LOCAL STRUCTURE OF Ge-Sb-Te AND ITS MODIFICATION
UPON THE PHASE TRANSITION

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Present-day multimedia strongly relies on re-writable phase-change optical memories. We
have found that $Ge_2Sb_2Te_5$ (GST), the material of choice in DVD-RAM, does not possess
the regular rock-salt structure but that Ge and Sb atoms are displacedfrom the ideal rocksalt
positions. Amorphisation of both GeTe and GST results in a significant shortening of
covalent bonds and a decrease in the mean-square relative displacement concomitant with a
drastic change in short-range order. The order-disorder transition in GeTe and GST is
primarily due to a flip of Ge atoms from an octahedral position into a tetrahedral position
without rupture of strong covalent bonds. It is this nature of the transformation that ensures
large changes in reflectivity, fast disk performance and repeatable switching over millions
cycles.

Present-day computers and numerous multimedia applications require faster and denser
memories. The ability of media to be used repeatedly, i.e. to be re-writable, is also an important
requirement. One of the most promising media for re-writable applications is phase-change materials.
The idea to use an amorphous-to-crystalline phase transition for information storage dates back to
the 1960s when S.R. Ovshinsky suggested a memory switch based upon changes in the properties of
amorphous and crystalline phases of multicomponent chalcogenides [1]. This technology became the
mainstream in optical disc production and in the late 1990s resulted in the commercialization by
Matsushita of 4.7 GB digital versatile disc random access memory (DVD-RAM) utilizing $Ge_2Sb_2Te_5$
(GST) as the recording medium [2]. The choice of GST was determined by its fast and stable
performance and large reflectivity changes between the crystalline and amorphous states.

The stable crystal structure of GST is hexagonal [3] but the structure of a thin laser-crystallized
layer is believed to be different. Based on x-ray diffraction (XRD) measurements, it was argued that
a crystallized GST layer possessed the rocksalt structure with Te atoms occupying sites on one fcc
sublattice with Ge and Sb randomly forming the other fcc sublattice (20% of the sites being
vacant)[4,5]. A lattice parameter of 6.02 Å was reported. The isotropic atomic displacements found via
the fitting process were quite large, 1.2 $Å^2$ and 3.2 $Å^2$, for Te, and Ge(Sb) species respectively. The
explicit structure of the amorphous phase has remained unknown and was tacitly assumed to be a
randomized rocksalt structure.

In order to develop better media, a much deeper understanding than presently available of the
local structure and its transformation is required. 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)[6].

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, additionally allows one to probe the local arrangement of atoms on a scale somewhat beyond the first-nearest neighbors, in particular, it is sensitive to the mutual arrangement of the neighboring 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 [7].

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 on *real-device structures*. The details of the sample preparation and main results have been reported in a recent Nature Materials publication [8].

The Fourier-transformed (FT) spectra for the Ge and Te edges of GST are shown in Fig. 1. The spectra measured at the Sb edge did not show any significant variation between the two states and are not shown here. (It should be noted that the r-space data shown in Fig. 1 are not real space radial distribution function data but the magnitude of the Fourier transforms (FTs) of the k-space EXAFS data. The peak positions in the figure are shifted from the actual interatomic distances toward lower r because of the photoelectron phase shift $\delta(k)$ in the phase factor of the EXAFS oscillations.) The data were fitted using the ab-initio multiple scattering code FEFF8 to simulate the theoretical spectra. A reader interesteed in knowing more about EXAFS is referred to a rather complete monograph [6].
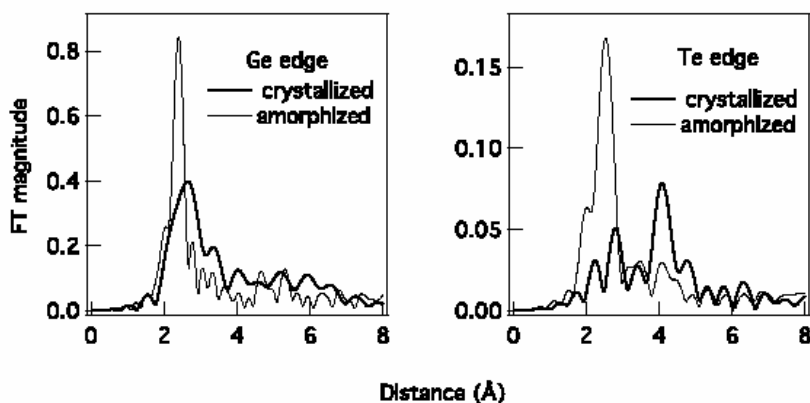

Fig. 1. Fourier-transformed EXAFS spectra for crystallized and laser-amorphized samples measured at the K-edges of Ge (left) and Te (right).

The results for crystalline GST are summarized below. We found two types of bond lengths, namely shorter and longer bonds that were for Te-Ge: 2.83 ± 0.01 Å, and 3.2 ± 0.3 Å and for Te-Sb: 2.91 ± 0.01 Å and 3.2 ± 0.3 Å. It should be noted here that the observation of splitting of the bond lengths into two groups is very similar to the case of GeTe. This similarity is significant becase GeTe is an end composition along the quasibinary GeTe – Sb_2Te_3 tie line to which GST belongs and demonstrates the importance of the GeTe component in the material. The uncertainties for the longer bonds are rather large. For this reason no definitive conclusions could be drawn about the longer bonds and in what follows we shall exclusively concentrate on the shorter bonds. The off-center location of Ge atoms means that there is a net dipole moment and suggests that GST is a ferroelectric material [9]. We also observed a second-nearest-neighbour Te-Te peak at 4.26 Å. The obtained results are in perfect agreement with previous XRD measurements taking the very large isotropic temperature factor B_0 into account.

The above results suggest the following structure model. The structure is similar to the rocksalt structure but due to differences in the covalent radii of the constituent species, Ge, and to a lesser extent Sb, are shifted from their corresponding fcc sublattice sites giving rise to a system of shorter bonds and longer bonds. The shorter bonds are more rigid and thus provide a framework for the local structure.

We now turn to the amorphous state. Unexpectedly, both the Te-Ge and Te-Sb bonds get *shorter* (2.61 Å and 2.85 Å, respectively) and *stronger* as evidenced by Fig. 1 (the peak in the amorphous phase is narrower and located at smaller distances). At the same time, the Te second-neighbor peak becomes considerably weaker but does not disappear completely. The MSRD value decreases from 0.02 Å^2 in the crystalline state to 0.008 Å^2 in the amorphous state.

To get further insight into the structure of the amorphous phase, we also performed XANES simulations and found that the best agreement with experiment was obtained when Ge was allowed to acquire its preferred tetrahedral surrounding in the amorphous phase [8].

This structural transformation is illustrated in Fig. 2 where a Ge atom is shown within the fcc structure formed by Te atoms. The Ge atoms occupy octahedral and tetrahedral symmetry positions in the crystalline and amorphous states, respectively. The stronger covalent bonds are shown with thicker lines than the weaker bonds (left). An intense laser pulse induces preferential rupture of the weaker bonds and the Ge atom flips into the tetrahedral position (right). Notice, that the three covalent bonds remain intact. This conservation of the system of stronger covalent bonds is crucial: the material is not molten in a conventional sense.
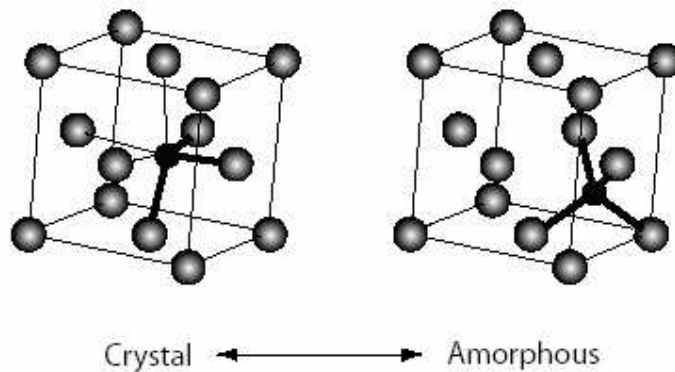

Crystal ⟷ Amorphous

Fig. 2. Fragments of the local structure of GeTe/GST around Ge atoms in the crystalline (left) and amorphous (right) states. Upon heating the sample by a short intense pulse (above the melting point, T_m) and subsequent quenching, the Ge atom flips from the octahedral to tetrahedral-symmetry position. Notice that the stronger covalent bonds remain intact upon the umbrella-flip structural transformation rendering the Ge sublattice random. Exposure to light that heats the sample above the glass-transition temperature (T_g) – but below T_m – reverses the structure.

Sb-edge XANES does not exhibit any significant changes upon amorphization (except for the Sb-Te bond shortening) implying that the local arrangement of atoms around Sb remains essentially unchanged in accordance with the above model. We believe that the Sb atoms mainly play the role of enhancing overall stability of the metastable crystal structure by participating in the over-all electron balance.

It is well known that lone-pair electrons subtended at chalcogen atoms plays a crucial role in local changes in the coordination number during reversible photostructural changes in S- and Se-based glasses and we believe that lone-pair electrons subtended at Te atoms may also play a role in the change of the bonding configuration discussed above.

Table 1. GeTe bond lengths determined from EXAFS analysis for the crystalline and amorphous states of various GeTe – Sb_2Te_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
GeTe	5.99	2.80 ± 0.01 3.13 ± 0.01	2.60 ± 0.01
$Ge_2Sb_2Te_5$	6.02	2.83 ± 0.01 3.15 ± 0.08	2.61 ± 0.01

We expect that the nature of the structural transformation discussed above – namely the switching of Ge atoms between octahedral and tetrahedral symmetry positions - is likely to be common for other phase-change media. In particular, very simialar changes in the Ge-Te bond length in the binary GeTe has also been observed (Table 1) [10,11].

References

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[1] S. R. Ovshinsky, Phys. Rev. Lett. **21**, 1450 (1968).

[2] T. Ohta, J. Optoelectronics Adv. Mater. **3**, 609 (2001).

[3] I. I. Petrov, R. M. Imamov, and Z. G. Pinsker, Sov. Phys. Cryst. **13**, 339 (1968).

[4] N. Yamada and T. Matsunaga, J. Appl. Phys. **88**, 7020 (2000).

[5] T. Nonaka, G. Ohbayashi, Y. Toriumi, Y. Mori, and H. Hashimoto, This Solid Films **370**, 258 (2000).

[6] *X-ray absorption*, edited by D. C. Koningsberger and R. Prins (John Wiley & Sons, New York, 1988) 683p..

[7] A. L. Ankudinov, B. Ravel, J. J. Rehr, and S. Conradson, Phys. Rev. B **58**, 7565 (1998).

[8] A. V. Kolobov, F. P., F. A., A. L. Ankudinov, J. Tominaga, T. Uruga, Nature Materials **3**, 703 (2004).

[9] J. Tominaga, T. Shima, M. Kuwahara, T. Fukaya, A. V. Kolobov, T. Nakano, Nanotechnology 15 (2004) 411.

[10] Y. Maeda, M. Wakagi, Jpn. J. Appl. Phys. 30 (1991) 101.

[11] A. V. Kolobov, P. Fons, J. Tominaga, A. L. Ankudinov, S. N. Yannopoulos, K. S. Andrikopoulos, J. Phys.: Condens. Matter 16 (2004) S5103.