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***In situ* study of the crystallization in GeTe<sub>0.26</sub>Se<sub>0.74</sub> thick film  
by synchrotron X-ray diffraction.**

P. Armand<sup>1,\*</sup>, R. Escalier<sup>1</sup>, J. Lizion<sup>1</sup>, C. Mocuta<sup>2</sup>, G. Silly<sup>1</sup>, A. Piarristeguy<sup>1</sup>

<sup>1</sup>: ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France

<sup>2</sup>: Synchrotron SOLEIL, L'Orme des Merisiers, Départementale 128, 91190 Saint-Aubin

\*Corresponding author: [pascale.armand@umontpellier.fr](mailto:pascale.armand@umontpellier.fr)

ORCID:	P. Armand	0000-0001-8921-5427
	A. Piarristeguy	0000-0002-8922-4566
	C. Mocuta	0000-0001-5540-449X
	G. Silly	0000-0001-8212-2359
	J. Lizion	0000-0001-9433-5394
	R. Escalier	0000-0003-4179-804X

**Abstract:**

Crystallization in unencapsulated GeTe<sub>0.26</sub>Se<sub>0.74</sub> amorphous 3 μm-thick films produced by thermal co-evaporation technique was studied by *in situ* temperature-dependent synchrotron powder X-ray diffraction from room temperature up to 418 °C and back to 30 °C. The experimental results obtained with a continuous heating rate of 2 °C/min under a protective nitrogen atmosphere showed that the crystallization process took place in several steps i) total crystallization of the amorphous phase to an intermediate crystallized phase, (ii) total transformation of the intermediate phase to a second crystallized phase. The intermediate phase corresponds to a solid solution with a metastable α-GeTe-like rhombohedral polar structure (*R3m*) presenting a uniaxial negative thermal expansion along the *c*-axis. The onset of crystallization to the polar structure is around 270 °C. The high-temperature phase

has a stable hexagonal structure with a  $P6_3mc$  space group. When cooling, until back to room temperature, the hexagonal structure is conserved. The effect of a changing heating rate from 2 to 0.1 °C/ min was also investigated. In this context, the crystallization scheme is modified.

**Keywords:** X-ray diffraction;  $\alpha$ -GeTe; Phase Change Material (PCM);  $\text{Ge}_4\text{Se}_3\text{Te}$ ; Negative Thermal Expansion (NTE)

## 1. Introduction

Phase Change Materials (PCMs) are characterized by their fast and reversible phase transformation between the amorphous and the crystalline state and by an exceptional difference in optic and electric properties between the two states [1 – 6]. The compound  $\alpha$ -GeTe is a well-known PCM model with a Ge–Te “metavalent-like” bond, an unconventional type of bonding in solids [7 – 9]. It has a rhombohedral structure ( $R3m$  space group), stable at ambient conditions, in which the Ge atoms have a distorted octahedral environment [10].

From a technological point of view, the brazing process during the integration stage of a PCM cell in embedded memories brings heat, thus high “amorphous state - crystallized phase” transition temperatures ( $\sim 260$  °C) of the PCM materials are required [11].

To overcome this technological problem,  $\alpha$ -GeTe material doped with light elements such as C or N, or Ge-Sb-Te films highly enriched in Ge have been considered [12, 13]. However, significant phase separations were observed during their crystallization. More recently, experimental studies have

focused on the role of Se in the enhancement of phase change properties of compositions synthesized in the GeTe-GeSe pseudo-binary [11 – 14, 16]. For example, Ren *et al.* [15] observed a fast (500 ns) and reversible electrical switching at about 270 °C for the GeTe<sub>0.74</sub>Se<sub>0.26</sub> (200 nm-thick film) sample with good data retention of 10 years at 208.5 °C. Structural measurements highlighted that GeTe<sub>0.74</sub>Se<sub>0.26</sub> (600 nm-thick film) had a metastable rhombohedral  $\alpha$ -GeTe-like structure with Se atoms randomly taking the place of Te atoms. Furthermore, Tomelleri *et al.* [11] explored the PCM potential of the entire GeTe-GeSe pseudo-binary. They managed to retain the metastable rhombohedral phase after annealing at 400 °C amorphous GeTe<sub>1-x</sub>Se<sub>x</sub> thin films (thickness ~ 80 nm) with  $0 \leq x \leq 0.84$ . It was observed that the contrast in resistivity between the amorphous and the metastable rhombohedral phase increased with Se content, reaching 11 orders of magnitude for the film with the highest Se content. For  $x = 0.84$ , very good data retention of 10 years at 272 °C was estimated.

These results are very promising for the development of PCMs with high transition temperatures and therefore, a more detailed study of these Ge-Te-Se solid solutions seems necessary in particular for the ternary compositions with high Se content.

According to the phase equilibria in the GeTe-GeSe pseudo-binary system established from bulk samples [17 – 19], three different crystal structures exist at room temperature as a function of the composition. The GeTe<sub>1-x</sub>Se<sub>x</sub> ( $0 \leq x \leq 1.0$ ) alloys are in the rhombohedral  $\alpha$ -GeTe structure for  $x \leq 0.5$ . Between  $x = 0.61 \pm 0.03$  and  $0.85 \pm 0.03$ , a single-phase of general composition GeTe<sub>0.25</sub>Se<sub>0.75</sub> (Ge<sub>4</sub>Se<sub>3</sub>Te) is observed with a hexagonal structure ( $P6_3mc$  space group) stable only below ~ 400 °C [20 – 22]. The coexistence of the two structures is reported between the rhombohedral and the hexagonal domains. For  $x \geq 0.95$ , the solid solutions present an orthorhombic structure as the pure covalent  $\alpha$ -GeSe phase with  $Pnma$  space group [23]. The small domain in composition between the hexagonal and the orthorhombic domains contains the two structures.

However, when the system is out of thermodynamic equilibrium, the GeTe-GeSe solid solutions synthesized as films switch between the amorphous phase and the metastable rhombohedral phase for chemical compositions where only the hexagonal phase is found when the system is in equilibrium [11, 15]. These out-of-equilibrium conditions are encountered in the PCM memories, and therefore these systems need to be studied in detail.

In the present work, we are studying the crystallization of a  $\text{GeTe}_{0.26}\text{Se}_{0.74}$  thick film at different heating rates by *in situ* synchrotron X-ray diffraction (XRD) measurements to examine the competition between the different types of bonds: the "metavalent bonds" announced in the rhombohedral phases [7 – 9] and the covalent bonds present in the hexagonal phases [20 – 22].

## 2. Experimental section

### 2.1 Samples synthesis

$\text{GeTe}_{0.26}\text{Se}_{0.74}$  3  $\mu\text{m}$  thick films were deposited on glass substrates by thermal co-evaporation of the pure elements (Ge pieces from Goodfellow, Te pieces, and Se granules from ChemPur, each one with a purity of 99.999%) using a PLASSYS MEB 500 device equipped with two current-induced heated sources and an electron beam evaporator. The two current-induced heated sources were used to evaporate selenium and tellurium, whereas the electron beam was used to evaporate germanium. Before the deposition, the chamber was evacuated down to approximately  $10^{-5}$  Pa. During the deposition process, the substrate holder was rotated and heated to approximately 90 °C using hot water circulation. The deposition rates of the three elements were automatically controlled with pre-calibrated quartz crystal monitors. The deposition was initiated once the deposition rates of the elements have been stabilized. The as-deposited  $\text{GeTe}_{0.26}\text{Se}_{0.74}$  films were found to be amorphous and were then characterized without annealing or capping. As it has been shown for GeTe films thicker

than 50 nm that the characteristic temperatures are not affected by oxidation [24], we have worked without protecting the films.

## 2.2 Characterizations

The chemical composition of the deposited films was measured at room temperature, before and after heat treatment, by energy-dispersive X-ray (EDX) spectroscopy with a Zeiss EVO HD15 instrument equipped with an Oxford Instruments X-Max N Si drift detector (SDD) EDX. EDX analysis is a semi-quantitative method that allows probing to a depth of about 1  $\mu\text{m}$ .

Synchrotron XRD patterns were collected *in situ* from room temperature up to high temperature on DiffAbs beamline at SOLEIL Synchrotron (Saint-Aubin, France). The X-ray beam (11.015 keV, wavelength of 1.1256 Å) was monochromatized using a Si (111) double crystal monochromator, and focused to a size of about  $180 \times 200 \mu\text{m}^2$  (Full width at half maximum, FWHM). An incident angle of  $6^\circ$  was used for all the reported measurements. The XRD measurements were performed using a 6-circle diffractometer (kappa geometry) and an XPAD-S140 two-dimensional detector [25, 26]. A compact furnace (Anton Paar model DHS-900) was used, consisting of a heating resistor encapsulated in the heating plate (AlN). An aluminum-made dome, equipped with Kapton® 12  $\mu\text{m}$  thick windows allows the performing of XRD experiments in reflection geometry while minimizing parasitic scattering. The sample was placed on the heating stage, held by a system of clips, and heated by thermal contact. A thermocouple encapsulated in the heating plate measures the temperature in real-time. All experiments were performed under nitrogen flow, to prevent sample oxidation and ensure good thermal homogeneity and a small temperature difference between the furnace and the sample. The diffractograms were recorded continuously during different temperature ramps ( $2^\circ \text{C}/\text{min}$ ,  $0.2^\circ \text{C}/\text{min}$ , and  $0.1^\circ \text{C}/\text{min}$ ), and different maximum temperatures were reached (between 285 and  $420^\circ \text{C}$ ) depending on the heating rate. For the cooling process, the furnace temperature was decreased

continuously at a rate of 50 °C/min down to about 150°C. Then, the inertial cooling became lower to reach room temperature.

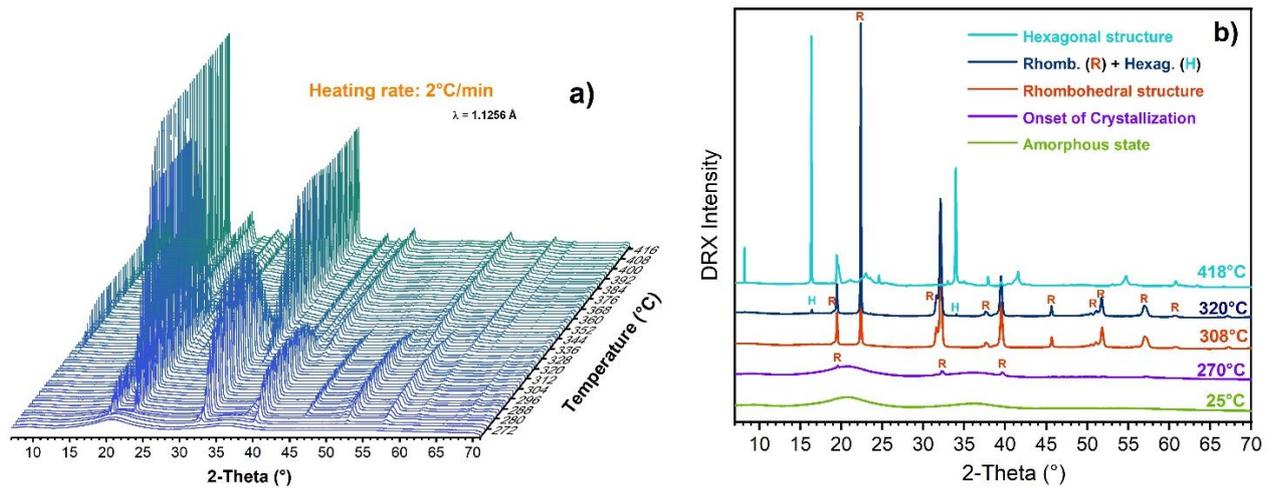
The lattice parameters of the crystalline phases were obtained by the refinement of the diffraction patterns with the LeBail method using the Fullprof program package [27].

### 3. Results

The room temperature chemical analysis of the 3 μm thick amorphous film deposited on a glass substrate leads to a composition of Ge<sub>50</sub>Te<sub>13</sub>Se<sub>37</sub> (GeTe<sub>0.26</sub>Se<sub>0.74</sub>) with an error estimated of ± 3 atomic % [28]. This composition is in the large domain of the existence of crystalline GeTe<sub>1-x</sub>Se<sub>x</sub> solid solutions having the stable hexagonal-type structure with  $0.61 \pm 0.03 \leq x \leq 0.85 \pm 0.03$  [20]. All the solid solutions in this large chemical domain of existence of the hexagonal single-phase in the GeTe-GeSe pseudo-binary have the general name “Ge<sub>4</sub>Se<sub>3</sub>Te” (GeTe<sub>0.25</sub>Se<sub>0.75</sub>). The temperature dependence on heating of the structural evolution of the amorphous GeTe<sub>0.26</sub>Se<sub>0.74</sub> film was followed by *in situ* synchrotron XRD measurements.

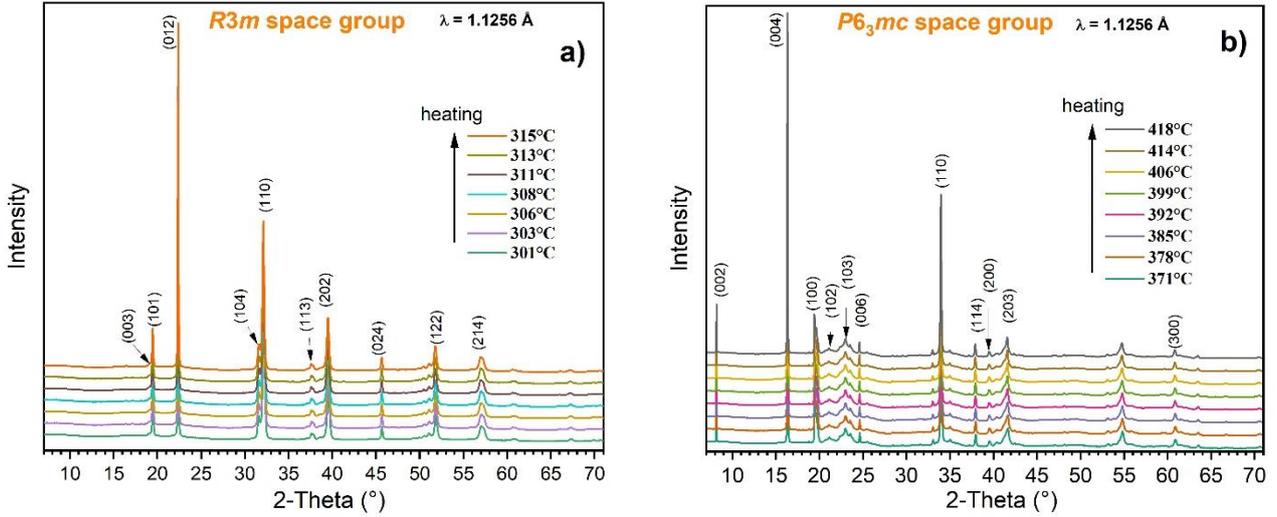
#### 3.1 Heating rate of 2 °C/min

The temperature ramp was 20 °C/min from 20 to 200 °C then, 2 °C/min up to 418 °C. The recorded X-ray scattered signals in the temperature domain from room temperature up to 268 ± 2 °C are characteristic of an amorphous state: with the absence of diffraction peaks and no significant evolution with the temperature being observed, Figure 1. The appearance of diffraction peaks starts at the temperature of 270 ± 2 °C corresponding to the onset of crystallization noted T<sub>x</sub>, Figure 1(b).



**Figure 1:** (a) A series of synchrotron diffractograms as a function of heating temperatures for an as-deposited  $\text{GeTe}_{0.26}\text{Se}_{0.74}$  thick film. (b) Selected temperatures to evidence the structural transitions from an amorphous state to rhombohedral-type and then to the hexagonal-type structure. H = hexagonal characteristic peaks, R = rhombohedral characteristic peaks.

In the temperature range  $270\text{ °C} \leq T \leq 298\text{ °C}$ , the amorphous part of the as-deposited sample decreases while the crystallized proportion increases to obtain a complete-crystallized sample with the rhombohedral structure from  $300 \pm 2\text{ °C}$  to  $315 \pm 2\text{ °C}$ , Figures 1 and 2(a). From  $317 \pm 2\text{ °C}$ , we may notice the apparition of new diffraction peaks compared to those already present, see Figure 1(b). These new peaks are due to the apparition of a second crystalline phase with a different structure, a hexagonal structure. For  $317\text{ °C} < T < 370\text{ °C}$ , the two phases coexist, Figure 1(b). Above  $370\text{ °C}$ , only the hexagonal structure is found, Figure 2(b).



**Figure 2:** Temperature range showing the evolution of XRD patterns of the GeTe<sub>0.26</sub>Se<sub>0.74</sub> crystalline phase with (a) a rhombohedral structure *R3m* (301 to 315 °C) and (b), a *P6<sub>3</sub>mc* hexagonal structure (371 to 418 °C). Only the main reflections were indexed on the graphs. The heating rate was 2 °C/min.

### 3.1.1 The rhombohedral “Ge<sub>4</sub>Se<sub>3</sub>Te” phase

Figure 2(a) highlights the temperature range of the existence of the intermediate phase, which corresponds to the metastable rhombohedral structure with the low-symmetry *R3m* structure of the general composition “Ge<sub>4</sub>Se<sub>3</sub>Te”. This non-centrosymmetric phase is present as a single phase only over a very narrow temperature range  $\Delta T = 14 \text{ °C}$  when continuously heating, with a rate of 2 °C/min, the GeTe<sub>0.26</sub>Se<sub>0.74</sub> thick film under nitrogen flow. The diffractograms do not show the presence of a parasitic crystalline phase as, for example, an elemental Ge one.

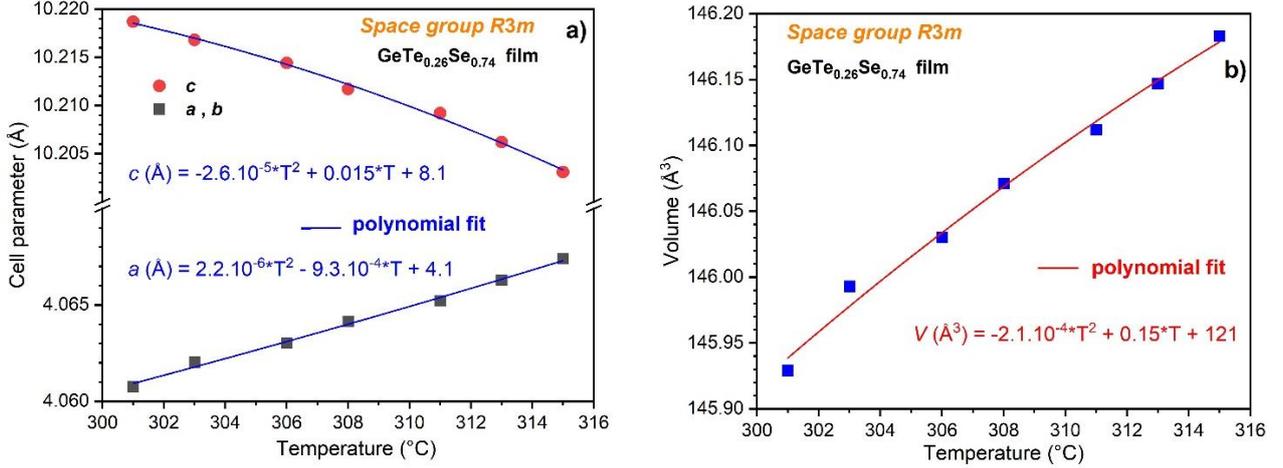
The temperature evolution of the rhombohedral structure of the GeTe<sub>0.26</sub>Se<sub>0.74</sub> thick film was analyzed in the 301 – 315 °C range with a LeBail-type refinement of the powder diffractograms (*a* and *c* in the hexagonal description of the rhombohedral lattice), Table I. The results pointed out cell parameter changes due to thermal expansion and deformation with increasing temperature. For comparison, room temperature parameters obtained from refinements by the Rietveld method of an X-ray powder

diffraction pattern of a “Ge<sub>4</sub>Se<sub>3</sub>Te” bulk sample obtained by the melt quenching method [14] or chemical vapor transport [22] are presented in Table I.

**Table I:** Lattice parameters ( $a$ ,  $c$ ), unit cell’s volume ( $V$ ), and  $c/a$  ratio in the function of the registered temperature on heating (2 °C/min) for the as-deposited GeTe<sub>0.26</sub>Se<sub>0.74</sub> film in the metastable rhombohedral structure  $R3m$  ( $a$  and  $c$  in the hexagonal description of the rhombohedral lattice). The data in *italic* are from [14, 22].

<b>T (°C)</b>	<b><math>a = b</math> (Å)</b>	<b><math>c</math> (Å)</b>	<b><math>V</math> (Å<sup>3</sup>)</b>	<b><math>c/a</math></b>
20 [22]	<i>3.9820(4)</i>	<i>10.374(2)</i>		<i>2.6052</i>
20 [14]	<i>4.01731</i>	<i>10.4293</i>	<i>145.71</i>	<i>2.5961</i>
301	4.0608(4)	10.2187(3)	145.929(5)	2.5165
303	4.0620(4)	10.2168(3)	145.993(5)	2.5152
306	4.0630(4)	10.2144(3)	146.030(5)	2.5140
308	4.0641(4)	10.2117(3)	146.071(5)	2.5126
311	4.0652(4)	10.2092(3)	146.112(5)	2.5114
313	4.0663(4)	10.2062(3)	146.147(5)	2.5100
315	4.0674(4)	10.2031(3)	146.183(5)	2.5085

Figure 3 presents the variations of the lattice parameters and unit cell’s volume in the temperature range 301 – 315 °C of the GeTe<sub>0.26</sub>Se<sub>0.74</sub> thick film. Both the  $a$  lattice parameter and the volume increase as a function of temperature, while the  $c$  parameter decreases.



**Figure 3:** Temperature range (301 to 315 °C) showing the evolution of (a) the lattice parameters  $a$  and  $c$ , and (b) the unit cell's volume  $V$  of the crystalline phase “ $\text{Ge}_4\text{Se}_3\text{Te}$ ” with a rhombohedral structure ( $a$  and  $c$  in the hexagonal description of the rhombohedral lattice). Solid lines are fitted curves of the experimental data. Error bars are smaller than the symbols. Heating rate of 2 °C/min.

The results of the two-degree polynomial fits of the curves are given in the graphs, Figure 3(a) for  $a$  and  $c$  experimental lattice parameters, and Figure 3(b) for the unit cell's volume  $V$ .

The mean linear thermal expansion coefficients  $\alpha$  – mean, at constant pressure, of the polycrystalline film, were calculated using the expression:

$$\alpha - \text{mean}(X) (\text{°C}^{-1}) = \frac{X_{\max} - X_{\min}}{T_{\max} - T_{\min}} \frac{1}{X_{\min}}$$

where  $X_{\max}$  and  $X_{\min}$  are either the lattice parameters  $a$  or  $c$  or the volume  $V$  of the cell at temperatures  $T$  maximum and  $T$  minimum.

The values calculated in the temperature range 301 – 315 °C are,  $\alpha\text{-mean}(a=b) = 1.16 \times 10^{-4} \text{ °C}^{-1}$  and  $\alpha\text{-mean}(c) = -1.09 \times 10^{-4} \text{ °C}^{-1}$ . We notice the anisotropy of the thermal expansion, with a positive coefficient of expansion following the  $a$  parameter, while that following  $c$  is negative, Figure 3(a).

The unit cell's volume  $V$  increases in the 301 – 315 °C temperature range, Figure 3(b), with  $\alpha\text{-mean}(V) = +1.24 \times 10^{-4} \text{ °C}^{-1}$ , and the  $c/a$  ratio decreases, Table I.

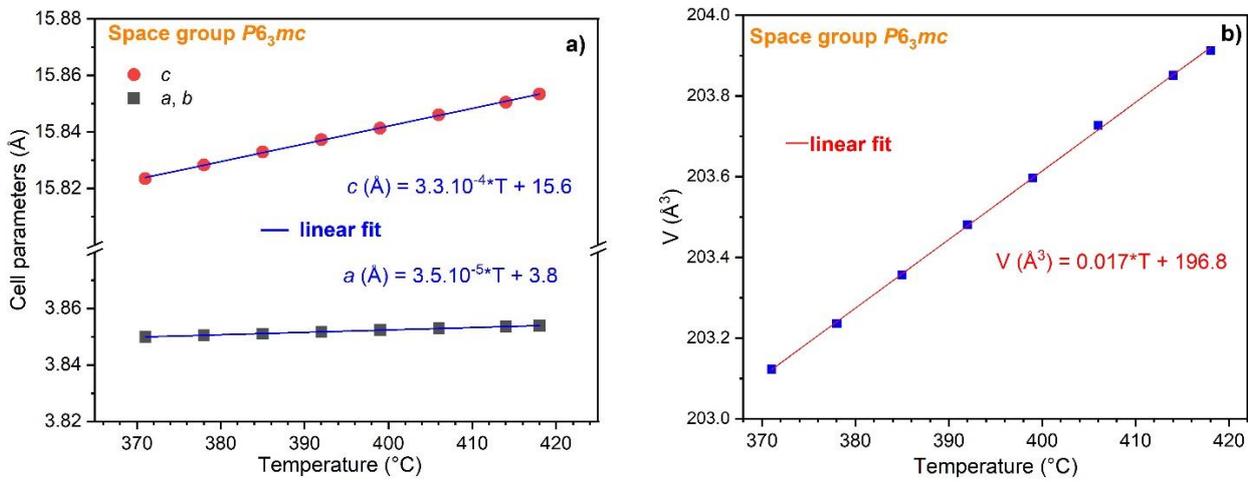
### 3.1.2 The hexagonal polymorph of “Ge<sub>4</sub>Se<sub>3</sub>Te”

A new polymorph with a hexagonal structure exists as the only crystalline phase from 371 °C to the highest recorded temperature of 418 °C, Figure 2(b). The high-temperature crystallized phase corresponds to the stable hexagonal “Ge<sub>4</sub>Se<sub>3</sub>Te” phase with the  $P6_3mc$  structure. Table II reports on the temperature evolution of cell parameters analyzed with a LeBail-type refinement of the powder diffractograms recorded between 371 °C and 418 °C. For comparison, room temperature lattice parameters obtained from bulk samples [18, 22] are presented in Table II.

**Table II:** Lattice parameters ( $a$ ,  $c$ ), unit cell’s volume ( $V$ ), and  $c/a$  ratio in the function of the recorded temperature on heating (2 °C/min) for the as-deposited GeTe<sub>0.26</sub>Se<sub>0.74</sub> film in the hexagonal structure with  $P6_3mc$  space group. The data in *italic* are from [18, 22].

T (°C)	$a = b$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )	$c/a$
20 [18]	<i>3.805</i>	<i>15.56</i>		<i>4.089</i>
20 [22]	<i>3.8071(1)</i>	<i>15.6376(2)</i>		<i>4.1075</i>
371	3.8500(6)	15.8235(3)	203.123(6)	4.1100
378	3.8505(6)	15.8283(3)	203.236(5)	4.1107
385	3.8511(6)	15.8329(3)	203.357(5)	4.1113
392	3.8517(6)	15.8373(4)	203.481(7)	4.1120
399	3.8523(6)	15.8413(3)	203.597(6)	4.1121
406	3.8530(7)	15.8461(4)	203.727(7)	4.1127
414	3.8536(8)	15.8505(4)	203.851(8)	4.1131
418	3.8539(9)	15.8534(4)	203.913(9)	4.1135

Figure 4 presents the evolution in the temperature range 371 – 418 °C of the hexagonal lattice parameters of the  $\text{GeTe}_{0.26}\text{Se}_{0.74}$  thick film as deposited on glass with a heating rate of 2 °C/min. From 371 to 418 °C, the parameters  $a$ ,  $c$ , and  $V$  increase continuously and linearly. The results of the linear fits of the curves are given inside the graphs, Figure 4(a) for  $a$  and  $c$  experimental lattice parameters, and Figure 4(b) for the unit cell's volume  $V$ .

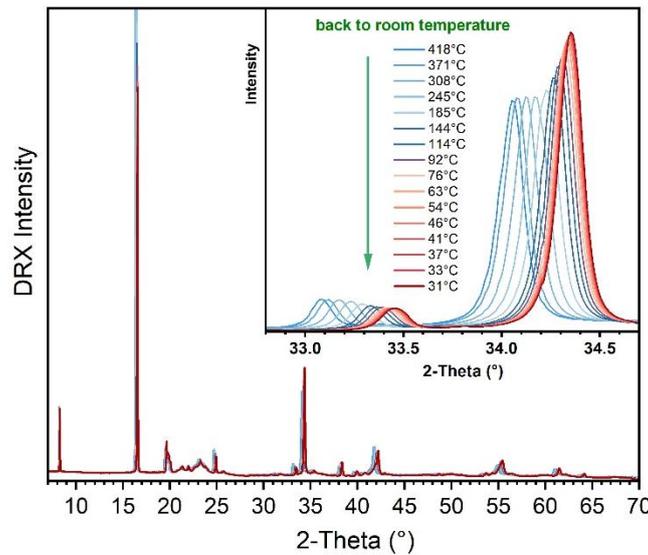


**Figure 4:** Temperature range showing the evolution of (a) the lattice parameters  $a$  and  $c$  and (b) the unit cell's volume  $V$  of the crystalline phase “ $\text{Ge}_4\text{Se}_3\text{Te}$ ” with a hexagonal structure (371 to 418 °C). Error bars are smaller than the symbols. The continuous heating rate was 2 °C/min. Solid lines are linear fittings of the experimental data.

The mean linear thermal expansion coefficients at ambient pressure calculated in the temperature range 371 – 418 °C, are  $\alpha\text{-mean}(a=b) = +2.93 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$  and  $\alpha\text{-mean}(c) = +4.18 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$ . All the lattice parameters present positive thermal expansions, Figure 4, as already reported for the hexagonal solid solutions [18]. The  $c/a$  ratio for the single-phase hexagonal solid solution  $\text{GeTe}_{0.26}\text{Se}_{0.74}$  is  $4.112 \pm 0.05$  % over the entire thermal region. A  $c/a$  ratio of  $4.109 \pm 0.5$  % was previously reported for the bulk  $\text{GeTe}_{1-x}\text{Se}_x$  solid solutions in the hexagonal domain ( $0.58 \leq x \leq 0.86$ ) recorded at ambient conditions [18].

### 3.2 Temperature decrease

After heating the thick film from room temperature to 418 °C, the temperature of the furnace was decreased continuously at a rate of ~50 °C/min down to ~150°C then slower, always under nitrogen flow. As expected, during cooling, the hexagonal-type structure of “Ge<sub>4</sub>Se<sub>3</sub>Te” which is the stable structure of this composition is conserved back to room temperature, Figure 5. We noticed a whole peak shift to larger values of 2 $\Theta$  corresponding to a decrease in the inter-reticular distances with cooling consistent with a contraction, see the insert in Figure 5.



**Figure 5:** Synchrotron ( $\lambda = 1.1256 \text{ \AA}$ ) diffractograms recorded in situ during cooling from 418 °C back to room temperature for the GeTe<sub>0.26</sub>Se<sub>0.74</sub> thick film deposited on glass.

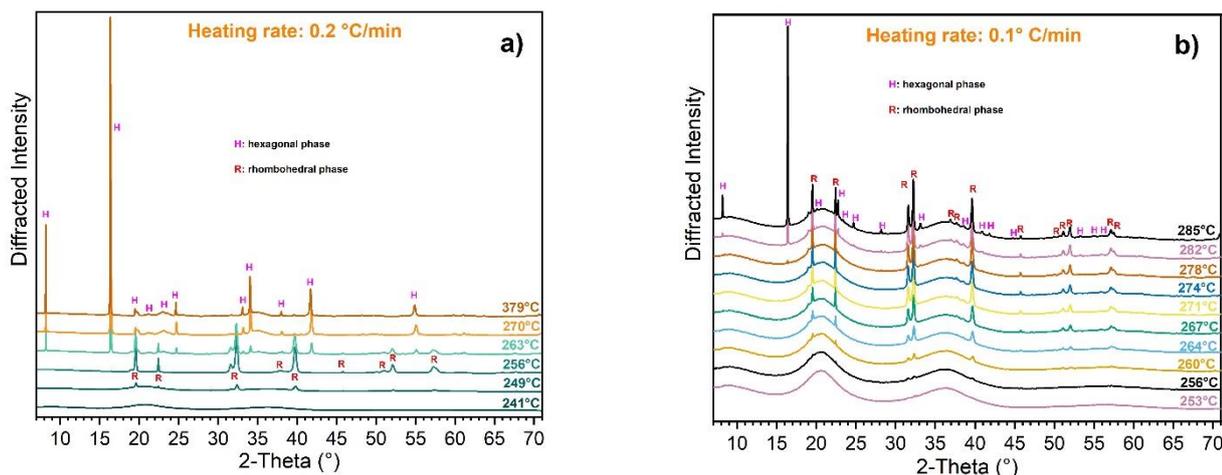
A recent work [11] on amorphous and encapsulated GeTe<sub>1-x</sub>Se<sub>x</sub> thin films (thickness ~ 80 nm) with  $0 \leq x \leq 0.84$  deposited at room temperature on Si (001) substrates by magnetron co-sputtering has studied their crystallization by annealing up to 400 °C at a heating rate of 10 °C/min and then cooling

down to room temperature. It has evidenced the metastable rhombohedral structure back to room temperature for all films [11]. This result differs from ours where the hexagonal-type structure is obtained at room temperature after the thick  $\text{GeTe}_{0.26}\text{Se}_{0.74}$  film was heated to 418 °C. The experimental conditions being rather different, the structural difference evolution may thus originate from the heating rate which was 2 °C/min here and 10 °C/min for Tomelleri *et al.* [11], from the film thickness (3  $\mu\text{m}$  for our film), the film preparation conditions, and/or the presence of a protected layer to avoid surface oxidation.

The chemical analysis performed on the back-to-room-temperature polycrystalline thick film is identical to the one before the thermal treatment. The LeBail refinement of the XRD pattern recorded at 31 °C after cooling gave, as hexagonal lattice parameters, the following values of the solid solution  $\text{GeTe}_{1-x}\text{Se}_x$  with  $x = 0.74$ :  $a = 3.8104(6)$  Å,  $c = 15.639(2)$  Å, and  $V = 196.646(3)$  Å<sup>3</sup>. These room temperature cell parameters are in very good agreement with previous works on bulk samples, see Table II [18, 22].

### ***3.3 Influence of the heating rate***

Several *in situ* synchrotron XRD patterns ( $\lambda = 1.1256$  Å) were collected under neutral gas (nitrogen) flow from room temperature up to high temperature with different heating rates to study the kinetic of the crystallization of a  $\text{GeTe}_{0.26}\text{Se}_{0.74}$  amorphous thick film. From ambient to 200 °C, the heating rate was 20 °C/min for each experiment and then, it was changed to 0.2 °C/min or 0.1 °C/min up to the highest recorded temperature, Figure 6.



**Figure 6:** A series of synchrotron diffractograms recorded *in situ* with  $\lambda = 1.1256 \text{ \AA}$  as a function of temperatures (a) with a heating rate of  $0.2 \text{ }^\circ\text{C/min}$  and (b), with a heating rate of  $0.1 \text{ }^\circ\text{C/min}$ , for the same as-deposited  $\text{GeTe}_{0.26}\text{Se}_{0.74}$  thick film.

Under the conditions of the continuous heating of the furnace, the heating rate (and thus the thermal budget) affects the kinetics of the crystallization behavior of uncovered  $\text{GeTe}_{0.26}\text{Se}_{0.74}$  thick films, Table III:

1) With a heating rate of  $2 \text{ }^\circ\text{C/min}$ , the onset of crystallization of the rhombohedral structure is  $T_{xI} = 270 \pm 2 \text{ }^\circ\text{C}$  and this “ $\text{Ge}_4\text{Se}_3\text{Te}$ ” polymorph is present as a unique and well-crystallized phase in the  $301 - 315 \text{ }^\circ\text{C}$  range before transforming to the hexagonal structure. For  $317 \text{ }^\circ\text{C} < T < 370 \text{ }^\circ\text{C}$ , the two polymorphs coexist, and above  $370 \text{ }^\circ\text{C}$ , only the hexagonal structure is detected, Figure 1(a).

2) With a heating rate of  $0.2 \text{ }^\circ\text{C/min}$ , Figure 6(a), the onset of transition from an amorphous state to the rhombohedral structure is  $T_{xI} = 249 \text{ }^\circ\text{C}$ . Only the rhombohedral form of “ $\text{Ge}_4\text{Se}_3\text{Te}$ ” is present as a unique phase at  $T = 256 \text{ }^\circ\text{C}$  before being completely transformed into the stable hexagonal structure at  $T = 270 \text{ }^\circ\text{C}$ . The onset of crystallization of the hexagonal structure is in the temperature range  $256 \text{ }^\circ\text{C} < T < 270 \text{ }^\circ\text{C}$ , Table III.

3) With a heating rate of  $0.1 \text{ }^\circ\text{C/min}$ , Figure 6(b), small diffraction peaks appear on the diffractogram recorded at  $T = 256 \text{ }^\circ\text{C}$  (onset of crystallization  $T_{xI}$ ) which are attributed to the rhombohedral form of the “ $\text{Ge}_4\text{Se}_3\text{Te}$ ” phase. Even with increasing the temperature from  $264$  to  $274 \text{ }^\circ\text{C}$ , the rhombohedral

phase was never obtained alone, a remaining amorphous part of the thick film is still present, Figure 6(b). At  $T_{x2} = 278$  °C, additional small diffraction peaks appeared which intensity increases with the temperature. In the 278 – 285 °C range, there is the cohabitation of three states, an amorphous state, a rhombohedral-like structure contribution, and the hexagonal polymorph of the general composition “Ge<sub>4</sub>Se<sub>3</sub>Te”.

**Table III:** Summary of crystallization onset temperatures observed in the function of the heating rate for the thick film of composition GeTe<sub>0.26</sub>Se<sub>0.74</sub>.

	<b>Heating rate</b>		
<b>Temperature</b>	<b>2 °C/min</b>	<b>0.2 °C/min</b>	<b>0.1 °C/min</b>
<b>T<sub>x1</sub></b>	270 °C <i>Rhombohedral form</i>	249 °C <i>Rhombohedral form</i>	256 °C <i>Rhombohedral form</i> + <i>Amorphous phase</i>
<b>T<sub>x2</sub></b>	318 °C <i>Hexagonal form</i>	256 °C < T < 270 °C <i>Hexagonal form</i>	278 °C <i>Rhombohedral form</i> + <i>Hexagonal form</i> + <i>Amorphous phase</i>

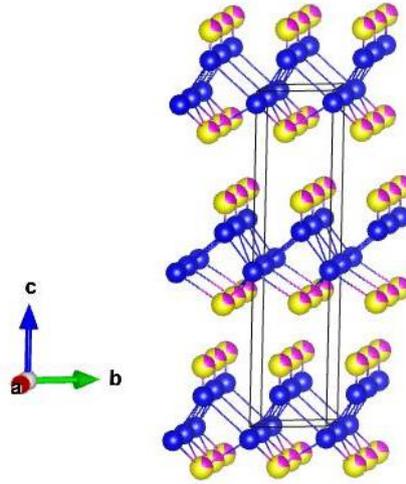
#### 4. Discussion

In atmospheric ambient conditions, the low-temperature ferroelectric  $\alpha$ -GeTe bulk crystal has a trigonal crystal system and the simple rhombohedron unit cell belongs to the non-centrosymmetric space group  $R3m$  [10, 29-33]. In the hexagonal setting, the unit cell parameters are  $a = b = 4.1719 \text{ \AA}$  and  $c = 10.710 \text{ \AA}$  ( $c/a = 2.567 > \sqrt{6}$ ). In  $\alpha$ -GeTe, the metavalent bond, a distinct nature of bonding located between the metallic and the covalent bond [9], promotes the atomic orbitals of the constituting atoms in some specific spatial directions. Consequently, the  $\text{Ge}^{2+}$  ion at the FCC primitive cell position is slightly off-center from the octahedral site.

Above the Curie temperature ( $\sim 400 \text{ }^\circ\text{C}$  in thermodynamic equilibrium [31]), the structural transition leads to the formation of the  $\beta$ -GeTe phase with a rock-salt cubic structure (space group  $Fm3m$ ). In the  $\beta$ -GeTe rhombohedral cell with an FCC configuration, the  $c/a$  ratio is  $\sqrt{6}$ . Ionic interactions, being less affected by thermal motion, prevail over some covalent characters in  $\beta$ -GeTe. This results in Ge atoms exactly positioned at the center of the primitive unit cell.

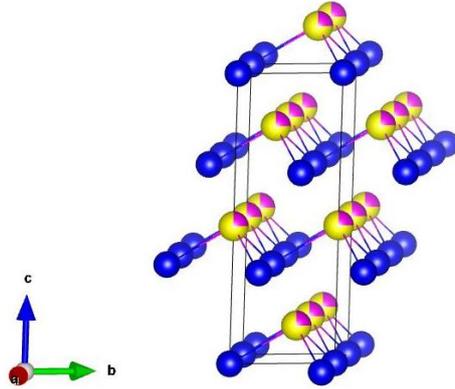
When replacing 75 % of the Te atoms with Se ones in pure GeTe, a completely different new-layered structure with a hexagonal lattice system is formed according to the phase equilibria in the GeTe-GeSe pseudo-binary system [17–19]. This “ $\text{Ge}_4\text{Se}_3\text{Te}$ ” hexagonal structure with the polar space group  $P6_3mc$  ( $Z = 1$ ) is announced as stable under  $\sim 400 \text{ }^\circ\text{C}$ . The existence of a stable rhombohedral structure at this composition has never been reported for a bulk solid solution under thermodynamic equilibrium.

The hexagonal structure is formed by 2D layers  $A\text{-Ge-Ge-A}$  ( $A = 3:1$  ratio of Se and Te) along the  $c$ -axis separated by van der Waals-like gaps, Figure 7 [21, 22]. Within one  $A\text{-Ge-Ge-A}$  layer, the coupling is strong and of covalent type. The short Ge – Ge contacts ( $d = 2.94 \text{ \AA}$ ) stabilize the crystal structure. This “ $\text{Ge}_4\text{Se}_3\text{Te}$ ” hexagonal structure does not present a portfolio of properties compatible with metavalently-bonded materials but with ordinary covalent bonding [8, 9].



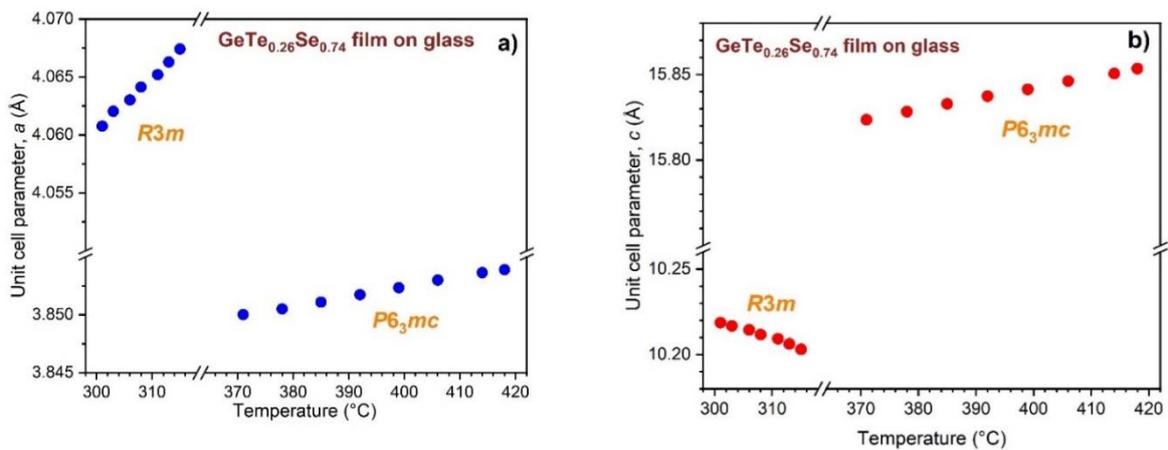
**Figure 7:** Side view of the hexagonal-like structure (space group  $P6_3mc$ ) of the “ $\text{Ge}_4\text{Se}_3\text{Te}$ ” material. Ge in blue, Se in yellow, and Te in pink. The black lines represent the unit cell.

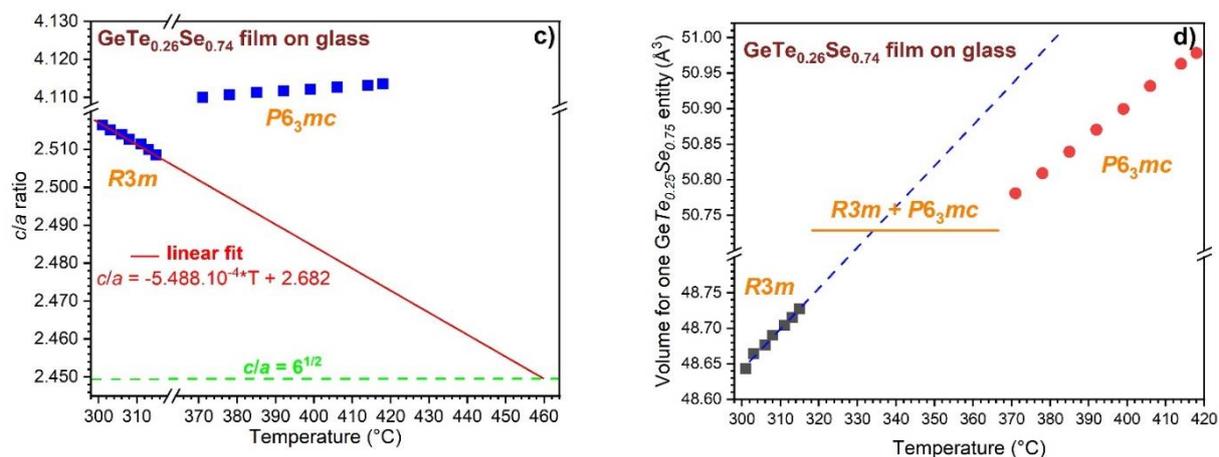
When an amorphous thick film of  $\text{GeTe}_{0.26}\text{Se}_{0.74}$  composition is heated at  $2^\circ\text{C}/\text{min}$ , it crystallizes near  $270^\circ\text{C}$  with a  $\alpha$ -GeTe-like rhombohedral structure, Figure 2(a). The crystallization of the metavalent “ $\text{Ge}_4\text{Se}_3\text{Te}$ ” rhombohedral structure has already been reported when heating or annealing solid solutions synthesized out-of-equilibrium as amorphous films [11, 15]. Its structure contains the same sheets as  $\alpha$ -GeTe but with the partial substitution of Te by Se atoms in a 1:3 ratio, Figure 8, thus, metavalent Ge-Te and Ge-Se bonds are present in the structure [22]. The rhombohedral lattice parameters of the solid solution, Table I, are smaller than the pure  $\alpha$ -GeTe as a consequence of the size difference between  $\text{Se}^{2-}$  (191 pm) and  $\text{Te}^{2-}$  (211 pm).



**Figure 8:** Side view of the hexagonal representation of the rhombohedral “ $\text{Ge}_4\text{Se}_3\text{Te}$ ” material (space group  $R3m$ ). Ge in blue, Se in yellow, and Te in pink. The black lines represent the unit cell.

Figure 9 shows the evolution of the lattice parameters and the reduced unit cell’s volume (volume occupied by one “ $\text{GeTe}_{1-x}\text{Se}_x$ ” entity) of the two polymorphs of “ $\text{Ge}_4\text{Se}_3\text{Te}$ ” function of the temperature.





**Figure 9:** Temperature range showing the evolution of (a) the lattice parameter  $a$ , (b) the lattice parameter  $c$ , (c) the  $c/a$  ratio, and (d) the reduced volume  $V$  of the crystalline phase “ $\text{Ge}_4\text{Se}_3\text{Te}$ ” with a rhombohedral structure  $R3m$  ( $a$  and  $c$  in the hexagonal description of the rhombohedral lattice,  $Z = 3$ ), and a hexagonal structure ( $P6_3mc$ ,  $Z = 1$ ). Error bars are smaller than the symbols. The continuous heating rate was  $2\text{ }^{\circ}\text{C}/\text{min}$ . Lines are fitting curves of the experimental data.

The rhombohedral structure phase exists only in a narrow temperature range as a unique phase ( $\Delta T = 14\text{ }^{\circ}\text{C}$ ) with our experimental conditions, Figure 2(a). The thermal evolution of the lattice parameters extracted by refinement of the in-situ XRD data ( $a$  and  $c$  in the hexagonal description of the rhombohedral lattice) pointed out a negative thermal expansion along the  $c$ -axis, Figure 9(b), while the  $a = b$  cell parameters have a positive thermal expansion, Figure 9(a). Consequently, the  $c/a$  ratio presents a negative evolution with temperature, Figure 9(c), as registered for the rhombohedral  $\alpha$ - $\text{GeTe}$  [29, 33]. While increasing temperature, the  $\alpha$ - $\text{GeTe}$ 's  $c/a$  ratio decreases toward  $\sqrt{6}$ , the ideal  $c/a$  ratio derived from the description of an ideal face-centered cubic cell ( $\beta$ - $\text{GeTe}$ ) of a primitive rhombohedral-centered cell in the hexagonal setting [30].

For the  $\text{GeTe}_{0.24}\text{Se}_{0.76}$  solid solution, a large deviation from the ideal  $c/a$  ratio, see Table I, indicates a more distorted structure than  $\alpha$ - $\text{GeTe}$  with respect to the FCC unit cell. With the increase in temperature, the deviation from the ideal  $c/a$  ratio is reduced, Figure 9(c). The extrapolation with a

linear regression leads to a cubic structure near 460 °C (not reached in our experiments) which is consistent with the phase equilibria diagram of the pseudo-binary GeTe-GeSe [17–19].

A negative thermal expansion (NTE) phenomenon (also known as “contraction upon heating”) in one crystallographic direction, here  $c$  in the hexagonal cell, is rare as atomic bonds are readily expanded, but they are difficult to shrink. In the planes perpendicular to the polar rhombohedral axis, Ge atoms are connected through chalcogenide atoms to form Ge-A-Ge bilayers ( $A = 3:1$  ratio of Se and Te), Figure 8. A possible scenario is that the Ge-A bonds will expand during heating, resulting in increased Ge-A-Ge angles and hence the reduced bilayer thickness. Simultaneously, electrostatic interactions between negative  $A$  anions and Ge cations of opposite bilayers will lead to a shortening of the distance between these bilayers which may explain the uniaxial NTE in the “Ge<sub>4</sub>Se<sub>3</sub>Te” rhombohedral structure.

The hexagonal structure of the “Ge<sub>4</sub>Se<sub>3</sub>Te” material is present as the only phase on a large range of temperature 371 – 418 °C for our film sample and with our experimental conditions (2 °C/min heating rate), Figures 2(b). Positive thermal expansion of the hexagonal lattice parameters and unit cell’s volume was registered upon heating. Above 370°C, a comparison of extrapolated rhombohedral structure volume (dashed line) with hexagonal structure volume in Figure 9 evidences that this later structure is more compact.

If the heating rate is reduced to 0.2 °C/min, the scenario of crystallization of the dense GeTe<sub>0.26</sub>Se<sub>0.74</sub> thick film is similar to the one with a 2 °C/min rate. However, the system has enough time to reorganize itself; thus, the thermal domain of coexistence of the metastable and stable “Ge<sub>4</sub>Se<sub>3</sub>Te” phases is reduced. With a lower rate of 0.1 °C/min, the rhombohedral polymorph is still the first to appear but the amorphous phase remains present up to the highest temperature studied, *i.e.* 285°C. This suggests that, from 256 °C, we are in the presence of a glass-ceramic material. It appears that the crystallization kinetics of the amorphous phase is not fast enough with this heating rate to ensure a complete crystallization of the thick film even at 278 °C. One explanation could be that a long time period spent

in the furnace induces some cracks in the film which decrease the contact with the heating plate and thus, limit the thermal transfer to the whole sample.

#### 4. Conclusions

Temperature-dependent *in situ* synchrotron XRD experimental study of unprotected  $\text{GeTe}_{0.26}\text{Se}_{0.74}$  amorphous thick film elaborated by the thermal co-evaporation technique has shown that the crystallization occurs in two steps when continuously heated at a rate of  $2\text{ }^\circ\text{C}/\text{min}$  from room temperature to  $418\text{ }^\circ\text{C}$ :

- First, the amorphous matrix transforms totally to an intermediate crystallized phase with an onset of temperature  $T_{x1} = 270 \pm 2\text{ }^\circ\text{C}$ . The two-dimensional “ $\text{Ge}_4\text{Se}_3\text{Te}$ ” metastable phase has a non-centrosymmetric rhombohedral structure ( $R3m$ ) with a negative thermal expansion along the  $c$  crystallographic direction ( $a$  and  $c$  in the hexagonal setting) which makes it attractive for fundamental research and industrial applications. This “ $\text{Ge}_4\text{Se}_3\text{Te}$ ” rhombohedral structure exists only because the as-deposited thick film is out of equilibrium,
- Then, a solid-solid phase transition occurs from the polar rhombohedral-type to the non-centrosymmetric layered hexagonal-type structure of “ $\text{Ge}_4\text{Se}_3\text{Te}$ ” which starts at  $T_{x2} = 318 \pm 2\text{ }^\circ\text{C}$ .

The measured diffractograms in the whole temperature range did not point out the existence of phase segregations (crystallized Ge or Te for example) in the experimental  $\text{GeTe}_{0.26}\text{Se}_{0.74}$  solid solution. On cooling to room temperature, the stable hexagonal structure of “ $\text{Ge}_4\text{Se}_3\text{Te}$ ” is maintained. When the heating rate is reduced, the crystallization schema is modified. At a heating rate of  $0.2\text{ }^\circ\text{C}/\text{min}$ , the thick amorphous matrix transforms totally to the unstable rhombohedral structure of “ $\text{Ge}_4\text{Se}_3\text{Te}$ ” alloy

but at a lower onset temperature of crystallization ( $T_{x1} = 249 \pm 2 \text{ }^\circ\text{C}$ ), and the transformation to the hexagonal stable phase occurs as soon as  $T_{x2} = 263 \pm 2 \text{ }^\circ\text{C}$ .

By heating quickly the amorphous 3  $\mu\text{m}$ -thick film, the system does not have enough time to reorganize and thus, the “metavalent bond” which persists would be trapped. With a slower heating rate, the structural evolution tends towards a quasi-static transformation and the system has time to reorganize, thus the domain of existence of the “ $\text{Ge}_4\text{Se}_3\text{Te}$ ” rhombohedral phase decreases. If the film would be heated very slowly ( $\ll 0.2 \text{ }^\circ\text{C}/\text{min}$ ) without mechanical degradations, as is necessarily the case in the construction of a phase diagram which, by principle, presents only phase changes at the thermodynamic equilibrium, then this metastable rhombohedral phase should not appear.

This work highlights the formation of the metastable rhombohedral phase (space group  $R3m$ ) of the general composition “ $\text{Ge}_4\text{Se}_3\text{Te}$ ” described as a distorted cubic structure when heating an amorphous thick film with close composition. This polymorph is of great interest since, like the  $\alpha$ -GeTe phase whose structure it derived, it is a promising material for PCM-type memories. Moreover, we have shown that the temperature of appearance of this phase as well as its domain of existence in temperature depends on the heating rate. The higher the heating rate, the larger the domain of temperatures of the existence of the rhombohedral form. As during the switching ‘amorphous to PCM-based chalcogenide structure’ extremely high heating rates are used ( $\sim 100 \text{ }^\circ\text{C}/\text{ns}$ ), we could then increase, in temperature, the range of existence of the “ $\text{Ge}_4\text{Se}_3\text{Te}$ ” metavalent phase and thus, increase the field of use of PCM devices at higher temperatures.

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[33] Persistence of the *R3m* Phase in Powder GeTe at High Pressure and High Temperature

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