

# Liquid $\text{Ge}_2\text{Sb}_2\text{Te}_5$ studied by extended x-ray absorption

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## Abstract

We report on x-ray absorption studies of the structure of the liquid phase of a prototypical phase-change material  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ . We demonstrate that the local structure of liquid  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  is very similar to that of amorphous  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ . Ge atoms in the liquid phase are found to be covalently bonded suggesting a semiconducting nature of the melt.

Ultra-fast phase-transitions in so-called phase-change materials are currently widely used in optical memories and are attracting growing attention as the basis of fast and dense non-volatile memory devices. Contradictory requirements such as high switching speed and long-term stability have singled out Te-based multicomponent alloys along the GeTe-Sb<sub>2</sub>Te<sub>3</sub> quasibinary tie-line with the material of choice for *both* electronic and optical memories being Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> (GST) [1]. The importance of phase-change materials for both present and future memory applications clearly requires better knowledge of their fundamental properties and the physics behind the utilized phase transition.

The current consensus on phenomenology of the phase change is simple and consists of the following. An intense laser (or electric) pulse excites the material, which is subsequently quenched into the amorphous state. It is tacitly assumed that exposure to a short intense pulse heats the material above the melting point although to date no direct evidence is available that the materials melts in the conventional sense. Exposure to a less intense pulse of longer duration leads to heating of the amorphous phase above the crystallization threshold reverting the material to the crystalline state. Property contrast between the crystalline and amorphous phases serves to store information. Since the properties are determined by the structure, precise knowledge of the structure is crucial.

While the stable crystalline structure of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> is hexagonal, the metastable cubic phase utilized in devices possesses a distorted rocksalt-like structure with Te atoms forming one face-centered cubic (fcc) sublattice and Ge/Sb/vacancies forming the other fcc sublattice [2]. In what follows we refer to this structure as cubic. Subsequent x-ray absorption studies and computer simulations have refined the local structure by demonstrating that the Ge and Sb atoms are not located at the center of the cell defined by the Te fcc sublattice but displaced from the center forming subsets of shorter and longer bonds [3][4]. This is similar to the structure of the binary GeTe that is an end point of the quasibinary tie-line GeTe-Sb<sub>2</sub>Te<sub>3</sub> to which Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> belongs.

EXAFS (extended x-ray absorption fine structure) studies have further suggested that during the phase transition the Ge atoms switch between octahedral (crystalline phase) and tetrahedral (amorphous phase) sites within the Te fcc lattice [3]. The presence of tetrahedrally coordinated Ge atoms in the amorphous phase has been confirmed by various groups [5, 6] and it was demonstrated that this change produces a large optical contrast between the two phases [7]. Alternative descriptions of the phase-change process have also

been suggested [6][8][9] where the presence of even-membered rings in both phases and conservation of the “octahedral” bonding angles is stressed.

At the same time, very little is known about the structure of the liquid state. Since the liquid state is believed to be key to the formation of the amorphous state it is clear that structural knowledge is of paramount importance. To date, the available information has been limited to diffraction studies [8][10] and *ab-initio* computer simulations [11][12][13] .

From the experimental diffraction studies it was concluded [10] that upon melting GST alloys of different compositions form octahedral liquids. The results of computer simulations are rather contradictory. While according to [11] in  $\text{GeSb}_2\text{Te}_4$  all atoms have octahedral coordination, the authors of [13] reported the coexistence of Ge atoms with both tetrahedral and octahedral bonding configurations and the coordination number for Ge of 4.3 has been reported in [12] for  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  .

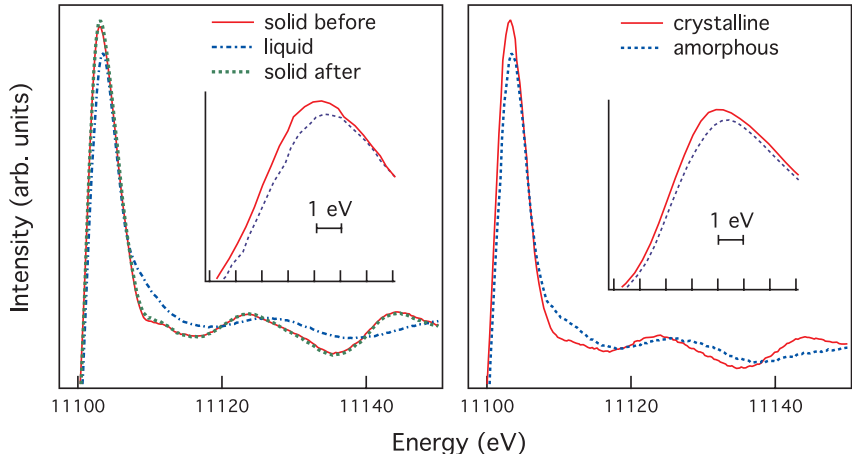


FIG. 1. XANES spectra of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  measured at the Ge K-edge for the solid-liquid (left) and crystalline-amorphous (right) transition. “Solid before” and “solid after” refer to XANES spectra taken at room temperature before and after the melting cycle. The insets show the edge positions on an extended scale. There is a shift of ca. 0.3 eV between the crystallized and amorphous phases associated with the larger band gap of the amorphous phase. The corresponding difference between the solid and liquid phases is much smaller (see text for details).

One of the very few techniques that can be applied to investigate the local structure of disordered systems such as a liquid is x-ray absorption spectroscopy. Extended x-ray

absorption fine structure (EXAFS) contains information about the short-range order such as the coordination number, first-nearest neighbor distances, bond disorder, and the chemical nature of the nearest neighbors around *each* constituent element. X-ray absorption near-edge structure (XANES) depends on multiple scattering and hence contains crucial information about the spatial arrangement of the neighbors around the absorbing atom that is not available through other techniques (hole lifetime effects limit the sampled volume to distances  $\leq 1nm$ .) In this Letter, we present the results of an x-ray absorption study of the melting of the prototypical phase change material  $Ge_2Sb_2Te_5$  .

The samples for the experiment were prepared as follows. A  $Ge_2Sb_2Te_5$  crystal with the stable hexagonal structure was ground into fine powder. In order to ensure high uniformity of the sample the powder was passed through a 20 micron-size mesh. The obtained powder was mixed with BN in ratios that were optimized for the measurements of the K-edges of all three constituent elements and placed into sealed quartz cells with ultrathin x-ray windows. The cell was filled with the  $Ge_2Sb_2Te_5$  -BN mixture and subsequently placed into a furnace and XAFS measurements were performed in transmission mode over a temperature range from room temperature to  $750^\circ C$  (the melting point of  $Ge_2Sb_2Te_5$  is  $615^\circ C$  ). Special care was taken to make sure that the spectra of the solid crystalline phase before and after melting were identical, i.e. no phase separation or oxidation took place upon heating  $Ge_2Sb_2Te_5$  and melting it in the cell).

The experimental results are shown in Fig. 1 (left-hand panel) that compares XANES spectra measured at room temperature before and after melting as well as the spectra of the liquid state measured at  $750^\circ C$  . One can see that the spectra in the hexagonal solid phase before and after melting essentially coincide indicating that phase separation or oxidation did not occur during the melting process and that the melting-solidification process is reversible. The same has also been confirmed for the Sb and Te K-edge spectra (data not shown). At the same time there are pronounced differences between the XANES spectra of  $Ge_2Sb_2Te_5$  in the (crystalline) solid and liquid phases clear demonstrating that the observed change is due to melting.

For comparison, the right-side panel shows the XANES spectra of  $Ge_2Sb_2Te_5$  in the laser-crystallized (cubic) and laser-amorphized states. As can be seen from an examination of the right- and left-side panels, the change in the XANES spectra during the melting process is very similar to that during amorphization.

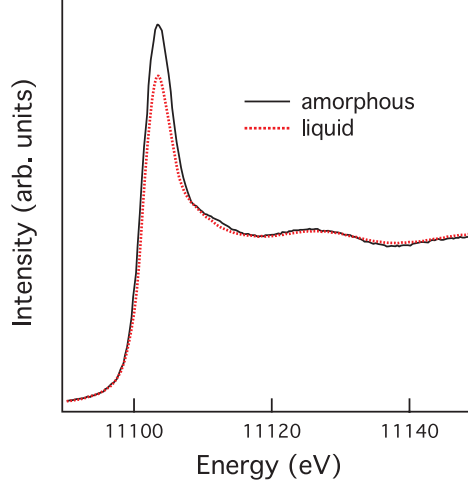


FIG. 2. Comparison of Ge K-edge spectra for the amorphous and liquid phases of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  demonstrating a lower white line intensity for the liquid phase and very similar features at higher energies

The fact that the comparison is made between the cubic and amorphous phases on the one hand and between the hexagonal and liquid phases on the other hand is due to the fact that it is impossible to directly melt the cubic phase or to quench the liquid phase into the cubic phase. The former is due to the rather slow heating rates in the furnace and the latter is caused by extremely high quench rates needed to generate the amorphous phase; the rate that is experimentally inaccessible except for thin film device structures. We have chosen this approach to include the *reversibility* of both the crystallization-amorphization and melting-solidification processes.

XANES spectra for the liquid and amorphous phases are directly compared in Fig. 2. One can see that while the white-line height is different for the two cases - which likely reflects a lower density of unoccupied states in the liquid phase where thermal excitation of charge carriers across the rather narrow band gap is efficient - the features above the white line that have structural origin are essentially identical.

At the same time, there is also a difference between the two sets of data. The Ge K-edge position for the amorphous phase is shifted by ca. 0.3 eV to higher energies with respect to that of the crystalline phase as a consequence of the larger band gap of the amorphous phase (inset). The spectrum for the liquid phase, however, is located at almost the same

position as that of the crystalline (solid) phase (inset). We attribute this difference in the edge position of the amorphous and liquid samples with respect to the crystalline sample to the fact that in the latter case the two spectra are taken at different temperatures (room temperature for the solid crystalline phase and 750 °C for the liquid phase) when the liquid state absorption edge may shift to lower energy due to temperature-induced decrease of the band gap (Moss-Burstein shift).

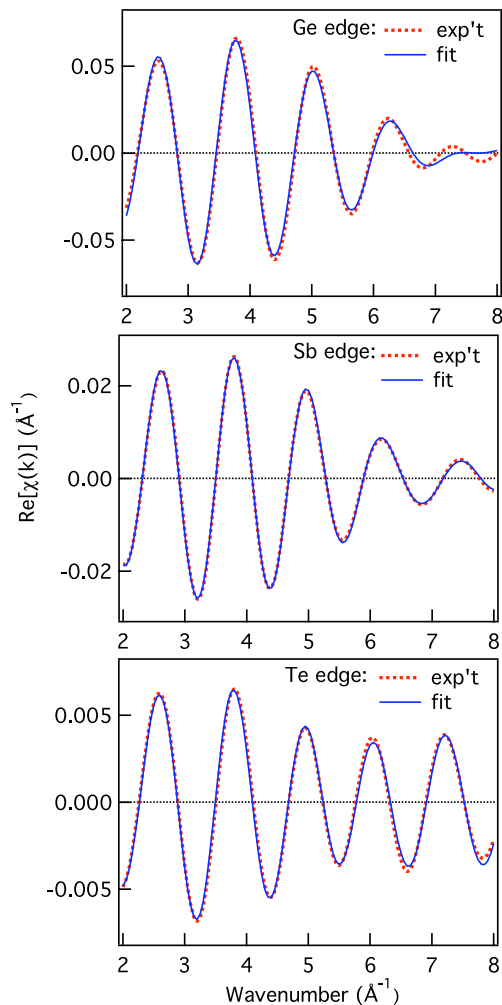


FIG. 3. Fitting results of EXAFS spectra in  $q$ -space for liquid  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  performed at the K-edges of all constituent atoms.

To get information about the short-range order we have analyzed EXAFS data measured at all three edges. While fitting of EXAFS data in general relies on use of an appropriate model, the fitting of the data for a liquid is additionally complicated by the fact that the

bond-length distribution may not be Gaussian. One way to tackle this problem is to use cumulants but in cases when anharmonicity is too large the use of cumulants is not always sufficient. An alternative approach is to use a technique like reverse Monte Carlo that allows the inclusion of different bonding geometries and their distributions. It should be noted, however, that from a statistical perspective the number of independent points in the EXAFS data for a liquid is rather limited because of the short  $k$ -range available, precluding the use of a large number of fitting parameters thus restricting the accuracy of the fit results, especially the coordination number, a quantity strongly correlated with disorder. A further complication is the choice of the proper background function. E.g. if a simple polynomial spline is used for the background subtraction, the coordination number can be strongly underestimated [14]. For this reason we have chosen a different approach.

While the exact structure of the amorphous phase is usually not unique, the optical properties of GST show very little or no variation from cycle to cycle or among various recorded bits suggesting that in this particular case the local structure that determines the optical properties is well defined. We have chosen to fit the liquid phase data using a *single representative configuration* that determines the properties of the liquid phase using the cumulant approach. In order to further enhance the reliability of the results and the number of degrees of statistical freedom, fitting was carried out simultaneously at all three edges. The fit results are summarized in Fig. 3. As one can see there is a very good agreement between the experimental and fitted spectra which provides an indirect justification of our approach.

Based on our analysis we conclude that the following bonds are present in the liquid phase: Ge-Te (2.64 Å), Sb-Te (2.85 Å). Additionally Ge-Sb correlations (3.04 Å) have also been detected. An important point that should be noted is that the obtained Ge-Te and Sb-Te bond lengths are similar to those in the amorphous phase (2.61 Å and 2.83 Å, respectively [3]) and also very close to the sum of the corresponding covalent radii [15] implying the bonds in the liquid phase have covalent nature and hence strongly suggesting that the liquid phase is semiconducting. While the fact that the bond length is equal to the sum of covalent radii is not an unambiguous proof of bonds being covalent, it is a very strong indication of this. For example, in the metastable cubic phase when the bonding is resonant the Ge-Te (2.83 Å) and Ge-Sb (2.91 Å) bonds length are significantly longer [3] than the sum of the covalent radii.

The semiconducting nature of the liquid phase of GST could not be *a priori* expected since many materials, in particular elemental Ge, become metallic in the liquid phase, while the amorphous phase is semiconducting in nature. Our conclusion is in agreement with the recent work on electrical conductivity of liquid GST when the observed temperature dependence of conductivity also suggested semiconductor nature of the molten phase [16].

In conclusion, based on EXAFS and XANES analyses we have demonstrated that the local structures of liquid and amorphous  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  are very similar which is in agreement with the assumption that the material is molten on its way to the amorphous state. At the same time, the fact that the white line height is different between the liquid and amorphous phases leaves open the question of whether this is purely thermal melting or whether there is an athermal component to it that is due to electronic excitation. A very important feature of the liquid phase demonstrated by this work is the covalent nature of bonds between the constituent atoms which determines its semiconducting behavior.

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