The evolution of atomic order in crystalline phase-change materials

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Abstract

Phase-Change materials are of technological interest due to their property contrast between the amorphous and crystalline phase and the fast transition mechanism. The large difference in electronic resistivity is particularly promising for the realization of non-volatile electronic memories. For the well-known phase-change material GeSb$_2$Te$_4$, it was recently shown that the electronic properties are heavily influenced by the atomic disorder in the crystalline phase. This disorder can even induce a metal-insulator transition within the stable hexagonal phase. The transition occurs as a function of the annealing temperature. This immediately raises the question if the phase transition can be related to a unique atomic rearrangement. Therefore, the atomic short range order and the symmetry of the unit cell have been investigated by extended x-ray absorption spectroscopy fine structure (EXAFS) and x-ray diffraction (XRD) as a function of the annealing temperature. EXAFS measurements were performed at 10 K in order to reveal static atomic displacements and at all three K absorption edges, allowing for an investigation of chemical ordering. The XRD patterns show that the lattice constant of the meta-stable rock-salt phase reduces rather continuously upon annealing. The complimentary analysis of EXAFS data reveals that the amplitude of static atomic displacements reduces rather continuously as well. This increasing order is closely related to the gradual decrease of resistivity upon annealing.

Key words: optical properties, atomic structure, local atomic displacements, Ge$_2$Sb$_2$Te$_4$

Motivation

Phase-change materials like the pseudobinary system (GeTe)$_x$·{(Sb$_2$Te$_3$)$_{1-x}$ with 0.8 $>$ x $>$ 0.3 (GST) belong to an interesting class of materials, because they are relevant to various topics in research and application. The large property contrast between their amorphous and crystalline phases, allows using them in non-volatile data storage devices [1][2]. Their low thermal conductivity even in the crystalline phase makes them interesting for thermoelectric applications [3]. Therefore, this manuscript will focus on the rare combination of macroscopic properties of these compounds and their origin from the atomic structure of the crystalline phases.

It was reported that the property contrast between the amorphous and crystalline phases originates from the prevalence of different chemical bonding mechanisms: Whereas purely covalent bonds govern the amorphous phase, resonant covalent bonds are formed in the crystalline phase with a higher optical dielectric constant [4] and longer interatomic distances [5]. Although the crystalline phase consists of well-defined unit cells, the variance of interatomic distances is even larger than in the amorphous phase [6]. This large variation is due to local atomic displacements [7], which are also considered responsible for a reduction of the optical dielectric constant [8]. The resulting atomic disorder was also made responsible for the localization of charge carriers [9], in that case leading to an electrically insulating behavior of the meta-stable crystalline phase. Therefore, atomic disorder is of great importance for the properties of crystalline GST materials.

It is instructive to compare the optical dielectric constant and the electrical resistivity of crystalline GeSb$_2$Te$_4$ (x=0.5) material annealed at different temperatures: Whereas the optical dielectric constant increases rather suddenly during the formation of vacancy layers at 500 K [10], the room-temperature electrical resistivity decreases continuously between 425 and 600 K by several orders of magnitude [9], although both effects are related to the atomic disorder. In this study, we present an investigation of the local atomic disorder as a function of annealing temperature by extended x-ray absorption spectroscopy fine structure (EXAFS) and by x-ray diffraction (XRD). We will finally discuss the correlation of both properties with atomic disorder.
Experimental

Samples of amorphous GeSb$_2$Te$_4$ were prepared by sputter deposition from stoichiometric targets using Ar atoms with a partial pressure of $5 \times 10^{-3}$ mbar. 800 nm of the material were deposited on Si substrates in order to perform XRD experiments in grazing incidence (GI) geometry using Cu K$\alpha$ radiation. The resulting diffraction patterns were refined using the WinPrep software. Samples for EXAFS experiments were deposited on spring steel from which the material was removed by mechanically bending the substrate. The resulting powder was ground, mixed with cellulose and pressed to pellets. The resulting pellets were cooled to 10 K in order to reduce the amplitude of thermal vibrations, which significantly dampen the amplitude of EXAFS oscillations even at liquid nitrogen temperatures. The samples were then measured in transmission geometry at all three K edges at the beamline CEMO [11] at Doris III, DESY, Hamburg. The EXAFS function $\chi(k)$ was extracted from the data as described by Kelly [12]. The resulting EXAFS function was refined using the path expansion formalism as implemented in the Artemis software [13], based on Ifeffit and Feff [14]. Each sample was annealed at a specific temperature in a tube furnace with Ar atmosphere. The samples were heated at 5 K/min and held at the final temperature for 30 min.

Results

It is well-known that many GST compounds crystallize in a meta-stable rocksalt-like atomic structure ($Fm\overline{3}m$), in which one sublattice is occupied by Tellurium atoms and the second sublattice contains Ge and Sb atoms. The remaining lattice sites remain vacant [15], thereby leading to absolute vacancy concentrations as high as 12.5% in GeSb$_2$Te$_4$. At elevated temperature, the meta-stable phase transforms to a stable hexagonal phase, in which the vacant sites are ordered on planes perpendicular to the cubic <111> directions. The resulting structure consists of alternating layers of Te and Ge, Sb and vacancies. The exact stacking sequence is still matter of debate, since a well-ordered sequence Te-Sb-Te-Ge-Te-Sb-Te-Vac has been proposed based on DFT calculations [16] and TEM analysis [17], whereas a remaining chemical mixing of Ge/Sb atoms has also been reported based on the rietveld refinement of x-ray diffraction data [15].

We have annealed the material at various temperatures and measured the diffraction pattern at ambient conditions. The resulting patterns were refined with the $Fm\overline{3}m$ space group for the meta-stable cubic phase and with the $R\overline{3}m$ group in the stable hexagonal phase. The resulting lattice constants are plotted in Fig. 1, where the structural transition is reflected by the change in space group. Our results are well in line with literature values, included in the plot as thin horizontal lines for the cubic [15] and hexagonal phases [18]. It is worth mentioning that a continuous reduction of the lattice constant with increasing annealing temperature was observed within the meta-stable cubic phase. Once transformed to the hexagonal phase, a reversed volume expansion of the unit cell was observed. The transition from the cubic to the hexagonal phase induces significant changes to the atomic long range order, since the diffraction patterns are clearly distinct. Several properties of the material, like the electrical resistivity do not show such distinct behavior in the meta-stable cubic and hexagonal phase, but rather change continuously [9].

It is therefore natural to wonder how the atomic short range order changes during the transition from the cubic to the hexagonal phase. We have therefore performed EXAFS experiments at all three absorption K edges of GeSb$_2$Te$_4$ powder, annealed at various temperatures. The Fourier transformed spectra are depicted in Fig. 2. They provide direct evidence that the local atomic ordering does not significantly change with the annealing temperature. We have refined the EXAFS spectra of all edges using the path expansion formalism based on a single atomic model for the compound. We refined only the first peak in the EXAFS data, because the signal-to-noise ratio is already too low at the second coordination shell (at 4.26 Å) due to large atomic displacements. Therefore, two distinct nearest neighbor distances were taken into account for each, Ge-Te and Sb-Te distances. With this model, the data could be refined up to a residual mismatch of 0.029. The parameters involved in this fit are presented in Tab. 1 together with their statistical error. It becomes clear that Ge-Te and Sb-Te distances are strongly distorted as compared to a perfectly cubic lattice. By comparing XRD and EXAFS data, we will now derive as much information on the atomic displacements as possible.
Fig. 1: The lattice constants of GeSb₂Te₄ were determined for different annealing conditions measured at ambient conditions (error bars smaller than point size). A clear transition from cubic to hexagonal diffraction patterns is observed, when the vacancies arrange on layers, thereby changing the stacking sequence and the atomic long range order. Changes within both phases proof the existence of continuous atomic rearrangements.

Let us first note that the EXAFS data presented in Tab. 1 and the XRD measurements in Fig. 1 are in good agreement, since the average interatomic distance \( \langle u \rangle \) from EXAFS compares well with half the cubic lattice constant \( a \) from XRD. The average interatomic distance is calculated using the numbers in Tab. 1 with the fraction of bonds of a specific type \( x_i \), as \( \langle u \rangle = 0.5 \cdot (x_{\text{Ge-Te}} (u_1 + u_2) + x_{\text{Sb-Te}} (u_3 + u_4)) = 3.02(1) \text{ Å} \), whereas half the lattice constant at the same annealing condition measured at 10 K is only slightly smaller: \( a = 2.998(1) \text{ Å} \). We are now in a position to analyze the atomic displacements in more detail.

Since the EXAFS measurements were performed at 10 K, where thermal vibrations are negligible, the observed atomic displacements must be of static nature and hence driven by a gain in electronic energy – and not by thermal vibrations. Together with the observation of the vibrational softening of interaction potentials upon crystallization [19], we can conclude that the atomic interaction potential has a rather flat shape, possibly with several local minima. But which atoms are actually displaced from their lattice site? Since every Ge and Sb atom is surrounded by exactly six Te atoms, the sum of short and long bonds gives the size of the local octahedra, i.e. the Te-Te distance across the octahedra. Therefore, we can obtain an estimate for the displacement of Te atoms by comparing the sizes of Ge-Te₆ and Sb-Te₆ octahedra. A calculation based on Tab. 1 results in the values 5.93(2) Å and 6.09(2) Å, respectively, which suggest that also the Te atoms are displaced from their cubic lattice sites. However, the static displacements are larger for the Ge/Sb atoms, since Fig. 2 shows a clear peak of Te-Te next nearest neighbors at approx. 4 Å, whereas no such next nearest neighbor peaks are observed for Ge/Sb-Ge/Sb interatomic distances.

<table>
<thead>
<tr>
<th>Scattering path</th>
<th>Coord. Number</th>
<th>Distance</th>
<th>Displacement param.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge-Te (short)</td>
<td>2.5(5)</td>
<td>( u_1=2.85(1) ) Å</td>
<td>0.006(1) Å²</td>
</tr>
<tr>
<td>Ge-Te (long)</td>
<td>3.5(5)</td>
<td>( u_2=3.08(1) ) Å</td>
<td>0.014(3) Å²</td>
</tr>
<tr>
<td>Sb-Te (short)</td>
<td>2.7(6)</td>
<td>( u_3=2.93(1) ) Å</td>
<td>0.005(1) Å²</td>
</tr>
<tr>
<td>Sb-Te (long)</td>
<td>3.3(6)</td>
<td>( u_4=3.16(1) ) Å</td>
<td>0.012(8) Å²</td>
</tr>
</tbody>
</table>
EXAFS data were measured at 10 K at all K absorption edges of GeSb$_2$Te$_4$ annealed at different temperatures after sputter deposition. The resulting Fourier transformed EXAFS spectra show only slight changes as a function of the annealing temperature. The most pronounced change at all edges is an increase in the height of the first peak.

Having reported the results at the lowest annealing conditions, we can in the following turn to the temperature dependence of the atomic displacement. Therefore, all EXAFS spectra were refined using the same model as reported above. It is worth mentioning that it always resulted in residuals of less than 0.03 and therefore describes also the local atomic environment in the hexagonal phase reasonably well. In order to quantify the amplitude of atomic displacements, the average splitting between short and long bonds, $\Delta u$ has been calculated by $\Delta u = 0.5 \cdot (x_{Ge-Te}(u_2 - u_1) + x_{Sb-Te}(u_4 - u_3)) = 0.115(3) \text{Å}$. This parameter is plotted in Fig. 3 as a function of annealing temperature and shows a decreasing trend until the hexagonal phase is reached. In the hexagonal phase, the displacement amplitude does not decrease further, proving that atomic displacements prevail in the hexagonal phase. These displacements are due to an irregular spacing of the various layers along the cubic <111> (or hexagonal <001>) direction. The irregular spacing can be equally described as correlated atomic displacements along the cubic <111> direction – just as the rhombohedral structure of GeTe, where layers are equally displaced along the cubic/rhombohedral <111> direction.

Fig. 3 also contains the value for the energy gap, obtained by ellipsometry and Fourier Transformed Infrared Spectroscopy (FTIR). Both values show a clear correlation and prove that some part of the electronic gap is due to Peierls-like atomic displacements.
Conclusion and discussion

Two different sources of atomic disorder have been identified in this study: The amplitude of atomic displacements from their lattice sites and the correlation of the direction of these displacements. The latter is most likely a direct consequence of the ordering of vacancies, since it was reported based on density functional theory (DFT), that atoms tend to fill the empty space of the vacancies [20]. Therefore, Te atoms next to a vacancy will displace towards the vacancy. Once the vacancies begin to align along planes, also the direction of atomic displacements will align.

Now, we can turn to the correlation of macroscopic properties with the local atomic displacements. Fig. 3 shows clearly that the displacement amplitude decreases continuously with increasing annealing temperature. The origin of these atomic displacements is a Peierls-like mechanism, which opens a gap in the band structure due to a gain in energy of the occupied electronic states. Therefore, once the amplitude of atomic displacements decreases, also the Peierls-driven energy gap should decrease. Since this is indeed the case, both results consistently reflect the reduction of local atomic displacements with increasing annealing temperature.

The optical dielectric constant, however, remains rather constant within the cubic phase and increases suddenly during the transition from the cubic to the hexagonal phase. It was pointed out that an atomic displacement localizes charge in the short bond and therefore reduces the optical dielectric constant [8]. Although a small trend is observed in the optical dielectric constant, the atomic displacements do not seem to influence the optical dielectric constant significantly. It is rather the ordering of vacancies in layers, and therefore the correlation of atomic displacements, which increases the magnitude of resonance bonding.

The electronic resistivity of GeSb$_2$Te$_4$ decreases continuously with increasing annealing temperature and shows an insulator-to-metal transition in the hexagonal phase. Since it is the atomic disorder, which localizes the charge carriers in the cubic phase and thereby turns the compound to an insulator, it is a consistent result that the reduction of local atomic displacements reduces the resistivity as well.

Based on the present data, we could explain the influence on local atomic displacement disorder on several macroscopic properties in GST compounds. The results emphasize the importance of atomic displacements for the properties of GST materials. It is worth mentioning that future studies should be performed to reveal the driving
force for the reduction of the atomic displacements. This driving force could be for example the gain in energy by the continuous diffusion of vacancies to layers within the cubic structure.

References


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