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Crystallization-induced short-range order changes in amorphous GeTe

A V Kolobov¹, P Fons¹, J Tominaga¹, A L Ankudinov², S N Yannopoulos³
and K S Andrikopoulos⁴

¹ Center for Applied Near-Field Optics Research, National Institute of Advanced Industrial Science and Technology, Tsukuba Central 4, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8562, Japan

² Department of Physics, University of Washington, Seattle, WA 98195, USA

³ Foundation for Research and Technology Hellas, Institute of Chemical Engineering and High Temperature Chemical Processes, (FORTH-ICE/HT), PO Box 1414, 26500 Patras, Greece

⁴ Physics Division, School of Technology, Aristotle University of Thessaloniki, GR-54124, Thessaloniki, Greece

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Abstract

By means of x-ray absorption fine structure and Raman scattering spectroscopies we demonstrate that the structure of amorphous GeTe is likely to be a mixture of 4(Ge):2(Te) and 3(Ge):3(Te)-coordinated structural units. Upon crystallization, a rhombohedral (distorted rocksalt) structure is established with about 10% of vacancies occurring on Ge sites. The vacancies are believed to play an important role in determining the ratio of 3(Ge):3(Te) and 4(Ge):2(Te) structural units.

1. Introduction

GeTe is a well-known ferroelectric material [1] and also a component material of phase-change optical memories [2]. In its crystalline form, GeTe possesses rhombohedral structure at room temperature. Both Ge and Te species are six-fold coordinated with three neighbours of the other kind located at 2.84 Å and three at 3.15 Å. A ferroelectric structural transition takes place around 650 K and at higher temperatures GeTe possesses rocksalt structure [3].

While in most cases the short-range order in amorphous solids resembles that of the corresponding crystal, GeTe seems to be an exception and its structure in the amorphous state has long been a matter of controversy. Whilst a large number of studies, such as x-ray [4] and electron diffraction [5] and Raman scattering [6] have indicated that a random covalent network with the local coordination of 4(Ge):2(Te) is the most appropriate model structure, neutron scattering [7] and Mossbauer spectroscopy [8] results suggest that amorphous GeTe is characterized by a 3(Ge):3(Te)-coordinated structure.

An ideal tool to directly investigate the local structure is the x-ray absorption fine structure (XAFS). The analysis of the extended x-ray absorption fine structure (EXAFS) allows one to

obtain information about the number of nearest neighbours (the coordination number), the bond lengths, degree of disorder, and also the chemical nature of the surrounding species. Tuning the x-ray energy to the absorption edge of different constituent species, one can independently probe the local structure around different constituent atoms, Ge and Te in this case. The x-ray absorption near-edge structure (XANES) is determined by multiple scattering and as a result additionally allows one to discuss the spatial arrangement of the nearest neighbours. It should be noted that the theoretical understanding of EXAFS and XANES has recently made significant progress and both EXAFS and XANES spectra can be simulated with very good accuracy [9].

In this paper, we present the results of an experimental study of the amorphous structure of GeTe and of the crystallization process using XAFS and Raman spectroscopies.

The samples were 3 μm thick films prepared by magnetron sputtering of a GeTe target onto both sides of 50 μm -thick Kapton substrates [10]. In order to obtain crystalline samples, the as-deposited films were annealed at 240 °C for 3 h in argon atmosphere. Measurements were performed at room temperature in transmission mode on a stack of samples with an optimized total sample thickness. Ge K-edge EXAFS spectra were taken at BL12C at the Photon Factory, Tsukuba, Japan and Te K-edge spectra were measured at BL01B1 at SPring8, Mikazuki, Japan.

Raman spectra were recorded with the aid of the 773 nm laser line emerging from a Ti:sapphire laser pumped by an Ar⁺ ion laser. To avoid photo-induced structural changes the laser power on the sample was kept very low. The backscattered light for the spectra shown in figure 4 was analysed by a triple monochromator (Jobin-Yvon T64000) operating at double subtractive mode and was then detected by a CCD cooled at 140 K. The spectrum presented in figure 3 was excited by a He-Ne laser and the scattered light was analysed by the same monochromator operating in the single configuration with the aid of a notch filter to achieve maximum throughput. The incident radiation was vertically polarized; however, no polarization analysis was used for the scattered light. The spectral resolution for the recorded spectra was set to 1 cm^{-1} in order to achieve maximum signal quality. Measurements were performed at ambient temperature.

2. Results and discussion

2.1. Extended x-ray absorption fine structure

Figure 1 shows k^3 -weighted raw EXAFS oscillations of amorphous GeTe at the Ge and Te K-edges. The data were analysed using the Athena and Artemis packages [11]. The theoretical amplitudes and phase shifts were simulated using FEFF8 [9]. To achieve better statistics and maximum confidence in the results, the two data sets were analysed simultaneously. Figure 2 compares the experimental and simulated EXAFS spectra for both measured edges.

The Ge-Te bond length was found to be 2.60 Å in the amorphous phase, a value that is in good agreement with previous studies [12]. For the average coordination numbers, we obtained the values of 3.3 ± 0.3 for Ge (with both Ge-Te and Ge-Ge bonds present) and 2.2 ± 0.2 for Te. The obtained values suggest that 4(Ge):2(Te) coordination is more likely to exist in amorphous GeTe although 3(Ge):3(Te)-coordinated structural units are also possibly present in smaller quantities.

The crystal structure resulting from the annealing of an amorphous GeTe film has been studied by us earlier [10]. It was demonstrated that the local structure around the Te species is indeed very well described by the rhombohedral structure reported in the literature earlier with 3 Ge neighbours located at 2.80 Å and another three at 3.13 Å. At the same time, fitting of the Ge-edge data using the same structural model failed to reproduce the experimental spectra.

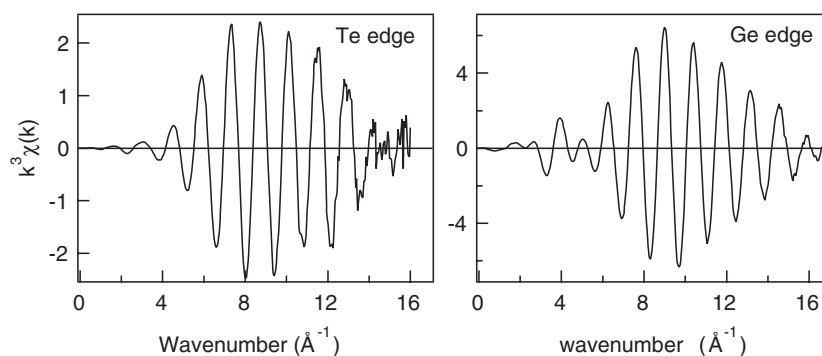


Figure 1. k^3 -weighted EXAFS oscillations at Ge and Te edges of an amorphous GeTe film.

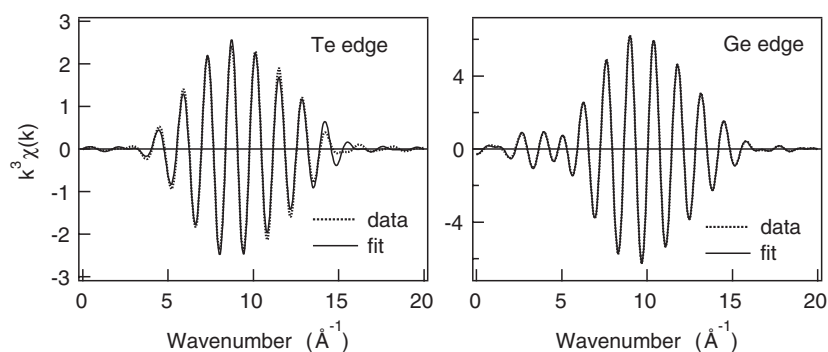


Figure 2. Experimental and simulated back-Fourier transformed EXAFS spectra for Ge and Te edges of amorphous GeTe.

In order to obtain a proper fit, we had to assume the presence of a certain number of Ge–Ge bonds. With this assumption, the fit quality was excellent [10]. It was found that about 10% of Ge had Ge as its first-nearest neighbour which implies that about 10% of Ge sites in the quasi rocksalt structure were vacant. The Ge–Ge distance obtained was 2.49 Å and may correspond to either an amorphous Ge–Ge phase or strained Ge–Ge bonds in a nanocrystalline phase.

We would like to note here that the bond lengths obtained for the crystalline phase are longer than the corresponding bonds in the amorphous phase (in perfect agreement with the results reported in [12]) which is rather unusual for covalently bonded solids. This result implies that there is more than simple disordering of the material when it transforms into the amorphous phase, suggesting significant differences in the local structure in the two phases.

2.2. Raman scattering

In order to get a deeper insight into the crystal structure, we have additionally measured the Raman scattering spectra of crystallized GeTe film. The results are shown in figure 3 where the peak located at 297 cm^{-1} is attributed to Ge–Ge bonds. For comparison, a spectrum of bulk Ge is also shown in the figure. The observed shift to lower wave numbers may be due to a variety of reasons, one possible explanation being the size effect.

Figure 4 compares the Raman spectra of amorphous and crystallized GeTe. The spectrum of the crystalline phase is characterized by two main peaks located at about 80 and 115 cm^{-1} in agreement with the results of [13]. On the other hand, the spectrum of the amorphous phase

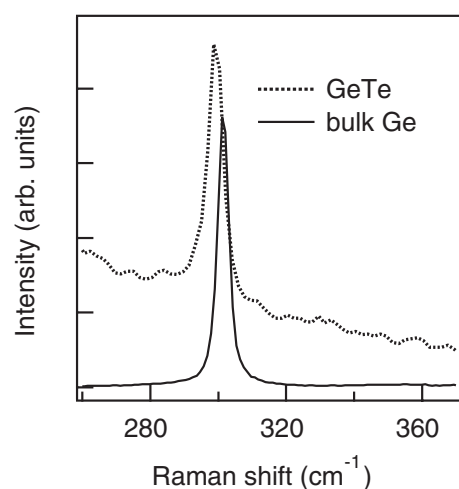


Figure 3. The Raman spectrum of a crystallized GeTe film. A spectrum for bulk Ge is shown for comparison.

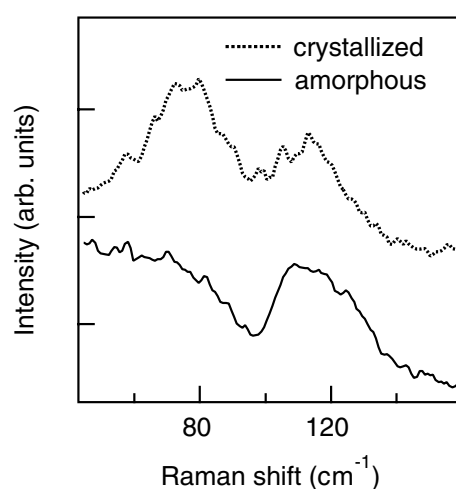


Figure 4. Raman spectra of amorphous and crystallized GeTe films.

apart from the two peaks mentioned above, displays also at low frequencies the usual broad features of the non-crystalline phases attributed to the low energy excitations. It is interesting to note that the intensity ratio I^{115}/I^{80} is drastically reduced in the transformation from the amorphous to the crystalline state. This is unusual for a typical covalently bonded solid and reminds one of a molecular solid such as selenium where the spectrum in the crystallized state is also characterized by a peak located at a lower (237 cm^{-1}) wavenumber compared to that in the amorphous state (255 cm^{-1}) [14, 15].

In the case of Se such behaviour has been attributed to weakening of interchain interactions and the resulting strengthening of intrachain interaction as the material is transformed from the crystalline to the amorphous state [14]. A similar situation can be seen in GeTe. Since there is a bond-strength hierarchy, namely, longer bonds are weaker, one can view GeTe as structural units formed by stronger bonds and kept together by weaker bonds. In the amorphous state, similar to the case of selenium, the weaker bonds become yet weaker and stronger bonds stronger resulting in a relative strengthening of the higher-energy Raman peak. This transformation thus leads to the 3(Ge):3(Te) structure dominating in the amorphous state.

2.3. X-ray absorption near-edge structure

To get more insight into the local structure, we have also measured XANES spectra. The experimental spectra measured at the Ge K-edge are shown in figure 5 (left panel). One can see that the spectra are very different, suggesting that local arrangements of atoms are also very different in the crystalline and amorphous phases. We simulated the XANES spectra (figure 5, right panel) assuming the distorted rocksalt structure for crystalline GeTe and tetrahedral coordination of Ge for amorphous GeTe (figure 6). As can be seen, the simulated spectra qualitatively reproduce the experimental results. The difference in amplitude of the features is partly due to the fact that thermal damping is not taken into account in the simulations. The obtained agreement between the experimental and simulated XANES spectra clearly demonstrates the existence of 4(Ge)-coordination for amorphous GeTe.

In order to further verify the feasibility of the tetrahedral-to-octahedral transformation upon crystallization, one can estimate the Ge–Te bond length in the amorphous state assuming that the Te atoms form a distorted fcc sublattice similar to that in the crystalline phase. The

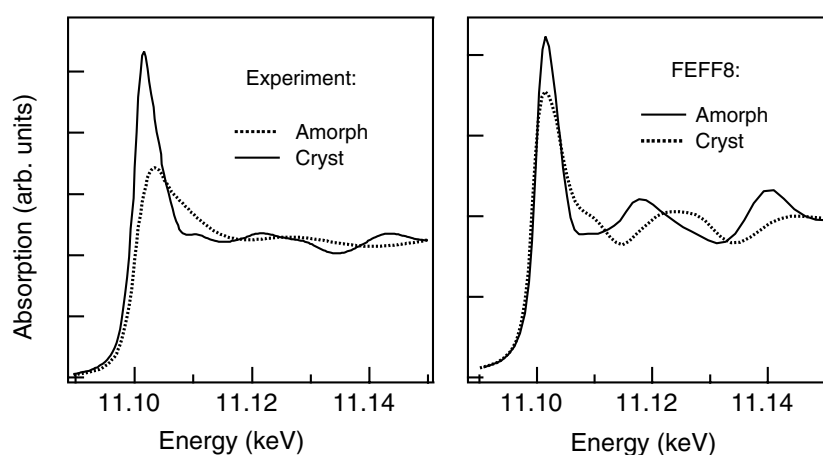


Figure 5. Measured and simulated XANES spectra for amorphous and crystalline GeTe.

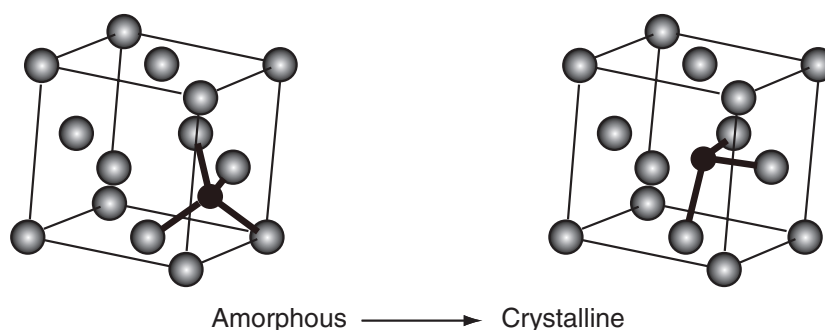


Figure 6. Modification of the local structure of Ge upon crystallization.

lattice parameter of the GeTe crystal is 5.99 \AA [3] giving 2.60 \AA for the Ge–Te distance, should the Ge atoms be located at tetrahedral symmetry sites of the Te fcc sublattice. These results are in very good agreement with the experimentally obtained value of $2.60 \pm 0.01 \text{ \AA}$.

We believe that it is this difference in the local structure (octahedral versus tetrahedral coordination of Ge) that is responsible for the large difference seen in the Raman spectra. Whilst the tetrahedrally bonded amorphous structure is rigid, the distorted rocksalt structure is much softer. One can here draw an analogy with mode softening typically observed in ferroelectrics.

The amorphous structure of GeTe can thus be viewed as follows. Weakening of longer GeTe bonds eventually leads to their rupture (as covalent bonds) and bonding between the structural fragments formed by the shorter (and stronger) GeTe bonds becomes more van-der-Waals like, similar to the case of amorphous selenium. Lone-pair electrons of the chalcogen may play an important role in this transformation. The structure in this situation assumes a 3(Ge):3(Te) coordination. The presence of vacancies on Ge sites as detected by our EXAFS and Raman measurements facilitate the relaxation of the local structure so that Ge atoms can move from energetically less favourable octahedrally coordinated sites (as in the distorted rocksalt structure) to (locally) more favourable tetrahedrally coordinated sites. This model agrees with an earlier suggestion [12] that the electronic configuration of Ge changes during crystallization.

The energy barrier separating the octahedral and tetrahedral sites is reduced should the Te atoms be displaced somewhat from their fcc positions. This motion is difficult in the continuously bonded rigid rocksalt structure and is more likely to occur at sites located close to Ge vacancies where the average local coordination of species is lower. Each vacancy facilitates the motion of six Te atoms (in the rocksalt structure). With about 10% of Ge sites being vacant and two Te atoms per unit cell one obtains at least about 30% of sites softening, i.e. about 30% of Ge atoms are likely to switch to the tetrahedral coordination. One can now make an estimate of the average coordination number in the amorphous phase. It is $4 \times 0.3 + 3 \times 0.7 = 3.3$, i.e. exactly the number we obtained from EXAFS analysis.

It should also be noted here that the characteristic activation energy of crystallization (in a 2.3–3.9 eV range, as detected by different techniques [16]) is much larger than the energy-gap in GeTe, the latter being the characteristic energy for solid state processes. This further supports our argument that the structural rearrangements taking place during crystallization occur locally and are of molecular-like nature.

3. Conclusions

EXAFS, XANES and Raman scattering studies suggest that the structure of amorphous GeTe is a mixture of 3(Ge):3(Te) and 4(Ge):2(Te)-coordinated structural units. Upon crystallization, GeTe assumes the rhombohedral (distorted rocksalt) structure with about 10% of Ge sites vacant. We believe that the concentration of vacancies on the Ge sites in the crystalline states is related to the ratio of the 3(Ge):3(Te) and 4(Ge):2(Te)-coordinated units in the amorphous phase. It is argued that atomic relaxation during the crystallization is a localized process of a rather molecular-like nature.

Acknowledgments

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