Local structure of amorphous and crystalline GeTe and GeSbTe

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1. INTRODUCTION

It's well known that the crystallization time of amorphous GeSbTe films is less than 100 ns [1,2]whereas amorphous GeTe films show slower crystallization speed [3]. The phase change is completed in the latter case within 300 ns after laser-pulse irradiation. In the present study, we have investigated the reason for this fast crystallization phenomenon and the origin of the crystallization behavior difference between the two materials.

The local structure of amorphous GeTe and amorphous GeSbTe and the change of the nearest-neighbor structure around each element during crystallization are analyzed by means of Ge, Sb and Te K-edge Extented X-ray Aborption Fine Structure (EXAFS).

2. EXPERIMENTAL PROCEDURE

Amorphous films were prepared by magnetron sputtering and crystalline films were, subsequently, prepared by laser annealing. The EXAFS measurements were carried out at BM29 line at the European Synchrotron Radiations Facilities (ESRF) in Grenoble.

The crystal structure of the annealed samples were previously analyzed by X-ray diffraction. We found that the GeSbTe material crystallizes into a NaCl type crystal structure. The atomic distribution proposed in the literature [4,5] for this structure is shown in figure.1; the Te atoms populate the sites indicated by black circles and the gray sites are randomly occupied by Ge and Sb atoms or vacancies with a different probability for each composition. In the case of GeTe films, the examined crystalline structure is rhombohedral (slightly distorted NaCl structure) and according to several authors [6,7,8,9], in this crystalline phase the Ge and Te atoms form three short bonds (solid lines) and three long bonds (dashed lines) with each other as shown schematically in figure 2 (the coordination is 3(Ge):3(Te)). .
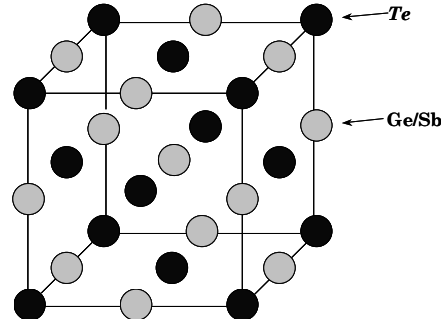
Figure 1: NaCl-type structure model of the metastable phse of GeSbTe ternary alloy
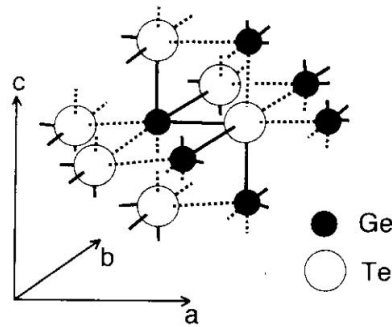

Figure 2: schematic views of the crystal structure of rhombohedral GeTe. Small black and large empty circles indicates Ge and Te atoms, respectively. Solid and dashed lines show the short and long bonds, respectively.

3. RESULTS

a) GeTe

-Amorphous GeTe:

Figure 3.a shows the EXAFS oscillations for the amorphous GeTe at the Ge K-edge and figure 3.b shows the corresponding radial distribution function after Fourier transformation. The peak around 2-3Å is related to the nearest-neighbor atoms around Ge. The interesting structural parameters, interatomic distance and coordination number, are determined by least-squares fitting of the theoretical expression of the EXAFS oscillations on the experimental spectrum. The fitted curve is shown in figure 4. From this analysis, we found that two types of bonds must be considered to obtain the best fit between the two curves. Both Ge-Ge and Ge-Te bonds exist in the nearest-neighbor shell of the Ge atoms in the amorphous state. A Ge atom is surrounded by two Ge atoms at a distance of 2.49Å and two Te atoms at a distance of 2.66Å (the errors of the interatomic distance and coordination number are considered to be within a few % and 20% respectively).
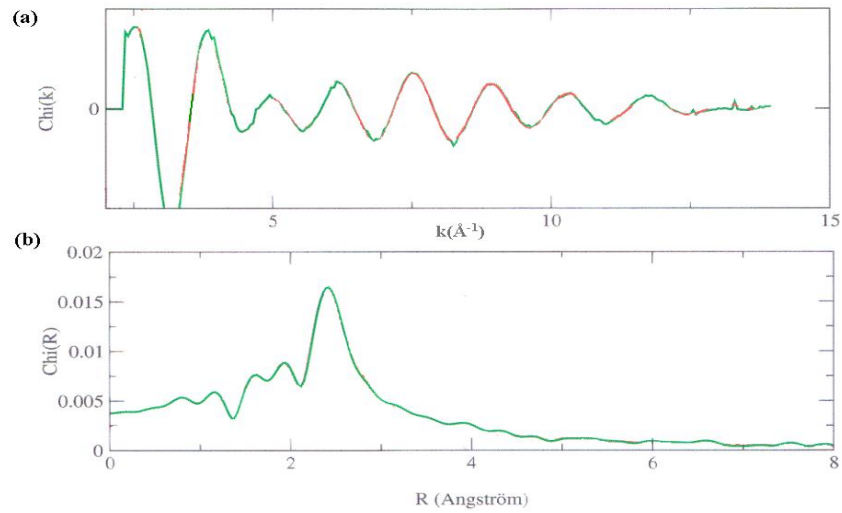
Figure 3: experimental Ge K-edge EXAFS spectrum (fig.a) and magnitude of the Fourier transform (uncorrected for phase shift) for the amorphous GeTe
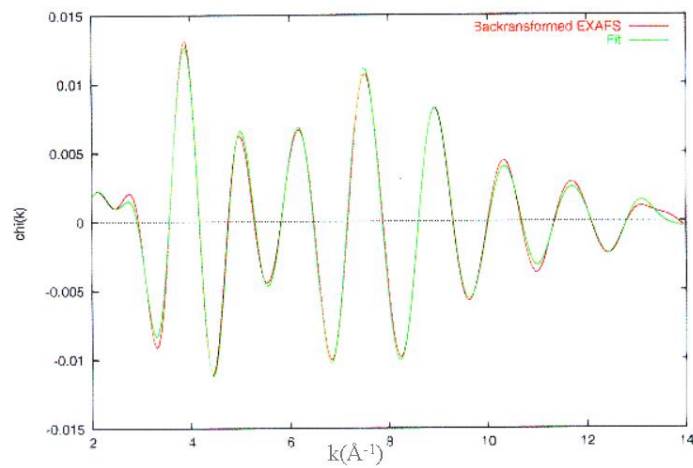

Figure 4: simulation of the EXAFS spectrum at the Ge-K edge. Red curve shows the experimental data and green curve shows the fitted function.

The results obtained at the Te-K edge of amorphous GeTe are consistent with the previous ones. A Te atom is surrounded by two Ge atoms at a distance of 2.61Å. The amorphous GeTe has 4:2 coordination with each atom satisfying its normal valence requirement.

The question is then to know whether the corresponding crystalline alloy has the same coordination or not.

-Crystalline GeTe:

Figure 5 shows the radial distribution function obtained from the EXAFS oscillations for the crystalline GeTe at the Ge-K edge. Compared to the signal obtained for the amorphous phase, the great changes implies that the short-range structure around Ge changes markedly at the crystallization. As described above, the crystalline GeTe has a slightly distorted NaCl

structure where the GeTe has the 3:3 coordination. By introducing this structural model in the simulation, figure 6 shows the corresponding theoretical calculated spectrum (green line). and the experimental one (red line). Despite the fact that the two curves don't fit very well, it seems that Ge atoms are surrounded by 6 Te atoms; three Te nearest neighbors atoms form with the central Ge atom three "short bonds" (the Ge-Te interatomic distance is 2.85Å) and three Te atoms form three "long bonds" (the Ge-Te interatomic distance is 3.16Å).
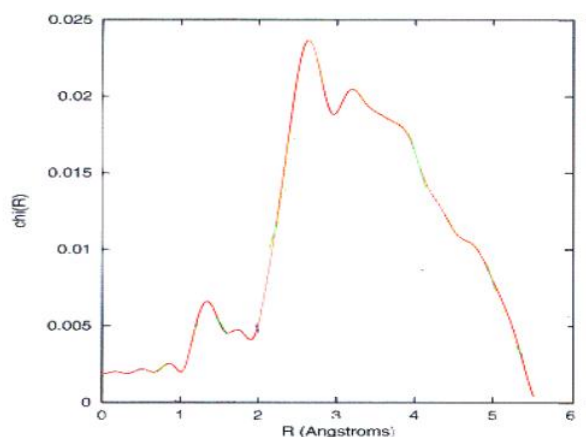
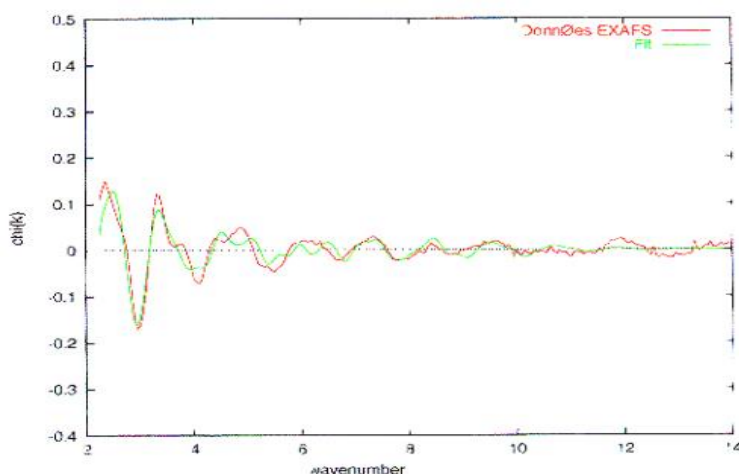**Figure 5:** magnitude of the Fourier transform for the crystalline GeTe at the Ge k-edge

Figure 6: simulation of the EXAFS spectrum at the Ge-K edge for crystalline GeTe. The experimental data are shown by red lines and the fitted curve by green lines

The crucial point of this study about the GeTe binary system is that, both Ge-Ge and Ge-Te bonds exist in the nearest-neighbor shell of amorphous GeTe and after crystallization, the homopolar Ge-Ge bonds disappear in the nearest-neighbor shell of crystalline GeTe.

b) GeSbTe

-Amorphous GeSbTe:

Figure 7 shows the EXAFS signal (red line) at the Ge K egde of amorphous GeSbTe, and the simulated signal (green curve). The main information obtained from this fitting is that the Ge atoms in the amorphous state are threefold coordinated by uniquely Te atoms (and/or Sb atoms) at a distance of 2.63Å (EXAFS measurements can not distinguish Te atoms from Sb atoms - when they have a backscattering role - because the atomic number of Sb is close to that of Te). There is no influence of homopolar Ge-Ge bonds .
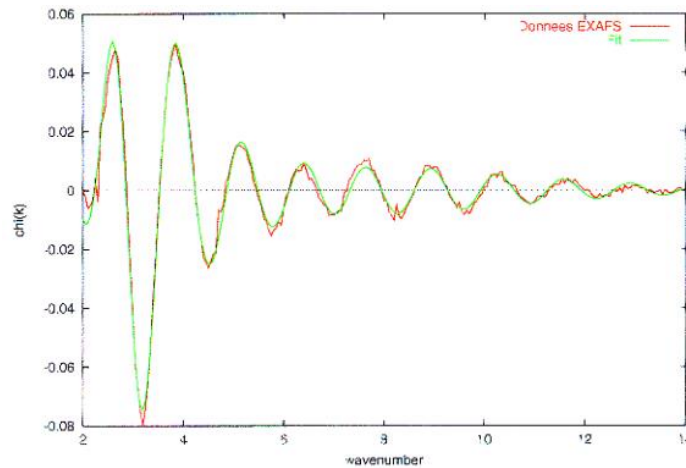

Figure 7: simulation performed on the amorphous GeSbTe at the Ge K-edge. The red line shows experimental data and the green curve shows the result of the simulation

In order to obtain a complete picture of the short-range ordering, we have investigated this amorphous system at the Te-K and Sb-K absorption edges. Our results are the following: there is no Ge atoms in the first coordination shell of the Sb atoms (the nearest neighbors are very likely Te atoms at the distance of 2.84Å), and the simulation at the Te-K edge shows that a Te atom has 2.5 nearest neighbors: 1 Ge atom (the bond length is 2.63Å) and 1.5 Te atom (the bond length is 2.63Å).

-Cristalline GeSbTe:

As previously mentioned and according to the literature, the crystalline GeSbTe has a NaCl type structure where the Te atoms occupy the first cfc lattice and the Ge/Sb atoms take place randomly on the sites of the second cfc lattice. Figure 7 shows the calculated EXAFS signal from the above model and the corresponding measured signal obtained at the Te-K edge in crystalline GeSbTe. We find that a Te atom is surrounded by 6 nearest neighbors: 3 Ge (at 2.94Å) and 3 Sb (at 3.04Å).

By considering the Exafs signal of the crystalline GeSbTe at the Sb-K edge, we agree with the proposed crystalline structure with regard to the first shell of coordination of the Sb atoms: a Sb atom has 6 Te nearest neighbors.
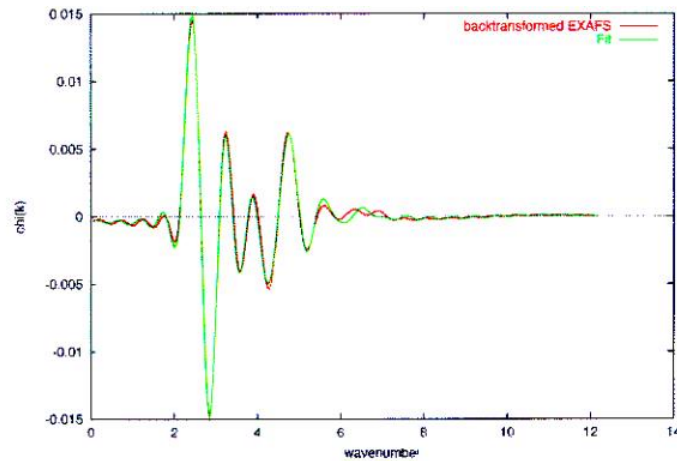
Figure 8: simulation performed on the cristalline GeSbTe at the Te K-edge. The red line shows experimental data and the green curve shows the result of the simulation

4. CONCLUSION:

These results show that the chemical short-range order (our study takes into account only the first coordination shell around each element) in the ternary GeSbTe system is almost the same in the amorphous phase and in the corresponding crystalline one. This chemical local order already present in the amorphous phase is likely responsible for the fast crystallization process. The phase change is indeed completed without appreciable atomic movement. The "amorphous" atoms move only on very small distances to reach the crystalline sites.

In turn, for the binary system, it appears that the local atomic order of both states are different. In the amorphous state, Ge atoms are fourfold coordinated by 2 Te and 2 Ge atoms (the Ge-Ge bond length is 2.19Å). When crystallization occurs the Ge-Ge bonds disappear in the nearest-neighbor shell of the crystalline GeTe, and Ge atoms are uniquely surrounded by Te atoms. The Ge nearest neighbors atoms around the central Ge are then located in the second coordination sphere at the minimum distance of 4.15Å. The phase transformation (amorphous state-crystalline state) requires the destruction of the Ge-Ge bonds and a significant movement of the Ge atoms to join the crystalline sites. This phenomenon limits probably the crystallization speed.

These results are in agreement with the measured crystallization times which are about 300ns for the GeTe material and less than 100ns for the GeSbTe material.

In summary, it seems that Sb added in the binary system GeTe doesn't accelerate the crystallization process but prevents the formation of the homopolar Ge-Ge bonds during amorphization which originate a slowing down in the crystallization behavior.

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