



Synthesis, high pressure behaviour and metastable phases of SixGe1-x alloys

Max Gerin

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Synthesis, high pressure behaviour and metastable phases of $\text{Si}_x\text{Ge}_{1-x}$ alloys

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Glossary

BM2 second-order Birch-Murnaghan. 102, 103, 107–109, 120, 121, 123, 126

BM3 third-order Birch-Murnaghan. 82, 102, 103, 107, 108, 120, 121

DAC Diamond anvil cell. 2, 83–87, 89, 99, 105, 109, 111, 121, 127, 134, 135

DFT Density Functional Theory. 89, 99, 108–111, 114, 116–119, 125, 126, 128, 134, 144

EDX Energy Dispersive X-ray spectroscopy. 3, 9, 15, 34–36, 42, 44, 49, 50, 54–58, 60, 61, 133

EOS Equation Of State. 82, 102, 103, 107–109, 120, 121, 123, 126

FWHM Full Width Half Maximum. 12, 33, 91, 98, 101, 102, 112, 120, 127, 139

HP High Pressure. 2, 3, 19, 45, 50, 73–78, 80, 81, 85, 89, 99, 111, 119, 121, 125, 127, 128, 134, 135, 141, 143

HT High Temperature. 2, 19, 26, 31, 38, 45, 46, 52–57, 59–63, 80, 121, 133, 134, 145

P-E Paris-Edinburgh. 2, 80–82, 85, 89, 93–95, 99, 100, 102–104, 120–122, 134, 135

PTM Pressure Transmitting Medium. 83–85, 89, 105, 111, 121, 127

SEM Scanning Electron Microscopy. 14, 15, 54, 55, 57, 58, 60, 61

SPS Spark Plasma Sintering. 20, 38–45, 52–56, 58, 63, 133

TEM Transmission Electron Microscopy. 68, 69

XRD X-Ray Diffraction. 3, 9–12, 14, 22–24, 26–28, 31–36, 41, 48, 49, 53, 54, 57, 59, 60, 69, 80, 85–87, 93, 94, 100, 101, 114, 117–119, 121, 127–129, 133–135, 138

General introduction

Modern technology is based on semiconductors, these materials are the heart of modern electronics and vital for communications, healthcare, transportation, energy and research. With new advances in these fields, new demanding and specialized applications require new materials, with flexible properties.

SiGe alloys in their stable diamond-like crystallographic form offer this flexibility, as their physical properties are tunable by varying their composition. The tunability of strain, bandgap [1] or thermal properties [2], made them materials of choice for a wide range of applications especially in semiconductor technologies. They are currently used for energy conversion in the space industry due to their thermo-electric properties [3, 4, 5], as well as in photonics [6] and micro electronics industry [7]. They are still subject of much research and show potential as new generation material for solar cells [8], or new high capacity anode material in Li-ion batteries [9].

Apart from their interesting properties in their diamond cubic form, new interest has been shown for new crystallographic phases of SiGe alloys such as tetragonal, rhombohedral or deformation of the ideal diamond cubic structures. In addition to the tunability of their physical properties, these phases exhibit different properties than the ones of the diamond cubic form such as a direct bandgap for wurzite phase [10], or different thermo-electric power [11].

High Pressure (HP) and High Temperature (HT) treatments are then of interest to explore and synthesize such phases. HP techniques have proven to be an effective means of inducing new crystallographic phases in materials. For example, it's well known that in germanium and silicon, metastable phases can be recovered at ambient upon pressure cycling in the 0-15 GPa region [12, 13, 14, 15, 16, 17, 15]. However the phase transition pathways remains almost unexplored in the case of SiGe alloys. This partially due the cost and difficulty to synthesize these alloys, especially germanium-rich materials.

The goal of my research project was first to find the synthesis pathway to obtain homogeneous SiGe alloys in laboratory. This was to compensate for the limited availability of different alloy compositions on the market, as well as the uncertainties about their quality or origin of synthesis. This synthesis work, was also intended to pursue a collaboration with the LN2 laboratory of Sherbrooke, Quebec, in providing new materials for anode active materials in lithium ion batteries. This part of my project could not be developed further due to the difficulties encountered during my thesis period because of the global Covid-19 pandemic.

Using the synthesised materials, our second main objective was to study the high-pressure behaviour of SiGe alloys of different compositions in order to complete the high-pressure phase diagram and to explore the thermodynamic conditions needed for the formation of new metastable SiGe phases that might have interesting properties. Using high pressure tools such as Paris-Edinburgh (P-E) press or Diamond anvil cell (DAC) coupled with *in situ* characterization techniques, we aimed to measure the mechanical, structural and vibrational properties of the diamond phase and, when possible, new phases of SiGe alloys.

Corresponding to the two main goals presented, this manuscript is organised in two main parts :

The **first main part** is dedicated to the synthesis work and the second part to the high pressure study of our materials.

In the **first chapter**, I briefly present the structural and vibrational properties of the natural diamond cubic phase of silicon, germanium and SiGe alloys. Along with the main laboratory techniques I used to characterize my synthesis products such as X-Ray Diffraction (XRD), Raman spectroscopy and Energy Dispersive X-ray spectroscopy (EDX).

In the **second chapter**, I first present the phase diagram of SiGe and a review of the techniques reported in the literature for the synthesis of SiGe alloys. Then, I detail the synthesis techniques and the experimental protocol I used along with the characterization of the synthesized materials.

The **third chapter** presents the different solutions I have found to achieve the desired materials by combining some of the previously introduced techniques, and I discuss the potential improvement of our synthesis protocols.

In the **fourth chapter**, I present the interest of germanium as potential new material in lithium ion batteries and report the synthesis of hybrid nanostructures of germanium and carbon using pulsed laser ablation in liquids.

The **second main part** of my manuscript begins with the fifth chapter which deals with the HP tools and the in-situ characterization techniques used during this work including the experimental setup, preparation protocols and large instrument used.

The **sixth chapter** presents a review of the known HP phases of silicon, germanium and SiGe alloys.

The **seventh chapter** presents our high pressure experiments performed on Ge, $Si_{0.8}Ge_{0.2}$ and $Si_{0.5}Ge_{0.5}$. I describe the *in situ* characterization of the diamond and the metastable phases of these materials, using Raman spectroscopy, XRD from a laboratory source or synchrotron. I focus particularly on pressure and temperature induced transitions that lead to the observation of metastable phases.

The main results of this synthesis and high pressure study of SiGe alloys are then summarised in the general conclusion section.

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Part I : Synthesis of SiGe alloys and nanostructured germanium

Structural and vibrational properties of Si, Ge and SiGe alloys and characterization techniques

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1.1 Introduction

In this chapter I briefly present the structural and vibrational properties of silicon, germanium and their alloys. This will allow a better follow-up of the discussion on the characterisation and properties of the synthesised alloys. I present the impact of alloying on the crystal structure and vibrational properties using theoretical and experimental results from literature. XRD, Raman spectroscopy and EDX techniques used to probe these properties are briefly presented, as well as the experimental setups used.

Production of silicon and germanium

Silicon composes 27.7% of the Earth's crust mass, rarely in pure form but rather in various silicate minerals. It was discovered in 1824 by the chemist Jöns Jacob Berzelius. It is mainly extracted from the mineral quartzite by reducing it in electric arc furnace. Each year more than seven millions tons of silicon are produced mostly in China (4.5 million of tons), Russia (0.6 million tons) followed by Norway and U.S (0.3 million tons)[18].

Germanium is relatively less present in earth crust, about 1.6 ppm compared to $\sim 280\,000$ ppm for silicon [19]. It was first detected by the German chemist Clemens Winkler in 1886 in the silver sulphide mineral argyrodite. Like silicon this element is not present on a pure form but extracted from waste residue of hydro metallurgical zinc processing operations [20]. 130 tons are extracted each year, mainly in China (85 tons) and Russia (five tons) [21]. Worldwide, about 30% of the total germanium consumed is produced from recycled materials. This value is even more important in manufactured electronic and optical devices, where more than 60% of the Ge metal used is routinely recycled as new scrap. Main industrial applications of germanium concern infrared technology and fiber optics (where new advances are still been done [22]).

Silicon germanium alloys are not present under natural conditions and are synthesized from silicon and germanium.

1.2 Structural properties

Silicon, germanium, and SiGe alloys crystallize in the same cubic diamond structure at ambient conditions. They belong to the $Fd\bar{3}m$ space group (227) also denoted with the suffix "-I" or prefix "dc" (Si-I or dc-Si). This structure can be described in two different ways :

- Two entangled FCC Bravais lattices, the second shifted by a vector $(\frac{a}{4}, \frac{a}{4}, \frac{a}{4})$, a being the cell parameter as shown in figure 1.1 a).
- Using one FCC lattice decorated with two identical atoms in $(0,0,0)$ and $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ positions as shown in figure 1.1 b).

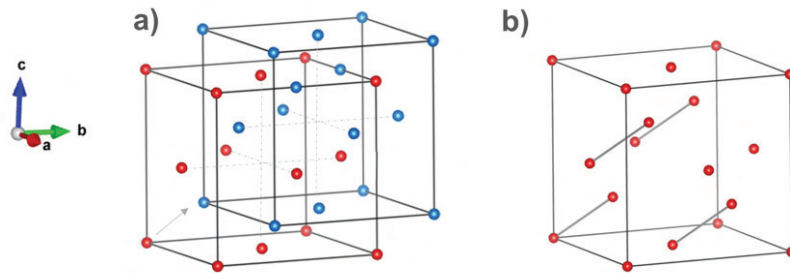


Figure 1.1: Construction of the diamond phase a) using two FCC lattices, one at the origin (in red) and another identical atom shifted by $(\frac{a}{4}, \frac{a}{4}, \frac{a}{4})$ (in blue) b) Using one FCC lattice where the repeated pattern is : one atom in $(0,0,0)$, another identical atom in $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ shown by a red-blue link . Using VESTA software [23].

In this structure, each atom is bond with four neighbour atoms (highlighted in figure 1.2).

Silicon and germanium cell parameters differ by 4% (5.658 Å for Ge and 5.430 Å for Si). They form a solid solution over the whole composition range. SiGe alloys are substitution alloy where occupancy of the sites depends on the composition of the alloy as depicted in figure 1.2 c. The cell parameter vary linearly between the cell parameter of the two pure components with the composition [24]. This Vegard law is almost verified for the SiGe system, where only a very small negative deviation around 0.002 Å has been measured for medium compositions ($x = 0.5$) [25].

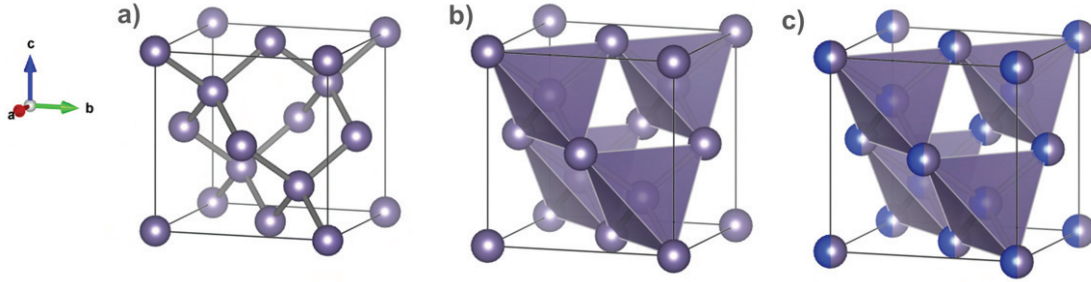


Figure 1.2: Simulated diamond structures showing a) Bonds b) Tetrahedrons c) Site occupancy's in $Si_{0.5}Ge_{0.5}$. Using VESTA software [23].

1.2.1 X-ray diffraction principle

XRD is a technique widely used to determine the structural properties of a crystalline material. The principle is to submit a sample to electromagnetic radiation noted λ . When this wavelength is of the same order than inter-atomic distances ($\sim \text{\AA}$) it is elastically diffused. Each atom composing the material acts as a diffusion centre. In case of crystalline samples, the periodicity of the atoms gives rise to coherent or incoherent diffusion of the incident waves. In the far field approximation (assuming that the source of diffusion is far from the detector), the intensity of elastic the diffusion by atoms can be written as :

$$I = \sum_{u,v,w} e^{-i(u\mathbf{a}+v\mathbf{b}+w\mathbf{c})\cdot\Delta\mathbf{k}} \quad (1.1)$$

With $\mathbf{a}, \mathbf{b}$ and $\mathbf{c}$ the vectors of the translations of the crystal, u, v and w the atoms positions in the crystal given by $\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$. $\Delta\mathbf{k} = \mathbf{k} - \mathbf{k}'$ is the difference between incident and diffracted wavevectors. In the case of elastic scattering : $|\mathbf{k}| = |\mathbf{k}'|$.

In order to have coherent interference the exponential term must satisfy the Laue condition :

$$\begin{aligned} \Delta\mathbf{k} \cdot \mathbf{a} &= 2\pi \cdot h \\ \Delta\mathbf{k} \cdot \mathbf{b} &= 2\pi \cdot k \\ \Delta\mathbf{k} \cdot \mathbf{c} &= 2\pi \cdot l \end{aligned} \quad (1.2)$$

When this equation is satisfied, $\Delta\mathbf{k} = \mathbf{G}$ is a vector of the reciprocal lattice, $\mathbf{a}^*, \mathbf{b}^*$ and $\mathbf{c}^*$ are the primitive vectors of translation of the reciprocal lattice. h, k and l represent the Miller indices indexing the planes.

This condition is equivalent to the Bragg law, stating that constructive interference happens when the travelled distance by X-rays $\Delta L = 2d \sin(\theta)$ is a multiple integer of the radiation wavelength.

$$\Delta L = 2d_{hkl} \sin(\theta) = n\lambda \quad (1.3)$$

By measuring the periodicity and positions of the reflections, information on the crystal cell parameters can therefore be obtained. A schematic representation of Bragg law and Laue conditions is presented in figure 1.3.

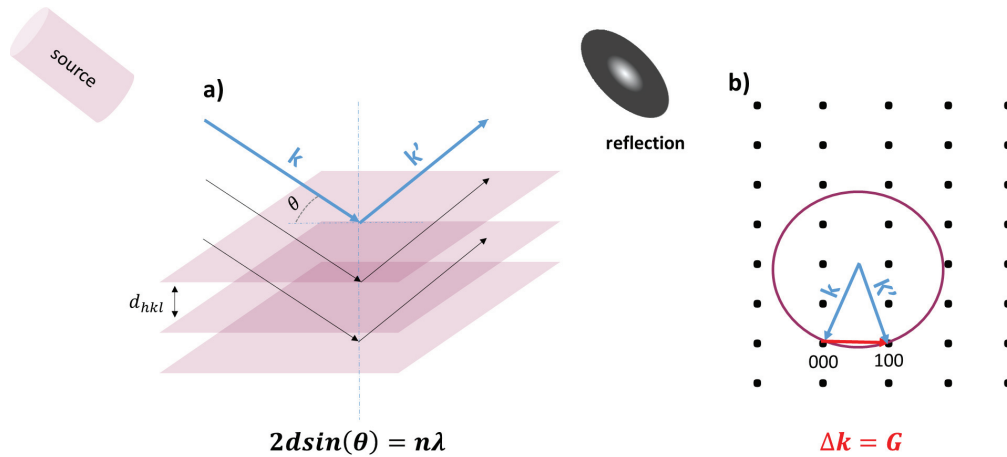


Figure 1.3: a) Illustration of the Bragg law $2dsin(\theta) = n\lambda$ b) Illustration of the Laue condition $\Delta\mathbf{k} = \mathbf{G}$ (in 2D)

Pure elements and some alloys have already been measured and crystal parameters are referenced in the PDF4+ database. Simulation of the XRD pattern of various compounds is presented in figure 1.4.

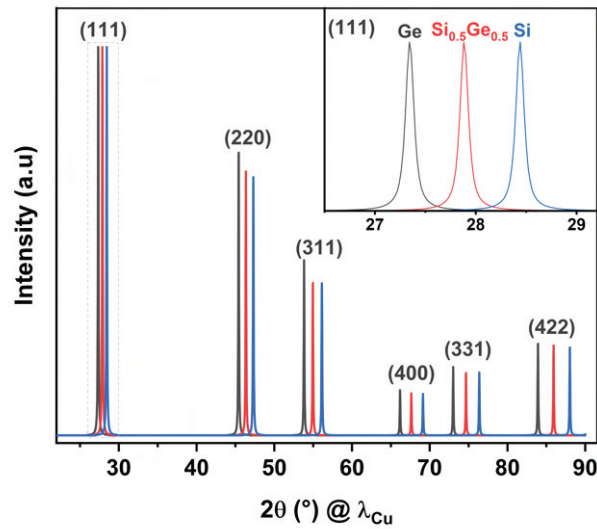


Figure 1.4: Simulated XRD patterns for monochromatic ($CuK_{\alpha 1}$) radiation wavelength. PDF4+ references used are Ge : 00-004-0545; Si: 00-005-0565 $Si_{0.5}Ge_{0.5}$: 04-005-9700.

1.2.2 Experimental setup

The XRD patterns presented in future sections are obtained using an Aeris Diffractometer in Bragg Brentano geometry. Radiation wavelength is $Cu_{K\alpha_1}$ at 1.5405 Å and $Cu_{K\alpha_2}$ at 1.5443 Å. The 2θ range is set to 10–80° with steps of 0.011°. For the incident beam a small divergence slit is used (1/16). A Nickel filter was placed before the detector to remove $K\beta$ signal. Extraction of the cell parameters was made using Maud Software version 2.99 [26]. The references of PDF 4+ data files used for structure simulation are the following : *Ge* : 00 – 004 – 0545 and *Si* : 00 – 005 – 0565 for raw materials and modified cif file *Si_{0.5}Ge_{0.5}* : 04 – 005 – 9700 for the other alloys. Further information on peak parameters such as Full Width Half Maximum (FWHM) and asymmetry were obtained using Fityk software version 1.3.1. (for more information see Appendix A).

1.3 Vibrational properties

1.3.1 Raman spectroscopy principle

The Raman effect also take advantages of the interaction between light and matter. The principle is to illuminate the sample with a monochromatic light, usually produced by a laser. The main part of the wave is elastically scattered, in this case the incoming and scattered wavelength are the same.

In Raman spectroscopy, the effect probed is the inelastic scattering of light by molecular vibrations (phonons). The energy of the scattered light is decreased/increased by the energy of the excitation created/annihilated. By measuring this difference, one can determine the frequencies of the vibrational modes in the material.

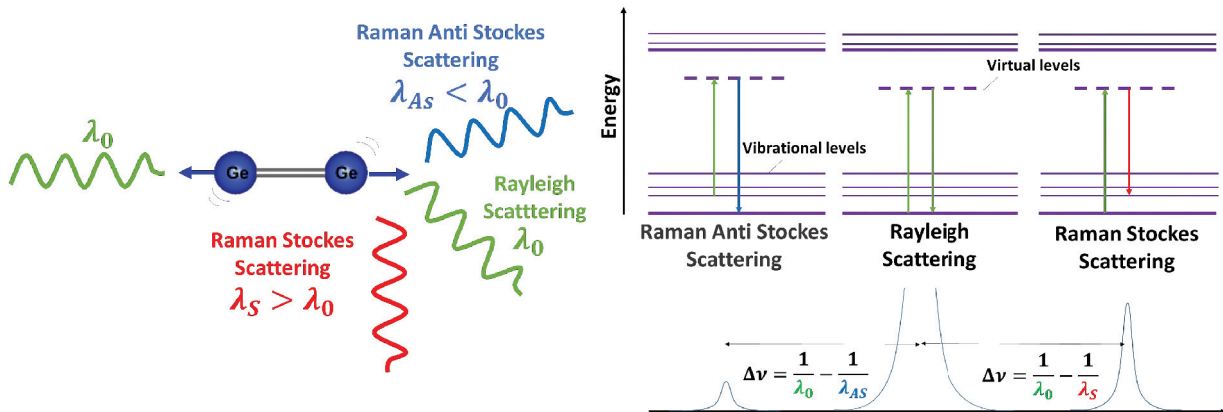


Figure 1.5: (left) Schematic representation of the interaction between an incident wavelength λ_0 scattered by a crystal lattice. (right) Jablonski diagram showing the origin of Rayleigh scattering (elastic), Stokes and Anti-Stokes Raman scattering (inelastic).

Directly inherited from the symmetry of the diamond structure, silicon and germanium typical vibrational spectra present only one vibration mode that is a longitudinal optic mode (LO) in figure 1.6. The germanium mode is usually measured at 300 cm^{-1} and the silicon mode at 521 cm^{-1} [27].

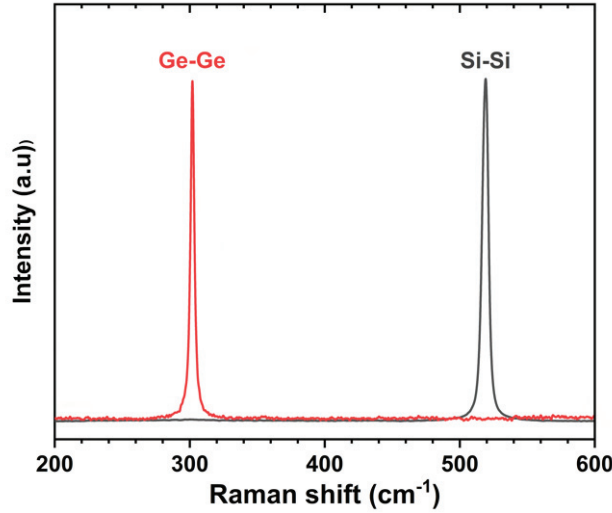


Figure 1.6: Typical Raman spectra of pure Si and Ge showing only one longitudinal optic mode at 300 cm^{-1} for germanium and 521 cm^{-1} for silicon.

Alloying of silicon and germanium has a huge impact on the vibrational spectra observed. Typical spectra of different compositions are presented in figure 1.7.

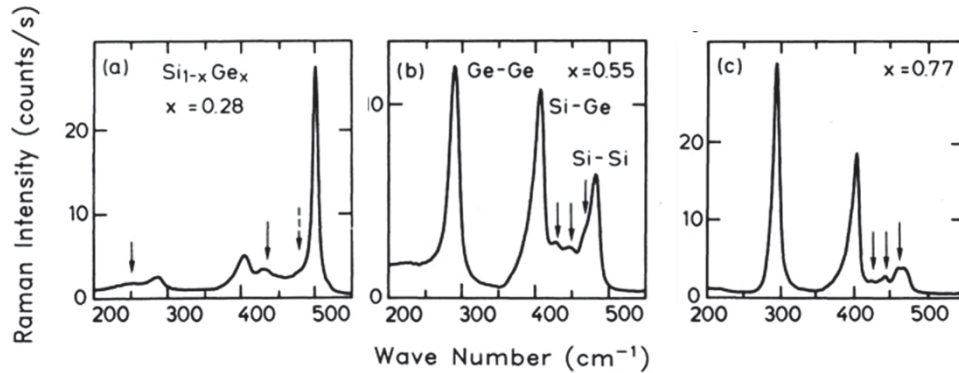


Figure 1.7: Raman spectra of $\text{Si}_x\text{Ge}_{1-x}$ for $x=0.28, 0.55, 0.77$. The longitudinal optic modes for Ge and Si are slightly shifted and vary in intensity depending on the composition. In addition a (Si-Ge) transverse optic mode is seen around 400 cm^{-1} . Depending on the alloy composition, several alloy induced peaks are visible, marked by arrows. Reproduced from ref [28].

First, three main modes corresponding to optical phonons associated with Ge-Ge, Ge-Si, and Si-Si vibrations are present around $300, 400$ and 500 cm^{-1} . They present an asymmetric shape because of the disorder introduced by the alloy that leads to a partial lifting of the selection rule and a contribution from the vibrational density of states [29, 30].

Between the Ge-Si mode at $\sim 400\text{ cm}^{-1}$ and the Si-Si mode at $\sim 500\text{ cm}^{-1}$, several modes are measured depending on the composition. In the literature those modes are associated to peculiar Si-Si local vibrational modes due to the fluctuations of the number of Ge atoms in the vicinity of Si ones [29, 31].

At frequencies lower than (Ge-Si) mode, a broad mode is present. This mode is less discussed in the literature and may arise from a local vibration of an isolated Si atom in a Ge matrix [32].

At frequencies lower than (Ge-Ge) mode, a broad feature is observed. This feature is often referred to as quasi-amorphous (q-a) because of a correspondence with a similar peak reported in amorphous alloys. This mode attribution is still discussed [28, 33].

1.3.2 Composition determination by Raman spectroscopy

Similarly to XRD, vibrational modes shift with the composition of the alloy. This dependence is particularly strong for the (Si-Si) mode that which express a linear shift with alloy composition as shown in figure 1.8 (reproduced from ref [28]). The composition of the sample can be estimated from the frequency of this mode using the following formula :

$$\omega_{Si-Si} = \omega_0 - 70 * (1 - x) \quad (1.4)$$

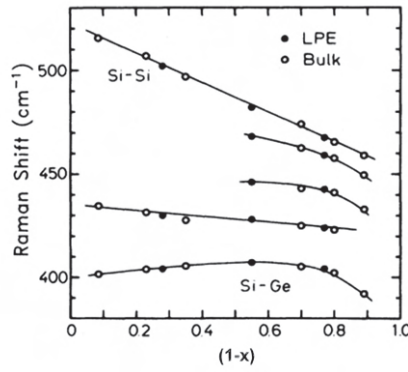


Figure 1.8: Raman shift of several Si_xGe_{1-x} vibrational modes as a function of composition reproduced from ref [28]. LPE stands for liquid phase epitaxy (the growth method used by authors to obtain single crystals) and Bulk other measurements made on polycrystalline samples. Si-Si mode show a strong linear variation as a function of the composition, used to estimate the alloy composition. Other modes also vary with composition, but this variation less marked and cannot be used efficiently to estimate the composition.

1.3.3 Experimental setup

Raman experiments were carried out using a Horiba Jobin-Yvon ARAMIS micro spectrometer in backscattering geometry. The laser wavelength used was 532 nm, diode laser power was adjusted in order to avoid heating effects on the samples and to improve signal over noise ratio. The laser beam was focused with a 50x objective and the signal was dispersed by a grating of 1800 grooves/mm, resulting in a spectral resolution of about $\sim \pm 1 cm^{-1}$.

1.4 Scanning electron microscopy and Energy dispersive X-ray analysis

The principle of Scanning Electron Microscopy (SEM) (in backscattering mode) is to focus a high energy electron beam on the sample surface by a set of electromagnetic lenses and to collect the backscattered electrons on a detector. The image contrast obtained strongly depend on the atomic number of the species present in the sample as shown in figure 1.9.

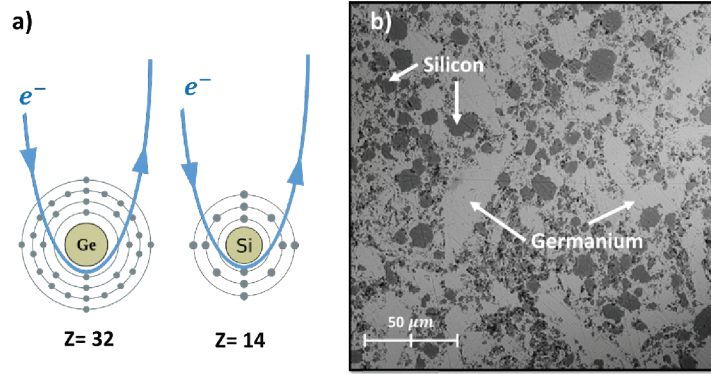


Figure 1.9: a) Schematic view of the incident electron backscattered by the interaction with the atom nuclei. This process is usually more efficient with heavy elements (that appears brighter). b) Typical image of compressed Si and Ge powders, showing germanium grains in light gray and silicon grains in dark gray.

Complementary to SEM imaging, EDX can also be performed. In this case, the incident primary electron beam excites some of the electrons of the inner shell of the atoms which are ejected, creating an electron hole. As this state is unstable, an electron of outer higher energy shell fills this hole. When the recombination occurs, the electron radiates specific X-rays that are characteristic of the difference of the energy between the two electronic shells. Those X-rays are detected by a energy-dispersive spectrometer. In our case X-rays emitted by germanium and silicon have very distinct signature spectra and the composition can be locally estimated in our sample as shown in figure 1.10 b).

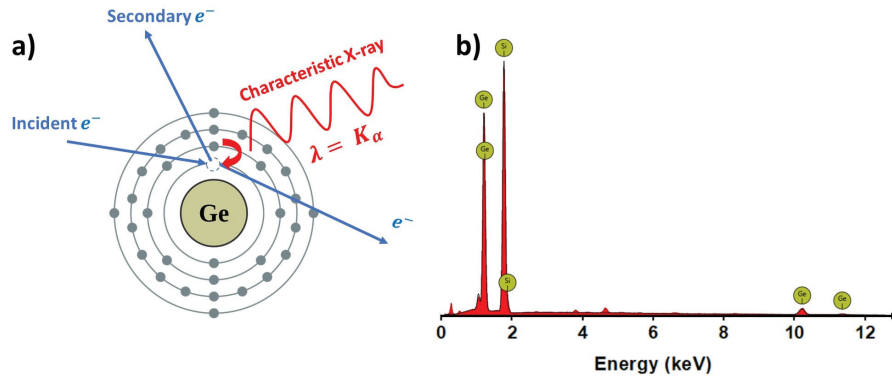


Figure 1.10: a) Schematic representation of the EDX physical process : i) ejection of an inner electron by an incident electron creating a hole in the inner shell ii) recombination of the electron hole with an electron of an higher shell iii) emission of X-ray radiation during recombination, with a wavelength characteristic of the atomic species b) Signature spectra of a sample composed of silicon and germanium.

1.4.1 Experimental setup

SEM pictures were obtained using a PHENOM pro bench scanning electron microscope in backscattering mode, equipped with a Silicon Drift Detector (SDD) with 25 mm^2 detection area and multi-channel analyzer of 2048 channels, 10 eV/channel. Global composition distribution was also determined using SEM. The contrast between germanium, silicon and their alloys allow us to observe the microstructure of the samples and the possible inhomogeneities. EDX measurements can be made both in point mode or mapping mode, allowing to estimate the composition of the sample at different scales.

Synthesis methods

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2.1 Introduction

In this chapter, I present the different methods and pathways used to synthesize SiGe alloys. Several issues motivated us to synthesise SiGe alloys in the laboratory in the context of this work. SiGe alloys are almost not commercially available. The few compositions available are very expensive, due to the fact that they are often high purity single crystals. Depending on the supplier, the method of synthesis may also vary or is not reported. In particular, germanium-rich alloys are extremely difficult to find commercially.

The objectives on the final product of synthesis were defined according to the type of study envisaged for the samples (in chapter 7 and 4). The goals of the synthesis work are the following :

- Find synthesis pathways toward the whole composition range.
- Synthesis time must be reasonable (about weeks).
- Small inhomogeneity can be present but less than 5% than the mean composition.
- The sample must present no residual stresses due to particle size or internal strain.
- The sample must contain no impurities (such as carbides or oxides).
- The techniques used will preferably be scalable for later use.
- The sample can be polycrystalline or monocrystalline and in different physical forms (powder, bulk). Control of the shape and density of the sample is a plus.

Given our synthesis objectives, the following sections aim to first present the SiGe phase diagram and then provide an overview of the different techniques used to synthesise SiGe alloys in literature. For each technique I will present its basic principle, describe the characteristics of the sample obtained and assess the potential advantages of using the technique. Finally by comparing the expected results to our synthesis objectives we will select which techniques are relevant and will define an experimental strategy.

2.1.1 SiGe phase diagram

At the base of each synthesis process, lays the phase diagram of the considered system. Three physical parameters (3 axes) are needed to plot the phase diagram : pressure, temperature and composition. For practical purposes, we consider here the phase diagram at ambient pressure.

For Si and Ge, the formation of a solid solution is expected as they obey the Hume–Rothery rules [34]. Si and Ge share the same cubic diamond structure with four valence electrons, have similar electronegativities (1.90 and 2.01 for Si and Ge respectively) and, finally, their atomic radii differ by less than 15% [35].

The phase diagram of SiGe system was experimentally measured for the first time by Stöhr & al in 1939 [36]. The phase diagram measured is shown in figure 2.1 b. This diagram is a typical binary phase diagram defined by three regions (liquid, liquid + solid, solid) separated by liquidus and solidus lines.

Liquidus and solidus lines are commonly determined using the solidification curves. For a pure compound, solidification is an exothermic process, which means that during the cooling of the melt, crystallisation occurs at constant temperature. In the case of alloys, this process happens in a temperature range that defines both liquidus and solidus lines as depicted in figure 2.1 a).

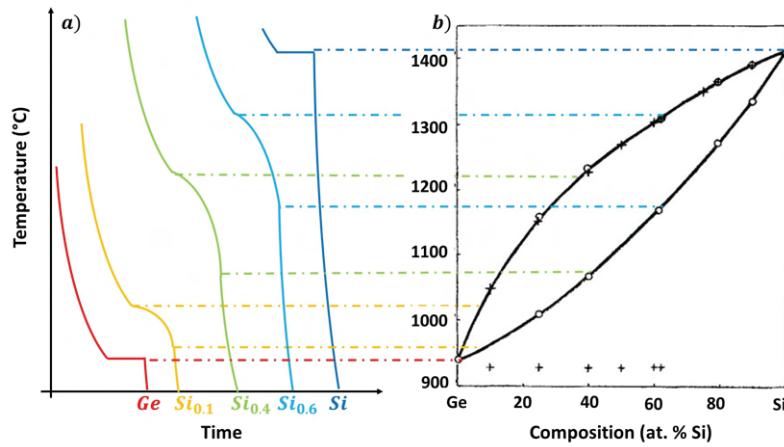


Figure 2.1: a) Schematic representation of cooling curves used to determine liquidus and solidus lines for SiGe alloys. b) Equilibrium phase diagram of the SiGe system, reproduced from ref [36].

The liquidus line was first determined using cooling curves of different SiGe compositions by Stöhr & al [36]. However the solidus line was found to be harder to measure for SiGe alloys. The authors report that the equilibrium between the formed crystals and the melt is not well established during cooling, which disturbs the measurement of the full solidification temperature. The SiGe system indeed tends to form "mixed crystals" meaning that during the solidification process, segregation occurs and different alloy compositions crystallize.

Instead, the authors tried to measure solidus line using heating curves. To determine the heating curves, homogeneous starting samples are needed. The authors obtained homogeneous alloys by annealing compacted powder mixtures of Si and Ge at relatively low temperature (920°C for Ge-rich samples) for months into quartz tubes. Then they recorded the heating curves of the homogeneous alloys to determine the solidus line. They noted that the separation in mixed crystal, seen during cooling, was not happening during heating, allowing them to measure a second time the liquidus line during this experiment. The phase diagram was not explored further except for the Ge-rich side in 1955 [37] and latter in 1984 [38]. The discovery of the phase diagram and confirmation of full miscibility of Si and Ge is the starting point of all synthesis process made later. This phase diagram is therefore used in this work.

These study highlight two major synthesis challenges that need to be overcome : i) if a mixture of germanium and silicon is brought to a liquid state, segregation will occur during the cooling procedure, preventing any homogenization of the sample; ii) in order to obtain homogeneous alloys using only solid state synthesis (without any melting) months are needed at temperatures below the germanium melting point (938°C).

2.1.2 Review of existing synthesis methods

Three different type of pathways can be used to synthesize SiGe alloys depending on the sample wanted. These pathways can generally be categorized as i) Gas phase reaction (thin layers) ii) liquid state reaction (single crystals), and iii) solid state reaction (polycrystalline samples).

Gas phase synthesis :

Chemical vapor deposition (CVD)[39, 40] and molecular beam epitaxy (MBE)[41] are methods widely used in the semiconductor industry for new generation electronic and optoelectronic materials. The principle is to expose a substrate to gas precursors (CVD) or sublimated Si and Ge (MBE) to form thin layer on the substrate. The advantages of these methods are the high control over the growth conditions, resulting in very pure thin layers of SiGe alloys deposited over a substrate (silicon wafer).

These methods are not of interest for us for several reasons : they do not produce bulk samples and the growth rate is slow (typically tens of nm/min)[42]. The substrate used is also part of the final product, and it is susceptible to induce strain on the sample because of lattice mismatch, as well as undesired signal in the future HP experiments. These techniques require specific/expensive equipment not accessible in our case.

Liquid phase synthesis

Different growing techniques were used to synthesize single crystals of SiGe alloys such as floating zone (FZ) [43, 44, 45], Czochralski (CZ) [46, 47], Bridgman [48], unidirectional growth [49] and classical cooling [50]. All these techniques are based on a very precise control of the growth conditions in order to get as close as possible to the equilibrium conditions. Besides the advantages of having single crystal samples, all of these methods are limited by the large gap between liquidus and solidus line, the reactivity of melted silicon with the crucibles, oxidation, segregation, gravity effects and slow growing rates. Even with recent advances in growth techniques, synthesis of SiGe alloys remains difficult and explains the low availability and high price of these materials on the market. Despite their interest, these methods are not accessible in our laboratory and are not used in this work.

On the opposite side of the spectrum, far from the equilibrium, experiments involving rapid melting and quenching are reported. In particular arc melting is a quenching method where the sample is melted with an electrical arc and cooled almost instantly in a cooled crucible. If the quenching speed is high enough, segregation can be avoided by passing from the liquidus to the solidus gap extremely quickly [51]. A study [52] mentions arc melting as an interesting method to obtain an intermediate state to form $Si_{0.8}Ge_{0.2}$ combined with spark plasma sintering (presented latter). Despite a lack of information about this particular method, arc melting is an interesting method and accessible in our laboratory and it will be described later 2.2.

Solid state synthesis :

Several techniques were used to synthesize polycrystalline samples. Most of the literature is focused on the silicon rich part of the phase diagram due to the interesting thermoelectric properties of $Si_{0.8}Ge_{0.2}$ alloy [53]. In these methods, the reaction between silicon and germanium is caused either mechanically or thermally.

Planetary ball milling is a commonly used method to prepare a powder mix and mechanically alloying Si and Ge [54, 55]. The principle is to mix Si and Ge powders in high-speed planetary ball mills. The energy of repeated impacts induces local alloying by the cold welding process [56]. The synthesized alloys are usually pre-reacted powders, presenting nano-sized crystallites and high internal constraints [55]. Due to the ball milling process the powders can present impurities like iron. These characteristics are not compatible with our objectives and this method is not of interest in our case.

Hot pressing was extensively studied to produce silicon rich alloys. The principle is to make Si and Ge powder mix reacts using HT (reaching 1400°C) and moderate pressures of ~ 100 MPa. The silicon and germanium powders used are often mechanically pre-reacted using planetary ball milling to enhance the hot pressing process. Only a few compositions were explored in the 80's : $Si_{0.7}Ge_{0.3}$ [57] and $Si_{0.8}Ge_{0.2}$ [57, 58, 59, 4, 60, 53]. The synthesis product is a dense cylindrical pellet of SiGe alloys. The characteristics of the samples are consistent with all our expectations, but this method is not accessible in our laboratory.

Spark Plasma Sintering (SPS) is a method similar to hot pressing regarding temperature and pressure range used. The main difference is that the high temperatures are created by passing a pulsed current through the sample. This current generates a plasma between the grains, resulting in highly localized temperatures. This method is extremely fast, with synthesis time of several hours. Most of the reported studies focus on the $Si_{0.8}Ge_{0.2}$ composition [61, 62, 63, 64, 65], but one study of Thompson & al. in 2012 reports the sintering process on different Si rich compositions [66]. There is globally a lack of knowledge about how this technique can be applied to the synthesis of other compositions than $Si_{0.8}Ge_{0.2}$. The characteristics of the synthesized samples fulfill our synthesis objectives, making SPS technique very interesting for our project. Though this method is not available in our laboratory, it was accessible in another laboratory for one week and it will be presented in section 2.4.

The Belt press is an apparatus that allows compressing a few mg of sample up to 5 GPa and temperatures up to 1600°C. Only one experiment has been proposed by Serghiou & al in 2014 [67]. Two symmetric compositions were explored $Si_{0.75}Ge_{0.25}$ and $Si_{0.25}Ge_{0.75}$. Despite the problems involved with melting at such high pressures, the results are dense homogeneous alloys of the two compositions. This is the only method that proposes a pathway to obtain polycrystalline germanium rich compositions. We carried a similar experiment in laboratory, that is presented in section 2.5.

In conclusion, most of the solid state techniques presented were used to produce larger quantities of samples. In the literature, most of the experiments were focused on the silicon rich part of the phase diagram. With the exception of crystal growing techniques that are limited by some factors, no a unique way to cover the entire compositional range of SiGe alloys is presented.

In conclusion, according to the literature, the main challenges are :

- Finding a way to overcome the wide gap between the liquidus and solidus lines, causing segregation when quenching down a melt.
- Expanding the accessible compositional range to germanium rich samples.
- Avoiding oxidation in our sample or contamination from reaction with crucibles.
- Limiting the processing time.

In the following section, we present the different techniques used. Four different technique were used : arc melting, solid state synthesis, SPS and Belt press. Arc melting is presented first as it is the one having the higher potential to form dense alloys over the whole composition range and is a relatively fast technique.

In all synthesis, the reactants are silicon powder (Particle size: 325 mesh, Purity: 99.999%, Strem chemicals) and germanium powder (Particle Size: 325 mesh, Purity: 99.99%, Sigma Aldrich).

2.2 Arc Melting

2.2.1 Introduction

The arc melting is a technique that appeared in the late 60's and was commonly used in the space industry to synthesize large amounts of titanium alloys [68]. Currently, this method open new pathways to synthesize high entropy alloys (HEA) composed of more than two elements [69]. A schematic view presenting the arc melting experimental setup is shown in figure 2.2.

The advantages of the arc melting are numerous :

- It is an extremely fast way to melt different elements together, even with large differences of melting temperature. This is a crucial parameter because in the case of silicon and germanium the difference in melting temperature is about 500°C.
- The sample does not react with the copper crucible that is water cooled, avoiding any contamination of the sample.
- Very fast quenching can help avoiding segregation of the different elements by directly going from liquid state that is homogeneous to the solid state [51].

A schematic view presenting the arc melting experimental setup is shown in figure 2.2. Typical arc melting apparatus is composed of several elements :

- A melting chamber, where the elements are melted.
- A vacuum pumping system that allows to remove the atmosphere of the chamber and fill it with argon.
- 2 electrodes : 1. A removable top tungsten electrode 2. A water cooled bottom electrode in copper, this electrode serves as crucible, holding the reactants.

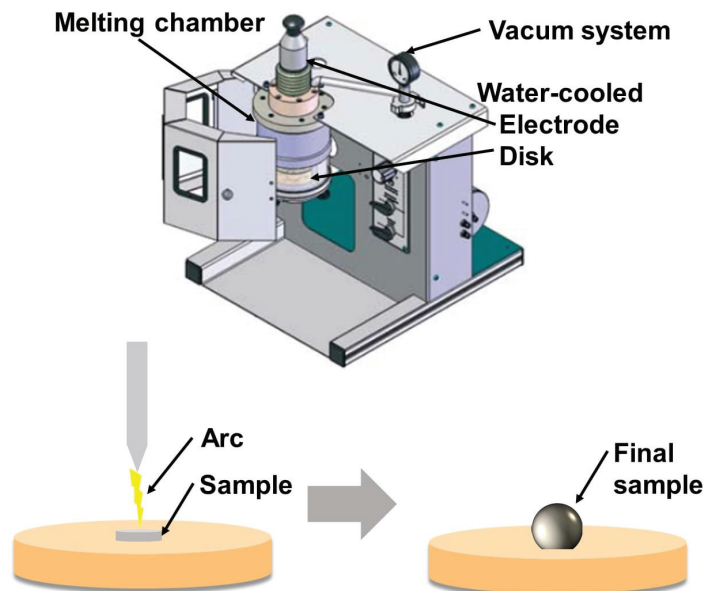


Figure 2.2: (Top) schematic representation of the BÜHLER Mini Arc Melting System type "MAM-1" reproduced from technical sheet. (Bottom) schematic representation of the arc melting process where an electrical arc is produced between top and bottom electrode, instantly melting the sample and quenched by contact with the copper cooled bottom electrode. The sample produced by this process are dense balls of approximately 200 mg mass.

2.2.2 Experimental protocol

The arc melting experiment was carried out using a BÜHLER Mini Arc Melting System type "MAM-1" placed in a glove box filled with argon atmosphere. For each composition, 200 mg of Si:Ge powders are prepared. The initial powders are intimately mixed together using an agate mortar and a crucible. The resulting mixture is then pressed to form pellets of 2 mm height and 8 mm diameter. The densification of the powder mix is a crucial step to avoid any pulverization of the powder by the electrical arc during the synthesis.

The pellets are placed on a water-cooled copper electrode inside the reaction chamber. After pumping and filling the reaction chamber with argon, a voltage is applied between the two electrodes. The upper tungsten electrode is manually moved close to the sample until the electrical arc appears. The arc instantly leads to the rapid melting of the whole sample. The liquid ball formed is cooled in a few seconds thanks to the contact with the copper disk. At this point, the bottom part of the sample in contact with the copper disk still contains some unmelted powder. The whole process is repeated three times, each time returning the ball to ensure full melting of the sample. After a sample is synthesized, the copper crucible and the whole chamber are cleaned to avoid any contamination of the next samples.

2.2.3 Results and discussion

The arc melting synthesized samples are a few millimeter diameter dense balls of reacted silicon and germanium powder. Depending on the sample, the final mass obtained is approximately 180 mg, due the ejected matter by the electrical arc. The resulting balls are cut using a diamond saw and polished or ground for analysis. In figure 2.3 we present three arc melting balls during the cutting process.

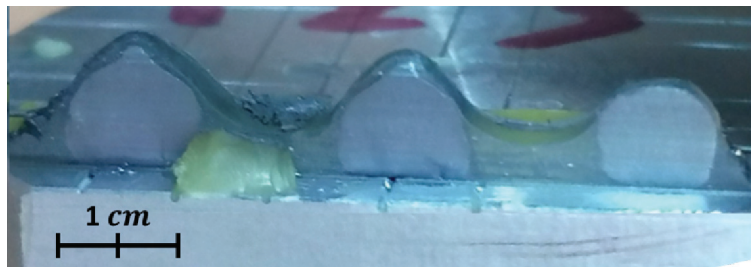


Figure 2.3: Picture of the balls synthesized with arc melting during the cutting process. The balls are embedded in a resin during the cutting process to keep the sample stable on the sample holder.

XRD patterns collected on ground samples obtained after the arc melting process are presented in figure 2.4. Two patterns of powdery germanium and silicon are shown for reference. The results indicate that the cell parameter of the sample is in between the germanium and silicon cell parameter. But none of the samples present a single (111) peak of diffraction indicating that composition in our sample is not homogeneous. The samples show broad diffraction peak indicating a strong composition gradient. The XRD results promote the idea that segregation is happening inside the sample during quenching process, despite the fast quenching. In the germanium and silicon rich samples ($x=0.1$ and $x=0.86$), the (111) reflections seems to be more defined, indicating that at both ends of the composition, segregation is less important. These results are consistent with the smaller gap between liquidus and solidus in these composition region. However, strong asymmetry is visible (left asymmetry for the Si rich sample, and right asymmetry for the germanium sample).

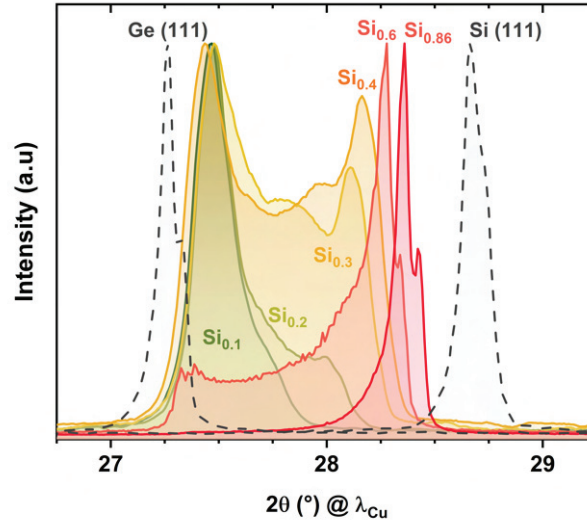


Figure 2.4: XRD patterns of the SiGe alloys obtained by arc melting zoomed on the first (111) reflection. Presence of broad peaks indicates that the composition in arc melting samples is not fixed. Pure silicon and germanium patterns are shown in dotted line for reference.

SEM micrographs were made on cut/broken and polished parts of the balls are shown in figure 2.5. The images shown are typical of the whole sample, and not specific to some regions (for example bottom or top part of the balls that may have experienced a different quenching speed). The images are consistent with the XRD results, showing a strong contrast between alloys rich in germanium (light gray) and silicon rich alloys (dark gray). No inclusions of pure silicon or germanium has been observed. We can note that, as the silicon content increases, the volume fraction of silicon rich grains increases at the expense of a germanium-rich matrix (as seen in XRD).

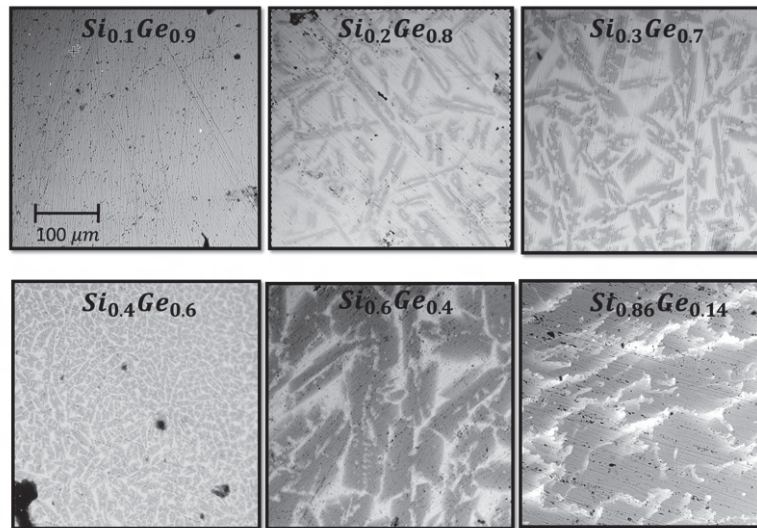


Figure 2.5: SEM images (in back scattering mode) of polished SiGe alloys obtained by arc melting. Light gray regions indicates the presence of germanium rich regions, dark gray indicates silicon rich regions. None of arc melting samples present a fixed composition.

2.2.3.1 Size effect/quenching effect

XRD and SEM experiment shown that segregation seems to occur for 200 mg pellets. We can make the hypothesis that quenching is having an effect but is not fast enough. To test this hypothesis, several samples of same starting composition $Si_{0.8}Ge_{0.2}$ with different starting mass were prepared. The goal is to decrease the quenching time by decreasing the sample size.

The results were analysed using XRD that is a faster way to see the segregation effect than SEM. The results shows that decreasing starting mass leads to a decreased left asymmetry of the (111) peaks and thus, to less segregation of germanium as shown in figure 2.6. These results indicates that a higher quenching speed leads to a better sample.

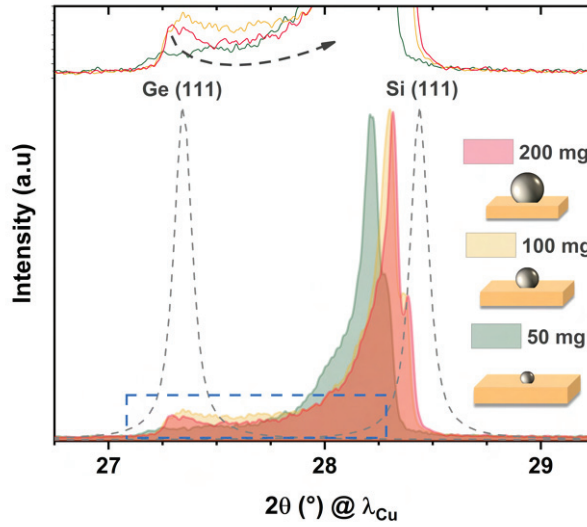


Figure 2.6: XRD pattern of three $Si_{0.8}Ge_{0.2}$ alloys of different starting mass obtained with arc melting. At the top an inset showing a zoom of the peak shoulder. The reduction of left asymmetry of the peak with decreasing sample mass is consistent with a reduced segregation effect with increasing quenching speed.

The obtained results indicates that reaching a faster quenching speed could improve the sample homogeneity, however this is difficult to achieve in our case. Using samples of less than 50 mg starting mass greatly increases the risks to pulverize the sample with the electrical arc. The installation of a vacuum suction system would be needed in order to increase the contact surface between the water cooled crucible and the melt, such device is not available in our lab.

2.2.4 Conclusion

In conclusion, using arc melting technique, we were able to make silicon and germanium powder react by rapid melting and quenching resulting into dense, spherical shaped samples. We observed using XRD and SEM that a gradient of composition is present in our sample with silicon rich and germanium rich regions. The quenching provided by arc melting is therefore insufficient to avoid segregation during the cooling process. Considering these results, we can say that for next experiments, the presence of melting in our sample should be avoided due to this high segregation effect. The next section will be dedicated to solid state synthesis, where we brought reaction between silicon and germanium powders while staying in the solid state region of the phase diagram, in the vicinity of the solidus line.

2.3 Solid state synthesis

2.3.1 Introduction

In this part we present the solid state synthesis process. Contrary to previous section, homogeneity is reached using a different path in the phase diagram. During the process, melting is prevented in order to avoid crossing the solidus line. This prevents segregation effects seen in previous section. This process shares some similarities with hot pressing method presented in the literature review section 2.1.2, except that we do not use pistons to apply pressure on the samples during heating.

The solid state reaction has been extensively studied in the literature. The diffusion process during solid state reaction is expected to be slow. The estimated diffusion coefficients of germanium and silicon inside SiGe alloys have been estimated [70], and follow an empirical Arrhenius law :

$$D = D_0 e^{-E_a/kT} \quad (2.1)$$

With D_0 the pre-exponential factor in cm^2s^{-1} , E_a the activation energy in eV, k the Boltzmann constant in eVK^{-1} and T is the temperature in Kelvin. The typical values of D_0 varies from 25 to 3000 cm^2s^{-1} and values of E_a varies between 3 eV for pure germanium to 4.8 eV for pure silicon [70]. The diffusion length is given by the equation :

$$L_{diffusion} = \sqrt{Dt} \quad (2.2)$$

The different parameters of this equation vary depending on the component considered (Si or Ge) and the medium in which the species are diffusing. The tab 2.1 gives some examples of calculated diffusion lengths using the previous equation of pure species (Si or Ge) into different media.

Medium	Temperature and duration	Calculated Ge diffusion length	Calculated Si diffusion length
Ge	1000°C 1h	-	970 nm
Ge	1300°C 1h	-	17 μm
Si	1000°C 1h	5 nm	-
Si	1300°C 1h	50 nm	-
$Si_{0.5}Ge_{0.5}$	1000°C 1h	44 nm	29 nm
$Si_{0.5}Ge_{0.5}$	1300°C 1h	2.1 μm	1.4 μm

Table 2.1: Calculated diffusion lengths of germanium or silicon species into Ge, Si or $Si_{0.5}Ge_{0.5}$ alloys media at different conditions, 1000°C and 1300°C, for a duration of one hour. Diffusion lengths are calculated using coefficient obtained in ref.[70].

To tackle the problem of slow diffusion, different strategies can be considered. A one step synthesis is not realistic as the reaction time to ensure a global homogeneity at the sample scale is too long. Instead, we plan to execute multiple annealing experiments at increasing maximum temperature, to avoid melting in our sample. To ensure a better reaction between Si and Ge powders, very intimate grinding of the powders are necessary between each annealing steps, promoting short diffusion paths and better reactivity of the powders. To further increase the contact surface between grains, a compacting device is also necessary.

Despite being long, this protocol has several advantages : i) The required equipment is easily accessible in the lab. ii) Since melting is avoided, silicon does not melt in the crucible and specific quartz boats are not necessary. iii) The sample size is only limited by the compacting device and boats used.

2.3.2 Experimental protocol : Si-rich samples

A schematic protocol is presented in figure 2.7. For each composition ($x = 0.5 - 1$ by step of 0.1), 200 mg of Si:Ge atomic mix powders are prepared. (Step 1) The powders are intimately mixed together using an agate mortar and a crucible. (Step 2) The resulting mixture is then pressed to form pellets of 2 mm height and 8 mm diameter. The pellets along with zirconium are placed inside an alumina crucible which is then inserted inside an alumina tube of an horizontal Carbolite (STF 16/180) oven. Zirconium serves as a local reductant due to its affinity with oxygen. The heating is ensured by joule effect using *SiC* resistances (step 3). To further protect the sample from oxidation, the atmosphere in the tube is pumped and filled with argon several times prior to annealing and a continuous flow of argon is used during the annealing. After each annealing step, steps 1 and 2 are repeated at different temperatures. The annealing temperature is progressively brought from 1000°C to the maximum annealing temperature by steps of 50°C or 100°C. The value of the maximum annealing temperature for each composition increases with the Si content (from 1150°C for $x = 0.5$ to 1350°C for $x = 0.9$). Calibration curves of the oven used are available in chapter C.

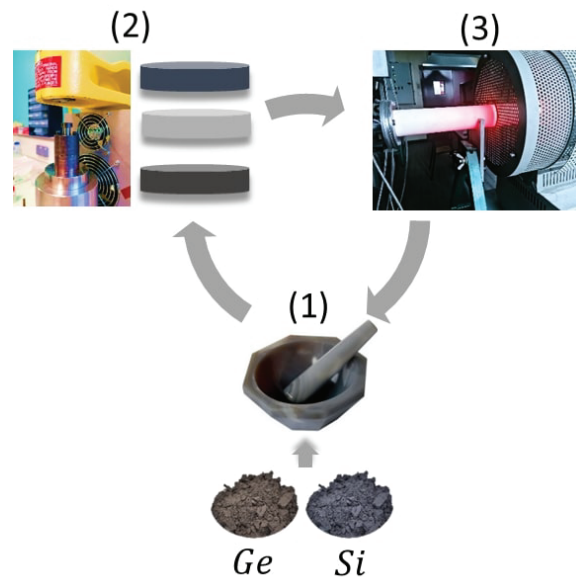


Figure 2.7: Schematic protocol for solid state synthesis : 1) intimate grinding of the Si:Ge atomic mix 2) compression at 200 bars of the powders into pellets 3) HT treatment. This process is repeated several times at increasing annealing temperatures.

2.3.2.1 Characterizations during synthesis steps

In order to follow the reaction, Raman spectroscopy and XRD measurements are performed after each annealing step to control that both local and global homogeneity are converging toward a mean value. XRD measurements were performed on $Si_{0.8}Ge_{0.2}$ sample and Raman spectroscopy on all the other samples ($x=0.5, 0.6, 0.7, 0.9$).

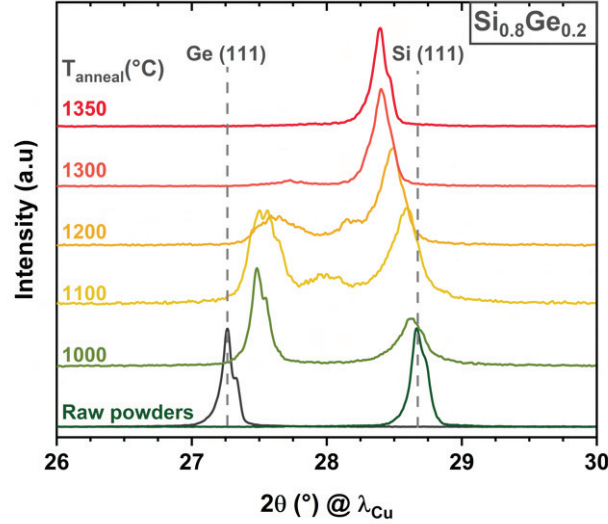


Figure 2.8: XRD pattern showing (111) reflection of the $\text{Si}_{0.8}\text{Ge}_{0.2}$ sample obtained after each annealing step. germanium and silicon raw powders are shown for reference.

The XRD patterns reveal that the reaction of the powders takes place gradually as the annealing temperature is increased. During the first annealing step at 1000°C, silicon and germanium react to create silicon rich and germanium rich alloys. This first step happens at a temperature higher than the germanium fusion point. The germanium melts locally and reacts with the surrounding silicon.

As we emphasize in a previous section, melting is something to avoid during synthesis if we want to avoid segregation. In our case, this is not detrimental as long as the melting occurs in the first step. Local melting of germanium allows us to create intermediate alloys in the sample. As an example, for a temperature of 1000°C, the composition extracted from X-ray analysis (shown in figure 2.9) indicates that pure germanium reacted to form $\text{Si}_{0.15}\text{Ge}_{0.85}$ (50% of the total area fitted). This alloy having a higher melting point, the next annealing steps can be made at higher temperatures without fully melt the sample. A second grain composition observed in the sample is very close to silicon (between 90-98 %), having a much higher melting point. Again, the melting is avoided during the following annealing steps. It should be noted that there is no trace of reaction between germanium and the crucible during this process, and that local melting of the sample does not pulverized germanium in the crucible either. The pellet overall composition remains close to the initial Si:Ge mix.

As the pellet is ground up, compacted and annealed several times, further reactions occur, and samples tend to form a unique composition marked by a single (111) reflection after the annealing step at 1350°C. The silicon content distribution after each annealing step during the synthesis process is shown in figure 2.9

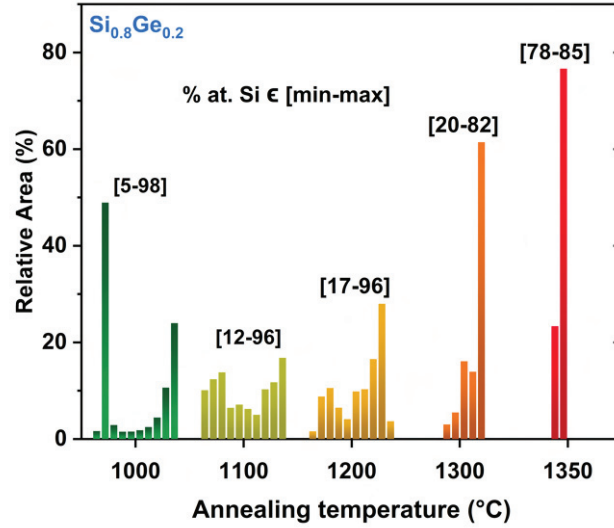


Figure 2.9: Distribution of the silicon content extracted from XRD patterns of $Si_{0.8}Ge_{0.2}$ after each step of the solid state reaction process. The composition is gradually converging towards the desired $Si_{0.8}Ge_{0.2}$ composition.

The fit of the diffraction patterns indicates that the sample is gradually reacting and gives indications on the compositions present in the sample. These information are crucial to correctly set-up the temperature steps.

The analysis of the weighted deviation σ defined in the equation 2.3 from the average value of the composition clearly shows that the overall composition of the sample tends to be more homogeneous at each step of the synthesis, ensuring that the process is converging close to a unique composition.

$$\sigma = \sum_{i \in \text{percentile}} |C_i - \langle C \rangle| * f_i \quad (2.3)$$

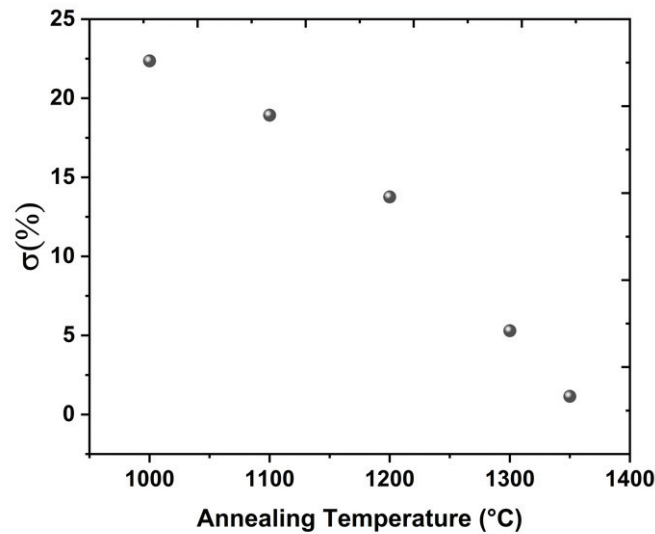


Figure 2.10: Deviation of the mean composition during the annealing steps, showing that the sample is converging toward an homogeneous composition.

Raman measurements performed on the other pellets ($x = 0.5, 0.6, 0.7, 0.9$) show similar results. The recorded spectra are slowly converging to a single composition (figure 2.11), confirming the gradual reaction of the powders. This can be seen following the Si-Si mode position during the annealing steps (see paragraph 1.3.2), gradually moving to lower frequencies due to the increase of germanium atoms in the local environment. The Si-Si stretching mode is shifted from its initial value (around 521 cm^{-1}) to a value determined by the alloy composition.

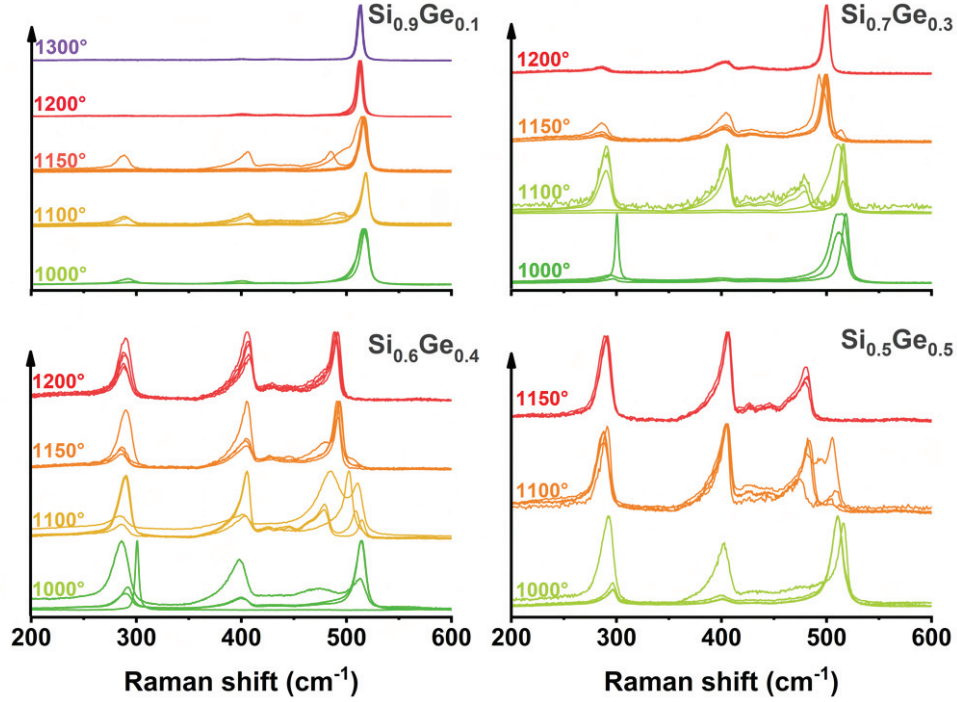


Figure 2.11: Raman spectra of $Si_xGe_{(1-x)}$ ($x = 0.5, 0.6, 0.7, 0.9$) during the solid state reaction process. After each annealing step, the Raman spectra taken at different points on the sample appears to converge towards a unique spectrum. The Raman spectra taken at the last annealing step show no clear variations over the whole sample.

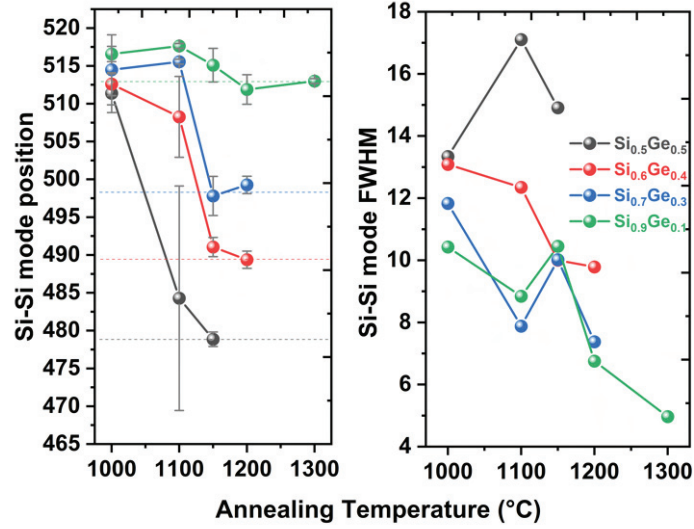


Figure 2.12: Position and Full width half maximum of the Si-Si mode deduced from Raman spectra as a function of the maximum annealing temperature. After each step of the solid state reaction process for $\text{Si}_x\text{Ge}_{(1-x)}$ ($x = 0.5, 0.6, 0.7, 0.9$). For each sample, the convergence of the Si-Si mode position is consistent with an improved homogeneity.

The Raman method being more local, the estimation of the composition is less precise during the first annealing steps and would require more measurements to improve the statistical analysis. But as the composition is converging, the uncertainty (error bars in the left pannel) tends to rapidly decrease to the experimental uncertainty determined by the Raman setup ($\pm 1 \text{ cm}^{-1}$) as shown in 2.12.

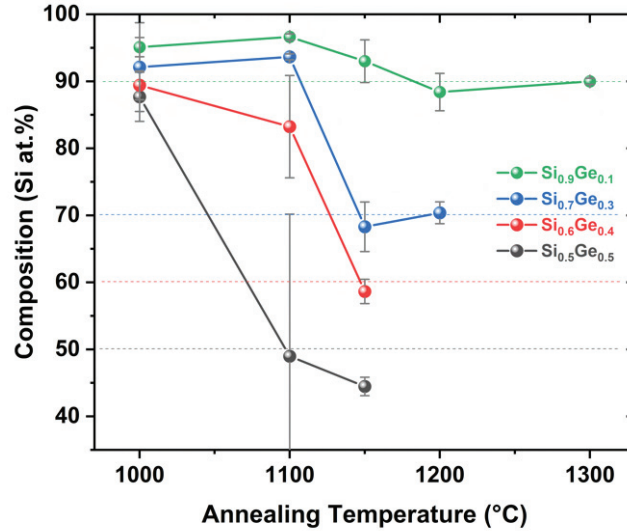


Figure 2.13: Estimation of the composition from Raman data for $\text{Si}_x\text{Ge}_{(1-x)}$ ($x = 0.5, 0.6, 0.7, 0.9$) samples after each step of the solid state reaction process.

2.3.2.2 Comparison of final samples

The overall processing time is long, considering at least that four HT treatments are necessary for each sample. Each annealing step takes more than 10 hours (accounting the time for the oven to cool down). Adding additional time for the grinding/compressing process, the overall time estimated to prepare the samples is about several weeks. But in comparison to as produced pressed pellets, final samples are mechanically stronger, and do not crumbled when handled. This mechanical strength allows us to polish the sample.

XRD patterns are obtained on the whole pellet after polishing, ensuring that the diffraction patterns shown in figure 2.14 are characteristic of the whole sample. A special care is taken to avoid any level effect (leading to a shift in 2θ of the pattern). Zoom on the (111) peaks shows that all the samples reflections are in between pure silicon and germanium, starting from the $Si_{0.5}Ge_{0.5}$ peak and distributed almost equally up to the pure silicon (111) peak. The different broadening of the peaks indicates that all the samples do not show the same micro structure or composition distribution. Nevertheless, no clear asymmetry is observed in the peaks. The samples composition are evenly centered on their respective predefined composition, showing no segregation in the samples as expected for solid state synthesis.

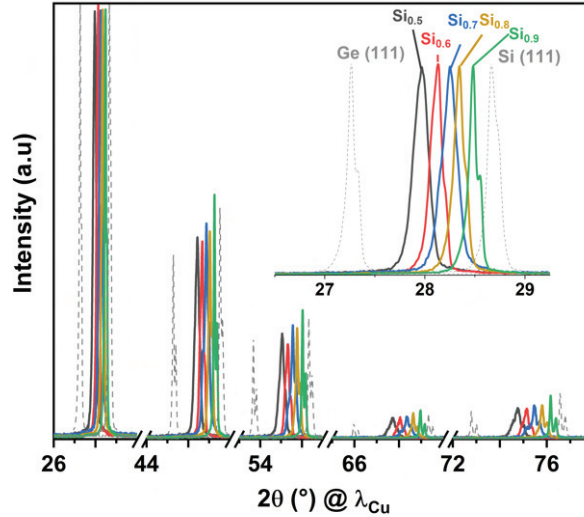


Figure 2.14: XRD patterns of $Si_xGe_{(1-x)}$ ($x = 0.5, 0.6, 0.7, 0.8, 0.9$) obtained after the solid state reaction process. Patterns and overall shape for the synthesized alloys are similar to these of silicon and germanium powders (shown in dotted lines), indicating that samples are homogeneous. Position of the reflections are consistent with a cell parameter proportional to silicon content in the alloy.

The analysis of the silicon content distribution from the XRD patterns is presented in figure 2.15 (see appendix A). The presence of two phases of close composition is suggested by the fitting procedure. Fits also show that samples richer in germanium ($x = 0.5, 0.6, 0.7$) present a greater proportion of the second composition presented in figure 2.15.

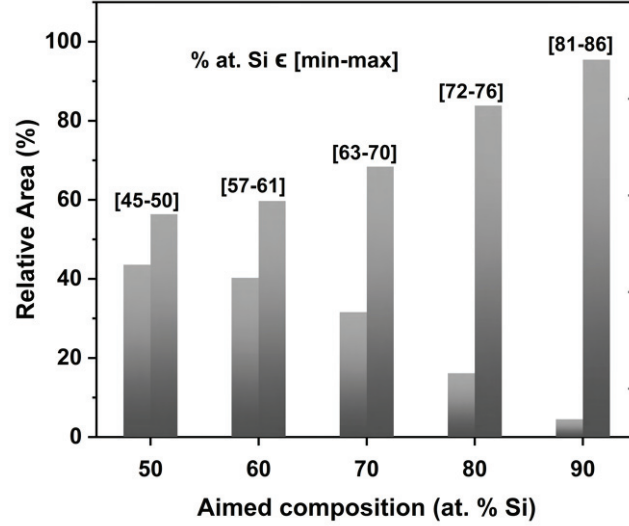


Figure 2.15: Distribution of silicon content obtained from XRD patterns. $Si_xGe_{(1-x)}$ ($x = 0.5, 0.6, 0.7, 0.8, 0.9$) samples obtained after the solid state reaction process show little composition variation using this method. Brackets indicates compositions interval estimated for each sample.

Peak broadening in XRD pattern suggest that the synthesis based on the solid state reaction is not efficient enough to reach homogeneity for an increasing content of germanium. These results can be explained by the lower temperature reached for germanium rich samples (due to a lower fusion point). To ensure that the fitting procedure is correct, we used three functions instead of two. The compositions estimated by both fits are almost the same indicating that two functions are enough to fit the whole pattern (shown in figure 2.16).

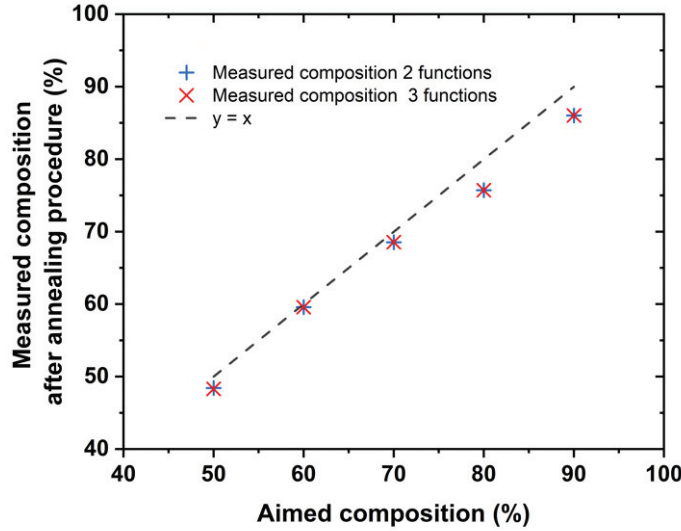


Figure 2.16: Mean silicon composition estimated for $Si_xGe_{(1-x)}$ ($x = 0.5, 0.6, 0.7, 0.8, 0.9$) obtained after the solid state process. Following the data analysis presented in appendix A, no difference are seen by using two or three functions in the fitting procedure of the XRD patterns.

It is important to notice that the fitting procedure proposed is more adapted to estimate composition distribution in inhomogeneous samples. The fitting procedure is not adapted to homogeneous samples as several parameters are fixed (like FWHM). The interpretation of these diffraction patterns using LeBail refinement and a single composition is possible. The table 2.2 shows the obtained cell parameter for each sample obtained by LeBail Refinement. The measured cell parameters are consistent with available PDF4+ references on similar compositions. The compositions estimated with XRD were calculated using the measured cell parameter of germanium and silicon and the Vegard law.

Sample	Measured cell parameter	Referenced cell parameter	Estimated composition [at.%Si]
Ge	5.658(1)	5.658(1)	0
$Si_{0.5}Ge_{0.5}$	5.543(2)	5.537(1)	51.5(8)
$Si_{0.6}Ge_{0.4}$	5.521(2)	-	61.1(8)
$Si_{0.7}Ge_{0.3}$	5.500(2)	-	70.2(8)
$Si_{0.8}Ge_{0.2}$	5.475(1)	5.465(1)	81.6(5)
$Si_{0.9}Ge_{0.1}$	5.454(1)	-	91.3(5)
Si	5.434(1)	5.430(1)	100

Table 2.2: Measured composition based on the cell parameter using LeBail refinement for $Si_xGe_{(1-x)}$ samples ($x = 0.5, 0.6, 0.7, 0.8, 0.9$) obtained from solid state reaction. The PDF4+ data files used are 00-004-0545 for Ge, 00-005-0565 for Si, 04-005-9700 for $Si_{0.5}Ge_{0.5}$, and 04-022-2155 for $Si_{0.8}Ge_{0.2}$.

SEM images (in back-scattering mode) show that some of the samples present a porous morphology that could be attributed to local melting discussed in the previous section 2.3.2.1. SEM images show little contrast between different regions, indicating that the obtained alloys are homogeneous.

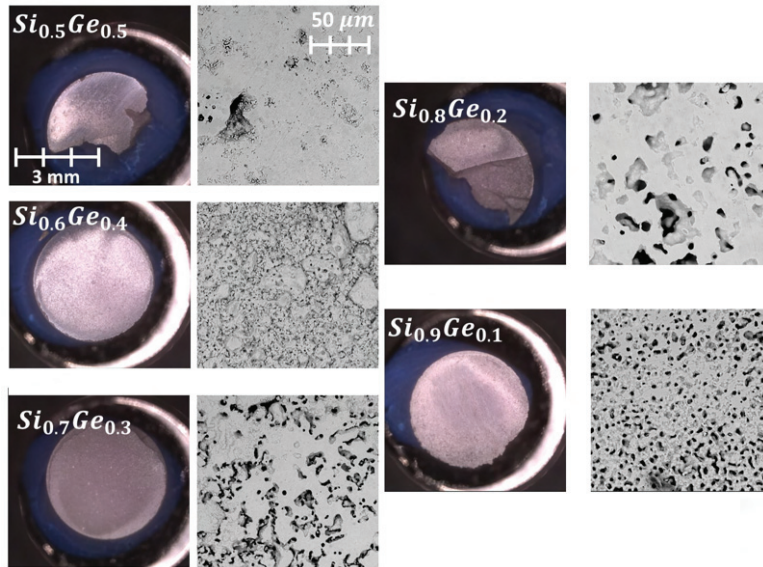


Figure 2.17: SEM images of $Si_xGe_{(1-x)}$ ($x = 0.5, 0.6, 0.7, 0.8, 0.9$) obtained after the solid state reaction process. Some samples show a porous morphology, but no clear variation of composition is seen. Black regions are due to topological artefacts.

EDX measurement were made on randomly chosen points on the surface. The average composition for each sample is presented in Tab.2.3. As the samples show some holes in their structure, these regions were excluded from the analysis to ensure no topological effects. It is the reason why a map analysis has been excluded. A few points shows the presence of unreacted grains or different composition, indicating that the grinding step can be improved. A majority of the sample is nevertheless homogeneous.

Sample name	Average composition [at.%Si]	Standard deviation [at.%Si]
$Si_{0.5}Ge_{0.5}$	51	3.9
$Si_{0.6}Ge_{0.4}$	59	2.0
$Si_{0.7}Ge_{0.3}$	63	2.0
$Si_{0.8}Ge_{0.2}$	79	2.1
$Si_{0.9}Ge_{0.1}$	90.5	0.4

Table 2.3: Si content from EDX for $Si_xGe_{(1-x)}$ ($x = 0.5, 0.6, 0.7, 0.8, 0.9$) samples obtained from solid state reaction.

Finally complementary to XRD and EDX, Raman measurements are made on the pellets and are presented figure 2.18. The Si-Si mode shows a standard deviation, lower than the $\pm 1cm^{-1}$ uncertainty of the experimental setup. Samples appear homogeneous from the Raman measurements. Larger dispersion is seen for samples richer in germanium, confirming that these samples are susceptible to be less homogeneous. Compositions evaluated using Raman spectroscopy are however consistent with the compositions obtained using other characterization techniques. However the fitting of the Si-Si stretching mode of germanium rich samples is complicated because of the lower intensity of this mode as the germanium content increases. Furthermore, the peak asymmetry increases with the Ge content. These results indicate that Raman spectroscopy is less efficient at estimating compositions than the other methods. The uncertainty will increase as the germanium content increases. The other modes (Ge-Ge, Ge-Si) are less sensitive to alloy composition and cannot be used to estimate the composition.

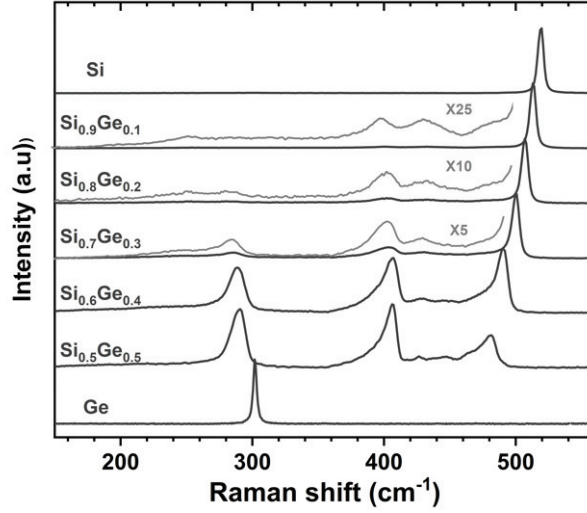


Figure 2.18: Typical Raman spectra of $Si_xGe_{(1-x)}$ ($x = 0.5, 0.6, 0.7, 0.8, 0.9$) samples obtained from solid state reaction. The shift of the Si-Si mode position and the appearance of new alloy-induced modes are consistent with the fact that alloys are more homogeneous as the silicon content increases.

Sample	(Si-Si) mode position [cm^{-1}]	Standard deviation [cm^{-1}]	Estimated composition [at.%Si]
Si	520.8	0.1	100
$Si_{0.9}Ge_{0.1}$	513.4	0.3	91
$Si_{0.8}Ge_{0.2}$	508.8	0.6	85
$Si_{0.7}Ge_{0.3}$	500.2	0.6	72
$Si_{0.6}Ge_{0.4}$	490	1.3	59
$Si_{0.5}Ge_{0.5}$	480	1.1	44

Table 2.4: Si content from Raman spectra for $Si_xGe_{(1-x)}$ ($x = 0.5, 0.6, 0.7, 0.8, 0.9$) samples obtained from solid state reaction. The composition is deduced from the (Si-Si) mode shift using ref. [28].

Figure 2.19 resumes the composition estimation from the different techniques. XRD is the only technique allowing a good estimation over the whole composition range. Both EDX and XRD techniques show good results and give similar compositions. The estimated Si content from EDX for $Si_{0.7}Ge_{0.3}$ is the only one showing a significant deviation from the expected value. This result could be due to a calibration error of the instrument.

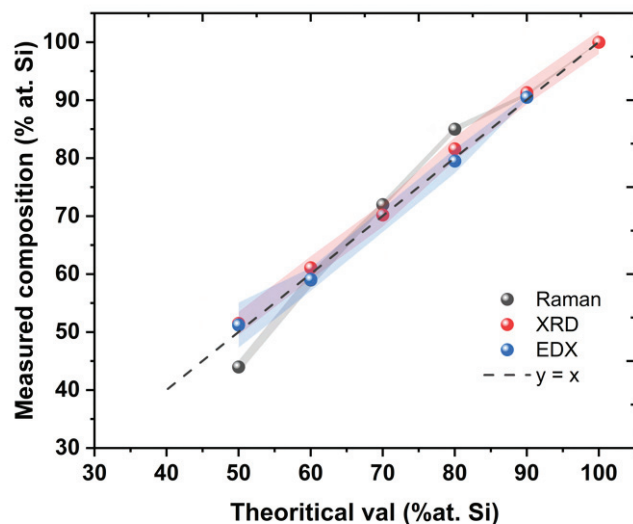


Figure 2.19: Comparison of the Si content estimated with Raman spectroscopy, XRD, and EDX.

2.3.3 Experimental protocol : Ge rich alloys

The previously described protocol is applied to germanium rich samples prepared in the same conditions. The first step in temperature of 1000°C was found to be detrimental to the samples (as shown in figure 2.20 c). According to these results, the melting of germanium did not produce the same effect with respect to the si-rich samples. Germanium is locally melted and the pellet is pulverized resulting in a degradation of the sample global composition and mechanical strength.

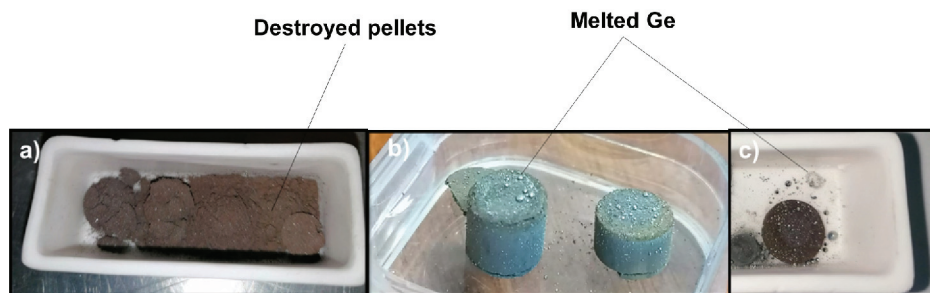


Figure 2.20: Typical pictures of Ge-rich samples after annealing. a) The crumbling of the pellet after the treatment. b) Apparition of melted germanium balls. c) germanium balls on the crucible walls due to melting.

Several strategies are attempted to overcome this issue. First, the temperature is lowered to 950°C, and even under the germanium melting point at 920°C, resulting in the lack of reaction, or in the destruction of the sample. Several reasons can explain these results :

- The first step applied in the case of silicon-rich samples consisted into going slightly above the melting point of germanium to force the reaction between molten germanium and silicon, resulting in the formation of a prealloyed sample. In the case of Ge-rich samples, an annealing at a temperature higher than the fusion point of germanium causes the majority of the pellet to melt and react with the crucible.

- If the temperature of the first annealing step is set below germanium point, no significant reaction occur between the powders, letting the sample unchanged. Increasing the annealing time to ten's of hours also did not produce any significant change on the sample except a slow degradation of the sample mechanical strength.
- Despite numerous efforts, oxidation of the samples was observed (see figure 2.21). Replacing the elements of the tubular oven, allowing the atmosphere to be controlled, did not impact the results.

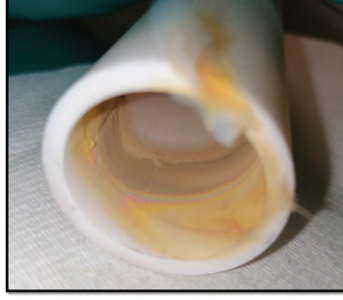


Figure 2.21: Residues present on the tube walls after the annealing experiments. Residues may be due to oxidation of germanium.

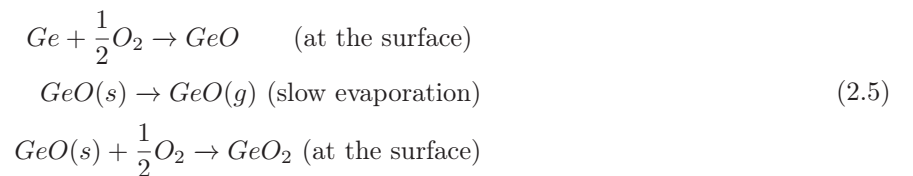
2.3.3.1 Oxidation of silicon, germanium and SiGe alloys

To better understand the presence of the residue on the walls previously seen (in figure 2.21, we have to consider the oxidation reaction of our materials.

For silicon, oxidation occurs at the surface by formations of an SiO_2 layer [71, 72] (eq. 2.4).



For germanium, oxidation follows a different path. The global oxidation mechanism is the following [73]: a GeO oxide layer first forms at the surface of the sample. This layer slowly evaporate and react with the atmosphere to form GeO_2 [74]. This mechanism is probably the cause to the residue observed on the tube walls during our experiment (figure 2.21). The monoxide layer that did not evaporate gradually react with the atmosphere to form a GeO_2 oxidation layer. This layer avoids further evaporation of Ge_0 , and partially protects the sample from further oxidation (eq. 2.5).



For SiGe alloys, oxidation occurs even differently. For germanium rich alloys ($x < 0.5$) the oxide layer formed during oxidation is only composed of SiO_2 [75], meaning that germanium is segregated away from the oxide SiO_2 interface and piled up on the SiGe alloy side of this interface. For silicon rich alloys, a two-layer oxide forms with a $(Si, Ge)O_2$ layer at the surface, and a pure SiO_2 layer underneath [76].

Thus, the residue seen on the tube walls in previous section is likely to be germanium monoxide, that is predicted to slowly evaporate during the annealing process, and crystallize on the tube walls.

2.3.4 Conclusion

In this section, we showed that the HT treatments works well with Si rich samples. The data acquired along the synthesis steps are consistent and show that gradual reaction of Si:Ge powder mix is possible. This protocol present a few advantages. The protocol is easy to implement. The shape of the samples is controlled by the compaction device. The samples show a good mechanical strength and no clear segregation occurs (or very localized). With our setup, approximately 200 mg can be produced for each pellet. This protocol has several limits. The treatment requires multiple steps (compressing, annealing, grinding) which last several weeks. The established protocol is not effective for germanium rich samples, mostly due to the low melting temperature and the high reactivity of germanium. The synthesized samples appear porous.

Considering these results, we can state that more controlled conditions are needed to make germanium rich samples in further experiment. According to the experimental setups available and the method reviewed in section 2.1.2, SPS method could solve these issues and will be presented in the following part.

2.4 Spark plasma sintering

2.4.1 Introduction

SPS is a method that became commercially available in the 80's even if patents on the subject goes back to the 1900[77]. The principle of this method is to use an electric discharge to accelerate densification or reaction of powders contained in a graphite die as depicted in figure 2.22. The heat is generated by the electrothermal effect and distributed only within the die.

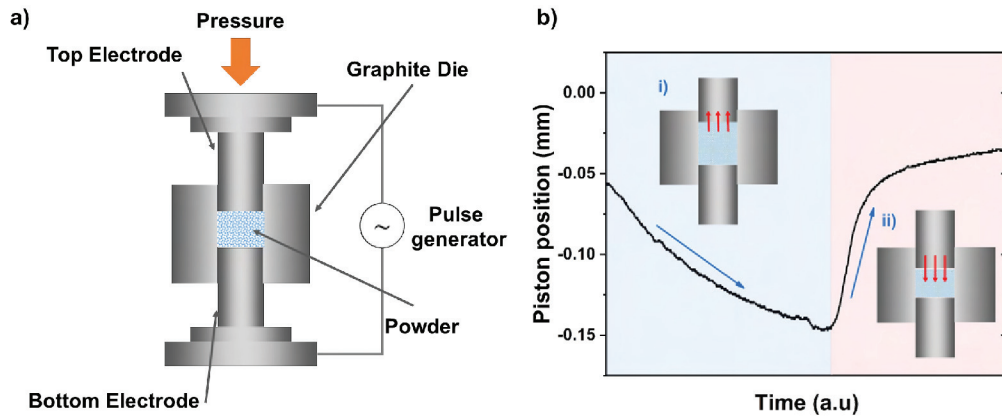


Figure 2.22: a) Schematic representation of SPS. b) Typical piston position curve showing in blue a negative displacement region where sample volume increase during heating, and in red a positive displacement region where the sample volume decrease during sintering.

By using SPS, several of the encountered problems with solid state reaction might be solved :

- For Si-rich samples : Decreases the number of steps in the synthesis protocol and the overall synthesis time while the density of the alloys is improved.

- For Ge-rich samples : Confines the powders during the reaction, avoiding uncontrolled melting of germanium. The high local temperature reached by SPS may also trigger reaction between the powders below germanium fusion point.
- Further protect the sample against oxidation by heating. Indeed, the sample is encapsulated inside a graphite die in a vacuum chamber.

2.4.2 Experimental protocol

Samples are synthesised using SPS from Syntex society, model 515S. Three Si:Ge powder mix corresponding to atomic ratio ($x = 0.2, 0.5, 0.8$) are prepared by intimately grinding Si and Ge powders using an agate mortar and a crucible. The powders are inserted into a graphite die of 15 mm in diameter, covered with thin graphite paper and closed by the two electrodes. Prior to heating, the chamber atmosphere was pumped and filled with argon. Heating is performed under vacuum. Uniaxial pressure is applied together with a high pulsed DC current between the electrodes and thus on the graphite die. The direct current pulsing duty cycle is set to 12 pulses on and two pulses off, for 3.3 ms each. During the SPS sintering, the heating rate is fixed at 100°C/min and the pressure is kept constant at 50 MPa.

During the experiment, piston position curves, pressure and temperature are recorded. These information give insights on the sintering process and will be presented in the following part.

2.4.2.1 Si rich alloys

The experimental curves corresponding to Si rich alloys ($x=0.5$ and $x=0.8$) are presented in figure 2.24 and 2.23. For both samples, increasing the temperature from room temperature to 900 °C did not show clear effects except the dilatation of the powder due to the temperature increase (decreasing the piston position).

For $Si_{0.5}Ge_{0.5}$ sample, the maximum temperature is limited to 1050 °C, i.e. the solidus line for this composition. During the first heating stage, a negative piston displacement is observed, consistent with a dilatation of the sample due to the increasing temperature. Increasing the temperature above germanium melting point resulted into quick densification of the sample shown by a positive piston displacement (shown by a dash line at 1010°C in figure 2.23). The sample is then cooled down to room temperature.

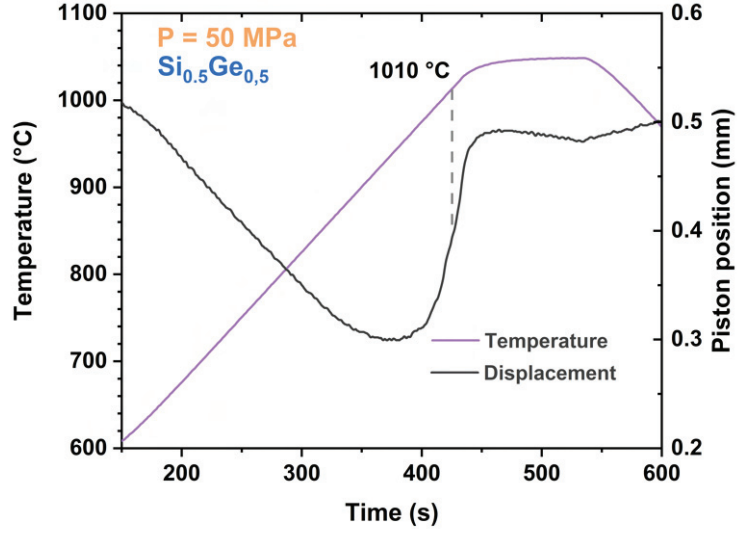


Figure 2.23: Experimental piston displacement curves and sample temperature as a function of time for the SPS sample $Si_{0.5}Ge_{0.5}$. The curves show first a dilatation of the sample followed by a rapid sintering at 1010°C.

For $Si_{0.8}Ge_{0.2}$ sample, the same behavior is noted upon temperature increases at 1020°C. After a 10 min plateau at 1120°C, the temperature is increased further to 1180°C, resulting again in a densification of the sample. After a dwell time at constant temperature, successively temperature and pressure are lowered to ambient conditions.

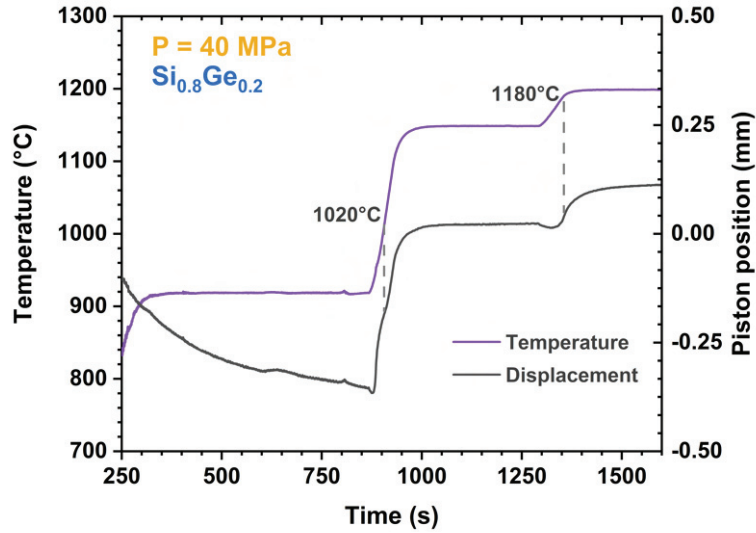


Figure 2.24: Experimental piston displacement curves and sample temperature as a function of time for the SPS sample $Si_{0.8}Ge_{0.2}$. Dilatation of the sample is seen up to 900°C followed by rapid sintering at 1020°C and 1180°C as the temperature is increased.

For both compositions melting of germanium did not produce any leaks, confirming that the confinement is efficient with this experimental setup as expected. Both of the samples are taken out of the graphite die and polished to remove top and bottom graphite sheet.

XRD patterns were taken directly on the polished pellets. The two samples show that compositions are close to the desired composition as shown in figure 2.25. In the case of $Si_{0.8}Ge_{0.2}$ sample, some regions of the samples are composed of Si-rich alloys that did not fully react with the germanium, spreading the silicon composition distribution from 71% to 86% (as shown in figure 2.26 right). In the case of $Si_{0.5}Ge_{0.5}$ sample, the results show greater homogeneity with a more centered large (111) reflection. The silicon composition distribution is estimated to be ranging from 38 to 51%, as shown in the left of figure 2.26.

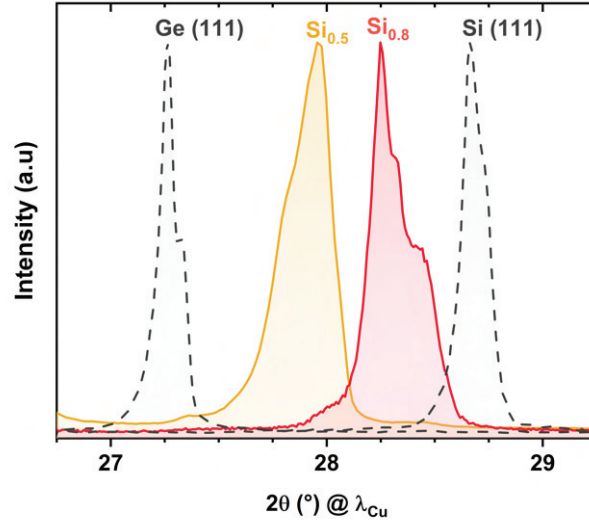


Figure 2.25: XRD patterns obtained on the SPS samples $Si_{0.5}Ge_{0.5}$ and $Si_{0.8}Ge_{0.2}$. In both samples no pure germanium or silicon are present showing that the powders reacted during the SPS process. Asymmetry of the (111) reflections indicates the presence of different compositions close to the aimed one. Pure silicon and germanium are shown in dotted line for reference.

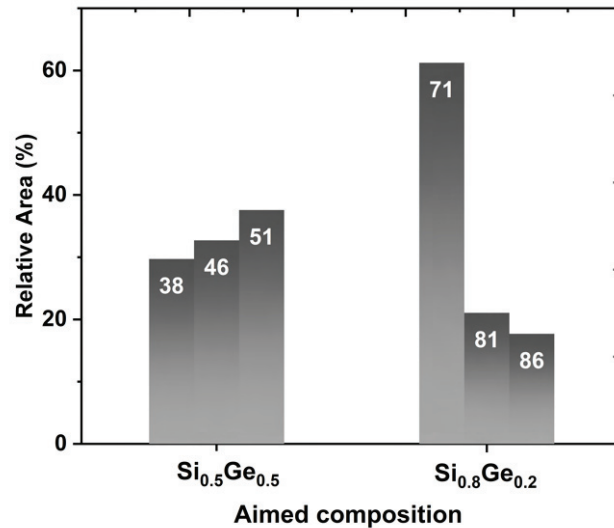


Figure 2.26: Silicon composition distribution obtained from XRD patterns. SPS samples $Si_{0.5}Ge_{0.5}$ and $Si_{0.8}Ge_{0.2}$ both show a distribution closed to the desired composition.

The SEM results confirm that both samples appear to be very compact and present almost no holes confirming that the sintering process is efficient. For $Si_{0.5}Ge_{0.5}$ samples, no clear contrast is seen between different regions (figure 2.27). Only a few light gray areas correspond to regions slightly richer in germanium. However, the global composition is homogeneous. Note that the dark points correspond to topological artefacts on the image color. Complementary EDX measurements indicates that atomic composition varies from $x=0.57$ to $x=0.42$.

For $Si_{0.8}Ge_{0.2}$ sample, dark gray regions indicates that some part are richer in silicon. According to EDX results, these dark regions are close to $x = 0.9-1$. The clear regions suggest that a majority of the sample composition is in the range $x = 0.66-0.75$.

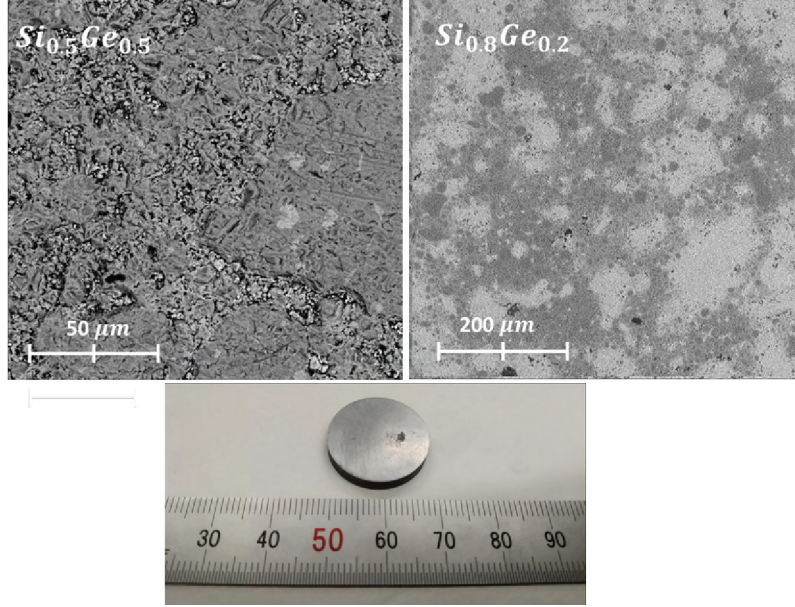


Figure 2.27: (Top) Typical SEM images of the SPS samples $Si_{0.5}Ge_{0.5}$ and $Si_{0.8}Ge_{0.2}$. (Top) Pictures of typical samples obtained by SPS. Light gray regions indicate germanium rich alloys and dark grey regions silicon rich regions. Black regions are due to topological artefacts.

Considering the results we can make hypothesis about the internal process happening during the SPS experiment, we can assume that melted germanium quickly react with the surrounding silicon to form SiGe alloys in $Si_{0.5}Ge_{0.5}$ and $Si_{0.8}Ge_{0.2}$.

For $Si_{0.5}Ge_{0.5}$, as the temperature is increased further (up to 1050 °C) even alloys with low silicon content are liquefied and react with all the silicon present. At this point two cases are possible :

- Case 1 : The major part of the sample is in solid state due to reaction with silicon (increasing the melting point).
- Case 2 : If not, it means that part of the sample is in liquid state, and another in solid state.

Case 1 is more likely and would explain the global homogeneity seen in the sample. Case 2 would suppose that the liquid part did not experienced segregation (as seen in arc melting section 2.2). The quenching time of 100°C /min being slower than in arc melting, the second case is unlikely. A possible improvement of this protocol would consist in keeping the sample at 1050°C for several hours to allow homogenization by solid state diffusion.

For $Si_{0.8}Ge_{0.2}$ sample, the same hypothesis can be made, the maximum temperature reached 1200 °C (VS 1250 for solidus line). In this case, the sample shows some traces of poorly or unreacted silicon that can be due to two effects:

- The lower germanium content and the surface contact between the Si powder and the melted alloys limit the reaction.
- The temperature is not set high enough to bring full reaction of the powders.

A possible improvement would be to set maximum temperature to 1250°C and use longer dwelling time like $Si_{0.5}Ge_{0.5}$.

In conclusion, Si-rich samples are accessible with SPS but the homogeneity is not sufficient for our applications. Nevertheless, SPS can achieve a fast reaction of the powders and formation of dense samples. The SPS experiment is not directly accessible in our laboratory and would require further experimental runs.

2.4.2.2 Ge rich alloys

Two experiments are conducted for Ge-rich alloys ($x=0.2$), a first one with a maximum temperature higher than the fusion point of germanium, and a second one with a maximum temperature lower than the melting point of germanium.

For the first experiment, the protocol followed consisted into first, go to 930°C then gradually increase the temperature to the desired alloy solidus temperature (980°C). The parameters curves are not shown, because the experiment has been stopped in emergency. During the first temperature increase to 930°C, a rapid piston displacement and leaking of melted germanium has been observed (figure 2.28). Surprisingly, melting of germanium is observed below its fusion point. This behaviour was not observed in previous experiment and could be due to a difference between sample internal temperature and thermocouple measurement. following these step, the sample was taken out of the die and was not analysed further.

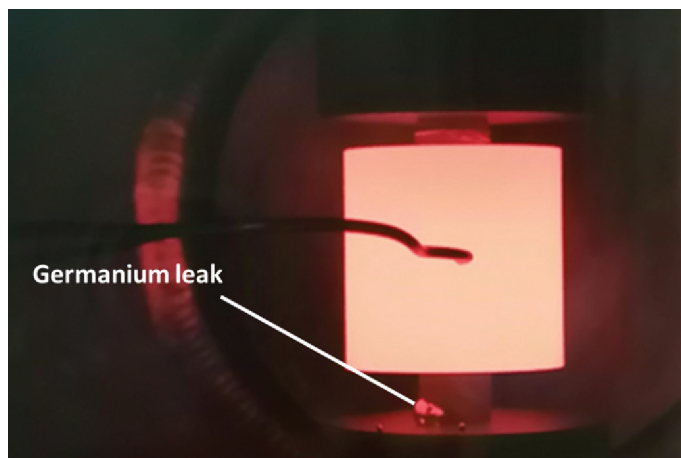


Figure 2.28: Picture showing a germanium leak during the SPS experiment on $Si_{0.2}Ge_{0.8}$ sample.

For the second experiment, the experimental parameters are presented in figure 2.29. The temperature is first increased to 700°C at a fast rate, then gradually increased to the temperature for which the sintering has been observed in the first experiment. Sintering is observed at temperatures close to 750°C, like in the first experiment. This time no leaking is observed. After a 10 min dwelling time, the temperature and pressure are successively decreased to ambient conditions. The sample is taken out, and polished for analysis.

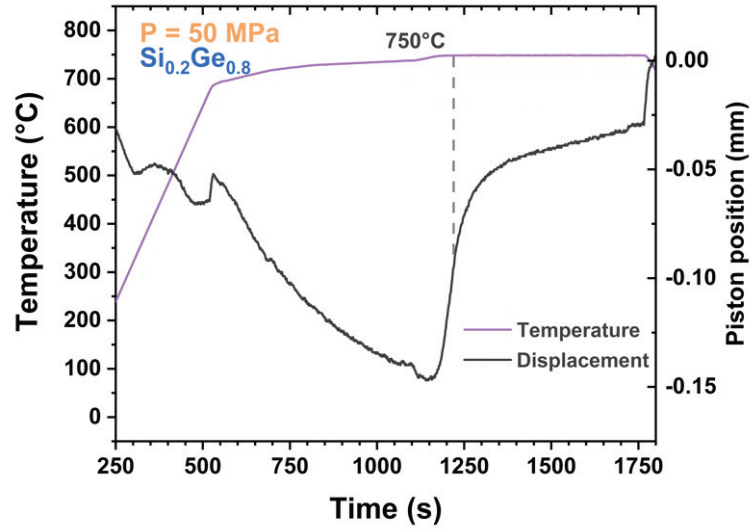


Figure 2.29: Experimental piston displacement curves and sample temperature for SPS sample $Si_{0.2}Ge_{0.8}$

SEM results obtained on the polished sample are shown in figure 2.30. The sample shows distinct grains having a large contrast between them EDX confirmed that the sample is composed of compacted silicon and germanium powders.

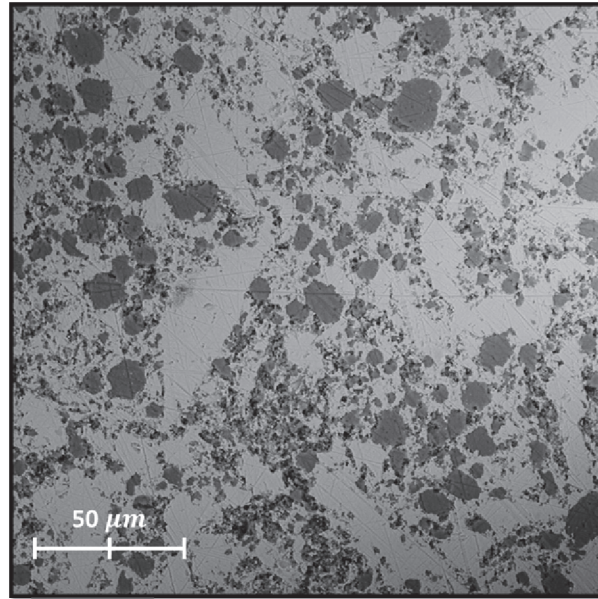


Figure 2.30: SEM image of the $Si_{0.2}Ge_{0.8}$ sample after SPS process. No reaction between the powders as showed by the presence of dark grains (germanium) and white gray grains (silicon).

Experiments made on germanium rich alloy ($x=0.2$) did not succeed. The reason is quite close to what happens in solid state synthesis. If the sintering temperature is too high, the majority of the sample melts and the confinement in the SPS is not efficient enough to avoid leaks. If the temperature is set to lower values, the reaction between germanium and silicon is not effective.

2.4.3 Conclusion

The SPS technique did answer to some of the problems encountered with previous methods. SPS allows to produce silicon rich samples, in a very fast time compared to solid state synthesis (hours of treatment). This is partially due to the confinement that contributes to contain alloys during their reaction in liquid/solid states. The samples obtained are very dense, shaped and mechanically resistant even if the homogeneity appears lower than the one obtained with solid state reaction. However, we saw that for germanium rich samples, the confinement is not enough to force the powders to react, and a quick premature melting of the sample leads to leaks. The situation involving an even greater confinement will therefore be explored in the following section dedicated to the Belt press experiment. Several improvement of the protocol have been proposed including refining the dwelling time at HT, or the maximum temperature reached.

2.5 High pressure - High temperature synthesis using a Belt press

2.5.1 Introduction

Belt apparatus is a method that appeared in the late 50's [78]. The principle of Belt press method is to combine the effects of HP (up to 5 GPa) and HT (up to 1700 °C) by confining the sample into a specifically designed gasket pressed by anvils. The objective is to force the reaction between silicon and germanium, but also contain the melt during the reaction. Several of the encountered problems might be solved :

- Similarly to SPS, the Belt apparatus has the advantage to confine the powders even further and to involve fast heating and quenching rates.
- Since solid state reaction is found to be ineffective at low temperature, this apparatus will allow to melt the mixture without produce leaking.
- The sample is protected from the atmosphere by the gasket itself.

In this particular experiment, the SiGe phase diagram must be modified to take into account the effect of pressure. Unlike regular elements, silicon and germanium present a decreasing melting point with pressure [79, 80]. Under 5 GPa, the melting point of germanium and silicon are decreased by almost the same percentage (20% for silicon and 27% for germanium), but silicon has a higher melting point. Working at 5 GPa would reduce the melting difference of the two elements. Extrapolated phase diagram at 5 GPa is presented in figure 2.31. The diagram is obtained by multiplying original values of solidus and liquidus lines by a factor varying linearly between pure germanium ratio (20 %) and pure silicon ratio (27 %).

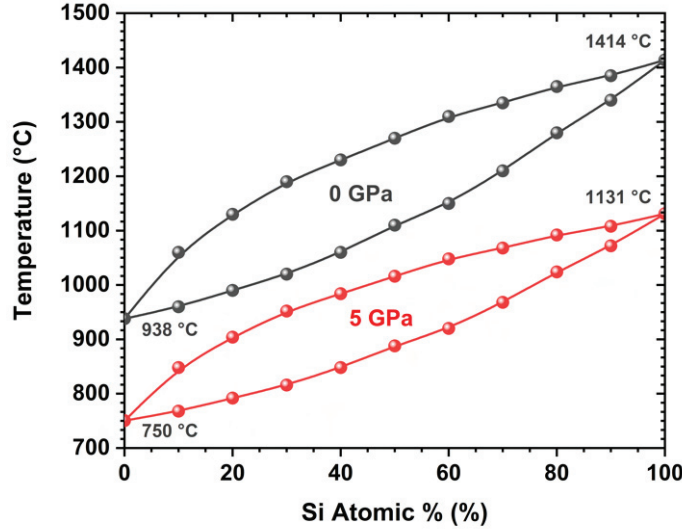


Figure 2.31: Si_xGe_{1-x} phase diagram at ambient pressure and at 5 GPa. Extrapolation to alloys was obtained using germanium and silicon melting curve as a function of pressure [79, 80].

2.5.2 Experimental protocol

Experiments are performed in a Belt apparatus [78]. The Belt press is a large volume press with a typical sample size of 70mm^3 . Pressure is calibrated against the room temperature fixed-point metal transitions, and at HT against the quartz-coesite transition [81]. Due to the design of the Belt press, temperature cannot be directly monitored with a thermocouple but is obtained from the calibrated relationship between input power and capsule temperature. The input power/capsule temperature relationship is calibrated at 1 and 5 GPa over a broad range of temperatures (25–1000 °C). The temperature uncertainty is estimated to be $\pm 4\%$. Approximately 200 mg of the 1:5 Si:Ge powder was loaded in a BN capsule (length 5 mm and diameter ca. 4 mm). These capsules are designed to seal in the Belt apparatus the powder while pressure is increased at ambient temperature. The powder is pressed to fill the entire capsule with a specially designed compacting device. The BN capsule is placed in an insulating boron nitride gasket inside a cylindrical graphite furnace, itself surrounded by a pyrophyllite gasket 2.32.

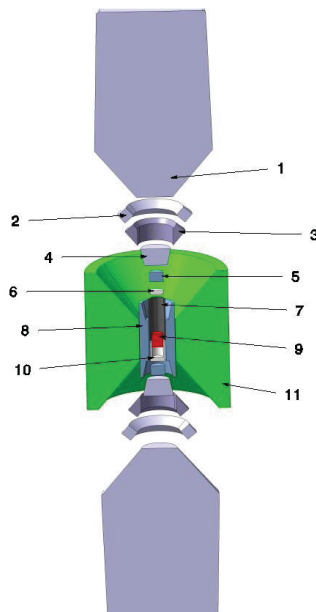


Figure 2.32: Schematic representation of assembly used in the "Belt" press experiment (exploded view). 1. WC anvils, 2. Teflon seal, 3. pyrophyllite gasket, 4. steel current lead, 5. pyrophyllite cylinder, 6. and 10. h-BN crucible or h-BN insulator + metal capsule (platinum, gold, tantalum, steel, Cu-Be alloy) 7. graphite carbon furnace, 8. central part of the pyrophyllite gasket, 9. sample (powder pellet: 4 mm in diameter and 5 mm in height), 11. Tungsten carbide belt.

2.5.3 Results and discussion

The different parameters measured during the Belt experiment are shown in figure 2.33. First the pressure is increased to 5 GPa, then temperature is increased at 20°C/min up to 1020 °C. As the temperature is increased, piston displacement curve shows a behavior change around 750°C with an increasing displacement rate. This is consistent with the predicted melting temperature of germanium at this pressure (see modified phase diagram at 5 GPa 2.31). At 1020°C and 5 GPa, the whole sample should be fully melted. As the temperature is lowered to 800°C the sample shows no clear sign of volume change. 800°C corresponds to the solidus temperature at this pressure and is kept constant for one hour. The resulting sample is manually extracted from the gasket, removing the different part of the capsule elements to be analysed.

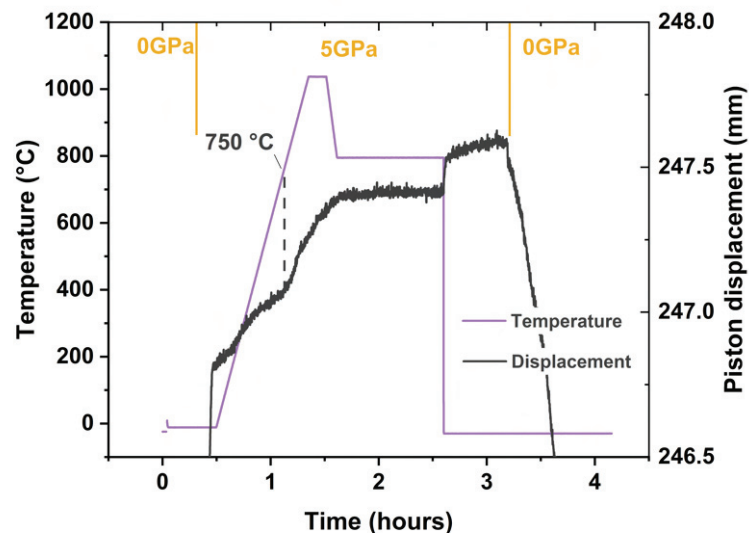


Figure 2.33: Experimental protocol and monitored parameters during the Belt press experiment. A rapid piston displacement is seen at 750°C. It is consistent with the melting point of germanium at 5 GPa.

Pictures of the sample surface obtained with an optical microscope show large grains (figure 2.34), with traces of solidification front (right picture).

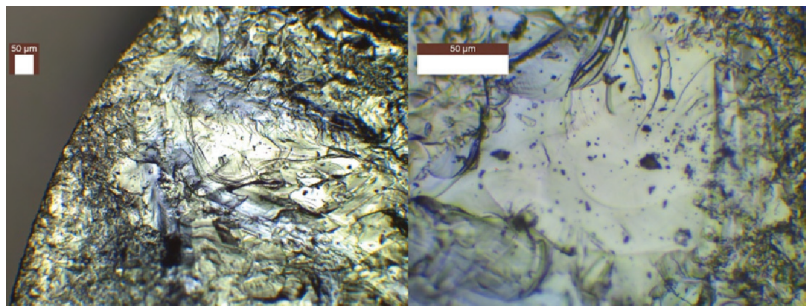


Figure 2.34: Pictures of the Belt press sample surface obtained with an optical microscope.

The X-ray diffraction patterns reveal that several grains of different compositions coexist in the sample (figure 2.35). Different peaks indicate that the grains themselves should be homogeneous, with a few silicon segregation (deduced from a right asymmetry of the main peak). An interesting fact is that all the silicon present in the sample reacted with germanium, forming a germanium rich alloy. The diffraction pattern obtained is very close to the $Si_{0.2}Ge_{0.8}$ pattern obtained by arc melting. The analysis of the composition from XRD shows that a major part of the grains should have a composition close to $Si_{0.2}Ge_{0.8}$.

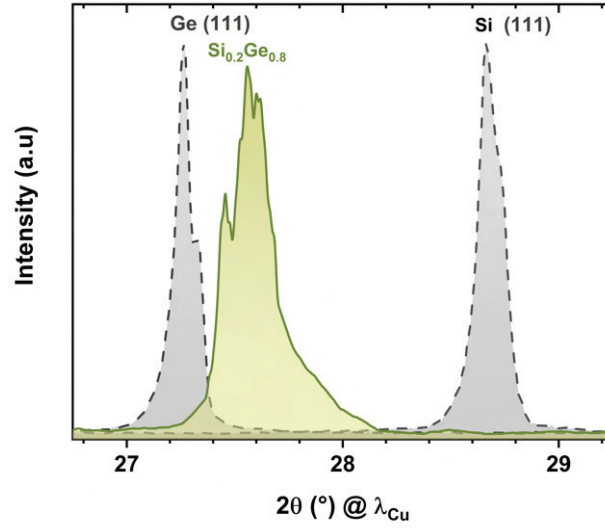


Figure 2.35: XRD pattern of $Si_{0.2}Ge_{0.8}$ Belt press sample zoomed on the (111) reflection. The presence of several peaks shows that grains of several germanium rich compositions are present in the sample. Pure silicon and germanium patterns are shown in dotted line for reference.

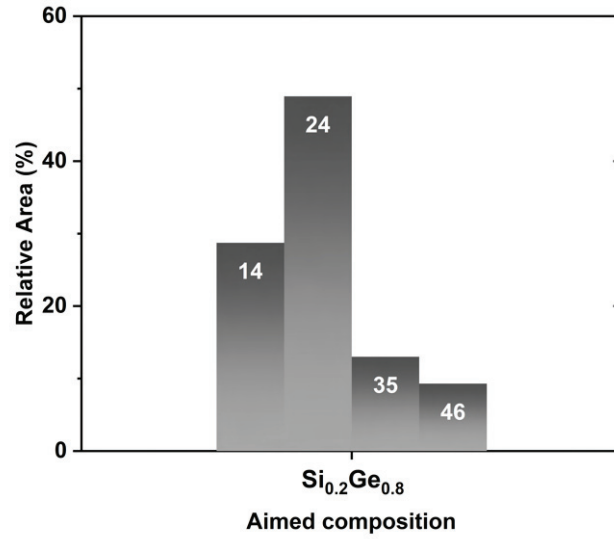


Figure 2.36: Silicon composition distribution extracted from XRD data for $Si_{0.2}Ge_{0.8}$ sample synthesized using the Belt press.

The SEM and EDX results (figure 2.37) suggest the growth of silicon rich grains during the solidification of the sample of different compositions ($x=0.3-0.5$). Around these Si rich grains, we can see a gradient of composition from Si rich to Ge rich alloy ($x=0.1$). The Ge rich part (in light gray in figure 2.37) constitute the majority of the sample. The silicon rich grains are expected to grow at an early stage when the liquid begins to solidify (see phase diagram). The Si rich gradient present around the grains attests the solidification of silicon impoverished liquid close to a nucleation center that is the grain early formed.

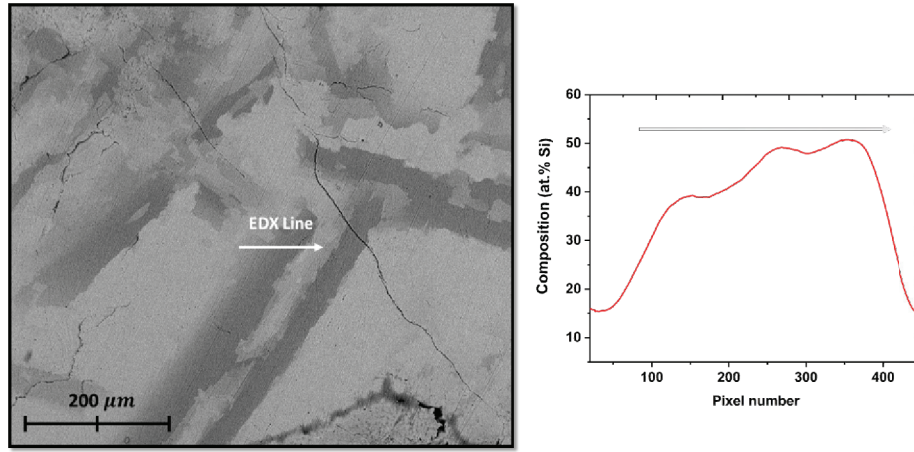


Figure 2.37: (Left) SEM image of the Belt press $Si_{0.2}Ge_{0.8}$ sample. (Right) EDX line made on a Si-rich grain slice.

2.5.4 Conclusion

In conclusion, in contrary to Spark plasma sintering, the confinement provided by the Belt press experiment is efficient to ensure a controlled reaction between germanium and silicon. The samples extracted show composition variations, with silicon rich grains. A better homogeneity should be reached with Belt apparatus by adding dwelling times at lower temperature after reaction. The HP involved into this process may enhance the diffusion process as well as the sample final density. More development is therefore needed to estimate the temperatures and times required to reach homogeneity in germanium rich samples. For this kind of experiment, very long dwelling times (about days) are not practically feasible and must be first assessed at ambient conditions to avoid unnecessary try and fails. Such annealing conditions will be explored in the next sections for germanium-rich samples at ambient conditions.

Combination of synthesis methods

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3.1 Introduction

Until now only one pathway to homogeneous silicon rich alloys has been found using solid state reaction. None of the techniques presented previously achieved homogeneity for germanium rich alloys, mainly due to the low melting temperature of germanium.

Nevertheless we saw that using arc melting and Belt press techniques can force germanium to react with silicon even with a high germanium content. Arc melting achieved this by fast melting/quenching, without control over the cooling conditions. Belt press achieved the reaction by melting the powders in a confined environment, allowing to control both reaction and cooling conditions. The alloys synthesized by these techniques are inhomogeneous but they present several good characteristics: they are dense, no pure germanium is present, and they exhibit a good mechanical strength.

All these characteristics indicate that these pre-alloys may be more suitable as precursors for solid state reaction due to :

- A higher melting point than germanium.
- A high density that can enhance diffusion process.
- A larger contact surface between grains or inhomogeneous regions.

Based on these considerations, we thought that the combination of different methods could lead to the desired results. The following section will be devoted to the description of the new synthesis routes we followed combining one of the technique presented in the previous section with a different technique mainly with solid state synthesis. The main goal is to find new pathways toward germanium-rich alloys, and to improve our control over the sample characteristics.

SPS technique is also presented in the following section, as it was found to be efficient to form pre-alloys for silicon rich compositions. Although the sample confinement provided by SPS did not allow us to synthesize pre-alloys for Ge-rich compositions, we considered that the higher density of the synthesized Ge-rich pellets may also be favorable for solid state reaction process.

The potential new promising pathways not explored during this work will also be discussed.

3.2 SPS and solid state reaction

In the SPS section 2.4; three compositions were tested : $Si_{0.8}Ge_{0.2}$, $Si_{0.5}Ge_{0.5}$ and $Si_{0.2}Ge_{0.8}$.

In the case of silicon rich samples ($x=0.8, 0.5$), alloys close to the desired composition were formed. These samples will allow us to test if a higher density and pre-alloying can enhance the HT treatment process for silicon rich alloys.

In the particular case of $Si_{0.2}Ge_{0.8}$ the sample obtained using SPS was composed of sintered powders of Si and Ge (unreacted). This sample will allow us to test if a high density without pre-alloying can positively affect the HT treatments for germanium rich compositions.

3.2.1 Experimental protocol

The solid state reaction protocol presented in the previous section 2.3 was modified to take into account the SPS sample characteristics. For silicon rich alloys, as the sample is composed of alloys close to the desired composition, only the last annealing step is applied to minimize processing time (1350°C one hour for $Si_{0.8}Ge_{0.2}$ and 1150°C one hour for $Si_{0.5}Ge_{0.5}$).

For the germanium rich composition, as the sample synthesized by SPS experiment is composed of dense unreacted powders, longer annealing time were used. The sample was first brought to 930°C at 5°C/min for 10 hours, then 950°C at 0.1°C/min for 24 hours, and finally at 980°C (the solidus line for $Si_{0.2}Ge_{0.8}$) with the same rate for 24 hours.

3.2.2 Results and discussion

XRD patterns of the silicon rich samples before and after the HT treatment are presented in figure 3.1. The (111) reflection of the sample after HT treatment appear narrower than the initial sample, without clear mark of asymmetry, this result indicates that a better homogeneity is reached after the HT treatment for both samples.

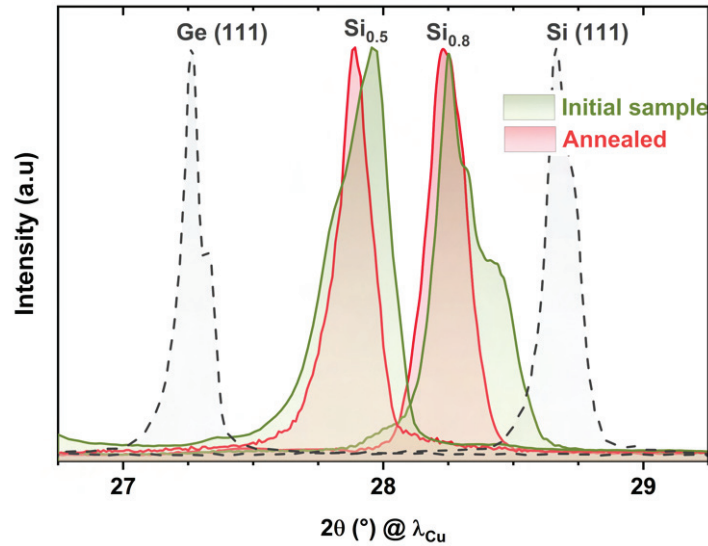


Figure 3.1: XRD pattern of $Si_{0.8}Ge_{0.2}$ and $Si_{0.5}Ge_{0.5}$ synthesized by SPS. (Green) Raw sample (Red) after HT treatments.

The silicon composition distribution analysis from XRD pattern is shown in figure 3.2, and the dispersion around mean composition is shown in table 3.1. For both samples, HT treatments resulted in a decrease in the standard deviation of the mean composition from 5-6 % to 2%. However, the mean composition is shifted downwards by 5% for these samples after annealing. This result is hard to explain because no matter was ejected from the samples during the annealing process, and may be due to a small experimental error during XRD measurements.

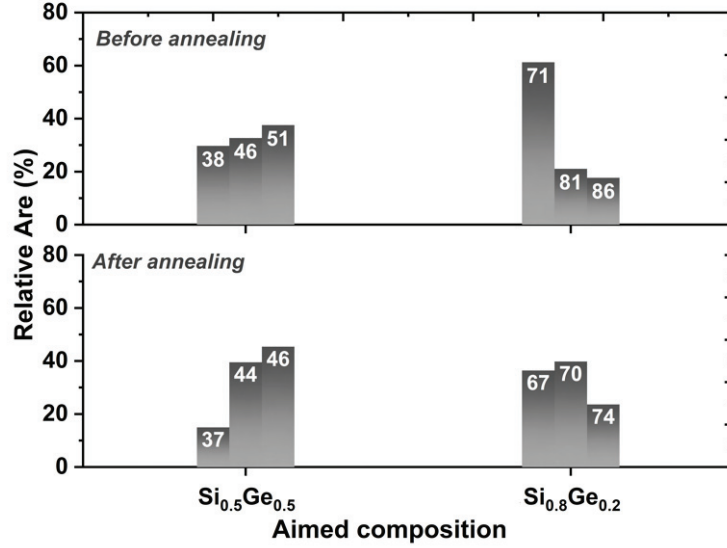


Figure 3.2: Distribution of the silicon content based on XRD patterns of $Si_{0.5}Ge_{0.5}$ and $Si_{0.8}Ge_{0.2}$ samples synthesized by SPS (top) Raw (bottom) After a HT treatment. Both samples show a reduced distribution range after the HT treatments consistent with a better global homogeneity.

Sample name	Estimated composition [at.%Si]	Standard deviation [%]
SPS $Si_{0.8}Ge_{0.2}$	75	6
SPS $Si_{0.8}Ge_{0.2}$ annealed	70	2
SPS $Si_{0.5}Ge_{0.5}$	46	5
SPS $Si_{0.5}Ge_{0.5}$ annealed	44	2

Table 3.1: Composition analysis from XRD pattern for $Si_{0.5}Ge_{0.5}$ and $Si_{0.8}Ge_{0.2}$ samples synthesized by SPS before and after the HT treatment. A better homogeneity is reached after the HT treatment, seen as a decrease in the standard deviation from 5-6 % to 2%.

SEM images and EDX mapping also confirm the global homogeneity of the sample after HT treatments (figure 3.3 and 3.4). However, in both samples the SEM images shows that small regions of different composition are still present after the HT treatment. This result is confirmed by EDX maps and point measurements, showing a standard deviation of ~ 8 % for $Si_{0.5}Ge_{0.5}$ and ~ 2 % for $Si_{0.8}Ge_{0.2}$. We also note the presence of very small inclusions of silicon rich alloy (in bright yellow in the EDX maps).

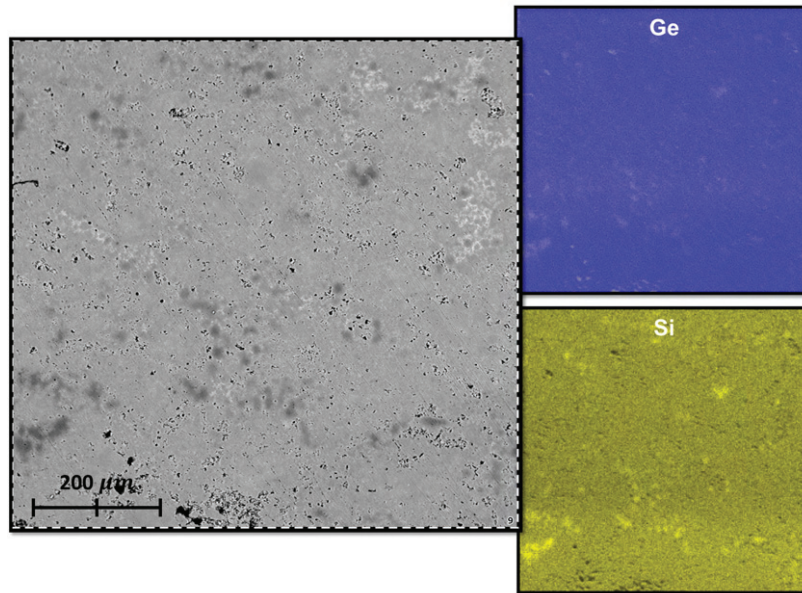


Figure 3.3: (Left) SEM images (Right) EDX maps of the $Si_{0.8}Ge_{0.2}$ sample synthesized by SPS after the HT treatment. The overall sample appear more homogeneous than before the HT treatment. However the presence of some darker and brighter regions indicate the presence of slightly different compositions. The composition difference measured using EDX is measured at less than 10%.

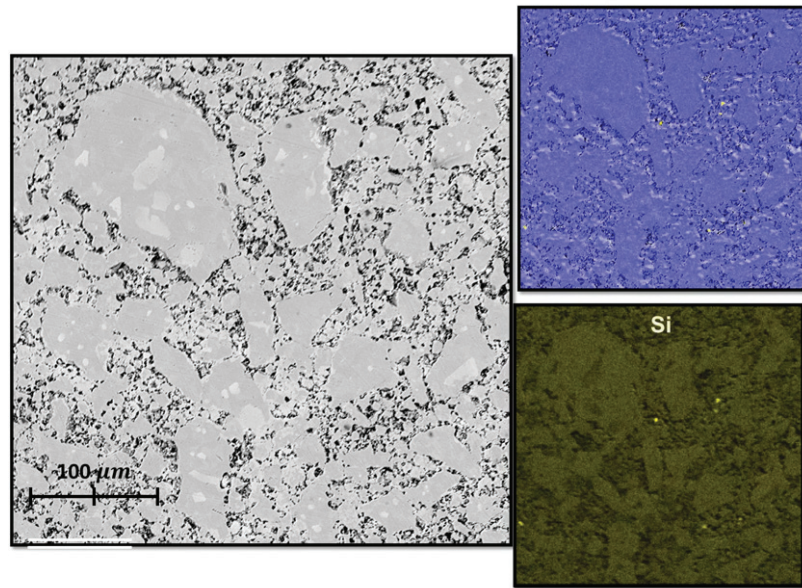


Figure 3.4: (Left) SEM images (Right) EDX map of SPS sample $Si_{0.5}Ge_{0.5}$ after the HT treatment. The overall sample appear more homogeneous than before the HT treatment. However the presence of some darker and brighter regions indicate the presence of slightly different compositions. The composition difference measured using EDX is measured to be less than 5%. Rare silicon inclusions are seen in EDX (in very bright yellow).

Name	Average composition [at.%Si]	Standard deviation [at.%Si]
<i>Si_{0.8}Ge_{0.2}</i>		
Maps	76	2.4
Points	77	2.3
<i>Si_{0.5}Ge_{0.5}</i>		
Maps	51	7.4
Points	52	8.0

Table 3.2: EDX measurements of the *Si_{0.5}Ge_{0.5}* and *Si_{0.8}Ge_{0.2}* samples synthesized by SPS after the HT treatment.

For *Si_{0.2}Ge_{0.8}* sample the annealing process resulted into pulverization of the sample, germanium balls were observed on the walls of the crucible used. The results are very similar to Ge rich experiments made on regular pressed pellets in section 2.3, and the sample was not analysed further. This result show that the density of the reactants alone cannot improve the annealing process, and the formation of Ge-rich alloys. Other pathways to synthesize homogeneous germanium rich samples will thus be explored in future sections.

3.2.3 Conclusion

In conclusion, combination of SPS and HT treatments allow us to combine advantages of both techniques. For Si-rich alloys, we showed that the samples present are dense and that they present a good global homogeneity. We showed however that some inclusion or inhomogeneity are still locally present in the samples. These results suggest that annealing times need to be increased. The synthesized samples fulfill almost all our synthesis objectives listed in section 2.1.

For germanium rich samples, we showed that density and mechanical strength of the initial sample does not affect the result of HT treatments resulting into pulverization of the sample. Other pathways to synthesize homogeneous germanium rich samples will thus be explored in future sections.

3.3 Belt press and solid state reaction

Sample of *Si_{0.2}Ge_{0.8}* synthesized with a Belt press present one supplementary feature not encountered in HT treatments until now. In previous annealing experiments on germanium rich alloys (section 2.3), we found that the low melting point of pure germanium was restricting the maximum annealing temperature. During the Belt press experiment, however, germanium reacted with silicon to form inhomogeneous germanium rich alloys. These alloys having higher melting points, they allow higher temperature treatments.

3.3.1 Experimental protocol

The sample was first brought to 930°C at 5°C/min for 10 hours, then 950°C at 0.1°C/min for 24 hours, finally at 980°C (the solidus line for *Si_{0.2}Ge_{0.8}*) for 90 hours with the same rate.

3.3.2 Results and discussion

For the first time, the $Si_{0.2}Ge_{0.8}$ sample was not destroyed or pulverized during the HT treatment. XRD pattern collected before and after the HT treatment are shown in figure 3.5. Compared to the initial sample, the annealed sample (111) reflection appears less broad, and the multiple peaks seen in the initial sample disappeared. We showed previously that the multiple peaks initially present were due to the presence of large grains of different compositions. The treatment was therefore efficient to homogenize the sample. However, the annealed sample still present a broad (111) reflection, combined with an asymmetrical shape. This suggest that required homogeneity is not fully reached for this sample.

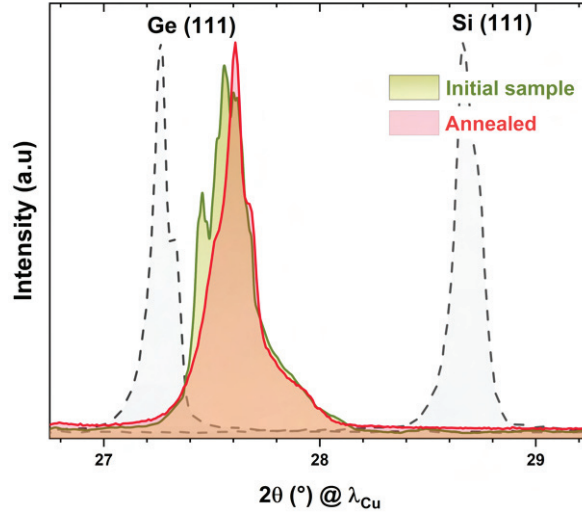


Figure 3.5: XRD pattern of $Si_{0.2}Ge_{0.8}$ synthesized in a Belt press. (Green) Raw sample (Red) annealed at 1020°C for 90h.

SEM and EDX measurements show a rather homogeneous sample at small scale (see figure 3.6). Some darker regions indicate that the sample composition is not perfectly defined. We can make the hypothesis that diffusion was not efficient enough in this sample to erase some of the initially present grains. This is consistent with the size of of grains measured in section 2.5 in the initial sample, some Si-rich grains were larger than $500\mu m \times 100\mu m$. EDX measurements indicate that the dark gray regions seen correspond to compositions higher than $x=0.3$. EDX measurements made on the homogeneous parts of the sample are listed in tab 3.3.

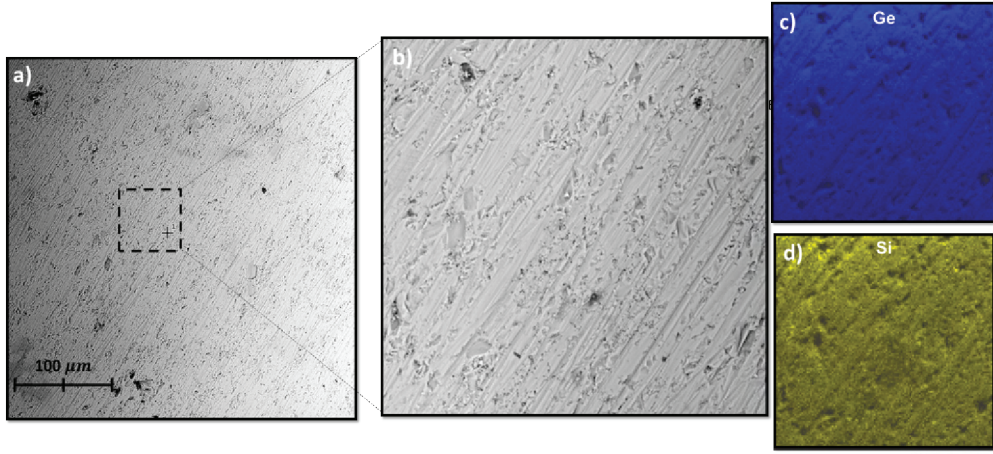


Figure 3.6: a), b) SEM image of the $Si_{0.2}Ge_{0.8}$ sample synthesized in a Belt press and annealed at 1020°C for 90h. c), d) EDX mapping. The results indicates that the silicon rich grains present in the sample before annealing (showed in section 2.37) almost disappeared. The composition appear to be more homogeneous in the majority of the sample.

Sample name	EDX Method	Average composition [at.%Si]	Standard deviation [%Si]
$Si_{0.2}Ge_{0.8}$			
	Maps	22	1.1
	Points	21	4.7

Table 3.3: EDX measurements of the $Si_{0.2}Ge_{0.8}$ sample synthesized in a Belt press and annealed 1020°C 90h.

3.3.3 Conclusion

We showed that annealing the $Si_{0.2}Ge_{0.8}$ sample synthesized in a Belt press produces good results. The hypothesis that not only the density, but also the presence of pre-alloys can enhance the annealing process is thus likely to be accurate. The sample synthesized corresponds to almost all the desired quality except that some regions present slightly different compositions. This may be attributed to the large grain domains existing in the sample prior to annealing, limiting the surface exchange between the grains of different composition. To obtain more homogeneous samples, modifications of the Belt press experimental protocol are needed, for example increasing the dwelling time at 800°C or higher temperatures to promote diffusion at high pressure instead of doing it with a post annealing treatment.

3.4 Arc melting and solid state reaction

As seen in previous sections, density and pre-alloying seems to play a key role in obtaining germanium rich homogeneous alloys. Following this idea, arc melting may offer one supplementary effect compared to SPS and Belt experiments. The SEM images presented in section 2.2 show that the contact surface between the different alloy compositions is greater in the arc melting synthesized samples than in the the Belt press synthesized sample.

3.4.1 Experimental protocol

Two samples were made for this experiment $Si_{0.2}Ge_{0.8}$ and $Si_{0.4}Ge_{0.6}$. The arc melting synthesis protocol to obtain the balls is identical to the one presented in section 2.2.

For the annealing post treatment, two distinct protocols were used. For the $Si_{0.2}Ge_{0.8}$ sample, the temperatures of 930°C 950°C and 980°C are successively reached, with dwelling time of one day for 930 and 950 and 2.5 days for the last temperature. The solidus temperature is 980°C for this composition.

For the $Si_{0.4}Ge_{0.6}$ sample, temperatures of 970°C, 1000°C, 1030°C and 1070°C are successively reached with dwelling time of one day for the first and 2.5 days for the last temperature. The solidus temperature is 1080°C for this composition.

3.4.2 Results and discussion

XRD patterns collected on the raw and annealed samples are shown in figure 3.7. The annealed samples show narrower peaks, with no clear marks of asymmetry. Analysis of XRD patterns show that the composition distribution inside the annealed samples is consistent with our objectives as shown in figure 3.8. For $Si_{0.2}Ge_{0.8}$ composition is estimated to $15\% \pm 2\%$. For $Si_{0.4}Ge_{0.6}$ composition is estimated to $41\% \pm 2\%$.

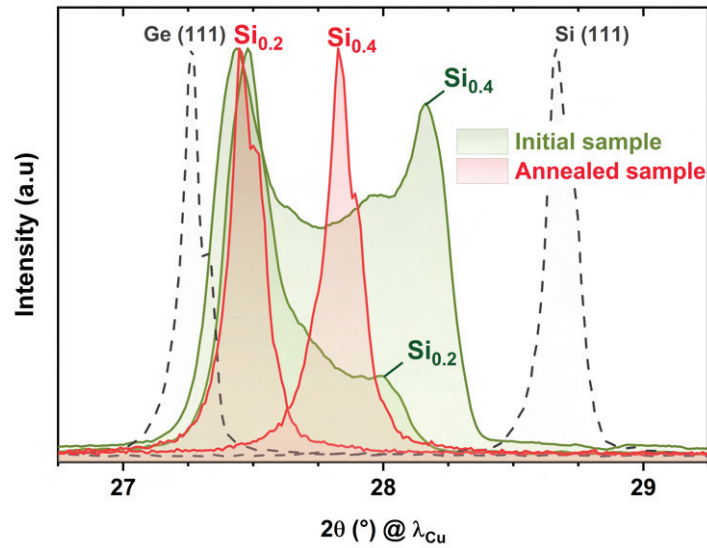


Figure 3.7: XRD patterns of $Si_{0.4}Ge_{0.6}$ and $Si_{0.2}Ge_{0.8}$ obtained with arc melting before (green) and after (red) the HT treatments. The composition gradient present in the initial sample is reduced after annealing, where the sample shows only one single reflection and therefore, one composition.

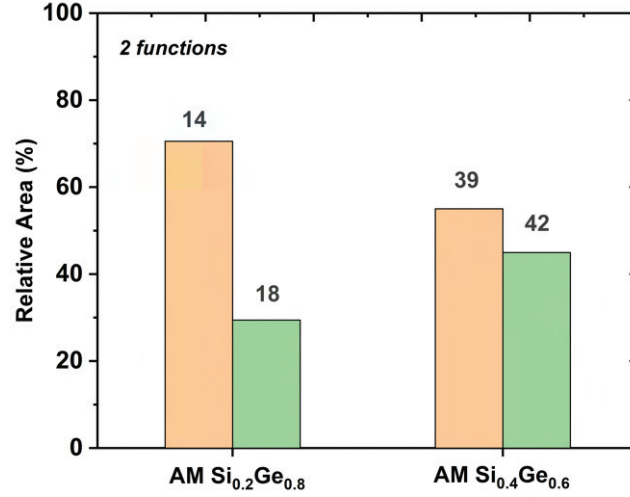


Figure 3.8: Distribution of the silicon content based on XRD patterns of $Si_{0.4}Ge_{0.6}$ and $Si_{0.2}Ge_{0.8}$ synthesized by arc melting after the HT treatments.

SEM images show that $Si_{0.2}Ge_{0.8}$ annealed sample is rather homogeneous, presenting some holes that have already been observed on the raw samples. EDX measurements obtained with maps and points at different regions of the sample confirm the global homogeneity (as shown in table 3.4). $Si_{0.4}Ge_{0.6}$ sample is marked by regions slightly richer in silicon than the main composition, but the measured variations between regions are less than 5%. Despite these defined regions, global homogeneity is reached at 37.6 %. The composition $Si_{0.2}Ge_{0.8}$ show similar characteristics, with some grains of slightly different compositions while keeping a global homogeneity in the our objectives of $\pm 5\%$.

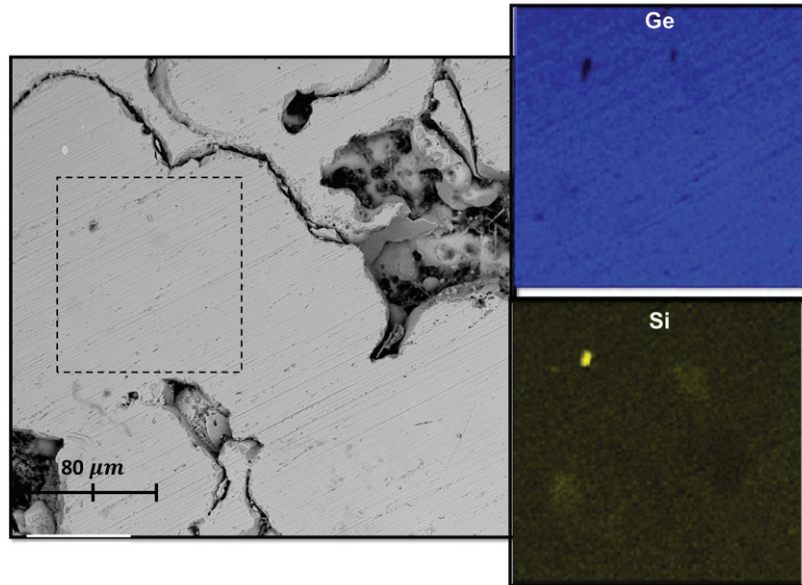


Figure 3.9: (left) SEM image of $Si_{0.2}Ge_{0.8}$ sample synthesized by arc melting after the HT treatment. The absence of contrast shows that the sample is rather homogeneous. (right) EDX maps showing that micro-metric inclusions of silicon rich alloys can be present in the sample.

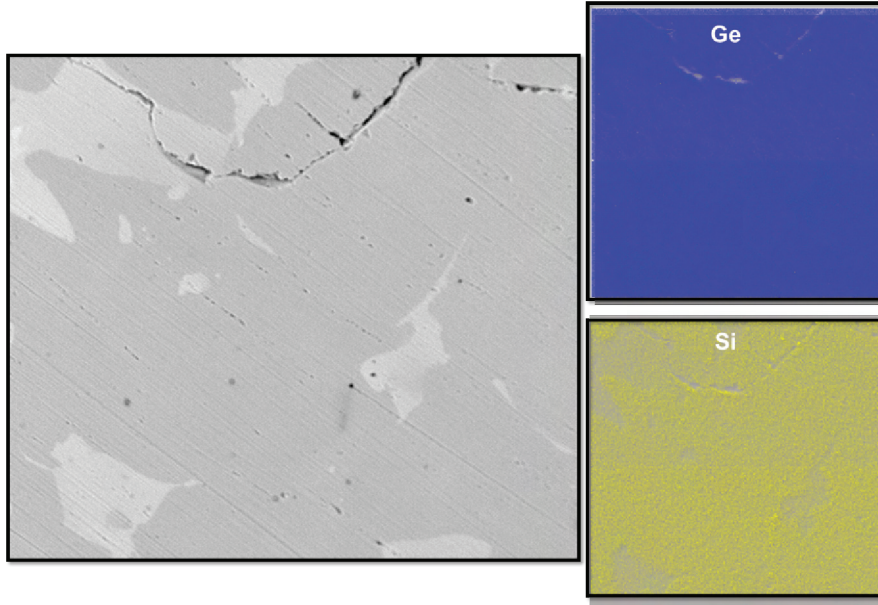


Figure 3.10: SEM image of $Si_{0.4}Ge_{0.6}$ sample synthesized by arc melting after the HT treatment, showing small regions with slightly higher germanium content (in white).

Sample name	Average composition [at.%Si]	standard deviation [at.%Si]
$Si_{0.2}Ge_{0.8}$		
Maps	19.3	0.6
Points	19	5.5
$Si_{0.4}Ge_{0.6}$		
Maps	38.2	0.5
Points	37	3.9

Table 3.4: EDX measurements made on the arc melting samples $Si_{0.2}Ge_{0.8}$ and $Si_{0.4}Ge_{0.6}$ after the HT treatments.

Raman spectra of the samples is shown in figure 3.11. Estimation of composition from Raman data are not made, due to the decrease of intensity of the Si-Si peak. In the case of germanium rich samples the composition cannot be well defined by Raman spectroscopy. Other modes are not composition-sensitive enough to be used.

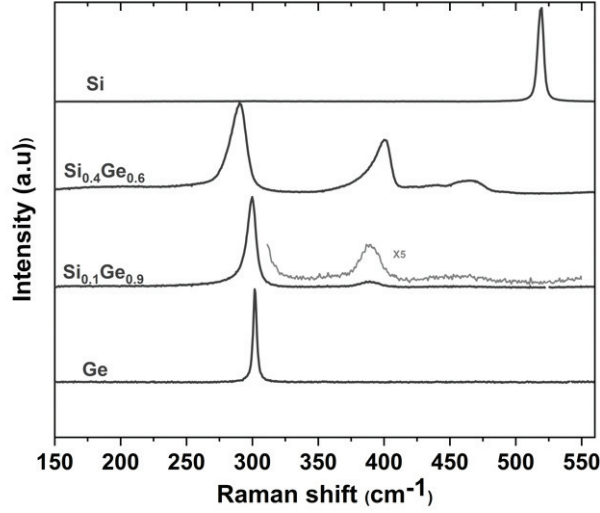


Figure 3.11: Typical Raman spectra of arc melting samples $Si_{0.2}Ge_{0.8}$ and $Si_{0.4}Ge_{0.6}$ after the HT treatments. The Si-Si longitudinal optical mode around 500 cm^{-1} is barely visible due to the low silicon content, making the composition estimation with Raman spectroscopy difficult.

3.4.3 Conclusion

Arc melting combined with annealing post treatments has been proven to be the only method allowing to reach homogeneity in the germanium rich samples. As expected, combined factor of density, pre-alloying as well as favorable surface contact between the grains enhance the diffusion process. These results can likely be expanded to silicon-rich samples, though this pathway hasn't been explored in this work. To obtain germanium rich samples, the overall processing time of the proposed method is several weeks. However, this protocol is only composed of two steps, arc melting and annealing, limiting the overall manipulation time.

As discussed in previous section 2.2, the arc melting process can be improved using faster quenching times using suction devices, resulting in more homogeneous pre-alloyed samples. With increased starting homogeneity, we can expect the post treatment time to be further reduced.

3.5 Conclusion on synthesis methods and materials

In conclusion, we were able to produce silicon germanium alloys of the whole composition range during this work. A pathway toward silicon rich alloys has been proposed involving several solid state reaction steps. Another pathway to synthesize germanium rich alloys has been found by combining both arc melting and solid state process. Both techniques used are scalable and open the way to perform other study on the polycrystalline sample produced.

Among all the methods presented in this work, arc melting has been proven to be the more versatile method as expected. This method also has the potential to synthesize more complex alloys [52, 82, 83]. The other techniques and results presented in this work constitute a rich set of information and should stimulate further investigations on possible improvement of our protocols and synthesis products.

Depending on the desired sample (shape, density, homogeneity, mass, composition) other combination of techniques and protocols are possible and haven't been explored in this work. For example, SPS or Belt press technique can be used with different starting reactants, and eventually homogeneous SiGe powders produced using the pathways presented. One could produce a sample combining the advantages of SPS technique (shape, density, mass) with homogeneity procured by the HT treatments.

The synthesized samples constitute a base for different kind of studies. For example, SiGe alloys have been proposed as new anode materials in lithium ion batteries. A partnership between our laboratory and the LN2 laboratory in Sherbrook Quebec lead to preliminary work on nanostructuration of germanium, which is presented in the following chapter 4. Extension of this work to SiGe alloys nanostructuration is therefore of interest.

The high pressure behaviour of the synthesized SiGe alloys is presented in the next main part of this work in section 7.

Hybrid nanostructure of germanium and carbon as anode material in lithium ion batteries

The goal of this section is to present preliminary results obtained on nanostructuration of germanium using pulsed laser ablation in liquids (PLAL). Here we develop the scientific interest of nanostructuring and the creation of hybrid structures for the search of new anode materials for lithium-ion batteries.. The principle of PLAL is presented, along with experimental protocol and synthesis results obtained.

4.1 Scientific background : germanium and silicon as high capacity materials for lithium ion batteries

A lithium battery consist of 3 main parts. An anode, separated from a cathode by an interface as shown schematically in figure 4.1. The production of current is based on electrochemical reactions taking place on either side of these elements. The interface between the two electrodes is electrically insulating but permeable to lithium ions and prevents a short circuit.

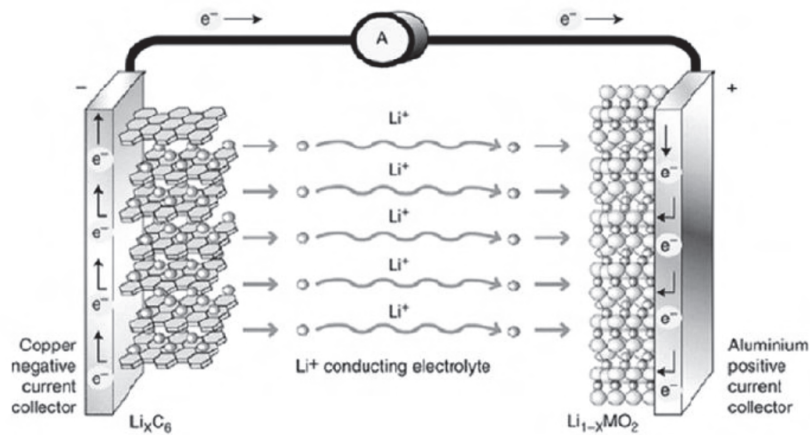


Figure 4.1: Schematic of a lithium-ion battery. Each lithium-ion battery consists of an anode and a cathode separated by an electrolyte containing dissociated lithium salts, which enables transfer of lithium ions between the two electrodes reproduced from ref [84].

A battery is charged when lithium is contained in the anode (here graphite). During the discharge process (delithiation), a lithium oxidation reaction takes place on the anode side shown in the equation 4.1 a). During this reaction electrons are released and captured by the current collector passing through an external circuit forming a useful current. The lithium positive ions move towards the cathode thus ensuring the balance of the charges. On the cathode side, a reduction reaction then occurs according to equation 4.1 b) during which the lithium ions are captured. During the charging process (lithiation), the opposite reactions occur.



The lifetime of a battery depends, among other things, on the reversibility of these reactions during lithiation and delithiation cycles. Among the parameters influencing the overall efficiency of a battery, two are crucial for the anode material: i) the capacity of the material measured in mAh/kg ii) the diffusion coefficient of lithium ions. These two parameters vary according to the anode active materials used. Currently graphite is mainly used as active material in commercial lithium-ion batteries. The capacity associated with the creation of the LiC_6 compound is 350 Ah/kg. Graphite has a diffusion coefficient ranging from 10^{-6} to $10^{-11} cm^2 s^{-1}$ [85].

Science underlying the fundamental technology is more-or-less unchanged since the commercialization in 1990 by Sony. In order to meet the increasing demand in power storage, greater energy density are required. Among the potential new high-capacity materials, silicon and germanium are particularly attractive due to their high capacity and complementary characteristics as shown in table 4.1 [86]. Germanium notably has a diffusion coefficient 400 times greater than silicon but is less abundant and more expensive.

Material	Graphite	Germanium	Silicon
Lithiated phase	LiC_6	$Li_{15}Ge_4$	$Li_{15}Si_4$
Specific capacity ($mAh.g^{-1}$)	372	1620	4200
Volumetric capacity ($mAh.l^{-1}$)	837	8600	9660
Volume expansion (%)	10%	280%	300%
Potential (V)	0.2-0.1	<0.5	0.1-0.2
Lithium diffusion coefficient Li^+ ($cm^2.s^{-1}$)	10^{-6} to 10^{-11}	10^{-10}	10^{-12}

Table 4.1: Main properties associated with silicon germanium and graphite. The specific/volumetric capacity are theoretical and indicated for the delithiated phase. Volume expansion is obtained with the ratio of the lithiated volume/ delithiated volume.[85, 87]

Lithiation of these materials produce a large volume change due to a insertion of lithium inside the structure [88]. These expansion effects are unavoidable and cause damage at different levels :

- Expansion can cause deformation of the current collector in contact with the anode and inflation of the battery.
- At the electrode level: repeated cycles of lithiation/delithiation can induce a gradual loss of contact with the current collector thus limiting the available capacity.
- At the particle level, volume changes induce mechanical stresses and fracture the active material particles.

The solution proposed here consists in studying hybrid structures composed of germanium nanoparticles trapped within a carbon matrix. This structure may solve the above mentioned problems appearing during lithiation. Two majors effects are expected, first nanostructuration has been proved to prevent the rupture of the material [89], ensuring better cycling performances. Second, the carbon matrix could allow to dissipate the mechanical stresses, ensuring electron conduction while keeping the contact with the current collector.

The following sections present the experimental protocol used to synthesize this hybrid material using pulsed laser ablation in liquid technique.

4.1.1 Pulsed laser ablation in liquids

Pulsed laser ablation in liquid (PLAL) method consists in focusing an intense pulsed laser beam on a solid target immersed in a solvent (figure 4.2). At the focal point, the concentrated energy of the beam creates a plasma, during its expansion the plasma cools down and allow the nucleation of nanoparticles. In our case, the solvent role is to provide a carbon source. During the nucleation of the particles, interactions with the solvent can induce the formation of carbon shells [90][91]. The laser ablation method involves complex processes occurring at different time scales, these processes are the subject of much research not discussed here [92, 93].

In this study, a Ge target is ablated in n-decane. n-decane is chosen as a carbon source, but also to avoid germanium oxide formation.

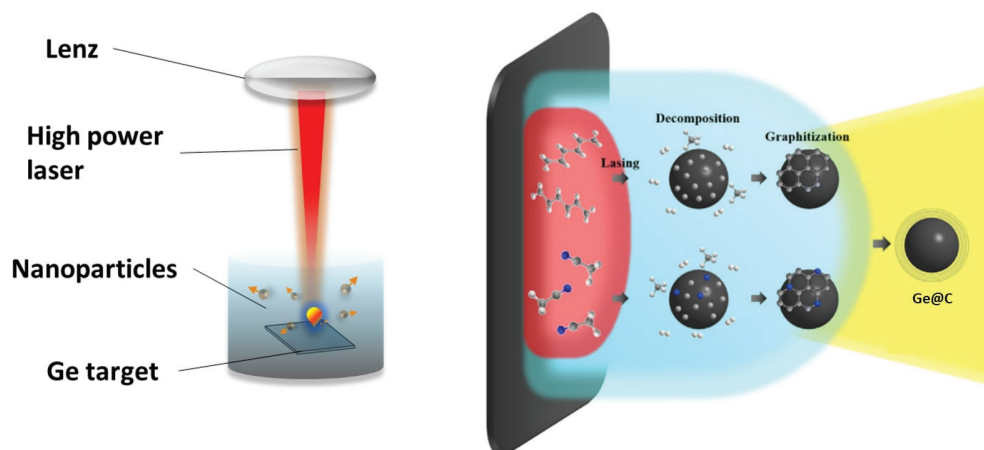


Figure 4.2: (left) Schematic drawing of the PLAL principle. A high power laser is focused on a germanium target immersed in a carbon rich solvent creating a plasma. (left) During its expansion, the plasma cools down allowing (nano) particles to nucleate. During this step, interaction with the solvent can produce core-shell structures.

4.1.2 Experimental setup

4.1.2.1 Optical setup

In the context of our experiment, a pulsed laser at 1kHz at 1064 nm is used. The pulse is 500 ps duration, with 1.5mJ/pulse and a fluency of $15J.cm^{-2}$ ($3^{10}W.cm^{-2}$). A schematic view of the optical scheme is presented in figure 4.3. The main pulsed laser is first redirected by 2 mirrors to define an optical axis, these two mirrors have a very high damage threshold due to the high power of the laser. A telescope is placed just after these mirrors to enlarge the size of the beam and avoid damaging the following mirrors. During this work, a laser used for the alignment at 532 nm was installed and adjusted to coincide with the optical axis of the main laser thanks to 2 mirrors. This laser goal is to allow low power alignment before the beginning of the ablation process with the high power laser. The alignment and ablation laser beams meet on a dichroic mirror reflecting the wavelength of the main laser and transmitting the wavelength of the alignment laser. Both lasers are redirected through a tower and then sent onto a system of mirrors controlled by a a galvo mirror systems . Connected to a computer, this galvo mirror Systems coupled with a F-Theta lens allows to scan the germanium target of approximately 1cm*2cm dimension. A $\lambda/2$ blade and a polarizing beam splitter is placed upstream to control the power of the laser. Finally, a camera is placed to observe the focal point and the ablation spot.

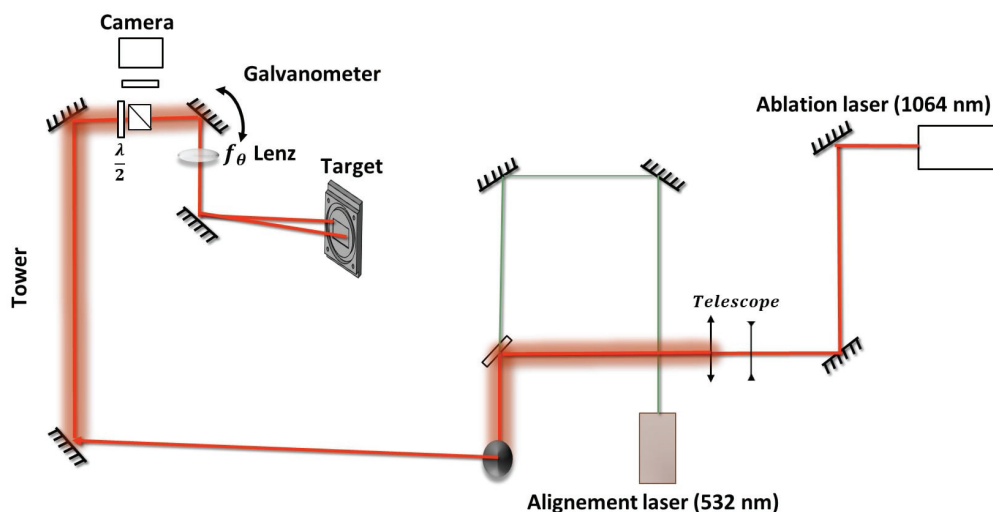


Figure 4.3: Optical scheme of the PLAL experiment. The ablation laser at 1064 nm is shown in red, the alignment laser at 532 nm in green. The ablation target is a germanium ingot.

4.1.2.2 Solvent circulation setup and extraction of the synthesis result

In order to produce a sufficient quantity of these nanoparticles allowing their study under different conditions, a circulation cell is set up to carry out the ablation continuously for several hours. The main parts of circuit are presented in figure 4.4.

This circuit is made up of a receptacle for the germanium target hermetically closed by a flow cell which is designed to have the most laminar flow possible (a). The circulation of the solvent is ensured by a peristaltic pump (b). The solvent containing the nanoparticles is then transported to a separating funnel where the nanoparticles aggregate and flocculate at the bottom. The whole solution is then centrifuged at 3000 revolutions per minute for 10 minutes (c). The centrifugation process is repeated until a fairly concentrated solution is obtained.

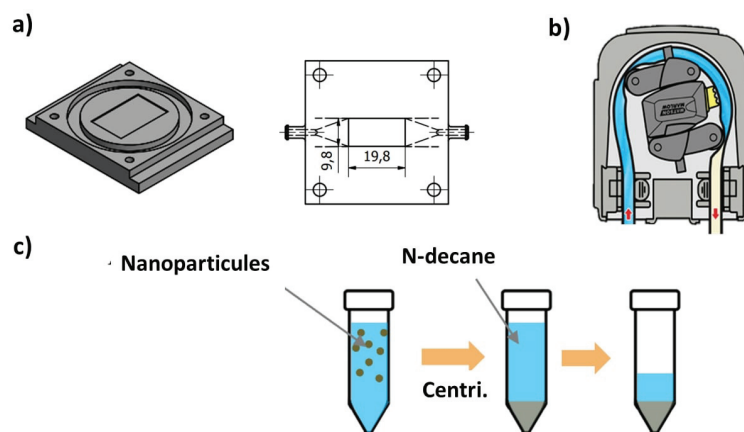


Figure 4.4: a) Receptacle containing the germanium target closed by the flow cell allowing circulation of the solvent b) Peristaltic pump c) Centrifugation of the solution

The concentrated solution is then dried out, and the resulting powder is analysed. The analysis results are presented in the next section.

4.1.2.3 Characterisation

During the synthesis process, a droplet of the liquid containing the nanoparticles is collected and deposited on a Transmission Electron Microscopy (TEM) grid (Ultra-thin carbon support film, 3nm, on a lacey carbon support film). TEM experiments were done on a JEOL 2100 HT microscope at a voltage of 200 kV. The images taken in high resolution are acquired using a Gatan Orius 200 camera. The resulting images are shown in figure 4.5. TEM images show large assemblies of nanoparticule and some isolated bigger particles of 500 nm diameter. Analysis of particle size using Fiji software [94] show that the nanoparticles radius is distributed around $9 \pm 4\text{nm}$. An amorphous carbon matrix (in light gray) surrounding the nanoparticles can be observed.

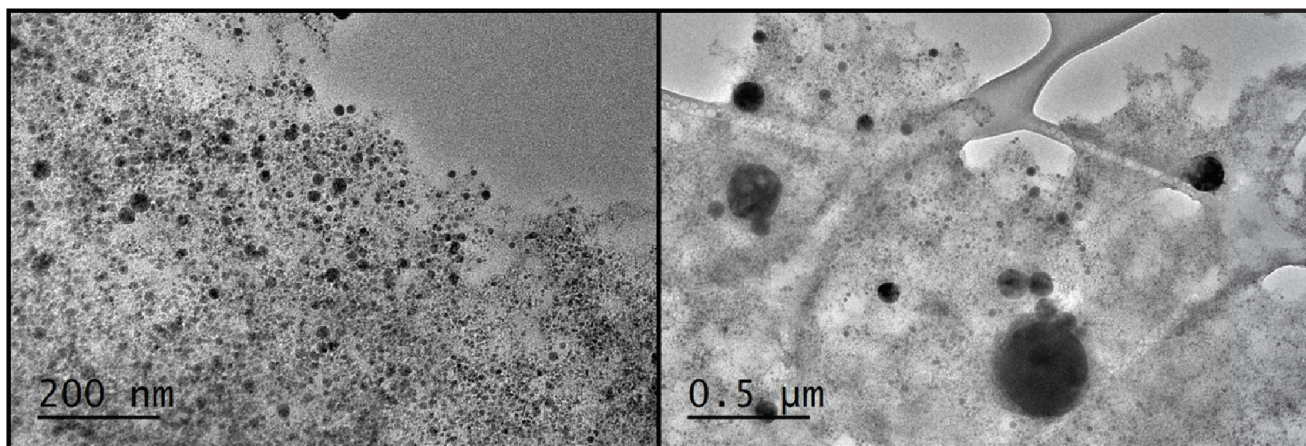


Figure 4.5: TEM image of the nanoparticle assembly obtained by pulsed laser ablation in n-decane. The nanoparticles (in black) appears to be surrounded by a carbon matrix (in light gray). The particle size is measured at $9 \pm 4\text{nm}$. Large particle of few hundreds of nanometer are sometimes observed.

Raman spectroscopy measurements made on the sample is shown in figure 4.6. The germanium mode usually located at 300 cm^{-1} appears downshifted and is measure at 295 cm^{-1} . This peak also show a strong asymmetry, with a full width half maximum ratio of $FWHM_{left}/FWHM_{right} = 1.83$. These results are consistent with the presence of nanoparticles of germanium [95]. The presence of amorphous carbon is evidenced by the presence of a broad D band measured around 1350 cm^{-1} , next to the G band at 1570 cm^{-1} .

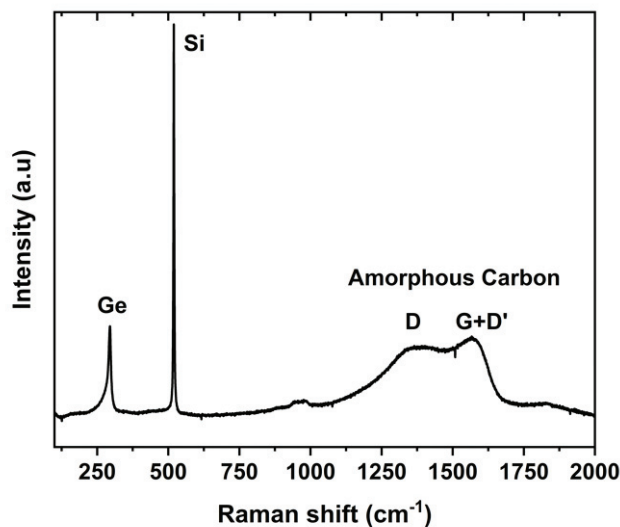


Figure 4.6: Raman spectrum of the sample synthesized by pulsed laser ablation in n-decane deposited on silicon wafer. The germanium mode appears blue-shifted and broad due to the nano-sized germanium particles present in the sample. Broad D and G bands of carbon appears at 1350 cm^{-1} and 1570 cm^{-1} confirm the presence of amorphous carbon.

The XRD measurements made on the sample only show the presence of germanium, no clear broadening is measured, possibly due to the strong signal of sub-micrometer Ge particles seen in TEM.

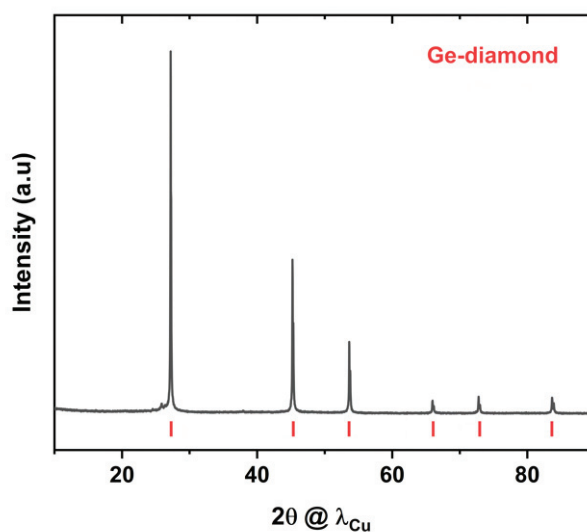


Figure 4.7: XRD pattern of the sample synthesized by PLAL. Only the reflections of germanium are seen.

4.2 Conclusion

Using PLAL method, we were able to synthesize a hybrid structure composed of nanoparticles of germanium embedded into a carbon matrix. The PLAL method was found to be an efficient pathway to synthesize a hybrid structure with carbon. One of the biggest advantages of PLAL method is that we can simply change the target to produce diverse nanoparticles assembly. For example, using the SiGe alloys synthesized using spark plasma sintering (section 2.4), synthesis of SiGe alloys nanoparticles could be proposed. This could lead to different studies for lithium ion batteries, but also a more fundamental study of the interactions between the carbon matrix and the nanoparticles using in situ Raman spectroscopy.

Preliminary experiments are currently conducted at the LN2 lab in Sherbrook, Quebec. The powders synthesized using PLAL were mixed with carbon black and assembled to make test batteries. Complementary batteries using regular germanium powder as active material are planned to be prepared in the same conditions to compare the electrochemical cycling behaviour.

PART II : High pressure studies of germanium and SiGe alloys

High pressure behaviour of Si, Ge and SiGe alloys : state of the art

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5.1 Silicon and germanium behaviour at high pressure

In this section, we present the HP behaviour of silicon and germanium and silicon germanium alloys. The HP behaviour of pure silicon and germanium is relatively well known and can provide insights on the possible transition pathway followed by SiGe alloys.

In this section and the following, phases of interest will be named after the compound and the crystallographic structure ex: *Si-R8*, *Ge-ST12* or simply "*R8*" or *ST12* when the compound is implicit. In the literature phases of silicon and germanium are sometimes noted using roman numerals, for example, Ge-I for the diamond phase of germanium. This notation can be confusing when comparing germanium and silicon as same crystallographic phases can have different roman numbers. Furthermore, the roman notation does not exist for SiGe alloys. I provided tables summarizing the different notations, that are presented in the following sections.

5.1.1 Transitions upon compression

The HP studies of silicon and germanium began in the early 60's with the development of new HP techniques allowing resistivity measurements at HP [96]. Notably, the early work made by Minomura & al. on germanium and silicon showed that at high pressure a resistivity drop of several orders of magnitude can be seen for Ge at 12 GPa and for Si at 20 GPa [15]. The authors stated that this phenomenon could be explained either by a melting of the compounds or a transition from the semiconducting diamond phase to a denser, metallic phase. Without direct *in situ* observations, this question was difficult to answer. The solution was brought with progress of *in situ* measurement methods. The development of new *in situ* XRD methods made by Jamieson & al. in 1962 [97] leads to measurements at pressures up to 15 GPa in germanium and silicon one year latter. This metallic behaviour at HP was found to be due to a phase transition from the diamond cubic phase to a tetragonal phase named Si- β or Ge- β . This name was inherited from the structure of the natural allotrope of Sn β -*tin* [98]. Latter using newly developed diamond anvil cells and *in situ* vibrational spectroscopy measurement techniques, this transition was further characterized in both silicon [99, 100] and germanium [101]. Using Raman spectroscopy this transition was however found to be challenging to observe due the metallic character of the β phase, leading to a very weak Raman signal.

This diamond to β transition has been observed to be very sluggish and sensitive to the presence of shear in both germanium and silicon [102]. Due these characters, the transition pressure reported in the literature varies widely. For Germanium it ranges from of 6.7 GPa (beginning) [103] up to 13.1 GPa (end)[104]. For silicon the observed transition pressure ranges from 8.3 GPa up to 16 GPa [105]. In general, the reported transition pressure for germanium are reported a few GPa lower than for silicon.

The transition mechanism from diamond to β phase is a reconstructive transition, characterized by a very large volume drop of $\sim 20\%$ for both Si and Ge [102, 106]. During the transition, the cubic cell is stretched along [100] and [010] directions and highly compressed in the [001] direction. The coordination number is changed from 4 to 6 as shown in figure 5.1.

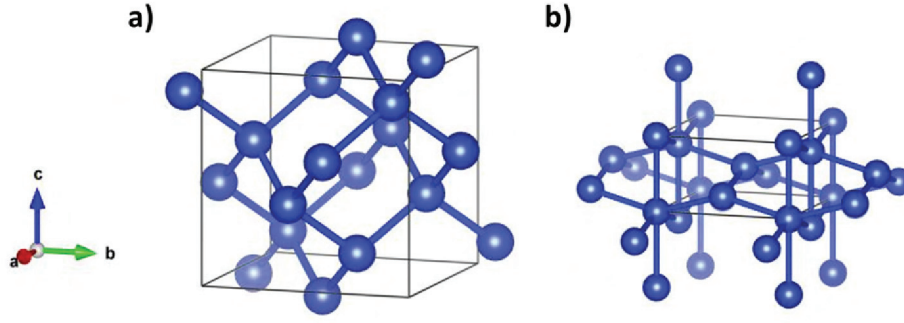


Figure 5.1: a) Diamond cubic structure b) Body-centered tetragonal (bct) β structure. During diamond cubic to β transition, the cubic cell is stretched along the $[100]$ and $[010]$ directions and highly compressed along the $[001]$ direction (dimension of cells are not to scale in the picture). Simulated using Vesta software [23].

With the new pressure tools available, silicon and germanium were studied at pressures greatly surpassing this metallic transition. For silicon, a rich variety of phases was found to quickly follow the β metallic phase [107, 108]. Interestingly, for germanium, a similar transition pathway is followed but at higher pressures [109], as shown in figure 5.2. The transitions between these HP phases were difficult to observe mostly due to their similar diffraction patterns, needing a fine control over pressure conditions and high resolution detection equipment. Study of these phases are beyond the scope of this study, but are depicted in figure 5.2.

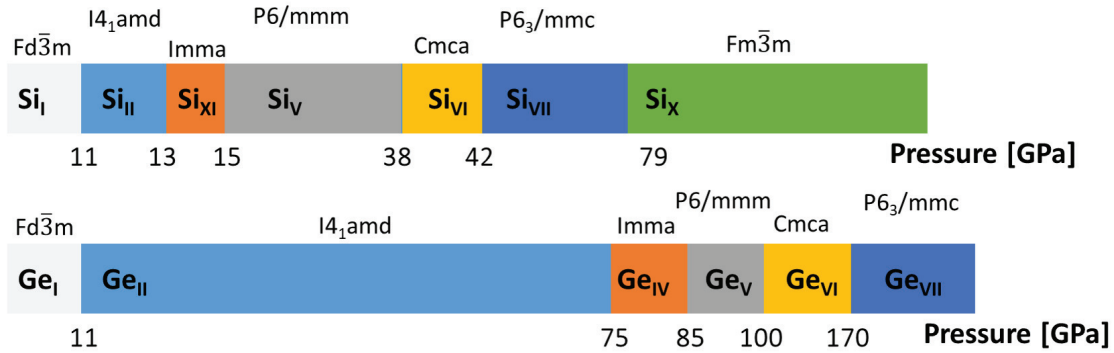


Figure 5.2: Accessible phases upon increasing pressure for silicon and germanium.

5.1.2 Transitions upon decompression from high pressure phases

More interestingly, notable effects were observed on the recovered samples upon decompression from β metallic phase. During the first studies of germanium and silicon, changes in density and resistivity were observed on the recovered samples after the pressure cycles [17, 15, 12]. These results raised the question of whether the transition from diamond to metallic β phase seen was reversible or not. For silicon, XRD measurements on recovered sample made by Wentof & al. [17] revealed the presence of one new phase of silicon the $Si - BC8$ phase. This body-centered cubic phase is similar to the diamond cubic phase, with eight atoms per cell, where each Si atom has four nearest neighbors, three at 2.39(1) Å and one at 2.30(1) Å in a distorted tetrahedral arrangement. This study also revealed that upon heating at 150°C for several hours this $Si - BC8$ phase does not transform toward diamond phase, but to another phase indexed as an hexagonal diamond structure noted $Si - hd$ (often called Lonsdaleite silicon).

Similar studies made on germanium interestingly showed a completely different behaviour. The sample obtained after decompression from the β metallic phase was found to be in tetragonal structure named $Ge - ST12$ by Bundy & al. [12]. $Ge - ST12$ phase has a complex tetragonal structure, with 12 atoms in the unit cell, formed by distorted tetrahedra and atoms in fivefold and sevenfold rings, the angular distortions of the ST12 tetrahedra are notably greater than for the BC8 structure. Upon annealing at a few hundreds of °C, the $Ge - ST12$ phase is found to transform back to the stable diamond cubic structure [13, 110, 111].

The different pathways observed in silicon and germanium were not explained at this stage. Especially the absence of BC8 and hexagonal diamond phases in germanium. Evidences of these phases in germanium were found under specific low temperature conditions [112]. Confirmation on the $Ge - BC8$ metastable phase was brought by Nelmes & al. [13]. The conditions required to form the $Ge - R8$ and $Ge - BC8$ phases were very fast decompression under hydrostatic conditions. At ambient temperature the $Ge - BC8$ phase was found to quickly transform to the diamond phase, contrary to $Si - BC8$ phase.

Later, using brighter sources offered by synchrotron experiments the pathway upon decompression from metallic phase to BC8 phase was clarified. An intermediate R8 phase between the β and BC8 phase was found in both silicon [113, 16] and germanium [14].

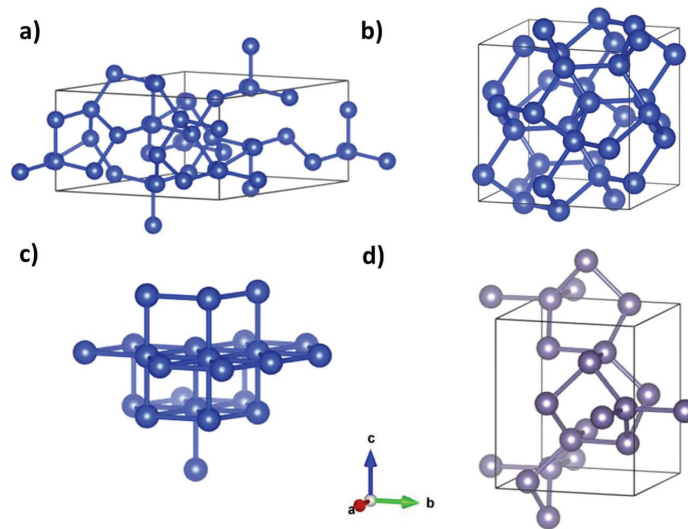


Figure 5.3: Metastable phases accessible upon decompression from β metallic phase a) R8 structure b) BC8 c) hexagonal diamond d) ST12 phase seen in germanium. Simulated using Vesta software [23].

A schematic view of the HP and metastable phases accessible is presented in figure 5.4. Phases accessible upon very HP (>20 GPa) are beyond the scope of this work but are reported in this figure. Group symmetry as well as references for each phase of silicon and germanium are presented in tables 5.2 and 5.1.

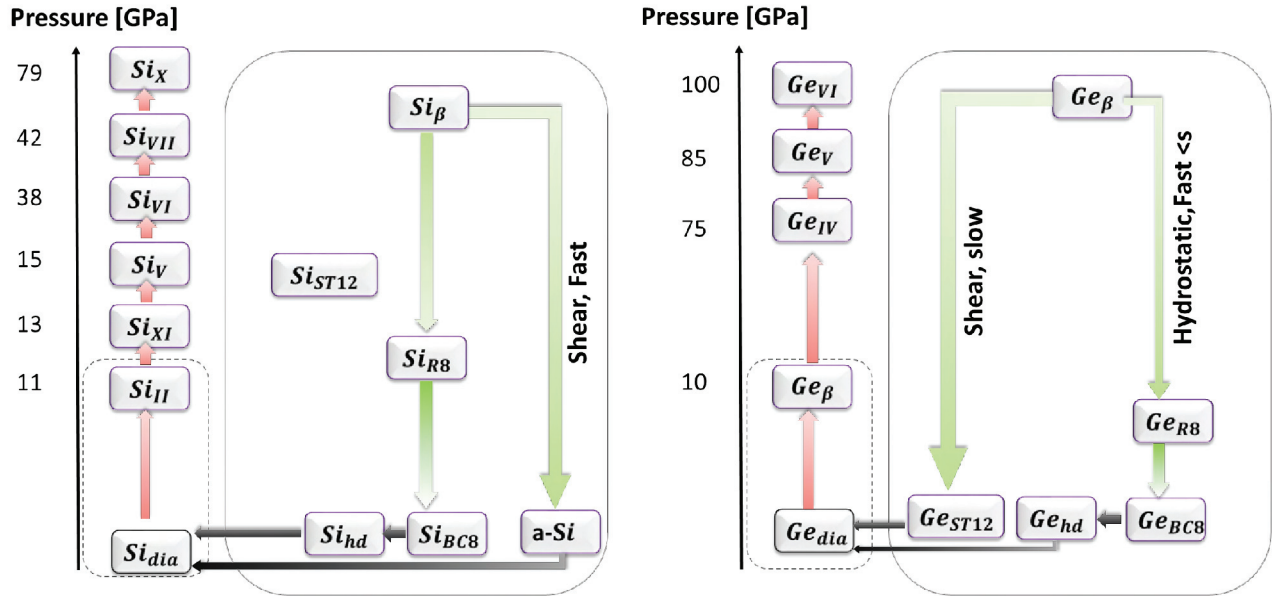


Figure 5.4: Schematic representation of phase transitions known in silicon and germanium. Red arrows indicates increasing pressure, green arrows decreasing pressures and black arrows thermally activated transitions. The phase transition happening upon decompression from the β phase are shown at the right of each diagram. For practical purposes some transitions are not shown.

Notation	Name	Space group
Ge_I	(cd), diamond cubic	$Fd\bar{3}m$
Ge_{II}	β -tin, metallic	$I4_1/amd$
Ge_{III}	Tetragonal , ST12	$P4_32_12$
Ge_{IV}	orthorhombic	$Imma$
Ge_V	Lonsdaleite/hexagonal diamond	$P6/mmm$
Ge_{VI}	Orthorhombic	$Cmca$
Ge_{VII}	Hexagonal compact, hcp	$P6_3/mmc$
Ge_{VIII}	BC8	$Ia\bar{3}$

Table 5.1: Table of HP and metastable phases encountered for germanium.

Notation	Name	Space group
Si_I	(cd), diamond cubic	$Fd\bar{3}m$
Si_{II}	Tetragonal β -tin, β -Sn, metallic	$I4_1/amd$
Si_{III}	BC8 Cubic	$Ia\bar{3}$
Si_{IV}	hexagonal diamond, lonsdaleite	$P6_3/mmc$
Si_V	(s.h), simple hexagonal	$P6/mmm$
Si_{VI}	Orthorombic	$Cmca$
Si_{VII}	hexagonal compact, hcp	$P6_3/mmc$
Si_X	(fcc), face centered cubic	$Fm\bar{3}m$
Si_{XI}	Orthorhombic	$Imma$
Si_{XII}	R8 rhombohedral	$R\bar{3}$

Table 5.2: Table of HP and metastable phases encountered for silicon.

The rich variety of metastable phases in silicon and germanium are of particular interest in many fields. Notably the pressure range needed to synthesize metastable phases enables large-scale synthesis for industrial use. Study of the optical properties of these phases are of interest in the photovoltaic industry in case of silicon R8 and BC8 phases [114, 115]. More recently, a huge interest on the optical properties of the hexagonal phase of germanium has been shown, due to its narrow direct bandgap of 0.3 eV [116]. These metastable phases properties are even more of interest in the case of SiGe alloys, because of the potential tunability they offer [10, 11].

5.2 Silicon germanium alloys at high pressure

SiGe alloys HP behaviour were explored later than germanium and silicon. Upon compression, the pathway followed by SiGe alloys was found to be close to silicon and germanium. The transition pressure to the metallic SiGe- β phase has been reported both theoretically [117, 118] and experimentally [119]. This transition pressure varies non-linearly in function of composition between silicon (~ 12 GPa) and germanium (~ 10 GPa) [120]. One study of Sui & al. [121] reports the pressure coefficients of 3 Raman modes of various alloy compositions, without any mention of the decompression behaviour.

In the case of SiGe alloys, only few recent studies mention the formation of metastable phases using HP techniques. In a recent study, Ikoma & al report the *ex-situ* measurement of $Si_{0.5}Ge_{0.5}$ - BC8 phase during HP torsion [122]. Morozova & al. reported for the first time resistivity measurements on Ge-rich ($x = 0.974$ and 1) and silicon rich samples ($x = 0, 0.02, 0.07, 0.13$) [11]. The samples were observed *ex-situ* after indentation, and reported to transform to ST12 phase for the Ge-rich samples, and BC8 phase for the Si-rich samples. Interestingly, they report the first *in situ* Raman spectroscopy measurement upon compression and decompression in diamond anvil cell on a silicon rich alloy ($x=0.974$). The transition pathway followed by $Si_{0.974}Ge_{0.026}$ appears very similar to pure Si with first a transition toward the $Si_{0.974}Ge_{0.026}$ - R8 phase ~ 4.2 GPa followed by a transition to $Si_{0.974}Ge_{0.026}$ - BC8 at 3 GPa. The BC8 phase was observed to be stable at ambient conditions.

In general, there is a lack of knowledge on the behavior of these alloys under pressure. If some works mention the compression behaviour or *ex-situ* measurement of metastable phases, almost no information is presented on full pressure cycle in SiGe alloys. The primary study presented however shows great interest on the exotic properties of SiGe metastable phases, notably germanium rich alloys hexagonal phase structure exhibits a tunable direct-bandgap, and shows efficient light emission [10, 123, 124]. Other metastable phases like R8 and BC8 structure may have an application in stress-controlled switches, as application of pressure leads to p-n inversion as evidenced by Morozova & al. [11].

This work can therefore bring insights on HP behaviour of SiGe alloys. The following section is dedicated to present the HP tools used to probe SiGe behaviour under pressure.

High pressure tools

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6.1 Paris-Edinburgh press

The P-E press is an hydraulic press developed in the beginning of the 90's. Originally developed for *in situ* neutron scattering [125, 126], it has been modified for *in situ* XRD studies [127]. This press allows compression of large volume samples (typically several mm^3) and is able to reach pressures up to 15 GPa and temperature up to 1500°C. In this work, P-E press is of interest because the pressure range accessible is consistent with the known pressure transition to the metallic phase of silicon, germanium and SiGe alloys. The low weight of this instrument (<50kg depending of the model) allows to install it on synchrotron beamlines for *in situ* study.

Two models of press have been used in this work, the first one is a V4 model that can apply 250 Ton-force on a piston of 100 cm^2 surface. The second is a lighter V5 model that can apply 160 Ton-force on a piston of 66.5 cm^2 surface. This latter press was installed on Elettra synchrotron at the XPress beamline for *in situ* XRD studies as described in section 6.1.1.

A schematic view of the press and the different components is shown in figure 6.1. Depending on the pressure and temperature conditions wanted, several experimental assemblies of anvils and gaskets are available. In our case, reaching pressures superior to 10 GPa requires to use sintered diamond anvils with a gasket of 5 mm outer diameter. Other setups using tungsten carbide anvils and larger gaskets up to 15 mm are available but are not suitable to our experimental requirements. The gasket containing the sample is composed of boron-epoxy. The studied powder samples can be loaded directly into the boron epoxy gasket for experiment at ambient temperature. If the use of high temperature is needed, supplementary encapsulation into a graphite oven and a protective boron nitride capsule is needed as shown in figure 6.1. The gasket is placed between the two sintered diamond anvils and installed in the press. Then the pressure is controlled by a hydraulic pump that injects oil in the lower part of the press. The oil pressure allows the movement of the lower piston. During the experiment, the resistance of the sample can be measured by placing electrodes on the upper and lower anvils.

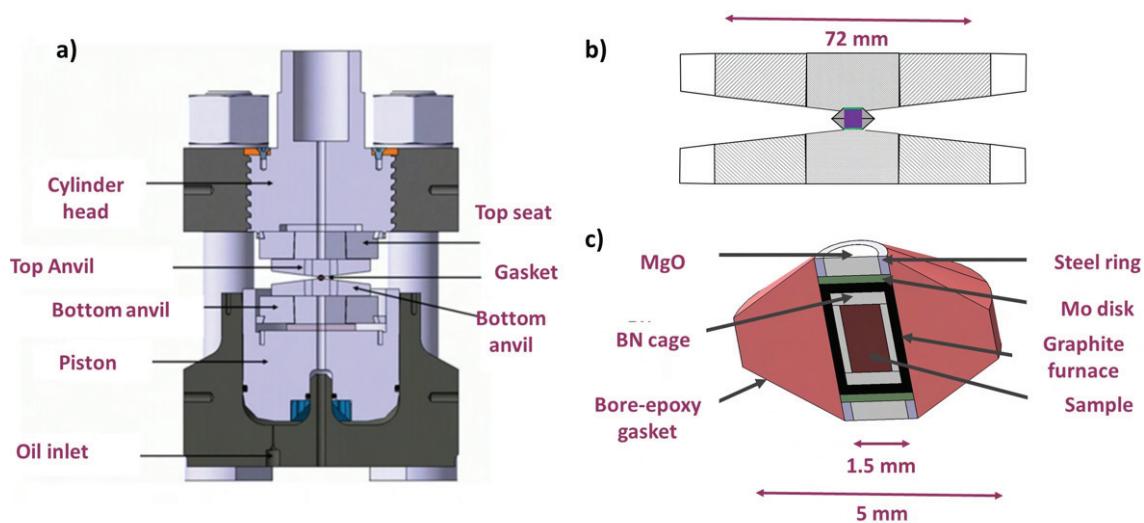


Figure 6.1: Schematic view of a) Cross section of a P-E press (model V5) and major components b) Diamond sintered toroidal anvils c) Assembly of 5 mm boron epoxy gasket : for a HP experiment the sample is loaded in the gasket and closed by two Mo disks. For HP-HT experiments, the sample is encapsulated into a graphite furnace and boron nitride capsule, closed by Mo disks and steel rings filled with MgO powder.

6.1.1 Installation of the Paris-Edinburgh press at XPress beamline at the ELETTRA Synchrotron, Trieste (Italy)

Elettra is a third-generation Italian synchrotron. In the storage ring, electrons traveling at nearly the speed of light through undulators, wigglers and bending magnets produce synchrotron radiation. The brightness of the light produced reach 10^{19} photons/s/mm²/mrad²/0.1%bw ten billion times brighter than that supplied by conventional laboratory radiation sources.

Xpress beamline is a dedicated HP diffraction beamline. A Si (111) monochromator is placed upstream to select an energy of 25 keV and focused in a 100 μ m monochromatic X-ray beam thanks to a toroidal mirror as shown in figure 6.2. The diffraction signal is collected on a PILATUS 3S 6M detector (from DECTRIS).

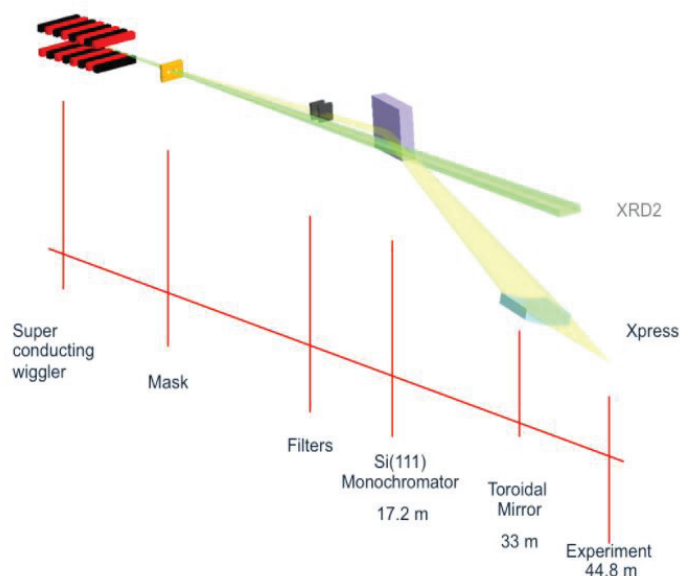


Figure 6.2: Optics layout of the XPress beamline. Reproduced from Elettra XPress beamline website.

During this work, we installed for the first time a large volume P-E press on XPress beamline. The equipment including the press, the pressurization system, the anvils, the gaskets, the current generator were brought to the facility. The press was placed on a dedicated seat and manually aligned using a vertical translation stage. The pressure was applied with a manual pump.

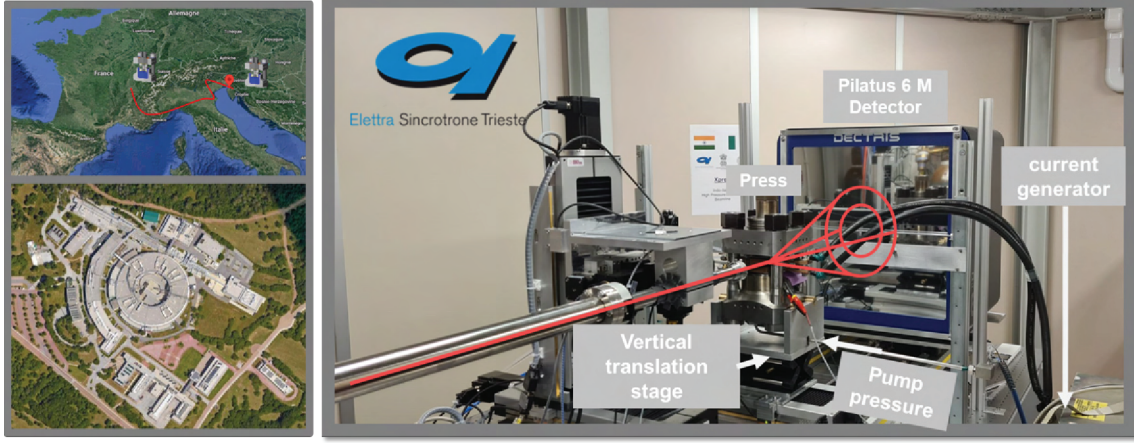


Figure 6.3: P-E V5 press installed on XPress beamline at Elettra. The anvils are connected to a current generator for high temperature experiments. The press height is set using a vertical translation stage in order to place the sample in the beam path. During the experiment, the pressure is controlled manually with a manual pump. The diffraction pattern was collected on a Pilatus 6 M detector.

Pressure calibration

In order to calibrate both pressure and detector position, a sample of silicon was prepared. A typical diffraction pattern obtained at ambient conditions is shown in figure 6.4. Due to the absorption of the anvils, a large part of the diffraction cones are not measurable. Good quality diffraction patterns can be collected in 80 seconds.

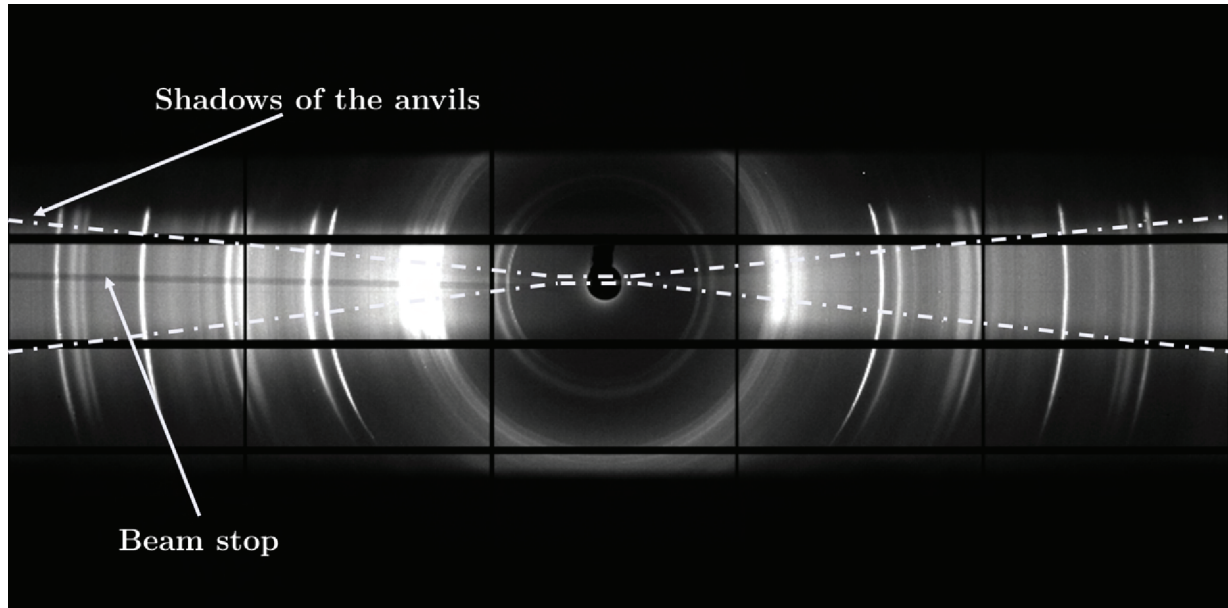


Figure 6.4: Diffraction image of a silicon sample under pressure obtained on the Pilatus 6M detector.

During the compression stage, the press height is regularly adjusted to compensate the piston displacement. The obtained silicon cell parameter as function of the oil pressure is presented in figure 6.5. Internal pressure is then calculated using a third-order Birch-Murnaghan (BM3) Equation Of State (EOS) :

$$P = \frac{3K}{2} \left[\left(\frac{V}{V_0} \right)^{\frac{7}{3}} - \left(\frac{V}{V_0} \right)^{\frac{5}{3}} \right] \left[1 + \frac{3}{4}(K'_0 - 4) \left(\left(\frac{V}{V_0} \right)^{\frac{2}{3}} - 1 \right) \right] \quad (6.1)$$

With P the pressure in GPa, $K=98.88$ GPa corresponding to silicon bulk modulus and $K'=4.24$ its pressure derivative [108]. The calculated internal pressure as function of the oil pressure was fitted using a second order polynomial equation $P_{intern} = \alpha P_{oil} + \beta P_{oil}^2$.

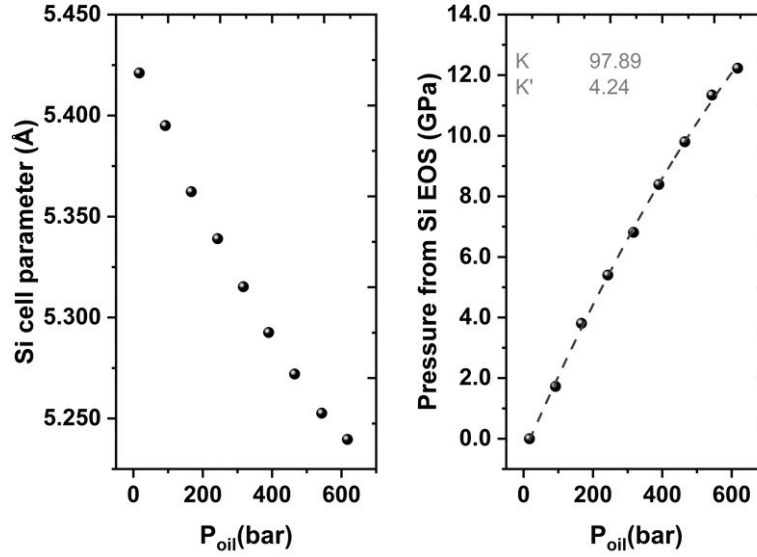


Figure 6.5: (left) Measured silicon cell parameter as function of the oil pressure applied to the piston (in bar). (right) Calculated internal pressure as function of the oil pressure based on equation 6.1

6.2 Diamond anvil cell

DAC have been developed in the late 50's. They constitute today one of the more versatile tools to apply pressure ranging from a few GPa to hundreds of GPa and temperature up to 5000 K. They are based on the simple equation $P = F/S$. In order to reach high pressures, the force must be applied on a very small surface typically less than 1 millimeter. Diamond, the hardest material known, is used to compress the sample. One major advantages of diamond is its transparency in a large range of wavelength from infrared to X-rays and gamma rays, allowing the to analysis of the materials using various *in situ* techniques [128]. The diamonds are also transparent in visible light, allowing observation of the sample using a regular microscope.

In practice, the preparation of a DAC is as follows (schematically shown in figure 6.6). 1) A $200\ \mu m$ thick steel gasket is pressed between the two diamonds to form a circular imprint of the size of the diamonds (typically from 250 to 600 μm). 2) At the center of this mark, a hole is drilled using an electro-erosion driller 3) The hole is then filled with the sample, a pressure calibrant and a Pressure Transmitting Medium (PTM) (described in following sections). 4) The cell is closed and ready to be used.

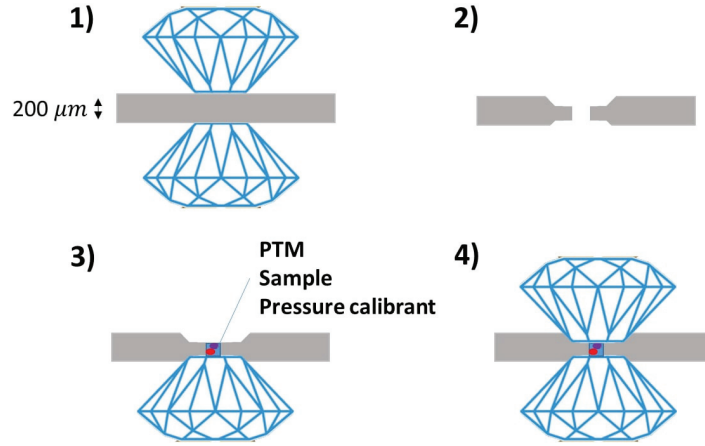


Figure 6.6: Preparation steps of a DAC experiment. 1) Indentation of the steel gasket with the diamonds imprint 2) Electro-erosion of a hole in the gasket that will be used as a pressure chamber 3) Loading of the pressure chamber with the sample, a pressure calibrant (ruby) and the PTM. 4) Closure of the cell

To apply the pressure, the upper diamond anvil is mobile, and usually moved thanks to an inflatable membrane, or mechanically using screws. In all of our experiments (unless mentioned), we used membrane high pressure cells. The gas used to inflate the membrane is helium, and pressure is controlled using a gas supply set-up. The different components presented are shown in figure 6.7.



Figure 6.7: (Left) a) Diamond anvil lower and upper part along with a circular steel gasket b) The metallic deformable membrane and capillary (Right) Helium gas supply setup allowing regulation of the pressure applied to the membrane.

During the experiment, the sample pressure is controlled by the membrane pressure. In this work we used typical maximum pressures of $\sim 20\ \text{GPa}$, corresponding to $\sim 100\ \text{bars}$ on the membrane (depending on the size of the diamonds and hole used). Upon compression, special care is taken to verify the gasket hole integrity during the experiment. Upon decompression, the pressure of the membrane is released gradually. Due to the plastic deformation of the steel gasket and friction between the piston and the cylinder the pressure inside the chamber is not directly lowered and an hysteresis is usually observed. Due to this effect, precise control of the internal pressure is harder during decompression. During this work it has been observed that even after decreasing the membrane pressure to $0\ \text{bars}$ the internal pressure measured is still of a few GPa. In this case we unscrew the cell, losing data in the low pressure regime.

6.2.1 Pressure calibration

Depending on the *in situ* method used, several calibrant can be used. In case of *in situ* Raman spectroscopy, the standard calibrant used is ruby. When ruby are doped with Cr^{3+} ions, a sharp fluorescent doublet can be measured when illuminated with a laser. This doublet can easily be measured using a spectrometer. The R1 line of this doublet is used to estimate the pressure using the following equation [129] :

$$P = \frac{A}{B} \left[\left(\frac{\lambda}{\lambda_0} \right)^B - 1 \right] \quad (6.2)$$

where P is pressure in GPa, and $A = 1876 \pm 6.7$ GPa, $B = 10.71 \pm 0.14$ parameters obtained in reference [129]. λ_0 is the measured wavelength of the R1 fluorescence line at ambient pressure and λ at higher pressures. The experimental uncertainty on pressure determination with this method is estimated at $\pm 5\%$. An example of measured redshift of R1 line is shown in figure 6.8.

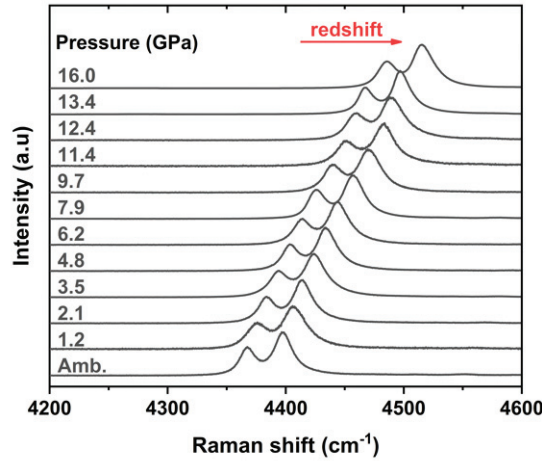


Figure 6.8: Measured ruby R1 and R2 fluorescence lines showing a redshift with increasing pressure. The calculated pressure using equation 6.2 is showed next to each spectra.

For HP XRD experiment at Soleil synchrotron, the pressure calibrants used was Au[130, 131]. The powdery Au is mixed with the sample inside the hole of the gasket. The pressure calibration can be done using equation of state presented previously 6.1 with the unit cell of Au measured at each pressure step during the XRD experiment.

6.2.2 Pressure transmitting medium

PTM plays a important role in Diamond anvils cell experiments. The choice of the PTM is often based on the pressure conditions needed (hydrostatic or not). In this work, paraffin oil is mostly used. This medium is known to solidify at rather low pressures of 5-7 GPa [132]. For comparison, standard 4:1 ethanol:methanol mix is known to solidify at higher pressures around 12-13 GPa [133].

In the case of this study, the use of paraffin oil is preferred because non hydrostatic conditions produce shear stress known to ease the transition towards metastable phases. For example in germanium, this non-hydrostaticity is known to lead to Ge-ST12 phase, whereas hydrostatic conditions can lead to Ge-R8 and Ge-BC8 transitions. In this work, the P-E press is also widely used, where the conditions are not hydrostatic. Therefore using this PTM allowed us to better compare DAC studies with P-E studies.

6.3 *In situ* Raman spectroscopy in DAC

All Raman experiments were carried out using a homemade spectrometer in backscattering geometry. The laser wavelength used was $\lambda = 532$ nm. The laser power was adjusted in order to avoid heating effects on the samples and to improve signal over noise ratio. The laser beam was focused with a 50x objective and the signal was dispersed by a grating of 1800 grooves/mm; the signal was collected on a Princeton Instruments Acton SP-2500i spectrometer. The spectral resolution of the setup is estimated to $\sim 1\text{cm}^{-1}$ and observation down to 10 cm^{-1} . A schematic view of the experiment is presented in figure 6.9.

During this work, maintenance of the equipment was made. Notably the CCD detector connected to the spectrometer was replaced after a technical failure. Once replaced, the CCD detector was calibrated using two atomic lines from a spectral mercury lamp at 546.075 nm and 579.067 nm. The calibration is regularly checked by measuring silicon and G band of graphite prior to each *in situ* measurement.

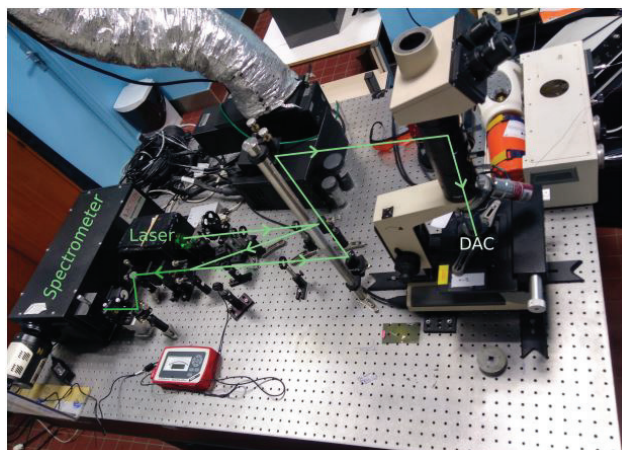


Figure 6.9: Micro Raman setup used for *in situ* measurements in DAC. The laser is shown in green.

6.4 *In situ* X-ray diffraction in DAC

Specifically designed DAC allow *in situ* diffraction measurements using laboratory sources of X-ray. During this work, we used an Almax-type DAC with an aperture angle of : 85° (top and bottom). Contrary to the DAC presented before, the pressure is controlled mechanically using a set of screws. This cell is mounted over a specifically designed support as shown in figure 6.10, and placed in the diffractometer.

The XRD data were collected using a microfocus Oxford Xcalibur Mova diffractometer. The X-rays are generated by a sealed tube, which is mounted on the goniometer and powered by the high voltage X-ray generator. The source used is molybdenum (K wavelength $\lambda = 0.70926$ Å). The X-ray optics consist of a high speed shutter located next to the tube shield, a monochromator for selecting a specified bandwidth from tube spectrum and a collimator in order to limit beam divergence. The beam diameter is approximately about $150\text{ }\mu\text{m}$ compared to a typical hole diameter of $100\text{--}200\text{ }\mu\text{m}$ in this configuration, the diffraction patterns show reflection of the steel gasket. Once placed, the sample can be viewed and aligned with the video microscope.

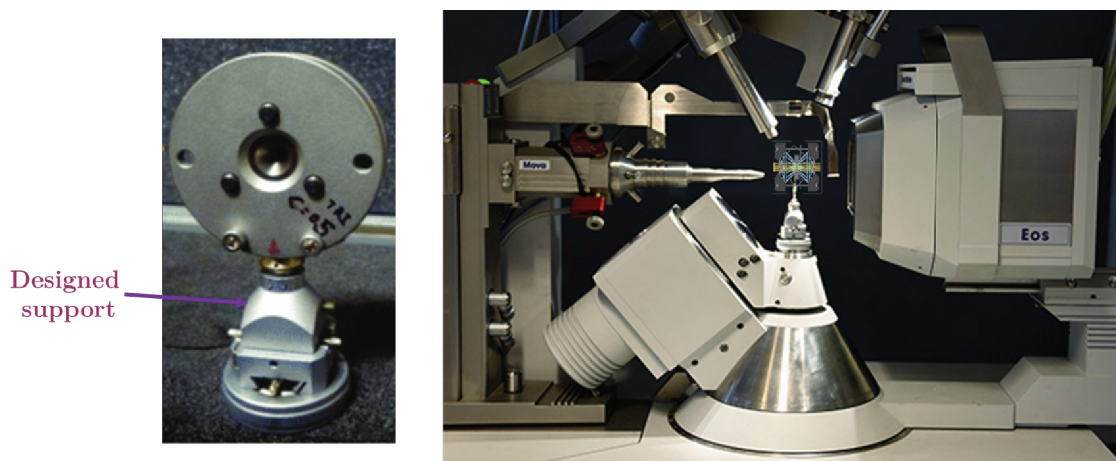


Figure 6.10: (left) Almax-type DAC mounted on the support allowing alignment in the diffractometer. (right) Four circle microfocus Oxford Xcalibur Mova diffractometer

For each pressure, three images are recorded on the detector and combined to form a 2D image using dedicated CrysAlisPro software. The reflections corresponding to the diamond anvils are removed from the image, and a 2D graph is reconstructed. A typical image obtained with this experiment is shown in figure 6.11.



Figure 6.11: Typical image obtained on Oxford Xcalibur Mova diffractometer. The diamond point reflections are hidden by the darker squares.

6.5 PSICHE beamline at the SOLEIL Synchrotron, Saint-Aubin (France)

This beamline is dedicated to XRD and tomography experiments under extreme conditions (pressure and temperature). The X-ray source is a multi-pole wiggler that provides a wide energy range white beam (15 to 100 keV). This wide energy range allows energy dispersive XRD measurements and tomography. In our case, we operated using a focused monochromatic mode for angular dispersive XRD measurements, with a beam size of $20\ \mu\text{m}$. The energy used is 33 keV equivalent to $0.3738\ \text{\AA}$. The powder XRD patterns were collected on a Pilatus CdTe image plate detector, with good quality diffraction patterns obtained in a few tens of seconds.

The experiment was performed in the framework of a Block Allocation Group (BAG) initiative proposed by the "réseau des technologies des haute pression" (<https://reseauhp.org/>). This BAG project is dedicated to group short-term projects using the same standardized setup, allowing a measurement time of 8 hours (1 shift). The BAG demand needs to be submitted as proposal and it is subjected to peer review committee as any other proposal.

High pressure properties and metastable phases in germanium and SiGe alloys

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7.1 Introduction

In this chapter, I will present the high-pressure studies of silicon-germanium alloys that I synthesised as described in the first part of the manuscript. 2. The main objectives are the definition of the stability domain of the diamond phase for different stoichiometries, the study of pressure induced phase transitions and the potential formation of metastable phases during compression and decompression cycles and, when possible, the study of the mechanical, structural and vibrational properties of the different phases. Using HP techniques described in previous chapter 6, we investigate the pressure behaviour of two different alloys: $Si_{0.8}Ge_{0.2}$ and $Si_{0.5}Ge_{0.5}$. To complete this study, experiments are currently made on $Si_{0.3}Ge_{0.7}$ composition and are not shown here. The pressure behaviour of germanium is also studied, while silicon is neglected as it is well documented. For each alloys, we tried to perform *in situ* X-ray diffraction studies (using either laboratory source or synchrotron radiation) to be able to determine the structure of phases appearing during compression and decompression cycles, and calculate the bulk modulus of different phases. The structural information was then combined with quantum-mechanical atomistic simulation work carried out in collaboration with a theoretician to better interpret the experimental data and the observed phase properties. *in situ* Raman experiments at HP were also undertaken and the vibrational properties of the samples are discussed with the preliminary Density Functional Theory (DFT) results.

7.2 High pressure study of germanium

In this section, we present the work made on pure germanium. As presented in the state of the art in section 5.1, the HP phase transition pathway of germanium is rather well known. Upon compression, diamond cubic germanium transforms to the $Ge - \beta$ metallic phase, and when decompressed from this phase it transforms predominantly into the $Ge - ST12$ phase at around 8 GPa [104, 134, 102, 103, 13]. Up to now, the experiments presented in the literature only report $Ge - ST12$ behaviour upon decompression, resulting in few pressure points. However, characterization of the $Ge - ST12$ vibrational properties shows some interesting features not discussed in the literature.

To investigate in more details the properties of the $Ge - ST12$ phase, and enlarge the accessible pressure region, two solutions were considered : i) to carry out a DAC experiment using two pressure cycles, one for synthesizing the $Ge - ST12$ phase, the second to explore its HP behaviour. ii) to synthesize $Ge - ST12$ phase using the P-E press, and carry out the HP experiment on the recovered $Ge - ST12$ sample. These experiments were also performed to give us new insights on how to perform future high-pressure experiments on SiGe alloys. The experiment in the P-E press is particularly interesting because it can potentially lead to the recovery of a large amount of metastable phase, thus opening up new possibilities of sample characterization. Germanium is a perfect candidate as it has the lower predicted transition pressure to the $Ge - \beta$ metallic phase among all the possible SiGe alloys, thus easier access to the metastable phases in large volume press.

7.2.1 Germanium behaviour during pressure cycling using *in situ* Raman spectroscopy

For the *in situ* Raman spectroscopy experiment, two pressures cycles were done. During the first cycle, we aimed to synthesize $Ge - ST12$ phase by compressing (and decompressing) a germanium wafer piece loaded in a DAC. During the second compression-decompression cycle, we intended to study the stability and vibrational properties of the synthesized $Ge - ST12$ phase on a wide pressure range. The experimental protocol is the following: a piece of high purity germanium wafer is loaded into a 100 μm hole in a steel gasket along with ruby as a pressure gauge. The PTM used is paraffin oil, as non hydrostatic conditions are needed to promote the transition toward the $Ge - ST12$ phase[14].

First pressure cycle :

Raman spectra obtained during the first pressure cycle are shown in figure 7.1. As no crucial data are needed during this step, the first compression stage is covered quickly. During compression the T_{2g} mode of germanium is observed up to 9.4 GPa. Total loss of Raman signal is observed at 12.1 GPa. This signal loss is consistent with a full transition toward the $Ge - \beta$ metallic phase, which has a very weak Raman signal. The two longitudinal and transverse optical modes of $Ge - \beta$ phase are not observed in our case [101]. Upon decompression from the metallic phase, no signal is observed down to 9.0 GPa where a new rich spectrum appears. A total of 12 new modes are measured and could be attributed to the $Ge - ST12$ phase [104]. The transition pressure is close to the pressures reported in literature that range from 7.3 to 10.3 GPa [102, 103, 111, 14, 104]. Initially, no coexistence with the diamond phase is observed, but as the pressure decreases, the presence of the diamond phase is observed at localized points in the sample. This coexistence is likely to be due to laser heating inducing a $Ge - ST12$ to diamond transition [110]. However, the majority of the sample show no traces of diamond. This observation illustrates the sensitivity of the $Ge - ST12$ phase to external conditions. Upon further decompression, the internal pressure could not be reduced below 1.0 GPa, even at 0 bar on the DAC's membrane.

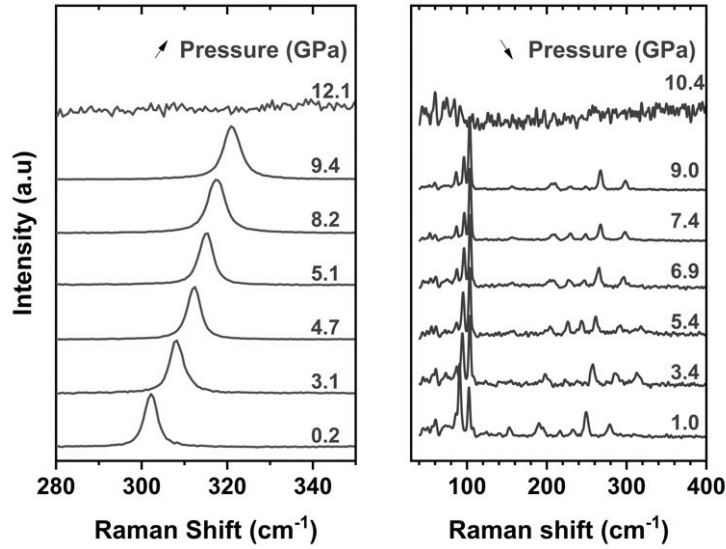


Figure 7.1: Raman spectra obtained during the first pressure cycle of a germanium wafer piece. Upon increasing pressure a transition toward a metallic phase is visible through a signal loss at 12.1 GPa. Upon decompression $Ge - ST12$ signature spectra is observed at 9.0 GPa.

Second pressure cycle :

During the second pressure cycle, the number of pressure steps is increased to follow the behaviour of the $Ge - ST12$ phase during compression. The obtained Raman spectra are showed in figure 7.2. Upon compression, the $Ge - ST12$ phase is observed up to 11.0 GPa where only one major mode is seen at 100cm^{-1} , above this pressure, no Raman signal is measured due to the transition to the metallic $Ge - \beta$ phase. The transition pressure observed is consistent with a fully reversible transition between $Ge - ST12$ and $Ge - \beta$ phase [103, 134]. Upon decompression, the reverse transition is observed at 10.4 GPa, slightly higher than the transition pressure measured during the first cycle.

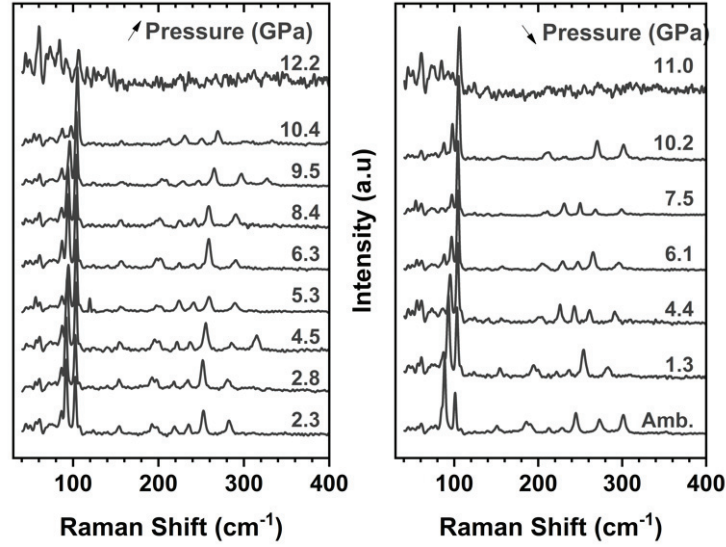


Figure 7.2: Selected Raman spectra obtained during the second pressure cycle of a germanium wafer piece. $Ge-ST12$ modes are observed up to 11.0 GPa, where the reverse transition $Ge-ST12$ to $Ge-\beta$ metallic phase takes place. Upon decompression, $Ge-ST12$ phase appears at 10.4 GPa and stays stable down to ambient pressure.

In order to complete this experimental work, simulation of the $Ge-ST12$ modes was made (obtained within the framework of a collaboration described in annex B) and is shown in figure 7.3. Interestingly, among all the simulated modes, two intense A_1 modes around 89 and 99 cm^{-1} exhibit a rare non-crossing behaviour upon increasing pressure. This effect has been observed in compounds such as Zirconia, AlSb and SbSI [135, 136], but this was never observed in the case of $Ge-ST12$ structure. This non-crossing event is caused by the fact that pressure (or temperature) forces two modes of the same symmetry to get closer. As these two modes get closer, they begin to interact strongly due to the fact that two modes of the same symmetry cannot take the same energy. This interaction result in hybridization of the modes, modifying both the intensity and the FWHM. During this event, the mode at lower frequency is predicted to exhibit softening whereas the other should behave normally.

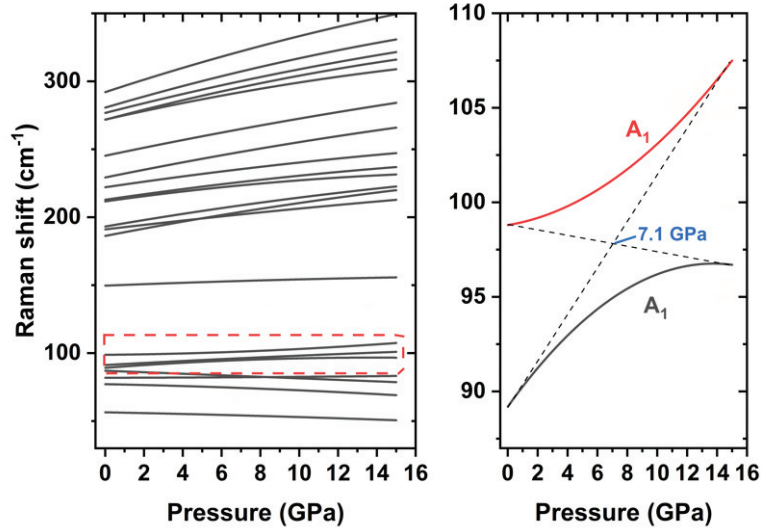


Figure 7.3: (left) Simulated pressure parameters for $Ge-ST12$ phase. (right) Two modes of same A_1 symmetry at frequencies around 100 cm^{-1} exhibit a non-crossing behaviour.

The measured positions of the two non-crossing modes during all the cycles are shown in figure 7.4. The results show no clear non-crossing behaviour during the cycles. We also observe that the pressure behaviour of the measured modes during the cycles is not exactly the same, which can be attributed to the fact that during the two pressure cycles, stresses accumulate in the sample, resulting in a slightly different pressure behaviour. A comparison between theoretical and experimental pressure behaviour of $Ge-ST12$ phase will be discussed in the following sections.

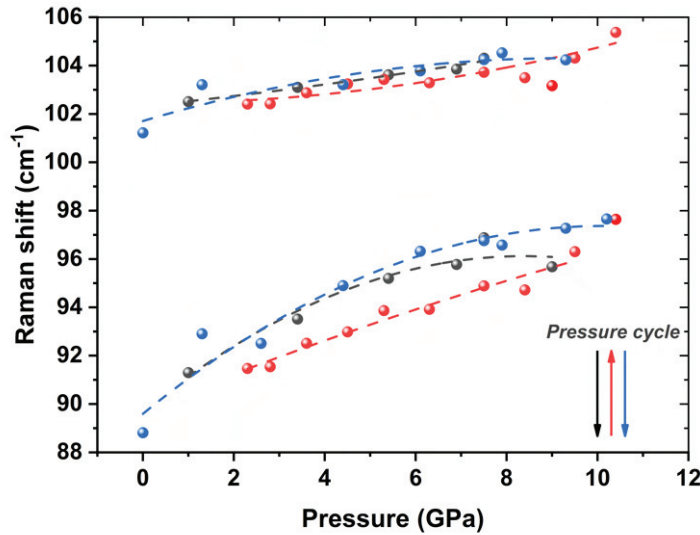


Figure 7.4: Raman shift of the two non-crossing modes in $Ge-ST12$ phase as a function of pressure. No clear non-crossing behaviour is observed during the pressure cycles, presumably due to the accumulation of stresses in the samples during the pressure cycles.

In the following sections, we will synthesise the $Ge - ST12$ phase using a P-E press and study the behaviour under pressure of the recovered sample. This method could be interesting for the study of non-crossing events, by removing one of the two pressure cycles and thus avoiding stress accumulation.

7.2.2 Synthesis of Ge-ST12 phase in Paris-Edinburgh press

For this experiment, a small piece of germanium wafer was grinded and the powder was loaded into a boron-epoxy gasket. The experiment was conducted in the following way: during compression, pressures of 4.5, 11.5 and 15.3 GPa are reached at a rate of 0.25, 0.07 and 0.016 $GPa.s^{-1}$. During decompression, pressures of 11.5 and 0 GPa are reached at a rate of 0.016 and 0.07 $GPa.min^{-1}$ respectively. The full cycle duration was approximately 13 hours. During the experiment, we measure the electrical resistance of the sintered diamond anvils and the sample by placing electrodes on the upper and lower anvils as depicted in figure 7.5.

The measured resistance as a function of the pressure is shown in figure 7.5. During compression a large resistance drop of resistance is seen around 9 GPa. A plateau at the minimum resistance is then reached at around 12 GPa, which is consistent with a transition to a metallic phase. During decompression, the resistance stays at its minimum value between 15 to 8 GPa, attesting that the sample is still in the metallic phase. At 8 GPa, the resistance rapidly increases by four orders of magnitude, due to a transition to a semiconducting phase.

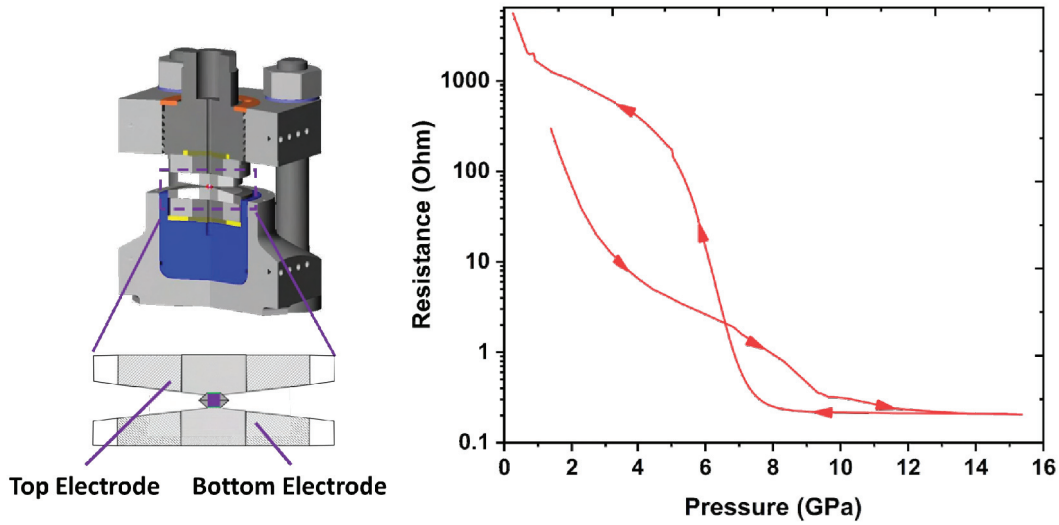


Figure 7.5: (left) Schematic view of the P-E press and of the position of the electrodes for resistance measurement. (right) Resistance measured during the pressure cycle of a germanium sample. During compression a large drop of resistance indicates that the sample transforms to a metallic phase. Upon decompression, resistance increases by 3 orders of magnitude around 6 GPa, consistent with a transition toward a semiconducting phase.

The XRD pattern obtained on the recovered and grinded sample is shown in figure 7.6. The diffraction pattern was successfully indexed with diamond and ST12 phases of germanium. LeBail refinement of the diffraction pattern indicates that the sample is composed of 75% of $Ge - ST12$ and 25% $Ge - diamond$. Two reasons can explain the presence of $Ge - diamond$ phase : i) an incomplete transition to the $Ge - \beta$ phase during the compression stage in the P-E press. ii) a reverse transition induced during the grinding of the sample before XRD measurements.

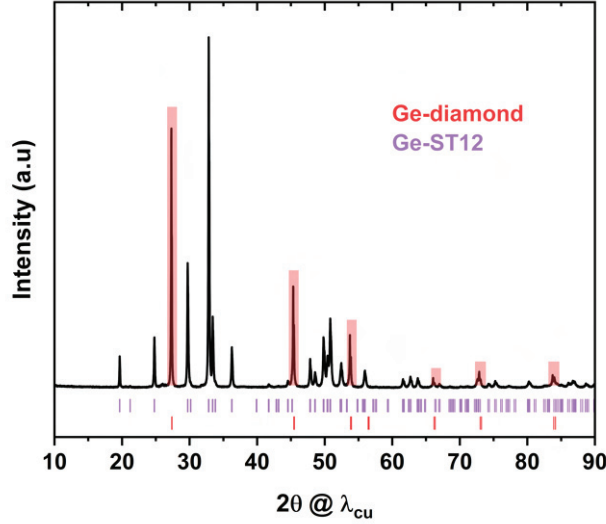


Figure 7.6: XRD pattern of the grinded Ge sample recovered after pressure cycling in a P-E press. LeBail refinement indicates that the sample is composed of $Ge - ST12$ and $Ge - diamond$ phase with a 75:25 mass ratio. Reflections of $Ge - ST12$ are shown in purple and of $Ge - diamond$ in red.

Raman spectra made on the raw (as recovered after the pressure cycle in the P-E press) and the grinded sample are shown in figure 7.7. The presence of the T_{2g} mode of the diamond phase on the raw sample indicates that the diamond phase is initially present after pressure cycling in P-E press. After grinding the sample, the measured Raman spectrum typically shows a more intense T_{2g} signal, indicating an increased proportion of diamond phase. The same result was obtained when the sample was annealed at 80°C for 30 min.

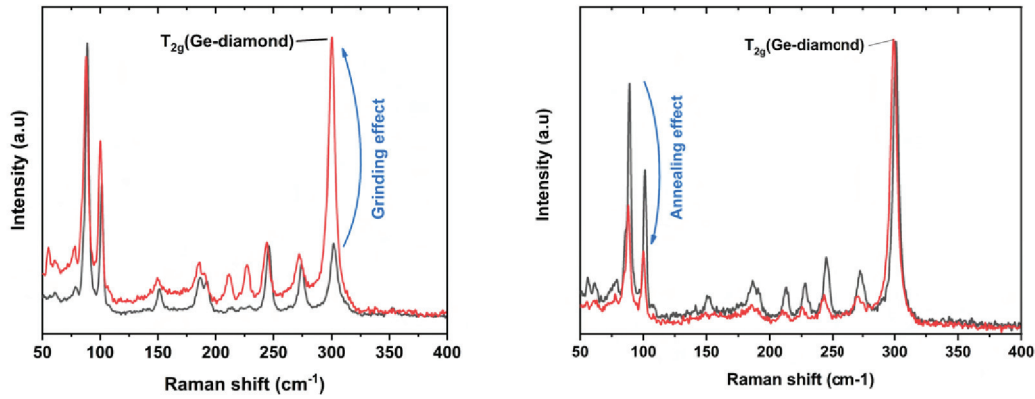


Figure 7.7: (left) Typical Raman spectra observed before grinding (black) and after (red). Recovered sample after pressure cycling in P-E press shows initially a lower diamond proportion (T_{2g} mode), this proportion appears to increase after the grinding process. (right) Typical Raman spectra observed before and after annealing at 80°C for 30 min. The signal of the $Ge - ST12$ phase is greatly diminished indicating that the transition to diamond phase is easily triggered even at low annealing temperatures.

Both grinding and annealing treatments show that the $Ge - ST12$ phase is particularly sensitive to external sources of energy. The presence of the $Ge - diamond$ phase in the sample synthesised using the P-E press can therefore be attributed to the presence of high shear forces during decompression. A slow transition from $Ge - ST12$ to $Ge - diamond$ phase at room temperature is also possible and was observed after months in the study of [13].

7.2.2.1 In situ high pressure Raman spectroscopy study of the synthesized Ge-ST12

Using the sample synthesized with the P-E press, an *in situ* Raman experiment was performed under similar conditions to these reported previously for a Ge wafer in a DAC. The Raman spectra obtained upon compression are shown in figure 7.8. For the first time, the *Ge* – *ST12* phase signal could be observed over an extended pressure region from ambient pressure to 12.3 GPa.

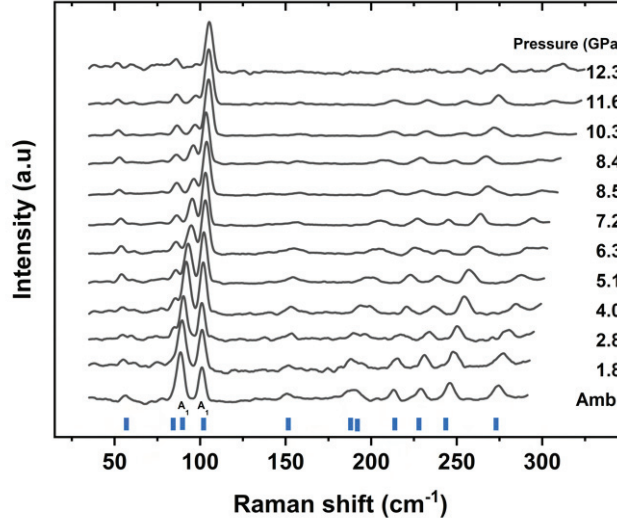


Figure 7.8: Raman spectra obtained upon compression of *Ge* – *ST12* sample synthesized using a P-E press. The two non-crossing A_1 modes are shown at respectively 90 and 100 cm^{-1} .

During this compression cycle, a total of 12 Raman modes are measured and followed upon compression. The pressure evolution of the modes were fitted using a second order polynomial function $\nu = \nu_0 + \alpha P + \beta P^2$. The results of both theoretical and experimental evolution of the modes is presented in the table 7.1. The measured parameters are in very good agreement with theoretical results.

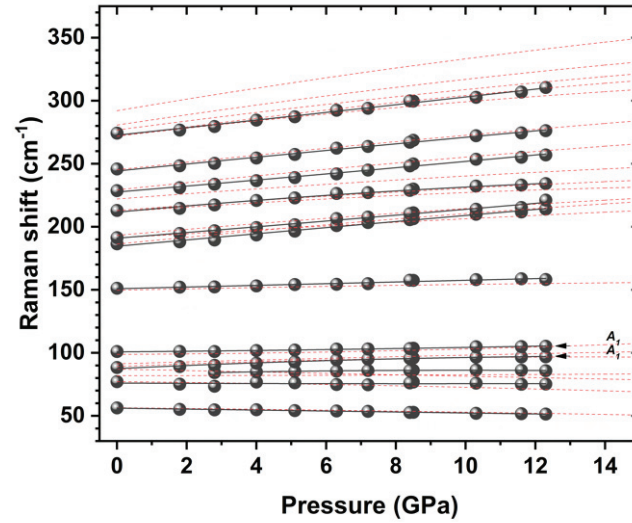


Figure 7.9: Measured $Ge - ST12$ mode shift (spheres) as a function of pressure along with calculated modes evolution (dashed lines in red). Second order polynomial fit of our experimental data are shown in (plain lines) parameters obtained are presented in table 7.1. A total 12 modes are measured of the 21 modes predicted.

Symmetry	Simulated parameters			Measured parameters		
	$\nu_0(cm^{-1})$	$\alpha(cm^{-1}GPa^{-1})$	$\beta(cm^{-1}GPa^{-2})$	$\nu_0(cm^{-1})$	$\alpha(cm^{-1}GPa^{-1})$	$\beta(cm^{-1}GPa^{-2})$
B1	56.5	-0.27(2)	-0.008(1)	56(1)	-0.37(6)	0
E	77.2	-0.27(5)	-0.018(2)	76(1)	-0.1(1)	0.01
E	81.9	0.03(2)	0.004(1)	83(1)	0.7(1)	-0.037(5)
B1	87.1	-0.56(2)	~ 0	-	-	-
A1	89.2	1.1(1)	-0.04(1)	88(1)	1.3(1)	-0.04(1)
B2	91.3	0.78(2)	-0.009(1)	-	-	-
A1	98.8	0.13(9)	0.030(4)	101(1)	0.23(7)	0.012(5)
E	149.7	0.57(2)	-0.011(1)	151(1)	0.7(2)	0
E	186.3	2.77(5)	-0.035(3)	185(1)	2.5(3)	0
B2	191.1	1.69(3)	-0.016(1)	-	-	-
A1	193.2	2.46(6)	-0.033(3)	191(1)	2.2(3)	0
B1	211.7	2.01(8)	-0.046(4)	212(1)	2.6(2)	-0.06(1)
B2	212.9	2.10(4)	-0.033(2)	-	-	-
E	222.1	2.11(6)	-0.029(3)	-	-	-
B1	229.3	2.91(5)	-0.031(2)	228(1)	2.3(3)	0
E	245.3	3.00(5)	-0.027(3)	244(1)	2.8(3)	0
A1	271.9	3.25(6)	-0.052(3)	273(1)	3.0(3)	0
E	271.8	3.82(8)	-0.058(4)	-	-	-
E	276.8	3.66(6)	-0.045(3)	-	-	-
B1	280.7	4.2(1)	-0.057(5)	-	-	-
B2	292.1	4.7(1)	-0.058(5)	-	-	-

Table 7.1: Simulation results for $Ge - ST12$ phase including symmetry of the mode, position at ambient conditions, pressure parameters. Same parameters are shown for our data and fits. Second order fit parameter β in $cm^{-1}.GPa^{-2}$ is 0 when no significant second order value is measured.

The evolution of the two non-crossing modes as a function of pressure is shown in figure 7.10. As expected, the non-crossing mode behaviour is more obvious in this experiment. The positions measured under ambient conditions are in agreement with the simulation data and are reported in table 7.1. During compression, these two modes show a non-crossing behaviour in the 5-7 GPa region. At higher pressures, the lower frequency mode shows less variation with pressure, which is consistent with a gradual softening of this mode. The coupling between the two modes is clearly visible by the variations in the relative intensity and FWHM. The lower frequency mode shows increasing intensity with pressure and both modes appear to have the same intensity at 4 GPa. The FWHM of the two modes appear to cross at 7.5 GPa, with a sharp decrease in the FWHM of the lower frequency mode.

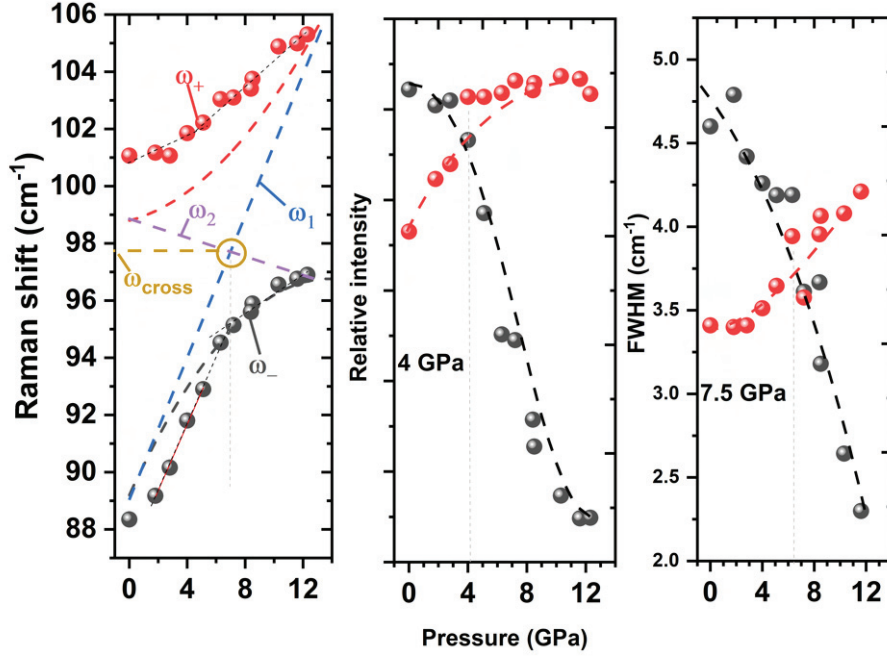


Figure 7.10: Fitted Raman shift, relative intensity and FWHM of the two non-crossing modes. The two modes show drastic modifications of intensity and FWHM in the 5-7 GPa region. Representation of the variables presented in equation 7.1 are displayed.

All these observations are consistent with an "exchange" of parameters between the two modes upon increasing pressure consistent with observation in literature [137]. In the case of coupled modes, the equation linking the observed frequencies is given by the following equation [138]:

$$\omega_{\pm} = \frac{1}{2}(\omega_1 + \omega_2) \pm \frac{1}{2}\sqrt{(\omega_1 - \omega_2)^2 + 4|\omega_{12}|^2} \quad (7.1)$$

With ω_1 and ω_2 the frequencies of the unperturbed modes, that can be obtained from a graphical representation. $\omega_{\pm}$ represent the higher (+) and lower (-) modes measured (coupled), and ω_{12} the coupling parameter. These different frequencies as a function of pressure are depicted in figure 7.10 along with our experimental and theoretical results.

Hence, if we consider the point where the frequencies of the unperturbed modes should cross (graphical interpretation) we have $\omega_1 = \omega_2 = \omega_{cross}$ as shown in figure 7.10 and equation 7.1 reduces to $|\omega_{12}| = \omega_{\pm} - \omega_{cross}$. Using this approach, the obtained coupling parameter is evaluated in between 2 to 7 cm^{-1} depending on the graphical representation of ω_1 and ω_2 .

This method is a first investigation and necessitates a better evaluation of unperturbed modes than the ones obtained by a graphical representation. This topic subject to more discussion using theoretical simulations.

7.2.3 Conclusion

With this study, we investigated, in more details, the conditions of formation and the pressure behaviour of the metastable $Ge - ST12$ phase. Performing two pressure cycles in a DAC by XRD we were able to synthesize the $Ge-ST12$ phase during the first cycle and study its pressure behaviour during the second cycle. We found that the diamond to β transition happens at 12.1 GPa during compression, and the reversible β to $ST12$ in the 9-11 GPa pressure range, upon decompression. The pressure behaviour of $Ge - ST12$ is sensitive to the accumulation of stresses due to the experimental conditions. Using a P-E press we were able to synthesise a larger amount of $Ge - ST12$ phase, this is important for further studies requiring a large mass sample. However, The $Ge - ST12$ phase was found to be particularly susceptible to re-transformation to the diamond phase during grinding or heat treatment. The vibrational properties under pressure of the synthesized $Ge - ST12$ sample were studied and are in agreement with the simulation work both at ambient and HP. Interestingly we report, for the first time, experimental evidences of a non-crossing behaviour under pressure of two modes with the same symmetry of the $Ge - ST12$ phase, this behaviour is currently discussed.

7.3 High pressure behaviour of $Si_{0.8}Ge_{0.2}$

In this section we present the HP diffraction experiments (*ex situ* and *in situ*) and the *in situ* Raman spectroscopy studies of $Si_{0.8}Ge_{0.2}$. Preliminary DFT simulations results will be used to help the discussion on structural and vibrational properties.

7.3.1 High pressure electrical resistance measurements using a Paris-Edinburgh press

A first experiment on $Si_{0.8}Ge_{0.2}$ using a P-E press is made, the goal of this experiment is to measure the *in situ* resistance during pressure cycles in P-E press and *ex situ* diffraction pattern of the recovered sample. This experiment previously allowed to synthesize a large amount of the metastable $ST12$ phase of germanium in section 7.2, and is repeated here for $Si_{0.8}Ge_{0.2}$ sample using the same experimental protocol. The $Si_{0.8}Ge_{0.2}$ sample is first ground and loaded into a boron-epoxy gasket. The pump pressure is set to perform a compression cycle to a maximum of 15 GPa corresponding to a higher pressure value than the expected transition to the metallic phase for this composition, predicted around 12 GPa [120, 118]. During the pressure cycle, the electrical resistance of the anvils and the sample is measured in order to follow the transition toward metallic phase.

Resistance measured during the pressure cycle is shown in figure 7.11. Upon compression, the resistance shows a large drop of two magnitude orders between 10 and 14 GPa, confirming that the sample transforms to a metallic phase, already predicted in this pressure range [118, 120]. The resistance behaviour is comparable to observations made on pure germanium sample during pressure cycles that led to $Ge - ST12$ phase. For $Si_{0.8}Ge_{0.2}$ the transition appears at higher pressure than germanium which is consistent with an increased transition pressure with silicon content in SiGe alloys as reported in literature [118, 120]. However, upon decompression, the resistance pathways followed by $Si_{0.8}Ge_{0.2}$ and germanium differs. For $Si_{0.8}Ge_{0.2}$ a large increase of resistance is measured at 3 GPa, and was previously measured at 6 GPa in germanium. This behaviour is consistent with a transformation toward a semiconducting phase for both samples.

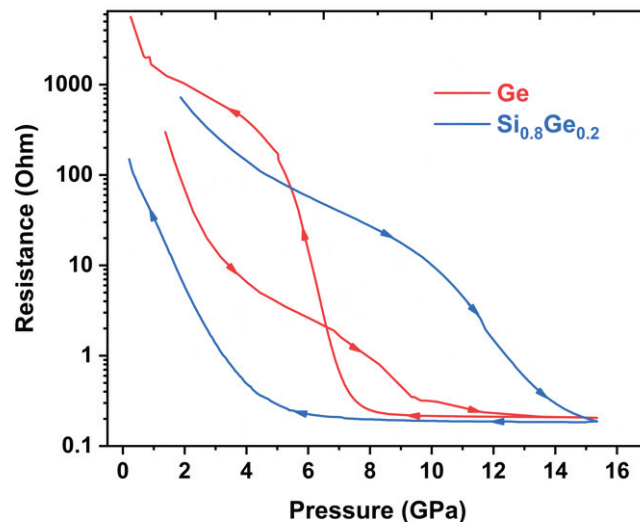


Figure 7.11: (blue) Resistance measurements of $Si_{0.8}Ge_{0.2}$ obtained in during the pressure cycle. During compression of $Si_{0.8}Ge_{0.2}$ a large drop of resistance around 13 GPa indicates that the sample transforms to a metallic phase. Upon decompression, resistance increases by 3 orders of magnitude around 2-3 GPa, which is consistent with a transition toward a semiconducting phase. (red) Resistance measurements of germanium sample during a similar pressure cycle in P-E press for comparison.

XRD pattern and Raman spectra obtained on the recovered sample after the pressure cycle did not show any signature of metastable phases. This absence of metastable phase is in contradiction with our previous P-E experiment on germanium that showed the presence of $Ge - ST12$ metastable phase upon decompression from the metallic phase. The most probable explanation is that the transition toward the metallic phase under compression is incomplete, leading to a reverse transition to diamond phase upon decompression. Another possible explanation is that the $Si_{0.8}Ge_{0.2}$ phase formed from the metallic phase transforms back to the diamond phase at ambient pressure. To answer these questions, HP-HT *in situ* XRD measurements using a synchrotron radiation in P-E press were conducted and are presented in the next section.

7.3.2 HP-HT XRD *in situ* study of $Si_{0.8}Ge_{0.2}$ using a PE press at Elettra synchrotron

In situ XRD measurements were performed at the XPress beamline at Elettra synchrotron using a V5 P-E press. For this experiment, the sample was prepared in the HP-HT setup as presented in section 6.1.1.

The diffraction pattern of the $Si_{0.8}Ge_{0.2}$ alloy obtained at ambient conditions is shown in figure 7.12 along with the pattern of the original Si powder used to test the set-up and as pressure calibrant. The $Si_{0.8}Ge_{0.2}$ pattern can be indexed to a diamond structure with $a = 5.457(5)$ Å in good agreement with the database cell parameter of 5.465(1) Å (PDF4+ ref Si0.8 - 04-022-2155).

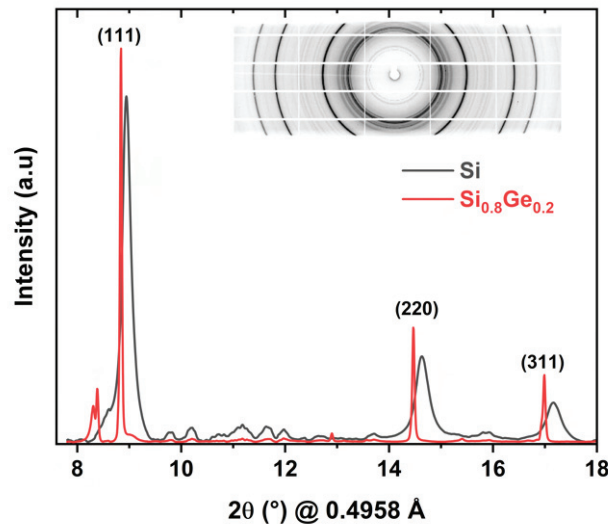


Figure 7.12: XRD patterns of $Si_{0.8}Ge_{0.2}$ and Si powder at ambient conditions measured at Elettra XPress beamline. Both patterns can be indexed to the diamond cubic phase with a cell parameter of $5.457(5)$ Å for $Si_{0.8}Ge_{0.2}$ and $5.422(5)$ Å for silicon.

The evolution of $Si_{0.8}Ge_{0.2}$ diffraction patterns with pressure is shown in figure 7.13. During the first compression stage, the diffractograms can be indexed with the diamond phase up to 7.4 GPa. Above this pressure, a phase transition is observed through the appearance of a weak signal at a 2θ angle of 12° . Interestingly, this transition is concomitant with the strong reduction of the FWHM of the $Si_{0.8}Ge_{0.2}$ -diamond phase diffraction peaks as shown in figure 7.13. This relaxation effect is believed to be due to elastic relaxation during the phase transition and has been already observed in germanium [139, 104]. However, to the best of our knowledge, this effect has not been reported in literature for SiGe alloys or silicon.

With increasing pressure, the signal from the high-pressure induced phase increases and can be assigned to the $Si_{0.8}Ge_{0.2} - \beta$ structure as observed in silicon and germanium. The onset transition pressure at 7.4 GPa is far lower than the one reported as a theoretical value obtained by Soma and al. of $\sim 12 \pm 2$ GPa [118] and the experimental value by Werner and al. of ~ 12 GPa [140, 120].

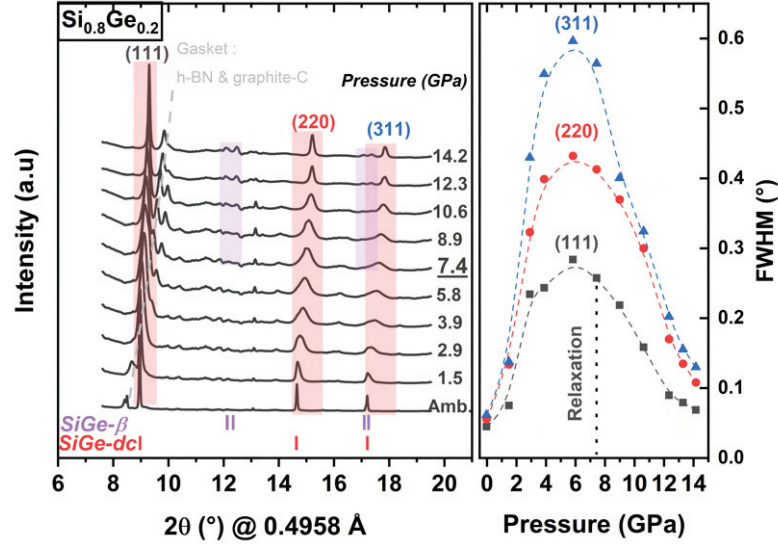


Figure 7.13: (Left) X-ray diffraction patterns of $\text{Si}_{0.8}\text{Ge}_{0.2}$ obtained upon compression in P-E press. A transition is seen at 7.4 GPa through apparition of a weak signal associated with $\text{Si}_{0.8}\text{Ge}_{0.2} - \beta$ phase. (Right) Measured FWHM of the three first reflections of $\text{Si}_{0.8}\text{Ge}_{0.2}$ -diamond phase as a function of pressure, showing a relaxation at 7.4 GPa, the transition pressure.

The beginning of the transition at rather low pressure can be attributed to multiple factors. i) the presence of shear stresses induced on the sample by the non-hydrostatic conditions, that are known to lower the transition pressure [139]. ii) early detection of the transition is eased by the indirect measurement of relaxation in the sample. This relaxation is believed to occur at a very early stage of the transition, when the β phase begins to nucleate at the grain boundary. [139].

During compression, $\text{Si}_{0.8}\text{Ge}_{0.2} - \beta$ mass ratio increases from 20% at 12.3 GPa to 36% at the highest reached pressure of 14.2 GPa, where $\text{Si}_{0.8}\text{Ge}_{0.2}$ -diamond and β phases still coexist. This coexistence can be attributed to the sluggish character of the transition as observed in silicon and germanium [141, 79].

The normalized volume evolution of diamond phase as a function of pressure is shown in figure 7.14. These data were initially fitted using a second-order Birch-Murnaghan (BM2) EOS model and we obtained a bulk modulus $K = 92(1)$ GPa. In a second step, a BM3 EOS model was used with K' fixed to 4.24 leading to $K = 91(1)$ GPa. The $K'=4.24$ value was chosen to be able to compare our bulk modulus with the one obtained recently for Si by Anzellini et al. [108]. Our measured bulk modulus are in very good agreement with a linear interpolation between germanium and silicon bulk modulus as shown in table 7.2.

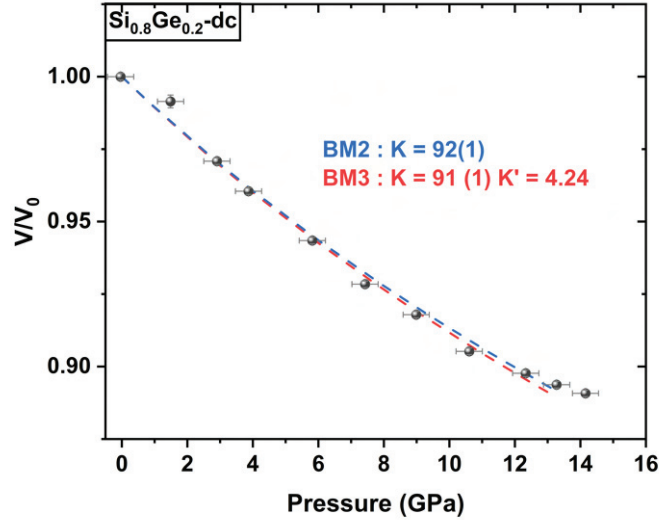


Figure 7.14: V/V_0 plot of $Si_{0.8}Ge_{0.2}$ -diamond phase as a function of pressure (points) along with a BM2 and BM3 EOS fitted to the data.

Sample	K (GPa)	K'	EOS	PTM	Method	ref
Si	101.5	3.45	BM3	He	XRD, DAC	[108]
Si	96.86	4.24*	BM3	He	XRD, DAC	[108]
Si	99.90	3.80	BM3	4:1 eth:meth	XRD, DAC	[107]
Si	97.88	4.23	BM3	-	Ultrasonic	[142]
Ge	74.37	4.76	BM3	-	Ultrasonic	[102]
Ge	76.0	4.373	BM3	4:1 eth:meth	XRD, DAC	[102]
Ge	74.9	3.0	BM3	4:1 eth:meth	XRD, DAC	[102]
$Si_{0.8}Ge_{0.2}$	92(1)	4.00 (fixed)	BM2	Boron-epoxy	XRD, P-E	this work
$Si_{0.8}Ge_{0.2}$	91(1)	4.24 (fixed)	BM3	Boron-epoxy	XRD, P-E	this work

Table 7.2: Comparison of bulk modulus obtained for $Si_{0.8}Ge_{0.2}$ -diamond phase using BM2 and BM3 EOS. K' parameter is fixed to make K value comparable with literature

$Si_{0.8}Ge_{0.2} - \beta$ unit cell parameters obtained at 12.3 GPa are: $a = 4.685(1) \text{ \AA}$ and $c = 2.590(1) \text{ \AA}$ with $c/a = 0.552$ in agreement with ref [118]. The measured parameters are consistent with a linear interpolation of the parameters of Si- β and Ge- β obtained in our simulations as shown in figure 7.15. With increasing pressure, no significant effect of pressure can be observed on the c/a ratio.

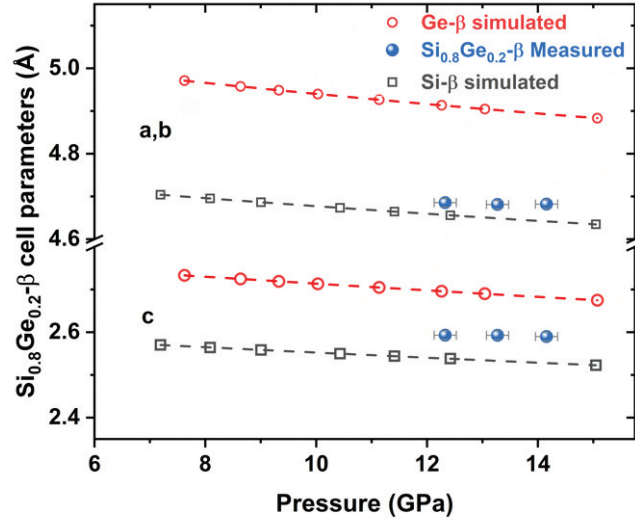


Figure 7.15: Evolution of the cell parameters as a function of pressure measured for $Si_{0.8}Ge_{0.2} - \beta$ phase (filled symbols) along with simulated parameters for $Si - \beta$ and $Ge - \beta$ phases (open symbols).

Interestingly, we observe that the transition from $Si_{0.8}Ge_{0.2} - diamond \rightarrow Si_{0.8}Ge_{0.2} - \beta$ phase is incomplete at 14.2 GPa. Dwelling times of several hours at this pressure did not affect the β proportion significantly. This partial transition explains the absence of metastable phase formation upon decompression observed in our previous P-E experiment in section 7.3.1. To find a pathway toward a complete transition to metallic phase, we decided to use temperature. The temperature was augmented from ambient to 255°C in 30 min with 10 min steps at 170 and 200°C. During these heating steps, no significant pressure variation was measured and stayed constant at 14.2 GPa. Diffraction patterns show that heating results in a rapid increase of β phase proportion as shown in figure 7.16.

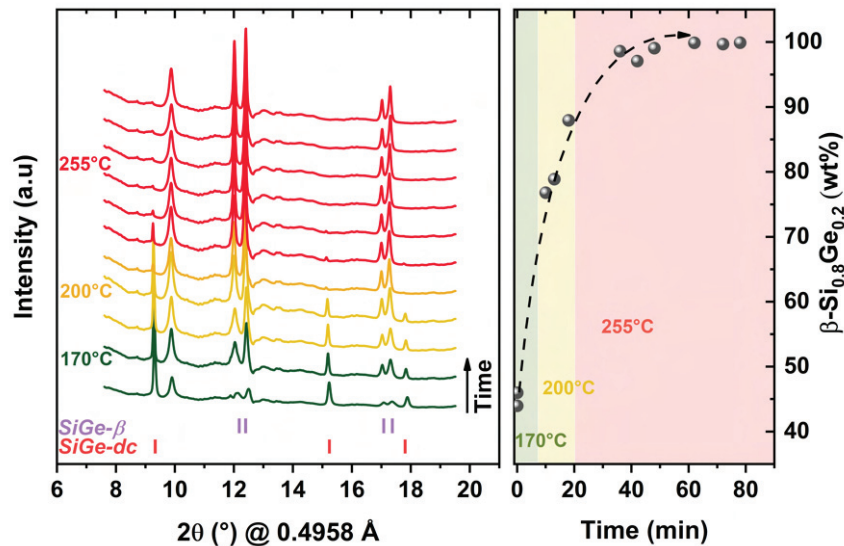


Figure 7.16: (Left) X-ray diffraction patterns of $Si_{0.8}Ge_{0.2}$ sample obtained upon heating at 14.2 GPa showing a rapid increase of the β phase signal. (Right) Evolution of the β phase mass ratio % as a function of time. Green, yellow and red colors symbolised the temperature at which diffractograms were taken (170°C, 200°C, 255°C).

After one hour at 255°C, no reflections from the diamond phase can be measured anymore, indicating the full transformation to β phase. The β phase appears to be stable even after decreasing temperature and staying one night at ambient temperature and constant pressure of 14.2 GPa.

The subsequent decompression was performed after re-heating the sample at 255°C from 14.2 GPa to observe the impact of decompression at constant temperature of 255°C. The reverse phase transition $\beta \rightarrow \text{diamond}$ is observed at 9.7 GPa. The two phases coexist down to 5.7 GPa. From this pressure down to ambient pressure only diamond phase is observed.

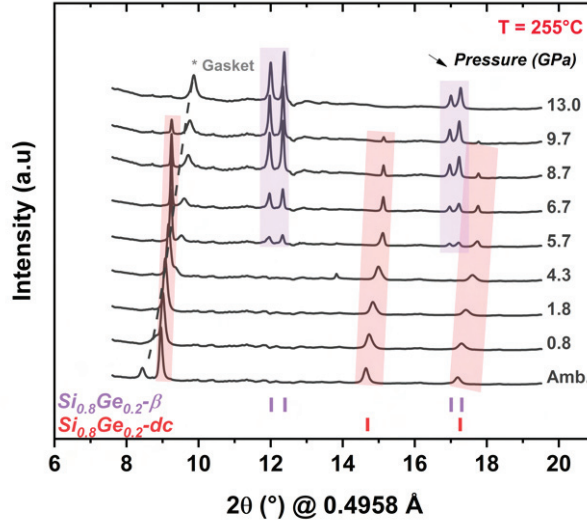


Figure 7.17: Diffraction pattern obtained upon decompression of $Si_{0.8}Ge_{0.2}-\beta$ phase at constant temperature of 255 °C. The reverse phase transition $\beta \rightarrow \text{diamond}$ is observed at 9.7 GPa

No metastable phase could be observed upon decompression at 255°C. They are usually formed with the help of shear stresses associated to non-hydrostatic conditions [14, 17], a situation that is studied in the next section.

7.3.3 *In situ* study of the high pressure induced metastable phases of $Si_{0.8}Ge_{0.2}$: an HP XRD experiment using a DAC

An experiment using a DAC was conducted to complement the previous results. The diffractograms were obtained using a laboratory source presented in section 6.4. For this experiment, a small piece of the $Si_{0.8}Ge_{0.2}$ sample was grinded and loaded in a DAC with diamond tips of diameters 350 μm with a stainless steel gasket (thickness: 80 μm , hole diameter: 100 μm) along with ruby as a pressure calibrant. Paraffin oil used as the PTM (providing hydrostatic conditions up to 4 GPa [132])

The first compression step, *i.e* the compression of the diamond phase, was covered rapidly, the focus being on the characterization of the $Si_{0.8}Ge_{0.2} - \beta$ phase and the transition sequence during the subsequent decompression. During compression the phase transition from $\text{diamond} \rightarrow \beta$ phase is observed above 10.0 GPa as shown in figure 7.18. Coexistence between the two phases extends from 10 GPa (1% mass ratio of β phase) to 17.2 GPa. The measured coexistence pressure range a few GPa higher than similar to the case of silicon [143, 108, 107, 101] and germanium [102, 139].

No other transition is observed up to 17.2 GPa, the highest pressure reached in this run, although other phase transitions have been reported in this pressure range [119], but without clear experimental evidence and crystallographic information.

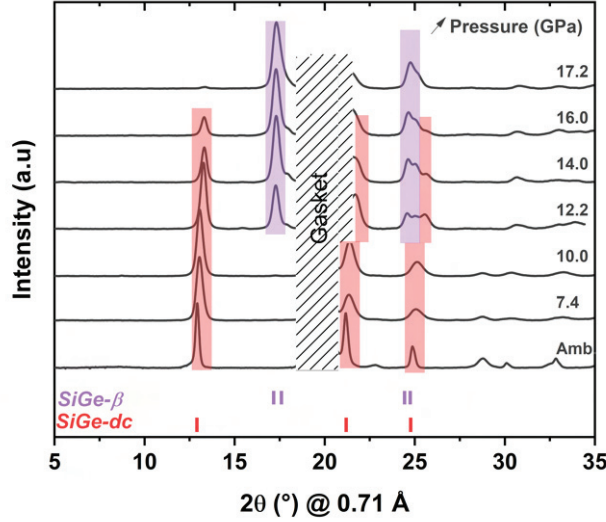


Figure 7.18: X-ray diffraction patterns of $Si_{0.8}Ge_{0.2}$ obtained upon compression in DAC. The phase transition from *diamond* $\rightarrow$ β phase is observed at 12.2 GPa.

Decompression patterns at room temperature are shown in figure 7.19. A first transition is seen at 10.3 GPa with clear new reflections appearing at 2θ angles of 9, 15 and 22.5°. This pattern was indexed using Leball refinement to a rhombohedral structure similar to the R8 phase of silicon [16, 113]. Phase unit cell parameters obtained for $Si_{0.8}Ge_{0.2} - R8$ at 10.3 GPa are $a = 9.16(1)$ Å and $c = 5.41(1)$ Å. They are in agreement with a linear interpolation based on theoretical results obtained for $Si - R8$ and $Ge - R8$ phases as shown in figure 7.20. Phase proportion obtained during the decompression indicates that $Si_{0.8}Ge_{0.2} - \beta$ and $Si_{0.8}Ge_{0.2} - R8$ phases coexist between 10.3 and 5.4 GPa. In pure silicon, full transition to $Si - R8$ phase has been recorded between 6.2 [113] and 8.2 GPa [16] (under more hydrostatic conditions).

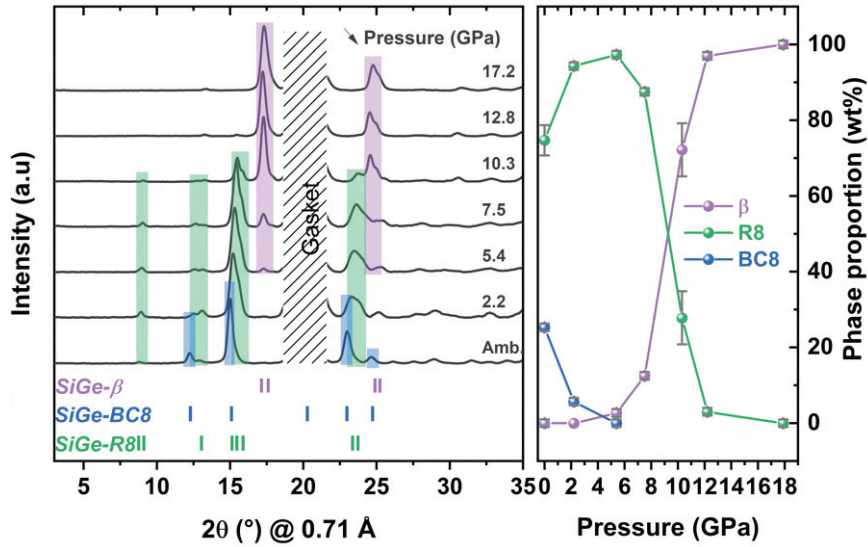


Figure 7.19: (Left) Diffraction patterns upon decompression at room temperature from $Si_{0.8}Ge_{0.2} - \beta$ phase. A first transition toward $Si_{0.8}Ge_{0.2} - R8$ is seen at 10.3 GPa, followed by another transition to $Si_{0.8}Ge_{0.2} - BC8$ phase at 2.2 GPa. Major reflections of the different phases are marked in color. (Right) Phase proportion in mass. % of the different phases observed upon decompression.

At lower pressures, the $Si_{0.8}Ge_{0.2} - R8$ phase partially transforms to another phase that can be indexed as a $Si_{0.8}Ge_{0.2} - BC8$ structure, showing that our alloy follows the same transition as silicon. It can be noted that the diffraction patterns of $Si_{0.8}Ge_{0.2} - R8$ and $Si_{0.8}Ge_{0.2} - BC8$ phases are very similar, however, the reflection at $2\theta = 9^\circ$ is only explained by the presence of R8 phase at ambient pressure.

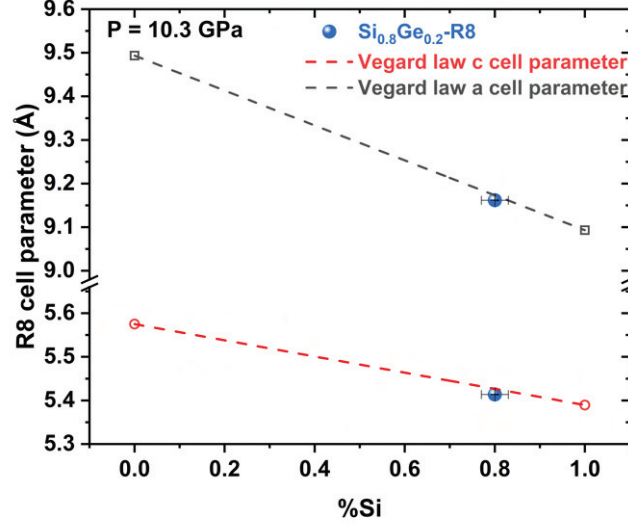


Figure 7.20: Simulated parameters at 10.3 GPa for $Si - R8$ and $Ge - R8$ (open symbols) along with measured parameters for $Si_{0.8}Ge_{0.2} - R8$ (filled symbols). Measured $Si_{0.8}Ge_{0.2} - R8$ parameters are consistent with a Vegard law (dashed lines).

A bulk modulus of $K = 80(2)$ GPa for the $Si_{0.8}Ge_{0.2} - R8$ is obtained using a BM2 EOS, in good agreement with the value we obtained by ab initio simulations on $Si_{0.8}Ge_{0.2} - R8$ phase. This value is also consistent with the linear interpolation of simulated values for $Si - R8$ ($K=83.0(6)$ GPa) and $Ge - R8$ ($K = 68.7(3)$). Our theoretical results for $Si - R8$ bulk modulus are lower than measurements of Piltz & al. [113]. They reported a bulk modulus of $K = 96(5)$ with $K' = 5$ (fixed), in order to compare this result, we fitted our values using a BM3 EOS with $K'=5$ resulting in $K = 76(2)$ GPa. The bulk modulus discussed in this paragraph are presented in table 7.3

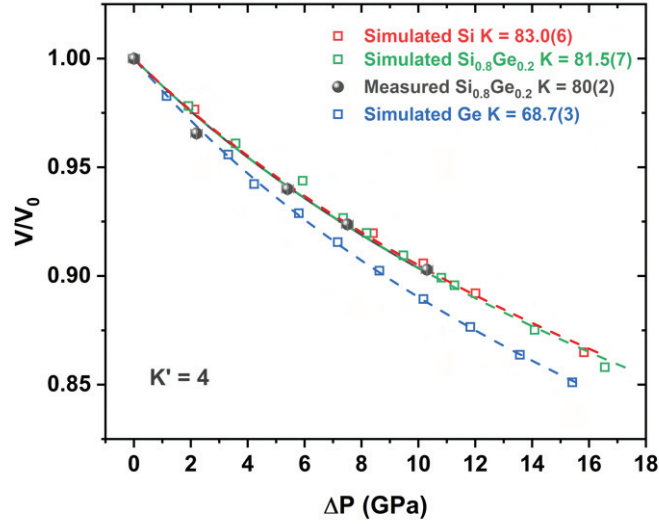


Figure 7.21: V/V_0 plot of $Si_{0.8}Ge_{0.2} - R8$ phase as a function of pressure (points) along with a BM2 EOS fitted to the data (plain lines). Theoretical data obtained for $Si - R8$, $Ge - R8$ and $Si_{0.8}Ge_{0.2} - R8$ are shown in open symbols and fitted using the same method (dashed lines).

Phase	Measured bulk modulus K (GPa)	Simulated bulk modulus K (GPa)	K'
$Ge - R8$	-	68.7(3)	4.00
$Si - R8$	-	83.0(6)	4.00
$Si_{0.8}Ge_{0.2} - R8$	80(2)	81.5(7)	4.00
$Si_{0.8}Ge_{0.2} - R8$	76(2)	76.7(9)	5.00

Table 7.3: Bulk modulus values for $Si - R8$ and $Ge - R8$ phases (DFT) $Si_{0.8}Ge_{0.2} - R8$ (measured). Obtained using BM2 and BM3 EOS fitted to the data with K' parameter fixed.

During decompression, although the global volume change of $Si_{0.8}Ge_{0.2} - R8$ phase is consistent with DFT simulations, the evolution of the cell parameters slightly deviates from simulated values. The c parameter shows a higher compressibility than the simulated value whereas for the a parameter, the compressibility is slightly lower. However, the overall agreement is quite good and these differences may arise from the fact that we used non-hydrostatic conditions during the experiment.

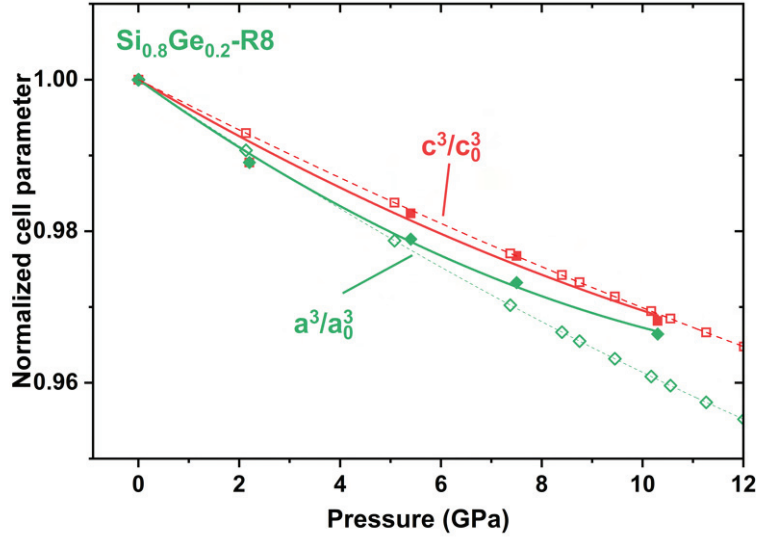


Figure 7.22: Normalized $Si_{0.8}Ge_{0.2} - R8$ individual cell parameters as a function of pressure. Plain symbols and lines represent respectively the measured and fitted data. Open symbols and dashed lines represent the DFT results and fitted data. The data were fitted using BM2 EOS.

The recovered sample diffraction pattern is presented in figure 7.23. The pattern analysis using a LeBail refinement shows that the sample is composed of a mixture of $Si_{0.8}Ge_{0.2} - BC8$ and $Si_{0.8}Ge_{0.2} - R8$ phase in almost a 75/25 mass ratio. No traces of other phases could be observed. Such coexistence of R8 and BC8 phases at ambient pressure has been reported for pure silicon in during of nanoindentation experiments [144, 145] and DAC experiments [16]. The cell parameters for both phases (R8 and BC8) of $Si_{0.8}Ge_{0.2}$ are presented in Table 7.4.

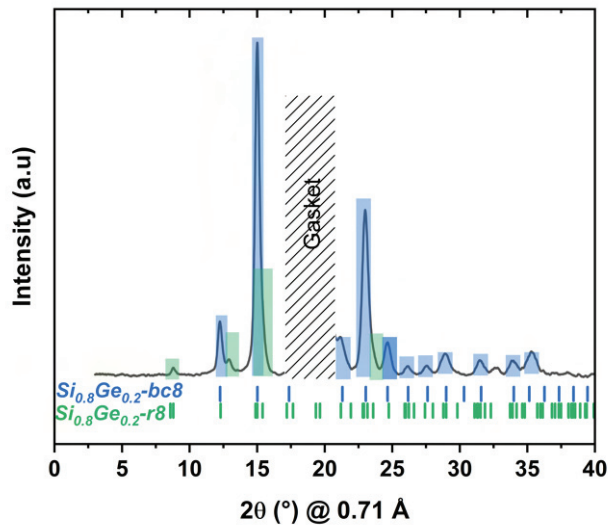


Figure 7.23: Recovered sample after the pressure cycle. LeBail refinement indicates that the sample is composed of two phases : $Si_{0.8}Ge_{0.2} - BC8$ and $Si_{0.8}Ge_{0.2} - R8$ in a 75:25 mass. % ratio mix.

Phase	Cell Parameter			Ref
	a	b	c	
$Si_{0.8}Ge_{0.2}$ -R8	9.48(1)	9.48(1)	5.59(1)	Exp. This Work
Si-R8	9.372	9.372	5.601	Theory This Work
Ge-R8	9.836	9.836	5.839	Theory This Work
$Si_{0.8}Ge_{0.2}$ -R8 (Vegard)	9.465	9.465	5.649	Theory This Work
$Si_{0.8}Ge_{0.2}$ -BC8	6.65(1)	6.65(1)	6.65(1)	Exp This Work
Si-BC8	6.636	6.636	6.636	[17]
Si-BC8	6.605	6.605	6.605	Theory This Work
Ge-BC8	6.932	6.932	6.932	[13, 122]
Ge-BC8	6.924	6.924	6.924	Theory This Work
SiGe-BC8 (vegard)	6.669	6.669	6.669	Theory This Work

Table 7.4: Cell parameter of $Si_{0.8}Ge_{0.2}$ R8 and BC8 metastable phases obtained using LeBail refinement along with simulated cell parameters for metastables phases of Si and Ge.

To confirm the experimentally observed phase sequence, DFT calculations of enthalpy of the different phases of $Si_{0.8}Ge_{0.2}$ were conducted. The enthalpy variations as a function of pressure for β , BC8 and R8 phases and of the diamond phase, used as reference, are shown in figure 7.24.

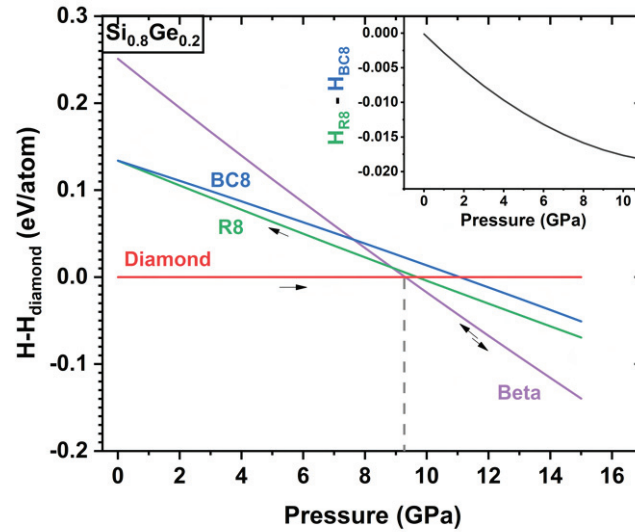


Figure 7.24: Enthalpy evolution as a function of pressure simulated for different phases of $Si_{0.8}Ge_{0.2}$. The diamond/ β crossing point is located at 9.3 GPa. The inset represent the enthalpy difference between R8 and BC8 phases, showing that at low pressures the enthalpy difference between the two phases decrease, explaining the observed coexistence of R8 and BC8 phase.

During compression, enthalpy of the diamond and β phases is predicted to be equal at 9.4 GPa, a few GPa higher than our measurement (12.2 GPa) for our experimental data. Upon decompression, even though the diamond phase is predicted to be the structure with the lowest enthalpy, R8 phase is formed due to a lower kinetic barrier (in case of Si ref [146]). This phase is more stable than the BC8. The predicted pressure of transition from β phase to R8 is around 10 GPa. We experimentally measured the β phase to R8 close to this value at 10.3 GPa. As pressure is reduced further, enthalpy difference between R8 and BC8 structures decreases by two orders of magnitude, and is almost zero at ambient conditions. This explains the coexistence of the two phases at ambient conditions. The mixture of R8 and BC8 at 2.2 GPa is consistent with what is found in pure silicon [16]. For germanium, however, the transition pathway is more difficult to observe and require very fast unloading (less than one second) in quasi hydrostatic conditions [14], in this case, the β to R8 phase transition happens at 7 GPa and to the BC8 at less than 1 GPa.

In conclusion, we demonstrated that the pressure induced phase transition pathway for $Si_{0.8}Ge_{0.2}$ is *diamond* $\rightarrow$ β upon compression, and $\beta \rightarrow R8 \rightarrow R8 + BC8$ upon decompression.

7.3.4 *In situ* HP Raman spectroscopy of $Si_{0.8}Ge_{0.2}$

To complement the X-ray diffraction investigations, Raman spectroscopy experiments under HP were conducted on the same alloy using a DAC. For this experiment, a small piece of the $Si_{0.8}Ge_{0.2}$ sample was grinded and loaded in a DAC with diamond tips of diameters 350 μm with a stainless steel gasket (thickness: 80 μm , hole diameter: 100 μm) along with ruby as a pressure calibrant, the PTM used for this experiment is a paraffin oil.

If previous Raman studies have reported the evolution of major modes Si-Si, Ge-Si or Ge-Ge during compression [121], to the best of our knowledge, there is no data on: i) the weaker peaks observed in the Raman spectra and shown in figure 7.25 for the diamond stable phase ii) the decompression path and the phases obtained upon decompression. Therefore, we propose here an analysis of the evolution of all Raman modes present during compression and decompression cycle, and a characterization of the vibrational properties of the metastable phases of $Si_{0.8}Ge_{0.2}$.

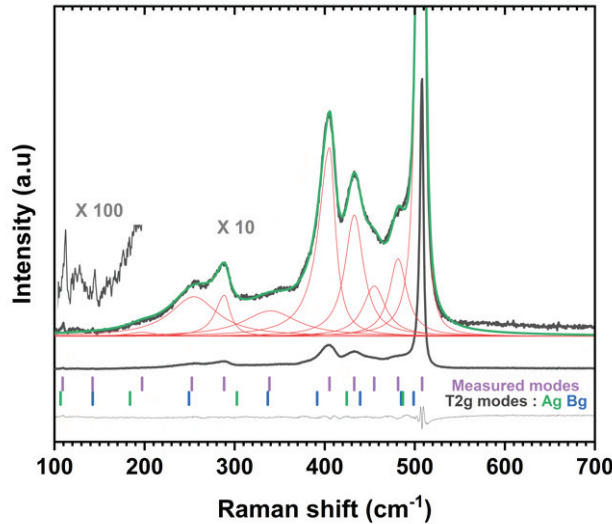


Figure 7.25: Typical Raman spectrum of $Si_{0.8}Ge_{0.2}$ at ambient conditions. The experimental spectrum is compared to the Raman frequencies obtained by DFT simulations on a $Si_{0.75}Ge_{0.25}$ alloy. Violet ticks indicates the measured modes, green and blue ticks represent the calculated Ag and Bg modes by DFT.

The Raman spectrum of $Si_{0.8}Ge_{0.2}$ measured at ambient conditions is shown in figure 7.25. The overall spectrum is in agreement with these from the literature [29]. First, three main peaks corresponding to optical phonons associated with Ge-Ge, Ge-Si, and Si-Si vibrations are present at 287 , 405 and 508 cm^{-1} , respectively. These three main modes are asymmetric because of the disorder introduced by the alloy that leads to a partial lifting of the selection rule and a contribution from the vibrational density of states [29, 30]. Using a split Lorentzian function to refine the ratio between left and right FWHM, a ratio of 1.58 for Si-Si, 1.86 for Ge-Si and 1.50 for Ge-Ge mode was measured, this ratio is fixed for the other fits performed in this work. The dependence of the Raman mode position on the chemical composition has been studied experimentally by [31, 28]. In our sample the most compositionally sensitive peak is the Si-Si mode (508 cm^{-1}) which corresponds to $x = 0.19 \pm 0.3$ using the method of [28]. Between the Ge-Si Raman mode at 405 cm^{-1} and the Si-Si peak at 508 cm^{-1} , three modes measured at 433 , 455 and 482 cm^{-1} were assigned in the literature to peculiar Si-Si local vibrational modes due to fluctuations of the number of Ge atoms in the vicinity of Si ones [31, 29]. The weak mode at 375 cm^{-1} is poorly discussed in the literature and may arise from a local vibration of an isolated Si atom in a Ge matrix [32]. In the lower frequency region, a broad feature is observed at 254 cm^{-1} . This feature is often referred to as quasi-amorphous (q-a) because of a correspondence with a similar peak reported in amorphous alloys [33]. This mode attribution is still discussed [28, 33, 29]. Finally, three weak peaks in the lower frequency region (197 cm^{-1} , 142 cm^{-1} and 109 cm^{-1}) are measured and have not been reported in literature.

Raman spectra upon compression are reported in figure 7.26. During the compression step, the signal of three weak modes present at low wavenumbers ($197, 142$ and 109 cm^{-1}), observed at ambient pressure, could not be followed due to a weak signal. At pressures above 15.7 GPa , only a very weak signal from the SiGe-diamond phase can be measured as it slowly transits to the metallic phase (as attested by the resistivity measurements presented in previous section 7.3.1). The Raman cross section of the metallic phase being very low, the signal loss at 15.7 GPa is a mark of total disappearance of the diamond phase.

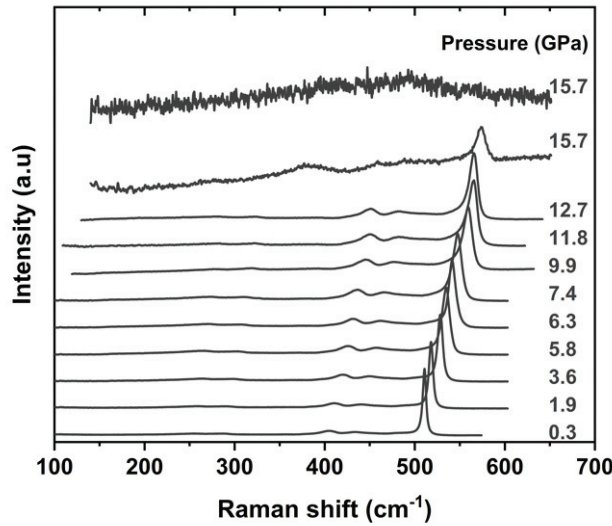


Figure 7.26: Raman spectra of $Si_{0.8}Ge_{0.2}$ -diamond phase obtained upon compression. At 15.7 GPa two spectra are shown at different region of the sample, where we observe a decrease or total loss of the signal due to the transition toward the β metallic phase.

The frequency of diamond phase modes measured as a function of pressure are reported in figure 7.27. The modes frequency shift were fitted using a quadratic equation $\nu = \nu_0 + \alpha P + \beta P^2$, and reported into table 7.5.

Mode	Measured parameters			Simulated parameters		
	ν_0	α	β	ν_0	α	β
A_g "Si-Si"	508(1)	5.1(3)	-0.06(2)	498	6.3	-0.09
B_g or A_g "Si-Si loc. Ge"	482(1)	5.1(6)	0.01(4)	Ag 485;Bg 487	6.2;6.0	-0.06;-0.06
A_g "Si-Si loc. Ge"	455(1)	5.5(4)	-0.07(3)	439	6.2	-0.09
B_g "Si-Si loc. Ge"	433(1)	4.9(2)	-0.07(2)	424	6.3	-0.08
A_g "Ge-Si"	405(1)	4.5(2)	-0.06(2)	392	5.4	-0.07
A_g	338(1)	6.1(5)	-0.22(3)	337	3.7	-0.05
B_g "Ge-Ge"	287(1)	3.6(2)	-0.06(1)	302	3.6	-0.04
A_g "Ge q-a"	252(1)	2.7(7)	-0.14(5)	249	3.4	-0.04
B_g	197(1)	-	-	183	-1.2	0.02
A_g	142(1)	-	-	142	-0.5	-0.02
B_g	109(1)	-	-	107	-2.0	-0.1

Table 7.5: Assignment of each measured mode of $Si_{0.8}Ge_{0.2}$ diamond phase, along with measured and simulated pressure coefficients using $\nu = \nu_0 + \alpha P + \beta P^2$ with ν_0 in cm^{-1} , α in $cm^{-1}.GPa^{-1}$ and β in $cm^{-1}.GPa^{-2}$.

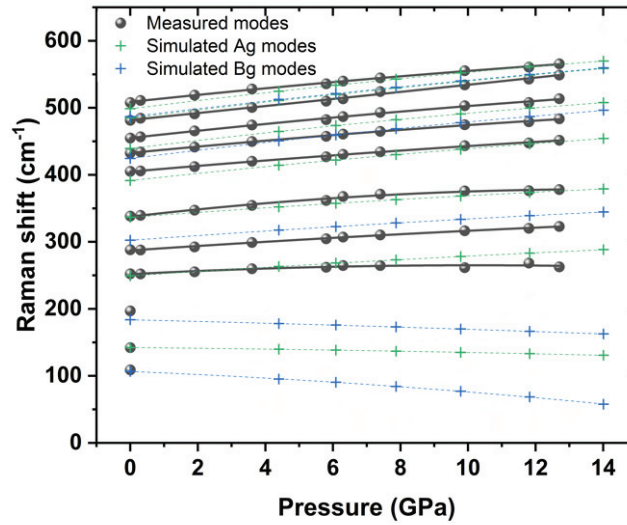


Figure 7.27: Measured Raman mode position as a function of pressure (plain lines and symbols) along simulated modes (dashed lines and cross symbol).

The mode shift behavior with pressure of the three main modes (Si-Si, Si-Ge, Ge-Ge) are in good agreement with measurements made by Sui & al. on close composition [121]. The pressure-evolution is in good agreement with our DFT simulations as shown in figure 7.27. This is a very good indication that the methodology used for DTF calculation and proposed in annex B can be extended to other solid solutions.

Raman spectra obtained upon decompression are presented in figure 7.28. During decompression special care was taken to reduce the laser power in order to minimize the heating of the sample. Exposition time was therefore augmented to several hours. During decompression no significant signal is measured down to 9.2 GPa where a totally new spectrum appears. This new spectrum remains unchanged down to 0.2 GPa when a new phase transition occurs. This transition sequence seems to be similar to what is observed by X-ray diffraction, *i.e.*, phase $\beta \rightarrow R8 \rightarrow R8 + BC8$. In our measurements, no modes are measured in the Si-Si region (520 cm^{-1}), indicating that no diamond phase is present in our sample during this decompression.

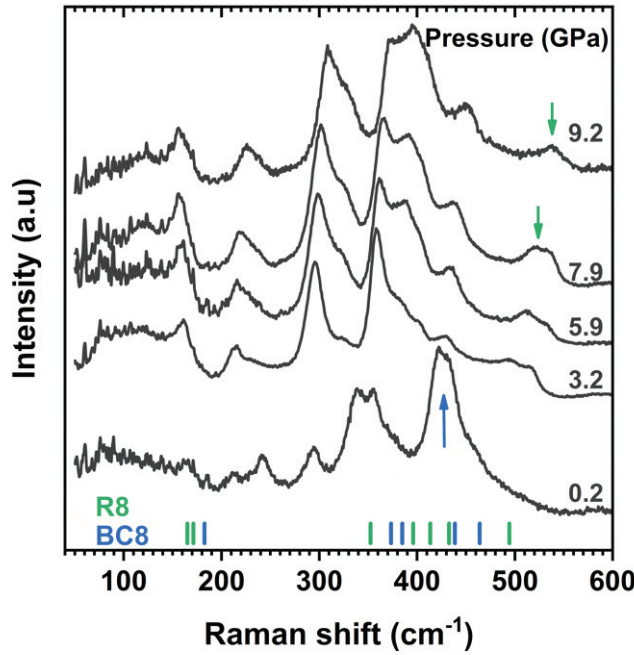


Figure 7.28: Measured Raman spectra upon decompression. A new spectrum is observed at 9.2 GPa. At ambient pressure the measured modes are similar to modes observed for Si-R8 and Si-BC8 phases according to [147], that are depicted by green and blue ticks.

As no spectra of $Si_{0.8}Ge_{0.2} - R8$ and $Si_{0.8}Ge_{0.2} - BC8$ exist in literature, analysis of mode shifts upon decompression is first done by comparison of the observed spectra with known spectra of $Si - R8$ and $Si - BC8$. During decompression, the presence of a strong peak around 350 cm^{-1} and one or two weaker peaks at 530 cm^{-1} (only visible at highest pressures and indicated with arrows in the figure) indicate that the sample first transforms to the R8 phase at 9.2 GPa. This R8 phase is the only metastable phase known in silicon for having peaks in this region and intensities [147]. This transition pressure is in agreement with the $\beta \rightarrow R8$ transition seen by XRD at 10.2 GPa. This mode and others belonging to this phase are still measured at ambient conditions as better shown in figure 7.29. At 0.2 GPa, one very strong mode appears at 430 cm^{-1} , close to the expected mode of the $Si - BC8$ phase. This result is coherent with the R8 to BC8 phase transition and the coexistence of the two phases observed by XRD at 2.2 GPa.

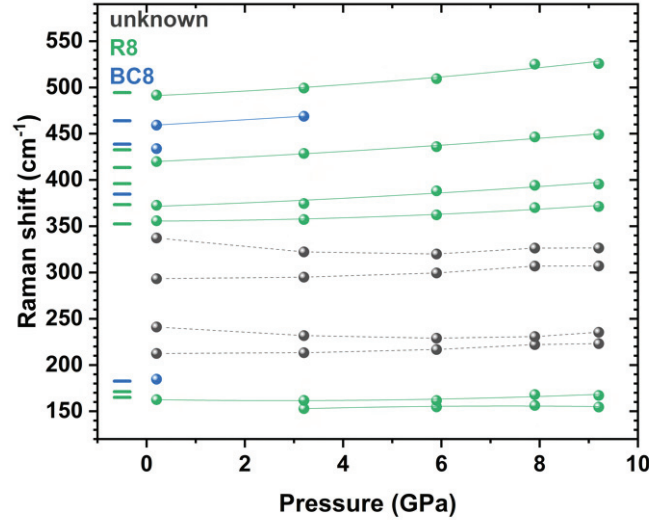


Figure 7.29: Raman frequencies of modes observed during decompression as a function of pressure (lines: measured evolution using a second order polynomial equation; ticks : modes of Si-R8 and Si-BC8 phases according to [147])

In table 7.6 are given the mode assignments based on the known modes for the $Si - R8$ and $Si - BC8$ phases. Interestingly, several modes observed for our sample in the region $200-350 \text{ cm}^{-1}$ cannot be attributed to any known modes of silicon phases and may therefore be attributed to the presence of germanium induced modes inside the structure. As no data is available for SiGe metastable phases, simulation of these structures is crucial to assign these new modes.

Phase and symmetry	$\nu_0(\text{cm}^{-1})$	$\alpha(\text{cm}^{-1}\text{GPa}^{-1})$	$\beta(\text{cm}^{-1}\text{GPa}^{-2})$	$\nu_0(\text{cm}^{-1})[147]$
R8 Eg	491	2.3	0.2	495 (Si)
BC8 Eg	458	3.2	-	463 (Si)
BC8 Tg	433	-	-	438 (Si)
R8 Eg or Ag	419	2.5	0.1	413 or 433 (Si)
R8 Eg	371	1.8	0.1	373 (Si)
R8 Ag	356	0.2	0.2	352 (Si)
unknown	337	-	-	-
unknown	293	-	-	-
unknown	241	-	-	-
unknown	213	-	-	-
BC8 Tg	184	-	-	182 (Si)
R8 Eg	163	-0.9	0.2	170 (Si)
R8 Ag	147 (estimated)	2.4	-0.2	165 (Si)

Table 7.6: Symmetry of the Raman modes of $Si_{0.8}Ge_{0.2}$, ambient measured position, pressure coefficient during decompression, predicted modes for Si-R8 and Si-BC8 modes according to [147].

Simulation of the vibrational properties of R8 and BC8 phases

The results presented in this section are DFT simulation of $Si_{0.8}Ge_{0.2}$ – R8/BC8 vibrational properties. Even if a full attribution of each Raman modes is not currently available, some features calculated by DFT are consistent with our measurements and can bring insights on the phases observed by Raman spectroscopy. We present here the main features allowing to support our experimental observations.

The figure 7.30 shows the decomposition of the partial spectral function at the Gamma point of the $Si_{0.8}Ge_{0.2}$ R8 and BC8 structures obtained by DFT. The attribution of the modes is not trivial due to a large number of modes. However, the newly discovered modes in the $200\text{-}350\text{ cm}^{-1}$ region are clearly present in our simulations. By decomposing the spectral function into the contributions of each chemical elements, we can deduce the contribution of the Ge-Ge or Si-Si bonds at the Gamma point. From this decomposition, it can be seen how Ge-Ge bond has an influence in the region of the newly observed modes (and in the lower frequency region in general) as shown in figure 7.30. Thus, the new modes observed are likely to be due to the presence of $Si_{0.8}Ge_{0.2}$ R8 and BC8 structures.

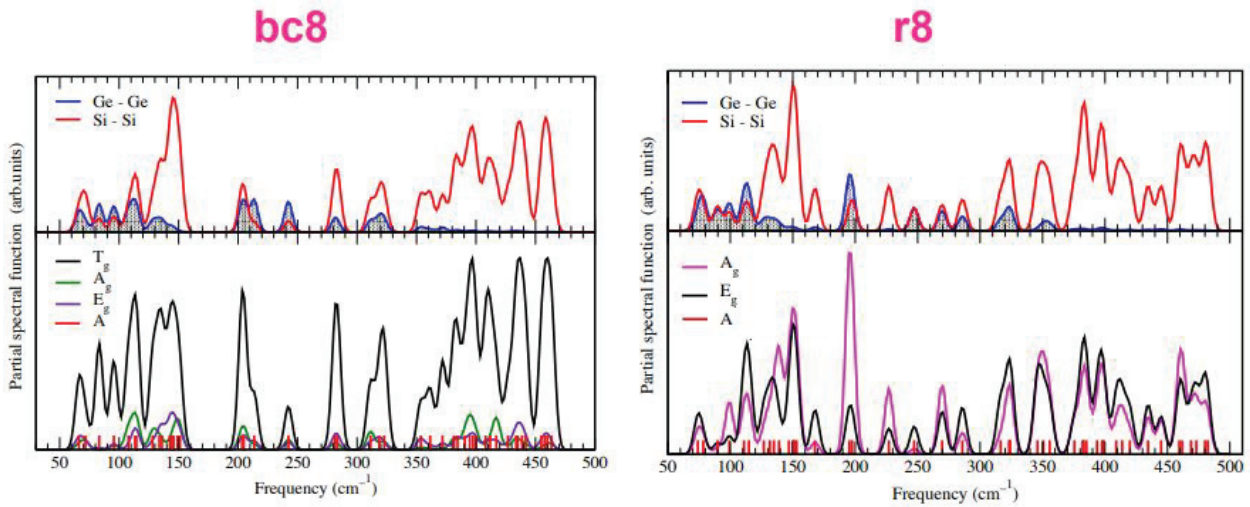


Figure 7.30: Decomposition of the partial spectral function at the Gamma point of the $Si_{0.8}Ge_{0.2}$ BC8(left) and R8(right) structures, along with contribution of the Ge-Ge or Si-Si bonds at the Gamma point.

The pressure evolution of calculated vibrational modes at the Gamma point for $Si_{0.8}Ge_{0.2}$ R8 and BC8 phases are shown in figure 7.31. Both structures exhibit a soft mode and become unstable at higher pressure that is consistent with our observations. Interestingly, it can be seen that $Si_{0.8}Ge_{0.2}$ – R8 phase is the only one having modes predicted in the $500\text{-}530\text{ cm}^{-1}$ region at pressures around 9 GPa. In our case, we observed modes in this region at high pressure (9.2 GPa), which slowly decrease in intensity as we decrease the pressure (see figure 7.28). This observation is consistent with a phase transition from $Si_{0.8}Ge_{0.2}$ – R8 $\rightarrow$ $Si_{0.8}Ge_{0.2}$ – BC8 as observed using *in situ* XRD.

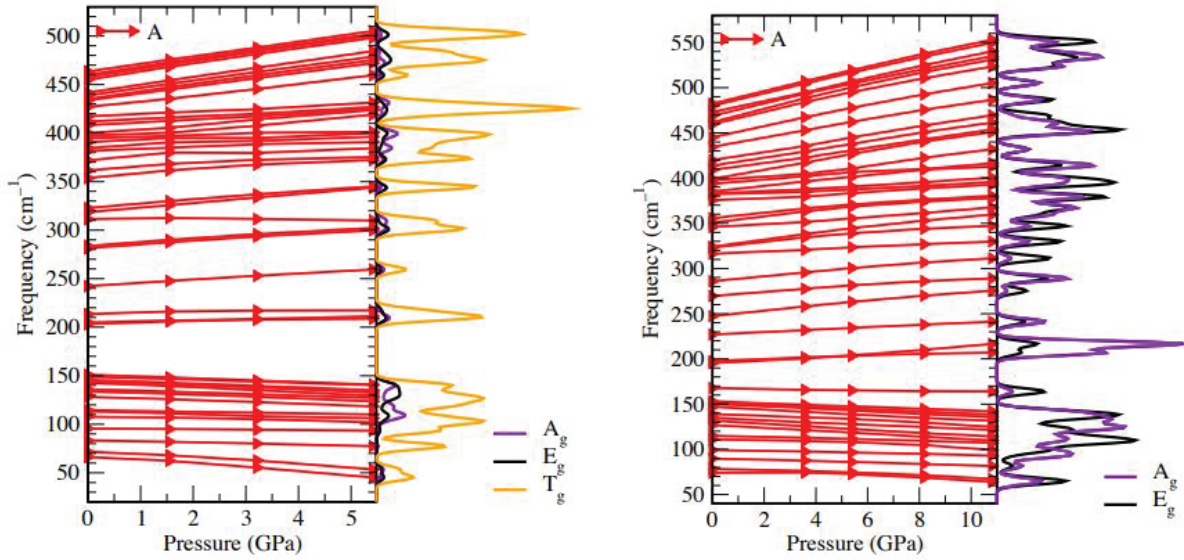


Figure 7.31: Simulated modes shift with pressure for the BC8 structure (left) and R8 structure (right) of $Si_{0.8}Ge_{0.2}$. The two phases show the presence of modes in the $200\text{--}350\text{ cm}^{-1}$ region where unassigned modes are observed.

In conclusion, if DFT simulation does not fully explain the observed spectra yet, evidences of the presence of $Si_{0.8}Ge_{0.2}$ – R8 and $Si_{0.8}Ge_{0.2}$ – BC8 phases as well as a phase transition upon decompression are supported by our simulations. Further work will probably allow to reinforce these evidences, and provide a full characterization of the vibrational properties of these new R8 and BC8 metastable phases.

7.3.5 Conclusion

In this section, structural, vibrational and mechanical properties of $Si_{0.8}Ge_{0.2}$ alloy were studied.

During compression, we measured the bulk modulus of the $Si_{0.8}Ge_{0.2}$ -diamond phase $K = 91(1)$ GPa, this value is consistent with a linear interpolation between silicon and germanium bulk modulus. The phase transition from the diamond to the β metallic phase was found to be a quite sluggish transition, where coexistence of the two phases is observed from 7.2 to 17 GPa depending on the experimental conditions. We report relaxations effects at a very early stage of this transition, probably due to the nucleation of β phase at the grain boundaries. The measured β structure parameters are in close agreement with a Vegard law between Si and Ge β structure. We also showed that the sluggish character of this transition can be promoted by using moderate temperatures, which allows a complete transition of the diamond to the β metallic phase at around 10 GPa.

Upon decompression, we observed in XRD the following phase transition pathway: $\beta \rightarrow R8 \rightarrow R8 + BC8$. The R8 phase appears first at around 9.2 GPa, followed by a partial transition toward BC8 phase around 3-2 GPa. The two phases coexist down to ambient pressure. The measured R8 bulk modulus ($K = 79(2)$ GPa) is consistent with both simulations and linear interpolation of Si and Ge bulk modulus. Small deviations from the theoretical unit cell parameters of the R8 phase were observed, attributed to the effect of the non-hydrostatic experimental conditions and the coexistence of multiple phases. The BC8 phase closely follows the theoretical simulations, with cell parameters consistent with Vegard's law.

Complementary Raman measurements combined with DFT calculations provided information of the vibrational modes seen in the diamond phase of $Si_{0.8}Ge_{0.2}$. The pressure behaviour of the diamond phase was found to be in excellent agreement with simulated modes and pressure coefficient. In situ Raman measurements under decompression showed a phase transition pathway similar to that observed by XRD, with the appearance of major modes that could be compared to the ones of silicon R8 and BC8 phases. New Raman modes, unexplained in literature, can have been induced by the alloying and are currently the subject of further investigation.

This work on $Si_{0.8}Ge_{0.2}$ could be extended in several ways, notably the use of both HT and HP in a large volume press can be repeated in the laboratory allowing the synthesis of a large quantity of metastable phases of $Si_{0.8}Ge_{0.2}$ and the potential scaling up. The sample could be characterised by other complementary techniques such as X-ray absorption spectroscopy (XAS) to investigate in depth the local geometric and electronic influence of alloying and their variation with pressure. Other interesting studies include investigating the effects of annealing on the recovered metastable phases. If the transitions follow the same rules as silicon and germanium, this could lead to the formation of new metastable phases and potentially the hexagonal phase of $Si_{0.8}Ge_{0.2}$.

7.4 High pressure study of $\text{Si}_{0.5}\text{Ge}_{0.5}$

In this section we present the *in situ* HP diffraction and Raman spectroscopy studies of $\text{Si}_{0.5}\text{Ge}_{0.5}$. Preliminary DFT simulations results will be used to help the discussion on structural and vibrations properties.

7.4.1 *In situ* HP XRD study of $\text{Si}_{0.5}\text{Ge}_{0.5}$ using a PE press at Elettra synchrotron

A first experiment on $\text{Si}_{0.5}\text{Ge}_{0.5}$ sample was performed at Elettra synchrotron XPress beamline. For this experiment, a piece of $\text{Si}_{0.5}\text{Ge}_{0.5}$ sample is grinded and loaded into a boron epoxy gasket using HP-HT assembly configuration. More details on the beamline and HP-HT assembly are provided in section 6.1.

For this experiment, the objective is to perform a pressure and temperature cycle similar to the one followed in section 7.3.2 for $\text{Si}_{0.8}\text{Ge}_{0.2}$. The experimental protocol is the following : first, to increase pressure to approximately 13 GPa where we expect the signal from β metallic phase to appear; second, to complete the transition by increasing the temperature to a few hundreds of °C at constant pressure of 13 GPa . Once the transition to the β metallic phase is complete, to decrease the temperature to room temperature and finally to decompress to ambient conditions. The goal of this cycle is to observe potential phase transition from β to metastable phases upon decompression at ambient temperature.

The diffraction pattern of the $\text{Si}_{0.5}\text{Ge}_{0.5}$ alloy obtained at ambient conditions is shown in figure 7.32 along with that of the initial Si powder used for the synthesis and taken as a reference. The measured $\text{Si}_{0.5}\text{Ge}_{0.5}$ cell parameter is 5.524(5) Å in good agreement with the database reference of 5.530(1) Å (PDF4+ database number 04-003-4732).

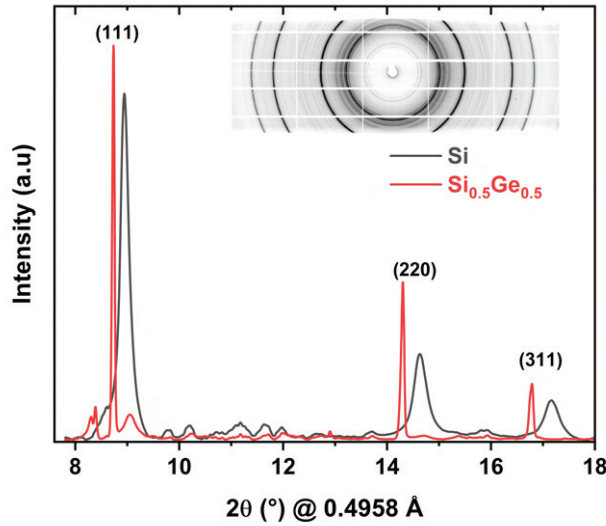


Figure 7.32: XRD patterns of $\text{Si}_{0.5}\text{Ge}_{0.5}$ and Si powder at ambient conditions measured on Elettra XPress beamline. Both patterns can be indexed to the diamond cubic phase with a cell parameter of 5.524(5) Å for $\text{Si}_{0.5}\text{Ge}_{0.5}$ and 5.422(5) Å for silicon.

The diffraction patterns obtained upon compression are shown in figure 7.33. During compression, the FWHM of $Si_{0.5}Ge_{0.5}$ reflections show a large decrease around 6 GPa. This is consistent with the observations made for $Si_{0.8}Ge_{0.2}$ in section 7.3.2, and with the onset of a phase transition toward β phase as reported in germanium [139, 104]. However, no reflections of the β phase were measured during increasing pressure, possibly due to i) higher sample absorption ($x=0.5$) resulting in a lower diffracted signal ii) an unfavourable detector position, where the border of the detector panel coincides with the expected positions of β phase first reflections.

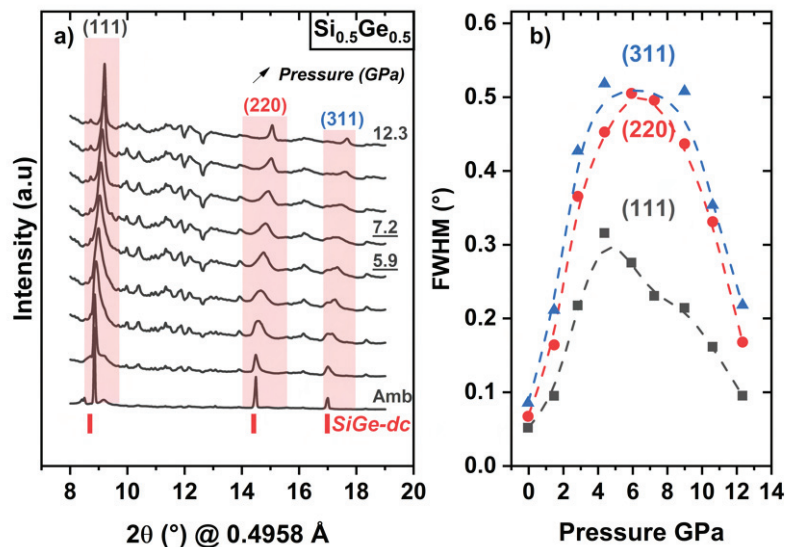


Figure 7.33: a) X-ray diffraction patterns of $Si_{0.5}Ge_{0.5}$ obtained under pressure in a P-E press. b) Evolution of the FWHM as a function of pressure of the first three reflections of $Si_{0.5}Ge_{0.5}$, showing a phase transition relaxation at around 6 GPa.

The volume contraction of the $Si_{0.5}Ge_{0.5}$ diamond phase as a function of pressure is shown in figure 7.34. The data were fitted using a BM2 and BM3 EOS so that the values could be compared with those of Anzelinni & al. [108]. The bulk modulus parameters obtained are $K = 84(2)$ with $K' = 4$ and $83(2)$ with $K' = 4.24$. This latter result is in agreement with a linear interpolation between the bulk modulus of silicon ($K = 97.88$ GPa, $K' = 4.24$) [108] and germanium ($K = 76.0$, $K' = 4.37$) [102].

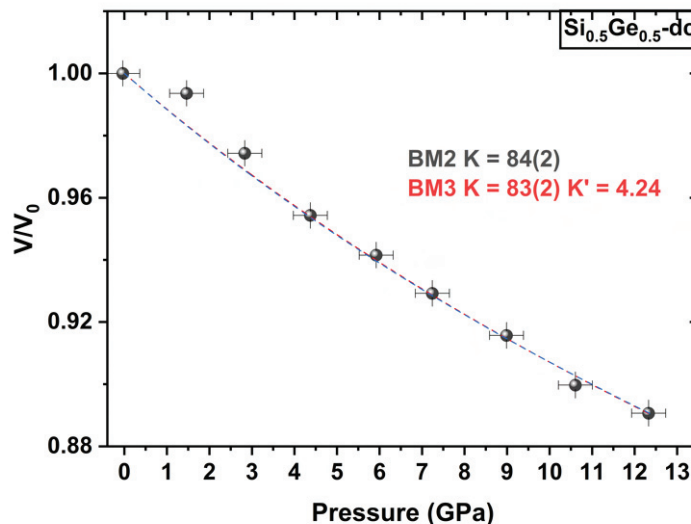


Figure 7.34: V/V_0 plot of $Si_{0.5}Ge_{0.5}$ diamond phase as a function of pressure along with a BM2 and BM3 EOS fitted to the data.

Unfortunately, the gasket containing the sample exploded when increasing the pressure above 12.3 GPa, and the sample could not be analysed further. Under ideal conditions, the maximum pressure that can be achieved in a P-E press using sintered diamond anvils is about 15 GPa. In practice, at pressures above 12 GPa, explosions can often occur damaging the anvils. In order to reach full transition to the β phase in large volume presses, high temperature is a key parameter as demonstrated in section 7.3.2 for $Si_{0.8}Ge_{0.2}$ sample. To avoid any risks of failure, it would notably be interesting to perform HT experiment at lower pressures in the 6-10 GPa pressure region to determine if the transition toward β phase can be completed at a lower pressure. Lowering the maximum pressure will allow to use tungsten carbide anvils, which would also allow access to a wider temperature range.

7.4.2 *In situ* synchrotron X-ray diffraction study of $Si_{0.5}Ge_{0.5}$ using a DAC

To obtain information on the potential metastable phases of $Si_{0.5}Ge_{0.5}$, *in situ* HP XRD measurements using a DAC were performed at PSICHE beamline at the synchrotron Soleil. For this experiment, a small piece of the $Si_{0.5}Ge_{0.5}$ sample was grinded and loaded in the hole of a stainless steel gasket (thickness: 30 μm , hole diameter: 100 μm) in a DAC with diamond tips of diameters 350 μm . Gold was used as a pressure calibrant and a 4:1 ethanol:methanol mixture as PTM.

Two pressure cycles were carried out as performed in section 7.2 for germanium. The first cycle is used to synthesise the metastable phase and the second cycle is designed to study the behaviour of the metastable phase under pressure.

In figure 7.35 is shown the diffraction pattern obtained at ambient conditions. Cell parameters, measured using LeBail refinement, are: 5.536(1) Å for $Si_{0.5}Ge_{0.5}$ sample in perfect agreement with the value of 5.537(1) Å (ref PDF4+ database : 04-003-4732) and 4.078(1) Å for the gold calibrant in perfect agreement with reference [148].

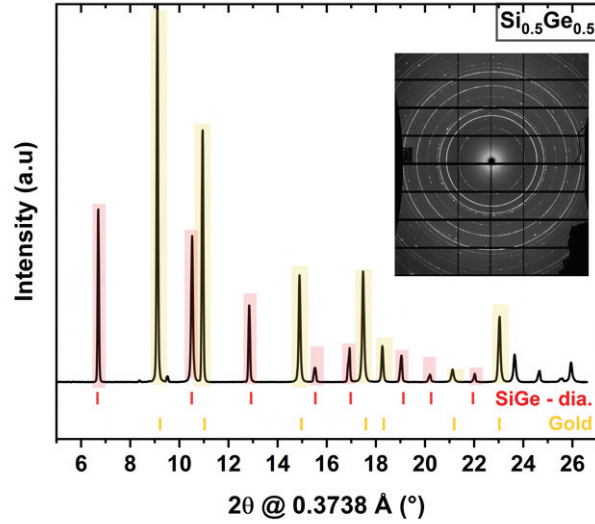


Figure 7.35: Diffraction pattern at ambient conditions of $Si_{0.5}Ge_{0.5}$ sample and gold used as a pressure calibrant. Cell parameters measured using LeBail refinement are 4.078(1) Å for gold and 5.536(1) Å for $Si_{0.5}Ge_{0.5}$.

First pressure cycle

The diffraction patterns collected under compression are shown in figure 7.36. Compression of the diamond cubic phase was rapidly covered as we had already collected data from a previous experiment using a P-E press (in previous section). The endpoint of the transition $Si_{0.5}Ge_{0.5}$ diamond phase to $Si_{0.5}Ge_{0.5} - \beta$ is measured at 14.0 GPa, where no reflections from the diamond phase could be observed anymore. Based on the definition of transition pressure by [140] in which the (111) reflection of the diamond phase has the same intensity as the (200) reflection of β phase, our transition pressure is situated at 12.1 GPa. This transition pressure is consistent with $Si_{0.8}Ge_{0.2}$ experiment (section 7.3.2) and reported theoretical [117, 118] and experimental values [140].

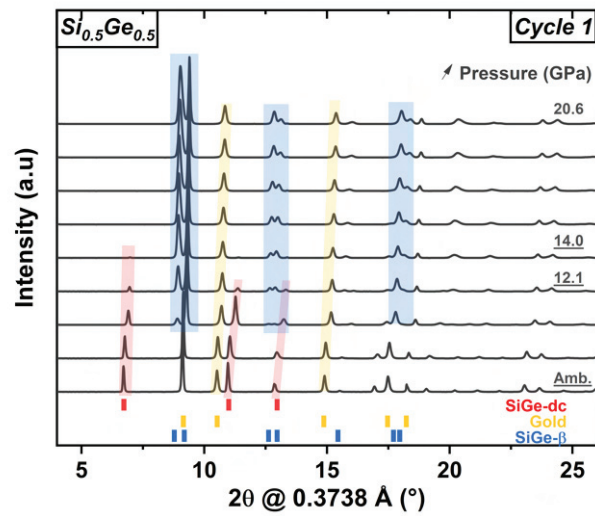


Figure 7.36: X-ray diffraction patterns of $Si_{0.5}Ge_{0.5}$ obtained upon compression. The transition from the $Si_{0.5}Ge_{0.5}$ diamond to the $Si_{0.5}Ge_{0.5} - \beta$ phase is estimated at 12.1 GPa. The main reflection of the phases in presence are indicated by tick marks.

The β phase appears to be stable up to 20.6 GPa. The evolution of normalized volume, V/V_0 , of $Si_{0.5}Ge_{0.5}-\beta$ as a function of pressure is shown in figure 7.37. Fitting the volume contraction using a BM2 function leads to $K = 138(1)$ GPa, a value between our theoretical results for $Ge-\beta$, $K = 116.3(1)$ and $Si-\beta$, $K = 147.5(1)$.

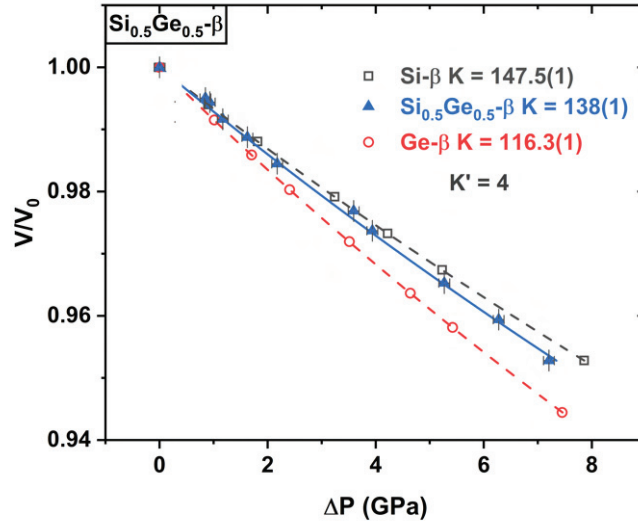


Figure 7.37: Normalized volume as a function of pressure of the β phase. (Plain symbols) Measured data for $Si_{0.5}Ge_{0.5}-\beta$. (Open symbols) Theoretical data for $Si-\beta$ and $Ge-\beta$. BM2 EOS fitted to the data (dashed lines) Theoretical data (Plain lines) Measured data.

The linear bulk modulus of the measured a and c unit cell parameters of the $Si_{0.5}Ge_{0.5}-\beta$ phase are shown in figure 7.38. The linear bulk modulus for a and b parameter is $K_{a,b} = 180(6)$ GPa, higher than theoretical values for $Ge-\beta$ ($K_{a,b} = 124.3(1)$ GPa) and $Si-\beta$ ($K_{a,b} = 160.5(1)$ GPa). For the c parameter the measured bulk modulus is $K_c = 91(2)$ GPa, lower than theoretical values for $Ge-\beta$ ($K_c = 103.0(1)$ GPa) and $Si-\beta$ ($K_c = 126.6(1)$ GPa).

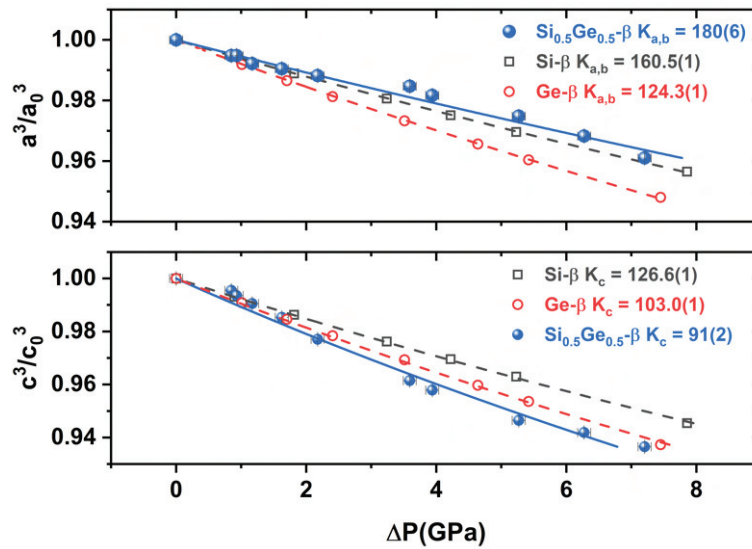


Figure 7.38: Normalized unit cell as a function of pressure of the β phase. (Plain symbols) Measured data for $Si_{0.5}Ge_{0.5}-\beta$. (Open symbols) Theoretical data for $Si-\beta$ and $Ge-\beta$. BM2 EOS fitted to the data (dashed lines) Theoretical data (Plain lines) Measured data.

The diffraction patterns obtained upon decompression from 20.6 GPa are shown in figure 7.39. During decompression from the $Si_{0.5}Ge_{0.5} - \beta$ phase, new reflections appear at low 2θ angles (5° and 12°) at 9.8 GPa. Upon further decompression, these reflections increase in intensity and the pattern can be indexed with a new $Si_{0.5}Ge_{0.5} - R8$ structure. This transition path is consistent with that of silicon [113, 16] and previously measured $Si_{0.8}Ge_{0.2} - R8$. In silicon this transition is reported at similar pressures between 8.2 and 10 GPa, for $Si_{0.8}Ge_{0.2} - R8$ we measured this transition at 10.3 GPa (in section 7.3.3). In $Si_{0.5}Ge_{0.5}$ sample, R8 and β phase appear to coexist down to 4.6 GPa where traces of the β phase remains. The stability domain of the $Si_{0.5}Ge_{0.5} - \beta$ phase upon decompression appears to be wider than for pure silicon, where the lower limit reported is 6.2 GPa [113, 16], but is consistent with the β and R8 coexistence measured down to 5.4 GPa for $Si_{0.8}Ge_{0.2}$ in previous section 7.3.3.

Further analysis of this new $Si_{0.5}Ge_{0.5} - R8$ phase pressure behaviour was performed during the second pressure cycle.

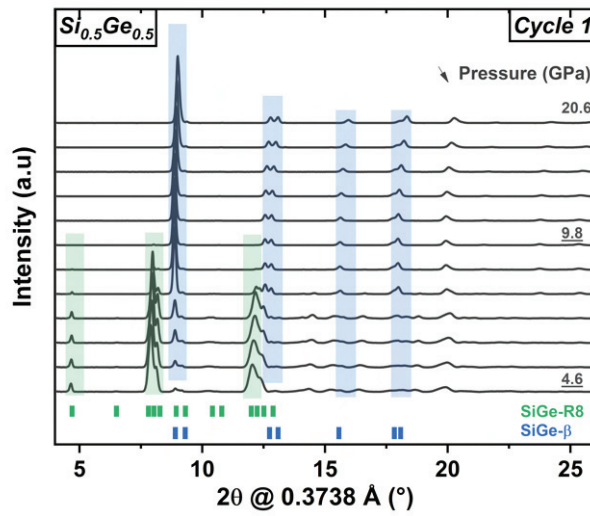


Figure 7.39: X-ray diffraction patterns of $Si_{0.5}Ge_{0.5}$ obtained during decompression. A phase transition from $Si_{0.5}Ge_{0.5} - \beta$ to $Si_{0.5}Ge_{0.5} - R8$ is observed at 9.8 GPa. The main reflections of the R8 and β phases are shown with green and blue tick marks, respectively.

Second pressure cycle

The diffraction patterns observed during the second pressure cycle are shown in figure 7.40. The reverse transition from R8 to β phase is observed upon compression at 11.3 GPa with an endpoint of the transition at 13.4 GPa. To the best of our knowledge, this reverse transition has not been observed in either silicon or germanium. Further compression up to 40 GPa was performed, showing a possible transition at pressure higher than 20 GPa.

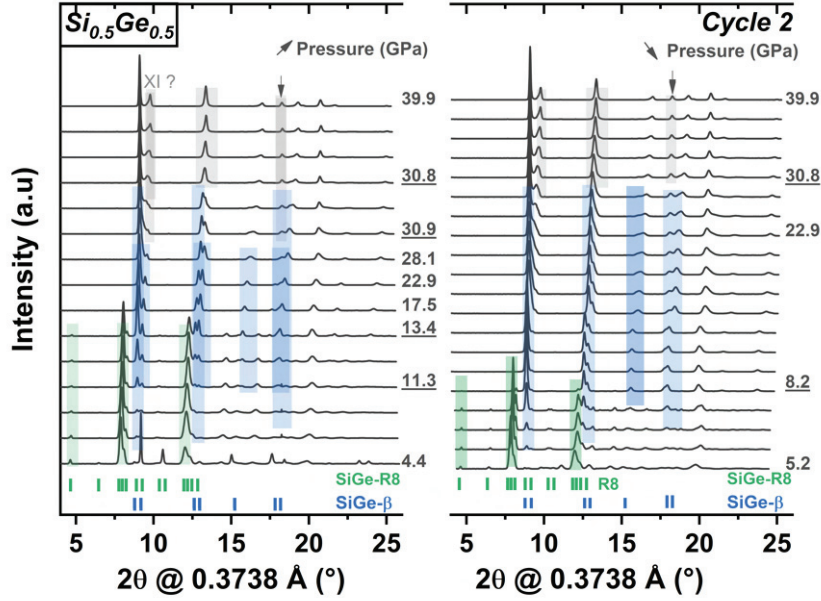


Figure 7.40: X-ray diffraction patterns of $Si_{0.5}Ge_{0.5}$ obtained during the second pressure cycle. (Left) Upon compression, the $Si_{0.5}Ge_{0.5} - R8$ phase fully transforms to $Si_{0.5}Ge_{0.5} - \beta$ at 13.4 GPa. Patterns obtained at pressures higher than 20 GPa could not be clearly indexed due to another transition happening. (Right) Upon decompression, the reverse $Si_{0.5}Ge_{0.5} - \beta$ to $Si_{0.5}Ge_{0.5} - R8$ transition is measured at 8.2 GPa.

The new phase may be due to a transition toward an orthorhombic $Imma$ structure, predicted to appear in the 18-22 GPa pressure range for $Si_{0.5}Ge_{0.5}$ [120]. As no detailed crystallographic data for $Si_{0.5}Ge_{0.5} - Imma$ phase are present in the literature, we have to compare our results to the well documented case of silicon and germanium. In silicon, this phase is reported in a narrow pressure region around 13 GPa often coexisting with two HP phases of Si : $Si - \beta$ and $Si - sh$ (Si-V, simple hexagonal) [108]. In germanium, this phase is stable at pressures above 70 GPa in a large pressure range of 15 GPa [109]. Due to the pressure difference between reported data, no direct comparison of the obtained cell parameters is possible.

However, as we can see in figure 7.41, where only the diffraction patterns collected at the highest pressures are shown, a few evidences of this phase are: i) a new reflection appearing close to a 2θ angle of 17° ; ii) a slowly decreasing of the intensity of the (312) reflection of the β phase at a 2θ angle of 22.5° . This reflection almost disappears at 39.8 GPa, indicating that the β phase may not be present at this pressure.

I therefore performed a LeBail refinement of the diffraction pattern at 39.8 GPa that could be successfully attributed to an orthorhombic $Si_{0.5}Ge_{0.5} - Imma$ phase with $a = 4.707(4) \text{ \AA}$, $b = 4.421(4) \text{ \AA}$ and $c = 2.523(4) \text{ \AA}$. The refinement did not work well for patterns collected at lower pressure due to the strong similarities between the β and $Imma$ phases, both of which are present. DFT simulations are currently underway to confirm the stability domain of this phase of $Si_{0.5}Ge_{0.5}$ and expected cell parameters evolution with pressure.

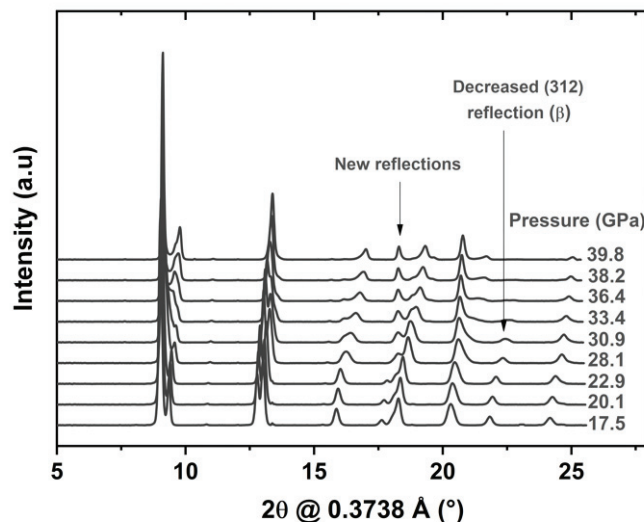


Figure 7.41: XRD patterns of $Si_{0.5}Ge_{0.5}$ and evidences of phase transition from $Si_{0.5}Ge_{0.5} - \beta$ to $Si_{0.5}Ge_{0.5} - Imma$ phase at pressures above 20 GPa.

Upon decompression from the *Imma* phase, the diffraction pattern of β phase is recovered, again around 20 GPa. This observation confirms the reversible transition $Imma \rightarrow \beta$. Upon further decompression, the diffraction patterns show, for the second time, the phase transition from the β to the R8 phase at 8.2 GPa, 1 GPa lower than for the first pressure cycle, as it can be seen in figure 7.40 and remains stable down to the lowest pressure reached (5.2 GPa).

The normalized volume evolution as a function of pressure measured for $Si_{0.5}Ge_{0.5} - R8$ phase is shown in figure 7.42. Using a BM2 EOS, a bulk modulus of $K = 76.2(9)$ GPa was obtained consistent with a linear interpolation between DFT results obtained for $Ge - R8$ ($K = 68.8(2)$ GPa) and $Si - R8$ ($K = 83.3(3)$ GPa).

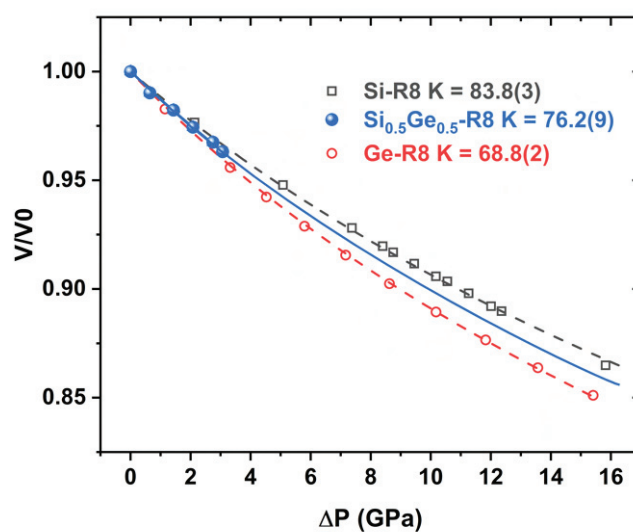


Figure 7.42: Normalized volume as a function of pressure of the R8 phase. (Plain symbols) Measured data for $Si_{0.5}Ge_{0.5}$ -R8. (Open symbols) Theoretical data for Si-R8 and Ge-R8. BM2 EOS fitted to the data (dashed lines) Theoretical data (Plain lines) Measured data.

The pressure in the sample chamber could not be decreased lower than ~ 5 GPa during the short available synchrotron beam time and therefore no XRD measurements at lower pressure were performed. The characterization of the sample inside the cell after further decompression was performed in the laboratory using Raman spectroscopy and will be presented in the next section. A complementary *in situ* HP Raman spectroscopy experiment on $Si_{0.5}Ge_{0.5}$ was also performed.

7.4.3 *In situ* Raman spectroscopy study of $Si_{0.5}Ge_{0.5}$

In situ HP Raman spectroscopy measurements were made on the $Si_{0.5}Ge_{0.5}$ composition. For this experiment, a small piece of the $Si_{0.5}Ge_{0.5}$ sample was grinded and loaded in the hole of a pre-indented stainless steel gasket (thickness: $80\ \mu m$, hole diameter: $100\ \mu m$) using a DAC with diamond tips of diameters $350\ \mu m$. Ruby chip was used as pressure calibrant, the PTM used for this experiment is a paraffin oil.

The Raman spectrum of $Si_{0.5}Ge_{0.5}$ measured at ambient conditions is shown in figure 7.43. The spectrum observed is identical with those from the literature [28, 29]. First, three main peaks corresponding to optical phonons associated with Ge-Ge, Ge-Si, and Si-Si vibrations are present at 291 , 408 , $485\ cm^{-1}$, respectively. Similarly to measurements made on $Si_{0.8}Ge_{0.2}$ composition, these three main modes are asymmetric, with a ratio between left and right FWHM of 1.46 for Si-Si, 4.42 for Ge-Si and 2.27 Ge-Ge modes. Interestingly, the measured asymmetry for this composition is higher than for $Si_{0.8}Ge_{0.2}$ (1.58 for Si-Si, 1.86 for Ge-Si and 1.50 for Ge-Ge). This result is consistent with an increased disorder in $x=0.5$ composition. Composition estimation [28] from the Si-Si mode places our sample at $x = 0.56 \pm 0.03$. Between the Ge-Si peak ($408\ cm^{-1}$) and the Si-Si peak ($482\ cm^{-1}$), three peaks are measured at 426 , 433 and $465\ cm^{-1}$ and are assigned to Si-Si local vibrational modes in different environment. These modes are more defined than for $Si_{0.8}Ge_{0.2}$, due to the increased germanium content [29, 31]. Similarly to $Si_{0.8}Ge_{0.2}$ a broad mode is seen at low frequency region around $210\ cm^{-1}$ called quasi-amorphous (q-a)[33].

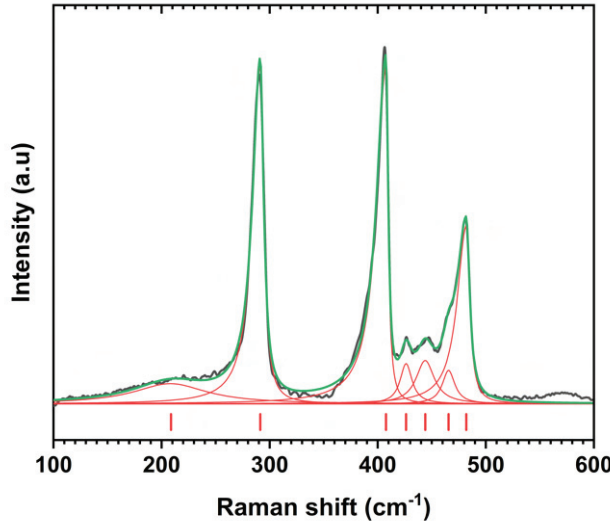


Figure 7.43: Typical Raman spectrum of $Si_{0.5}Ge_{0.5}$ at ambient conditions. The Lorentzian functions used to fit the modes are shown in red. The three Si-Si Ge-Si and Ge-Ge major modes are fitted using asymmetric Lorentzian profile.

Raman spectra obtained upon compression are reported in figure 7.44. At pressures above 13.4 GPa, no signal from the SiGe-diamond phase can be measured as it slowly transforms to the metallic phase. The Raman cross section of the metallic phase being very low, the signal loss above 13.4 GPa is a mark of the total disappearance of the diamond phase. This transition is consistent with the pressure domain of the diamond phase measured using XRD in previous section 7.4.2.

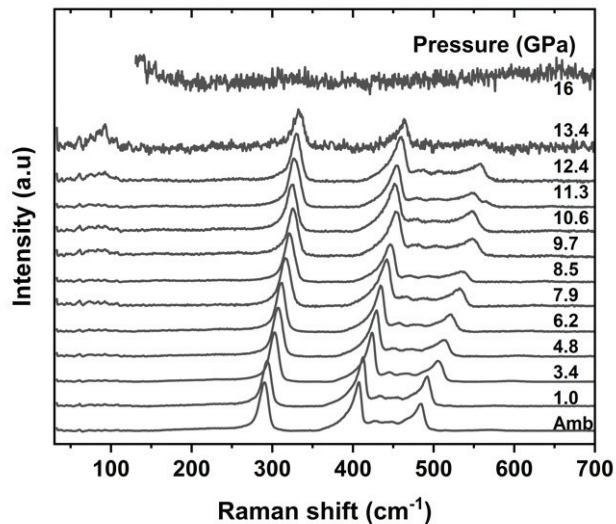


Figure 7.44: Raman spectra of $Si_{0.5}Ge_{0.5}$ upon compression. A signal decreased of the diamond phase is observed at 13.4 GPa followed by a total loss at higher pressures.

The evolution of the mode positions as a function of pressure are shown in figure 7.45, and the pressure parameters are reported in table 7.7. For this composition, the simulated number of modes is greater than for $Si_{0.8}Ge_{0.2}$ composition, the modes predicted in the lower frequency region $<200\text{ cm}^{-1}$ are not seen as well as the ones in the middle frequency region $(320-400)\text{ cm}^{-1}$. For the measured modes, the pressure behaviour is in global agreement with DFT results. In particular, the measured linear pressure dependency (in $\text{cm}^{-1}.\text{GPa}^{-1}$) of the three main modes (Si-Si: 6.8, Si-Ge: 5.1, Ge-Ge: 3.9) are in good agreement with reported results by Sui & al (Si-Si: 7.0, Si-Ge: 5.1, Ge-Ge: 4.0) on a close composition ($x=0.55$) [121]. The lowest measured mode at 210 cm^{-1} at ambient pressure is not clearly observed at HP due to its low intensity and broadness.

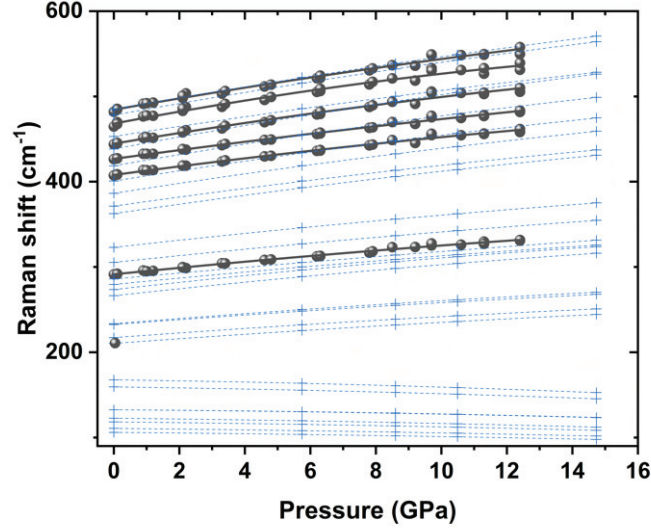


Figure 7.45: Measured Raman mode positions as a function of pressure for $Si_{0.5}Ge_{0.5}$ sample (plain lines and symbols) along simulated modes for this composition (dashed lines and cross symbol).

Mode	Measured parameters			Simulated parameters		
	ν_0	α	β	ν_0	α	β
Ge q-a	196(5)	-	-	-	-	-
Ge-Ge	291(1)	3.9(2)	-0.05(1)	286	3.5	-0.03
Ge-Si	408(1)	5.1(1)	-0.07(2)	401	6.1	-0.08
Si-Si loc. Ge 1	427(1)	5.2(5)	-0.06(2)	419	6.7	-0.09
Si-Si loc. Ge 2	445(1)	6.5(1)	-0.10(3)	438	7.3	-0.09
Si-Si loc. Ge 3	468(1)	7.4(5)	-0.15(4)	478	6.9	-0.07
Si-Si	485(1)	6.8(5)	-0.08(3)	485	6.9	-0.07

Table 7.7: Mode denomination of each measured mode of $Si_{0.5}Ge_{0.5}$ diamond phase, along with measured and simulated pressure coefficients using $\nu = \nu_0 + \alpha P + \beta P^2$ with ν_0 in cm^{-1} , α in $cm^{-1}.GPa^{-1}$ and β in $cm^{-1}.GPa^{-2}$.

Raman spectra measured upon decompression are shown in figure 7.46. During this decompression stage, no signal is measured down to 8.2 GPa, where new modes appear at 200 and 300 cm^{-1} . This transition pressure is consistent with the R8 stability domain observed during previous XRD measurements. The signal over noise ratio appears to gradually increase during decompression steps, indicating that the amount of R8 phase increases when lowering the pressure but the metallic phase is potentially still present down to low pressures (4.2 GPa). This result is consistent with the large pressure region coexistence of these two phases observed by XRD in the previous section 7.4.2. Upon decompression from 4.2 GPa to ambient pressure a new spectrum is observed, with clear new peaks indicated with arrows in figure 7.46. This last spectrum is complex to analyse, possibly due to the coexistence of three phases.

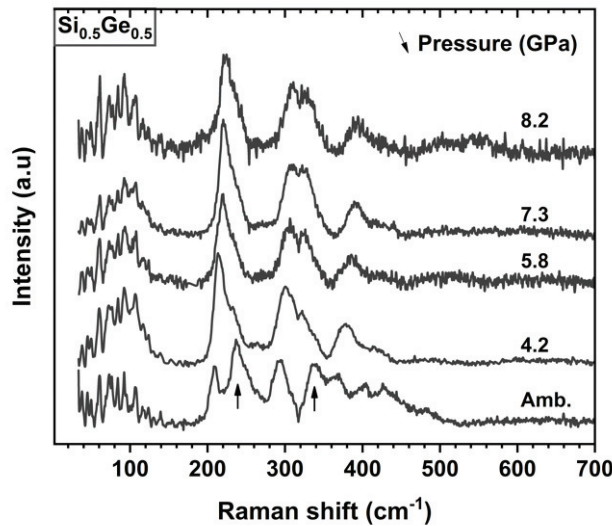


Figure 7.46: Raman spectra of $Si_{0.5}Ge_{0.5}$ sample as a function of pressure during decompression.

Some spectra collected at ambient pressure showed the presence of diamond phase modes. The presence of the diamond phase can be due either to a low stability of the observed phases or to laser heating despite working with a very low laser power and long acquisition times. It is hard to unambiguously determine which phases are present at ambient pressure. What we can say is that some of the low frequency modes can be attributed to a new phase. In fact, they do not belong to the diamond phase and they do not follow the R8 modes pressure behaviour. These modes are situated at 236, 250, 265 337 cm^{-1} . The modes at 209, 298 and 365 cm^{-1} can, instead, be attributed to the R8 phase, and are consistent with the pressure evolution of R8 modes seen at higher pressure. The measured mode positions as a function of pressure, with their respective attribution is presented in figure 7.47.

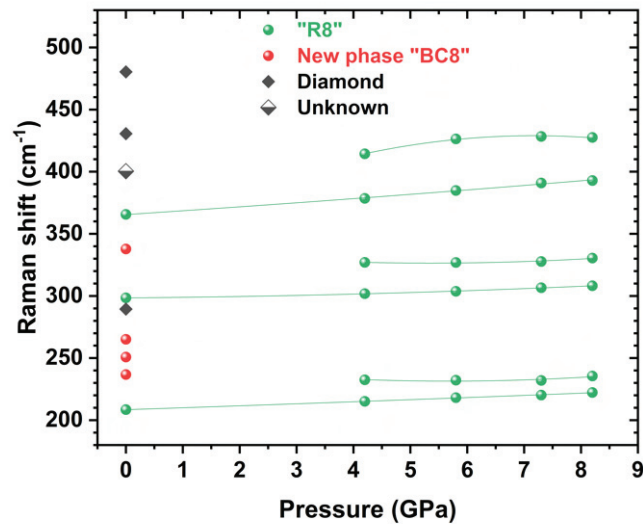


Figure 7.47: Raman frequencies observed under decompression as a function of pressure. (Lines) measured evolution using a second order polynomial equation. The modes positions attributed to each potential phase are indicated with specific symbol.

Complementary Raman measurements were made on the sample inside the cell used in the previous section 7.4.2 after the two pressure cycles at Soleil. Decompression from 5 GPa was made manually by unscrewing the cell. The spectrum obtained is shown in figure 7.48. Interestingly, this spectrum extremely similar to the ones observed between 8.2 to 4.2 GPa previously in figure 7.46 and attributed to the $Si_{0.5}Ge_{0.5} - R8$ phase. This observation indicates that upon decompression in hydrostatic conditions, the sample may stay in the R8 phase, without further transition.

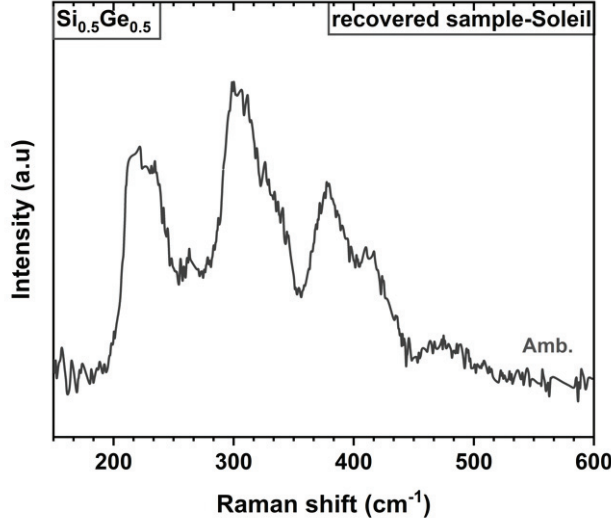


Figure 7.48: Raman spectrum of $Si_{0.5}Ge_{0.5}$ sample recovered after pressure cycles (described section 7.4.2)

7.4.4 Conclusion

With this high pressure study, we were able to observe three phases of $Si_{0.5}Ge_{0.5}$. Upon compression, the phase transition from the diamond to the β metallic phase was found to occur in a large range of pressure. The transition starts as low as 6 GPa in non hydrostatic conditions and is fully completed at 14 GPa in hydrostatic conditions. The bulk modulus of $Si_{0.5}Ge_{0.5} - diamond$ phase was measured to be $K = 84(2)$ GPa, lower than the one of $Si_{0.8}Ge_{0.2} - diamond$ and in agreement with the linear interpolation of the simulated ones of Si and Ge. The fitted $Si_{0.5}Ge_{0.5} - \beta$ bulk modulus was $K = 138(1)$ GPa in agreement with a linear interpolation between simulated $Ge - \beta$ and $Si - \beta$ bulk modulus. This β phase is observed to be stable up to 20.6 GPa. At higher pressure, this phase appears to slowly transform into a new phase which could be indexed as $Si_{0.5}Ge_{0.5} - Imma$ phase at 39.8 GPa. Upon decompression we report the following transitions $Imma \rightarrow \beta \rightarrow R8$. The $Si_{0.5}Ge_{0.5} - \beta$ to $Si_{0.5}Ge_{0.5} - R8$ phase transition was observed, during two different pressure cycle, at pressures of 9.8 and 8.2 GPa. The reverse transition $R8 \rightarrow \beta$ happens at 13.4 GPa. The $R8$ phase coexists with the β phase down to 4.4 where only traces of β signal are observed. No clear evidence of the appearance of the phase BC8 was detected by Raman spectroscopy for this composition contrary to what observed for the $Si_{0.8}Ge_{0.2}$. Further study by XRD or other techniques in the lowest pressure range after decompression are needed. The measured bulk modulus for $Si_{0.5}Ge_{0.5} - R8$ phase is $K = 76.2(9)$ GPa in good agreement with theoretical values for $Si - R8$ and $Ge - R8$ simulated parameters.

7.5 Conclusion

In conclusion, the pressure behaviour of two alloys with different compositions, $Si_{0.8}Ge_{0.2}$ and $Si_{0.5}Ge_{0.5}$, was studied in such depth for the first time in the literature, to our knowledge. Both samples show similar behaviour under compression with a linear variation of the bulk modulus as a function of composition. Upon compression, the two samples follow the same transition from the diamond to a metallic β phase. We showed that this transition is first seen indirectly by relaxation of sample stresses, and is found to coexist with the diamond phase to higher pressures than expected in literature. We report for the first time that, upon decompression of this metallic phase, metastable phases are formed in SiGe alloys with a successive transition to the R8 and BC8 phase. According to our results, the structural and mechanical properties of this metastable phases follow a linear law with their structural equivalent silicon and germanium. Importantly, we provide insights into how to ensure a complete transition to the metallic phase in a large volume press using moderate temperatures, opening up pathway for synthesizing large quantity of metastable phases. This could lead to easier characterisations of the recovered sample using *ex-situ* characterization techniques and potentially to the scaling up of the metastable phase for various applications.

General conclusion and perspectives

In this manuscript, I presented the synthesis and the high-pressure studies I carried out during my PhD research project on silicon and germanium alloys.

Since SiGe alloys of different compositions synthesised under the same conditions are difficult to obtain commercially, much of my initial research was spent trying to synthesise them in the laboratory. I have succeeded in developing an experimental protocol that allows me to obtain alloys that are homogeneous over the entire composition range.

I first observed that due to their different physical properties, especially with regard to melting point, the reaction between silicon and germanium is difficult to implement. For Si-rich alloys, I presented a protocol using repeated grinding, compaction and HT treatments at progressively increasing temperatures. Using XRD, Raman spectroscopy and EDX, three characterisation techniques easily available at ILM, I showed that the synthesized alloys of composition ($x \sim 0.5$; 0.6; 0.7; 0.8; 0.9) are homogeneous, with, however, a low density and porous surface. The quantity and quality were sufficient to perform high-pressure experiments requiring only powdered samples. This synthesis method was ineffective in synthesising low-melting Ge-rich samples. In these samples, germanium was found to limit the annealing temperature and thus the reaction of the powders. We report either oxidation or destruction of the Ge-rich samples during HT treatments, due to the high proportion of germanium in these samples and its low melting point. Two pathways were then proposed to overcome these issues: i) confinement of the powders during reaction; ii) quasi-instantaneous melting and quenching in controlled atmosphere.

I investigated the effect of confinement of the powders during the reaction using two techniques: spark plasma sintering and HP-HT Belt apparatus. The confinement provided by SPS was found ineffective in containing the germanium during melting for Ge rich samples, leading to leakage and could not force the powders to react. We however found an efficient way to synthesize dense and quasi-homogeneous Si-rich samples using SPS method. We notably showed that these samples can be homogenized using HT post-treatments. This technique has therefore the potential to fill the gaps of the proposed method for Si-rich alloys (based on multiple annealing steps), as it promotes a fast reaction rate and high density end products. The other confinement technique proposed, the Belt apparatus, was found efficient enough to confine the powders during reaction but the results were dense inhomogeneous Ge-rich alloys. The experimental protocol proposed for the Belt experiment can be improved to promote a better homogeneity, but need further experimental research.

On the other way, to overcome germanium early melting, we proposed quasi instantaneous melting and quenching of silicon and germanium using an arc melting setup, but this technique leads to inhomogeneous alloys. We stated that the "pre-alloy" synthesized with arc melting have good characteristics for HT treatments : a high density, a higher melting point than germanium and a large surface of contact between the different compositions coexisting in the sample. We were therefore able to synthesize two Ge-rich alloy compositions using arc melting combined with HT post treatments. We provided evidences that modifications to the experimental setup, including a faster quenching system, could lead to more homogeneous alloys and a reduction in the processing time of post-annealing treatments. The arc melting method, combined with HT post treatments has great potential and could be further explored to create dense and homogeneous alloys across the composition range.

I also presented the interest of germanium as new high capacity anode active material for lithium ion batteries. We report the successful synthesis of a hybrid structure composed of nanoparticles of germanium embedded into a carbon matrix using pulsed laser ablation in liquids. The synthesized materials are currently being tested upon lithiation and delithiation cycles at the LN2 laboratory at Sherbrooke. If the tests are conclusive, this work can be extended to nanostructured SiGe alloys by changing the germanium ablation target with the SPS synthesized pellets. This could lead to different interesting studies for new electrodes in lithium ion batteries, but also to more fundamental study on the interactions between the carbon matrix and the nanoparticles under stress using in situ Raman spectroscopy or XRD.

The main part of my PhD research project was to study the behaviour under pressure and the occurrence of new metastable phases of the synthesised alloys. I managed to study pure germanium to complement some information in the literature, $Si_{0.8}Ge_{0.2}$ and $Si_{0.5}Ge_{0.5}$ using a P-E press or a DAC coupled with *in situ* XRD and Raman spectroscopy techniques. I also performed some preliminary HP experiments on $Si_{0.3}Ge_{0.7}$, the results of which require proper analysis and further investigation and are not reported in the manuscript.

Using P-E press and a pressure cycle up to 14 GPa we could synthesize large quantity of the Ge tetragonal metastable phase called $Ge - ST12$. We performed HP *in-situ* Raman spectroscopy experiments in a DAC to study the pressure behaviour of this phase up to 12.3 GPa. A unique non-crossing behaviour of two low frequency modes with same symmetry was observed for the first time confirming predicted theoretical data. Under decompression, we observed that the transition between the pressure induced metallic phase $Ge - \beta \leftrightarrow Ge - ST12$ is reversible in the 9 and 11 GPa pressure region. The $Ge - ST12$ phase can easily transit back toward the diamond phase by grinding or low temperature annealing.

Following the study on germanium, we performed HP experiments on SiGe alloys of two compositions. We first showed that, contrary to the case of Ge, the synthesis of a large amount of metastable phases was not possible using cold compression in a P-E press for $Si_{0.8}Ge_{0.2}$ and $Si_{0.5}Ge_{0.5}$ alloys. Our XRD data collected upon increasing pressure shows that the diamond to β phase transition begin at lower pressure compared to reported values for Ge or Si and is very sluggish, with coexistence of the two phases over a wide pressure range. We notably observed, for the first time, a very early relaxation of sample stresses near 6 GPa, at the beginning of this transition, consistent with the nucleation of $SiGe - \beta$ phase at its early stage. For the stable diamond phase, we measured a bulk modulus of $K = 92$ and $K = 84$ GPa for the $x = 0.8$ and $x = 0.5$ composition, respectively. Known values for Si and Ge are $K = 97.9$ and $K = 74.4$ GPa, respectively [108, 149]. We also report the $SiGe - \beta$ phase bulk modulus of 138 GPa for $Si_{0.5}Ge_{0.5}$ which we compared to our DFT results of 147.5 and 116.5 GPa for Si and Ge. Both bulk modulus and cell parameters follow a linear law as a function of composition.

With a HP-HT experiment in a PE press we demonstrated that the sluggish character of the β phase transition can be overcome by the application of a moderate temperature (255 °C), thus paving the way for the synthesis of large amount of metastable phases of SiGe alloys.

The compression behaviour of both SiGe samples was also studied by *in situ* Raman measurements, combined with preliminary DFT calculations. The pressure behaviour of the $Si_{0.8}Ge_{0.2}$ diamond phase was found to be in excellent agreement with simulated modes and pressure coefficient. For $Si_{0.5}Ge_{0.5}$, some of the predicted modes were not measured, however the global pressure behaviour was consistent with close DFT-predicted modes. For both composition, we observed a transition toward the metallic phase at high pressure, with traces of diamond phase still present at 15.7 GPa for $Si_{0.8}Ge_{0.2}$ and 13.4 GPa for $Si_{0.5}Ge_{0.5}$, both consistent with the sluggish character of the transition observed in XRD. At higher pressures, we report evidences of $Si_{0.5}Ge_{0.5} - \beta \rightarrow Si_{0.5}Ge_{0.5} - Imma$. This transition appears to be sluggish as well, coexisting with β phase on a wide pressure range.

Upon decompression, a first transition from $SiGe - \beta \rightarrow SiGe - R8$ phases, happens in both of our samples in a similar pressure range of 10-8 GPa, confirmed by XRD and Raman spectroscopy measurements. We observed that this new $SiGe - R8$ phase coexists with $SiGe - \beta$ phase down to ~ 5 GPa for both compositions. We report that the cell parameters and bulk modulus of both our alloys in R8 phase varies as function of composition in between calculated Si-R8 and Ge-R8 parameters. We measured R8 bulk parameters of $K = 76$ and 80 GPa for $x = 0.5$ and 0.8 respectively, in between calculated $K = 68.7$ and 83.0 for Ge and Si.

For $Si_{0.8}Ge_{0.2}$ the apparition of a new Raman spectrum at 9.2 GPa appeared comparable with the Si R8 reported modes in the literature. Interestingly, we observed new modes in the low frequency region which are unknown for the Si-R8 phase. These new modes are attributed to the presence of germanium in the Si structure as confirmed by our DFT calculations. For $Si_{0.5}Ge_{0.5}$ a similar spectra was observed at 8.4 GPa, but it was harder to attribute to the R8 phase due to the lack of known Raman signature for this sample. Future simulation work could shed light on the observed modes.

For $Si_{0.8}Ge_{0.2}$ composition we were able to measure diffraction patterns down to ambient pressure, showing that the phase transition $Si_{0.8}Ge_{0.2} - R8' \rightarrow SiGe - BC8$ occurs at approximately 2 GPa. Also R8 and BC8 phase were found to coexists at ambient pressures. This result was confirmed by enthalpy simulation showing that the enthalpy difference between R8 and BC8 converge to almost zero as the pressure decrease.

The same transition pathway was also confirmed for $Si_{0.5}Ge_{0.5}$ by Raman spectroscopy. New modes, similar to modes reported for the $Si - BC8$ structure, were observed to appear in the spectra at low pressure. Complete decompression to ambient led to another phase transition, which could not be clearly assigned due to coexistence of multiple phases. The sample was found extremely sensitive to laser heating. Future theoretical simulations on the new R8 and BC8 of $Si_{0.5}Ge_{0.5}$ structure, including the partial spectral function at Γ point, may clarify the attribution of each mode measured.

This HP work on SiGe alloys could be extended in several ways. The transition pathway found using a P-E press combining both temperature and pressure could be reiterated and optimized, allowing the synthesis of a large amount of SiGe metastable phases which can then be characterised by different techniques. This method could lead to further studies, including the study of the effects of annealing on the recovered metastable phases and could also allow a better analysis of the structural vibrational and mechanical properties in a DAC as performed for $Ge - ST12$. If transitions obey to the same rules than silicon and germanium, this could lead to the formation of new metastable phases and potentially to the hexagonal phase of SiGe alloys, which is interesting because Ge-rich alloys should have a direct band gap allowing efficient light emission as for Ge [10].

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Thanks to the people who are reading these lines, I hope that you enjoyed reading this manuscript as much as I enjoyed making all these crazy experiments.

Composition determination of SiGe alloys from X-ray Diffraction

1 Introduction

The goal of this part is to explain the fitting protocol used to estimate the different compositions present of a non homogeneous alloy. This method is a useful tool to estimate the compositions present in a sample during the synthesis steps. The general idea is to find a function suitable to fit pure Ge or pure Si XRD patterns, extract the parameters of this function and replicate this function to fit a composition gradient. Fityk software was used for this purpose, using Levenberg-Marquardt algorithm [150].

2 Fitting process

2.1 Function used

A SplitVoigt function is used to fit correctly the following problems :

- Using a conventional copper source, two wavelength are present λ_{α_1} and λ_{α_2} at 1.544390 and 1.540598 Å. The intensity of the λ_{α_1} is half the intensity of λ_{α_2} .
- The center of the second peak is function of the center of the first peak, this function is given by the Bragg law :

$$\begin{cases} 2d\sin(\theta_1) = n\lambda_{\alpha_1} \\ 2d\sin(\theta_2) = n\lambda_{\alpha_2} \end{cases} \rightarrow \frac{\lambda_1}{\lambda_2} = \frac{\sin(\theta_1)}{\sin(\theta_2)} \rightarrow \arcsin\left(\frac{\lambda_2}{\lambda_1} * \sin(\theta_1)\right) \quad (\text{A.1})$$

- The peak shape of X-ray data is usually a combination of Gaussian and Lorentzian profiles. Here we use a Pseudo-Voigt function which is the sum of a gaussian and lorentzian profiles having the same area. The proportionality factor between the two is noted η the Lorentz parameter.

$$PV(\text{height}, \theta, hwhm, \eta) = \text{height} \left[(1 - \eta) \exp\left(-\ln(2) \left(\frac{x - \theta}{hwhm}\right)^2\right) + \frac{\eta}{1 + \frac{x - \theta}{hwhm}} \right]^2 \quad (\text{A.2})$$

- To take into account experimental asymmetry measured for silicon and germanium, we use a Split Voigt

with different left and right FWHM. This function is defined as a Split-PV :

$$Split - PV = \begin{cases} PV(height, \theta, hwhm_L, \eta) & \text{if } x < \theta \\ PV(height, \theta, hwhm_R, \eta) & \text{if } x > \theta \end{cases} \quad (\text{A.3})$$

- The final function is the sum of two Split-PV, to take into account the two wavelengths considered.

In figure A.1 is presented different Split-PV function with different parameters.

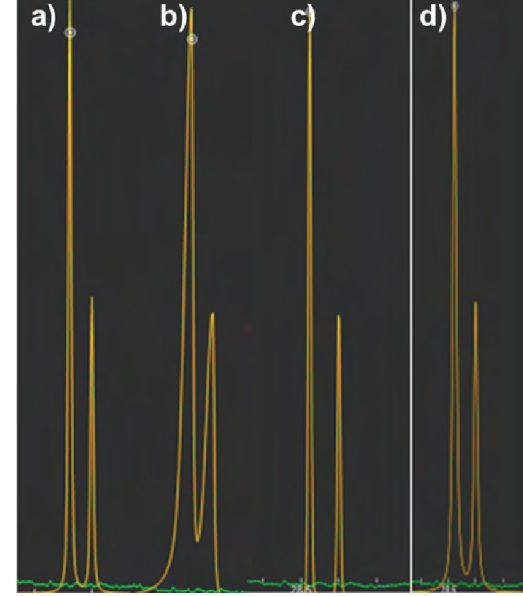


Figure A.1: a) symmetric half Gaussian Lorentzian $\eta = 0.5$ b) Same with left asymmetry $HWHM_{left} = 4 * HWHM_{right}$ c) Gaussian $\eta = 0$ d) Lorentzian $\eta = 1$

2.2 Extraction of parameters

The protocol used to fit an inhomogeneous alloy is presented in figure A.2. First we proceed to a fit of a reference, in our case silicon is used. Then, we fix all the parameters of this function (except height and position). Finally, we replicate this function as many time as needed to fit the diffraction pattern of a inhomogeneous alloy.

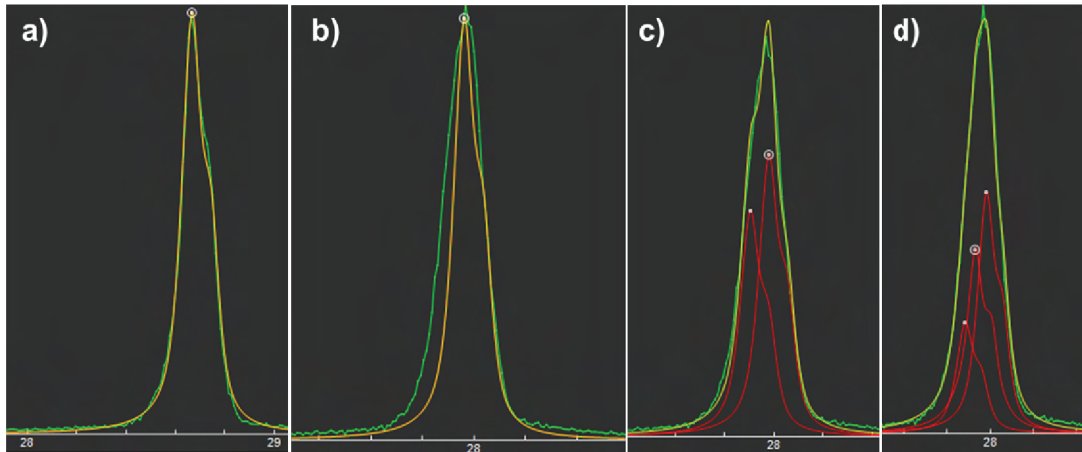


Figure A.2: a) One function fitting of pure Silicon. b) Reproduction of this same function to fit an homogeneous alloy c) d) adding multiple "Si-like" functions in order to fit the inhomogeneous alloy.

The extracted parameters are the following :

- With the peaks positions we can estimate the compositions using a Vegard law.
- With the area of each peak, we can obtain the fraction corresponding to each composition.
- With both parameters we can therefore obtain proportion of each composition in the inhomogeneous alloy.

The results obtained for our example are shown in table A.1.

Function number	Center [2 θ]	Area [a.u]	Composition [at.%Si]	Composition proportion [%]
Func.1	27.871	0.040	43.22	18
Func.2	27.927	0.077	47.24	36
Func.3	27.982	0.099	51.17	46

Table A.1: Fitting results of an inhomogeneous alloy using three functions.

The results are displayed on a bar chart as shown in figure A.3, the y axis represent the composition proportion (in % of the total area fitted). Each bar represent a given composition (in % of silicon). On the x axis, the name of the aimed composition and measured composition distribution are displayed. When the number of different compositions present in a inhomogeneous sample is too large, a composition interval is displayed.

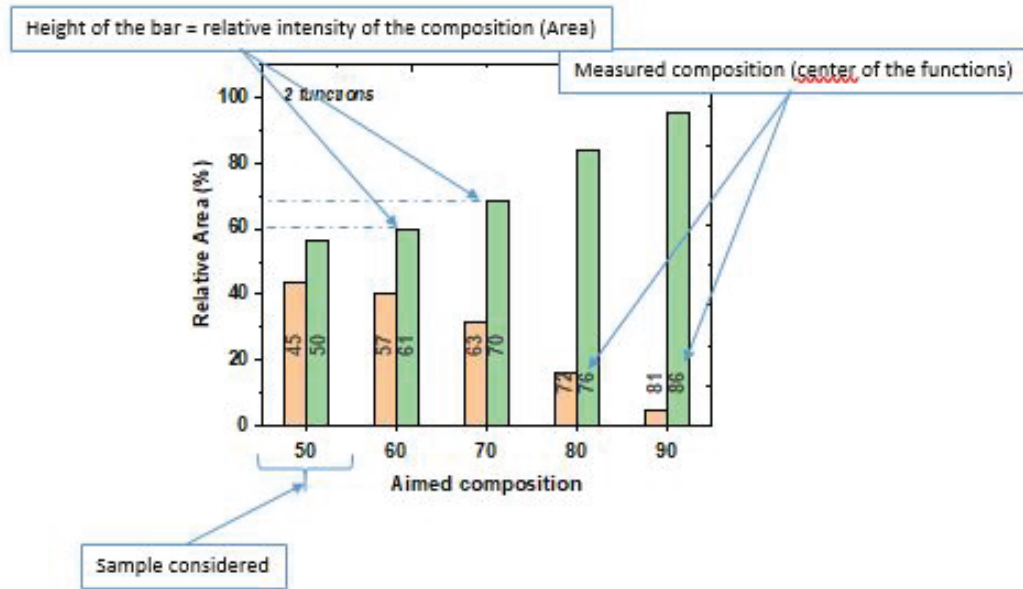


Figure A.3: Typical presentation of fitting results.

This method is used to estimate the different compositions inside a SiGe alloy sample, and is not meant to extract other sample properties. This method is however a useful tool during the synthesis, to represent visually the compositions present in an alloy.

Simulation tools

In the context of this work, ab initio simulations of SiGe alloys were made in collaboration with Silvana Elena Radescu Cioranescu, professor at the University de La Laguna (Spain). The results shown here have not been simulated by me, but are the result of a collaborative work and many discussions, where experimental observations and theoretical simulations are guiding each other.

As discussed in Section 1.2 SiGe alloys can be understood as a random alloy whose lattice parameters obey Vegard's law. The Raman spectra of SiGe alloys can be obtained within the harmonic approximation using a cluster expansion method [151]. However, due to the disorder associated with the solid solution, the symmetry of the simulation clusters is lower than that of the crystallographic phase. Typical simulation supercells with this method have often just the trivial identity as the only symmetry operation (SG1). Therefore, all the calculated Γ modes of the simulated alloy are Raman and Infrared active. This give rise to a very high number of modes, and it is not likely to be a good representation of the real alloy.

The solution used in the simulation is to decompose the modes of the disordered structures according to the irreducible representations of the modes corresponding to the proper symmetry "ideal-ordered" structure. This approach was recently proposed by Ikeda et al. [152] and proved efficient for different disordered alloys such as CuAu. With this method, the modes obtained at the zone center (Γ point) can be analyzed in a rather similar form as for an ordered system (with its high crystallographic symmetry). The positions of the peaks of the spectral function curve are then obtained by the unfolding method [152], which reflects the crystallographic symmetry. With this method, a complete vibrational analysis of disordered SiGe alloys is possible, from the ambient pressure to HP.

Simulation results

The results here are given as an example for the composition $Si_{0.75}Ge_{0.75}$. They are compared to our experimental measurements in section 7.3.

One first result that can be obtained from the simulations is the vibrational density of state (or phonon density of state). This gives information on the distribution of phonons in the energy scale. In our case, it is possible to discriminate between the contributions to the vibrational dynamics of Si and Ge as shown figure B.1. It can be observed, for example, that the contribution of Si is relevant in the high frequency range, contrary to Ge.

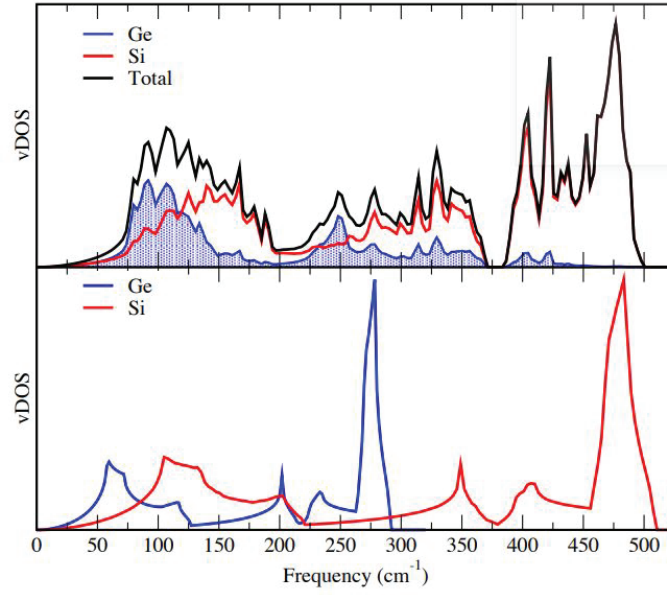


Figure B.1: Calculated vibrational density of state for $Si_{0.75}Ge_{0.25}$.

A second result is the frequency of the optical phonon at the zone center (Γ point). The symmetry analysis of the eigenvectors associated with each mode is made in order to identify Raman or infrared activity. Apart from the mode assignment at ambient pressures, these calculations can be extended at a range of volumes and respective pressures allowing the study of the evolution of the frequencies of the different modes under compression as shown in figure B.2.

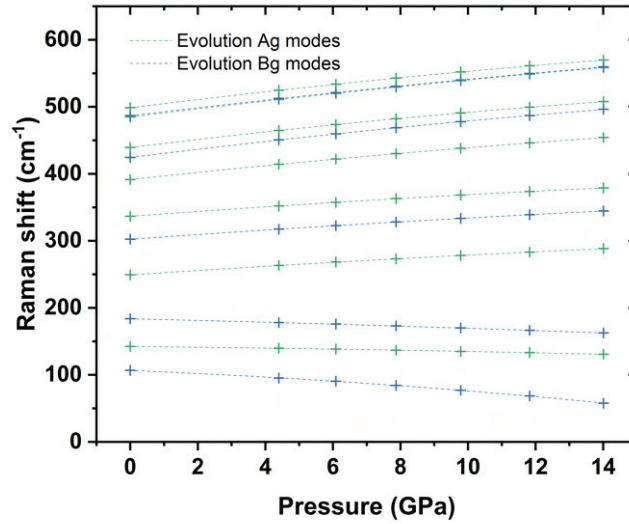


Figure B.2: Calculated pressure evolution of the calculated modes for $Si_{0.8}Ge_{0.2}$.

A third result is the decomposition of the partial spectral function at Γ point for the disordered Si-Ge alloys shown in figure B.3. With this, we can attribute to each of the frequencies obtained the contribution of the Ge-Ge or Si-Si bonds.

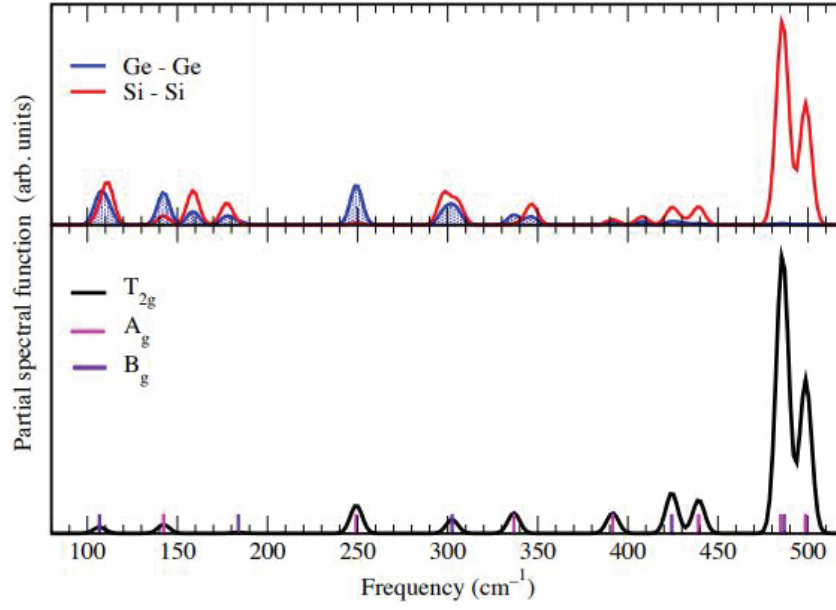


Figure B.3: Partial spectral function at Γ point for $Si_{0.75}Ge_{0.25}$ composition. The ticks represent each of the frequencies obtained from the disordered structure. It can be seen how each peak of the partial spectral function corresponds to the irreducible mode of the disordered alloy.

Finally the enthalpy of the different phases at ambient conditions and HP can be obtained. The relative enthalpy differences give information on the possible pressure-driven transitions and coexistence pressures between the different phases as shown figure B.4.

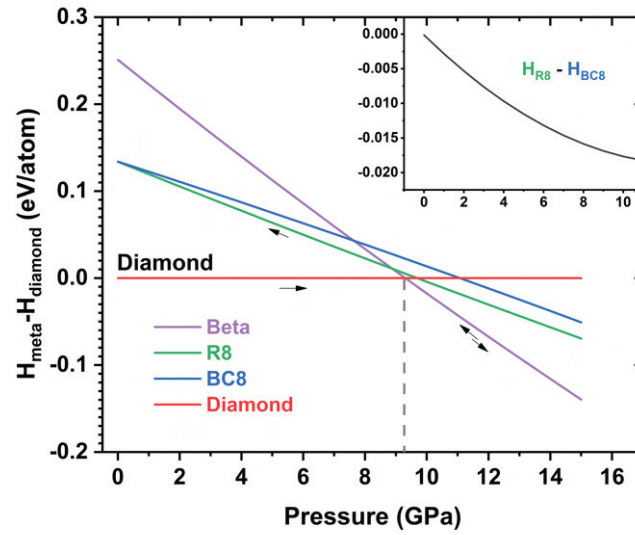


Figure B.4: Enthalpy of various structures of $Si_{0.75}Ge_{0.25}$ alloy in function of pressure. Showing that during compression, enthalpies of the diamond and β phases are predicted to cross at 9.4 GPa. A pressure induced transition between diamond and β phase is therefore predicted at this pressure.

In conclusion, ab-initio simulations provides the framework to not only predict structural properties and stability domains of different phases but also gives information on band structure and vibrational properties of our materials. The analysis of the disordered alloys for each phase within the framework of the band unfolding method allows the study of the simulated system in terms of the symmetry and the irreducible modes of the real material. A further analysis of all the alloys simulations is still in progress but preliminary results are shown in this manuscript in the respective section of each alloys.

Technical details

All the DFT calculations for the analysis of the SiGe alloys were performed using the Vienna ab initio simulation package (VASP) [153, 154, 155]. A projector-augmented-wave scheme (PAW) [156] was used and explicitly included the semicore d electrons of Ge as well as the outermost s and p electrons, adopting the so-called PBEsol generalized gradient approximation (GGA) for the exchange and correlation functional. The cutoff in the plane waves basis set was taken at 375 eV. For the integration over the Brillouin zone a 10x10x10 Monkhorst-Pack grid was used. The SiGe alloys were simulated by means of the ATAT cluster expansion scheme [151], with cluster sizes up to 16 atoms, which is necessary to obtain accurate cluster convergence (the cross validation score was 0.34 meV). To calculate the phonons, a post processing Phonopy [157] package to analyze the vibrational modes was used.

Oven calibration curves

This section contains information about the oven used for HT treatments of the synthesis results presented chapter 2. Two different ovens were used, the first one is able to reach temperatures up to 1600°C, the second 1200°C. Both were tubular ovens, specially designed for HT treatments under a protective atmosphere (see in figure C.1). Knowledge about internal temperature versus "set" temperature is crucial both for the conduction of the experiment, and the reproducibility of HT treatments in other ovens.

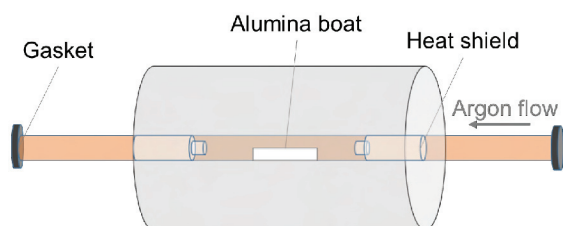


Figure C.1: Schematic view of a tubular oven

1 Horizontal Carbolite (STF 16/180) tubular oven $T_{\max} = 1600^{\circ}\text{C}$

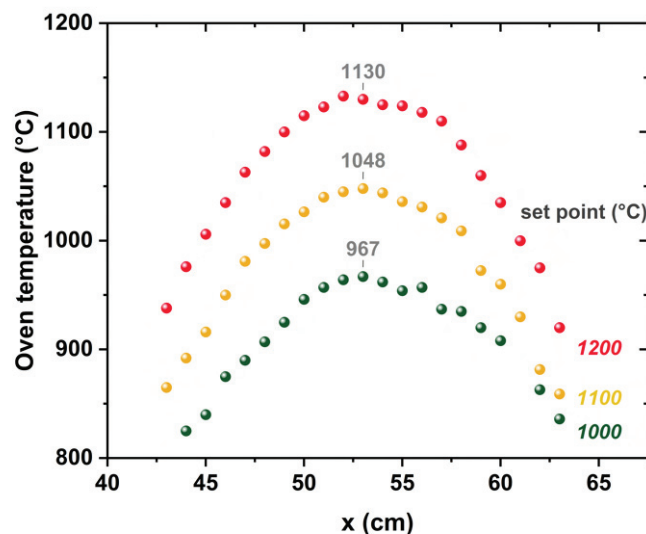


Figure C.2: Calibration curve determined for the horizontal Carbolite (STF 16/180) oven measured at different positions in the oven tube.

As solid state reaction is a slow process, annealing at optimal maximum temperature is extremely important. The oven calibration were measured using a K type thermocouple allowing temperature measurements up to 1200°C . For the measurement one of the two heat shield (see in figure C.1) was removed to insert the thermocouple. It is possible that a modification of the reached temperature appear during the shield removal and should be seen as an asymmetry in the temperature gradient.

The calibration curve of set values VS measured values is shown in figure C.3. The curve follows a linear tendency in the range $1000\text{--}1200^{\circ}\text{C}$. Assuming that this linear dependence is valid outside this region, we can predict the values outside the measured range. There is a large difference between the set temperature and the reached temperature especially at high temperature. The focus point where temperature reaches a plateau is very narrow ($<5\text{ cm}$) inherent to the capacity of the oven to go at very high temperatures. During annealing, these temperatures differences, and focused region length are taken into account. No clear asymmetry is measured, indicating that removing one of the two heat shields does not produce a significant modification of the internal temperature or is limited to regions outside the focused region where the highest temperature is reached.

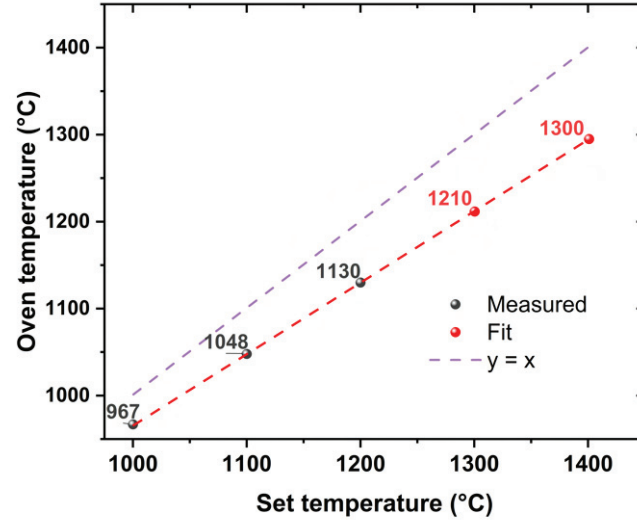


Figure C.3: Calibration curve of the temperature measured at the middle of the Horizontal Carbolite (STF 16/180) oven versus set temperature.

The relation between set and measured internal temperature of the oven in the 967- 1130°C temperature region is given by $T_{meas} = 0.815(1) * T_{set}$.

2 Horizontal Carbolite (CTF12/75/700) tubular oven $T_{max} = 1200^{\circ}\text{C}$

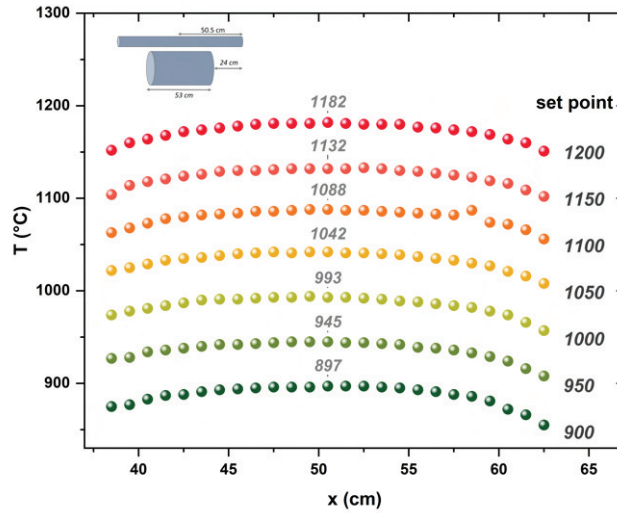


Figure C.4: Horizontal Carbolite (CTF12/75/700) tubular oven temperature measurements as a function of the position in the tube.

This oven is made for reaching temperature up to 1200 °C, and show an extremely precise internal vs "set" temperature and a large region where the temperature is centered around the set temperature (~ 10 cm) . These parameters indicate that, despite a lower maximum temperature of 1200°C, annealing in this oven are more flexible than in the previous one, allowing larger sample.

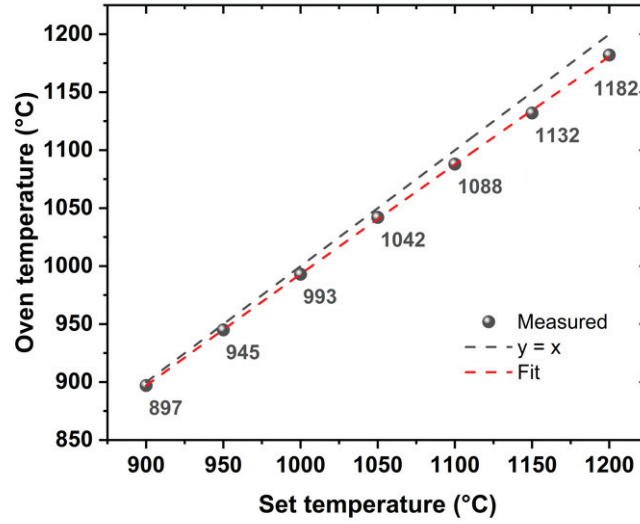


Figure C.5: Horizontal Carbolite (CTF12/75/700) tubular oven calibration curve.

The relation between set and measured internal temperature of the oven in the 900-1200°C temperature region is given by $T_{meas} = 0.945(5) * T_{set}$.

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Synthesis, high pressure behaviour and metastable phases of Si_xGe_{1-x} alloys

Abstract : Understanding the transition pathway toward metastable phases in SiGe alloys is a key issue for future generations of semiconductor and energy-related technology. High pressure techniques have proven to be a very efficient method of exploring new phases and properties in germanium and silicon, leading to the discovery of a large number of metastable phases with exotic properties. However, there is only a few experimental reports on the high-pressure behaviour of Si_xGe_{1-x} alloys, mainly due to the difficulty to synthesize homogeneous SiGe alloys of good quality. In this study, we first present synthesis pathways toward homogeneous polycrystalline SiGe alloys of different compositions using arc melting and high temperature treatments. Then, we report the high pressure behaviour of Ge and SiGe alloys studied using Paris-Edinburgh press and diamond anvil cells coupled with in-situ characterization techniques such as Raman spectroscopy and X-ray diffraction. Upon compression, the behaviour of the stable SiGe diamond phase is reported along with transition toward the β -metallic phase. During decompression, the formation of new metastable structures named SiGe-R8 and SiGe-BC8 is observed in SiGe alloys. Temperature is discussed as a key parameter to drive the diamond to β -metallic transition in large volume presses, possibly allowing synthesis of large quantities of metastable phases. The experimental results are discussed in comparison to those reported in the literature and using DFT simulations.

Keywords : [SiGe alloys, synthesis, high pressure, metastable phase]

Synthèse, comportement haute pression et phases métastables du système Si_xGe_{1-x}

Résumé : Comprendre les mécanismes de transition vers les phases métastables des alliages silicium germanium est un levier clé pour les futures avancées technologiques dans le domaine des semi-conducteurs et de l'énergie. Les techniques haute pression ont démontrées leur efficacité pour explorer les propriétés ainsi que les nouvelles phases du silicium et du germanium, menant à la découverte de nombreuses phases métastables ayant des propriétés exotiques. Cependant, peu de travaux expérimentaux existent sur le comportement et les phases métastables accessibles des alliages silicium germanium. En effet, la synthèse d'alliages homogène et de bonne qualité est compliquée à mettre en œuvre expérimentalement. Dans cette étude, nous présentons d'abord un protocole permettant de synthétiser diverses compositions d'alliages en utilisant la fusion par arc suivie de traitements thermiques. Nous présentons ensuite les comportements à haute pression du germanium et des alliages SiGe en utilisant des expériences Paris-Edimbourg et cellule enclumes diamant couplées avec des techniques de caractérisation *in situ*, comme la diffraction des rayon X et la spectroscopie Raman. Durant la compression, nous analysons les propriétés structurales, mécaniques et vibrationnelles de la phase naturelle diamant des alliages SiGe, ainsi que le mécanisme de transition vers la phase β métallique. Lors de la décompression, nous observons la transition de nos alliages vers de nouvelles structures SiGe-R8 et SiGe-BC8. Le contrôle de la est un paramètre clé facilitant la transition dans les presses gros volumes, ouvrant la voie à des stratégies de synthèse des phases métastables. Les résultats expérimentaux sont discutés avec ceux de la littérature ainsi que des résultats obtenus par DFT.

Mots clefs : [Alliages silicium germanium, synthèse, haute pression, phase métastable]