Ordering in Crystalline Ge-rich Ge-Sb-Te Alloys:
A story of different length scales

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ABSTRACT

Observations of ordering in crystalline Ge-rich Ge-Sb-Te (GST) alloys indicate the presence of significant thermally-induced disorder that manifests differently on varying length scales. While it is tempting to assume that the average structure of GST alloys is representative of ordering on shorter length scales, recent measurements indicate the presence of structural unit rearrangements on intermediate and short-range length scales with temperature. In this report, we focus on two GST alloys, GeTe and $Ge_8Sb_2Te_{11}$ and examine ordering on different length scales using both x-ray absorption spectroscopy (XAFS), Bragg diffraction (BD), and total scattering (TS) techniques. The combination of these techniques reveal that the apparent ferroelectric transitions in the GST alloys, as observed by BD, are a consequence of the rearrangement of structural units on shorter length scales, an order-disorder transition. The confirmation of significant thermal rearrangements of the structural units making up crystalline GST alloys may also provide some insight into the effects of disorder on electrical transport in phase-change material devices.

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

1. INTRODUCTION

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.[1] 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 $x_c \sim 0.86$, 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.[2]

A recent temperature dependent x-ray absorption study (XAFS) of the local structure about Ge atoms of the tie-line endpoint compound GeTe demonstrated that the local symmetry did not change from rhombohedral to cubic even upon heating beyond the Curie temperature. The study concluded that the average structure as measured by BD and the local structure as measured by XAFS were different and the ferroelectric transition was in fact an order-disorder transition and not a displace transition as had been previously thought.

In the current paper, the local structure in GeTe is further investigated by total scattering which goes beyond BD and includes semi-coherent or diffuse scattering contributions to the scattering intensity so as to include pair-correlation information on intermediate and short length scales.   In addition we have investigated the local structure about Ge, Sb, and Te of another the GeTe rich GST8211 compound by XAFS. Temperature dependent XAFS measurements through and above T_C showed no change in local bonding coordinate from rhombohedral symmetry of the low-temperature phase as explained below.

2. EXPERIMENTS

Thin film samples of GeTe and GST8211 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)=2π r ρ_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.

XAFS measurements of GST8211 were carried out in transmission mode using beamline BL01B1 at SPring-8 in a thin film geometry at the Ge Kα, Sb Kα, and Te Kα edges.   The sample thickness was adjusted to achieve a unity

edge jump at the edge.   The sample temperature was varied using an inline furnace with a continuous flow of N_2 to prevent oxidation.   XAFS spectra were subsequently analyzed using the athena/artemis software suite.[6]

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.
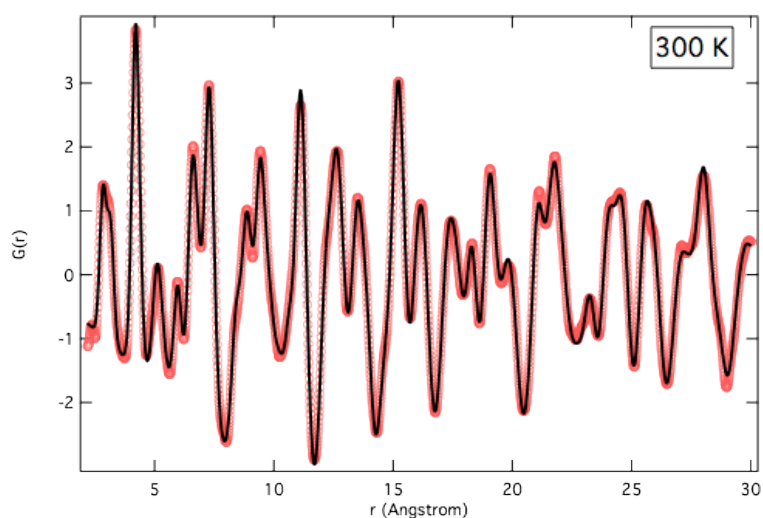

Figure 1. The experimental 300 K reduced radial distribution function G(r) obtained by a Fourier transform of the experimental S(Q) scattering function is shown in red (circles).   The best fit to the experimental data using the simplified model described in the text (continuous line) is shown superimposed on the experimental data.
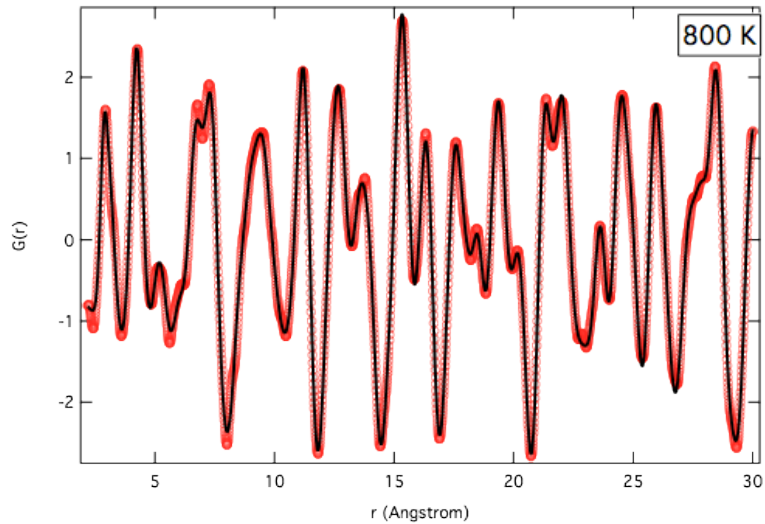
Figure 2. The experimental (above the Curie temperature) 800 K reduced radial distribution function G(r) obtained by a Fourier transform of the experimental S(Q) scattering function is shown in red (circles). The best fit to the experimental data using the simplified model described in the text (continuous line) is shown superimposed on the experimental data.
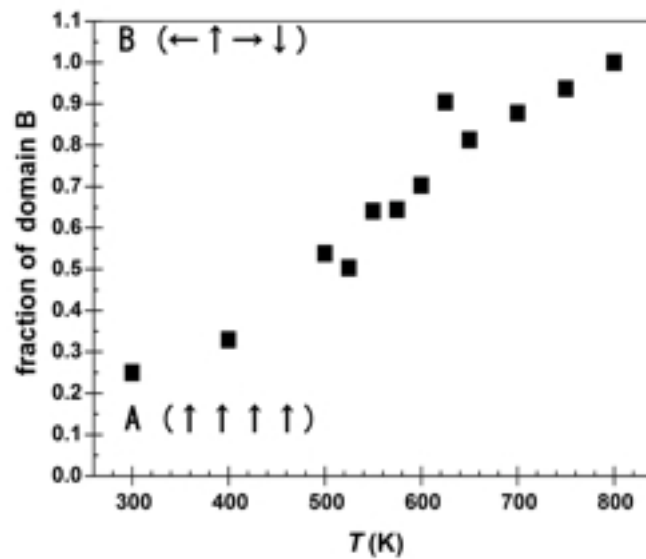

Figure 3. A plot of the relative volume fraction of the displacive versus "small cell" model as described in the text. The results clearly show the presence of a order-disorder transition.

XAFS measurements of the Fourier transform of the χ(k) function for both Ge and Sb edges in GST8211 are shown in Figure 4 as a function of temperature from below to above the Curie temperature. Note that there is no indication of a sudden "displacive transition" with temperature. The characteristic features of a local rhombohedral symmetry bonding arrangement are preserved for all temperatures strongly suggesting the rhombohedral to cubic phase-transition observed by BD is in fact an order-disorder transition.
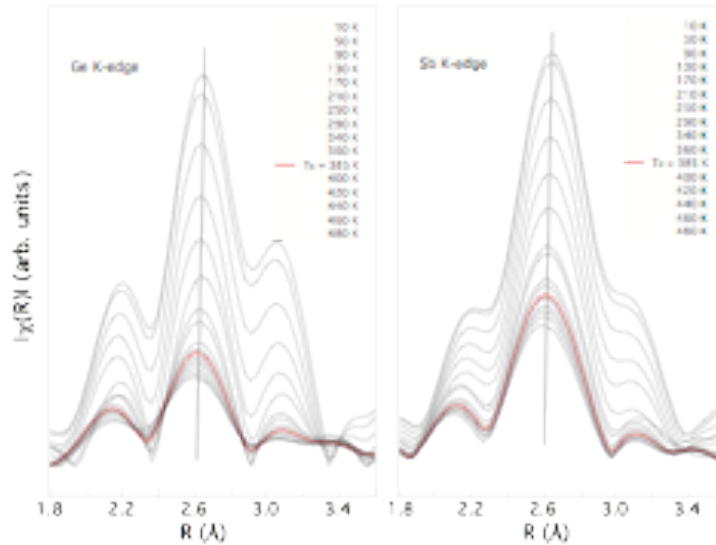
Figure 4. Fourier transformed plots of Ge Kα and Sb Kα XAFS spectra for GST8211 crystalline thin film samples as a function of temperature. No change in the local structure (other than Debye-Waller related damping) can be observed in the vicinity of the Curie temperature (indicated by a thicker red line). Note that due to interatomic potential phase-shifts, the peaks are shifted to smaller values.

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. A series of XAFS observations on the x=8/9 GeTe-rich GST8211 compound also strongly suggested a similar thermally activated disordering mechanism is active. 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. 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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Biographies

Paul Fons graduated from the University of Illinois at Urbana-Champaign in 1990 writing his thesis on the growth and electronic structure of metastable semiconductor alloys. Subsequently, he became a research fellow at the University of Tsukuba in Japan. In 1993, he joined the National Institute of Advanced Industrial Science & Technology (AIST) also located in Tsukuba.   While at AIST, he has carried out extensive work in molecular beam epitaxy, photoluminescence, and structural measurements using synchrotron radiation including diffraction, x-ray absorption, and high-pressure, and ultra-fast time-resolved studies as well as density-functional theory calculations.   He is currently working in the functional materials group at AIST on phase-change materials.