Why Phase-Change Media Are Fast and Stable: A New Approach to an Old Problem

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Present-day multimedia strongly relies on re-writable phase-change optical memories. We find that, different from current consensus $Ge_2Sb_2Te_5$ (GST), the material of choice in digital versatile discs—random access memory (DVD-RAM), possesses a structure similar to ferroelectric GeTe, namely that Ge and Sb atoms are located off-center giving rise to a net dipole moment. 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 the short-range order. We demonstrate that 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. [DOI: 10.1143/JJAP.44.3345]

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1. Introduction

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.[2,3] 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[4] 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).[5,6] A lattice parameter of 6.02 Å was reported. The isotropic atomic displacements found via the fitting process were quite large, especially for the Ge and Sb sites. Indeed, in the XRD analysis it was found that the isotropic temperature factor values B_0—which is a measure of atomic displacements from the ideal crystalligraphic positions due *e.g.* to thermal vibrations—for Te, and Ge(Sb) species were 1.2 Å^2 and 3.2 Å^2, respectively, which corresponds to atomic displace-

ments of 0.1 Å and 0.2 Å for Te and Ge(Sb) species, respectively. These fitting results were later confirmed by other groups.[7,8]

It was suggested[9] that the cubic structure of GST (which is rather isotropic and more similar to the amorphous structure than any other crystalline structure) was the reason for high-speed switching and stable performance. The explicit structure of the amorphous phase has remained unknown and was tacitly assumed to be a randomized rocksalt structure. The crystallization process into the metastable cubic phase of GST is characterized by an activation energy of typically 2.3–2.7 eV[10] (>3 eV for the binary GeTe[11]).

The above scenario of events has lead to the paradoxical situation in which a device such as an optical disc is functional and commercially available but the structural changes behind the utilized transition are unknown. In particular, the following questions need to be answered.

Why are the atomic deviations so large (~7% of the bond length) in a solid crystalline phase, in other words, is the structure really rocksalt? If the structures of the crystalline and amorphous phases are similar, why is the reflectivity difference so large? Why is the activation energy of crystallization almost an order of magnitude larger that the energy gap? (the energy-gap being the characteristic energy of any solid-state process) Why are crystalline regions more reflective than amorphous regions? (usually, in the amorphous state chalcogenide semiconductors possess the band gap that is smaller—and the resulting absorption and reflectivity larger—than in the crystalline state[12])

In order to answer these questions, 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).[13]

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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.[14]

2. Experimental Details

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 GeTe that is a constituent material of the quasi-binary GeTe-Sb_2Te_3 used in commercial optical memories.

Measurements on GST were performed on real-device structures. The details of the sample preparation can be found elsewhere.[15] For GeTe, as-deposited and thermally crystallized 3-micron thick films were used.

3. Results and Discussion

The Fourier-transformed (FT) spectra for the Ge and Te edges of GST are shown in Fig. 1. The spectra measured at
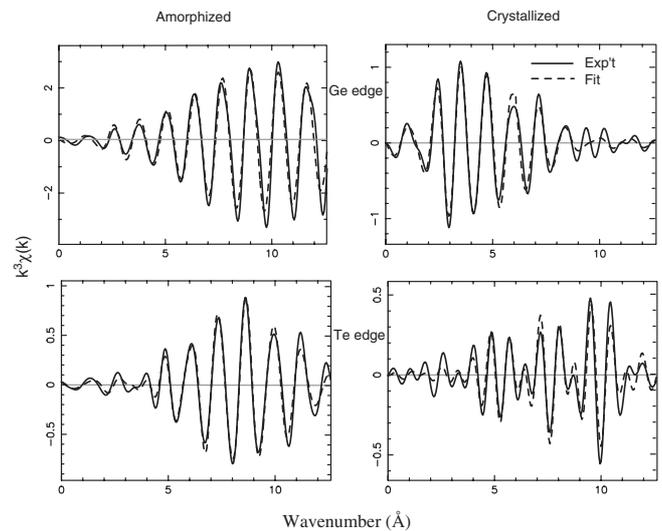
Fig. 2.   Comparison of experimental and simulated EXAFS at Ge and Te K-edges for crystallized and laser-amorphized samples (in the back-FT space).

Table I.   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		Activation energy, eV
		Crystal	Amorphous	
GeTe	5.99[26]	2.80 ± 0.01	2.60 ± 0.01	∼3
		3.13 ± 0.01		
$Ge_2Sb_2Te_5$	6.02[5,6]	2.83 ± 0.01	2.61 ± 0.01	
		3.15 ± 0.08		2–3
$Ge_1Sb_2Te_4$	6.04[27]	2.88 ± 0.02	2.64 ± 0.02	

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 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. The reader interested to know more about XAFS is referred to ref. 13. A comparison of the experimental and simulated EXAFS spectra is shown in Fig. 2. and the main results for the materials are summarized in Table I.

3.1   Local structure of the crystalline state

As regards the crystalline phase we used the rocksalt structure as the starting structural model for data fitting. By varying the corrections to the ideal rocksalt structure distances, we obtained the following results.

For GeTe we found that each atom has 6 neighbors of the opposite types located—in groups of three—at two different distances, namely, there are two different Ge-Te bond length: 2.80 ± 0.01 Å and 3.13 ± 0.01 Å. These data reveal
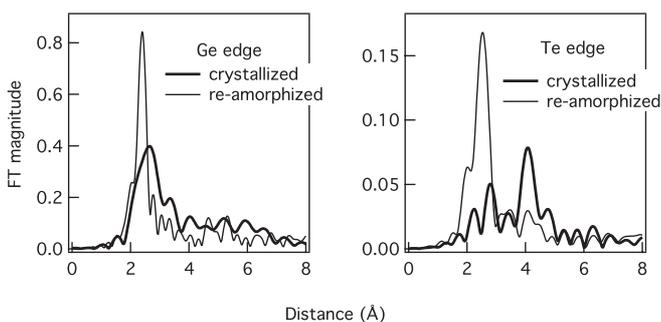

Fig. 1.   Fourier-transformed EXAFS spectra for crystallized and laser-amorphized samples measured at the K-edges of Ge (left), Sb (middle) and Te (right).

that GeTe possesses a rhombohedral structure. This result is in perfect agreement with previous studies. We have additionally found that the Ge sublattice contained about 10% vacancies.[16]

The obtained results for crystalline GST are summarized below. As in the case of GeTe, we found several types of bond lengths, namely 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. 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.

No Sb-Ge bonds were detected in agreement with the fact that Sb and Ge do not intermix in the solid phase but we clearly observed a second-nearest-neighbour Te-Te peak at 4.26 Å.

It should also be mentioned that the isotropic atomic displacements of single atoms obtained from XRD, especially for Ge and Sb species, are quite large ($\langle u^2 \rangle = 0.04$ Å^2). Indeed, this number is more than twice larger than the corresponding value for the analogous binary compound.[6] In contrast, the mean-square relative displacements (MSRD) of the Te-Ge bond length obtained in EXAFS are considerably lower (0.02 Å^2). This result demonstrates that Ge and Sb atoms deviate from the ideal rocksalt positions not in a random way but in a strongly correlated manner with respect to the neighboring Te atoms, i.e. the crystalline structure is in fact a distorted rocksalt-like structure similar to the case of the ferroelectric GeTe. The off-center location of Ge atoms means that there is a net dipole moment and suggests that GST is a ferroelectric material.[17]

Another key point to note is that the MSRD value for the Te-Te pair (the second-nearest neighbor) is considerably smaller than that for the first nearest neighbor (Ge-Te or Sb-Te).[15] This is rather atypical for a solid and strongly suggests that the Te sublattice is inherently more stable than the Ge-Te or Sb-Te local structure. Further studies in this direction are currently underway.

The obtained results are in perfect agreement with previous XRD measurements taking the very large isotropic temperature factor B_0 into account. Yet better evidence of the consistency of the two techniques is a comparison of Te-Te distances. The lattice parameter of 6.02 Å obtained from XRD implies a Te-Te distance of 4.26 Å which is in excellent agreement with the direct Te-Te distance measurement by EXAFS (4.26 ± 0.01 Å).

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 the corresponding fcc sites giving rise to a system of shorter bonds and longer bonds in an overall buckled structure.[18] The shorter bonds are more rigid and thus provide a framework for the local structure. It is worth mentioning that a similar mechanism, namely weaker back-bonding to second-nearest neighbors has been argued[19] to be the reason for cohesion between the layers in the rhombohedral structure of IV–VI compounds.

3.2 Local structure of the amorphous state

We now turn to the amorphous state. In GeTe, the Ge-Te bond lengths were found to be shorter (2.60 Å) in the amorphous state than in the crystalline state. This result is in good agreement with previous XAFS measurements.[20] In the ternary GST we also found that Te-Ge and Te-Sb bonds get shorter (2.61 Å and 2.85 Å, respectively) and stronger as evidenced by Fig. 1. 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.

Inclusion of Ge-Ge, Sb-Sb, Te-Te, and Ge-Sb first-neighbor correlations in the starting model did not lead to any improvement in the fit quality based on which we conclude that such bonds are not present in either crystalline or amorphous phases.

Such behavior is highly unusual for typical three-dimensional covalently bonded solids as due to the anharmonicity of interatomic potentials, disordering typically results in an increase of the bond lengths and the bond-length disorder. The obtained results reminds one of the case of molecular solids where the presence of intermolecular and intramolecular bonds determines the crystallization/amorphization behaviour.

In the current case, a bond strength hierarchy also exists and the following model of structural rearrangement can be envisaged. Upon melting, the longer Te-Ge (and Te-Sb bonds) are broken and as a result the shorter bonds become even shorter and stronger, i.e. the amorphous phase is locally more ordered than the crystalline phase. Our Raman scattering experiments provided further grounds for this model, namely, the Raman measurements for both GeTe[21] and GST (Fig. 3) showed that the spectra for the crystalline films are dominated by a peak located at lower wavenumbers, i.e. "mode softening" takes place upon crystallization. This situation can be compared with the case of Se or Te when interchain interaction is weakened giving rise to a Raman peak located at higher wave numbers.[22] It should be mentioned that an increased local bond order in the amorphous phase was also observed for selenium.[23]

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 sur-
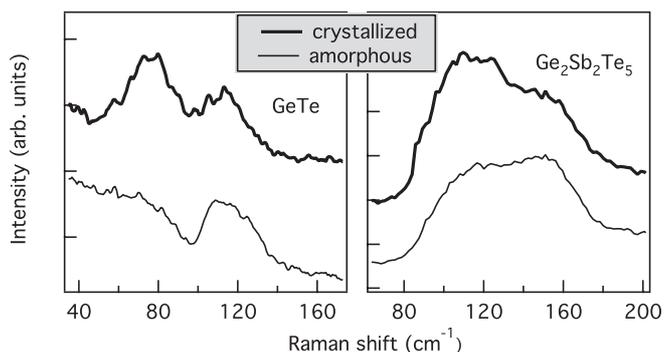

Fig. 3. Raman scattering spectra for amorhous (dotted line) and crystallized (solid line) GeTe (left) and Ge$_2$Sb$_2$Te$_5$ (right) layers.
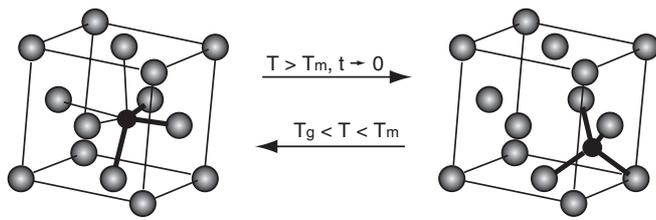
Fig. 4.   Fragments of the local structure of GeTe/GST around Ge atoms in the crystalline (left) and amorphous (right) states. Upon heating the sample by a short intense pulse (above the melting point, T_m) and subsequent quenching, the Ge atom flips from the octahedral to tetrahedral-symmetry position. 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.
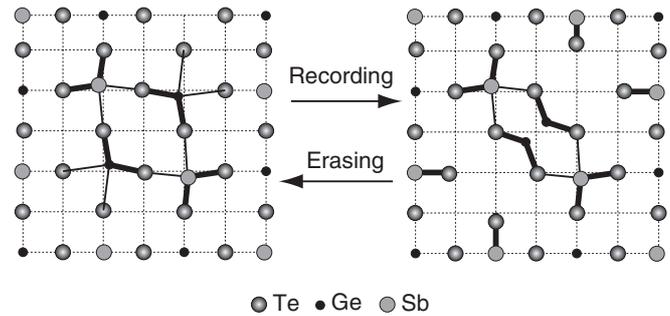

Fig. 5.   Schematics of medium-range-order changes in the structure of GST upon reversible amorphization-crystallization. The umbrella-flip of Ge atoms from the initially distorted rocksalt structure in the crystalline state (left) results in a shortening of Sb-Te bonds and subsequent distortions in the Te fcc sublattice (amorphization) (right).

rounding in the amorphous phase.[15]

This structural transformation is illustrated in Fig. 4 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 (Fig. 4 left). An intense laser pulse induces rupture of the weaker bonds and the Ge atom flips into the tetrahedral position (Fig. 4 right). An alternative description of the structural transformation upon melting is an umbrella-flip distortion resulting in disordering of the Ge sublattice. 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.

To support the aforementioned transformation we proceed to an estimate of the Ge-Te distance from the crystallographic data. Using a lattice parameter of GST (6.02 Å, refs. 5, 6), the Ge-Te distance (Ge atoms being in tetrahedral symmetry positions) can be easily calculated to be 2.61 Å, i.e. exactly the value obtained from the EXAFS analysis. Very similar values can be obtained for GeTe. This consistency between the results obtained using two different structural techniques is the ultimate proof of the suggested structural modification as well as the generality of the structural modification in GeTe-based alloys.

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.

3.3   Intermediate-range-order changes

The structural change on an intermediate-range-order scale can be speculated to be the following (Fig. 5). After rupture of the weaker Ge-Te bonds the Ge atoms flip into the tetrahedral symmetry position forming the GeTe$_4$ tertahedra. At the same time, the broken weaker Ge-Te bonds no longer counterbalance the Sb-Te bonds on the opposite site and, as a result, the Sb-Te bonds become structure determining. The structure relaxes making the Sb-Te bonds shorter (just as in amorphous Se the intrachain bonds get shorter upon

amorphization, i.e. rupture of Van-der-Waals interaction between the chains[23]). The Sb-Te bond shortening upon amorphization has been observed experimentally.[15] This can be viewed as the local formation of the Sb-Te phase. Finally, the structure relaxation causes a slight distortion in the Te fcc sublattice. We can thus describe the complete "amorphization" process as Ge-flip-induced nanophase separation accompanied by distortion of the Te fcc sublattice. As a total result, the long-range order is destroyed but the structure does not become random. It is important that the amorphous phase possesses a well-defined (single-state) structure without long-range periodicity. We believe that the well-defined local structure of the amorphous state is the reason for the overall stability of the GST-based optical media.

4.   Related Issues

Although it is generally assumed that the role of a laser pulse is to simply heat the material, we believe that electronic excitation creating non-equilibrium charge carriers is crucial for the weakening and subsequent rupture of the subsystem of weaker Ge-Te bonds.[15]

It should be stressed that the above structural transformation involves a change in the hybridization from p-type bonding in the rocksalt to sp^3-hybridization in the amorphous state. Indeed, in GeTe the bond ionicity—almost negligible in the amorphous phase[20]—was found quite significant in the crystalline phase.[24] This substantial change in the electronic states accounts for the very large change in optical and electrical properties of GST upon the crystallization-amorphization transition.

It should also be noticed here that the unveiled structural modification can also account for another issue that has never been discussed in literature. Typically, amorphization results in bond-weakening and an appearance of tail states leading to a decrease of the band gap.[12] A decreased band gap means higher absorption and, consequently, higher reflectance in the amorphous state. In GST the situation is reversed, namely, it is the crystalline regions that possess a smaller gap and higher reflectance. The above model provides a clear explanation for this highly unusual behavior. Indeed, the crystal structure consists of shorter and longer bonds. The longer (and hence weaker) bonds are characterized by a smaller energy splitting between the

bonding and antibonding states and thus determine the positions of the valence and conduction band edges (and the width of the band gap) in the crystal. In the amorphous phase, on the other hand, the initially weaker bonds break and disappear altogether and the initially stronger bonds get even shorter and stronger. As a result, the splitting between the bonding and antibonding states increases producing a larger band gap—and lower reflectivity—as compared to the crystalline phase.

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 that take place entirely within the amorphous phase.[25] While the underlying mechanisms of the photostructural changes and phase-change are different, we believe that lone-pair electrons subtended at Te atoms play a significant role in the change of the bonding configuration discussed above.

We expect that the nature of the structural transformation discussed above is likely to be common for other phase-change media. The mechanism for the structural phase transition disclosed here provides potentially critical insight in the search for better performing materials for the next generation of faster and denser optical and Ovonic memories.

Note added in proof—After this manuscript has been submitted, a paper reporting large displacement of Ge atoms in crystalline $Ge_2Sb_2Te_5$ has appeared.[28] The reported displacements are in perfect agreement with the results reported in the present manuscript.

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