

## Nanometer-scale mechanism of phase-change optical recording as revealed by XAFS

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### Abstract

We demonstrate that the Ge(Sb)–Te bond lengths in crystallized cubic Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> (GST) are significantly lower than the values expected from the previous X-ray diffraction (XRD) analysis. At the same time, the second nearest-neighbour Te–Te distances are in perfect agreement with XRD. We conclude that the structure of GST is a *distorted* rocksalt structure. Upon amorphization, Ge–Te and Sb–Te bonds get *shorter and stronger*. This unusual behaviour is due to a switch of Ge atom from an octahedral symmetry position in the crystalline state into a tetrahedral symmetry position in the amorphous state. It is this switching of the Ge atoms that is responsible for the fast and stable media performance.

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One of the most exciting technological developments today is the ever spreading use of multimedia and the Internet. In order to satisfy the continuously increasing requirements for data storage, fast and stable recording media are needed. It should be stressed here that the requirements of high speed and high stability are intrinsically a tradeoff. Whilst fast speed requires an easy transition between the two binary states, high stability requires that the energy barrier separating the two states is high enough to prevent spontaneous erasure of the recorded information. At the same time, a fast transition between the two states often suggests that the structural modification of the system upon the transition is rather small. On the other hand, one requires significant changes in properties of the materi-

als in order to record information with a high carrier-to-noise (CNR) ratio, e.g. to significantly change the electronic structure. The possibility of using the same media many times, i.e. reversible recording, is another important requirement. As follows from the introduction, the ideal medium should possess rather specific properties.

One of the most promising approaches to-date is optical phase-change memory. The idea of optical phase-change recording is rather simple and dates back to 1960s when a switch based on a change in the electrical properties of Te-based materials between crystalline and amorphous states was first suggested by Ovshinsky [1].

When a melt is cooled down slowly, such that the structure always remains in thermal equilibrium, upon reaching the crystallization temperature the material crystallizes, i.e. is transformed into a solid state with well-defined periodic structure. If, on the other hand, the cooling rate is fast, then at a certain temperature the viscosity of the liquid increases to a degree when the structure can no longer relax following the changes in temperature; one obtains a

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supercooled liquid and then a glass. Different from the crystallization temperature, the glass-transition temperature is not well-defined. A range of temperatures exist and the particular temperature of the glass transition – and hence the glass structure – depends on the cooling rate.

Once in the solid state, the glass, if kept at a temperature close to the glass-transition temperature long enough, crystallizes. On the other hand, rapid heating of the crystalline material to a temperature above the melting point and subsequent rapid cooling (quenching) can produce a glassy state. This glass-formation diagram is demonstrated in Fig. 1.

The material can also be heated by light. Exposure of an amorphous material to laser light to the extent that the material is heated to above the glass-transition temperature results in its crystallization while short and intense laser pulses melt the material and – provided the heat dissipation rate (quench rate) is fast enough – an amorphous recorded bit is formed.

It follows from the above description that many materials can be used in the phase-change memories. In practice, however, the best performing materials are  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  (used in digital versatile discs random access memory, DVD-RAM) and  $\text{AgInSbTe}$  (used in DVD-RW) [2]. They show the best performance in terms of speed (the slowest process is the crystallization of a bit which takes place on a time scale of 30 ns) and stability (DVD-RAM allow for over 1,000,000 cycles of recording). The important question that arises is why these two materials are the best. It is difficult to believe that the process behind the phase change is a simple disordering of the covalent network of a solid.

In order to understand the nanometer-scale mechanism of the underlying structural changes one has to know the detailed local structure of the materials in both crystalline and amorphous states. In this paper we concentrate on  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  (hereafter referred to GST).

The stable structure of GST is hexagonal. We would like to stress that the details of even the stable structure are still unclear. In one of the first studies it was concluded that the stacking sequence of the layers was  $-\text{Sb}-\text{Te}-\text{Ge}-\text{Te}-\text{Te}-\text{Ge}-\text{Te}-\text{Sb}-\text{Te}-$  [3]. In a rather recent work this conclusion was challenged and it was deduced, that the stacking sequence was different [4]. Finally, in the latest study using

powder diffraction and synchrotron radiation the conclusion was that the Ge and Sb sites were not unique, but that were randomly occupied by Ge and Sb [5]. We would like to note here that the sample preparation was different in the studies reported here which could account for the observed differences but, whatever the reason, an important issue is that even the stable structure still merits further investigation.

The situation with thin layers crystallized starting with the amorphous phase is even more complicated. It has been demonstrated, using X-ray diffraction, that the arrangement of atoms is similar to the rocksalt structure with Te atoms occupying sites on one face-centered cubic (fcc) sublattice and Ge and Sb forming the other fcc sublattice with 20% of the sites on the Ge/Sb lattice being vacant [6]. The lattice parameter was determined to be 6.02 Å and the fitted thermal factor  $B_0$  (which was assumed to be isotropic) was as large as 3.2 Å<sup>2</sup> for the Ge and Sb species. The latter parameter – which in this case characterizes the degree of disorder in the sublattice – corresponds to atomic displacements of Ge/Sb species of 0.2 Å (i.e. 7% of the bond length) with respect to the ideal rocksalt positions.

The structure of the amorphous state was not known and it was tacitly assumed that it was formed by disordering the underlying rocksalt structure. It was further argued that high symmetry of the cubic structure of GST was the reason behind the fast phase-change transition during the amorphization [7].

In this paper, we report our results of a study of the local structure of GST in both crystalline and amorphous states. An ideal tool to investigate the local structure of a material and its changes on the atomic scale independent of the state of the material (crystalline or amorphous) is X-ray absorption fine-structure (XAFS) [8] spectroscopy.

Extended X-ray absorption fine structure (EXAFS) spectroscopy allows one to obtain information about the local structure around selected chemical species, such as the average coordination number, the bond lengths, the chemical nature of the neighbouring species, as well as the bond length disorder parameter, or mean-square relative deviation (MSRD) of the bond length. The technique is selective to the absorbing atom, which allows one to probe the local structure around different constituent elements independently.

X-ray absorption near-edge structure (XANES), which involves multiple scattering, additionally allows one to probe the local arrangement of atoms on a scale somewhat beyond the first-nearest neighbours, in particular, it is sensitive to the mutual arrangement of the neighbouring atoms in space, i.e. includes bond angle information. As XANES features are also a consequence of transitions from occupied core states to unoccupied conduction-band states, the spectra also contain information about the density of unoccupied conduction-band states. It should be mentioned that recent advances in theory have made it possible to simulate EXAFS and XANES spectra with good accuracy [9].

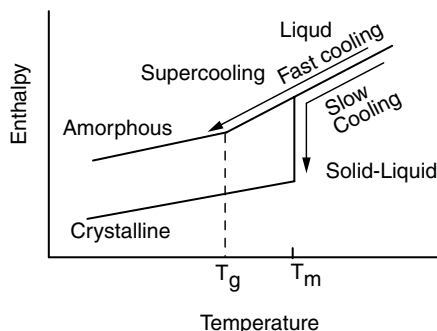


Fig. 1. A glass-formation diagram.

In order to investigate the structure of crystallized GST and its modification upon laser-pulse-induced amorphization, we have measured EXAFS and XANES spectra at the K-edges of all three constituent species. Measurements were performed in fluorescence mode for the Ge K-edge (at beamline BL12C at the Photon Factory, Tsukuba, Japan) and in conversion electron yield mode for the Sb and Te K-edges (at beamline BL01B1 at SPring-8, Mikazuki, Japan). To achieve better statistics and maximum confidence in the results, the data obtained for the three edges were analyzed concurrently. As a reference, we have also investigated the structure of the binary Ge–Te that is an end point material of the quasibinary Ge–Te–Sb<sub>2</sub>Te<sub>3</sub> used in commercial optical memories.

Fig. 2 shows raw EXAFS oscillations obtained at the Ge, Sb and Te K-edges after subtraction of the smooth background and normalization to the edge jump. The Fourier-transformed (FT) spectra for the all three edges are shown in Fig. 3. There are several striking features visible in the FT spectra. First, the peak position shifts to shorter distances in the amorphous state. Second, the peak intensity becomes significantly higher and, finally, the peaks become narrower in the amorphous state. Such changes implies that the bonds get shorter and stronger in the amorphous state, i.e. the *local* order increases. Such a situation is very unusual for covalent solids where, due to anharmonicity of interatomic potentials amorphization is typically accompanied by an increase in the interatomic distance and decreased *local* ordering (peak lowering and broadening).

Also of interest is the fact that while the second-nearest-neighbour peak is clearly observed in the Te fcc sublattice, it is completely smeared out in the Ge/Sb sublattice, suggesting that the Te sublattice is inherently much more stable than the Ge/Sb sublattice.

Quantitative structural analysis of EXAFS data was performed [10] using a non-linear least square fitting method as implemented in IFEFFIT that utilizes theoretical scattering amplitudes and phases of the photoelectron calculated by FEFF6 code [11]. To calculate the  $f_i^{\text{eff}}(k)$  and  $d_i(k)$  for each edge (Te, Ge and Sb), we assumed the NaCl structure containing 100% Te on Na sites, and 40% Ge, 40% Sb and 20% vacancies on the Cl sites as the starting structural model for the crystalline state. The actual atomic positions may be dif-

ferent from those assumed in the initial model, but if such differences are small, the same model functions of  $f_i^{\text{eff}}(k)$  and  $d_i(k)$  will adequately describe the actual structure, due to the principle of transferability of photoelectron amplitude and phase [12]. The fitting procedure was performed using the Artemis program [13] which utilizes the IFEFFIT engine. Since 20% of sites on the Ge/Sb sublattice are vacant, the model coordination numbers used were  $N_i = 4.8$  for Te and  $N_i = 6$  for Ge and Sb.

During the fits, we varied the following parameters: the backscattering amplitude  $S_0^2$ , the  $\Delta E_0$  (correction to the photoelectron energy origin  $E_0$  initially assumed to be located in the middle of the absorption edge jump for all edges),  $\Delta R_i$  – corrections to the model pair distances, as well as their mean-square relative displacements (MSRD's)  $\sigma_i^2$ . The fitting results are summarized in Table 1. One can clearly see that, indeed, the Ge–Te and Sb–Te first-nearest bond lengths are significantly shorter than the corresponding values expected from XRD. On the other hand, the second-nearest Te–Te distance is exactly the same as that expected from XRD data. At the same time, the coordination numbers are about half than those expected from the rocksalt structure.

The coordination numbers were obtained using the following procedure. The amplitude of the EXAFS oscillations is equal to  $S_0^2 \times N_i$ , where  $S_0^2$  is the passive electron reduction factor. The  $S_0^2$  values obtained within this assumption for the crystallized phase, where the coordination numbers of Ge and Sb were fixed at 6 and Te at 4.8, were 0.22(5), 0.42(7), and 0.44(9) for Te, Ge and Sb atoms, respectively, i.e. dramatically reduced compared to their most expected range, between 0.7 and 1.0. Similar reduction was observed for  $S_0^2$  the obtained in the re-amorphized samples: 0.18(2), 0.20(4) and 0.24(5), respectively. Such drastic reduction in  $S_0^2$  can sometimes be explained by self-absorption effect in concentrated samples. In our case, however, the samples were thin and uniform. Since the obtained  $S_0^2$  values are significantly outside their physically reasonable range, we concluded that our assumption of the octahedrally coordinated absorbing atoms in the rocksalt structure was incorrect and the actual coordination numbers are smaller than 6 (for Ge–Te and Sb–Te) and 4.8 for Te–(Ge,Sb). To break the correlation between  $S_0^2$  and

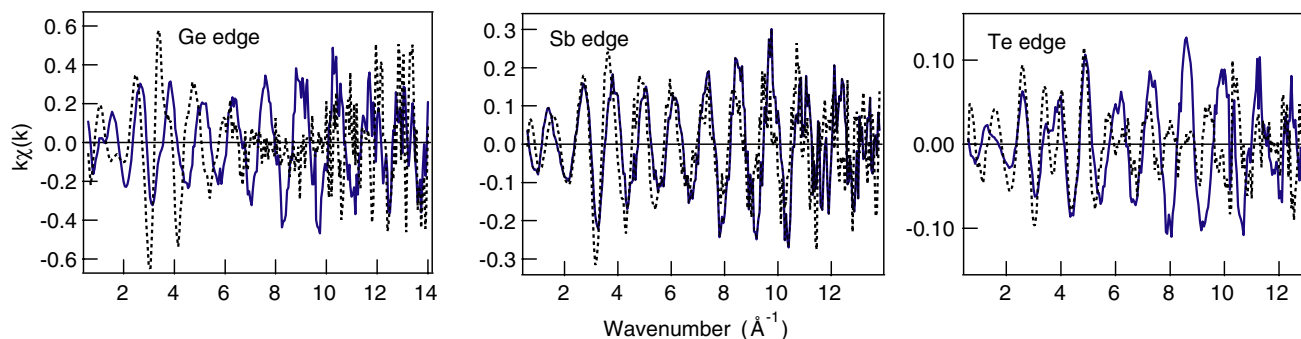


Fig. 2. Raw EXAFS oscillation at all three edges for the crystallized (dashed lines) and laser-amorphizes (solid lines) states.

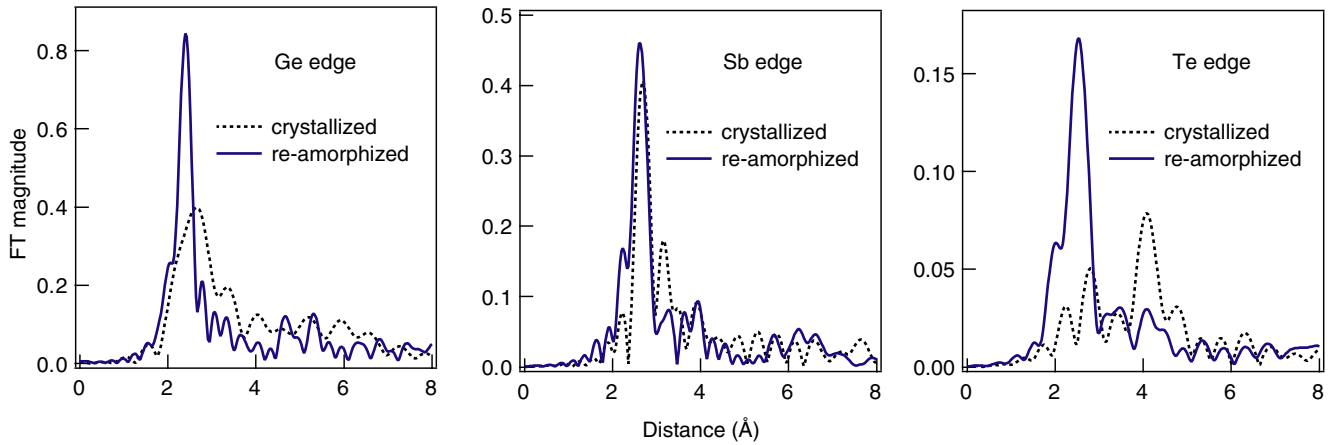


Fig. 3. Fourier-transformed spectra for the crystallized and laser-amorphized states for all three edges.

Table 1  
Structure parameters of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  obtained through data fitting (C – crystalline state, A – amorphous state)

	Ge–Te		Sb–Te		Te–Te (2nd)	
	C	A	C	A	C	A
$R_i$ (Å) ( $\pm 0.01$ )	2.83	2.61	2.91	2.85	4.26	–
$\sigma_i^2$ (Å <sup>2</sup> ) ( $\pm 0.002$ )	0.019	0.008	0.015	0.007	0.011	–
	Ge–Te		Sb–Te		Te–(Ge,Sb) (1st)	
	C	A	C	A	C	A
$N_i$ ( $\pm 30\%$ )	3.6	1.7	3.8	2.1	1.5	1.3

$N_i$  and to obtain the  $N_i$  values, we fixed the  $S_0^2$  to be 0.7 and allowed the  $N_i$  to vary in the fits. The coordination numbers that were obtained by using this procedure are tabulated in Table 1.

The obtained bond lengths were  $2.83 \pm 0.01$  Å for Ge–Te and  $2.91 \pm 0.01$  Å (cf. Table 1), i.e. significantly shorter than expected based on the unit cell values obtained from diffraction measurements.

It should also be noted that MSR value for the second-nearest Te–Te neighbour is *smaller* than those for the first-nearest Ge(Sb)–Te neighbours. This result seems unusual for the covalent network where disorder accumulates with increasing distance.

Based on the above results, one can deduce the following local structure for the crystalline state. The Te atoms form a rather stable fcc sublattice with Ge and Sb located close to the corresponding rocksalt positions but displaced from the center of the rocksalt cell. The structure is thus similar to the well known structure of GeTe where Ge (and to a lesser extent Sb) atoms are displaced from the center of the cell (rhombohedral structure) having three Te neighbours located at a shorter distance (2.80 Å) and three more Te neighbours located at a longer distance (3.14 Å). The crystal structure of GST is schematically shown in Fig. 4(a) where one Ge atom is shown at a position slightly displaced from the octahedral vacancy in the Te fcc lattice.

The fitting of the GST data assuming a local structure similar to GeTe gives a small improvement in the fit quality and the three longer Ge(Sb)–Te distances were obtained to be  $3.2 \pm 0.1$  Å. The rather large uncertainties in the obtained values do not allow us to draw any significant conclusions about the longer bonds and for this reason in what follows we concentrate on the shorter bonds.

We would like to note here that displacements of Ge and Sb atoms in real crystals are likely to be stochastic and – for this reason – the previously suggested rocksalt structure [6,14] remains the best description of the average long-range arrangement of atoms. It should also be noted that since Ge atoms are located off center the symmetry of the structure is different from that of the rocksalt and a more appropriate way to refer to the crystal structure is as a *distorted* rocksalt structure. Significant displacements of Ge atoms has recently also been confirmed by neutron scattering [15]. Exact determination of the long-range crystal structure and symmetry requires knowledge of intermediate range order, such as mutual arrangement of Ge, Sb and vacancies, and remains one of the major challenges. While several likely speculations have been made [10,16], the existing body of data is insufficient to allow one to draw any definitive conclusions.

We now turn to the amorphous state. As seen from Table 1, the Ge–Te and Sb–Te bonds do indeed get stronger (and more ordered) upon amorphization. This very

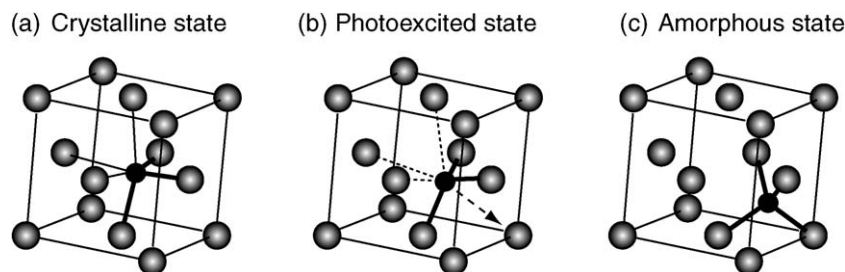


Fig. 4. Switching of a Ge atoms from a (displaced) octahedral symmetry position in the crystalline state (a) through an intermediate photoexcited state (b) into a tetrahedral symmetry position in the amorphous state (c). The arrow in the middle frame (b) indicates the force acting on the Ge atom after the rupture of the longer Ge–Te bonds.

unusual behaviour suggests that the structural modification is more complex than simple disordering of the covalent network. We would like to mention here that bond shortening upon amorphization has been previously observed by EXAFS [17] and Raman [18] spectroscopies for molecular solids such as Se and Te. There is a significant similarity between the structures of Se and Te and the structure of GST. In both cases, there are two kinds of bonds. In Se (Te) there are stronger covalent (*intrachain*) bonds and weaker van-der-Waals (*interchain*) bonds. Upon amorphization, the weaker van-der-Waals bonds break and the interchain bonds dominate the local structure getting stronger and shorter. A similar bond hierarchy also exists in GST where shorter (stronger) and longer (weaker) Ge(Sb)–Te bonds co-exist.

It is not unnatural to imagine that weaker bonds break upon photoexcitation – just as interchain bonds break in photoexcited selenium [19]. Since the Ge–Te bonds in the crystalline state are longer than the sum of Ge and Te covalent radii (1.22 Å and 1.35 Å, respectively), they are strained. Following the rupture of the longer bonds there is a net force acting on Ge atoms (Fig. 4(b)). As a result, the Ge atom is likely to flip into a tetrahedral symmetry position preserving the three strong Ge–Te bonds and forming a new bond. Ge atoms thus acquire their preferred tetrahedral coordination (Fig. 4(c)). It should be noted that the above picture is rather schematic. In reality, after the rupture of the longer Ge–Te bonds that no longer counterbalance the forces acting on Te atoms, the Sb–Te bonds somewhat shrink (cf. Table 1) and the Te sublattice gets distorted. This accounts for strong damping of the second-shell peak as seen in Fig. 3(c).

To verify the suggested structural transformation, we can estimate the Ge–Te bond length. Based on the lattice parameter of 6.02 Å, the center of the tetrahedral vacancy is located at 2.61 Å from the corner Te atoms. The experimentally measured Ge–Te bond lengths in the amorphous state (4.26 Å, see Table 1) is in excellent agreement with the estimation based upon XRD structure determination.

The switching of Ge atoms into tetrahedral symmetry position is further confirmed by analysis of XANES spectra [10] (Fig. 5). One can see that there is a reasonably good agreement between experimental and simulated spectra.

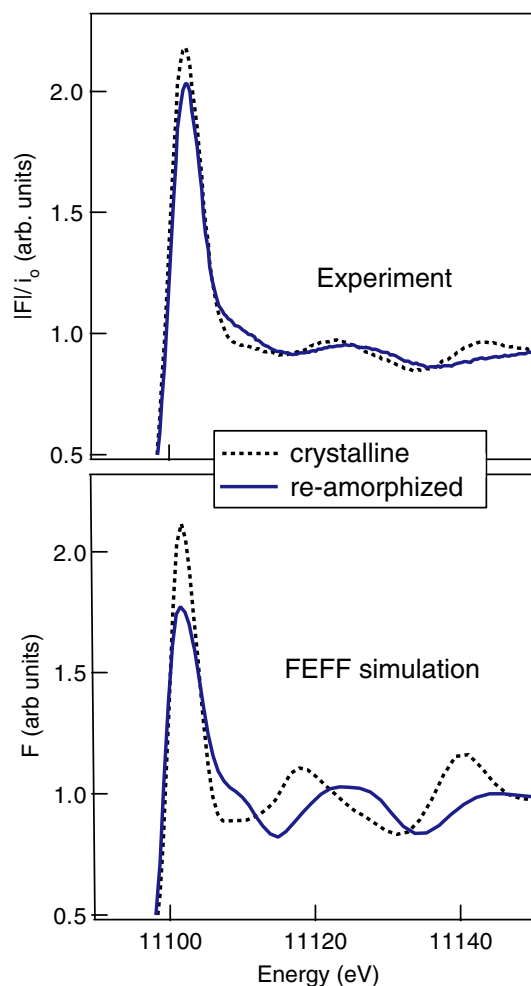


Fig. 5. Experimental (top) and simulated (bottom) Ge-edge XANES spectra in crystalline and amorphous state. In the simulations, Ge is placed in the octahedral and tetrahedral symmetry positions in the crystalline and amorphous states, respectively.

The difference in the amplitude is due to the fact that thermal damping has not been taken into account during the simulations.

As the Sb-edge XAFS does not exhibit pronounced changes, we suggest that the local structure of Sb atoms does not change significantly during the crystal-to-amorphous



Table 2  
Ge–Te bond length in the crystalline and amorphous states of different materials along the GeTe–Sb<sub>2</sub>Te<sub>3</sub> quasibinary line

Material	Lattice parameter (Å)	Ge–Te bond length (Å)	
		Crystal	Amorphous
GeTe	5.99 [20]	2.80 ± 0.01	2.60 ± 0.01
		3.13 ± 0.01	
Ge <sub>2</sub> Sb <sub>2</sub> Te <sub>5</sub>	6.02 [6,14]	2.83 ± 0.01	2.61 ± 0.01
		3.15 ± 0.08	
Ge <sub>1</sub> Sb <sub>2</sub> Te <sub>4</sub>	6.04 [21]	2.88 ± 0.02	2.64 ± 0.02

transition, namely, the Sb atoms preserve their (distorted) octahedral coordination.

The role of Sb atoms in the phase-change process (the presence of Sb makes the crystallization process significantly faster) is not quite clear. It is likely that its role is limited to ensuring the overall electron balance necessary to stabilize the rocksalt structure.

A study of another quasibinary material – GeSb<sub>2</sub>Te<sub>4</sub> – and of the binary GeTe has revealed very similar changes in the Ge–Te bond lengths upon the crystallization–amorphization transition (Table 2). In all cases, Ge–Te bonds get shorter upon amorphization, the observed changes being of similar magnitude. This similarity suggests that the nature of the structural transformation during the phase transition is similar in all Ge-containing materials and consists primarily of Ge atom switching between octahedral and tetrahedral symmetry positions within the Te fcc sublattice.

It is this nature of the transition that is responsible for the very fast structural change. The structure does not have to be molten in a conventional sense. It is a simple rupture of weaker Ge–Te bonds that is sufficient for the atomic switching. The Te sublattice is essentially preserved and ensures the stability of the media.

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