

# Nanometer-scale mechanism of phase-change in Ge-Sb-Te alloys probed by XAFS

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We have performed XAFS measurements at all three edges of Ge-Sb-Te on real device DVD structures. We found that in the crystalline state GST possesses a *distorted* rocksalt structure while in the amorphous state Ge atoms switch into the tetrahedral symmetry positions within the Te fcc sublattice. The switch is triggered by the strained Ge-Te bonds in the cubic GST phase. It is this switching of the Ge atoms – as opposed to laser-induced conventional melting – that ensures fast and stable performance of phase-change optical discs.

## 1. Introduction

The phenomenology of the phase-change is simple and consists of the following. 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 the solid state with a 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 to follow the changes in temperature in which case one obtains a supercooled liquid and then a glass. The material can also be heated by light. Exposure of an amorphous material to a laser light such that heats it above the glass-transition temperature results in its crystallization while short and intense laser pulses melt the material and - provided the heat dissipation rate is fast enough - an amorphous recorded bit is formed.

It follows from this description that almost any material can be used for phase-change recording. However, just a very limited number of materials are suitable in terms of speed and stability. The best materials to-date are Ge-Sb-Te (used in DVD-RAM) and AgInSbTe (used in DVD-RW) [1]. What makes these two materials special? Interestingly, the nanometer scale mechanism behind the phase-change has remained unclear for almost 10 years after DVDs became commercially available.

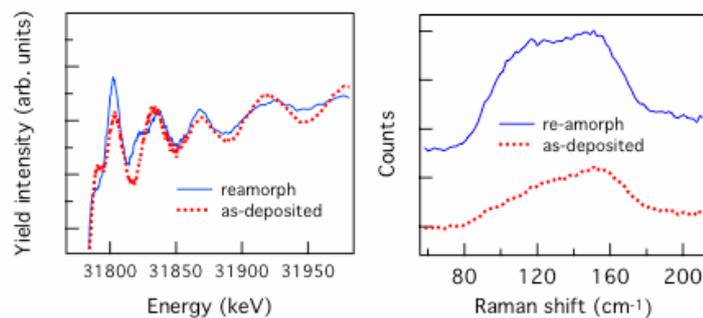
Previous x-ray diffraction (XRD) studies [2,3] have demonstrated that thin layers of GST crystallize into a structure that is similar to rocksalt. While this was a very important step forward it left open questions about the *local* structure and its transformation upon the phase transition. In this paper we present the results of an investigation of the local structure of Ge-Sb-Te 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 spectroscopy (XAFS) [4]. 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 neighboring species, as well as the bond length disorder parameter, or mean-square relative displacement (MSRD). 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, is additionally sensitive to the mutual arrangement of the neighboring atoms in space. As XANES features are 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.

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. Two main materials, namely  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  and  $\text{GeSb}_2\text{Te}_4$  have been studied. As a reference, we have also investigated the structure of the binary GeTe that is a constituent material of the quasi-binary  $\text{GeTe} - \text{Sb}_2\text{Te}_3$  used in commercial optical memories. Measurements were performed on real device structures.

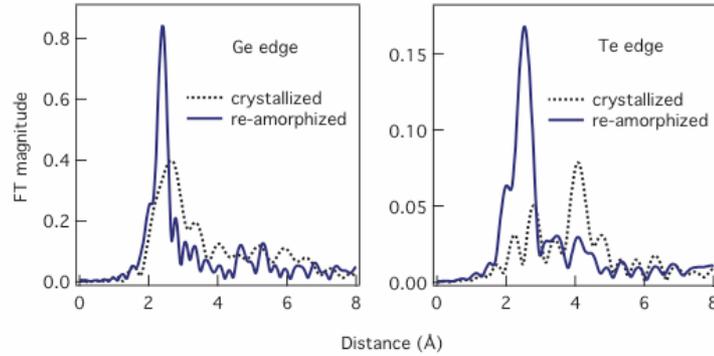
## 2. Results and discussion

The structure of GST has previously already been investigated by XAFS [5] but it is important to note here that those experiments were performed on thicker films and using the as-deposited amorphous films. It is not obvious that the as-deposited structure is identical to the reversibly obtained laser-amorphised structure. In fact, since the *as-deposited amorphous* structure is obtained under rather non-equilibrium conditions we may expect that it is different from the laser-amorphised state. To address this issue, we have measured XANES and Raman spectra of as-deposited and laser-amorphised layers. Figures 1(a,b) compare XANES spectra and Raman spectra of as-deposited and laser-amorphised GST. One can see that the as-deposited amorphous state possess spectra different from those of the laser-amorphised state. Whilst the detailed analysis of the differences is beyond the scope of the present work, it is obvious that the two amorphous structures are different.



**Figure 1:** Comparison of XANES (a) and Raman scattering (b) spectra of as-deposited and laser-amorphised  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  layers demonstrates that the two structures are different.

Figure 2 shows Fourier-transformed spectra measured at Ge and Te K-edges for the crystallised and laser-amorphised states of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ .

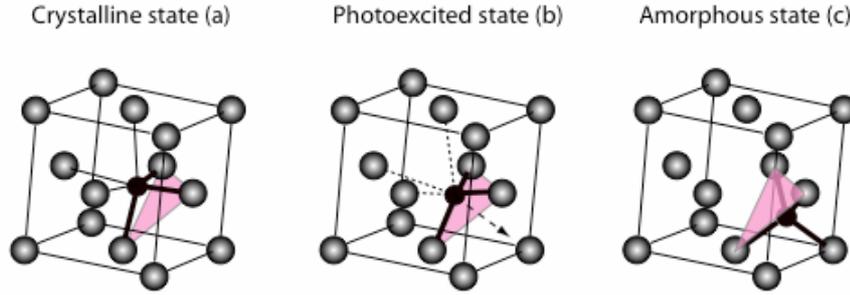


**Figure 2:** Fourier-transformed EXAFS spectra of laser-crystallised and laser-amorphised  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  layers.

### 2.1 Crystalline state

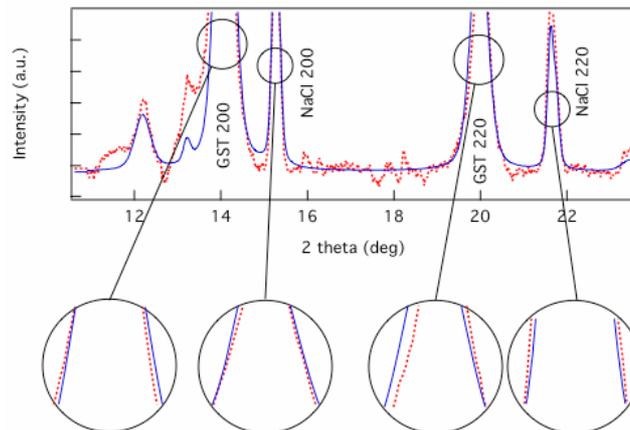
We used the rocksalt structure as the starting model for the fitting process [6]. The results obtained for Ge-Te bonds are summarised in Table 1. One can clearly see that the Ge-Te first-nearest bond lengths are significantly shorter than the corresponding values expected from XRD. On the other hand, the second-nearest Te-Te distance of  $4.26 \text{ \AA}$  is exactly the same as that expected from XRD data [6]. The coordination numbers were found to be about half the value expected for the rocksalt structure. It should also be noted that the 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 a covalent network where disorder typically accumulates with distance.

Based on the above results, one can deduce the following local structure for the crystalline state of GST. The Te atoms form a rather stable fcc sublattice with Ge and Sb located close to – but not exactly on – the corresponding rocksalt sites, being displaced from the center [6,7]. The structure is thus strictly speaking not rocksalt (since it does not possess rocksalt symmetry) but similar to the well known structure of GeTe where Ge atoms are displaced from the center of the cell (rhombohedral structure) having three Te neighbours located at a shorter distance ( $2.83 \text{ \AA}$ ) and three more Te neighbours located at a longer distance ( $3.13 \text{ \AA}$ ) [8]. The crystal structure is schematically shown in Fig. 3a where a Ge atom is shown within the Te fcc lattice. Based on the above model, we have further fitted the structure assuming two pairs of distances (shorter and longer bonds) for both Ge-Te and Sb-Te pairs. The fit quality was somewhat improved and the longer Ge-Te and Sb-Te distances were found to be  $3.15 \pm 0.2 \text{ \AA}$ , the values similar to the longer Ge-Te bonds in GeTe. The rather large uncertainties in the obtained values do not allow us to draw more specific conclusions about the longer bonds.



**Figure 3:** Local structure of GST in the crystalline (a) photoexcited (b) and amorphous (c) states. The Ge atom (black) is shown within the Te fcc lattice). The arrow in panel (b) indicates the net force acting on the Ge atom from the strained Ge-Te bonds after rupture of longer bonds.

To get some insight into the long-range order structure we have performed x-ray diffraction measurements on a *mixture* of GST and the rocksalt (NaCl) with subsequent Rietveld refinement. The result is shown in Fig. 4. While the usual way to judge about the refinement quality is to estimate the difference between the experimental and simulated spectra, such an approach has some limitations. In particular, if the sample contains larger grains, relative intensities of the lines may be different from those in a perfect powder sample. We thus only looked at how well the peak *positions* are reproduced by the fit since this is only determined by the interplane distances and is not influenced by a possible preferred orientation. As one can see, the fitted position of the NaCl peaks are in perfect agreement with the measurement. However, the GST peak positions cannot be fitted. There is a systematic deviation in the peak positions: namely, the experimental 200 peak is located to the left and the 220 peak is located to the right of the simulated peaks. We believe that the reason for this are displacement of Ge and Sb atoms from the ideal crystallographic positions.



**Figure 4:** X-ray diffraction spectrum of a mixture of GST and NaCl (red dotted line) and Rietveld refinement (blue solid line). While the peak positions of NaCl are fitted very well, the experimental GST peak positions differ from those of the rocksalt structure model fit.

An important issue that still remains open is whether the Ge (Sb) atoms are displaced randomly or in a correlated way and also whether the displacements are static or dynamic. Experiments to answer these questions are currently underway. In either case, at this moment a *distorted* rocksalt structure remains the best way to describe the long-range atomic arrangement in GST.

Other implications from the above results are the following. Firstly, the fact that Ge (Sb) atoms are located off center implies that there is a net dipole moment and Ge-Sb-Te is potentially a ferroelectric material. The possible ferroelectric nature of GST may be key to understanding the super-resolution read-out mechanism in super-resolution near-field structure (Super-RENS) optical disks [9]. Secondly, it should be noted that Ge(Sb)-Te bond lengths are longer than a sum of the corresponding covalent radii, i.e. the bonds are strained. We believe that this strain causes frustration in the cubic structure of GST rendering it unstable and is a major reason for a fast phase transformation [11].

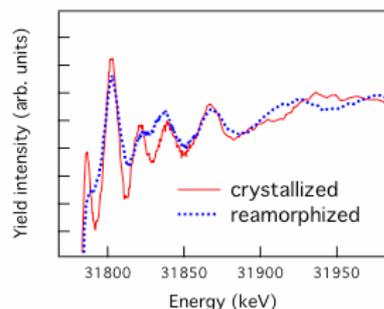
## 2.2 Amorphous state

We now turn to the amorphous state. One can imagine that the weaker bonds break as a result of photoexcitation [11] (similar to photo-induced melting of selenium when photoexcitation leads to rupture of interchain bonds and subsequent photo-induced athermal melting of the material). Following the rupture of the weaker bonds, Ge atoms become three-fold coordinated (Fig. 3b) and due to forces acting on the Ge atoms due to presence of the strained bonds it becomes possible for Ge atoms to flip through the plane between the three Te atoms and acquire the preferred tetrahedral coordination (Fig. 3c). Light-induced heating leads to an increase in the lattice constant which favours this process making the strain larger and the energy at the pinchpoint lower. The net result of such a structural transformation is a switch of a Ge atom from an octahedral symmetry site into a tetrahedral symmetry site.

A test for the final state of such a transformation is an estimate of the Ge-Te bond length. With the lattice parameter of 6.02 Å [3,4] the distance to the center of the tetrahedral site can be calculated in a straightforward manner to be 2.61 Å which agrees perfectly with the Ge-Te bond length in the amorphous state measured experimentally ( $2.61 \pm 0.01$  Å).

As was stated earlier, XANES – different from EXAFS – depends on multiple scattering, i.e. is sensitive to mutual arrangement of the scattering atoms in space. Our Ge K-edge XANES measurements (and analysis) confirmed [6] that Ge atoms switch into the tetrahedral symmetry sites upon amorphisation.

Figure 4 shows Te K-edge XANES spectra for the crystallised and laser-amorphised layers. One can see that the Te-edge spectrum also undergoes a very significant change. This is not surprising, since Te-Ge(Sb) interactions are significantly modified upon rupture of the longer Ge-Te bonds and subsequent relaxation. Since XANES probes transitions between the core level state and the lowest unoccupied state (bottom of the conduction band) this result demonstrates that the density of states associated with Te is significantly modified upon amorphisation. A drastic change in DOS associated with Te atoms has also been obtained through computer simulations [12].



**Figure 4:** Te K-edge XANES spectra of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  in the crystalline and amorphous states.

To check how general the above changes are we have investigated another GST compound, viz.,  $\text{GeSb}_2\text{Te}_4$  and a binary  $\text{GeTe}$  that is an end point of the quasi-binary  $\text{GeTe-Sb}_2\text{Te}_3$  tie-line. The measured Ge-Te bond lengths are shown in Table 1. As one can see, the changes are very similar in all cases and scale rather well with the lattice parameter. We thus conclude that the mechanism of phase-change recording consists primarily of the Ge atom switching between the octahedral and tetrahedral symmetry positions.

**Table 1:** GeTe bond lengths determined from an EXAFS analysis of the crystalline and amorphous states of various  $\text{GeTe} - \text{Sb}_2\text{Te}_3$  quasibinaries. It should be noted that the bond lengths for the crystalline state agree well with XRD data (taking the very large  $B_0$  values into account).

Material	Lattice parameter, Å	Ge-Te bond length, Å	
		Crystal	Amorphous
$\text{GeTe}$	5.99	$2.80 \pm 0.01$ $3.13 \pm 0.01$	$2.60 \pm 0.01$
$\text{Ge}_2\text{Sb}_2\text{Te}_5$	6.02	$2.83 \pm 0.01$ $3.15 \pm 0.08$	$2.61 \pm 0.01$
$\text{Ge}_1\text{Sb}_2\text{Te}_4$	6.04	$2.88 \pm 0.02$	$2.64 \pm 0.02$

### 3. Future challenges

There are several important issues still to be investigated. What is the role of Sb? Since the Sb surroundings do not change upon amorphisation we believe that Sb is necessary to ensure overall electron balance and stabilizing the distorted rocksalt structure of GST. Whether or not this is the only role of Sb remains to be explored.

One of the most important challenges is the establishment of the intermediate- and long-range order (symmetry) in GST beyond the rocksalt approximation. Some suggestions about possible

intermediate-range order have been recently made [13]. They require further verification and the understanding of the intermediate-range order is likely to lead to development of more advanced materials. This is where XAFS and XRD can complement each other.

Finally, what changes are taking place in Ge-free phase-change materials? What is the nanometer-scale origin of structural changes in Ag-In-Sb-Te? While some similarities between GST and AIST have been established, e.g. 'cubic' arrangement of atoms and presence of shorter and longer bonds [14], the details of the *local* structure of both crystalline and amorphous phases of AIST are still not sufficiently understood. Our preliminary XAFS measurement have shown that XAFS spectra at Sb and Te edges have features similar to those in GST but the data quality obtained does not allow to draw more significant conclusions. Further measurements are currently underway.

#### 4. Conclusions

We have demonstrated that the photo-induced phase change in Ge-Sb-Te consist primarily of Ge atom switching between octahedral and tetrahedral symmetry sites within the Te fcc lattice. The driving force for the flip to the tetrahedral site are strained Ge-Te bonds present in the cubic phase of GST. It is this switching that ensures fast and stable performance of phase-change optical discs.

#### Acknowledgements

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