium Ba²⁺ (135pm), potassium K⁺ (138pm), strontium Sr²⁺ (118pm) and rubidium Rb⁺ (148pm), as well as silver Ag⁺ (115pm). The increase in the size of the cation results in a decrease in the inclination of the TiO₆ octahedra and in the distortion of the oxygen octahedra, which results in a decrease of the Curie temperature [94].

Concerning the impact on the piezoelectric constant, the replacement of Na^+ (102 pm) and / or Bi^{3+} (103 pm) by Ba^{2+} (135 pm), where the cations having different valences occupy the **A** sites, leads to vacancies in the matrix; which facilitates the movement of the walls of the cell and thus greatly improves the piezoelectric properties.

The decrease in the size of cation **A** causes an increase in internal stress [92], [95] as well as that of the rotation, tilt and distortion of TiO_6 octahedra, which results in the distortion of the matrix and an increase in piezoelectric coefficient [91], [95] – [97]. Gai et al. [82] have noted the increase of the size of the matrix causing as previously the distortion of the matrix and thus the improvement of the piezoelectric properties. Even though there is a distortion of the matrix, there is no change in structure [95], [98]. On the other hand, the smaller the ionic radius of the substituent, the greater the distortion of the matrix [92].

The addition of rare-earth (RE) element probably has multiple influences on NBT:

- Reduction of bismuth volatilization during the sintering process [91], [98], [99],
- Ceramic densification with RE-O bonds much stronger than those Bi-O [93], [98], these stronger bonds are due to a difference in electronegativity between Bi and O which is lower than that between the RE and O [92],
- Cerium has one more role, which is that of maintaining the overall load of the structure, neutral, with the creation of vacancies of Bi [82], [90], [91], and the decrease of the number of oxygen vacancies allowing the compensation of ionic defects [91], [97] making the movement of the walls easier and thus improving the piezoelectric, ferroelectric and electrical properties.

In addition, the improvement of the piezoelectric properties can also be attributed to the decrease in dielectric loss $\tan(\delta)$ [93], [97].

Regarding the Curie temperature, it decreases due to the distortion of the matrix, by the decrease of the electronegativity and the electronic configuration [97]. The decrease in the size of the cation **A**, resulting in an increase of the distortion of the octahedra and thus decreasing the symmetry of the last. By doping with the erbium [97] or europium [96] from the lanthanides group, the increase of the temperature was observed.

Regarding structural defects, according to Jiang et al. [96], in ceramics, the elements Bi and Na are known to evaporate easily and simultaneously with the creation of oxygen vacancies to compensate the charges. These vacancies are considered to be one of the mobile charge transports. On the other hand, for Rehman et al. [99], only Bi evaporates during high-temperature sintering. Conductive electrons and charged oxygen vacancies are created during the ionization of oxygen vacancies that play an important role in conduction and relaxation phenomena in Bi-based materials.



V_O° corresponds to the first ionization of oxygen deficiency and $V_O^{\circ\circ}$, to the second.

The electrons can be trapped by Ti^{4+} ions (61 pm) or Bi and (or) O vacancies:

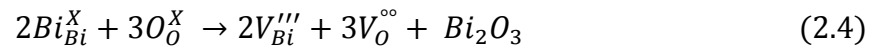


The oxygen vacancies in ceramics can be "trapped" after annealing under an oxygen atmosphere and be created after annealing under argon atmosphere. The concentration of conductive electrons and ionized defects contributing to dielectric polarization and conduction processes varies according to annealing atmospheres.

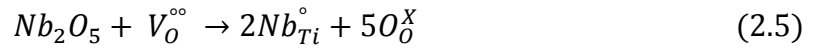
2.4.2 Substitution of site B

Concerning the substitution of site **B**, 7 transition metals were used: cobalt, chromium, iron, manganese, niobium, vanadium and tungsten. Among these elements, niobium (Nb^{5+} (64 pm)), vanadium (V^{5+} (54 pm)) and tungsten (W^{6+} (60 pm)) are donor dopants while the other four are acceptor dopants: Mn^{3+} (65 pm), Cr^{3+} (62 pm), Fe^{3+} (55 pm) et Co^{3+} (55 pm). The last has long been considered to have a valence of +2, but Wang [100] has shown that it was, in fact, the Co^{3+} ion (55 pm), which could be easily formed in an oxidizing atmosphere (in air) during sintering.

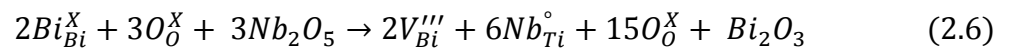
The addition of larger donor elements (Nb^{5+} to Nb^{3+} (64 to 72 pm) or W^{5+} to W^{4+} (62 to 66 pm)) than the titanium (61 pm) in the structure results in the distortion of the matrix and the expansion of the volume of the matrix as well as changes in the crystal structure, which results in increased Curie temperature (when low doping), piezoelectric coefficient and dielectric permittivity [101]. The addition of Nb^{5+} (64 pm) [92] results in a local disorder in TiO_6 octahedra due to ion mass, charge, internal stress, and distortion caused by substitution. This engenders an increase in grain size as well as an improvement in ferroelectric properties. This is also due to the elimination of the generation of oxygen vacancies, which makes it possible to reduce the concentration of mobile charges. Identical as for the substitution of site **A**, during the sintering process, there are vacancies of Bi and O due to the loss of mass in Bi_2O_3 . According to the Kröger-Vink equation:



Ion donor doping such as Nb^{5+} (64 pm) at the site can fill the oxygen vacancies in the NBT according to the equation:



The overall balanced reaction in mass and charge is:



Where Bi_{Bi}^X , O_O^X , Nb_{Ti}° , $V_O^{\circ\circ}$ and V_{Bi}''' denote, respectively, a zero charge on bismuth, a zero charge on oxygen, an Nb ion with a positive charge at the Ti site, an oxygen vacancy with two positive charges and a bismuth gap with three negative charges. From the above equations, the trivalent negative electric centers generated by the bismuth vacancies are neutralized by the Nb_{Ti}° and the generation of oxygen vacancies is suppressed by doping with ions of higher valence Nb^{5+} in Ti sites of NBT [92].

Substitution of the **B** site by the donor ion V^{5+} (54 pm) allows the improvement of the ferroelectric properties [102], [103], this is explained by the decrease of the chemical defects such as the oxygen and bismuth vacancies [103], [104]. It should be noted that oxygen vacancies are

considered in ferroelectric materials as a mobile charge that causes domain pinning and therefore prevents a change in polarization. These defects can be eliminated by substitution on site **A** with lanthanide or substitution with donor ions for **B** sites [32], – [34].

Regarding the substitution with acceptor ions, the addition of iron or chromium improving ferroelectric and dielectric properties with a greater polarization and a low leakage current density. It results in the microstructural changes that are consequences of the disorders in the TiO_6 octahedra due to the internal tensions, as well as to the formation of the defect complexes which minimizes the intercalations between the chemical defects and the walls of the matrix [106].

The Mn^{3+} ion (65 pm), behaves as an acceptor creating oxygen vacancies in the matrix. The grain size increases and the ceramic thus becomes harder resulting in the enhancement of the piezoelectric coefficient d_{33} , which can be attributed to the improvement of the densification of the ceramics. On the other hand, this causes a decrease in Curie temperature [107].

Moreover, the origin of ferroelectricity in the bismuth phases is related to the inclination of the TiO_6 octahedron on the c -axis and the rotation in the a - b plane. When the ionic radius of the dopant is greater than that of the substituted ion, this leads to the distortion of the TiO_6 octahedra, whereas when the ionic radiuses are similar, this results in a strong inclination and rotation of the TiO_6 , which results in significant improvement of piezoelectric properties of NBT ceramics.

Similarly, when the radius is smaller than that of the Ti^{4+} matrix, the piezoelectricity is increased. Thus, in the case of cobalt, the radius of Co^{3+} (55 pm) being lower than that of Ti^{4+} (61 pm), the enhancement of piezoelectric properties is partly due to a greater densification of ceramics (CoO oxide presented in the solution behaves like a fondant) and the increase of the residual polarization [100].

2.4.3 Conclusions

Since cations at **B** sites are similar in size and do not play a major structural role in the polarization process of bismuth phases, several authors [99], [104], [105] believed that site **A** substitution had more impact than the substitution of site **B** for the improvement of ferroelectric and piezoelectric properties. However, as we have just shown, the substitution of sites **A** and **B** is

possible in order to improve these properties. A schematic of these substitutions is shown in Figure 2.6.

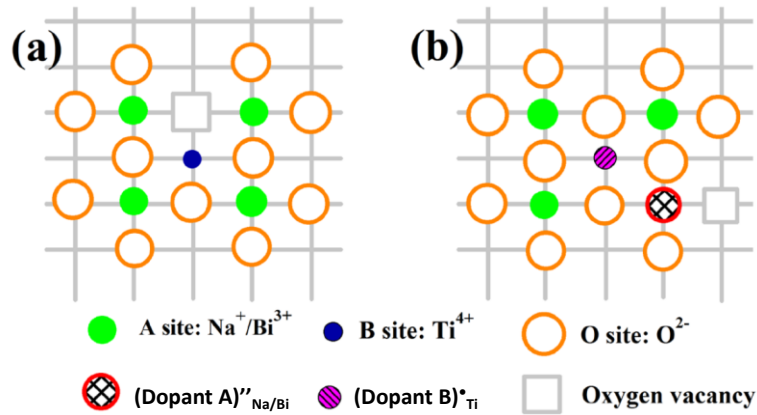


Figure 2.6 – Schematic representation of the local perovskite structure for NBT doped ceramics on sites A and B.

(a) production of oxygen vacancies, (b) substitution on sites A and B

Some of the dopant materials have a stronger effect on sodium bismuth titanate properties enhancement. In Table 2.2, the summary of the state of the art of NBT, $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$, ceramic substitution is presented.

Table 2.2 – Doping of $\text{Na}_{0,5}\text{Bi}_{4,5}\text{Ti}_4\text{O}_{15}$ ceramic and results obtained in terms of piezoelectric response and Curie temperature.

Doping element	Starting product	Fabrication technique	Substituted site	Material formula obtained	d_{33}	T_C	Applications	Ref
-	-	Solid-state	-	$\text{Na}_{0,5}\text{Bi}_{4,5}\text{Ti}_4\text{O}_{15}$	16	638-668		[93]
Ba^{2+} (135pm)	BaCO_3	Solid-state	A	$\text{Ba}_x(\text{Na}_{0,5}\text{Bi}_{0,5})_{1-x}\text{Bi}_4\text{Ti}_4\text{O}_{15}$			-	[94]
				0,03	8	648		
				0,06	11	645,9		
				0,09	16	641,2		
				0,12	21	635,6		
Nd^{3+} (98pm) $\text{Ce}^{3+}/\text{Ce}^{4+}$ (101/87pm)	Nd_2O_3 CeO_2	Solid-state	A	$\text{Na}_{0,5}\text{Bi}_{4,5-x}(\text{Nd}_{0,5}\text{Ce}_{0,5})_x\text{Ti}_4\text{O}_{15}$			High temperature	[93]
				0,1	20	636		
				0,2	28	630		
				0,3	19	621		
				0,4	17	618		
$\text{Ce}^{3+}/\text{Ce}^{4+}$ (101/87pm)	CeO_2	Solid-state	A	$\text{Na}_{0,5}\text{Bi}_{4,5-x}\text{RE}_{0,5}\text{Ti}_4\text{O}_{15}$			High temperature	[90]
				0,25	19	658		
				0,5	28	655		
				0,75	22	654		
				1	21	653		
$\text{Ce}^{3+}/\text{Ce}^{4+}$ (101/87pm)	CeO_2	Solid-state	A	$\text{Na}_{0,5}\text{Bi}_{4,5-x}\text{Ce}_x\text{Ti}_4\text{O}_{15}$	16	640	High temperature	[89]
				0,02	23	630		
				0,03	26	628		
				0,04	18	615		
$\text{Ce}^{3+}/\text{Ce}^{4+}$ (101/87pm)	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	Chemical solution deposition	A	$\text{Na}_{0,5}\text{Bi}_4\text{RE}_{0,5}\text{Ti}_4\text{O}_{15}$	Improvement of electrical and ferroelectric properties		-	[92]
Pr^{3+} (99pm)	$\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$							
Tb^{3+} (92pm)	$\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$							
Er^{3+} (89pm)	Er_2O_3	Solid-state	A	$\text{Na}_{0,5}\text{Bi}_{4,5-x}\text{Er}_x\text{Ti}_4\text{O}_{15}$	14	636	Multifunctional optoelectronic sensor High temperature	[97]
				0,05	15	652		
				0,1	15	659		
				0,2	17	676		
				0,3	13	669		
				0,4	12	666		
Eu^{3+} (95pm)	Eu_2O_3	Solid-state	A	$\text{Na}_{0,5}\text{Bi}_{4,5-x}\text{Eu}_x\text{Ti}_4\text{O}_{15}$	-	640 to 711	High temperature piezoelectric sensor and electro-optical integration	[96]
				0 to 0,4				

Li ⁺ (76pm) Ce ³⁺ /Ce ⁴⁺ (101/87pm)	Li ₂ CO ₃ CeO ₂	Solid-state	A	(NaBi) _{0,5-x} (LiCe) _{x/2} [] _{x/2} Bi ₄ Ti ₄ O ₁₅	13	640	High temperature	[82]
				0,06	17	641		
				0,1	28	641		
				0,15	20	643		
Li ⁺ (76pm) Ce ³⁺ /Ce ⁴⁺ (101/87pm)	Li ₂ CO ₃ CeO ₂	Solid-state	A	(NaBi) _{0,46} (LiCe) _{0,04} Bi ₄ Ti ₄ O ₁₅	30	640	High temperature	[91]
Tm ³⁺ (88pm)	Tm(NO ₃) _{3,5} H ₂ O	Chemical solution deposition	A	Na _{0,5} Bi ₄ Tm _{0,5} Ti ₄ O ₁₅	Improvement of ferroelectric properties		-	[95]
Yb ³⁺ (87pm)	Yb(NO ₃) _{3,5} H ₂ O			Na _{0,5} Bi ₄ Yb _{0,5} Ti ₄ O ₁₅				
Lu ³⁺ (86pm)	Lu(NO ₃) _{3,x} H ₂ O			Na _{0,5} Bi ₄ Lu _{0,5} Ti ₄ O ₁₅				
La ³⁺ (103pm)	La(NO ₃) _{3,6} H ₂ O	Chemical solution deposition	A	Na _{0,5} La _{0,5} Bi ₄ Ti _{3,97} V _{0,03} O _{15-δ}	Improvement of ferroelectric properties		-	[104]
V ⁵⁺ (54pm)	VO(OC ₃ H ₇) ₃		B					
Nd ³⁺ (98pm)	La(NO ₃) _{3,6} H ₂ O	Chemical solution deposition	A	Na _{0,5} Bi ₄ Nd _{0,5} Ti _{3,97} V _{0,03} O ₁₅	Improvement of ferroelectric properties		-	[103]
V ⁵⁺ (54pm)	VO(OC ₃ H ₇) ₃		B					
V ⁵⁺ (54pm)	VO(OC ₃ H ₇) ₃	Chemical solution deposition	B	Na _{0,5} Bi _{4,5-x/3} Ti _{4-x} V _x O ₁₅	Improvement of ferroelectric properties		-	[102]
Mn ³⁺ (65pm)	MnCO ₃	Solid-state	B	NBT-Mn _x	Possible application up to 500		High temperature	[107]
				0,125				
				0,25				
				0,375				
				0,5				
				0,75				
Cr ³⁺ /Cr ⁴⁺ (62/55pm)	Cr(NO ₃) _{3,9} H ₂ O	Chemical solution deposition	B	Na _{0,5} Bi _{4,5} Ti _{3,97} Mn _{0,03} O ₁₅	Improvement of electrical and ferroelectric properties		-	[106]
Fe ³⁺ (55pm)	Fe(NO ₃) _{3,9} H ₂ O		B					
Co ²⁺ /Co ³⁺ (65/55pm)	CoO	Solid-state	B	Na _{0,5} Bi _{4,5} Ti _{4-x} Co _x O ₁₅	High temperature up to 500 ° C		[108]	
				0,2				
				0,3				
				0,4				
				0,5	27	668		
Co ²⁺ /Co ³⁺ (65/55pm)	CoO	Solid-state	B	Na _{0,5} Bi _{4,5} Ti _{3,7} Co _{0,3} O ₁₅	33	663	High temperature	[100]
W ⁶⁺ (60pm) Nb ⁵⁺ (64pm)	WO ₃ Nb ₂ O ₅	Solid-state	B	Na _{0,5} Bi _{4,5} Ti _{4-x} (WNb) _{x/2} O ₁₅	11		High temperature	[101]
				0,015	26	645		
				0,02	28	645		
				0,025	24	645		
				0,04	22	645		
Nb ⁵⁺ (64pm)	Nb(OCH ₂ CH ₃) ₅	Chemical solution deposition	B	Na _{0,5} Bi _{4,5} Ti _{3,94} Nb _{0,06} O ₁₅	-	-	High density data storage devices	[105]

2.5 Conclusions and the choice of the dopants for the NBT ceramic

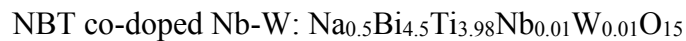
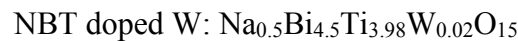
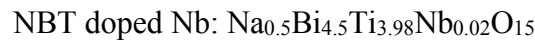
In order to improve the piezoelectric properties of NBT, it is possible to substitute site **A** and (or) site **B** of the perovskite mesh. The intercalation of the $(\text{Bi}_2\text{O}_2)^{2+}$ sheets with the three perovskite blocks $(\text{A}_{m-1}\text{Ti}_m\text{O}_{3m+1})^2$ was not established, thus it is not presented.

The nature of the substituent element by its size, its charge and the substitution rate influence the piezoelectric properties (d_{33} , $\tan(\delta)$, T_c) of the final chemical compound and its conductivity.

Overall, the more distortion or modification of the structure, (ex. an inclination of the octahedron), the higher the piezoelectric properties.

Regarding the Curie Temperature, T_c , which we seek to increase, the effect of substitution is less obvious. The data collected show that the distortion of the matrix (with the decrease of electronegativity) causes a decrease in the Curie temperature, T_c , and induces the increase of piezoelectric properties. Many studies show that with regard to the substitution of the **A** site with a small element such as lanthanides, the Curie temperature, T_c , can be increased by europium doping and the elements from the same group: Gd, Tb, Dy, Er, Tm, Yb, Lu [92], [95], [96].

Taking into account the data summarized in Table 2.2 and state of the art presented in subsection 2.4, the NBT raw powder that will be used in material/transducer fabrication by screen-printing method was decided to be doped by niobium Nb^{5+} (64 pm), tungsten W^{6+} (60 pm) and co-doped by Nb^{5+} (64 pm) & W^{6+} (60 pm) with the ratio of NBT-x (0.02), which was found to be an optimal in the literature [101]. The obtained chemical formulas are as follows:



For sensor fabrication, the pure and doped NBT materials will be used. Their properties will be compared to the state of the art (chapter 3).

Chapter 3. Fabrication and characterization of piezoelectric materials

In the previous chapter, we explained the choice of piezoelectric materials. However, the development of sensors requires a certain number of in-depth studies on the technique itself. The screen-printing method is a technological opportunity which is used in electronics to produce hybrid circuits, multilayer systems, and thick layers of dielectrics and conductors, which complements the need of the medium-scale deposition technique between thin layers ($<5\text{ }\mu\text{m}$) and bulk element ($>500\text{ }\mu\text{m}$).

In addition to the intrinsic parameters, related to the chemical composition (chapter 2), the condition of fabrication influences the final properties of the material. The purpose of the studies, described in this chapter, is to define the fabrication conditions of NBT material by the screen-printing method and suggest the material that will be used in the fabrication of a prototyped device.

To eliminate the influence of substrate during the characterization of material properties, NBT ceramics were produced in the form of detached disks with the electrodes deposited by a physical vapor deposition method. Overall, 5 versions of pure and 3 versions of doped NBT material were fabricated and characterized on their morphological, electric, dielectric and piezoelectric properties. Each version of the NBT material was produced progressively during the research period of this dissertation, with the purpose of material-fabrication conditions optimization. The summary of the results, for each NBT material, shows the optimum conditions for NBT ceramic elaboration by the screen-printing method and is the first step in the development of ultrasonic sensors.

In this chapter, the data of fabrication and characterization are represented as follows.

- First, the description of the fabrication process and preliminary characterization of raw materials, and samples dimensions are presented (section 3.1.)

- After the description of the fabrication protocol for NBT versions, characterization tools and measurements performed are summarized (section 3.2).
- By comparison of the fabrication parameters and measurement results, the optimal candidate among NBT materials, produced by the screen-printing method, will be determined (section 3.3).

3.1 Fabrication protocol and method

Disregarding the nature of the materials deposited with the screen-printing method (a piezoelectric element, an electrical conductor, a dielectric, or materials for more conventional applications) the manufacturing process is performed as follows:

1. ink development
2. material deposition
3. sintering process
4. polarization (in the case of a piezoelectric element; electrodes deposition is required)

In the previous dissertations of Dr. Very, the development of lead zirconate titanate (PZT) piezoelectric sensors was described [109]. It was shown that the properties of piezoelectric materials, fabricated by the screen-printing method, can be determined through the fabrication of detached piezoelectric elements. Hence, in this work, the fabrication of detached NBT elements follows the same protocol detailed in [109] and is based on the technique proposed for suspended element fabrication by H. Debeda et al. (international patent number WO2007/077397) [110]. The principle of detached element fabrication follows three fundamental steps (Figure 3.1):

- the deposition and consolidation of the "sacrificial thick layer"
- the deposition and sintering of the structural layers (e.g. NBT)
- the elimination of the "sacrificial layer" by dissolution, heat treatment, ultrasound, etc. or a combination of these methods.

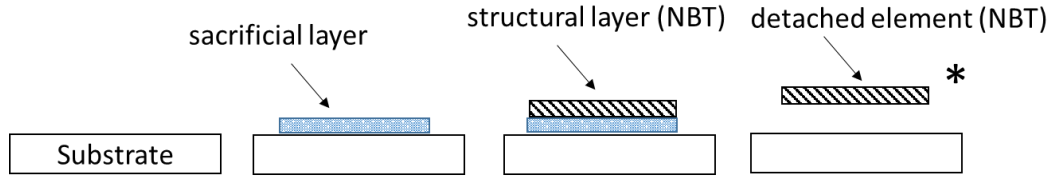


Figure 3.1 – Schematic diagram of the fabrication procedure of detached elements.

** For NBT material fabrication, the sacrificial layer is dissolved during a sintering process*

3.1.1 Raw material production

In the course of this work, 5 pure and 3 doped NBT powders were produced by the hydrothermal method. The starting materials: Bi_2O_3 (99,8% purity), TiO_2 (99,5%) and Na_2CO_3 (99,49%) were mixed in a specific proportion. Then, the chemical element mixture was calcined in a Carbolite RWF1100 furnace. The initial powder grain size was different for each of the produced powders (Table 3.1). These values were compared with the properties of fabricated NBT materials (refer to the discussions in section 3.3).

The analysis with X-ray diffractometer reveals the crystal structure of samples [111]. The general principle of this method is to use the interaction of the X-ray and matter, measuring the intensity of X-rays that are scattered according to orientation in space. The scattered rays interfere with each other; the intensity, therefore, has maxima in certain directions; this phenomenon is called diffraction. The detected intensity is recorded as a function of the deflection angle 2θ of the beam, the curve obtained is called the diffractogram. The angle reveals the atomic structure according to the Bragg law:

$$2d\sin(\theta) = k\lambda \quad (3.1)$$

where d is an interplanar distance between aligned lattice points (in Å), θ is an angle of the strongest constructive interference (in rad), λ is an incident wavelength from RX source (in nm) and k is a positive integer number.

For NBT powders, the analysis was made with a Malvern Panalytical X-Pert PRO diffractometer [112]. The data were compared with the sodium bismuth titanate pattern from the

International Center for Diffraction Data (ICCD) [113]. In Figure 3.2, an example of X-ray diffractogram (XRD) of fabricated NBTv1 powder is shown. According to the pattern from ICCD, peaks of the BLSF phase are presented, with the peak of maximum intensity in (119) plane.

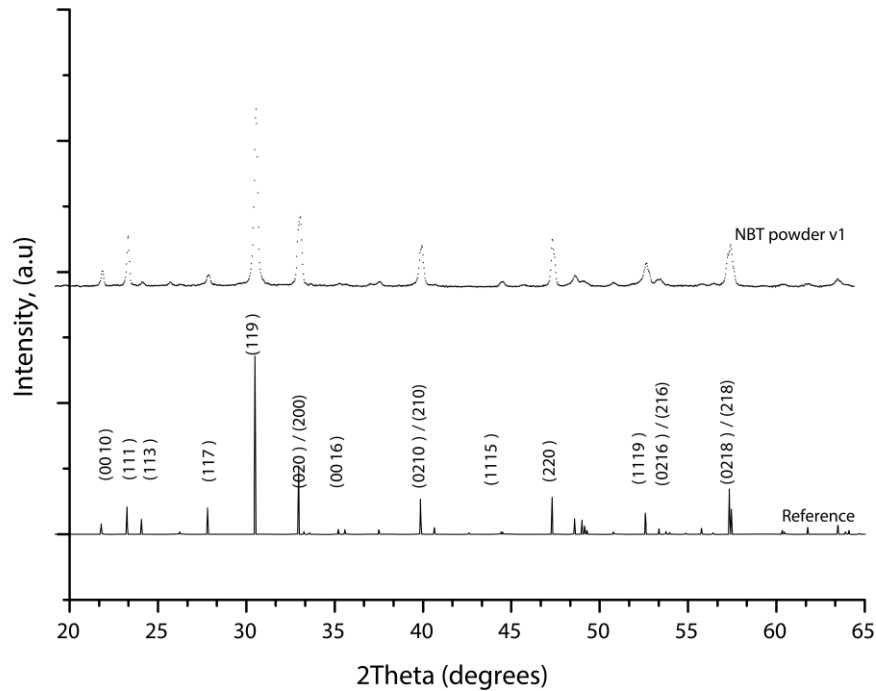


Figure 3.2 – An example of X-ray diffraction patterns of NBT powder produced and reference data.
The measured diffractogram of NBT powder produced corresponds to the available materials' diffractograms from the International Center for Diffraction Data (ICCD).

The standard examination by XRD includes the determination of interplanar distance (the perpendicular distance between two successive planes in a particular direction) and average crystallite size [114]. The first parameter is determined with the Bragg law (equation 3.1) and depends on the angle θ of interference peak observed.

The average crystallite size can be determined through analysis of an XRD pattern. If grain does not contain sub-grains and (or) defects the crystallite size will match the grain size. However, in the case of anisotropic grain structure (i.e. BLSF structure) inside a crystalline material, the crystallite dimension depends on the material microstructure, which includes grains, sub-grains, and defects [115]. Indeed, in this case, the crystallite size can be approximated through sub-grain

representation. The first approximation, which can estimate a microstructure of the material is generally described by Scherrer formula [116]:

$$\beta(rad) = \frac{\lambda}{L_d \cos(\theta)} \quad (3.2)$$

where β is a broadness of the ray from the diffraction pattern in rad, L_d is a lattice parameter which corresponds to the crystallite size (in Å), θ is an angle of the strongest constructive interference of the same ray (in rad) and λ is the wavelength of the incident wave from X-ray source (in nm).

To be noted that the Scherrer's equation is the particular case of the Williamson-Hall method. It assumes that all the particles have the same shape and size which does not correspond to the real conditions. Furthermore, this approximation does not consider the instrumentation broadening error, which leads to the error in the determination of the crystallite size [115].

The limitations of Scherrer's equation make this method inappropriate for material characterization. However, in this work, the equation 3.2 was used for rough estimation. The dependence between three parameters:

- grain size (measured with SEM),
- interplanar distance, d , in the particular plane (119) corresponded to the peak of maximum diffraction,
- crystallite size, L_d , can be correlated.

3.1.2 Ink fabrication and characterization

In screen-printing, ink viscosity and composition are elements that determine material properties. Close attention should be paid to the homogeneity of its component mixture and the reproducibility. In case of sodium bismuth titanate ink development, three components (raw NBT powder produced in laboratory conditions, sealing glass CF7575 [117] and organic vehicle ESL400 [118]) were mixed in a specific proportion. The ink was homogenized with three roll milling machine, Exakt80E [119], until the desired viscosity (in our case, this value is in the range of 10-100 Pa*s depending on the applied shear rate) was obtained.

Rheological properties of fabricated inks were measured with a rheometer RheolabQC of Anton Paar [120]. The ink was introduced into a plane-plane geometry of rheometer. The deformation was applied to the ink by rotation and the shear stress was determined by the measured torque force after the imposed deformation. Indeed, the viscosity was plotted as a function of shear rate.

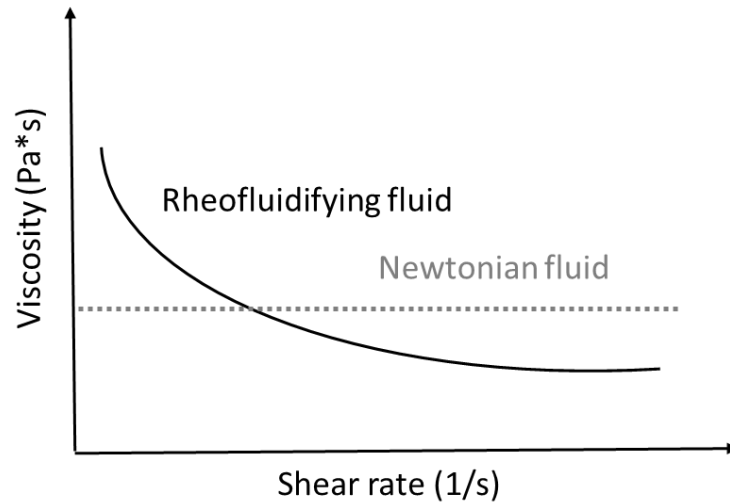


Figure 3.3 – Viscosity measurement. Newtonian and the rheofluidifying fluid’s behaviors.

Fluids react in different ways depending on mechanical stress. The rheological behavior of the fluid establishes this reaction and shows the relationship between deformation and applied constraints. In Figure 3.3, the behaviors of two fluid types, so-called Newtonian and Rheofluidifying, are presented. Rheofluidifying or pseudoplastic fluids, such as screen-printing inks, possess a very high viscosity at low shear rates, which decreases non-linearly as a function of the stress. In our case, the proportion of organic vehicle is the main factor influencing the rheology of the ink. Therefore, it is important to adjust its amount during ink production.

3.1.3 Screen-printing

Screen-printing is a fabrication method by which ink is deposited onto a substrate by moving a squeegee on top of a screen with a certain mesh (Figure 3.4 (a)). In this work, the screen-printing machine DEK248 was used for NBT materials fabrication (Figure 3.4 (b)). During the process, each deposited layer was followed by leveling and drying process of 15 and 10 minutes respectively.

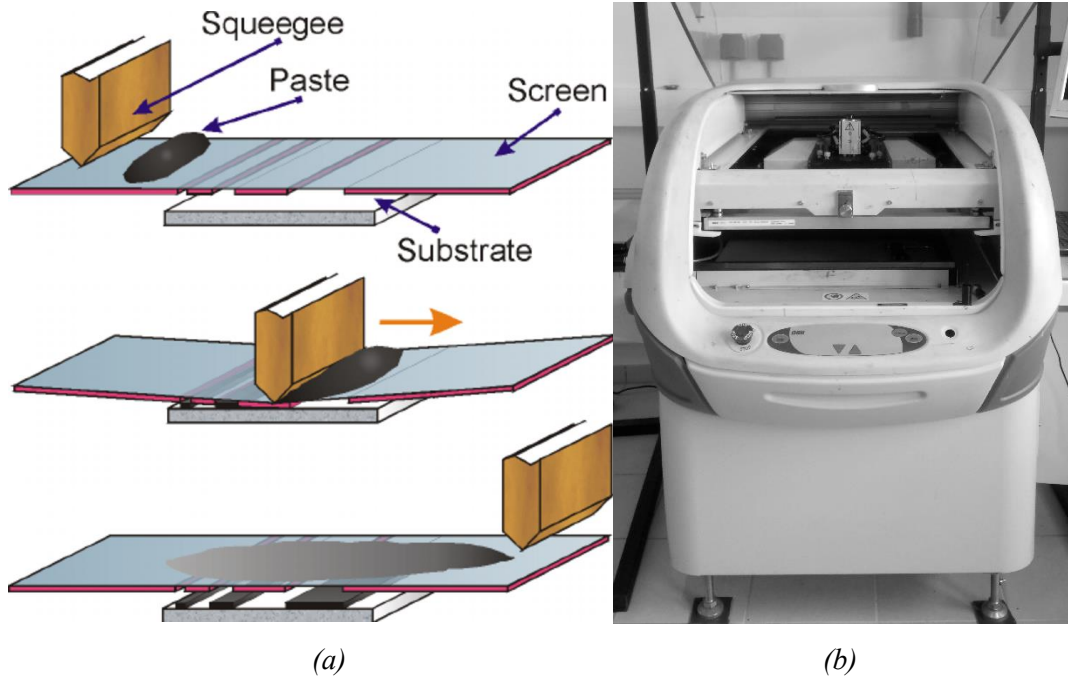


Figure 3.4 – Screen-printing method (a) used for the fabrication of NBT material with screen-printing machine DEK248 (b).

Based on the previous studies with PZT material [109], it was shown, that the desired thickness for characterization of detached elements is in the range of 100 μm . Hence, for our samples, subsequently, after the deposition of the sacrificial layer (ink based on the SrCO_3 – epoxy mixture in proportion 55% to 45%), the layers of piezoelectric ink were deposited to form the layer of 100 – 120 μm in thickness (before sintering).

For the characterization of primary materials, in the form of detached elements, the screen pattern was designed, in Layout Editor software [121], forming the disk patterns of 5 and 10 mm in diameter (Figure 3.5 (a)). The screens specifically manufactured by DB Product [122] was designed for the deposition of 30 μm per layer (Figure 3.5 (b)); thus, 3-4 layers were needed for deposition of 100 μm .

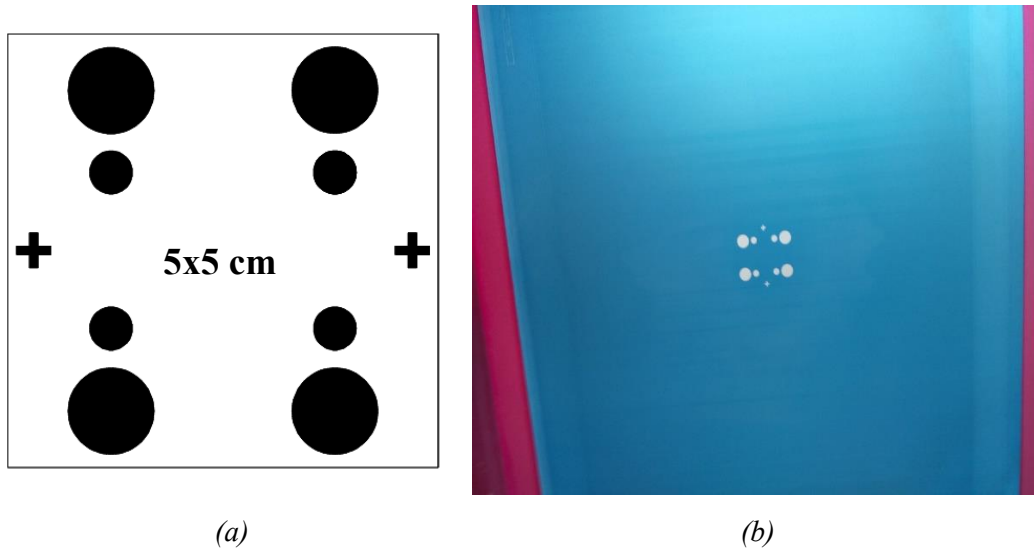


Figure 3.5– Screen-printing screens definition.

(a) The pattern used for the detached element fabrication designed in LayoutEditor software; (b) Manufactured screen by DB Product from the given pattern (allows deposition of $30\ \mu\text{m}$ per one movement of squeegee).

3.1.4 Sintering

Once the material has been formed by the screen-printing method, the sintering is required. Sintering anticipates in the formation of material properties and is a mandatory process in ceramic elaboration (Figure 3.6).

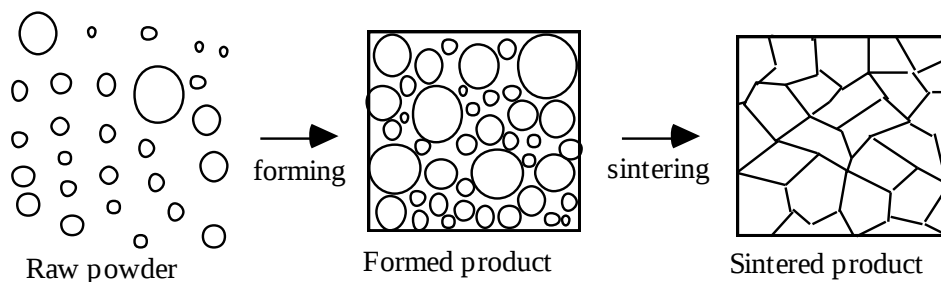


Figure 3.6 – Schematic representation of the sintering process [123].

The sintering of crystalline material can be done by several methods (i.e. atomic transport paths and their associated sources and sinks): vapor transport, surface diffusion, lattice (volume diffusion, grain boundary diffusion, and dislocation motion). The particles interaction during

sintering process is commonly made between densifying (grain boundary diffusion, lattice diffusion from the grain boundary and dislocation motion) and non-densifying mechanisms (surface diffusion, lattice diffusion from the surface, vapor transport). NBT ceramics have an anisotropic grain structure. For this structure-type, the densifying mechanism dominates [124].

The sealing glass, CF7575, added into piezoelectric ink, plays an important role in the sintering phase of sample fabrication. At the temperatures of 500 – 550 °C the grains of CF7575 start melting and, thus, improving the kinetics of NBT grains. Hence, the NBT material, fabricated from piezoelectric ink, containing CF7575 (a binder), can be sintered at lower temperatures. (In the state-of-the-art technologies, the sintering temperature for NBT bulk material exceeds 1000 °C [77], [89], [91], [125]).

In this work, for NBT ceramics formation, the conventional sintering method was used. During this step, an NBT material, in the form of a detached disk, was placed inside a Carbolite RWF1100 furnace and sintered under a bismuth-saturated atmosphere.

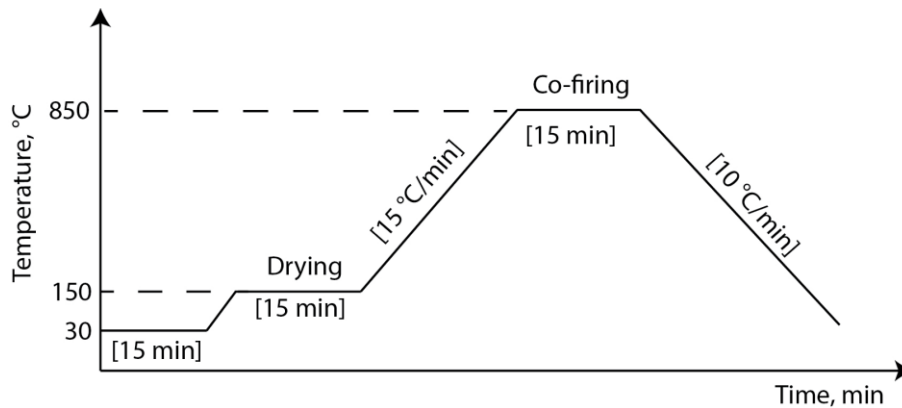


Figure 3.7 – Standard sintering protocol used for fabrication of NBT detached elements.

The sintering protocol used for ceramic fabrication is shown in Figure 3.7 with the dwell period at 850 °C of 15 minutes. The time and temperature of sintering was adapted according to the protocol of Ag/Pd 9693-G [126] conductive ink and was successfully used for PZT components in previous studies [109]. During sintering, the volatilization of organic vehicle implies the reduction of the post-fabrication thickness. Therefore, the thicknesses of screen-printed detached

films after sintering were about 80 μm for most of the fabricated samples. Nevertheless, the value of 80 μm is in the range of 100 μm and is favorable for NBT samples characterization.

3.1.5 Polarization

Polycrystalline ceramics can be represented as the complex of grains with the randomly oriented dipoles. By the application of the high electrical field, all dipole moments may be oriented in the same direction. It is, so-called spontaneous polarization P_s (C/m), expressed in a capability of electrical charge generation per unit area. A ferroelectric material is a specific case of polycrystalline ceramics where spontaneous polarization has two equilibrium states and can be reversed by application of an external electric field. Therefore, the polarization of material depends not only on the electric field applied but also on its direction, yielding a hysteresis loop (Figure 3.8) [127].

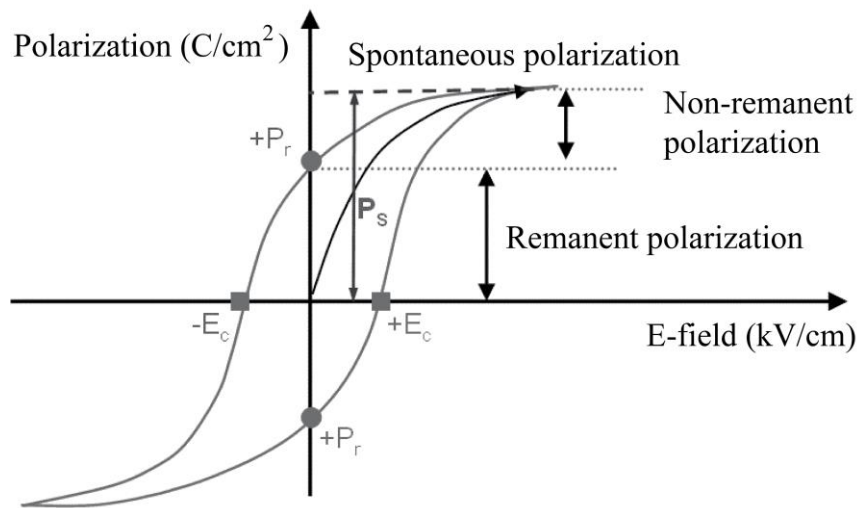


Figure 3.8 – A typical hysteresis loop of ferroelectric ceramic.

By measurement of the ferroelectric ceramics' hysteresis loop, the properties of the material and the polling process can be studied. Spontaneous polarization P_s is a value, obtained under application of a high electric field. When the electric field is removed, the dipole moments will persist and keep their orientation. The value of the polarization will be reduced to the state called remanent (residual) polarization P_r . In this state, no electric field is required to support its value and the material may be used as piezoelectric.

The value of the electric field required for the ceramic polarization may be determined from the hysteresis loop, whereby electrical coercive field E_c (V/m) indicates the energy needed for domain orientation switching. The optimal electric field for ferroelectric material polarization must exceed the electric coercive field by the factor of 2. However, this value may be reduced by the increase of the temperature, in this case, the dipole switching occurs under a lower electric field and grains are more easily oriented.

In previous studies, with screen-printing PZT material, the evolution of the piezoelectric charge coefficient, d_{33} , was studied as a function of applied electric field and poling temperature at 100 °C, 150 °C and 200 °C. It was found that an optimal temperature for PZT ceramic polarization is approximately 150 °C. The electric field required for optimal polarization of PZT elements was found to be in the range of 30 kV/cm [109].

Shujun Zhang and Thomas R Shrout in their studies of the single perovskite crystals [128] reported that the value of the coercive field for domain orientation switching is linearly proportional to the Curie temperature (T_c).

Indeed, the NBT material ($T_c \sim 650$ °C) requires a higher electric field in comparison with PZT ceramic. E.g., Wand et al. reported the value of 130 kV/cm for 200 °C. In this work, the screen-printed detached NBT elements piezoelectric coefficient, d_{33} , dependence from the E-field was found to be in the same range (refer subsection 3.2.4 for details). Hence, the configuration for NBT samples polarization is described as follows:

To make electrical contact, the deposition of electrodes (200 nm) was carried out by a physical vapor deposition method (PVD) on both sides of the detached disk. The poling cycle takes around 25 min. After stabilization of temperature at 150 °C an electric field, in the range from 120 kV/cm to 150 kV/cm (depending on the NBT version thickness), from Keithley 2657a Source Meter [129] was applied. For safety reasons, the samples were polarized inside Signatone Power Pack [130]. To prevent the breakdown in the air, each version of NBT ceramic was polarized in silicon oil. After the electrical field was removed, the material became functional. The polarization test bench is presented in Figure 3.9.

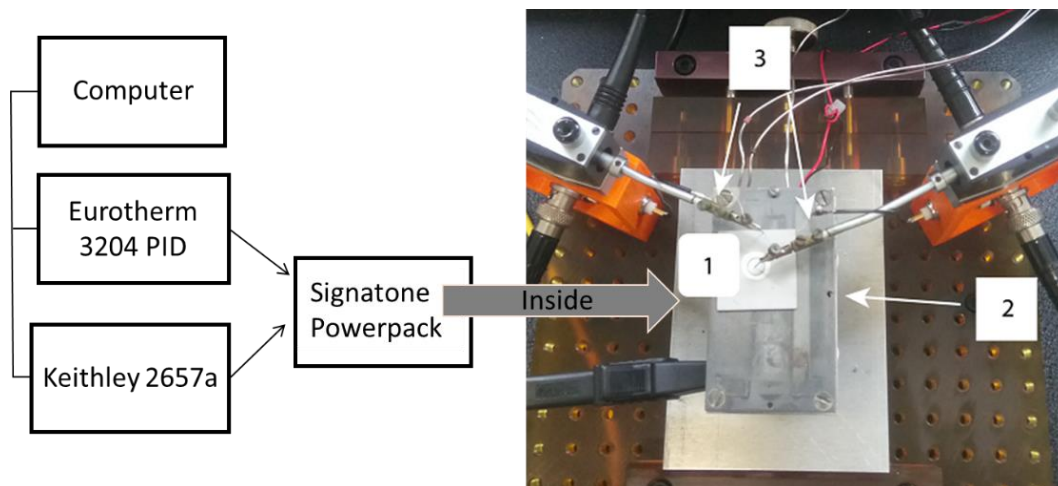


Figure 3.9 – Experimental test bench setup for polarization and resistivity measurement of piezoelectric elements.

Eurotherm 3204 PID is a temperature controller. (1) is the detached piezoelectric element placed onto the hot plate (2). The electric contact from both sides is taken with gold contact points (3).

3.1.5 Fabrication parameters of sodium bismuth titanate materials.

Summary and conclusions.

This synthesis of fabrication properties shall be seen via the view of in long-term development through the process cycle described as fabrication -> characterization -> modification of fabrication parameters -> new characterization -> comparison and conclusions.

The attempt to produce the material with superior properties in comparison to the previous version attributed in development of 5 pure and 3 doped NBT materials. The overview of fabrication parameters is presented in Table 3.1. It has to be noticed, that XRD analysis of NBT powders, introduced in this section, is a step in the characterization of material properties. However, to clarify the document, these data are discussed in this subsection, and later will be analyzed again in conclusions to the chapter (section 3.3).

The overview of fabricated NBT elements is shown in Annex A. Some notes, in their production, for particular versions are summarized here as follows:

The NBTv1 was the first attempt in the production of the material. The purpose of its development was to demonstrate the possibility of NBT ceramic fabrication capable to withstand

high-temperature conditions. By taking into the consideration the effect, that the sintering of dense bulk NBT ceramic is exceeding 1000°C for several hours [77], [89], [91], [125], the samples of NBTv1 were sintered under 850 °C for 10 hours. After successful tests with the NBTv1 material, it became clear, that NBT piezoelectric element can be fabricated through a realization of piezoelectric ink by screen-printing technique.

However, as was mentioned in Subsection 3.1.4, in sensor production, for the electrodes of commercial conductive ink of Ag/Pd 9693, which is desired to be used for sensor fabrication, (already proved its reliability for PZT composites) suggests the sintering time of 10-15 minutes. Hence, after demonstration of the screen-printing method applicability for NBT detached elements fabrication, the other versions of NBT materials were sintered for 15 minutes.

Among their production, the particular note has to be given to the NBTv2, in which the powder calcination time was adjusted, for NBTv1 protocol optimization, to 5 hours at 750°C. The powder agglomerations islets of NBTv2 powder was observed by scanning electron microscope. During detached elements sintering, agglomerations led to the development of the relatively porous ceramics, in which the volume was suggested to be increased through sintering (The value of 160 µm was obtained from 100-120 micrometers of deposit material). The properties of this material version were found to be inferior in comparison to NBTv1 (refer to section 3.3 for more details), and the powder calcination protocol was changed to 5 hours at 700°C for subsequent NBT versions (from NBTv3 to NBTv8).

In the case of NBTv5 fabrication, the problems with deposition occurred. It led to the production of detached elements of 25 µm in thickness. Due to the high value of resonance frequency, it was not possible to perform the analysis from impedance data (due to the low thickness, resonance appears above the frequencies of an impedance analyzer). However, the set of other parameters were successfully measured and are compared with other versions of NBT material (section 3.3).

The grain size of NBT powders was observed with an Inspect S50 scanning electron microscope (SEM) (Table 3.1). The effect of the grain size on the electric properties of bismuth titanate from BLSF ceramics was investigated by H. Shulman in her dissertation work [38]. Indeed, for the NBT material, the grain size of powders can be correlated with material properties evolution (section 3.3).

Table 3.1 – Summary of the fabrication conditions of NBT ceramics.

NBT version	Powder calcination	Powder grain size, μm	Ink composition: NBT-CF7575-ESL400, % mass	Sintering conditions @ 850 °C	Thickness after sintering, μm
v1	3 hours at 700 °C follow by 5 hours at 750 °C	0.5 – 1.2	63-4-33	10 hours	80
v2	by 5 hours at 750 °C	0.5 – 2.2	67-4.2-28.8	15 minutes	160
v3	by 5 hours at 700 °C	0.1 – 0.5	58-3-39	15 minutes	80
v4	by 5 hours at 700 °C	0.3 – 1.5	66.3-4.4-29.2	15 minutes	80
v5	by 5 hours at 700 °C	0.1 – 0.3	60.9-3.6-35.5	15 minutes	25
v6 doped with Nb	by 5 hours at 700 °C	0.2 – 1	64-4-32	15 minutes	80
v7 doped with W	by 5 hours at 700 °C	0.3 – 1.5	63.5-3.5-33	15 minutes	80
v8 co-doped with Nb & W	by 5 hours at 700 °C	0.1 – 0.3	58.2-3.5-38.3	15 minutes	70

The analysis of X-ray diffractogram for each type of the NBT powder demonstrates the presence of a single-phase bismuth layer structure ferroelectric (BLSF) [131] with the highest intensity of diffraction peak at (119) for each type of powder (Figure 3.10). It was reported that this structure possesses high Curie temperature and materials from this family are promising candidates for high-temperature applications [77].

The average crystallite size was determined by analyzing the broadness of the ray β in (119) plane (Figure 3.11) and application of equation 3.2. The broader peaks indicate the finer domain size structures. Furthermore, the peak shift to the lower angles indicates the increase of the interplanar distance between interatomic layer structure (equation 3.1).

The comparison of the grain size, the interplanar distance between aligned lattice points d and the crystallite size L_d for each type of NBT material, can be seen in Figure 3.11 with the calculation presented in Table 3.2. It was observed that the powder grain size increment leads to the increase of crystallite size and reduction of interplanar distance. Consequently, a cell structure for finer grain NBT materials is more compacted.

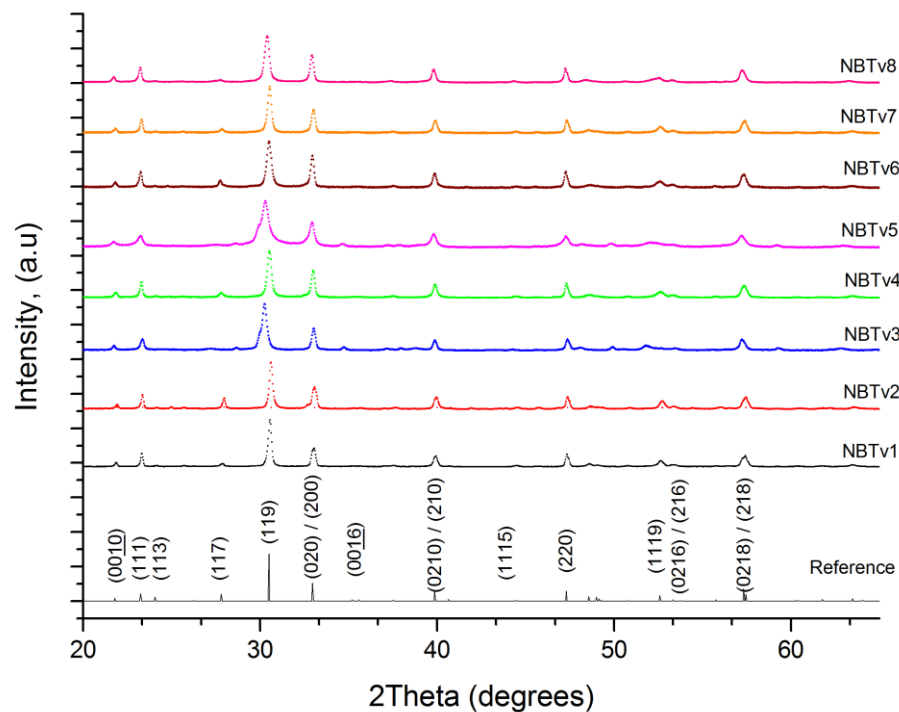


Figure 3.10 – X-ray diffraction patterns of produced NBT powders and reference data.

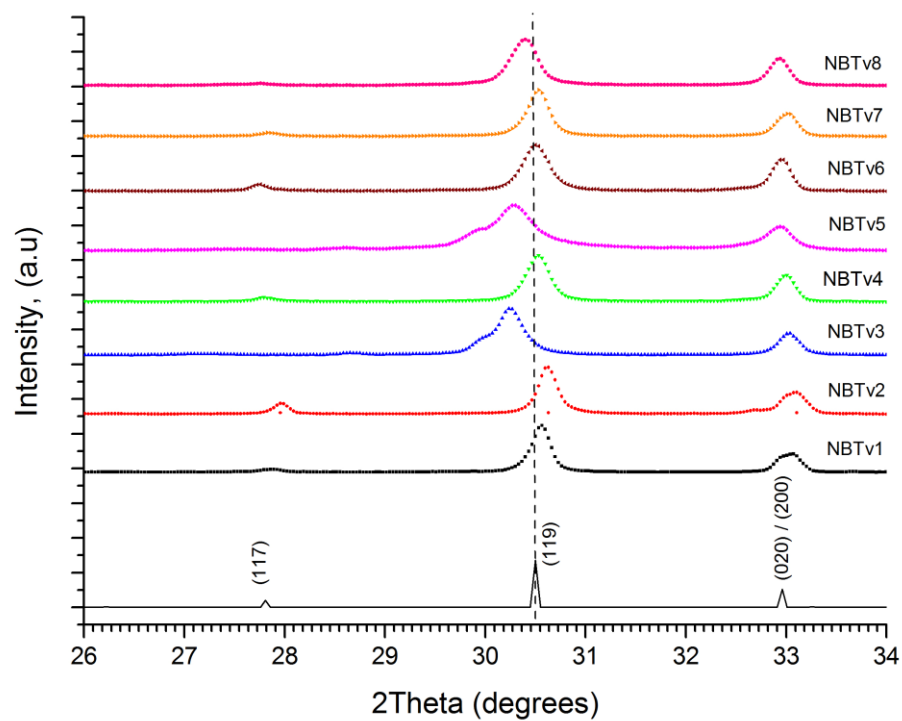
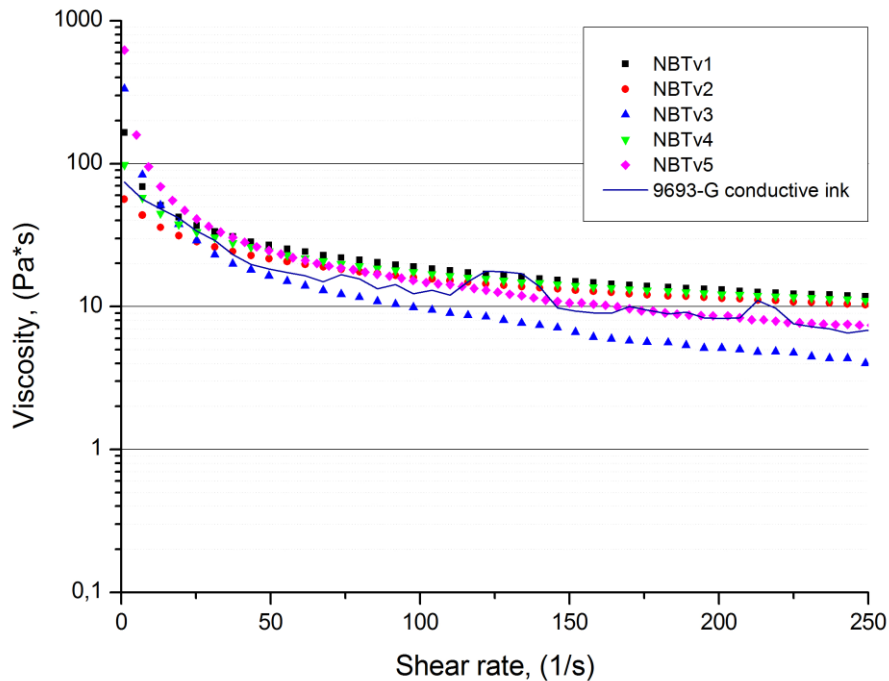


Figure 3.11 – X-ray diffraction patterns of produced NBT powders and reference data. The zoom on the peak of maximum intensity.

Table 3.2 – Microstructure of NBT ceramics

NBT version	Powder grain size, μm	Interplanar distance in 119 plane, Å	Estimated crystallite size, nm
v1	0.5 – 1.2	21,7	12,4
v2	0.5 – 2.2	21,6	13,3
v3	0.1 – 0.5	22,3	7,5
v4	0.3 – 1.5	21,8	10,8
v5	0.1 – 0.3	22,1	6,5
v6 doped with Nb	0.2 – 1	21,9	10,4
v7 doped with W	0.3 – 1.5	21,8	10,8
v8 co-doped with Nb & W	0.1 – 0.3	22	9,3

Each version of NBT ink was produced in order to obtain a solution with the rheofluidifying properties. Indeed, the produced NBT inks show the rheofluidifying behavior (Figure 3.12) with the value in the range of commercial conductive ink of Ag/Pd 9693-G [126]. The viscosities of NBT inks produced from doped powders (NBTv6, NBTv7, and NBTv8) were in the same range (for image clarity, they are not presented in the manuscript).

**Figure 3.12 – Viscosity of fabricated NBT inks.**

Based on the analysis of the fabrication properties it was shown that the raw materials, which followed the same (or similar, depending on version type) protocol in their production, have

different morphologies (grain size), slightly different crystallography (interplanar distance between lattice points and crystallite size) and the viscosities in the range of commercial conductive ink Ag/Pd 9693-G.

3.2 Experiment and methods for material characterization

The characterization process of piezoelectric material contains numerous methods, i.e: XRD, chemical analysis, morphology, electric, mechanical, dielectric, ferroelectric and piezoelectric properties. All the parameters may be measured with different approaches, depending on desired applications.

In this section, the characterizations performed with screen-printed piezoelectric materials, with examples of results are highlighted. After the introduction to the morphological analysis for NBT detached elements (subsection 3.2.1), we will present the methods adapted for resistivity (subsection 3.2.2) and dielectric properties (subsection 3.2.3) evaluation. The measurement techniques used for the evaluation of piezoelectric and electromechanical properties will be presented in subsection 3.2.4. The methodology and a few examples of materials properties determination as a function of temperature will be highlighted in subsection 3.2.5.

With an intention of properties optimization and a better understanding of fabrication parameters, the sintering studies were carried out for doped ceramics of NBTv6 (doped with Nb), NBTv7 (doped with W) and NBTv8 (co-doped with Nb-W) (subsection 3.6).

Section 3.2 describes the experiments and methods of measurements performed for characterization of NBT materials does not contain the results for the set of NBT versions. An example of measurement will be given prior to characterization parameter. The set of results will be summarized and compared in section 3.3.

3.2.1 Morphological analysis

Microstructural crystal morphology affects strongly the macroscopic electromechanical properties of polycrystalline ceramics [132]. E.g., it exists numerous types of PZT ceramics, and

the desirable properties for specific applications were obtained by alteration of chemical and morphological parameters of the material [133].

The morphological analysis of NBT material was carried out with Inspect S50 scanning electron microscope. The structure was measured in the magnification range from 2000x to 25000x which allows observing defects in the material and estimates the mean grain size. The overview of fabricated morphologies is presented in Annex B.

The NBT ceramic lattice orientation structure is represented by a grain anisotropy sheet-like texture formation (Figure 3.13), in which, four perovskites layers between two layers of bismuth oxide form an orthorhombic structure with cell c direction of 4.065 nm, 80 times bigger than in a (0.5427 nm) and b (0.5459 nm) directions (chapter 2). Swartz et al. showed that the conductivity in a -, b - axis is one order higher than in c -direction [134]. Hence, for grain-oriented ceramics, the different piezoelectric properties can be obtained through poling in a particular direction.

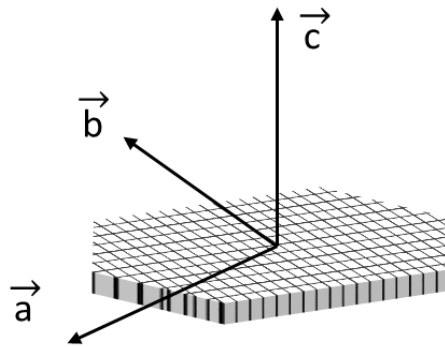


Figure 3.13 – Schematic grain representation of the NTB material after sintering.

The anisotropy in c -axis represented the formation of the bismuth oxides $(\text{Bi}_2\text{O}_2)^{-2}$ structure, hence, the grains form sheets.

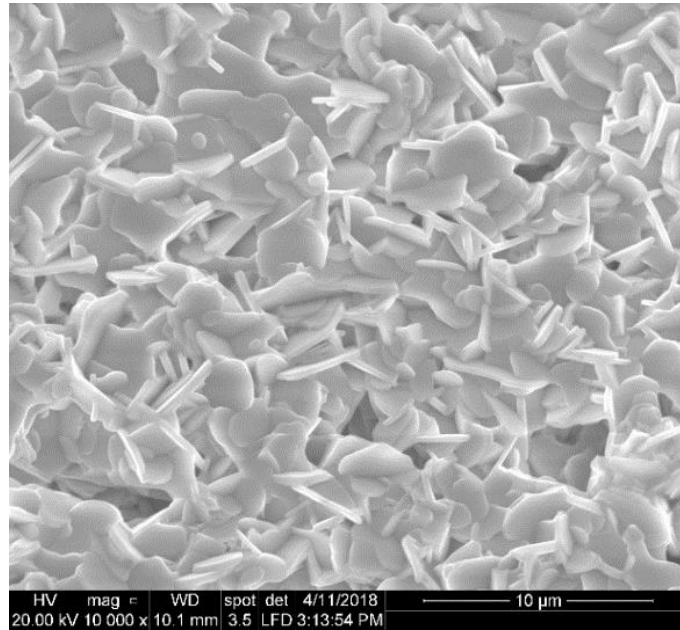


Figure 3.14 – NBT ceramics formed with screen-printing method and sintering under 850°C for 15 minutes. Image magnitude x10000.

The screen-printing NBT ceramics is characterized by the sheets-like structure grain formation.

An example of the measured morphology is presented in Figure 3.14. The micrograph shows the partially oriented sheets-like grains structure. This morphology is typical for an NBT and is similar to results obtained for bulk ceramics by other authors [89] – [91].

3.2.2 Resistivity measurement

Piezoelectric materials operating at high temperatures must generally be polarized under high electric field and temperature. Hence, for piezoelectric ceramic, high resistivity is a key parameter, which allows the application of a larger electric field while it is also required for high-temperature applications [135].

For fabricated detached disks, resistivity assessment was performed by measuring the leakage current with the Keysight 2657A source meter. The experimental set-up is presented in Figure 3.9 and is the same as for the polarization process. A sample is placed into a metallic plate. The gold points are connected to electrodes and the electric field from the source meter is applied.

The resistivity, ρ (Ohm*cm), is determined from the leakage current density by application of the local Ohm's law:

In general case:

$$\vec{J} = (\sigma + i\omega\epsilon)\vec{E} = \sigma\vec{E} - \omega\epsilon''\vec{E} + i\omega\epsilon'\vec{E} = (\sigma - \omega\epsilon'' + i\omega\epsilon')\vec{E}, \quad (3.3.1)$$

In DC mode, the equation 3.3.1 is simplified to:

$$\vec{J} = \sigma\vec{E}, \quad (\text{A/m}) \quad (3.3.2)$$

where, $\vec{J}$ is a measured leakage current expressed by the current density from electrodes area (in A/cm), $\vec{E}$ is an electrical field applied (in V/cm) and σ (S/cm) is a material conductivity inverse proportional to the resistivity ($\sigma = 1/\rho$); $i\omega\epsilon$ defines the stored charge in capacitance as a function of an angular frequency ω , ϵ is a permittivity of dielectric material (in F/m), ϵ' and ϵ'' are real and imaginary part of the permittivity.

Piezoelectric material of certain dimension will exhibit the resonance maximum according to its vibration frequency, which introduces the non-linearity to the current density distribution as a function of frequency. Its response can be modeled with the resistor-capacitor circuit as shown in Figure 3.15. The current density will depend on permittivity evolution (charging of capacitor) with frequency and expressed with the equation 3.3.1.

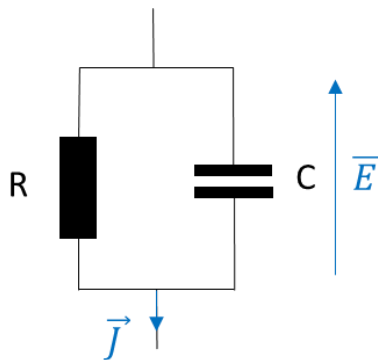


Figure 3.15 – R-C resonance circuit.

Equation 3.3.1, which presents the relation between permittivity and conductivity, is applied for measurements of AC-conductivity. In the studies with the screen-printed NBT material, the resistivity was measured in the DC-mode, hence, the simplified equation 3.3.2 is used.

The reliability of the resistivity measurement was evaluated with a repeatability test (Table 3.3). The first row is the results of 10 measurements on the same sample, where the sample was removed from the metallic plate, turned through 180 degrees and replaced. The second row is an example of measurements performed for different samples from the batch of NBTv4 ceramic. The electrode's area was calculated from the measured radius of 2.75 mm and is the same for each element. The sample thicknesses were measured by SEM, for one of the samples, and was found to be 80 μm . Hence, thicknesses for other samples were estimated to be 80 μm . The relatively high error of measurement (50%) is explained by thickness measurement incertitude for the samples set and low values of leakage current (in the order of 10 pA).

Table 3.3 – Repeatability of the resistivity measurements for the NBT detached disks fabricated by the screen-printing method.

	Mean $\pm$ standard deviation @ 30°C
10 measurements; one sample NBTv4	3E13 $\pm$ 14%
8 fabricated disks of the NBTv4 material	4.2E13 $\pm$ 50%

The set of measurements is shown in Figure 3.16, where the measurement of one sample is plotted with the standard deviation covering the row dispersion of NBTv4 samples. It worth to be noticed that the resistivity remains constant under applied E-field (up to 25 kV/cm) indicating stability of electric properties in this range.

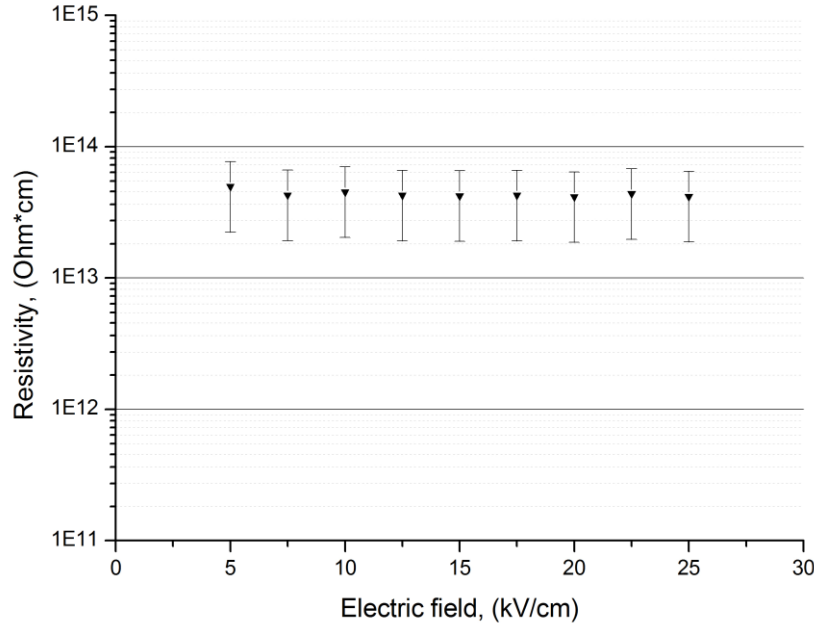


Figure 3.16 – Mean value of the resistivity, measured from the 8 samples of the NBTv4 material, as a function of applied electric field.

3.2.3 Dielectric properties

The term dielectric was first applied by Faraday to describe a charging process of a capacitor. From his description, the dielectric can be defined as an insulator or a material with high resistivity. Later, at the beginning of the 20th century, the studies of atomic and molecular structure carried out by Debye led to the determination of the dipole moment [136]. The subsequent works of Onsager [137], KS Cole & RH Cole [138], Frohlich [139], expanded the understanding of dielectric theory and dipole moment.

The classification of dielectric materials can be summarized according to the paper published in 1952 by Pr. Bouix [140]. It is based on a determination of the electronic moment $\vec{m}$ of the molecule and described by three dielectric categories:

- The substances which contain only optical polarization and external electric field produce solely the electron displacement (dielectric materials where molecules contain one type of the atom. i.e. noble gases, diamond, oxygen).

- The substances which contain optical and infrared polarization. They can contain the dipolar atomic structure, but only IR and optic polarization can occur (i.e. CO₂, benzene C₆H₆ etc.).
- The substances which contain both polarizations mentioned and polarization that occurs from dipole orientation. Characteristically for solid-state materials (i.e. ZnO, quartz, polymers etc.).

As was already mentioned previously, NBT material is a member of the class of BLSF ceramics. It belongs to the “third” dielectric category capable of dipole polarization and possesses a high permittivity.

The crystalline structure of ferroelectric material has a crystallographic polar axis in which occurs the reversible spontaneous polarization P_s . Each ferroelectric material characterized by one or multiple ferroelectric domains, which characterized by an area of oriented spontaneous polarization. By application of the electric field, the domains exhibit changes in their structure knowing as polarization effect (subsection 3.1.5). The material ability to store the electrical energy under given frequency is described by the relative permittivity ϵ_r (equation 3.4). This coefficient is related to piezoelectric properties of materials (i.e. high values of relative dielectric permittivity is desirable for actuator applications). The inherent dissipation of electromagnetic energy is presented through dielectric loss tangent $\tan(\delta)$ [141]. The measured complex dielectric properties can be represented by these two parameters.

Relative permittivity is expressed by the ratio of the material permittivity ϵ to the permittivity of vacuum ϵ_0 (equal to 8.85E-12 (F/m)) with an equation:

$$\epsilon_r = \frac{\epsilon}{\epsilon_0} \quad (3.4)$$

The dielectric loss can be expressed through the relationship between imaginary ϵ'' and real ϵ' components of permittivity:

$$\tan(\delta) = \frac{\epsilon''}{\epsilon'} \quad (3.5)$$

Depending on the frequency, the dielectric properties of the material is associated with different phenomena. Dielectric relaxation in the frequencies range between 1–100kHz represents the dipole interaction within the particle and is of interest during the characterization of ferroelectric ceramics. It provides information about polarizability in dipole region and related to the piezoelectric effect and conductivity [142].

For NBT material, fabricated by the screen-printing method, the relative dielectric permittivity in the longitudinal operational mode, ϵ_{33} , was obtained from capacitance and loss $\tan(\delta)$ measurements.

The experiment was performed with three apparatus:

- PM300 Piezotest d33 PiezoMeter Systems [143]
- ModuLab XM MTS - Materials Test System [144]
- E4990A Impedance Analyzer [145]

In Table 3.4, the repeatability of 10 measurements for one screen-printed NBTv6 sample with capacitance equal to 400 pF and $\tan(\delta)$ loss of 0.008 at 1 kHz is presented. The reliability of measurements was shown through the error below 3 % for $\tan(\delta)$.

Table 3.4 – Repeatability the dielectric measurements with each apparatus.

	PM300 (Standard deviation)	ModuLab XM MTS (Standard deviation)	E4990A (Standard deviation)
C, (F)	0,15%	0,01%	0,02%
$\tan(\delta)$	0,75%	1,75%	2,75%

The correlation of results obtained was performed by measurements of 6 samples from NBTv6 with each apparatus (Figure 3.17). It was demonstrated that the measurements with three test benches are in good coherence. Hence, dielectric data registered with PM300 Piezotest d33 PiezoMeter Systems, Modulab XM MTS, and E4990A Impedance Analyzer can be compared and analyzed.

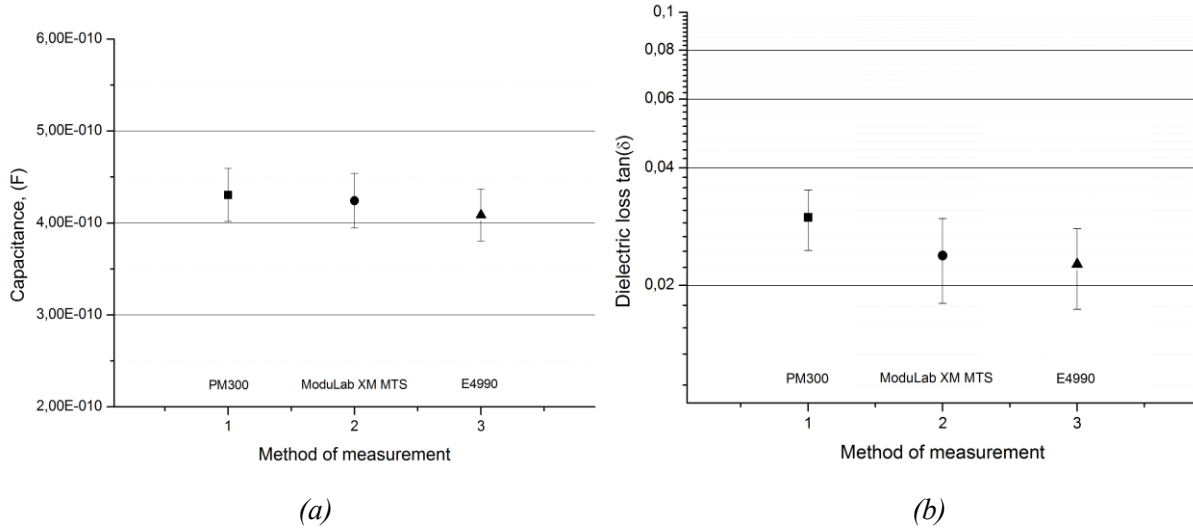


Figure 3.17 – Capacitance (a) and dielectric tangent loss (b) measured at 1 kHz for 6 NBTv6 detached disks.

Due to the simplicity of the method, at room temperature, dielectric properties measurements were carried out with PM300 Piezotest d33 PiezoMeter Systems accordingly to the measurement procedure detailed in [146]. The relative permittivity was determined through the equation:

$$\varepsilon_r = \frac{lC}{\varepsilon_0 S} \quad (3.6)$$

whereby, C is the measured capacitance (in pF) at 1 kHz, l is the disk thickness (in μm), S is an electrode area (in cm^2).

3.2.4 Piezoelectricity

Piezoelectric effect associates electrical and mechanical phenomena, in which three types of coefficients establish material properties. Piezoelectric ceramic characterization can be done regarding its electrical, mechanical and piezoelectric properties. These coefficients are associated through piezoelectric constitutive equations [147]:

$$D_i = \varepsilon_{ik}^T E_k + d_{ikl} T_{kl} \quad (3.7)$$

$$S_{ij} = s_{ijkl}^E T_{kl} + d_{kji} E_k \quad (3.8)$$

whereby, the electric displacement vector D_i (C/m²), electric field vector E_k (V/m), dielectric permittivity under constant stress second order tensor ε_{ik}^T (F/m), are electric coefficients; strain second order tensor S_{ij} (dimensionless), stress second order tensor T_{kl} (N/m²), and mechanical compliance measured under constant dielectric displacement fourth order tensor s_{ijkl}^E (m²/N) are mechanical coefficients; and d_{ikl}, d_{kji} (C/N), the piezoelectric charge coefficients third order tensors.

According to the IEEE standard on piezoelectricity [147], the performance of the piezoelectric device can be evaluated in terms of its Curie temperature T_c , piezoelectric coefficient d_{ikl} , permittivity ε_{ik}^T , dielectric loss $\tan(\delta)$ and electromechanical coupling factor k_{ijk} .

The electromechanical coupling factor describes the efficiency of energy conversion from mechanical to electrical state and vice-versa. For the dynamic conversion, the coupling factor can be found with the equation:

$$k_{ijk}^2 = \frac{d_{ikl}^2}{s_{ijkl}^E \varepsilon_{ij}^T} \quad (3.9)$$

where d_{ijk} , s_{ijkl}^E , ε_{ij}^T are the aforementioned piezoelectric charge coefficient, mechanical compliance, and dielectric permittivity.

In the case of screen-printed thick films, the piezoelectric material operates in thickness-extension mode [147]. Therefore, the equation for the piezoelectric charge coefficient can be written:

$$d_{33} = k_{33} \sqrt{\varepsilon_0 \varepsilon_{33} s_{33}^E}, \quad (\text{C/N}) \quad (3.10)$$

where ϵ_0 is a vacuum permittivity, ϵ_{33} is a relative permittivity and s_{33}^E is a mechanical compliance under constant dielectric displacement in the longitudinal operation mode.

High piezoelectric charge coefficient is desirable for materials used as actuators, where a high mechanical force is needing to be generated. In case of sensing application, the high voltage value in a response to mechanical stress is desirable. This value is determined with a piezoelectric voltage g_{33} (V/N) coefficient, which is related to the piezoelectric charge coefficient by the following equation:

$$g_{33} = \frac{d_{33}}{\epsilon_0 \epsilon_{33}} = \frac{k_{33} \sqrt{s_{33}^E}}{\sqrt{\epsilon_0 \epsilon_{33}}}, \quad (\text{V/N}) \quad (3.11)$$

From the equation (3.10) the piezoelectric charge coefficient, d_{33} , depends on the square root of the permittivity. Its value is opposite to the piezoelectric voltage coefficient, g_{33} , which are inversely proportional to the square root of the permittivity. Hence, the measurement of the permittivity as a function of temperature is one of the parameters which provides information about transducer operability [148].

3.2.4.1 Piezoelectric characterization

In this work, the dielectric charge coefficient, d_{33} , is measured with PM300 Piezotest d33 PiezoMeter Systems. The method of measurement is the same as described in subsection 3.2.3.

By previous work with PZT screen-printing sensors [109], it was shown, that the value of d_{33} is lower in comparison to PZT bulk material. Such difference can be explained by the relatively low sintering temperature of 850°C and the additive of CF7575 sealing glass. Indeed, it was observed that microstructures of NBT element, fabricated by the screen-printing method, contain the voids in the place of CF7575 and are relatively porous (Annex B).

A screen-printed NBT material polarizability was examined by measurement of d_{33} after application of gradually increasing electric field at 150 °C. The optimal polarization electric field was found to be in the range of 130 kV/cm which is in coherence with the state of the art [125].

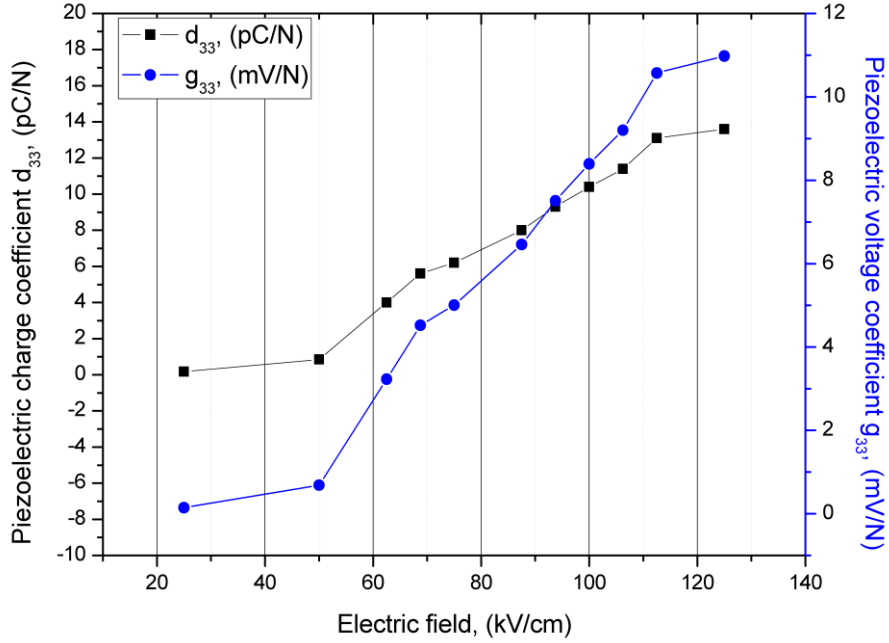


Figure 3.18 – Piezoelectric charge coefficient, d_{33} , and piezoelectric voltage coefficient, g_{33} , evolutions as a function of applied electric field for screen-printed NBTv1 detached disk.

During these studies, the value of the permittivity value was observed to be unchanged before and after polarization. Hence, g_{33} evolution is linearly proportional to d_{33} enhancement with E-field increment and was calculated using equation 3.11. Their evolutions as a function of the applied electric field are shown in Figure 3.18.

The impedance of polarized NBT ceramic was measured with E4990 Impedance Analyzer. The NBT material, in the form of a detached disk, was placed between two tips as shown in Figure 3.19. An example of the impedance curve shown in Figure 3.20.

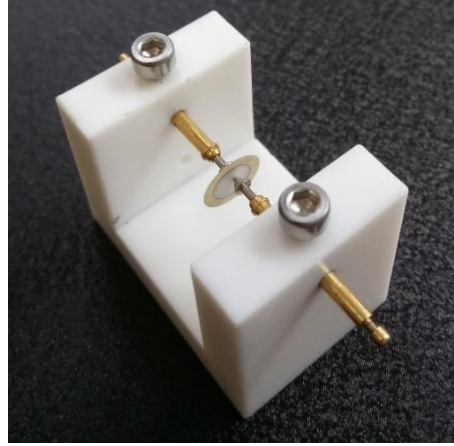


Figure 3.19 – Positioning system with NBT detached disk used for impedance measurement.

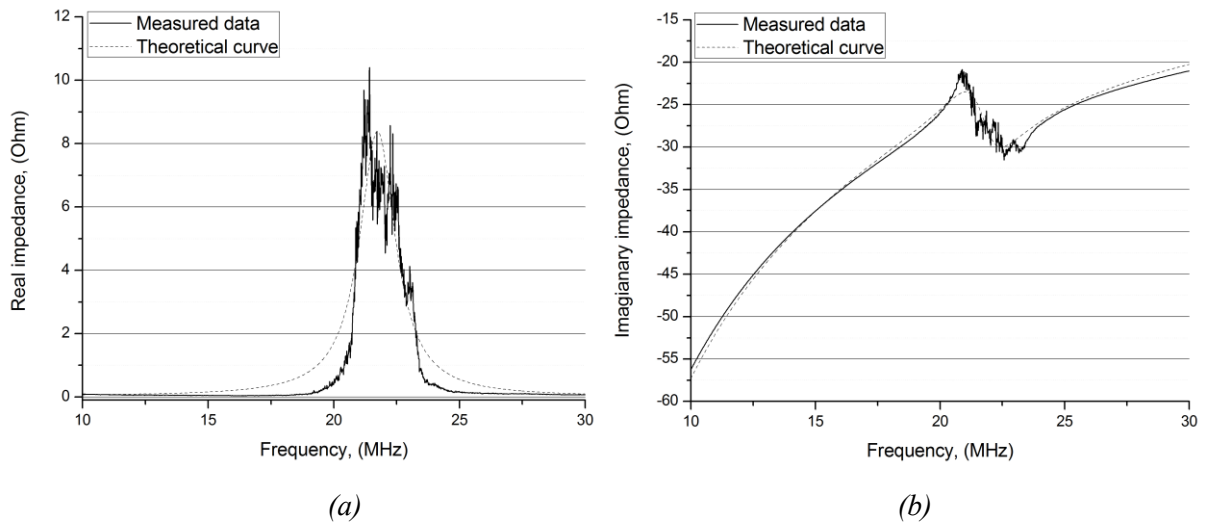


Figure 3.20 – Electrical impedance (a) real part and (b) imaginary part of NBTv1 detached disk polarized under the electrical field of 120 kV/cm with an associated fit.

3.2.4.2 Electromechanical parameters obtained from the fit of an impedance

Since all the parameters (electrical and mechanical) of piezoelectric material are correlated, it is important to describe these dependencies through a theoretical model matching experimental data. The classical approach, allowing simulation of all the coefficients from experimental impedance is Krimholtz, Leedom, and Matthaei (KLM) model [149]. Due to the reversibility of the piezoelectric effect, the equations from the KLM model can be rewritten with different coefficients.

Following a theoretical approach, based on the KLM model, the electromechanical parameters of the piezoelectric detached disk were calculated by matching experimental measurement with theoretical values. Three complex parameters, parallel frequency (Fp^*), electromechanical coupling factor (kt^*), capacitance (C^*) were adjusted using the Matlab software in order to fit measured data.

Complex values of these parameters can be found from the standard equations of piezoelectricity [150]:

$$Fp^* = Fp \left(1 + \frac{i}{qFp} \right), \quad (\text{Hz}) \quad (3.12)$$

$$kt^* = kt \sqrt{1 - i/qkt^2} \quad (3.13)$$

$$C^* = capa \left(1 - \frac{i}{qcapa} \right), \quad (\text{F}) \quad (3.14)$$

where Fp is the parallel frequency (in Hz), qFp is the mechanical quality factor, kt is the electromechanical quality factor, qkt is the electromechanical loss, $capa$ is the capacitance (in F) and $qcapa$ is the dielectric loss (inversely proportional to $\tan(\delta)$). Frequency constant in thickness mode was determined by the following equation:

$$N_t = Fp * l_{NBT} \quad (3.15)$$

where l_{NBT} is the thickness of the active element (in μm).

Theoretical impedance was determined by the following equation:

$$Z_{elec}^* = \left(-\frac{1i}{C^*\omega} \right) \frac{\left[1 - (4Fp^*kt^{*2}\tan\left(\frac{\omega}{4Fp^*}\right)) \right]}{\omega}, \quad (\text{Ohm}) \quad (3.16)$$

where ω is an angular frequency (in Hz).

Table 3.5 – Electromechanical parameters of NBTv1 disk fitted with Matlab software and their comparison with calculation and measurements.

Symbol	Quantity	Fitted value	Measured with another method
F_p	parallel frequency	21.75 MHz	21.75 MHz [151]
N_t	frequency constant	2175	2175
qF_p	mechanical quality factor	23	15 [151]
kt	electromechanical coupling factor	0.17	0.15 [151]
$capa$	Capacitance	266 pF ($\epsilon_{33} = 105$)	275 pF (d33 Meter) ($\epsilon_{33} = 110$)
$qcapa$	dielectric loss	188 ($\tan(\delta) = 0.005$)	125 (d33 Meter) ($\tan(\delta) = 0.008$)

An example of fitted electromechanical parameters is displayed in Table 3.5. The coherence of fit with direct measurements and calculations from the impedance curve (F_p , qF_p , kt) [151] and dielectric properties measured with PM300 Piezotest d33 Meter validates the reliability of the theoretical model.

3.2.5 Material characterization as a function of temperature

The evolution of material properties as a function of temperature defines its applicability for use in high-temperature environment. Hence, to complete the characterization, the experiments with piezoelectric material parameters observation with temperature are necessary.

Sodium bismuth titanate ceramics was extensively studied as a candidate for a high temperature sensor [77], [89] – [91], [125], [152] – [157]. It was shown, that in case of a bulk dense ceramics the NBT material can be used for sensing application up to 500-550 °C. The studies demonstrate that the electric, dielectric, piezoelectric and electromechanical properties are correlated and parameters degradation with temperature increasing occurs simultaneously. In this work, to examine screen-printed NBT material properties behavior in a harsh environment, measurements of electrical resistivity and dielectric properties as a function of temperature were carried out.

3.3.5.1 Resistivity

Resistivity evolution as a function of temperature reveals materials insulating properties under harsh environmental conditions. The stability of this parameter indicates material endurance to a high electric field as well as polarizability of the samples.

The test bench for resistivity measurement as a function of temperature was the same as for the measurements at room temperature (Figure 3.9). The temperature was gradually changed by heating of a hot plate and the resistivity measurements were performed through registration of the leakage current at given temperatures. For each NBT version, the resistivity was measured from 30 °C to 175 °C.

For the NBTv5, a material with the highest resistivity, the measurements were carried out up to 350 °C. The measurement example is shown in Figure 3.21. The resistivity plot was correlated with the experiment for NBT bulk material reported in [152] (refer to section 3.3 for more details).

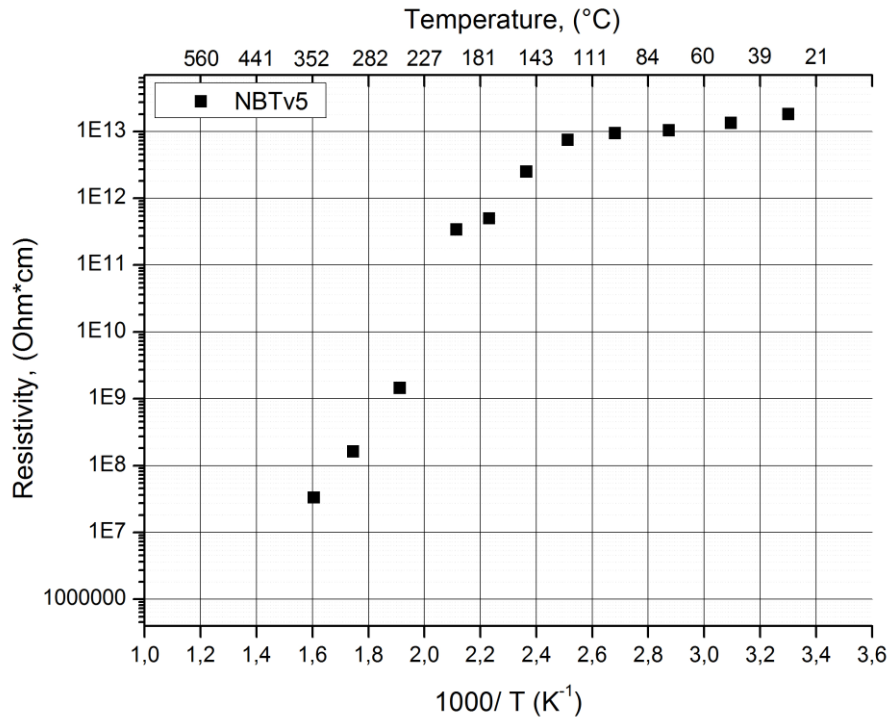


Figure 3.21 – An example of the resistivity measurement performed for a detached disk of NBTv5.

The behavior of resistivity, for detached elements of NBTv5, as a function of temperature follows the Arrhenius law:

$$\rho = A \exp(-E_a/k_B T), \quad (\text{Ohm} * \text{m}) \quad (3.15)$$

where A is a pre-exponential factor constant, E_a is the activation energy of the mobile charge carriers (in eV), k_B is a Boltzmann constant ($1.38064852 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$) and T is an absolute temperature (in Kelvin).

3.3.5.2 Dielectric properties

The evolution of dielectric properties as a function of temperature was carried out with ModuLab XM MTS [144] in the range from 30 °C to 350 °C. The sample was put on a hot plate and connected through two points to ModuLab XM MTS impedance analyzer. The measurement was performed in high impedance material testing mode, in the frequency range from 100 Hz to 100 kHz (Figure 3.22). Indeed, the values of 1 kHz and 10 kHz were treated. The value of 1 kHz was chosen because it is a standard to measure a low-frequency dielectric data and it is the same frequency measured by Berlincourt method [158]. The frequency of 10 kHz is another measurement frequency (as a function of temperature) which can be found in the literature for an NBT ceramics [89] – [91], [125], [152] – [156].

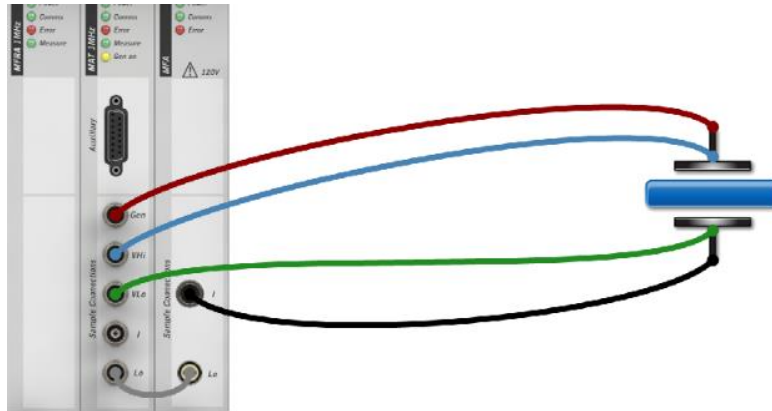


Figure 3.22 – High impedance material testing configuration used in the experiment.

The impedance material testing configuration contains a basic module for material characterization with frequency up to 1 MHz with femto ammeter option which allows current measurement up to 10^{-15} A .

The example of the dielectric properties evolution as a function of temperature carried out at 1 kHz, is shown in Figure 3.23.

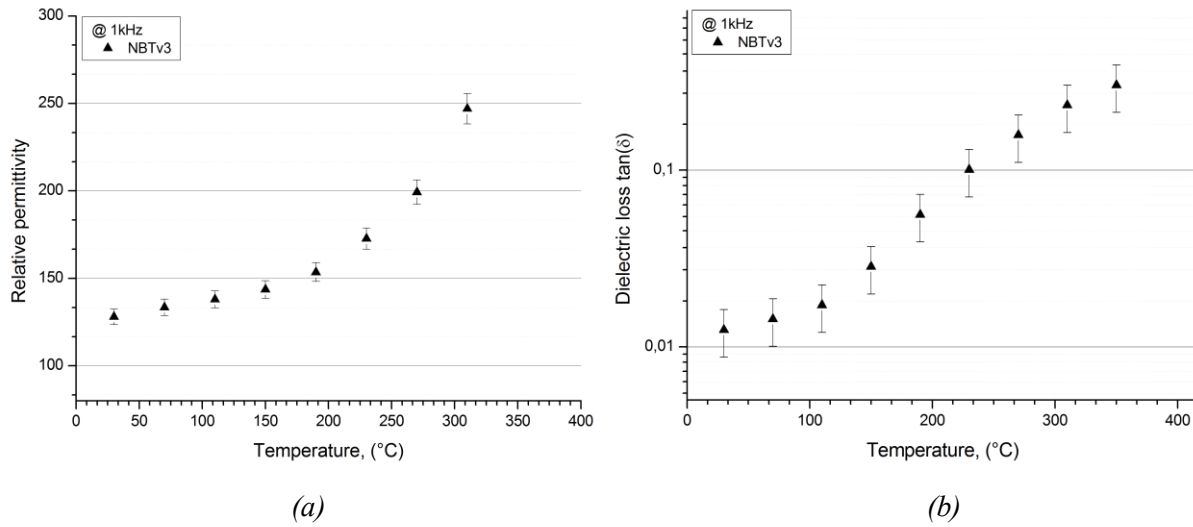


Figure 3.23 – Dielectric properties evolution for NBTv3 sample as a function of temperature at 1 kHz.
 (a) relative permittivity and (b) loss tangent $\tan(\delta)$.

3.2.6 Sintering studies

As was mentioned in section 3.1, the sintering protocol was adapted to match the requirements of the ceramic-electrodes co-firing process in sensor fabrication. Following the perspective in material development for the future works, dedicated to parameters optimization, and for a deeper understanding of the screen-printing parameters in NBT sensor development, the preliminary sintering studies were performed. The choice of doped NBT materials in the experiment was explained by two factors:

- The properties of NBT detached disks doped by Nb and W (NBTv6 and NBTv7 correspondingly) were in the range of un-doped NBT ceramics. It could be related to the fabrication process. If it is the case, by changing the sintering time, we might be able to obtain the material of superior properties.
- The NBT doped ceramics were the last fabricated materials in course of this thesis work. The fabrication of some of the un-doped versions was already impossible.

Samples were sintered for 1 and 2 hours. The measurements of piezoelectric, dielectric and electromechanical parameters were compared with the materials sintered for 15 minutes.

3.2.7 Conclusions

In this section, we discussed the characterizations performed for screen-printing NBT material (in a form of a detached disk). The experiments of morphological, electric, dielectric, piezoelectric analysis are presented with an example of measurement. Results for each NBT version are summarized in section 3.3.

3.3 Results and discussions

3.4.1 Introduction

With the aim to develop an ultrasonic sensor for high-temperature environment 8 versions of screen-printed NBT material were tested. All along their fabrication and characterization important questions were addressed considering the screen-printing NBT sensor development:

1. What is the most important parameter in the choice of NBT version for sensor production? To answer this question, we must consider the concept of high-temperature material where the properties stability as a function of temperature determines the functionality.

2. Dr. Shulman in her thesis work, by studying the conductivity of bismuth titanate ceramics (most studied material of BLSF) as a function of the grain size observed that the conductivity value depends on oxygen vacancies in the material. The finer grain bismuth titanate material showed the conductivity of one-decade lower compared to the coarse grain ceramics. The conductivity of both equalized at higher temperatures, in which the oxygen migration in the finer grain materials intends to increase [38]. Would we observe the same dependency for our samples? Does it relate to the fabrication process?

3. Previous research with PZT material, indicate that the PZT ceramics produced by screen-printing method possess the lower dielectric and piezoelectric properties in comparison to bulk materials. Do we observe the same effect for NBT screen-printed detached elements? Is it crucial for their operability at high temperatures? To answer these questions, the measurements of electrical resistivity and dielectric properties will be compared to the state of the art and measurements carried out with Pz46 commercial piezoelectric element dedicated for high-temperature applications.

4. Due to the screen-printing process, the sintering procedure of NBT ceramics is differing from that for bulk materials [89] – [91], [125], [152] – [156]. Does the change in time treatment enhance the properties of screen-printed NBT ceramic? Hence, the NBT materials with different sintering protocols are compared.

3.4.2 Results

The morphologies of NBT elements after sintering, can be seen in Annex B. Through optical observation two conclusions were made:

- Under given sintering condition (850 °C for 15 minutes), ceramic grain size is depending on the raw powder dimension. The finer powders anticipate in the formation of ceramics with smaller grain structures.
- The sample morphologies contain defects which are due to the sealing glass CF7575 presented in the ink.

The measurement of electrical resistivity at 30 °C and 175 °C are shown in the Figure 3.24 and compared with the value for commercial piezoelectric element Pz46 (dedicated to high-temperature measurements) [159]. It is shown that NBT detached disks fabricated with screen-printing method possess resistivity in the range of Pz46. An NBT material fabricated from fine grain powders, NBTv5, has the best resistivity at 175 °C with a higher value compare to Pz46.

The resistivity measured for NBTv5, material which has the lowest conductivity among NBT versions, were compared to the state of the art [152], [160] (Figure 3.25). It was found that the resistivity of screen-printed disks at the temperatures of 300 °C and 350 °C is two decades' lower compare to bulk ceramics, which expected to be related to the relatively low density of the screen-printed NBT ceramic and morphological defects (voids appeared in places of sealing glass CF7575).

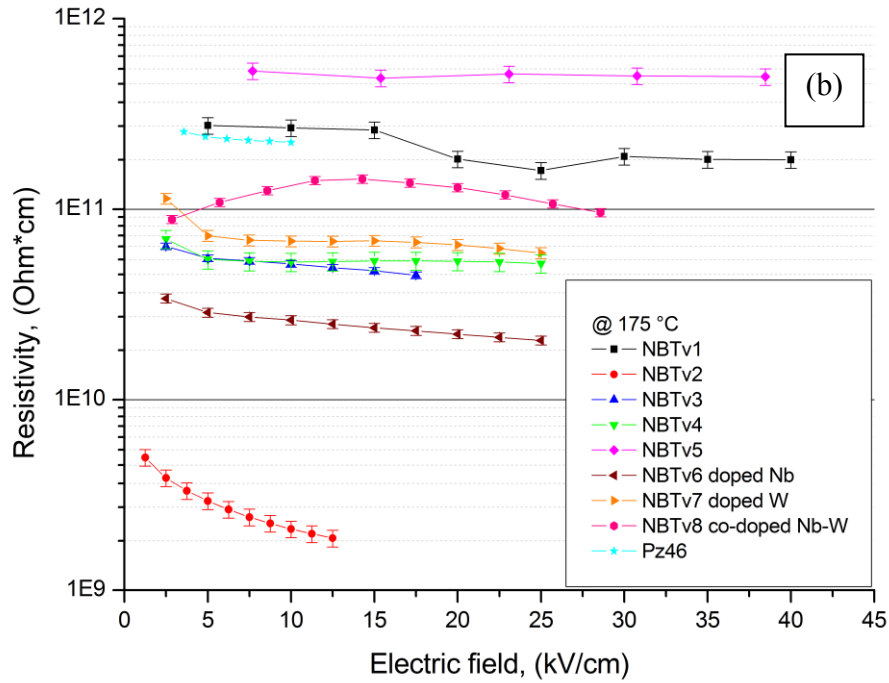
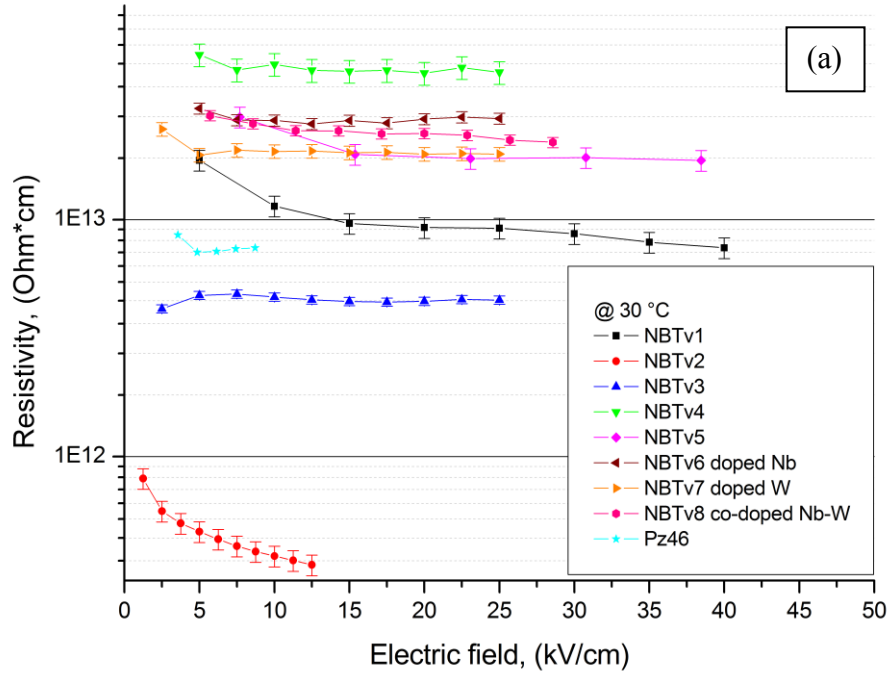


Figure 3.24 – Resistivity as a function of applied electric field for screen-printed NBT detached elements in comparison with a Pz46 commercial element.

Measurements at 30°C (a) and 175°C (b). For image clarity, standard deviation from the mean value, for each measurement, was reduced to 20 % from the determined value.

The existence of two different conduction mechanism in the ferroelectric region was shown. The same effect was observed by Kumar and Varma in their studies of La-doped NBT material. It was suggested that at lower temperatures the conduction mechanism is due to the electrons/holes migration while at high temperatures, the contribution of thermally activated oxygen vacancies to the electric conductivity is increasing [160]. Nevertheless, activation energies calculated from Arrhenius plots were 0.27 eV and 0.88 eV in the 30°C - 200°C and 200 °C - 350 °C temperature ranges, correspondingly, which are in accordance with the results reported in the literature [152], [160].

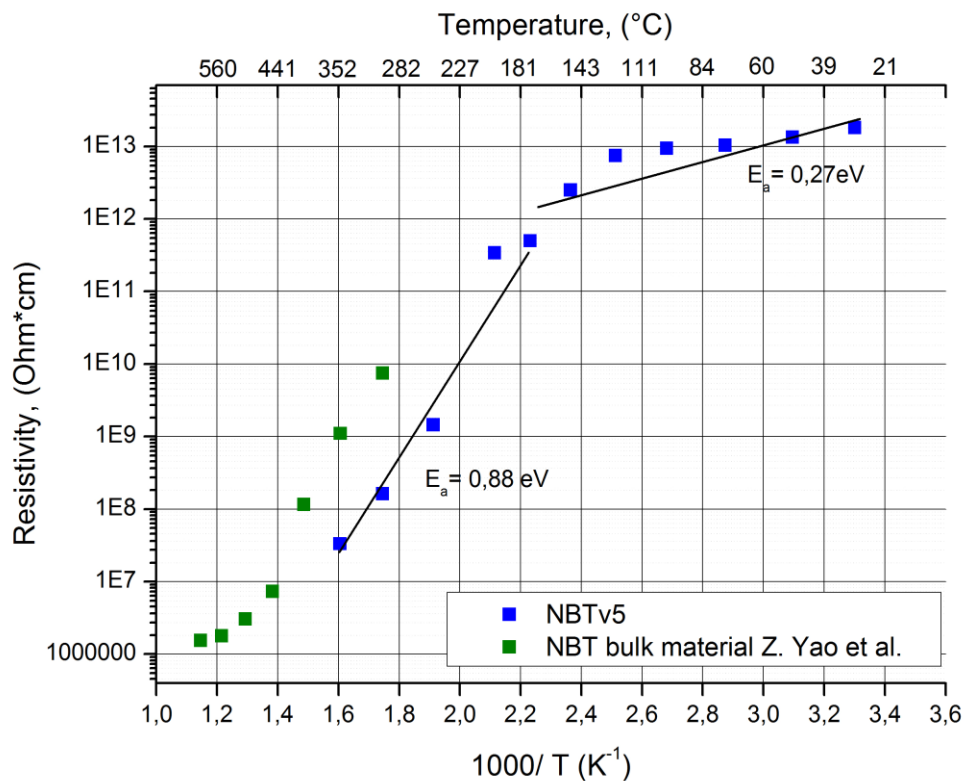


Figure 3.25 – Resistivity evolution of fabricated material as a function of temperature in comparison with bulk NBT ceramics [152].

The observation of dielectric properties as a function of temperature at 1kHz (Figure 3.26 (a) and Figure 3.27 (a)) and at 10 kHz (Figure 3.26 (b) and Figure 3.27 (b)) for the series of the samples shows that all the versions, except NBTv2, withstand to high-temperature conditions. Again, the best stability was found for the fine grain powder based NBTv5 material.

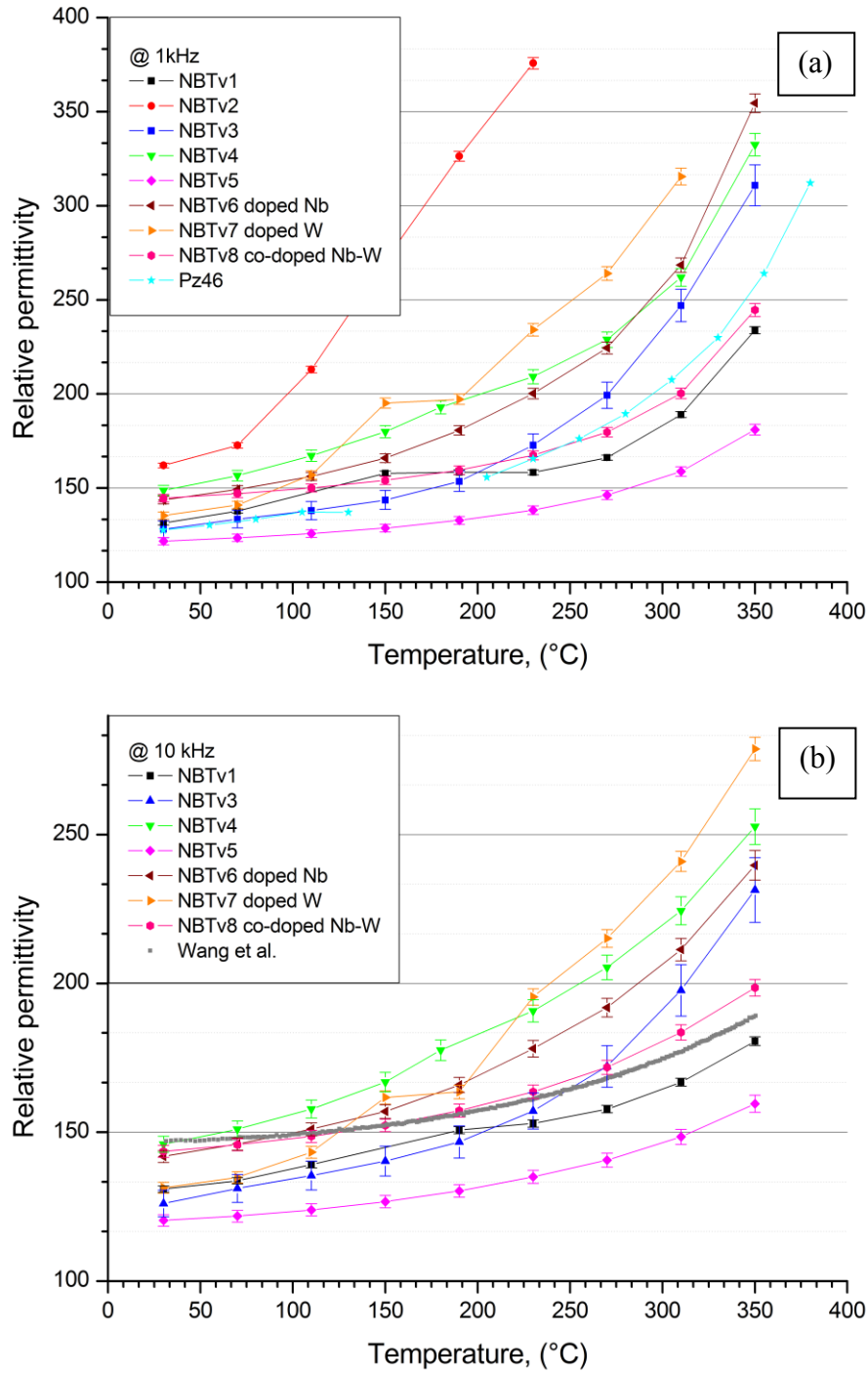


Figure 3.26 – Relative permittivity as a function of temperature for screen-printed NBT detached elements in comparison with the state of the art and Pz46 commercial element.

Measurements at 1kHz (a) and 10 kHz (b). For image clarity, standard deviation from the mean value, for each measurement, was reduced to 20 % from the determined value.

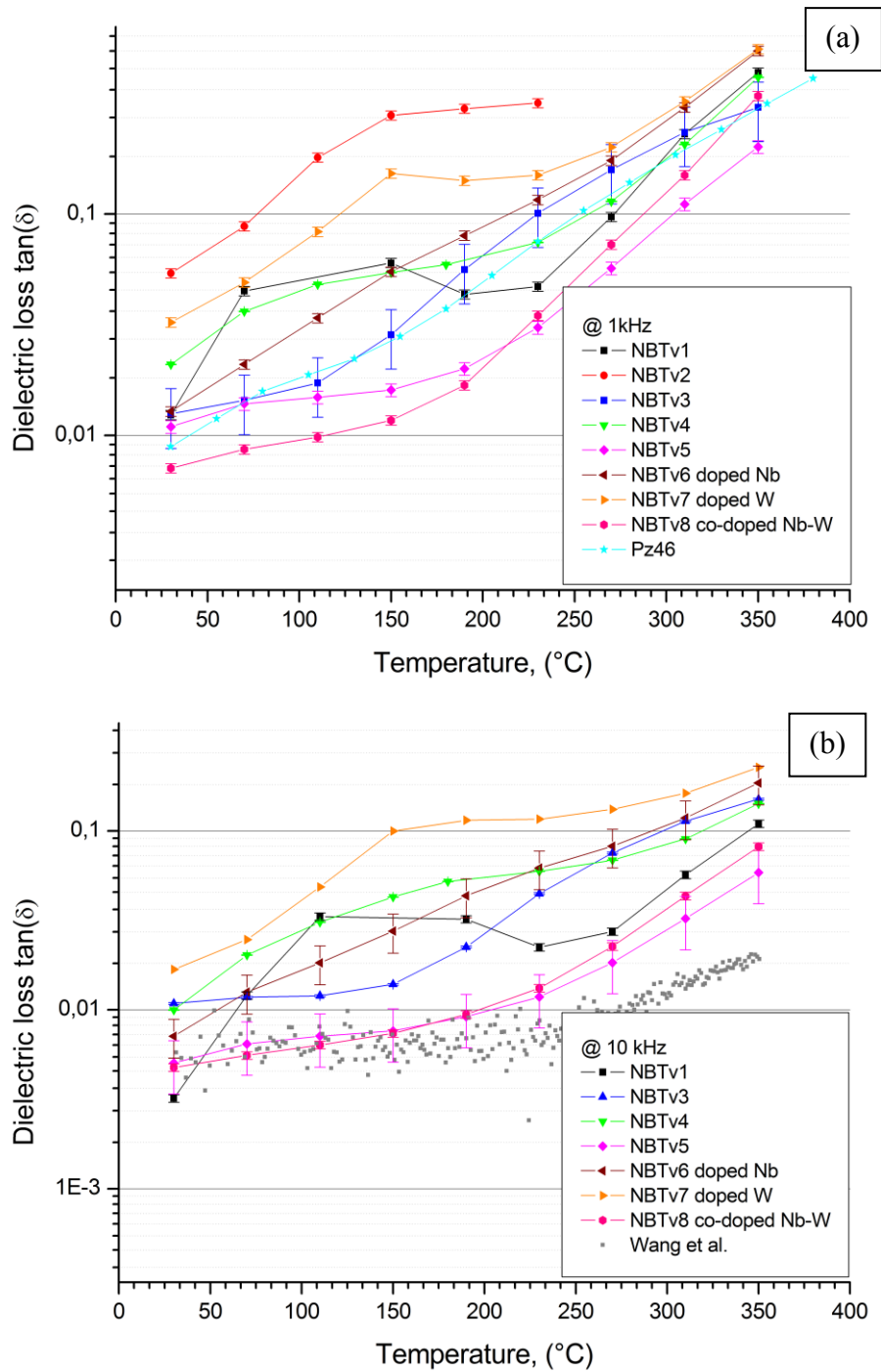


Figure 3.27 – Dielectric tangent loss as a function of temperature for screen printed NBT material in comparison with the state of the art and Pz46 commercial element.

Measurements at 1 kHz (a) and 10 kHz (b). For image clarity, standard deviation from the mean value, for each measurement, was reduced to 20 % from the determined value.

At room temperature, the versions of the NBT material were compared on their grain size, dielectric (ϵ_{33} , $\tan(\delta)$), piezoelectric (d_{33} , g_{33}) and electromechanical properties (qFp , kt) (Table 3.6). The parameters of NBT screen-printing detached disks approaching the properties of the Pz46 element. The notable difference in quality factor (qFp) is believed to be related to the screen-printing process, which characterized by an imperfection in material densification.

Table 3.6 – Overview of NBT ceramic properties at room temperature.

NBT version	Powder grain size, μm	Sintering time	ϵ_{33}	$\tan(\delta)$	d_{33} , pC/N	g_{33} , mV/N	qFp	kt
v1	0.5 – 1.2	10 hours	140 ± 10	0.008 ± 0.003	13.1	10.5	23	0.17
v2	0.5 – 2.2	15 min	162	0.05-0.6	8.5	5.9	31	0.14
v3	0.1 – 0.5	15 min	135 ± 10	0.01 ± 0.002	14.1	11.8	25	0.14
v4	0.3 – 1.5	15 min	140 ± 10	0.019 ± 0.001	12.3	9.9	30	0.12
v5	0.1 – 0.3	15 min	125 ± 10	0.009 ± 0.001	13	11.7	n.a	n.a
v6 doped with Nb	0.2 – 1	15 min	160 ± 15	0.02 ± 0.01	11.8	8.3	27	0.12
v7 doped with W	0.3 – 1.5	15 min	155 ± 5	0.04 ± 0.01	11.4	8.3	23	0.15
v8 co-doped with Nb & W	0.1 – 0.3	15 min	150 ± 10	0.0085 ± 0.001	20	15.0	66	0.22
Pz46			125	0.01	20	18	>600	0.2

n.a – not available. Due to the low thickness of the fabricated detached elements, the resonance curve appears above 50 MHz, which exceeds E4990A Impedance analyzer frequency range. Hence, the electromechanical properties were undetermined.

The sintering studies were performed for NBT doped materials of v6, v7, and v8. They are highlighted with micrographs (Figure 3.28), electrical impedance response (Figure 3.29) and are summarized in Table 3.7.

The SEM micrographs of NBT ceramics obtained from sintering protocols of 15 min, 1 hour and 2 hours reveal the evolution of the grain sizes with sintering time increment. It was observed that for three versions of NBT ceramic the average grain size of ceramic sintered for 1 hour and 2 hours are bigger in comparison to the sintered with 15 minutes.

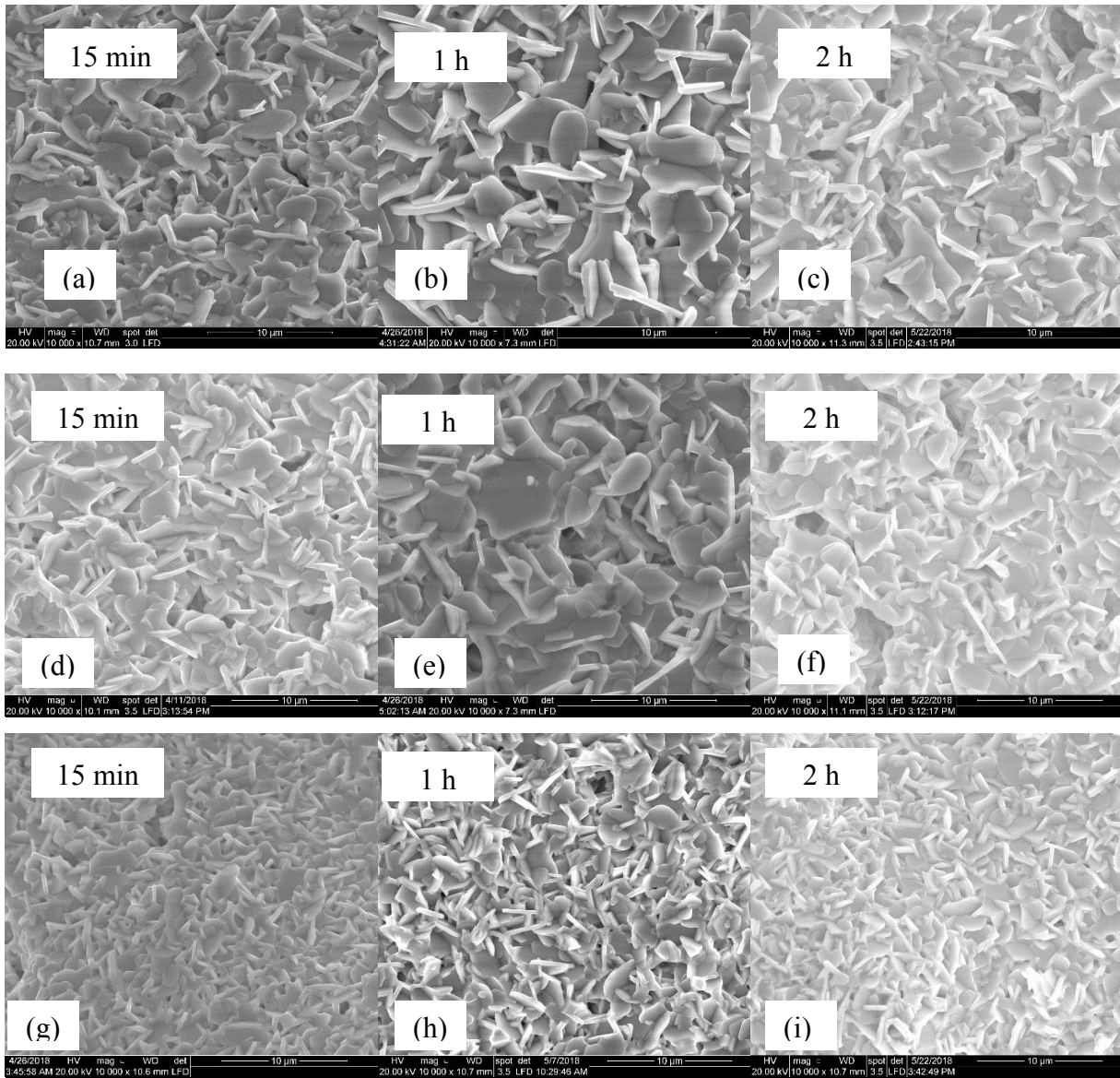


Figure 3.28 – Micrographs of doped NBT ceramics, under magnification of $\times 10000$, obtained from different sintering protocols.

(a), (b), (c) – Corresponds to NBTv6 doped by Nb; (d), (e), (f) – NBTv7 doped by W; (g), (h), (i) – NBTv8 co-doped with Nb&W.

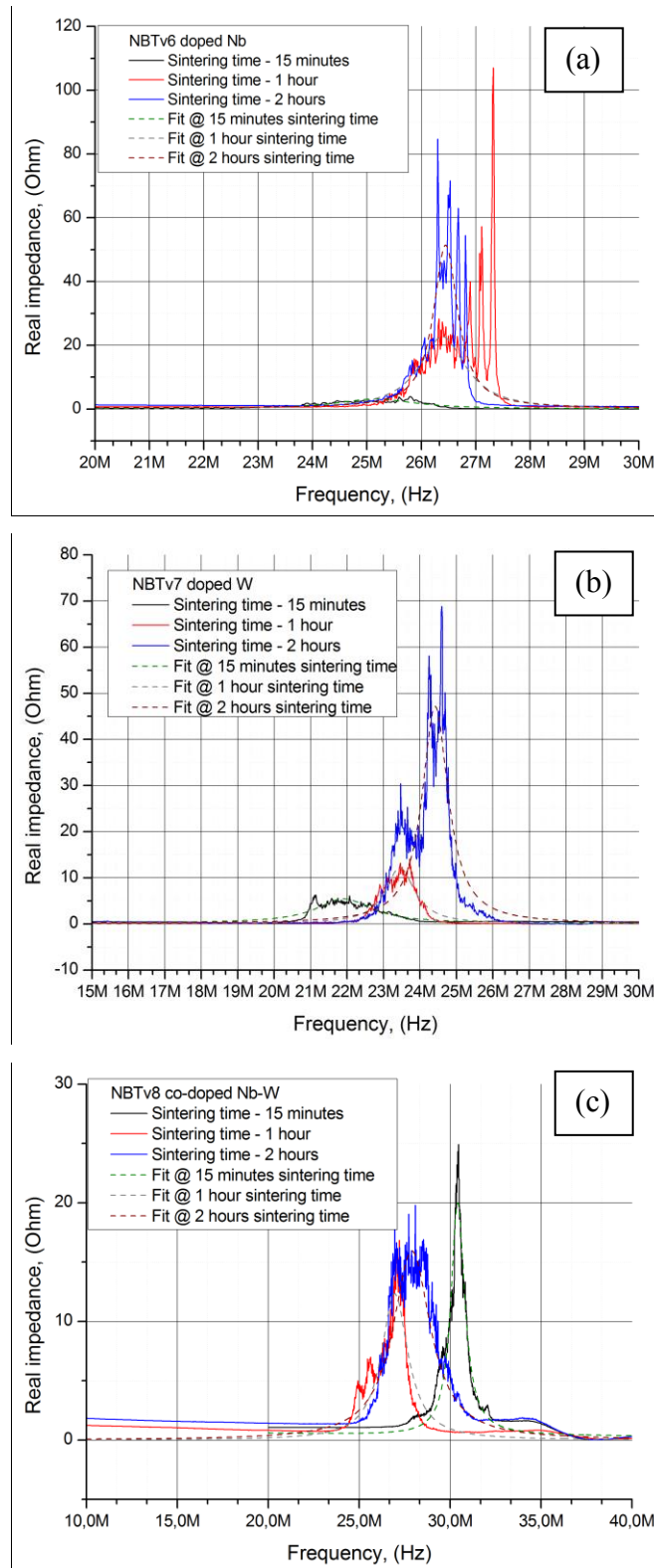


Figure 3.29 – Evolution of impedance as a function of sintering time for doped NBT ceramics.

(a), (b) and (c) corresponds to NBTv6 doped by Nb, NBTv7 doped by W and NBT co-doped by Nb-W respectively.

The analysis of the impedance curves, for NBTv6 and NBTv7 coarse grain ceramics, shows that the electrical response is enhanced by the increase of the sintering time to 1 hour and (or) 2 hours. However, the impedance curves of the NBTv8 material, produced from the finer grain powders remained at the same level.

Table 3.7 – Evolution of NBT ceramic properties as a function of time sintering at room temperature.

NBT version	NBTv6 doped Nb			NBTv7 doped W			NBTv8 doped Nb-W		
Sintering time	15 min	1 h	2 h	15 min	1 h	2 h	15 min	1 h	2 h
ϵ_{33}	160 ± 10	160 ± 10	160 ± 10	155 $\pm$ 5	155 ± 5	155 $\pm$ 5	150 $\pm$ 10	150 ± 10	150 ± 10
$\tan(\delta)$	0.02 ± 0.01	0,0115	0,02	0.04 ± 0.01	0,0108	0,0171	0.0085 ± 0.001	0,0136	0,0085
d_{33} , pC/N	11.8	11	11.5	11.4	13.6	14.4	20	18	18
g_{33} , mV/N	8.3	8.2	8.3	8.3	9.9	10.4	15.0	13.5	13.5
qFp	27	24	15	23	43	53	66	26	15
kt	0.12	0.15	0.17	0.15	0.17	0.16	0.22	0.23	0.25

The acoustic response for three versions of NBT as a function of sintering time of the samples was studied with a theoretical model that will be detailed in chapter 4. The model allows simulating the sensor response for an ideal case, in which the NBT materials sintered for 15 min, 1 h, and 2 h were stacked with alumina substrate and integrated into an acoustic cavity filled by Helium gas. The signal treatment, adapted in chapter 4, reveals the theoretical response of so-called “tempographs” shown in Figure 3.30.

Table 3.8 – Piezoelectric coefficient of fabricated material relative to the value for Pz46 commercial element

Material version	d_{33} % efficiency compare to Pz46	g_{33} % efficiency compare to Pz46
v1	65	77
v2	42	32
v3	70	62
v4	61	51
v5	65	67
v6 doped with Nb	59	51
v7 doped with W	55	51
v8 co-doped with Nb & W	100	86

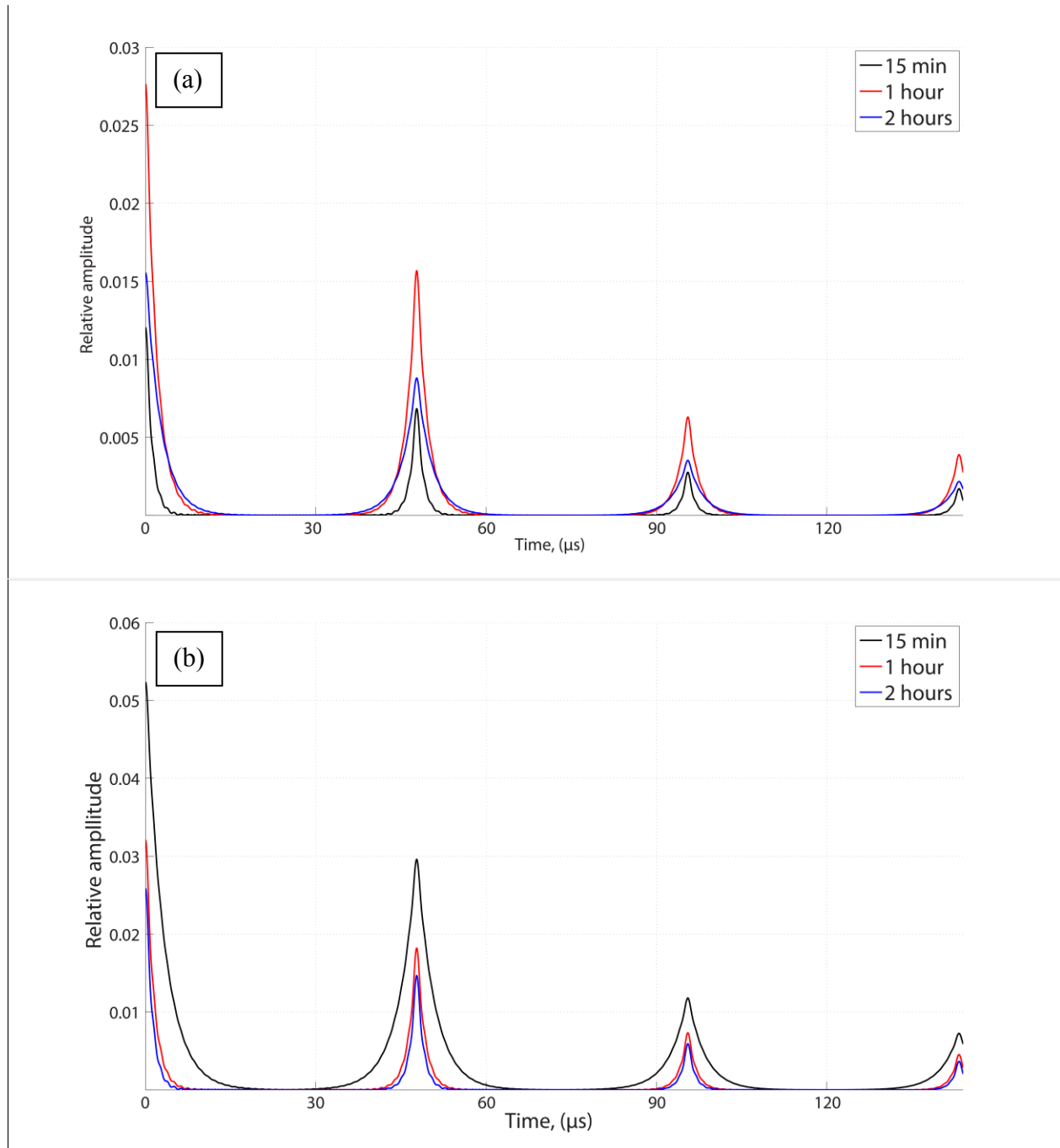


Figure 3.30 – Theoretical acoustic response of NBT materials as a function of time sintering.

NBTv7 coarse grain (a) and NBTv8 fine grain (b) materials coupled with alumina substrate and integrated into an acoustic cavity filled by Helium gas.

The quantitative measure of piezoelectric material efficiency is described by direct and inverse piezoelectric effects. The piezoelectric responses for each NBT material version are summarized in Table 3.8 in comparison to the Pz46 commercial piezoelectric element. The NBTv8

co-doped with Nb and W has the highest value of d_{33} and g_{33} . Its piezoelectric coefficient, d_{33} and g_{33} , are in the range of Pz46 commercial element (of 100 % and 86 % respectively).

3.4.3 Conclusions

The set of measurements shows that certain versions of screen-printed NBT material possess slightly better electric, dielectric and (or) piezoelectric properties. The origin of this dependencies can be related to several factors: a raw material composition, a grain size, a microstructure, the difference in a fabrication process, etc.

To summarize the fabricated materials, let's correlate the results on the conductivity phenomenon observed by Dr. Shulman in bismuth titanate ceramics. According to her observation, the materials of a finer grain structure possess lower conductivities. In this work, there were three NBT types with fine grain structures: NBTv3, NBTv5, and NBTv8 (co-doped by Nb-W). Analyzing separately un-doped and doped ceramics, one can observe, that indeed, the NBTv5 and NBTv8 possess better resistivity in comparison to other coarse powders materials (Figure 3.24 and Figure 3.25).

However, the NBTv3 resistivity value is in the range of coarse NBT materials. It can be explained by NBTv3 microstructure (Annex B). NBTv3 is the material of a porous structure with no sheets-like grain structure formation. The grain/pore percolation is suggested to be a reason for its higher conductivity [161].

The NBT powders were doped with one ratio of dopant. Hence, it is difficult to conclude on fabricated NBT doped ceramics. Indeed, the parameters of NBTv6 and NBTv7 doped by Nb and W were found to be in the range of un-doped NBT ceramics fabricated from coarse grains. The superior piezoelectric properties were obtained for NBT material co-doped by Nb and W. It is suggested that co-doping by Nb and W in B-site produces the lattice distortion in the pseudo-perovskite block resulting in slight monoclinicity, which implies the enhancement of electric and piezoelectric properties [157].

The evolution of dielectric properties as a function of temperature (Figure 3.26 and 3.27) are in accordance with resistivity measurements. The comparison of dielectric properties evolution as

a function of temperature with the commercial piezoelectric element Pz46 and NBT bulk material [125], suggests that the samples possess the similar behavior, which indicates their applicability for high-temperature applications. Contrariwise, morphological defects, related to the CF7575 additive in ink production, may be the reason for NBT properties degradation with temperature (resistivity, quality factor).

It was shown, through the sintering studies with 3 versions of NBT, that the material properties can be altered through the application of different sintering protocols (Table 3.7). The theoretical acoustic response of the sensor indicates that the acoustic measurements are possible with materials sintered by each protocol. Hence, in the first stage of sensor development, it is rational to keep the use of the sintering protocol of 15 min during 850 °C. As the theoretical model presents an “ideal” case in which the imperfections of coupling did not considered, properties dependencies on sintering protocol need to be evaluated regarding the material deposition onto a substrate.

Overall, eight versions of the NBT ceramic were fabricated with a slightly different protocol and the repeatability of their production was shown through parameters comparison. It was found that an NBT ceramic fabricated with the screen-printing method is a promising solution in the field of high-temperature application and the materials formed from the finer grain size powders possess good parameters endurance at 350 °C.

Owing to these studies, two important results were obtained:

- Through the set of characterizations of the properties of the 8 versions of NBT material, the general knowledge about production and parameter control were achieved. The “optimal” protocol developed to produce NBT detached element will be used in sensor device fabrication.
- Among tested NBT materials, the piezoelectric properties of NBTv8, co-doped with Nb and W, detached elements were found to be superior to other NBT versions, approaching the value of the Pz46 commercial element. Hence, the choice of this material is attributed and envisaged for the development of the sensor device.

Chapter 4. Development of piezoelectric sensor

The studies on NBT material fabrication with a screen-printing method demonstrated the reliability in its production. Electric, dielectric, piezoelectric properties measurements and the monitoring of their evolution as a function of temperature were carried out for detached elements. Hence, the effective material and a fabrication process were established (chapter 3). The following step consists in the integration of piezoelectric ceramics on a substrate for an acoustic signal generation.

As was mentioned in chapters 1 and 3, the transducer's performance depends on the difference of the coefficient of thermal expansion (CTE) between piezoelectric material and substrate. Moreover, its importance was observed through the experiment with the REMORA sensor [10], [44]. To overcome the coupling problem, the screen-printing method was chosen due to its advantage in direct deposition into a substrate. Hence, intermediate layers such as brazing are not necessary.

Alumina, Al_2O_3 , ceramic substrate has a CTE value similar to that of the piezoelectric ceramics (Table 4.1). Consequently, no cracks and no delamination emerge during the sintering process. For this reason, the alumina substrate was chosen by our research group for the PZT sensor fabrication [109], [146], with properties range corresponding to state of the art [162] – [164].

Nowadays, new sensors are under development for applications in a harsh nuclear environment. The stainless steel 316L is the common substrate candidate used in these conditions [15], [18], [21], [44]. The mismatch of CTE between ceramics and metal, in this case, suggests the use of intermediate layers [165].

A model, which allows the comparison between both candidates, namely “alumina substrate” and “stainless steel 316L substrate”, is implemented in this chapter. We will see in section 4.1 that a deposit of NBT material on alumina allows getting performances needed for acoustic measurements. After the simulations, the sensors were fabricated. Their characterizations are reported in section 4.2 and section 4.3. The acoustic measurements in liquid (to demonstrate feasibility) and gas environment, devoted to establishing the possibility of in-situ gas measurement under the temperature of 350 °C, are reported in section 4.4. Finally, the constraints for the prototype design integration in an experimental environment of MTR reactors is discussed in section 4.5.

4.1 Alumina substrate as an alternative to the stainless steel

4.1.1 Introduction

During the development of new sensors, the choice of the appropriate materials defines the functionality and reliability. In chapters 1 and 3, the main problem in an association between two different materials for high-temperature sensor development was discussed. Indeed, no standard solution exists, and the approach depends on the application area [63].

Table 4.1 – Coefficient of thermal expansion, at ambient temperature, for materials envisaged to be used in sensor fabrication.

Substance type	Piezoelectric ceramic	316L stainless steel	Alumina
CTE @ ambient temperature	$7 \cdot 10^{-6} / \text{K}$ [166]	$16 \cdot 10^{-6} / \text{K}$ [167]	$8 \cdot 10^{-6} / \text{K}$ [168]

The theoretical model allowing the study of sensor response can be seen as complementary to the free state model used for the fit of piezoelectric detached elements (chapter 3). It consists of adding material layers to the 1D representation of the free piezoelectric element. In the case of this study, we introduce alumina and electrodes layers into the simulation model. Propagation of waves can be modeled by application of the impedance matching equation (described in details in [19]):

$$Z_{in} = Z_c \frac{Z_{out} + jZ_c \tan(\varphi)}{Z_c + jZ_{out} \tan(\varphi)} \quad (4.1)$$

whereby, Z_{in} and Z_{out} is the impedance seen at the input and output of a passive layer (in Ohm), Z_c – acoustic impedance of a passive layer (in Pa*s/m), φ – impedance phase velocity.

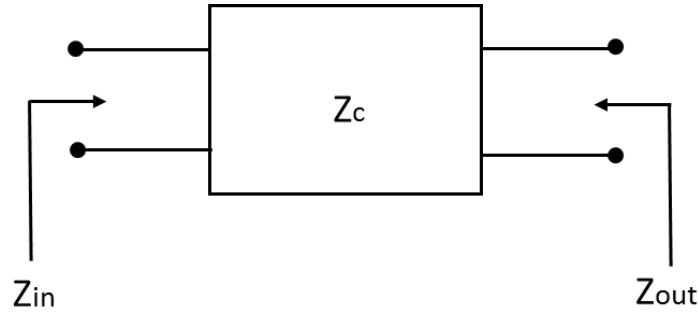


Figure 4.1 – Modeled layer of passive material seen as a quadrupole.

This model allows calculation of the different resonance mode. Indeed, the influence of each layer modified the response of the system (Figure 4.2). The single active piezoelectric element, operating in the longitudinal mode, will exhibit a frequency resonance mode, which appears according to longitudinal celerity and thickness (Figure 4.2 (a)). When an active element is coupled with a substrate, waves propagate in elastic solid, the interference within intermediate layers is generated. It results in maximums and minima in certain frequencies, which positions are depending on elements thicknesses, sound celerity, and densities. The overlap of frequencies reveals in multi-frequency resonance response (Figure 4.2 (b)). The active element and substrate coupled together define the sensor functionality.

The acoustic measurements are performed, by placing the sensor onto a cavity, in which the waves propagate. Waves propagation in liquid and (or) gaseous medium result in overlapping of the system response creating multi-resonances on top of the impedance response (Figure 4.2 (c)).

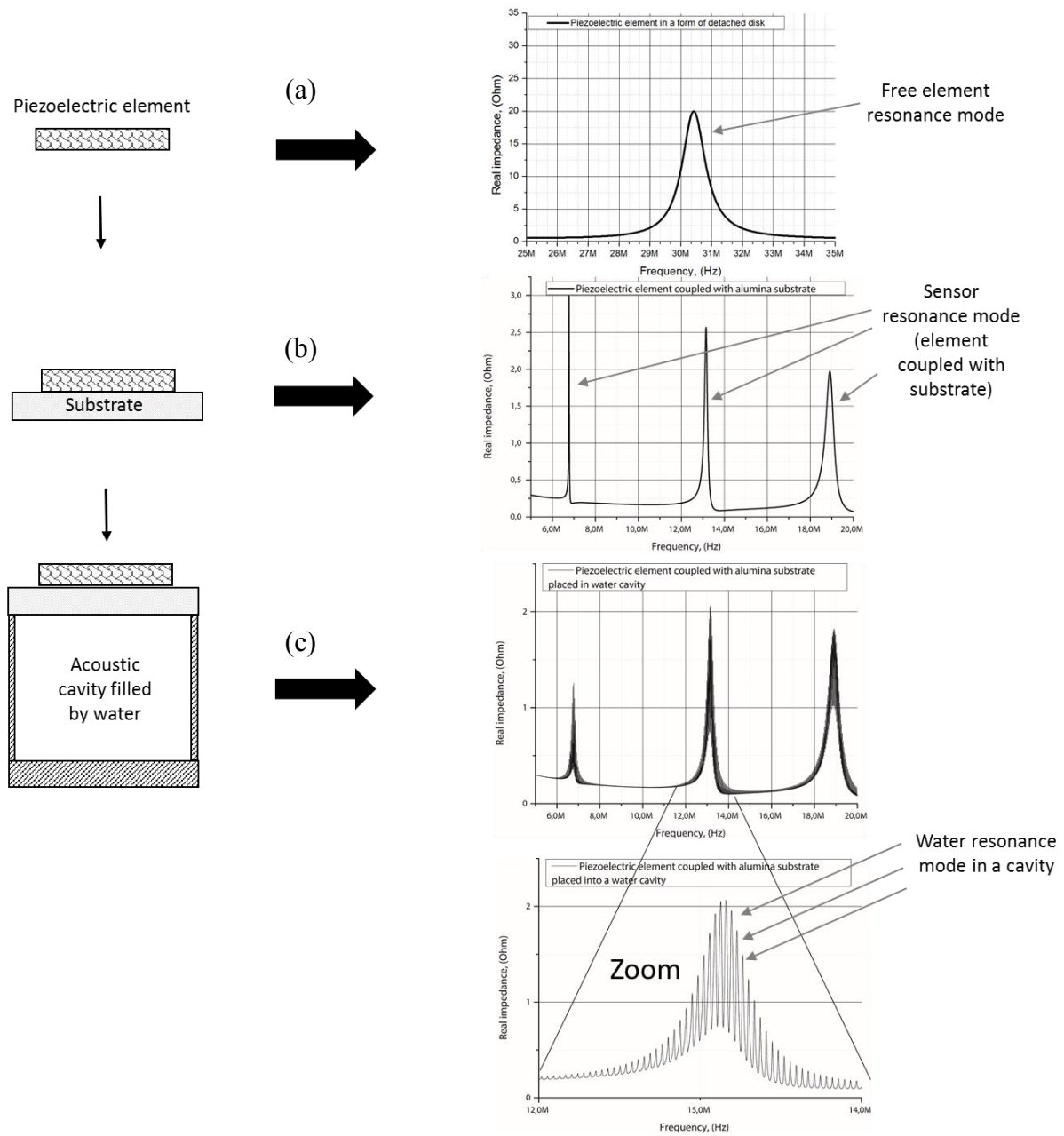


Figure 4.2 – An example of a theoretical response of the single active element (a), coupled with a substrate of a certain thickness (b), and introduced onto acoustic cavity (c).

In this work, to model the acoustic properties, the propagation medium is introduced by an acoustic cavity of centimetric dimensions.

The model concept was already demonstrated in previous publications [7], [44]. Taking as an example, REMORA sensor (designed for fission gas measurement in-situ in experimental reactors), in which commercial piezoelectric material was brazed with 2 cm thick stainless steel

plate and the assembly was welded to an acoustic cavity (Figure 4.3). By registration of echogram and additional signal treatment, the speed, thus the quantity of released gasses was determined through the equation:

$$c = \sqrt{\frac{\gamma RT}{M}} = \sqrt{\frac{\gamma RT}{xM_{Xe} + (1-x)M_{He}}} \quad (4.2)$$

where c is the speed of sound (in ms^{-1}), T – temperature (in K), M – molar mass, R – universal gas constant and γ – adiabatic index ($=5/3$ for monoatomic gas).

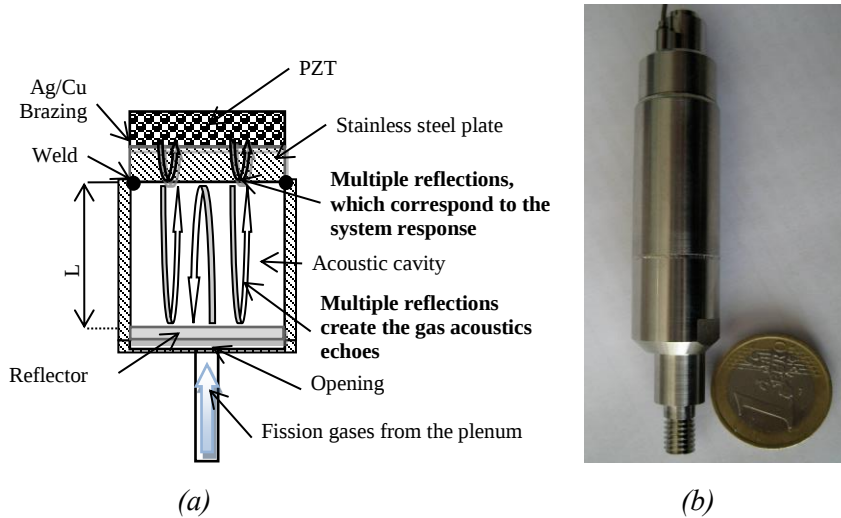


Figure 4.3 – REMORA acoustic gas sensor.

(a) Schematic representation. (b) Sensor overview.

4.1.2 Theoretical comparison of sensor response according to the substrate type

First of all, let's justify the choice of an alumina substrate, for which the theoretical model, described in details in section 4.4, is used. For this purpose, the comparison of the theoretical response of deposited NBT material on stainless steel and alumina substrate was performed (Figure 4.4).

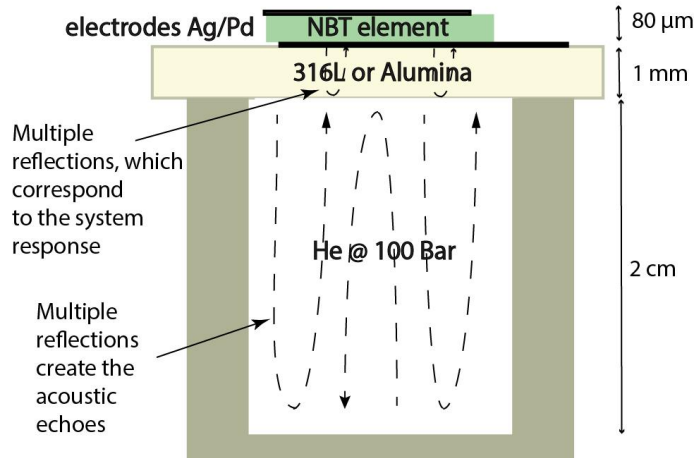


Figure 4.4 – Model of a screen-printed sensor for acoustic response simulation as a function of substrate type.

Table 4.2 – Parameters used for simulation of screen-printing sensor response as a function of the substrate type.

Case	NBT thickness	Substrate type & thickness	Cavity thickness	Acoustic medium
1	80 μm	Stainless steel 316L of 1 mm	2 cm	Helium gas @ 100 Bars
2		Alumina of 1 mm		

The acoustic theoretical response can be represented in terms of “tempograph”, which is a filtered acoustic signal (for more details, see section 4.4). The data, for both cases (stainless steel 316L and alumina substrates), are shown in Figure 4.5.

The signal amplitude increased by approximately 40 % in the case of deposition onto an alumina substrate (Figure 4.5). Not only **alumina substrate** is having CTE approaching that one of piezoelectric NBT ceramics, but it was also found to be a better candidate for acoustic energy distribution.

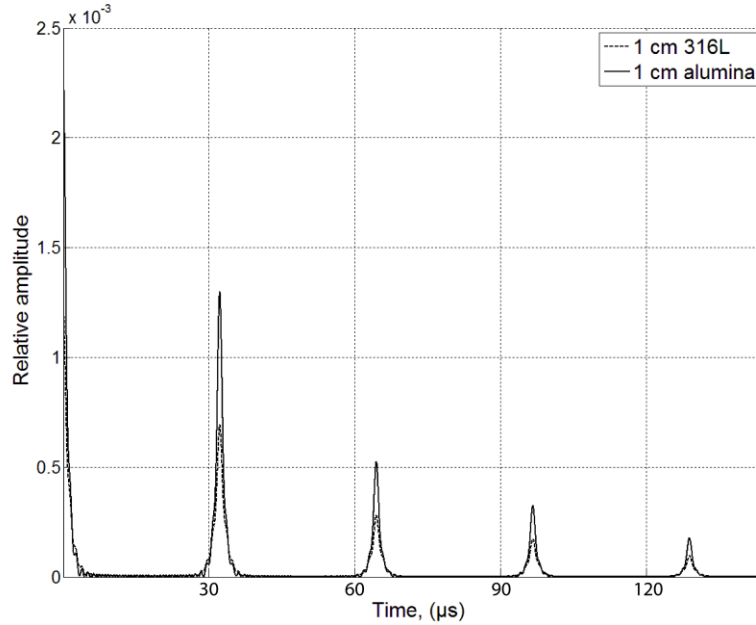


Figure 4.5 – “Tempographs” obtained from theoretical acoustic measurement of gas inside the cavity with the 316L stainless steel or the alumina substrate configuration.

4.1.3 Theoretical comparison of sensor response as a function of substrate thickness

The sensor acoustic response depends on various parameters, i.e., substrate type, thicknesses of the active element and substrate, cavity size just a few to mention. In subsection 4.1.2, the advantage of using alumina substrate for sensor casing was shown. Hence, the alumina plates of 700 μm thickness used for PZT sensor fabrication in previous researches [109] might be an appropriate candidate for NBT sensor device development. To justify the choice of substrate thickness, an acoustic response was modeled as a function of substrate thicknesses (500 μm , 700 μm , and 1000 μm).

Table 4.3 – Screen-printed acoustic sensor. Validation of substrate size.

Case	NBT thickness	Alumina thickness	Cavity thickness
1	80 μm	1000 μm	2 cm
2	80 μm	700 μm	2 cm
3	80 μm	500 μm	2 cm

The “tempographs” as a function of alumina thickness is shown in Figure 4.5. The alumina in the thickness from 500 μm to 1000 μm can be used for sensor fabrication. Overall, the compromise between slightly better sensitivity (500 μm) and durability (1000 μm) has to keep in mind.

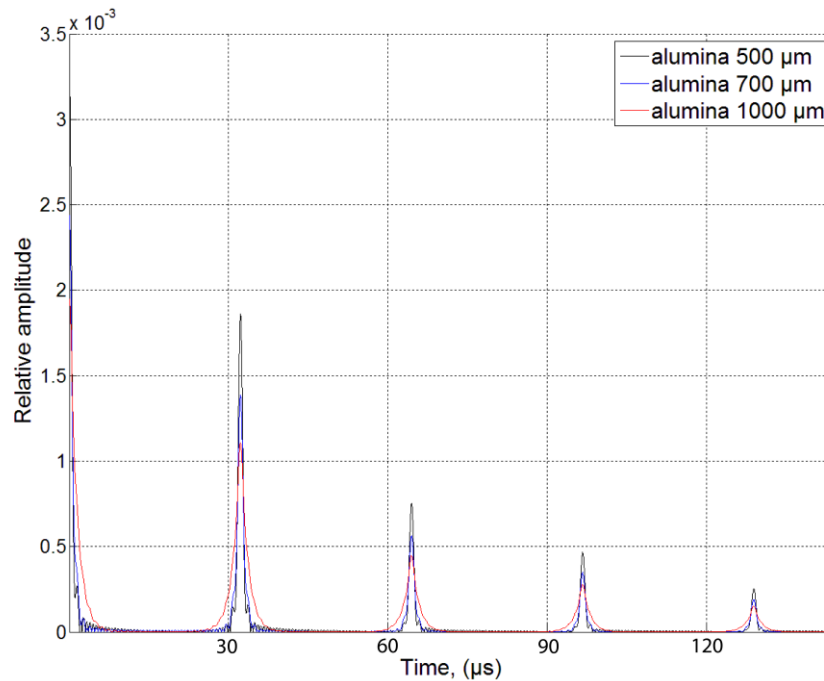


Figure 4.6 – “Tempograph” as a function of alumina substrate thickness, obtained from theoretical acoustic measurement of gas.

The decreasing of substrate thickness leads to better sensitivity for the aforementioned screen-printed sensor.

4.1.4 Conclusions

The sensors configuration was validated by studies based on the method detailed in section 4.4. The sensor concept was established as follows:

- Alumina substrate of 700 μm used for PZT sensor production is an appropriate candidate to be used in sensor fabrication.
- The studies show that by coupling an active element with an alumina substrate, an acoustic signal theoretically amplifies by 40% (for a given configuration).

4.2 Sensor fabrication and characterization

Development of sodium bismuth titanate ceramics detached elements, produced by the screen-printing method, was investigated in chapter 3. Eight versions of piezoelectric materials were produced; manufacturing conditions were optimized. Each material was characterized on its morphological, chemical, electric, dielectric, piezoelectric and electromechanical properties. With a temperature test, it was demonstrated that the NBT material fabricated from the fine grain size powders is a favorable candidate for use under 350 °C.

For sensors fabrication and characterization, the same protocol, as described in chapter 3, was used. In subsection 4.2.1 a brief description of their fabrication is presented. Subsection 4.2.2 describes the measurements carried out. The comparison of results obtained with a detached disk (of the same material) is performed.

4.2.1 Fabrication of NBT sensors

Several NBT sensors on an alumina substrate (700 μm thickness) were fabricated using a standard screen-printing process [164] where layers form a stack: alumina-electrode-NBT-electrode as shown in Figure 4.7. The NBTv3 was used as an active material in sensor development.

In this section, measurements data are presented for one sample with the best properties and a relative error obtained from the complex of measurements. The overview of fabricated sensors is presented in Annex A.

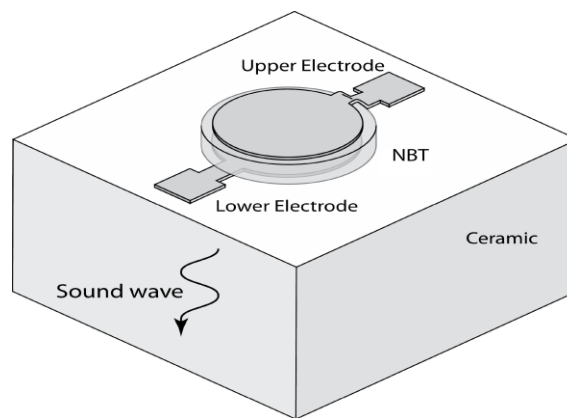


Figure 4.7 – Schematic representation of the fabricated NBT sensor.

During the fabrication process, the desired thickness of the active element (after sintering) is in the range of 100 μm . However, the ink of NBTv3 contained a high value of the organic vehicle. Consequently, during sintering at 850 $^{\circ}\text{C}$ for 15 minutes, the thickness of the NBT layer was reduced more than twice. The thicknesses of the NBTv3 layer on alumina substrate after sintering were about 40 μm , with electrodes on Ag/Pd (conductive ink ESL 9693-G) of 5 μm on each side. The electrodes diameter is 4 mm.

4.2.2 Measurements of NBT sensor properties

4.2.2.1 Morphological analysis

The micrographs reveal the small grain size porous structure of ceramics (Figure 4.8). The holes on top of the NBTv3 layer is related to the imperfections of the fabrication process. Sealing glass CF7575, playing the role of a constituent that decreases the sintering temperature, are of coarse grains (more than 10 μm for some particles). At a temperature of 500 $^{\circ}\text{C}$, grains of CF7575 start to melt, and voids appear in their place. Such microstructure suggests degradation of electrical and mechanical properties.

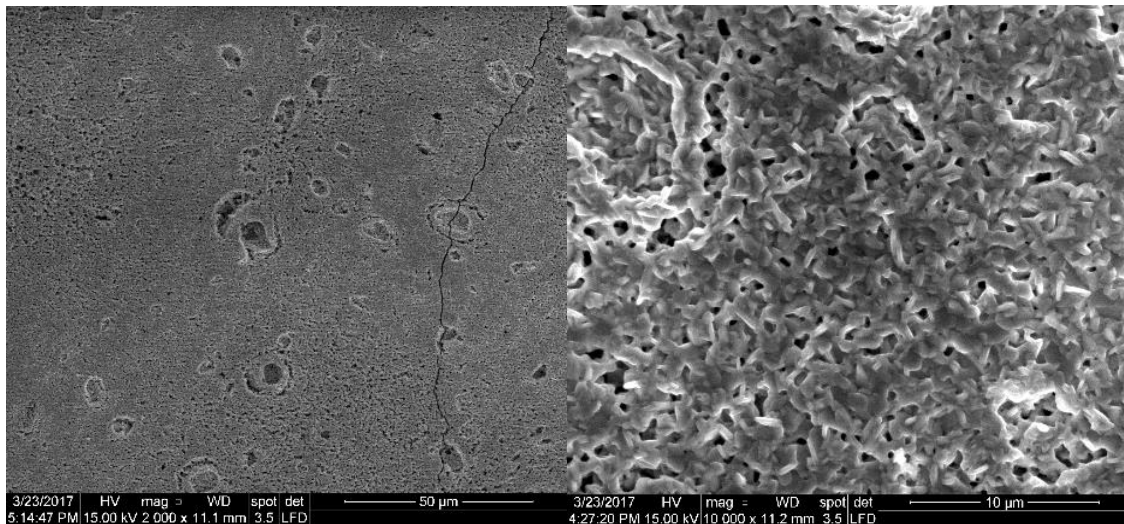


Figure 4.8 – Morphological analysis of NBTv3 sensor.

Image (a) at Magnitude of x2000; (b) at Magnitude of 10000x. The surface of NBTv3 ceramic is damaged, the holes and cracks are observed. Such microstructure suggests degradation of electrical and mechanical properties.

Nevertheless, it was found, that the parameters of NBTv3 sensors were enhanced compared to the results obtained for detached elements (subsection 4.2.2 and section 4.3). It believed to be due to good adhesion between NBT and alumina layers, which strengthened the grain bonds and densifies the structure in the intercalation between ceramics.

4.2.2.2 NBT sensor. Resistivity

The resistivity was measured with the same test bench used for detached elements (Figure 3.9). The leakage current was measured with a Keysight 2657A source meter, and the resistivity was calculated from Ohm's law (subsection 3.2.2). The resistivity at room temperature for an NBTv3 sensor on alumina substrate increased from 4E12 Ohm*m (for detached disk) to 1E13 Ohm*m. Its evolution as a function of temperature is presented in subsection 4.3.1.

4.2.2.3 NBT sensor. Dielectric properties

The sensors dielectric properties, at room temperature, were measured both by a PM300 Piezotest d33 PiezoMeter Systems and an E4990 Impedance Analyzer at 1 kHz. The dielectric permittivity ϵ_{33} measured for NBTv3 was found to be by 19 % lower compared to detached NBT material of the same version (Table 4.4). The dielectric loss $\tan(\delta)$ also decreased from 0.01 to 0.008 (Table 4.4). Measurements of relative dielectric permittivity and dielectric loss $\tan(\delta)$ as a function of temperature was carried out with a ModuLab XM MTS in the range from 30 °C to 350 °C and are presented in subsection 4.3.2.

Table 4.4 – Dielectric properties of an NBTv3 sensor fabricated by the screen-printing method in comparison with a detached element, state of the art and Pz46 commercial element.

NBT type	NBTv3 sensor on alumina substrate	NBTv3 material detached disk	NBT Wang et. al. [90]	Pz46
Relative dielectric permittivity, ϵ_{33}	104 ± 4	135 ± 10	145	125
Dielectric loss, $\tan(\delta)$	0.0075 ± 0.002	0.01 ± 0.002	0.0078	0.01

4.2.2.4 NBT sensor. Piezoelectricity and electromechanical parameters

The piezoelectric charge coefficient, d_{33} , is measured with PM300 Piezotest d33 PiezoMeter Systems. In the case of alumina substrate component, a contact with the bottom electrode was made by application of conductive silver paste.

The measurement of d_{33} with PM300 Piezotest d33 PiezoMeter Systems is validated for the massive piezoelectric components (of thickness from 500 μm). For the piezoelectric NBT element deposited by the screen-printing method, the measurement of piezoelectric charge coefficient in longitudinal mode is affected by charges from d_{31} related to the substrate thickness. Therefore, the measured coefficient d_{33} is the effective measurement of the stack. N. Torah et al. [169] determined the relation between this d_{33} effective measured coefficient and real d_{33} of a piezoelectric element:

$$\frac{\partial D_3}{\partial T_3} = d_{33}^{effective} = d_{33} + 2d_{31} \left(\frac{-\frac{v_{sub}}{Y_{sub}} - s_{13}^E}{s_{33}^E + s_{12}^E} \right) \quad (4.3)$$

where D_3 is the electric displacement and T_3 is a mechanical stress in polar axis 3; Y_{sub} and v_{sub} are respectively the Young modulus and the Poisson coefficient of the substrate. This remains an indicative title because, in the rest of the work, we will not use this equation. We will keep the d_{33} displayed by apparatus and comparisons with the state of the art will be the same, since most publications indicate the coefficient measured by the device.

The d_{33} coefficient as a function of the applied electric field (during polarization) for an NBTv3 sensor is presented in Figure 4.9. The same value as for detached element of 14 pC/N was obtained by application of the electric field of 170 kV/cm. However, under the field of 170 kV/cm, the break down occurs thus the samples and the samples required the polarization in the silicon oil. For this reason, most of the sensors were polarized at 150 kV/cm under air conditions, which simplifies the set-up.

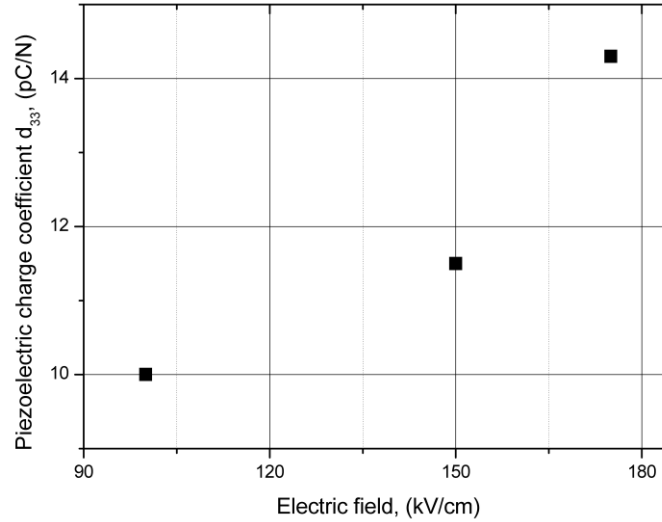


Figure 4.9 – Piezoelectric charge coefficient evolution as a function of applied electric field for a screen-printed NBTv3 sensor.

The impedance of NBTv3 sensor on the alumina substrate was observed with an E4990 Impedance Analyzer. Different resonance modes of the piezoelectric element coupled with a substrate then appear (Figure 4.10). The parameters of the stacks (mainly for the alumina substrate) such as speed of sound, density, and thickness are introduced after measurement. The theoretical model introduced in section 4.1 was used to fit measured impedances. The theoretical peaks overlap the measured data of a sample of NBTv3, which indicates the feasibility of the model. Electromechanical properties found for an NBTv3 active element, in this particular case, are represented in Table 4.5.

Table 4.5 – Electromechanical parameters of NBTv3 sensor fitted with Matlab software.

Symbol	Quantity	Value NBTv3
F_p	parallel frequency	55 MHz
N_t	frequency constant	2220
qF_p	mechanical quality factor	10
kt	electromechanical coupling factor	0.12
$capa$	capacitance	245 pF ($\epsilon_{33} = 80$)
$qcapa$	dielectric loss	450 ($\tan(\delta) = 0.002$)

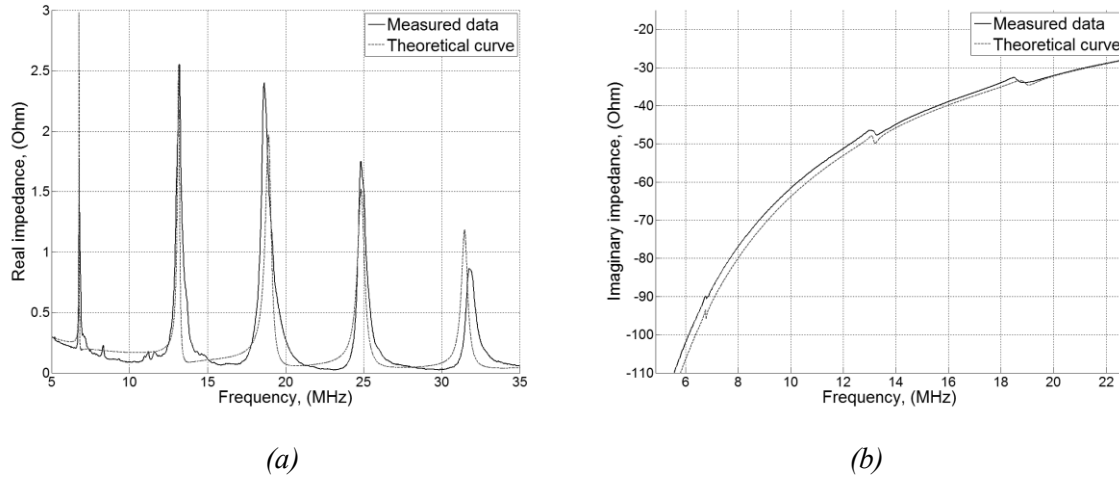


Figure 4.10 – Electrical impedance of NBT sensor polarized under the electrical field of 150 kV/cm with an associated fit.

(a) real part; (b) imaginary part.

4.2.3 Conclusions

Sensors made from NBTv3 material were characterized on their electric, dielectric and electromechanical properties. They are represented with measurements performed for one sample with relative errors from the stack of measured data. The comparison with the measurement carried out for a detached element (of the same material version) indicates the enhancement of resistivity and dielectric properties for on alumina sensor. The electric response of the polarized sample is in agreement with theory (section 4.1), whereas the resonance modes from the alumina substrate have appeared. Overall, the properties of NBTv3 sensors were found to be superior to detached elements, which may be explained to the coupling phenomenon within alumina and piezoelectric ceramics.

4.3 Characterization of sensor properties as a function of temperature

In chapter 3, the evolution of resistivity and dielectric properties as a function of temperature were investigated for NBT materials. For screen-printed sensors, the same measurements were carried out, and the data are compared with measurements for NBT detached disks. Likewise, to section 4.2, measurements are presented for one sensor of NBTv3 with appropriate relative errors.

The impedance response of a sensor indicates the possibility to carry out an acoustic measurement. Hence, complementary to resistivity and dielectric properties measurement, the impedance was registered up to 350 °C (subsection 4.3.3). Its evolution as a function of temperature reveals the behavior of electrical impedance response. In addition, the electromechanical properties monitoring can be performed from the theoretical model introduced in section 4.1 and described in details in section 4.4.

4.3.1 Screen-printed sensor. Resistivity evolution as a function of temperature

The resistivity was measured in the range from 30 to 175 °C. This range includes the polarization temperature and is the same used for detached elements characterization. Hence, the measurements performed for the NBTv3 sensor was compared with the previous characterization of NBTv3 material. In Figure 4.11, the measurement at 30 °C and 175 °C are shown.

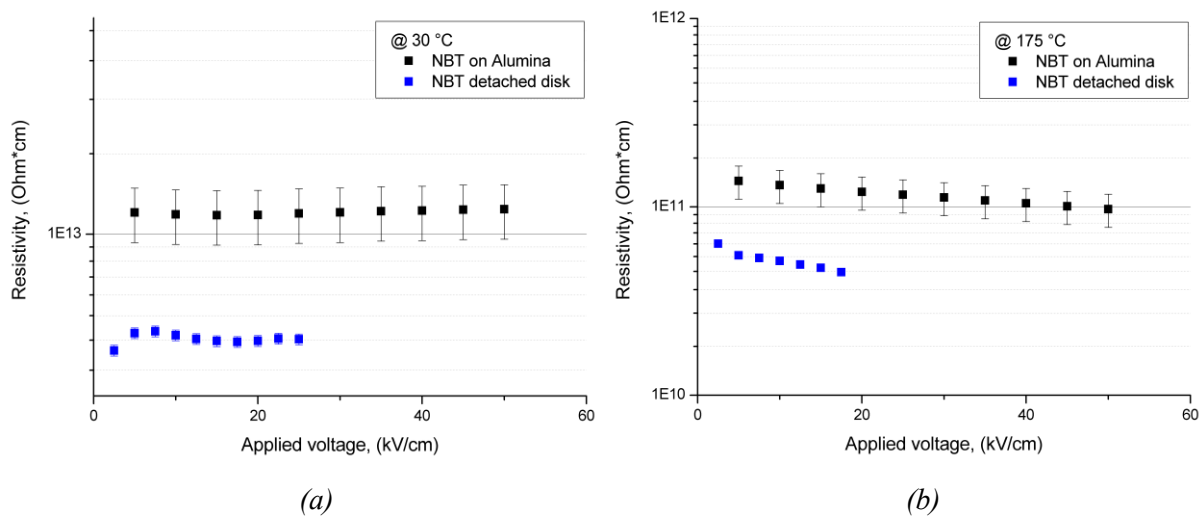


Figure 4.11 – Resistivity evolution of screen-printed on alumina sensor in comparison with NBT detached disk of the same material (NBTv3) as a function of temperature.

(a) at 30 °C; (b) at 175 °C.

The increase in the resistivity at 30 °C and 175 °C for the sensor on an alumina substrate in comparison to detached disk was observed. It suggests that the sensor of NBTv3 possess the stability of the properties in this range of temperature (up to 175 °C) and can be easily polarized.

4.3.2 Screen-printed sensor. Dielectric properties evolution as a function of temperature

Dielectric properties were measured following the same process described in subsection 3.3.2. The NBT screen-printed sensor was put into a hot plate, and the measurement was carried out in the range from 30 °C to 350 °C by gradually increasing the temperature (Figure 4.12).

For the NBTv3 sensor, the evolution of relative permittivity as a function of temperature was found to be lower compared to the detached disk of the same material. Dielectric permittivity is one of the parameters which establish and rely upon piezoelectric charge coefficient d_{33} and piezoelectric voltage coefficient g_{33} (equations 3.10 and 3.11). Its evolution with temperature can be an indicator of relative stability for the piezoelectric coefficients as a function of temperature (electromechanical coupling factor k_{33} and elastic compliance s_{33}^E are another two). The dielectric loss $\tan(\delta)$ stability with a temperature was enhanced with the value below 20 % at 350 °C.

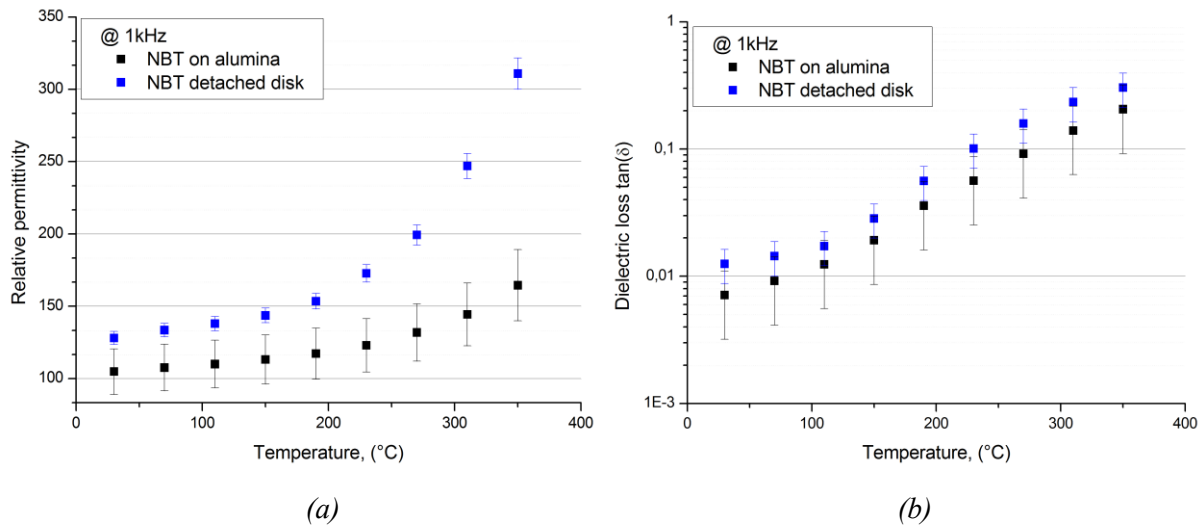


Figure 4.12 – Dielectric properties (at 1 kHz) evolution of screen-printed on alumina sensor in comparison with NBT detached disk of the same material (NBTv3) as a function of temperature.
 (a) Relative permittivity ϵ_{33} ; (b) Dielectric loss $\tan(\delta)$.

4.3.3 Screen-printed sensor. Impedance evolution as a function of temperature

The sensor was placed on a hot plate, as described in the previous experiment. The measurements of electrical impedance as a function of temperature were carried out from 30 °C to 350 °C by gradually increasing of temperature and instantaneous measurements (subsection 4.3.3.1) and regarding impedance observation as a function of time under given temperatures (subsection 4.3.3.2).

4.3.3.1 Response on instantaneous solicitation

The measurements were carried out instantaneously after a sample reaches the corresponded temperature. To better observe impedance variation, we focused on the second zone of the resonance, which is in the frequency range of 12-13 MHz (Figure 4.13). With temperature increasing the resonance of the screen printed NBT sensor decrease in frequency and amplitude. The impedance curve was fitted, and the electromechanical coefficients evolution was studied. In Table 4.6 the parameters at 30 °C (before temperature cycle), at 350 °C and after the temperature cycle (30 °C) are presented.

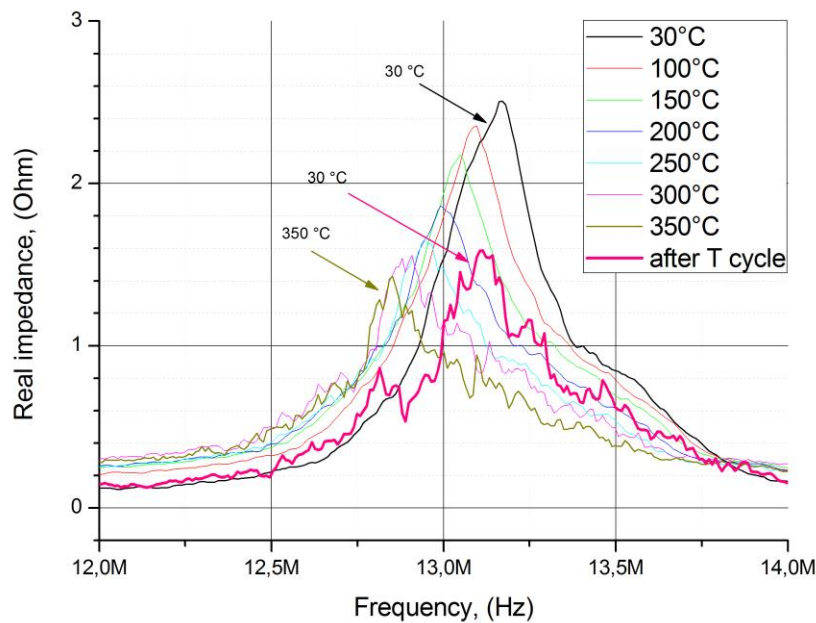


Figure 4.13 – NBTv3 sensor. Impedance evolution as a function of temperature.

Table 4.6 – Electromechanical parameters of NBTv3 screen-printed sensor evolution from 30 °C to 350 °C.

Temperature	qFp	qFp evolution, %	Fp evolution, Mhz	kt	Capa, pF	Loss, $\tan(\delta)$	d_{33} , pc/N
30 °C	10			0.12	245 pF ($\epsilon_{33} = 80$)	0.002	10,5
350 °C	6	50%	0.32	0.12	330 pF ($\epsilon_{33} = 96$)	0.004	
After T cycle @ 30 °C	6	45%	0.06	0.12	245 pF ($\epsilon_{33} = 80$)	0.004	10,4

By this experiment, the degradation in signal impedance amplitude was observed with temperature increment. The implemented theoretical model shows that this degradation in amplitude is related to the decrease in mechanical coupling factor qFp . The deterioration occurred with temperature increases and the level of amplitude did not restore after temperature cycle, whereby, the electromechanical coupling factor, kt , was found to be stable up to 350 °C. The slight increase in a relative permittivity ϵ_{33} at 350 °C was observed. The piezoelectric properties (presented by measurement d_{33} piezoelectric charge coefficient) and permittivity ϵ_{33} before and after temperature cycle remained unchanged.

4.3.3.2 Response evolution on time

The degradation of impedance amplitude with time at high temperatures (100 – 400 °C) can be a limiting factor in the lifetime of samples. Therefore, the endurance to a high temperature for the screen-printed sensor was studied by observing impedance evolution under heat as a function of time following the methodology:

a) The sample, tested up to 350°C, was put into a hot plate for 1 hour at 100 °C, 200 °C, and 300 °C.

b) A second sample (after polarization) was put into a hot plate for 8 hours at 300 °C.

a) The impedance stability under 100 °C, 200 °C, 300 °C for one hour of measurement were determined. The impedance degrades at the beginning of temperature shock, then stabilized in its value. At 300 °C, the fluctuation of the impedance value is presented.

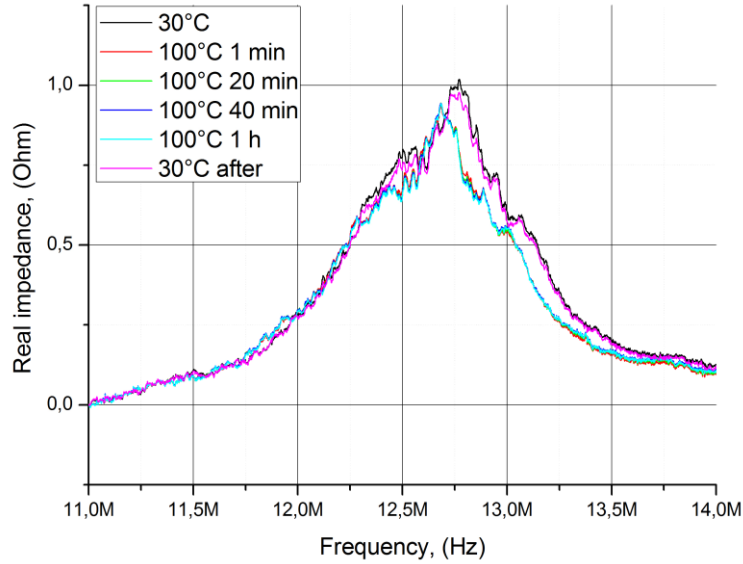


Figure 4.14 – NBTv3 sensor. Impedance evolution. 1 hour at 100 °C.

Slight changing in amplitude and resonance frequency is observed.

There is no significant alteration of the response when the device is at 100 °C (Figure 4.14). The degradation of peak value enhanced with temperature increasing as can be seen in Figures 4.15 and 4.16. Nevertheless, the impedance at 300 °C is still distinguishing, indicating the possibility of the measurement to be carried out.

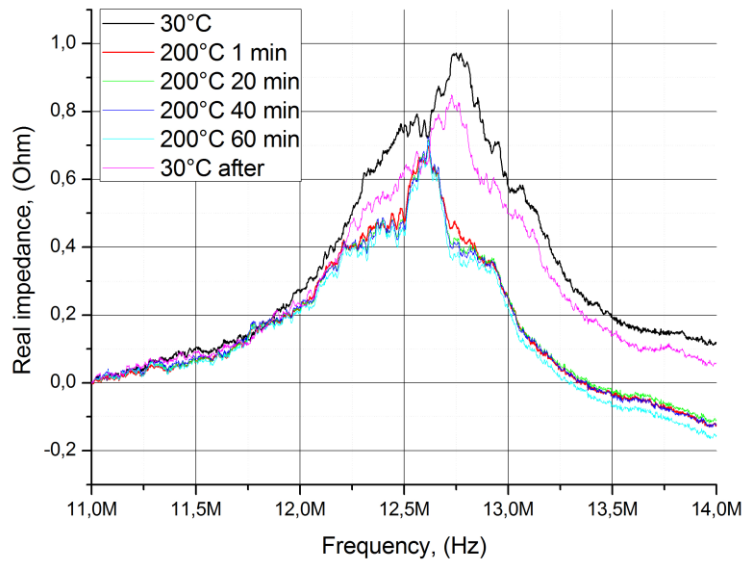


Figure 4.15 – NBTv3 sensor. Impedance evolution. 1 hour at 200 °C.

The signal degrades more in comparison to the measurement performed at 100 °C. After the temperature cycle, the overall impedance value is slightly degraded.

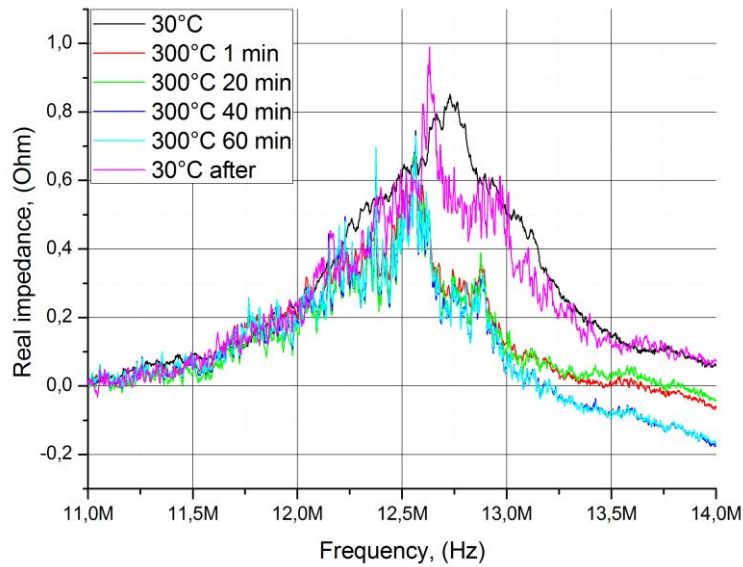


Figure 4.16 – NBTv3 sensor. Impedance evolution. 1 hour at 300 °C.

The oscillation of the resonance due to the heating process of material can be clearly seen. The impedance is degraded at 30 °C after exposition on temperature.

b) The impedance curve was monitored during the 8 hours' period at 300 °C. The value of electrical response was stable (Figure 4.17) which indicates the reliability of the measurement under the time conditions of, at least, up to 8 hours.

The possible explanation in impedance degradation is related to the aging of material properties. It appears that the fabricated NBTv3 materials are soft ceramic with expressed high rate extrinsic contributions related to domain wall motion as a function of temperature [170]. For stabilization of an impedance response, densification is required.

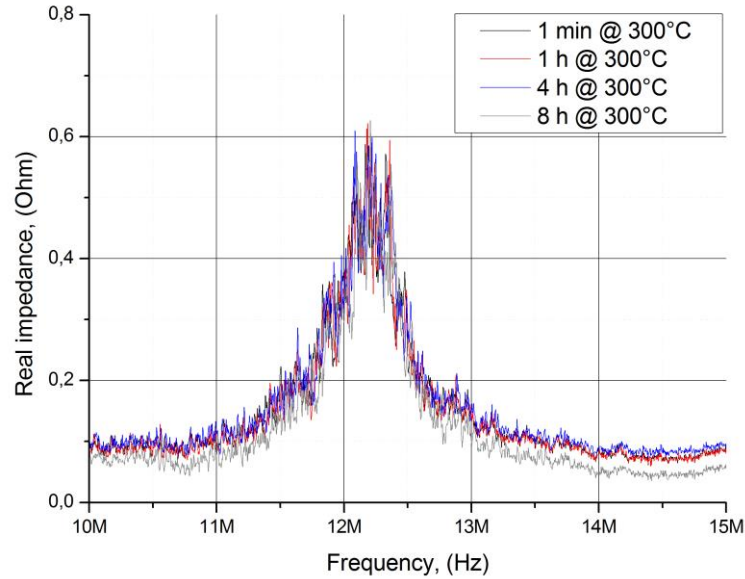


Figure 4.17 – NBT sensor. Impedance evolution at 300 °C during 8 hours of observation.

The electrical impedance remains unchanged revealing the system properties stabilities with time under high temperatures.

4.3.4 Conclusions

The measurements of resistivity, dielectric properties, and impedance as a function of temperature were carried out. The electrical and dielectric properties of the NBTv3 sensor on the alumina substrate were found to be superior to the detached element of the same material. Dielectric measurements of the NBT sensor sample are in good correlation with previous researches on bulk NBT material [90], [91], [125] with the dielectric loss under 20 % at 350 °C. The system response impedance evolution was studied as a function of temperature (Figure 4.14 – Figure 4.17). The impedance remains detectable at 350 °C thus the acoustic measurements are theoretically possible. Furthermore, impedance stability under the temperature of 300 °C for 8 hours indicates sensor reliability in high-temperature environments. Acoustic tests performed with fabricated sensors are presented in section 4.4.

4.4 Acoustic measurements

For acoustic tests, an Olympus computer-controlled pulser/receiver 5800PR and a Tektronix TDS3032 oscilloscope were used correspondingly for signal excitation and acquisition. The possibility of acoustic measurement with the fabricated sensor was shown, first, in a liquid environment (subsection 4.4.1). Based on these measurements, the theoretical model, applied in subsection 4.4.1, was validated. The possibilities for gas detection at room and high temperature (350 °C) are confirmed by application of the same theoretical model (subsection 4.4.2). The measurement of pressurized Helium gas at room temperature are presented in subsection 4.4.3.

4.4.1 Acoustic measurements in liquid

The acoustic pulses propagate reflecting inside the cavity. They are recorded as echograms. Theoretically, the speed of sound can be measured from echogram using the following equation:

$$c = \frac{2L}{\Delta_t}, \quad (m/s) \quad (4.4)$$

where Δ_t is the time (in s) of pulse propagation in a cavity in both directions, L is the cavity depth (in cm)

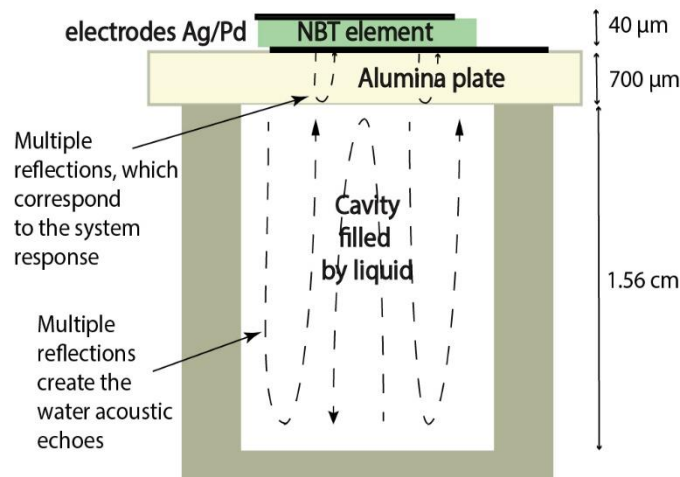


Figure 4.18 – Schematic representation of the acoustic test bench.

The piezoelectric element is placed on the top of a cylindrical cavity filled with water.

The measurement of sensor response in the liquid is an important step which provides information about its sensitivity. For screen-printed NBT sensor on alumina substrate, a first experiment of wave propagation in the cavity (under room temperature conditions), filled with water and ethanol, was carried out. Test bench configuration is shown in Figure 4.18.

The acoustic test, carried out in the cylindrical cavity of 1.56 cm depth, shows a good sensitivity in signal detection (Figure 4.19). The echograms of the measurement are clear and easy to read. Time of flight (TOF) can be used to define measurement Δt . Application of equation 4.4 was used to calculate the speed of waves propagation in liquids. For water and ethanol, the values are, respectively, 1495 and 1250 m/s. These values are in the range of theoretical data for the measured substances [171], [172].

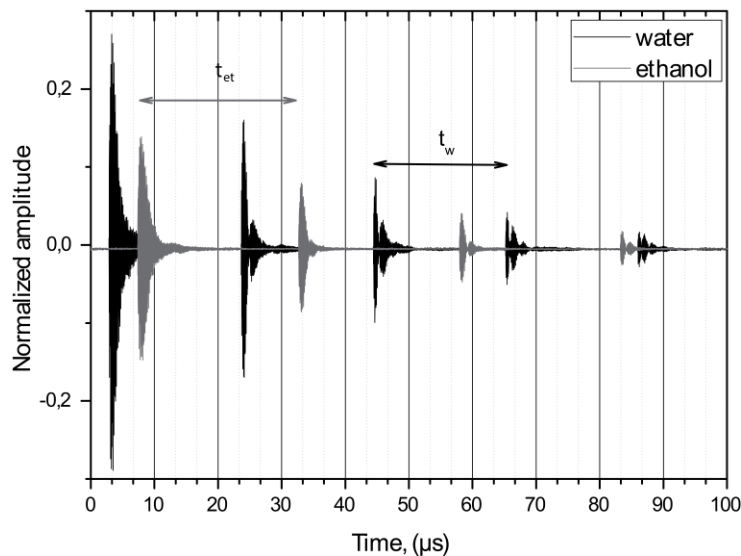


Figure 4.19 – Echogram of NBT sensor in the cavity filled with water or ethanol.

Under harsh measurement conditions, the influences of system noise, temperature, radiation, etc., complicate signal registration. The sensitivity of gas detection is lower. Furthermore, the measurement of mixtures requires additional signal treatment.

It is worth noting that the usual methods of measurement of speed of sound in the time domain cannot be accurately applied to such echograms. The dispersion of ultrasonic signal leads

to a deformation of echoes that prevents the use of intercorrelation methods (Figure 4.19). Therefore, for a precise measurement of speed of sound, a specific signal processing is needed.

The generation of plane waves in the entire range of frequencies and their sum in the cavity produces a stationary wave pattern. A liquid shows resonance at the frequencies $f_n = nc/2L$, whereby c is the speed of sound, L the length of the resonator, and n is an integer number. Using the frequency approach, the principle of the acoustic signal measurement treatment in the close cavity for gas qualification is described in [7] and [44]. Data processing, for our measurements, was carried out with application of the same approach.

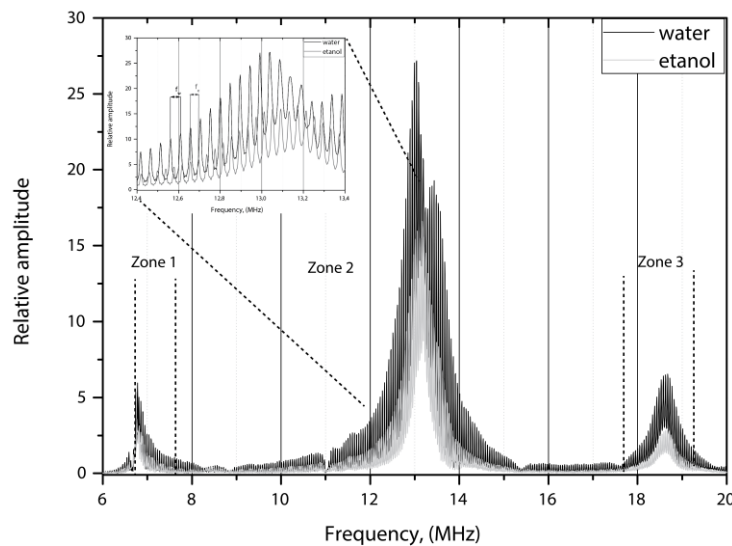


Figure 4.20 – Initial water and ethanol spectra obtained from the modulus of FFT of the echogram

Figure 4.19.

Zone 1, zone 2 and zone 3 – illustrate the interest for operation.

Initially, the part (beginning part) of the echogram signal due to the resonance of piezoelectric material coupled to the alumina substrate is removed. Then, the modulus of the fast Fourier transform (FFT) of the remaining signal is performed. Thus, one could obtain a spectrum containing the peaks of resonance of the fluid under study (Figure 4.20), with the amplitude modulated by the response of the system (corresponding to the resonance of the piezoelectric disc coupled with the alumina substrate). Then, the zone that has the highest sensitivity to the fluid to be characterized is suitably chosen. This last operation allows to filter the signal and rejects some

nondesirable parasitic resonances. The last inverse fast Fourier transform (IFFT) is done and one could obtain, in the time domain, a filtered signal (what we called the “**tempograph**”) on which it is straightforward to measure the TOF, by measuring the time between two peaks, or multiple peaks for more accuracy in results (Figure 4.21).

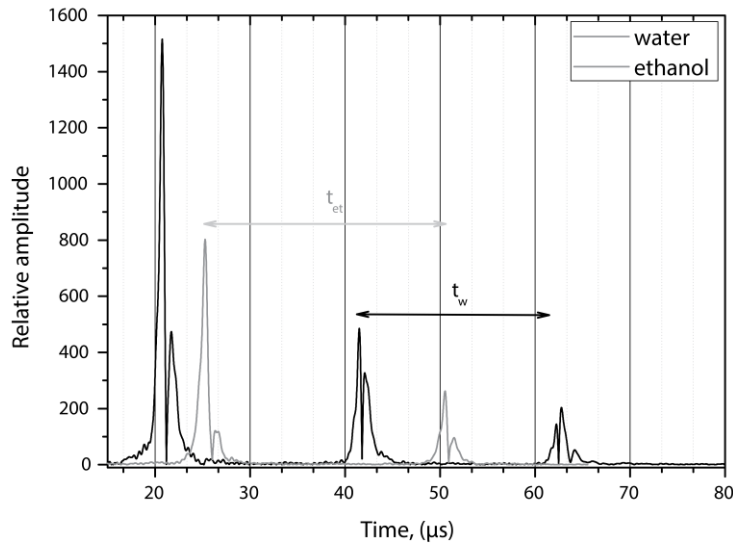


Figure 4.21 – Experimental “tempographs” obtained from the echograms of Figure 4.19 in the frequency range from 12.4 to 13.4 MHz.

It should be noted that the registered signal value primarily depends on the chosen “tempograph” zone. The measurements show three zones in which a signal can be detected and treated. In Figure 4.21, high sensitivity to water and ethanol measurement in the second zone from 12.4 to 13.4 MHz for NBT device is shown.

By the experiment with liquid substances, it was demonstrated that as long the “tempograph” can be registered the measurements are possible. Hence to justify sensor properties for gas measurement, the simulation data are represented in the form of a “tempograph”.

4.4.2 Theoretical examination of the NBT sensor for gas measurement under high temperature

To validate the theoretical model and its reliability, we introduce into our stack model a cavity of water medium. Thus, the theoretical test bench looks like in Figure 4.18.

By application of the same approach as in section 4.1 for impedance matching, the theoretical resonances in the water around resonance frequency of the NBT device were shown and compared with the experimental observation (Figure 4.22). In order to confirm the theoretical model, an inverse FFT treatment was applied to the modeled data (Figure 4.23).

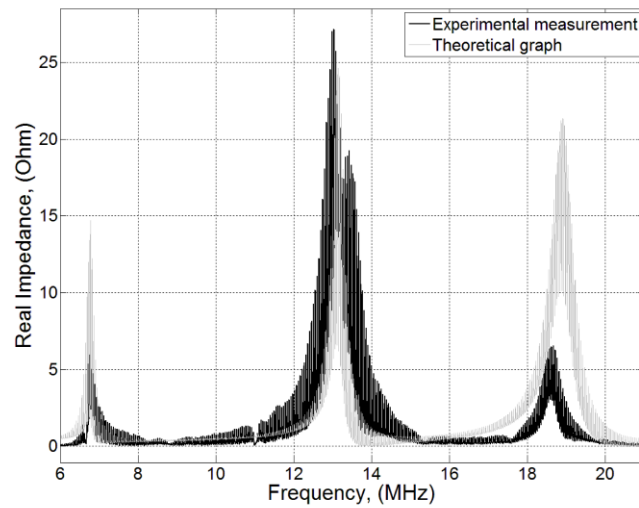


Figure 4.22 – Validation of the model. Theoretical and experimental impedances of the NBT sensor with a cavity filled with water.

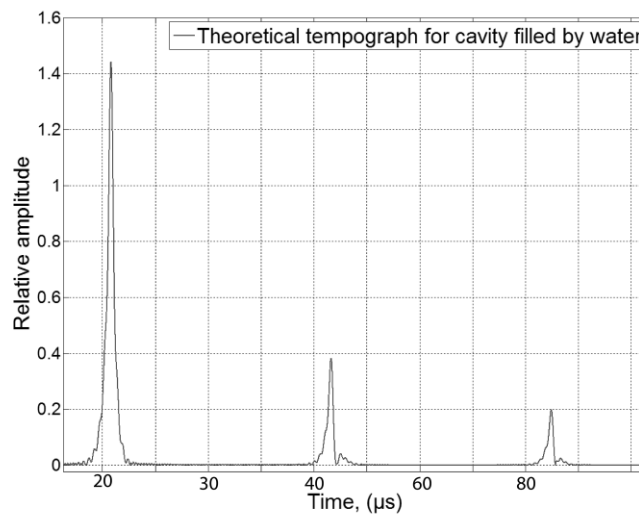


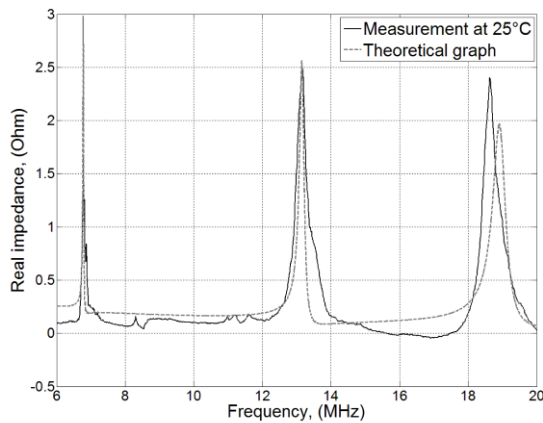
Figure 4.23 – Validation of the model. “Tempograph” obtained from the theoretical impedance in Figure 4.22 in the broad frequency zone.

The feasibility of implementing the developed sensor in harsh environmental conditions for gas measurement is validated theoretically as follows. The sensor is introduced into a cavity (the same length of 1.56 cm) filled by helium. As experimentally it is not yet possible to carry out the measurements at 350 °C with gas, the impedance measured at this temperature was injected into the model.

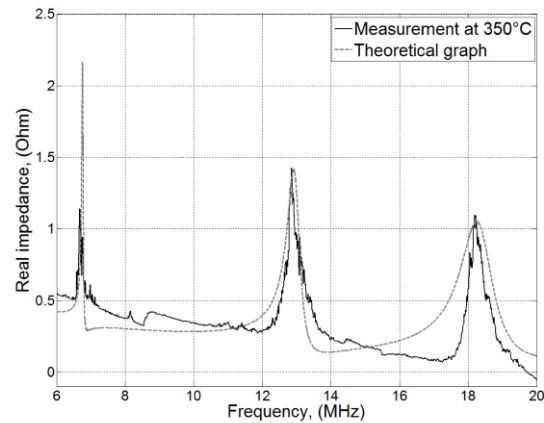
The values of fit shown in Table 4.7 are injected into a gas model. It enables obtaining of electromechanical parameters for two temperatures. Theoretical and experimental impedance curves are represented in Figure 4.24 (a) and Figure 4.24 (b) for respectively 25 °C and 350 °C.

Table 4.7 – Electromechanical parameters of NBTv3 sample for gas measurement.

Symbol	Quantity	@ 25 °C	@ 350 °C
F_p	parallel frequency	55 MHz	43 MHz
N_t	frequency constant	2120	1720
qFp	mechanical quality factor	10	6
kt	electromechanical coupling factor	0.12	0.12
$capa$	capacitance	245 pF ($\epsilon_{33} = 80$)	330 pF ($\epsilon_{33} = 96$)
$qcapa$	dielectric loss	450 ($\tan(\delta) = 0.002$)	210 ($\tan(\delta) = 0.004$)



(a)



(b)

Figure 4.24 – Measured and theoretical impedances of NBT sensor.

(a) for 25 °C; (b) for 350 °C.

To take into account the fact that the properties of a gas change with temperature, the ideal gas law $PV = nRT$ was applied. Gas speed will be different at 25 °C and 350 °C. The speed of helium at 25 °C and 350 °C can be determined from the website of National Institute of Standards

and Technology [173]. Its values were introduced into the model (1045 and 1482 m/s for 25 °C and 350 °C, respectively).

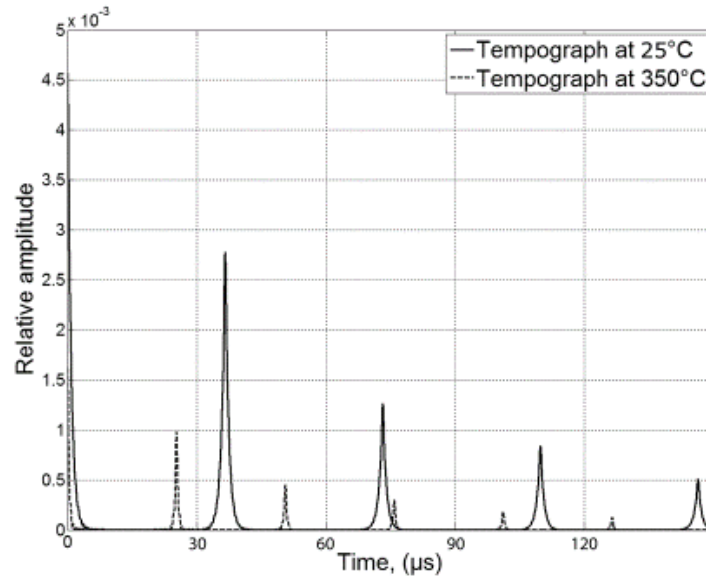


Figure 4.25 – Theoretical “tempographs” of gas detection with fabricated device at 25°C and 350°C.

Figure 4.25 shows that even when the measurement is carried out at 350 °C, the determination of gas properties is still possible.

4.4.3 Gas composition measurement demonstration at ambient temperature

To demonstrate the possibility of gas detection with the fabricated sensor, the liquid cavity was replaced by the metallic rod tube of 14 mm depth glued to the alumina substrate. The first device for gas measurement was constructed by joining the NBT sensor with the cylindrical acoustic cavity.

The set was put inside a pressurized enclosure which enables to establish the pressure up to 70 bar. The signal from the sensor was acquired by the wires passing through a sealed passage. The measurements of pure Helium were carried out under room temperature conditions for the pressure from 48 to 61 bar. The registered echograms (Figure 4.26) were treated in Matlab software. An

FFT and inverse FFT to the corresponding zone of the spectra were applied to carry out the measurements with the “tempographs” (Figure 4.27). Equation 4.4 was applied to “tempograph’s” peaks. The speed in the Helium was found about 1000 m/s which is in accordance with the theory [174].

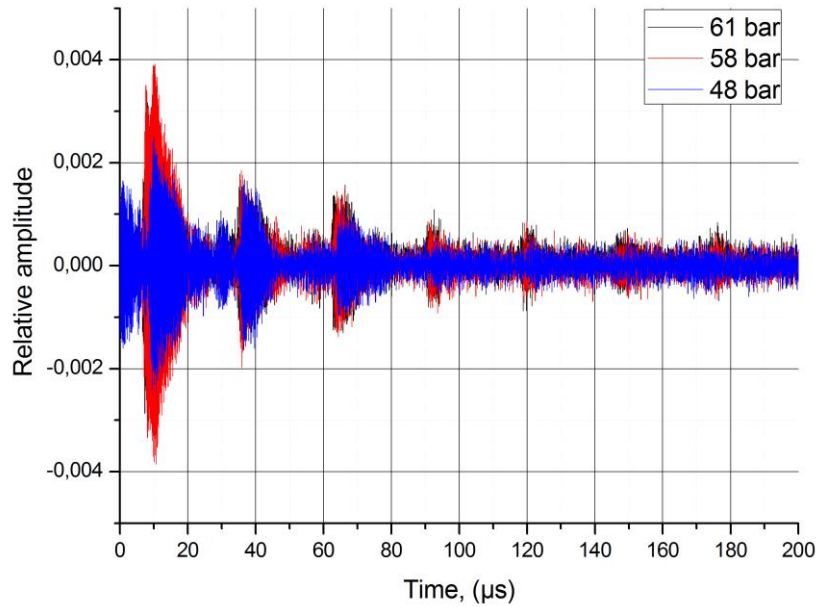


Figure 4.26 – Measurement of helium gas. Registered echograms.

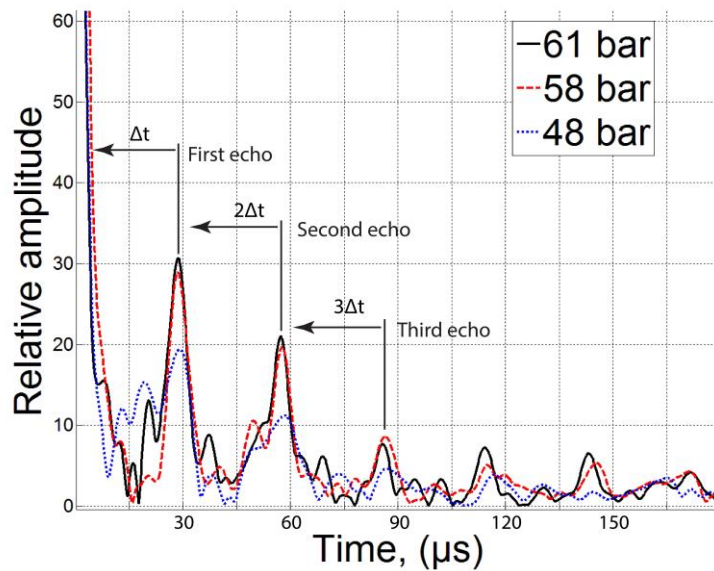


Figure 4.27 – Measurement of helium gas. “Tempographs” obtained from echograms in Figure 4.26.

4.4.4 Conclusions

The fabricated and characterized NBT sensor on the alumina substrate was tested on its acoustic response in the liquid and gaseous environment. The measurement in the liquid environment was intended to show sensor deployment to in-situ gas measurement. Sensor's sensitivity evaluation and confirmation of the theoretical model were done based on this experiment (subsection 4.4.1). The measurement of Helium gas in-situ at room temperature in the pressure range corresponding to real conditions in an experimental reactor (50 to 70 bars) was carried out (subsection 4.4.3). In subsection 4.4.2, the possibility to do the acoustic measurement of released gases at a high temperature of 350 °C was shown with the theoretical model.

4.5 Prototype design

The prototype design is envisaged in the course of this thesis work and is under review for the patent deposition. Hence, in this section, the details of the prototype configuration are omitted. Miniaturized sensors were manufactured. Their characterizations are presented in the given subsection are confirming the possibility of prototype operability under experimental conditions.

The acoustic experimentations carried out under room temperature conditions and the temperature test carried out for screen-printed NBT sensor on alumina substrate confirmed the possibility for in-situ gas measurement with the given device in experimental reactor facilities (MTR) (sections 4.3 and 4.3). In this section, the first view of the new prototype development of sensor integration for measurement in-situ is presented. In subsection 4.5.1 the experimental conditions of Jules Horowitz MTR reactor are briefly described. In subsection 4.5.2 the dimensional constraints to prototype development are presented. The fabrication and characterization of the miniaturized sensor then described (subsection 4.5.3). The temperature test establishes sensor possibility to be integrated for in-situ measurements under a harsh environment in Jules Horowitz experimental reactor (subsection 4.5.4).

4.5.1 Experimental conditions in Material Testing Reactor

The Jules Horowitz Material Testing Reactor (JHR) is a 100 MW pool-type reactor with a compact core which is currently under construction on the CEA Cadarache site. The reactor facility is designed to provide large experimental capacity and flexibility (Figure 4.28). The design of the core provides 10 irradiation cavities (7 of small diameter of 30 mm and 3 of large diameter of 80 mm) located in the core, 100 irradiation cavities located in the Beryllium reflector zone (surrounding the core) and 4-6 irradiation cavities (depending on the core configuration) located in water channels.

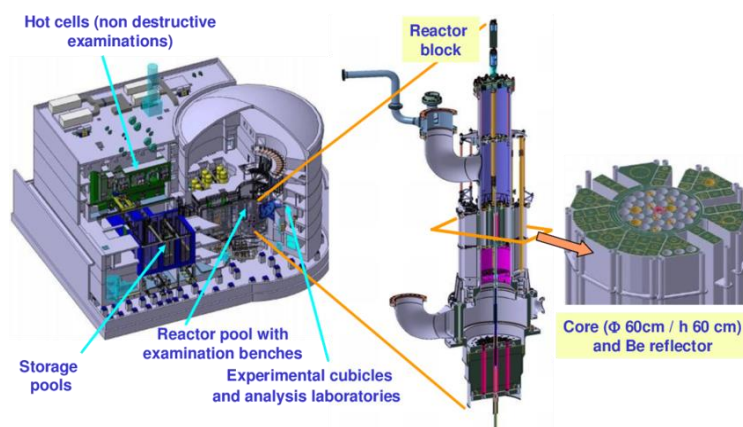


Figure 4.28 – View of the JHR facility [175].

The important role in JHR is devoted to the fuel test devices dedicated to Generation VI reactors [17]. They are represented by three devices:

- MADISON device dedicated to the investigation under nominal conditions, (evolution of fuel microstructure clad corrosion, fission gas releases...)
- ADELIN device dedicated to off-normal situations with extreme power ramps.
- LORELEI device dedicated to accident situations.

The NBT screen-printed sensor, developed for the fission gas measurement experiment in the temperature conditions of up to 400 °C, is expected to be tested in MADISON device (temperature of water loop of 320 °C) and ADELIN device (temperature of 345°C ± 10° of fuel rod).

4.5.1.2 MADISON device

The experiment device is dedicated to fuel studies under standard pressure conditions. A water loop, implemented in a cubicle of the reactor building, will feed the in-pile part with water of well-controlled conditions [175]. Depending on the experimental need, the design of water loop can provide water of Pressurized Water Reactor (PWR) (155 bars, temperature lower than 320°C) or Boiling Water Reactor (BWR) (75 bars, temperature lower than 290°C) conditions. The in-pile part will be installed on a displacement system in the Beryllium reflector and is made of a pressure flask capable of maintaining the highly pressurized fluid (Figure 4.29 (a)) [175]. The internal diameter of the pressure flask is 62 mm which offers a large volume dedicated to the important panel of experimental programs. Depending on instrumentation dimensions' irradiation rigs of 1-2 samples or of 4 samples can be used. An example of an irradiation rig is shown in Figure 4.29 (b).

Besides the fission gas measurement, MADISON device will contain the instrumentation for temperature, clad/fuel elongation, diameter gauge, gas pressure, neutron flux measurements etc... The adequate environment conditions (linear power, temperature, mechanical stress profiles) during irradiation will be maintained.

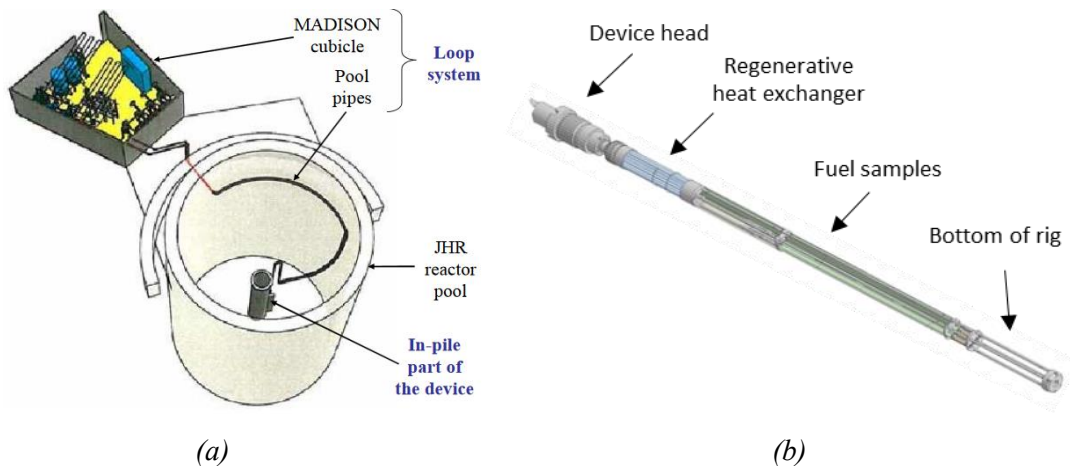


Figure 4.29 – View of MADISON experimental device in the JHR facility.

(a) Experimental cubicle; (b) Irradiation rig.

4.5.1.3 ADELINe device

Likewise, MADISON device, ADELINe is dedicated to Light Water Reactor (LWR) fuel. It is made of an in-pile part and out-of-pile water loop. The objective of the ADELINe experiment is to investigate fuel behavior of a single rod under off-normal conditions (high pressure and temperature) which can lead to clad failure. The device characterized with high thermal balance accuracy (of 6% at 2 s) with a maximum power of 620 W/cm (390 W/cm for burnup bigger than 90 GMj/t).

High power is reached by using zirconium alloys as a material for the test device structure. The representative cladding temperatures are obtained by adapting the thermal-hydraulic parameters. The instrumentation dedicated to temperature, pressure measurement, rod elongation, and rupture investigation is just a few to mention that will be integrated into ADELINe device.

4.5.2 Requirements for prototype configuration

Along the experimental conditions in MTR reactor it is compulsory that the instrumentation has to be miniaturized. The sensor for fission gas measurement shall be placed inside a fuel rod. The fuel rod will be integrated inside MADISON and (or) ADELINe device. The developed screen-printed NBT sensor shall be integrated close to the plenum part (upper part of a fuel rod dedicated to released gases collection) with the inner diameter restriction of 13 mm. Envisaged configuration concept is shown in Figure 4.30.

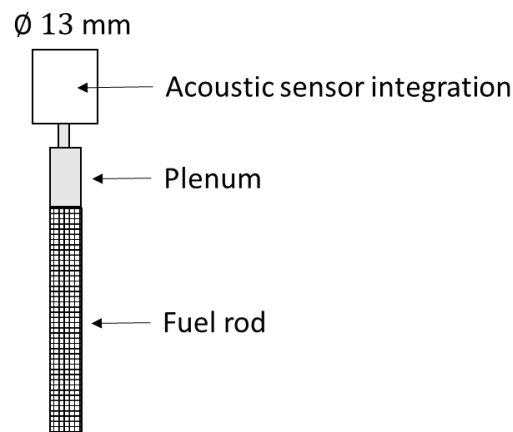


Figure 4.30 – Acoustic sensor integration inside a combustion rod.

Based on the fabrication process specification on active element deposition into an alumina substrate, the first step is to reduce the dimensions of a sensor. Thus the active element on a substrate can be integrated inside the pressurized enclosure (connected to plenum).

4.5.3 Fabrication and Characterization of the miniaturize sensor

The screens with adjusted pattern dimension, for the screen-printing process, was designed in LayoutEditor. The electrodes were maintained at 4 mm in diameter. However, the length between the boards, from one electrode to another, was changed to 10 mm. The screens were manufactured by DB Product. The fabrication process of the NBT miniaturized sensor was similar to NBTv3 sensor manufacture. After deposition of the “bottom” electrodes, 7 piezoelectric layers were deposit on-top, forming the layer of 100 μm thickness. The superior electrode was deposit to finish the process, and the samples were sintered in a bismuth-saturated atmosphere at 850 $^{\circ}\text{C}$ during 15 min. The view of the miniaturized device is shown in Figure 4.31.

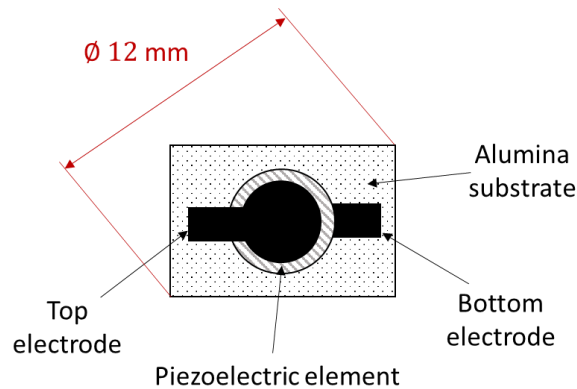


Figure 4.31 – Miniaturized sensor device. View from the top.

For miniaturized sensor fabrication, the ink of NBTv8 co-doped with Nb-W was used. The piezoelectric properties (d_{33}) of the detached elements from this material reached 20 pC/N which is relevant to the value for the Pz46 commercial element.

The main purpose of this fabrication was to demonstrate the capability in the manufacturing of a miniaturized device with the properties of NBT material. Hence, the electric field applied during polarization was adjusted to 100 kV/cm. In this particular set-up, no silicon oil for

polarization process is required. With the applied E-field of 100 kV/cm, the piezoelectric charge coefficient d_{33} of 10 pC/N was obtained. This value was sufficient to perform the preliminary impedance analysis (Figure 4.32). By increasing of an electric field to the range reported for NBTv8 detached disks (150 kV/cm – 170 kV/cm) one could expect the similar value of d_{33} for NBTv8 miniaturized sensor.

The electrical response of the miniaturized sensor is shown in Figure 4.32. Its response is similar to the NBTv3 sensor response of bigger dimensions. It is suggested that NBTv8 miniaturized sensors have similar acoustic properties.

Table 4.8 – Miniaturized NBTv8 screen-printing sensor characteristics comparison with detached NBTv8 element, state of the art, and Pz46 commercial element.

NBT type	Miniaturized sensor (NBTv8)	NBTv8 material detached disk	NBT Wang et. al.	Pz46
Resistivity, (Ohm*m)	1.7E13	2.3E13		7.5E12
Relative dielectric permittivity, ϵ_{33}	135 $\pm$ 4	150 $\pm$ 10	145	125
Dielectric loss, $\tan(\delta)$	0.011 $\pm$ 0.002	0.0085 $\pm$ 0.001	0.0078	0.01
d_{33} , pC/N (E-field applied during polarization)	10 (100 kV/cm)	20 (150 kV/cm)	28	20

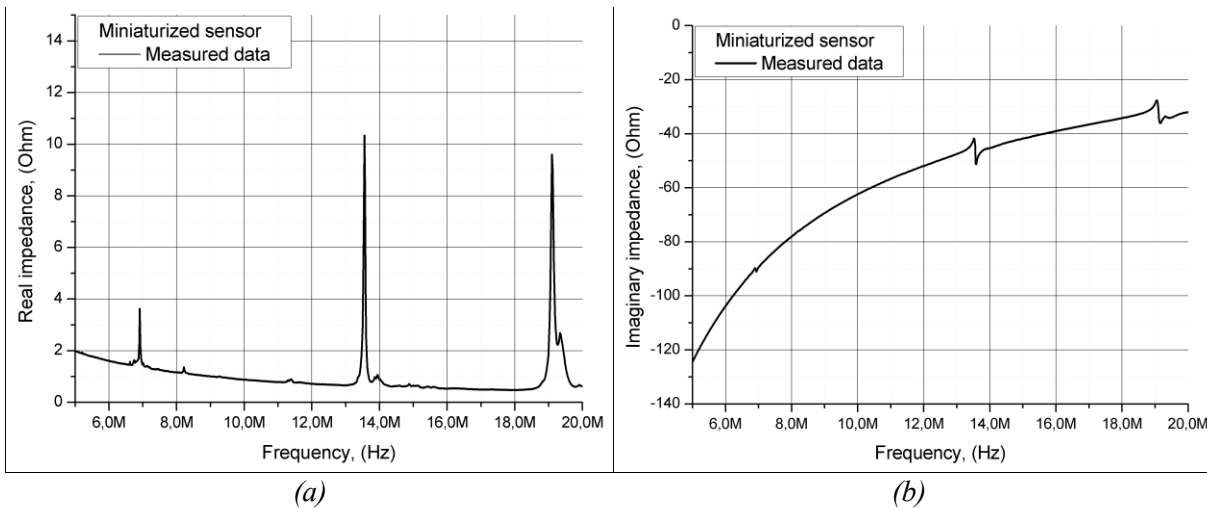


Figure 4.32 – Electrical impedance of NBT miniaturized sensor

(a) real and (b) imaginary part.

4.5.4 Temperature test with miniaturized sensor

The measurement of resistivity and dielectric properties of the miniaturized sensor confirmed its applicability in the temperature range of up to 350 °C. In Figure 4.33, the resistivity evolution as a function of an electric field applied for 30 °C and 175 °C is shown and compared with the detached disk of the same NBT version. The dielectric properties evolution is represented in Figure 4.34. Overall, as was expected, the sensor possesses the properties of NBTv8 material.

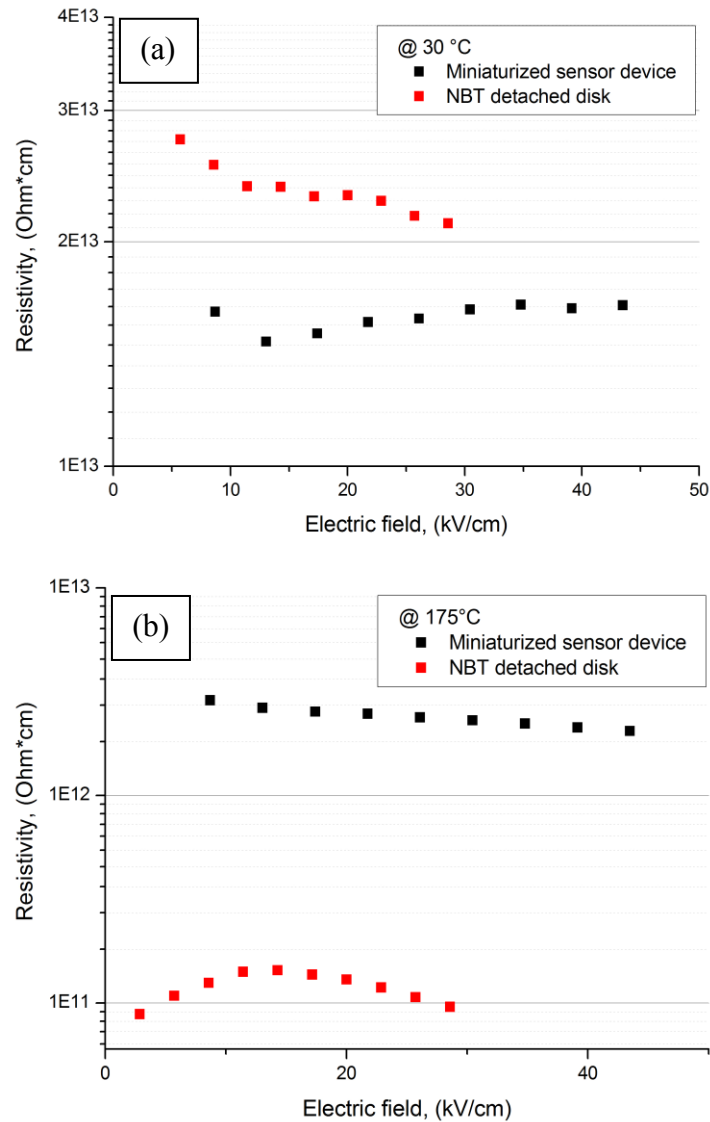


Figure 4.33 – Resistivity evolution of the miniaturized sensor in comparison with an NBT detached disk of the same material (NBTv8) as a function of temperature.

(a) 30 °C; (b) 175 °C.

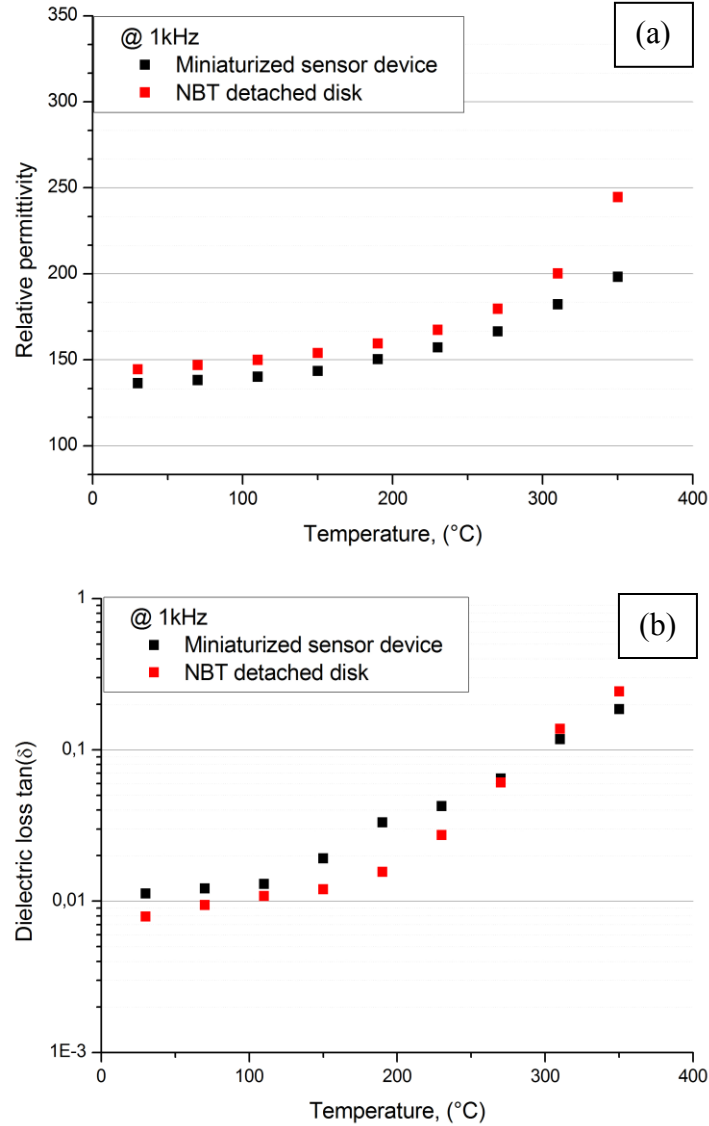


Figure 4.34 – Dielectric properties evolution of the miniaturized sensor in comparison with an NBT detached disk of the same material (NBTv8) as a function of temperature.

(a) Relative permittivity ϵ_{33} ; (b) Dielectric loss $\tan(\delta)$.

4.5.5 Conclusions

The miniaturized sensor consists of the same elements as the previously tested sensor (alumina substrate, NBT material, and electrodes) and are capable of in-pile integration into an enclosure with the near diameter restriction of 13x13 mm. Its performance was measured and the properties of the device for a high-temperature application were reported. The integration into an acoustic cavity is expected to be performed prior to the next phase of device development.

4.6 Conclusions

Based on fabrication of NBT screen-printing sensors an alternative approach in the development of instrumentation for harsh environmental conditions is introduced. The tests with NBTv3 on the alumina substrate show the reliability of the sensor under high temperatures (section 4.2 and section 4.3). The measurements of pressurized Helium gas under ambient temperature confirmed sensors functionality. Furthermore, by the introduction of the theoretical model, the possibility of measurements up to 350°C was demonstrated (sections 4.3 and 4.4). The miniaturized sensor configuration was discussed in the frame of in-pile integration inside a combustion rod in the Jules Horowitz experimental reactor (section 4.5). The results with such sensor, made from NBTv8 ink, reveals its possible implementation for fission released gas measurement in MTR experimental facilities.

Conclusions and Perspectives

The previous studies, of our research group in partnership with CEA, on fission released gas measurement, validated the concept of measurements with an ultrasonic method. The main goal of this thesis work was to develop a new ultrasonic sensor with a measurement capability up to 200 °C - 400 °C in Material Testing reactors.

Conclusions

In the course of this work, a deeper understanding of the screen-printing method for high-temperature ceramics of anisotropic structure, the relationship between fabrication and material parameters, and the development of ultrasonic sensors, able to withstand to required temperature conditions, has been achieved. The important results could be summarized as follows:

1. The repeatability in NBT sensors fabrication using the screen-printing method was shown, first in the form of detached elements (material in a form of a disk) and then on an alumina substrate (sensor).
2. The comparison of the manufacture parameters and characterization of eight NBT versions permit to choose a potential candidate material for sensor development. Properties of NBT materials were found to be dependent on grain size dimensions. According, to the observation, the materials fabricated from finer powders have a better electric (resistivity), dielectric and piezoelectric properties in comparison with the coarse grains based sintered ceramic.
3. The bibliographic studies on doping of NBT ceramics revealed multiple choices for substitution of **A**- and **B**- site of the perovskite structure. Based on these studies, 3 dopants were used for NBT ceramic production. The co-doped by Nb-W NBT ceramic showed the piezoelectric

charge coefficient, d_{33} , of 20 pC/N and is in the range of commercial Pz46 piezoelectric element. The use of such co-doped Nb-W NBT materials is envisaged for final sensor devices.

4. The electromechanical model based on electrodynamics formula and impedance matching equation, used in previous research experiments, was successfully applied to the NBT screen-printing sensor. The model allowed monitoring of electromechanical, piezoelectric coefficients and was used to validate the sensor concept.

5. The acoustic tests carried out with NBT sensors, ensure high sensitivity of liquid substance detection (water and ethanol) and the reliability in measurement of pressurized gas in centimetric acoustic cavities. These experiments demonstrated the feasibility for fabrication of NBT sensor and its applicability for the speed of sound measurement under ambient temperature conditions.

6. As it is not yet possible to perform gas measurements in high-temperature environment, the measurements under the temperature of 350 °C were validated by the application of the theoretical model used for monitoring of electromechanical coefficients of sensors. Until the electrical impedance can be registered, the acoustic measurements at high temperature remain theoretically possible.

7. The study of impedance response as a function of temperature validates sensor applicability for the temperatures of 300 - 350°C for a period of minimum 8 hours, whereas the measured impedance remained stable through the period of observation.

8. Based on the validated NBT screen-printing sensor, a new prototype concept was proposed. It is currently under development and is planned to be covered by an international patent in the near future.

Suggestions for future work

From this work, several axes for future development can be suggested.

1. To produce NBT sensors of enhanced properties, a better understanding of fabrication parameters is required.

a) The sealing glass CF7575 of coarse grain size (contained in ink) leads to surface degradation after sintering. It is suggested that amelioration of surface homogeneity will lead to an increment of material electric, dielectric and piezoelectric properties. Few approaches are suggested:

- The coating of powders with sol-gel will increase the binding force between the grains, and it is expected to behave as the sealing glass, reducing the sintering temperature.
- The application of isostatic pressure to deposited layers (before sintering) shall increase their densities by reduction of inter-grain cavities.
- Alternatively, the CF7575 sealing glass may be replaced with another Pb- and (or) Bi-based composites of smaller grain particles.

b) Properties of NBT ceramics can be enhanced by doping. Even though for the screen-printed NBT material co-doped by Nb and W the properties were improved, for optimization of NBT material, the complementary studies of doping mechanism with different dopant ratios are required.

c) The properties evolution as a function of sintering conditions was reported in the thesis. A complementary sintering study for un-doped and doped NBT ceramics can reveal in the material with enhanced parameters and give a better understanding of the powder size impact during the fabrication.

2. Additional temperature studies.

a) Temperature tests in this work were limited by 400 °C. The monitoring of parameters evolution as a function of temperature up to the phase transition in Curie temperature will give the approximation on the maximum operating temperature for screen-printing NBT sensors.

b) In the current work, the measurements of sensor properties as a function of time and temperature were carried out. The test at 300°C for 8 hours ensures properties stabilities for the given conditions. However, to evaluate the influence of a heat-rate on the NBT sensor, the tests under longer time periods are necessary. This will not only allow the estimation of the aging and lifetime for the sensor but can also be used for the model development for in-situ gas monitoring in an experimental reactor facility.

3. Evolution of sensor properties in a radiative environment carried out for screen-printing sensors of PZT-type and commercial elements Pz46 confirmed the potential applicability in high neutron and gamma fields. The similar campaign in irradiation reactor will be performed for NBT screen printing sensors.

4. Gas characterization in laboratory conditions.

a) In order to complete acoustic measurements with screen-printing sensors, the new experimental test bench allowing the gas composition evaluation from 40 to 150 bar pressure range is currently under development.

b) In addition, acoustic tests as a function of temperature & pressure can be performed in CEA. Acoustic data may be used during in-situ experiment reactor measurements.

Résumé

Les travaux présentés dans cette thèse concernent le développement d'une nouvelle génération de capteurs acoustiques pour la caractérisation des gaz de fission dans les conditions difficiles présentées au cœur des réacteurs d'irradiation technologiques. L'optimisation de la durée de vie des barres de combustible nucléaire, sans réduction des marges de sécurité (par exemple, en minimisant la corrosion ou l'augmentation excessive de la pression interne) nécessite un meilleur contrôle de la libération d'hélium et des gaz de fission dans les volumes libres d'un crayon de combustible. La présence de gaz de fission relâchés influe directement sur le comportement du combustible nucléaire. Des programmes expérimentaux performants et une instrumentation innovante pour les réacteurs d'essai de matériaux (MTR) ont permis de mieux comprendre la mécanique et la thermophysique du combustible nucléaire.

Traditionnellement, l'évaluation des gaz de relâchement de fission, dans le crayon de combustible d'un réacteur expérimental, consiste en une mesure simultanée de la pression interne du crayon et de la température du combustible. Cependant, la simple mesure de la pression ne fournit pas d'informations sur la nature des gaz libérés, informations nécessaires à la compréhension des modifications subies dans le combustible, lors de l'irradiation. C'est pourquoi, en collaboration avec une équipe du CEA, l'IES a développé et breveté un système de mesure acoustique permettant de surveiller en temps réel lors d'une irradiation, la masse molaire du gaz contenu dans les crayons combustibles expérimentaux. Ce capteur acoustique a été conçu pour fonctionner dans des conditions hostiles.

Ce capteur a été testé sur crayon expérimental à fort *burn-up*, extrait d'un barreau de combustible français à réacteurs à eau sous pression irradié pendant cinq cycles. Par la suite, ce crayon expérimental a été irradié une fois de plus (expérience REMORA 3) dans le réacteur expérimental OSIRIS (Saclay 2010). Nous avons pu mesurer, en cours d'irradiation, la cinétique de libération des gaz de fission jusqu'à une température de 190 °C.

Cependant ce type de capteur possède une température limite de fonctionnement à 200°C par sa conception intégrant une brasure de l'élément piézoélectrique sur une plaque métallique. Cela rend impossible son utilisation dans le nouveau réacteur d'essai de matériau (MTR) du CEA, le réacteur Jules Horowitz. Sur la base de cette limitation et de la nécessité d'opérer à des températures plus élevées, une seconde approche a consisté à appliquer un processus de sérigraphie à la production de l'élément actif. Dans le cadre de sa thèse, F. Very a travaillé avec du titanate de zircone de plomb (PZT) ; la possibilité de fabrication, de caractérisation et de mesures par ultrasons a été démontrée, à température ambiante.

Ce travail de thèse s'inscrit dans la continuité des précédentes études et s'intéresse au développement d'une génération de capteur pouvant fonctionner à plus haute température.

Le premier chapitre présente l'état de la technique en matière de développement de capteurs acoustiques (transducteurs) pour les environnements difficiles. Après la description d'un concept de base des transducteurs acoustiques, une étude bibliographique du développement des capteurs est présentée selon trois perspectives : l'instrumentation nucléaire acoustique, les transducteurs pour les mesures dans un environnement à haute température et les études sur les matériaux composant les transducteurs en environnement radiatif.

Dans le second chapitre, un état de l'art sur les recherches récentes sur les céramiques ferroélectriques à structure de couche de bismuth (BLSF) est présenté. Ces matériaux possèdent une température de Curie élevée, ce qui en fait une solution prometteuse pour les applications automobiles, aérospatiales et nucléaires. Pour obtenir un coefficient piézoélectrique relativement élevé et de faibles pertes diélectriques, les multiples approches en développement de matériaux sont abordées. Sur la base des difficultés de polarisation du titanate de bismuth, $\text{Bi}_3\text{Ti}_4\text{O}_{12}$, des céramiques de la phase Aurivillius, le sodium titanate du bismuth, $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$, a été choisi comme matériau piézoélectrique alternatif.

Afin d'améliorer les propriétés piézoélectriques du sodium titanate du bismuth (NBT), une étude bibliographique des dopages et de leurs impacts sur ces propriétés a été réalisée. Le mécanisme de dopage proposé est présenté. Il est possible de substituer le site A et / ou le site B du réseau pérovskite. La nature de l'élément, sa taille, sa charge et le taux de substitution influencent les propriétés piézoélectriques et électrique du composé chimique final. En ce qui

concerne la température de Curie que nous cherchons à augmenter, l'effet de la substitution est moins évident. Les données recueillies montrent que la distorsion de la matrice (avec la diminution de l'électronégativité) entraîne une diminution de la température de Curie et induit l'augmentation des propriétés piézoélectriques. De nombreuses études montrent qu'en ce qui concerne la substitution du site A par un petit élément tel que les lanthanides, la température de Curie, TC, peut être augmentée par le dopage à l'euprasiu et les éléments du même groupe. Compte tenu de ces données, notre choix s'est porté sur 3 poudres brutes de NBT optimisées : dopage par niobium Nb^{5+} , par tungstène W^{6+} et co-dopage par Nb^{5+} et W^{6+} .

Dans les chapitres précédents, nous avons expliqué le choix des matériaux piézoélectriques et introduit le processus de fabrication. Cependant, le développement de transducteurs piézoélectriques avec la méthode de sérigraphie nécessite un certain nombre d'études approfondies sur la technique elle-même. C'est une opportunité technologique utilisée dans l'électronique pour produire des circuits hybrides, des systèmes multicouches et des couches épaisses de diélectriques et de conducteurs. Ce procédé complète les besoins en terme de dépôt à moyenne échelle entre couches minces ($<5\text{ }\mu\text{m}$) et éléments massifs ($> 500\text{ }\mu\text{m}$). Dans le troisième chapitre, nous discutons de la fabrication par sérigraphie et de la caractérisation de céramiques NBT pures et dopées sous forme de disque. L'analyse de la taille des grains de poudre brute, des paramètres de frittage, de la taille des grains de céramique et de la composition chimique du titanate de sodium et de bismuth est présentée. Nous discutons des expériences effectuées et de leur importance dans le cadre de l'analyse des propriétés du capteur pour les applications à haute température. Nous proposons une évaluation des propriétés des échantillons en fonction de la température. Les paramètres de fabrication et les propriétés mesurées sont analysés pour différentes versions du matériau. Cette analyse montre les conditions d'élaboration des céramiques au titanate de sodium et au bismuth par sérigraphie et permet de d'envisager la conception et le développement de capteurs à ultrasons.

Les études sur la fabrication du matériau NBT avec la méthode de sérigraphie démontrent la fiabilité de sa production. Par conséquent, les processus de production optimisés ont été établis. Dans le chapitre 4 nous nous intéressons à l'intégration des céramiques piézoélectriques sur un substrat pour la génération de signaux acoustiques. La performance finale du transducteur dépend notamment de la différence du coefficient de dilatation thermique entre le matériau piézoélectrique

et le substrat. Pour surmonter ce problème, le procédé de sérigraphie a été choisi en raison de son avantage dans le dépôt direct dans un substrat. Par conséquent, une couche intermédiaire telle que le brasage n'est pas nécessaire. Le substrat céramique d'alumine, Al_2O_3 , a une valeur de coefficient de dilatation thermique approximativement similaire à celle des céramiques piézoélectriques. Après les simulations, des capteurs ont été fabriqués. Leur caractérisation complète est décrite et des mesures de tenue en température ont été réalisées. Des mesures acoustiques en milieu liquide et gazeux ont aussi démontré le principe de fonctionnement d'un tel dispositif. La corrélation des propriétés de capteur mesurées à haute température (jusqu'à 350 °C) avec un test acoustique à température ambiante a permis de démontrer théoriquement une utilisation possible en haute température.

Enfin des perspectives sont présentées :

1. Pour la production de capteurs NBT dotés de propriétés améliorées, il peut être nécessaire d'optimiser les paramètres de fabrication.

- l'enrobage des poudres avec des sol-gel devrait augmenter la force de liaison entre les grains et réduire la température de frittage.

- L'application d'une pression isostatique sur les couches déposées avant le frittage pourrait augmenter leurs densités par rétrécissement des cavités inter-grains ce qui se traduirait par modification de la densité, donc des propriétés de la céramique.

2. Des études de température complémentaires seront menées :

- les essais en température dans ce travail étaient limités à 400 °C. Le suivi de l'évolution des paramètres en fonction de la température jusqu'à la transition de phase dans la température de Curie donnera l'approximation de la température maximale de fonctionnement pour les capteurs NBT sérigraphiés.

- Dans les travaux en cours, l'évolution des propriétés du capteur en fonction du temps à une température donnée a été réalisée à 300 °C pendant 8 heures. Il sera nécessaire d'effectuer un test de température sur des périodes plus longues. Cela permettra non seulement d'estimer le vieillissement et la durée de vie d'un capteur particulier, mais sera également utilisé pour l'élaboration d'un modèle de surveillance de gaz in situ dans un réacteur expérimental.

3. L'évolution des propriétés des capteurs en environnement radiatif réalisée pour les capteurs de sérigraphie de type PZT et les éléments commerciaux Pz46 a confirmé leur application dans les champs de neutrons et de gamma élevés. Une campagne similaire pour cette dernière génération de capteurs permettrait de démontrer son implantation en réacteur de recherche.

4. La production de nouveaux prototypes avec les tests et les étalonnages associés ouvrira la fenêtre de l'industrialisation.

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ANNEX A

OVERVIEW OF FABRICATED SAMPLES WITH MEASUREMENTS CARRIED OUT

NBT version	NBT sample reference	thickness	relative permittivity	dielectric loss	applied E-field	d33	resistivity @30C	permittivity on T	resistivity on T	impedance	fit	acoustic test (notes)
	d – detached disk											
	s – sensor on alumina substrate				kV/cm	pC/N	Ohm*cm					
NBTv1	-											
	d1.1											
	d1.2	100	151	0,0071	80	10,2				yes	yes	
	d1.3											
	d1.4	100	142	0,011	70	8						
	d2.1	100	130	0,0053	100	12,4				yes	yes	
	d2.2	100	143	0,0069	100	13,6		yes		yes	yes	
	d2.3	100	139	0,0081	110	14	1,00E+13		yes	yes	yes	
	d2.4	100	134	0,0085	100	11,2		yes			yes	
	d3.1											
	d3.2											
	d3.3	100	180	0,0068	70			yes		yes		
	d3.4											
NBTv2			before - after poling									
	d1.1	160	1356-128	1,4-0,11	40	4,6				yes		
	d1.2	160	135	no-0,2	55	2	7,35E+10					
	d1.3	160	188-512 (9.6)	0,46-0,6 (0,4)	60	4,3						
	d1.4	160										

	d2.1	160	295-130	0,6-0,35	50	7,5	4,30E+09				yes	
	d2.2	160										
	d2.3	160	183	0,25	70	9	4,00E+11	yes		yes		
	d2.4	160										
	s1.1	65	15									
	s1.4	65		0,4	50		2,00E+10					
NBTv3												
	s1.1											
Gas test Nov2017	s1.1p	39	92	0,0078	150	11				yes	yes	yes (after T of 400°C)
	s1.2											
Gas test Nov2017	s1.2p	40	95	0,0075	150		1,00E+13	yes		yes		yes (after T of 375°C)
	s1.3											
Gas test Nov2017	s1.3p	35	75	0,0106	150	11,7				yes		yes
	s1.4											
Gas test Nov2017	s1.4p	37	83	0,0086	150	12				yes		yes
	s2.1											
	s2.1p	37	77	0,0106	170	14,3				yes	yes	yes
	s2.2	35	78	0,0078	140							
	s2.2p								yes			yes
	s2.3											

	s2.3p											
	s2.4											
	s2.4p											
	s3.1											
	s3.1p	37	117	0,0093	160	14	1,41E+1 3	yes	yes	yes	yes	yes
	s3.2											
	s3.2p	35	114	0,0071			2,56E+1 3					
	s3.3											
	s3.3p	35	114	0,008			1,65E+1 3	yes	yes			
	s3.4											
	s3.4p	36	114	0,0081			1,30E+1 3					
	d1.1											
	d1.2	80	147	0,017								
	d1.3	80	139	0,011			yes	yes	yes			
NBTv4												
	d1.1	80	136	0,02								
	d1.2	80	129	0,0197	135	12,3	2,00E+1 3		yes	yes	yes	
	d1.3	80	129	0,0195								
	d.1.4	80	147	0,0189								
	d.2.2	80	161	0,0179			5,00E+1 3		yes			
	d.2.3	80	132	0,0179								
	s1.1	42	117	0,03								

	s3.1	55		0,05								
	s3.1p	55		0,05			2,50E+09					
	s7.1	20		0,07								
	s.7.4p	20		0,04				yes	yes			
NBTv5												
fabrication 1 (f1)												
fabrication 2 (f2)												
	d3.1	25	130									
	d3.1p	25	125		150	13	1,30E+13					
	d3.2p	25	120				1,00E+13	yes	yes			
	d3.3p											
	s.1.1	35	124	0,0074	200	12	1,00E+14	yes	yes	yes	yes	yes
	s1.1p	35		0,004								
	s1.2	30	120	0,0074			1,00E+14	yes	yes	yes		
	s1.2p	35		0,05								
	s.1.3	20		0,005								
	s1.3p	28		0,0074			1,00E+10		yes			
	s1.4	30		0,012								
	s1.4p	30		0,0075								
	s.2.1			0,027								
	s2.1p			0,064								
	s2.2			0,016								

	s2.2p			0,048								
	s.2.3			0,017								
	s2.3p			0,047								
	s2.4			0,057								
	s2.4p			0,333								
fabrication 3 (f3)	s.1.1	22		0,0071								
	s1.1p											
	s1.2			0,0077								
	s1.2p	38		0,014								
	s.1.3	15		0,0062								
	s1.3p	34		0,009								
	s1.4	24		0,0067								
	s1.4p	35		0,01								
	s.2.1	28		0,0074								
	s2.1p			0,006								
	s2.2	38		0,005								
	s2.2p			0,006								
	s.2.3			0,0047								
	s2.3p	28		0,0061								
	s2.4			0,0065								
	s2.4p	35		0,0047								
	s4.1	40		0,0058								
	s4.1p	38		0,033								
	s4.2	44		0,0065								
	s4.2p	30		0,042								
	s.4.3	26		0,0054			2,50E+13	yes	yes			

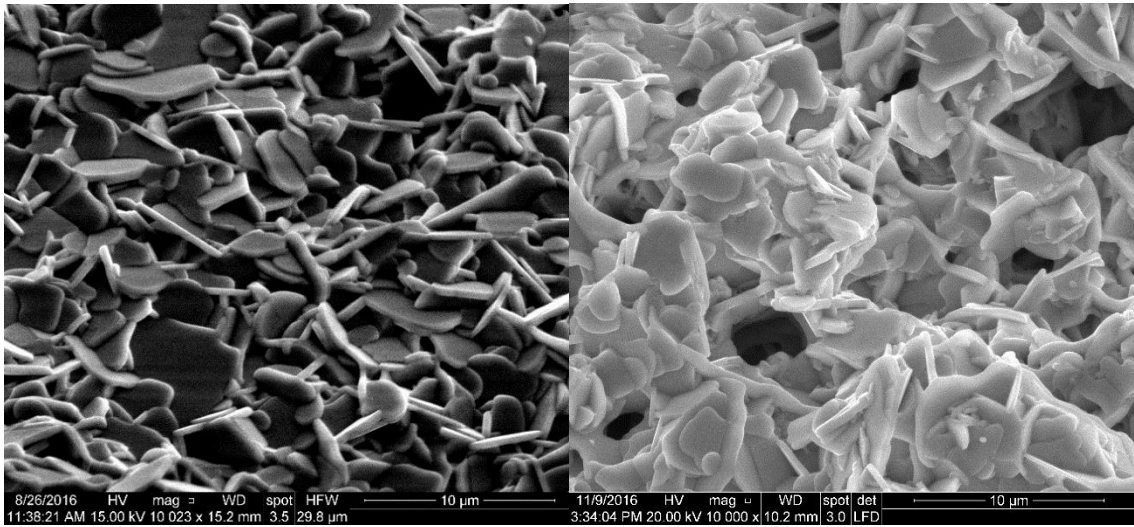
	s4.3p											
	s4.4	50		0,00615								
	s4.4p	25										
	s.5.1	32		0,008								
	s5.1p											
	s5.2	20		0,0062								
	s5.2p	28		0,006								
	s.5.3	25		0,006								
	s5.3p	29		0,007								
	s5.4	28		0,0076								
	s5.4p	30		0,0094								
	d1.1	26	120	0,0092								
	d1.2	26	120	0,0109								
	d1.3	26	110	0,0105			1,30E+1 3					
NBTv6 doped with Nb												
	d1.1	80	175	0,035								
	d1.1p	80	145,72126	0,035								
	d1.2	80	157	0,035								
	d1.3	80	145	0,021	150	11,8	3,00E+1 3	yes	yes	yes	yes	
	d2.1	80	174	0,031								
	d2.1p	80	138,05172	0,0259								
	d2.2	80	164	0,0286								
	d2.3	80	165	0,0279								
	s.1.1	50		0,054								
	s1.1p											
	s1.2	55		0,12								
	s1.2p											

	s.1.3			0,084								
	s1.3p											
	s1.4			0,071								
	s1.4p											
	s.2.1	60		0,075								
	s2.1p	55		0,11								
	s2.2	65		0,081								
	s2.2p	50		0,129								
	s.2.3	70		0,087								
	s2.3p	55		0,124								
	s2.4	55		0,087								
	s2.4p	55		0,121								
	s3.1	50		0,077								
	s3.1p	58		0,118								
	s3.2	48		0,076								
	s3.2p	54		0,09								
	s3.3	50		0,076								
	s3.3p	55		0,09								
	s3.4	55		0,078								
	s3.4p	45		0,096								
	d5	80	181	0,0128							yes	
	d5p	80	160	0,0115								
	d6	80	168	0,0207							yes	
	d6p	80	160	0,0231								
NBTv7 doped with W	d1	80	157	0,0561								
	d2	80	154	0,0467								
	d3	80	152	0,0632								

	d4	80		0,0449								
	d5	80	158	0,0108	150	11,4	2,00E+1 3			yes	yes	
	d6	80	138	0,0165	150	13,6						
	d7p	80	161	0,0171								
	d8p	80	158	0,0225	150	14,4				yes	yes	
NBTv8 co-doped with Nb- W	d1	60	148	0,0123								
	d2	60		0,6634								
	d3	60	163	0,027								
	d4	60	150	0,0136	150	20	2,20E+1 3	yes	yes	yes	yes	
	d1p	60	155	0,0105	150	17,9						
	d2p	60	155	0,0085								
	d3p	60	142	0,0092								
	d4p	60	155	0,0092								
	d5	60	136	0,0136	150	18	yes			yes	yes	
	d5p	60	145	0,02								
	d6	60	148	0,0085	150	17,6	yes			yes	yes	

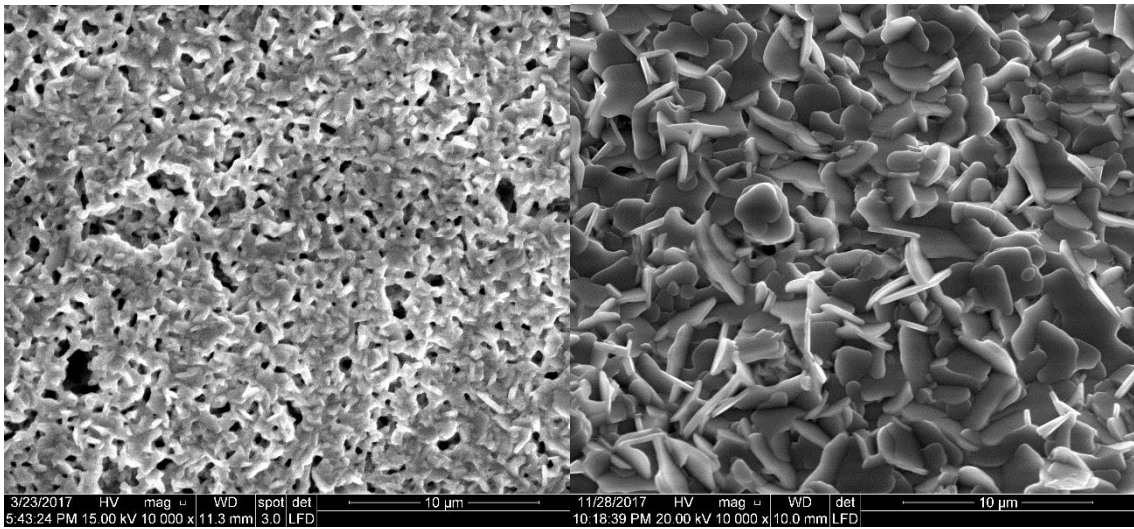
ANNEX B

MORPHOLOGY OF SCREEN- PRINTED NBT MATERIALS



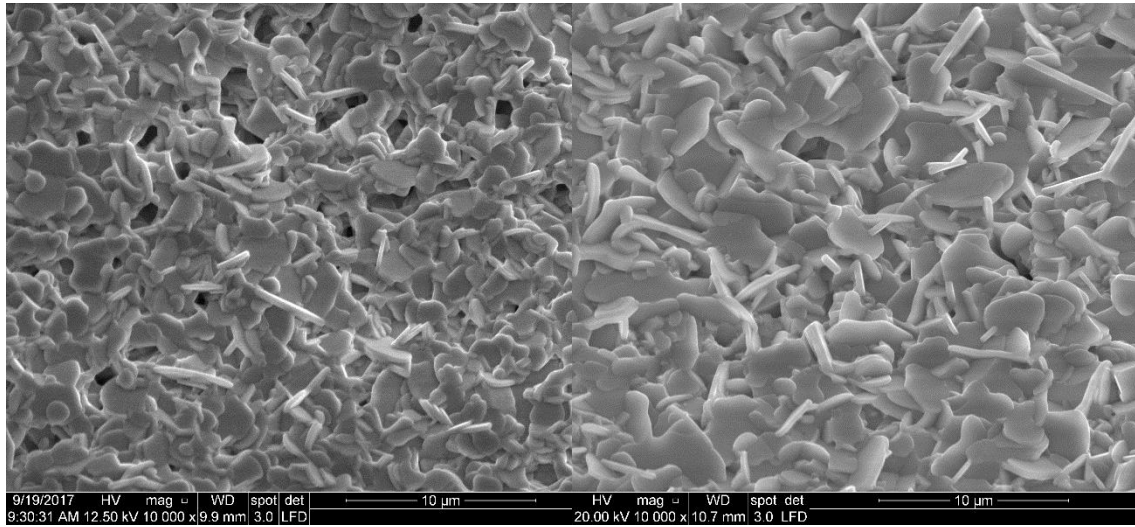
(a)

(b)



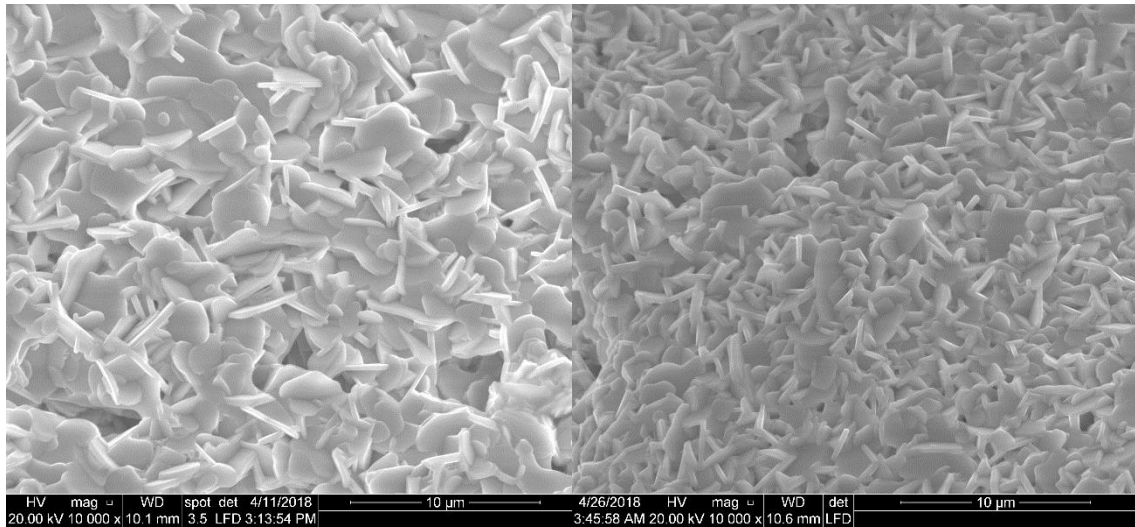
(c)

(d)



(e)

(f)

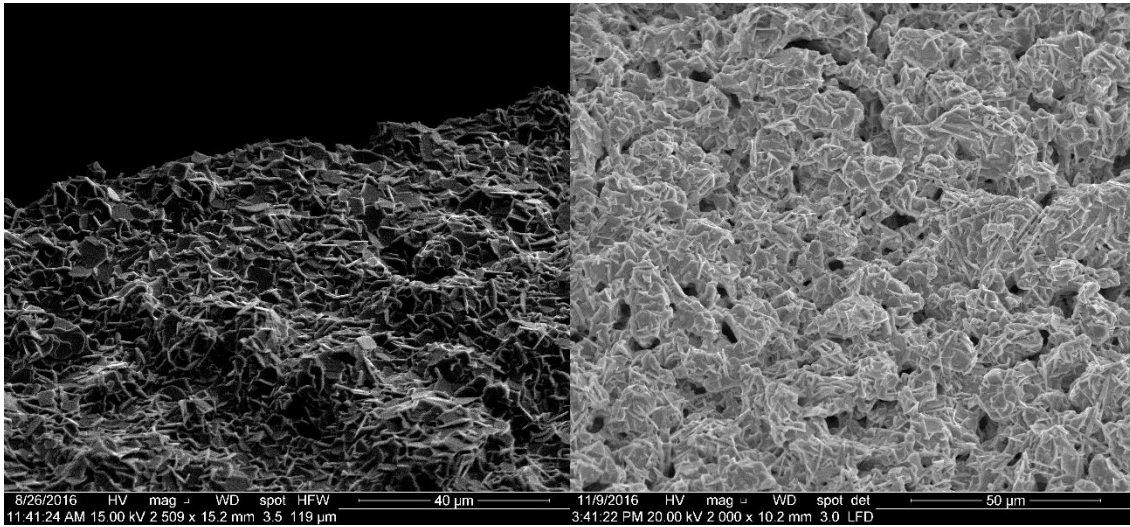


(g)

(h)

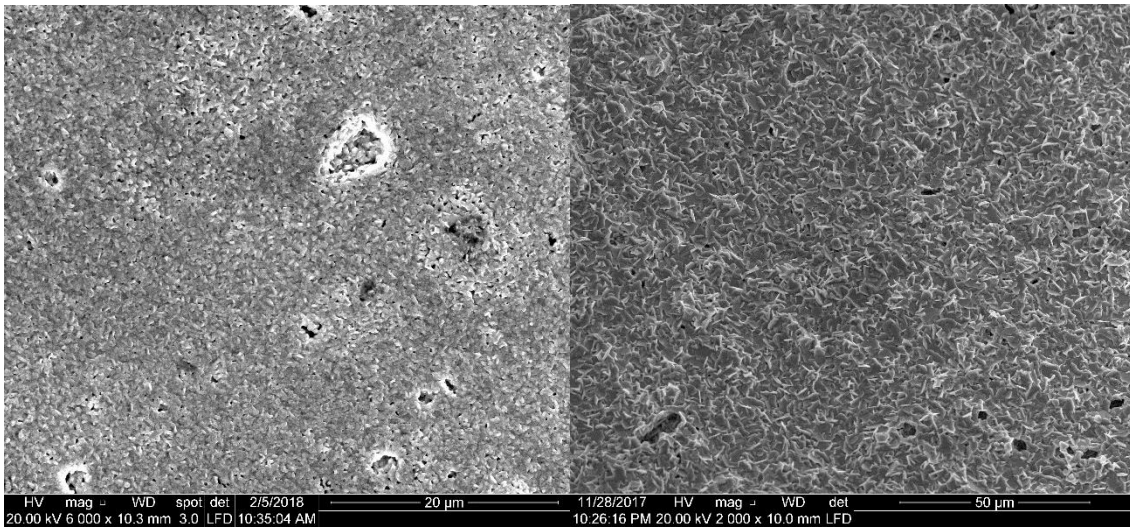
Figure B.1 – Morphology of sintered NBT ceramics observed under magnification $\times 10000$.

(a) NBTv1 (sintered 10 hours), (b) NBTv2 (powder agglomeration), (c) NBTv3, (d) NBTv4, (e) NBTv5, (f) NBTv6 doped with Nb, (g) NBTv7 doped with W, (h) NBTv8 co-doped with Nb-W.



(a)

(b)



(c)

(d)

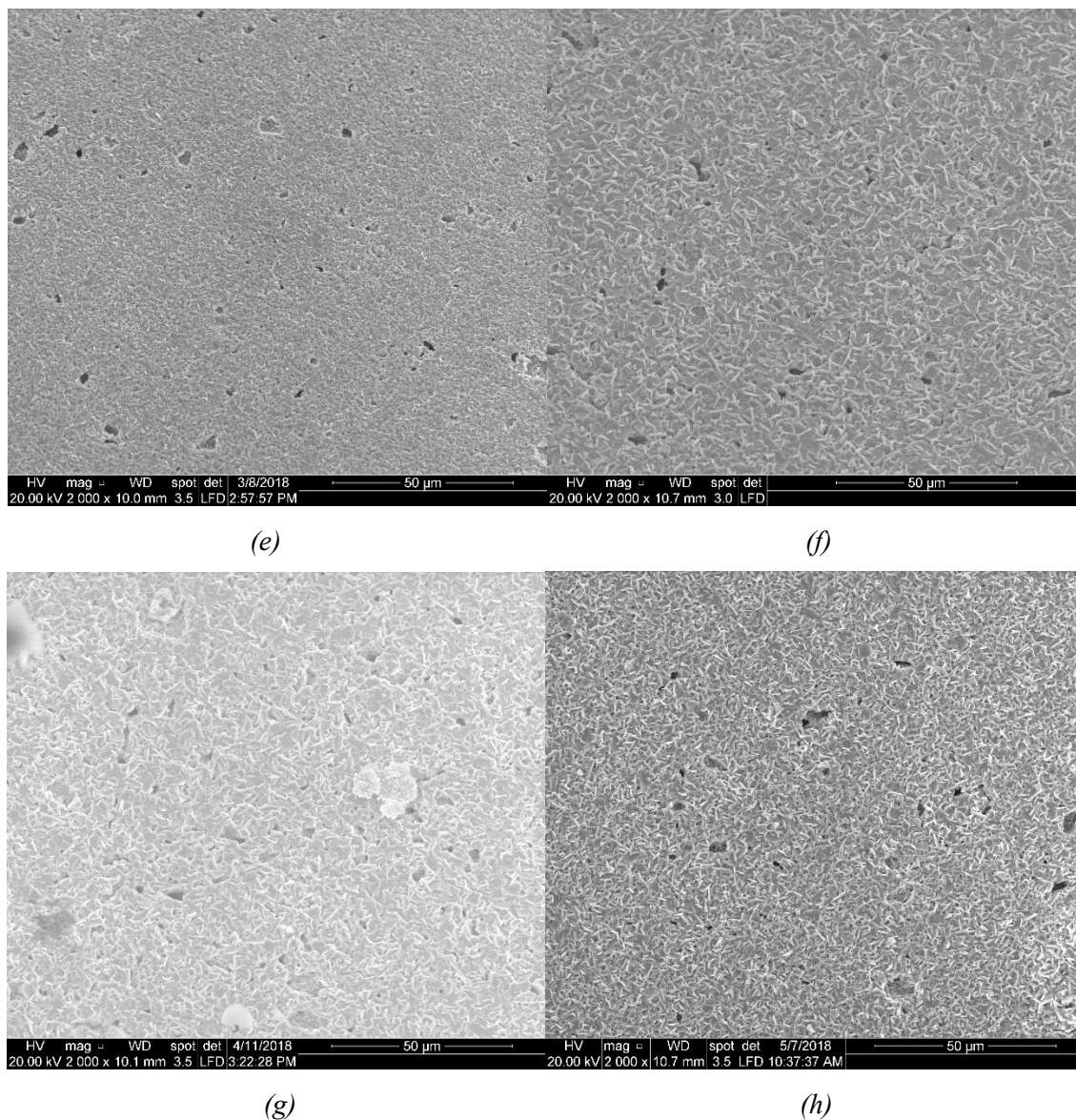


Figure B.2 – Morphology of sintered NBT ceramics. Observed under magnification x2000.

(a) NBTv1 (sintered 10 hours), (b) NBTv2 (powder agglomeration), (c) NBTv3, (d) NBTv4, (e) NBTv5, (f) NBTv6 doped with Nb, (g) NBTv7 doped with W, (h) NBTv8 co-doped with Nb-W.

Development of acoustic sensors for the extension of measurements to high temperature in the experimental reactors

Abstract: This Ph.D. thesis is dedicated to the development of a new generation of ultrasonic sensors devoted to fission gas characterization. More generally, these studies concern the development of instrumentation for the Jules Horowitz material testing reactor (JHR) aiming to perform in-situ control of the released gas composition for optimization of burn-up rate and fuel rod lifetime. The operation temperature of this new reactor will be in the range of 200 °C - 400 °C. Hence, the main problem concerns the development of piezoelectric material, able to operate in the required temperature range, and its integration with a sensor device.

To resolve this problem, we propose to use the sodium bismuth titanate (NBT) ceramic material developed by the screen-printing technique. Several versions of piezoelectric materials were produced during this research, with the purpose of optimizing material manufacturing conditions. Each material was characterized (morphological, chemical, electric, dielectric, piezoelectric and electromechanical parameters) and “tests as a function of temperature” were carried out. After demonstrating repeatability in material fabrication, the protocol for NBT sensor production was determined and a prototype of the ultrasonic sensor was fabricated.

The sensor was fabricated by deposition of an active material onto an alumina substrate. After characterization of sensor properties, acoustic tests showed a high sensitivity of measurements at ambient temperature (25 °C). Furthermore, by integration of sensors into a pressurized enclosure the possibility of gas detection in the range from 50 to 70 bars was demonstrated. To verify the sensor’s applicability to gas detection under harsh temperature environment, a theoretical model based on electromechanical properties and impedance matching equations was introduced. It was theoretically demonstrated that the sensor is able to perform gas measurements from ambient temperature up to 350 °C.

Key-words: ultrasonic sensor, piezoelectricity, screen-printing, fission gas measurement, high temperature application, sodium bismuth titanate.

Développement de capteurs ultrasonores pour l’extension des mesures acoustiques aux hautes températures dans les réacteurs expérimentaux

Résumé : Ce travail de thèse porte sur l’étude et la réalisation d’une nouvelle génération de capteurs ultrasonore dédiés à la caractérisation des gaz de fission. Plus généralement, ces études concernent le développement de l’instrumentation du réacteur d’essai des matériaux Jules Horowitz (RJH), visant entre autre à effectuer le contrôle *in situ* de la composition du gaz libéré afin d’optimiser la durée de vie du combustible et le taux de combustion. La température de fonctionnement de ce nouveau réacteur devant se situer dans la plage entre 200 °C à 400 °C, la principale problématique concerne donc le développement d’un matériau piézoélectrique, capable de fonctionner dans la plage de température requise, et son intégration à un dispositif de détection.

Nous proposons l’utilisation du sodium titanate de bismuth (NBT) développé par la méthode de la sérigraphie. Dans le but d’optimiser les conditions de fabrication des matériaux, plusieurs versions de matériaux piézoélectriques ont été produites au cours de cette thèse. Chacun des matériaux a été caractérisé (paramètres morphologiques, chimiques, électriques, diélectriques, piézoélectriques et électromécaniques) et des tests en fonction de la température ont été conduits. Après avoir démontré une bonne répétabilité dans la production du matériau, le protocole de fabrication des capteurs a été déterminé et un prototype de capteur ultrasonore a été réalisé.

Ces capteurs ont été fabriqués par dépôt du matériau actif sur un substrat d’alumine. Après caractérisation des propriétés des capteurs, des essais ont montré une sensibilité acoustique importante à température ambiante. De plus, la possibilité d’une détection de gaz sur une gamme de pression de 50 à 70 bars a été démontrée par l’intégration d’un capteur dans une enceinte. Pour vérifier la possibilité d’application du capteur à la détection de gaz dans des environnements hostiles (haute température), un modèle théorique basé sur les propriétés électromécaniques et les équations d’adaptation d’impédance a été introduit. Il a été démontré théoriquement que le capteur est capable d’effectuer des mesures de gaz de la température ambiante jusqu’à 350 °C.

Mots-clés : capteur d’ultrason, piézoélectricité, sérigraphie, mesure du gaz de fission, application haute température, sodium titanate de bismuth.