Simultaneous Measurements of Short and Long-range order in GeTe

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ABSTRACT

GeTe is an endpoint of the technologically important pseudobinary tie line $(GeTe)_x(Sb_2Te_3)_{(1-x)}$ that is widely used for both re-writable optical recording as well as nonvolatile phase-change electrical memory. Until recently, it had been believed that GeTe underwent a displacive ferroelectric to paraelectric transition at T_c~ 700 K, however recent temperature-dependent XAFS results suggested that the first-nearest neighbors maintain a rhombohedral (3+3) disordered octahedral coordination through T_c. In the current paper, we carry out a temperature-dependent pair-distribution function analysis using x-rays to study order in GeTe on a variety of different length scales in a single measurement and show that the transition is of an order-disorder nature with significant levels of disorder present even at room temperature. These results suggest that GeTe and possible other phase-change materials on the pseudobinary tie-line experience significant temperature activated dynamic disorder. These results are expected to be present in partially transformed amorphous phase as well and may have important consequences for electrical transport in phase-change materials.

Keywords: order-disorder, pair-distribution function, scattering

1. INTRODUCTION

GeTe is a phase-change material and constitutes one of the endpoints of the technologically important GeTe-Sb_2Te_3 pseudobinary tie-line. Compounds along this tie-line exhibit unusually large changes in electronic properties between disordered (RESET) and ordered (SET) states that have made them the materials of choice for both optical and electrical non-volatile storage devices. The phase-change process occurs on the order of nanoseconds and for domains on nanometer length scales. GeTe based non-volatile electrical memory has been shown to switch[i] on the order of 10~ns, a writing speed on the same order as the dynamic memory of the recent past, underscoring the industrial interest in these materials. The switching mechanism is now being debated and the details of the structure on different length scales may well play an important role in the phase-change mechanism and its optimization in commercial devices. The extent of thermally-induced disorder is also of interest as it has been shown both theoretically and experimentally that temperature-induced disorder may couple with photo-induced excited-state effects to induce the formation of the so-called amorphous phase via athermal pathways[ii,iii]. The short temporal and small spatial domains make modeling of changes in electronic properties using *ab-initio* quantum mechanical techniques attractive. Quantum mechanical calculations of changes in material properties have been used to unveil the underlying mechanisms behind the large changes in material properties undergone by phase-change materials between SET and RESET states as well as for the design of novel artificial structures with more ideal switching attributes.[iv]

GeTe is a narrow band gap semiconductor and at room temperature assumes a simple rhombohedral structure (α-GeTe) with two atoms in the unit cell. The α phase of GeTe can be visualized as a rocksalt structure with a small sheer relaxation along the pseudo-cubic [111] direction. In α-GeTe, both Ge and Te atoms are nominally octahedrally coordinated with two triplets of shorter (2.83 Å) and longer (3.15 Å) bonds, a structure that has been described as a Peierl distortion due the quasi one-dimensional nature of the p-orbital based bonding in GeTe.[v]

Ge-Sb-Te alloys along the pseudobinary $(GeTe)_x(Sb_2Te_3)_{1-x}$ tie-line are well known phase-change alloys that exhibit large changes in electrical and optical properties when transformed between amorphous and crystalline phases. $Ge_2Sb_2Te_5$ (GST225) for example is considered a prototypical phase-change alloy in that it is used both in optical storage devices (DVD-RAM) as well as in phase-change electical memory (PC-RAM). Research on the GeTe rich side of the tie-line has recently increased due to the higher crystallization temperatures potentially allowing PC-RAM operation in high-temperature environments. Additionally, the enhancement in the reflectivity difference between crystalline and amorphous phases near the 408 nm operating wavelength of Blu-Ray discs have made the $Ge_8Sb_2Te_{11}$ (GST8211) phase the material of choice over GST225 for Blu-Ray re-writeable optical disc applications.

The structures of phase-change compounds crystallized from as-deposited material with compositions lying along the tie-line ranging from 1 to 0.85 were observed by temperature dependent BD (Bragg diffraction) to initially crystallize upon laser-irradiation into a rhombohedral (s.g. R3m) structure.[vi] The rhombohedral structure results in a distorted octahedral local environment in which can be described as 3+3 or three shorter and three longer bonds as typified by the A7 structure of elemental Sb. Upon further heating, a ferroelectric to paraelectric transformation to cubic symmetry (s.g. $Fm\bar{3}m$) was then observed. From this change in symmetry it was concluded that the local 3+3 distorted octahedral bonding configuration transformed at T_C to a ideal octahedral coordination in which all six bonds were identical in length. In these BD measurements, a gradual decrease in the transition (Curie) temperature Tc was observed with increasing x leading to the prediction that for tie-line compositions above the critical composition x_c~0.86, no trigonal-cubic phase transition would exist and the average structure would be cubic upon laser-crystallization. It should be noted in passing that the bulk phase of GST8211 is reported to consist of a 21-layer stack that is inaccessible kinetically for the temperatures discussed here.[vii]

Changes in local structure associated with the ferro- to para-electric phase transition in GeTe have also recently been observed by x-ray absorption fine-structure measurements (XAFS).[viii] This experiment which observed changes in local structure about Ge atoms, concluded that there was no change in the local rhombohedral symmetry even behyond the Curie temperature. The change from rhomobohedral to cubic symmetry observed by BD was attributed to averaging effects and that in fact, the transition was not displacive in nature, but of an order-disorder character.

Here we simultaneously investigate changes in atom correlation over a wide range of length scales in a single measurement using a pair-distribution function analysis by utilizing both diffuse and coherhent diffraction contributions.

2. EXPERIMENTS

Thin film samples of GeTe of 1 μm thickness were grown by RF sputtering in an argon atmosphere from composite targets and deposited onto high-purity quartz substrates at room temperature. The samples were subsequently crystallized by annealing in a nitrogen ambient for two hours at 180°C. For the GeTe total scattering measurements, the GeTe sample was scraped off the substrate and loaded into a 200 micron diameter quartz capillary tube that was then sealed to prevent oxidation. The samples were then measured at beamline BL02B2 at the Japan Synchrotron Radiation Research Institute (SPring-8); details of the beamline setup have been described elsewhere.[4] The incident beam energy was 29.5 keV and the diffractometer imaging plate distance afforded an angular resolution of 0.02°. The sample temperature was varied from 300 to 800K by immersing the sample in a N_2 jet of the required temperature. The incident beam energy was calibrated using a standard CeO_2 powder sample at room temperature. A background reference spectra was taken at room temperature without the GeTe sample present. The reduced structure factor G(r) was obtained from the raw diffraction data using the program PDFgetX2 and modeling of the

underlying pair distribution was carried out using the program PDFgui.[5] The reduced structure factor G(r) is

$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin(Qr)dQ$$

directly related to the observed structure function S(Q) by

The reduced structure factor is related to the pair-density distribution function g(r) by $G(r)=2\pi r \rho_0 (g(r)-1)$. The

$$G(r) = \frac{1}{Nr}\sum_i\sum_{i\neq j}\left[\frac{b_i b_j}{\langle b\rangle^2}\delta(r-r_{ij})\right] - 4\pi r\rho_0$$

measured G(r) is modeled by summing over all possible atom pairs in the model or

where the sum is over all atom pairs i and j, b_i and b_j are the scattering lengths of atoms i and j, and <b> is the average scattering length of the model. The details of the model used are described in the Results and Discussion section.

3. RESULTS & DISCUSSION

As a first approximation a simple "small cell" model based upon the earlier fitting results of the temperature dependent GeTe XAFS measurements was constructed.[3] The basic premise of the model was the relative "dipole moments" of the Ge-Te dipoles should average to zero along each of the pseudocubic <111> directions. A key point of this simple model is that it is consistent with the short-range rhombohedral symmetry as observed by the XAFS measurements. A key question the fit of the model to experiment answers is whether or not such a simple model can properly describe the experimentally observed changes in not only short, but also intermediate range pair-correlations with temperature. Two competing models, the aforementioned "small cell model" as well as a displacive transition model in which the rhombohedral primitive cell is allowed to gradually transform to a cubic symmetry cell with temperature were constructed. For each temperature, the relative weight of each model, the lattice parameters, and isotropic Debye-Waller factors were allowed to vary to match both the full G(r) experimental spectra. Figures 1 and 2 show plots of the experimental G(r) data for 300 and (above the Curie temperature) 800 K respectively. The circles represent experimental data while the continuous line represents the "small cell" model described above. As can be seen in the plots, the experimental model describes both the short and intermediate-range order quite well suggesting that the transformation of GeTe from a rhombohedral to a cubic bonding arrangement is, in fact, a reversible order-disorder transition.

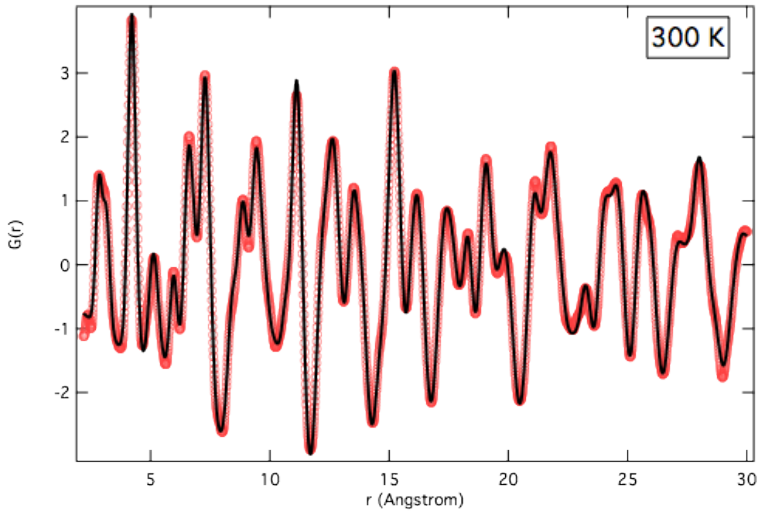

Figure 1. The experimental 300 K reduced radial distribution function G(r) obtained by a Fourier transform of the experimental S(Q) scattering function is shown in red (circles). The best fit to the experimental data using the simplified model described in the text (continuous line) is shown superimposed on the experimental data.

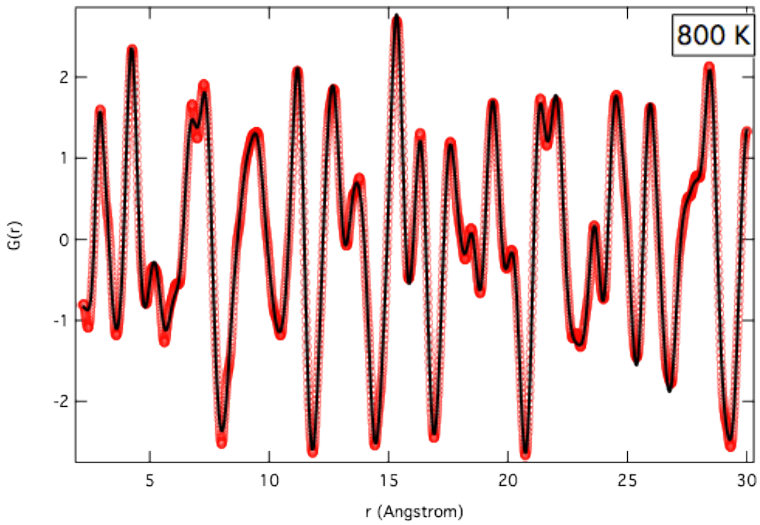

Figure 2. The experimental (above the Curie temperature) 800 K reduced radial distribution function G(r) obtained by a Fourier transform of the experimental S(Q) scattering function is shown in red (circles). The best fit to the experimental data using the simplified model described in the text (continuous line) is shown superimposed on the experimental data.

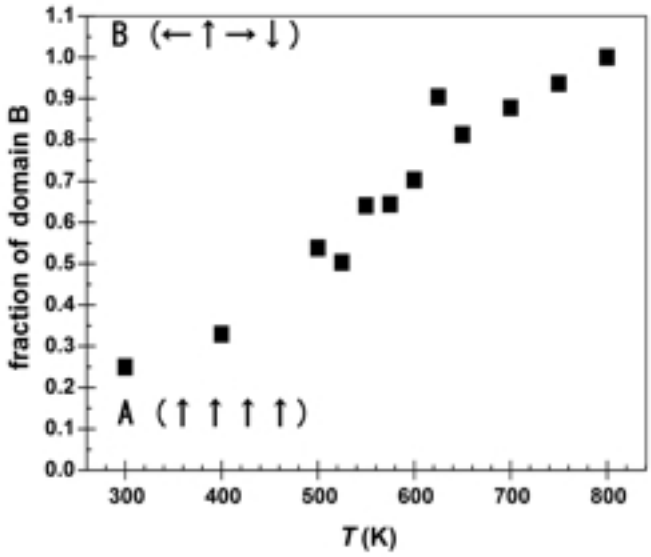

Figure 3. A plot of the relative volume fraction of the displacive versus “small cell” model as described in the text. The results clearly show the presence of a order-disorder transition.

4. **CONCLUSION**

The results of total scattering measurements that probe both short and intermediate range order in the crystalline phase of GeTe as a function of temperature are consistent with earlier XAFS results indicating the presence of significant thermally activated disorder. The simplest possible model consistent with both XAFS and BD results was constructed in which the average "dipole moment" of the rhombohedrally distorted Ge-Te bond was zero at the Curie temperature. The model was found to be in excellent agreement not only with experimentally observed short-range order, but intermediate-range order as well. Collectively these observations suggest that the local structure in $(GeTe)_x(Sb_2Te_3)_{1-x}$ alloys is dynamic and constantly in a state of rearrangement. This conclusion also has ramifications for the application of *ab initio* methods for the prediction of the properties of phase-change materials in showing that the heretofore utilization of well ordered GeTe structures is insufficient. These observations of temperature induced variations in local order with temperature are also likely to play a role in electrical transport. It is also tempting to speculate that similar effects may be present in the disordered phase which in turn may play a role in the localization of charge carriers and possibly in the drift observed in the resistivity of the RESET state in electrical devices.

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