Real structure of metastable Ge-Sb-Te and Ge-Bi-Te materials

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ABSTRACT

Metastable bulk samples of GST and GBT materials were prepared by rapid quenching, chemical transport reactions and high pressure synthesis. HRTEM and in situ temperature dependent single crystal diffraction experiments yield insight into real structure phenomena such as two-dimensionally extended cation defect ordering and associated local distortions.

Key words: GST materials, GBT materials, crystal structure elucidation, real structure

1. INTRODUCTION

Ternary antimony and bismuth tellurides have received much attention from materials scientists as this class of compounds dominates the field of phase-change materials (PCMs) for data storage media and non-volatile RAM devices.[1] Metastable phases of Ge-Sb-Te (GST) and Ge-Bi-Te (GBT) materials with rocksalt-type average structures are important in the write-erase cycle of PCMs, whereas stable modifications often show long-periodically ordered layered structures, some of which exhibit interesting thermoelectric properties.[2] Structural motifs known from the stable phases can be found in metastable modifications, e. g. distorted rocksalt type slabs with Te occupying the anion and Ge, Sb/Bi or voids occupying the cation positions. However, many questions regarding the element distribution, vacancy ordering and associated local distortions still remain open. As the properties strongly correlate with the real-structure effects on the atomic and on the nanoscale, detailed knowledge of the real structures is essential.

2. EXPERIMENTS

Samples of stable GST and GBT materials were obtained by melting stochiometric mixtures of the elements in argon atmosphere, quenching and annealing. Metastable single crystals of GST phases were grown at ~500 °C by chemical transport reactions using iodine as transporting agent. Metastable bulk material of GBT was obtained by melting stable phases in a multi anvil press and quenching under pressures up to 15 GPa. The samples were fully characterized by PXRD, HRTEM and EDX. In situ temperature dependent single crystal diffraction experiments were performed at the ID11 beamline of the ESRF (Grenoble).

3. RESULTS & DISCUSSION

GeTe-rich GST materials, e.g. $Ge_{\sim 0.8}Sb_{\sim 0.2}Te$, contain low concentrations of cation vacancies and exhibit a cubic high-temperature phase which upon rapid quenching does not transform into the corresponding stable phase.[3a] The metrics remains pseudocubic as strain arising from the metric distortion hinders further relaxation.[3b] Twinned single crystals grown in the stability range of the cubic high temperature modification and subsequently quenched exhibit a rhombohedral α-GeTe-type average structure despite the cubic metrics. Diffuse scattering and HRTEM indicate cation defect ordering extended in two dimensions and associated local distortions (cf. Fig. 1, left) along $<111>_{cubic}$, which are characteristic for stable phases as well. Similar nanostructures have been observed in samples of metastable $Ge_{0.25}Bi_{0.5}Te$ (cf. Fig. 1, right), which were synthesized by quenching under high pressure. They do not exhibit a cubic high-temperature phase at ambient pressure but always form the stable layered structure if common techniques of solid state synthesis are used. According to Rietveld refinement, GBT samples obtained under high pressure conditions exhibit an α-Hg-type average structure, however, planar defect ordering and local distortions are very pronounced.

Figure 1: HRTEM image of $Ge_{\sim 0.8}Sb_{\sim 0.2}Te$ with finite cation defect layers (left, similar structures have been observed for $Ge_{0.25}Bi_{0.5}Te$) and of $Ge_{0.25}Bi_{0.5}Te$ (right) showing domains with different arrangements of defect layers and also without defect layers.

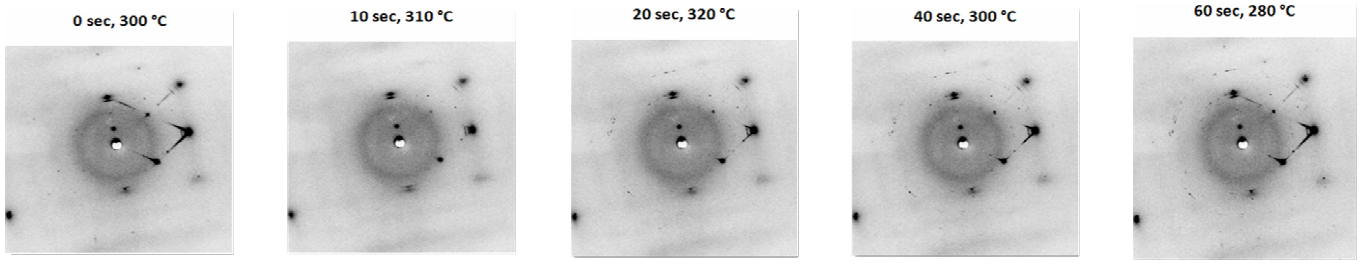

Figure 2: Temperature and time dependent change of the diffuse scattering of a $Ge_{\sim 0.8}Sb_{\sim 0.2}Te$ single crystal (same oscillation with $\Delta\varphi$ = 1°, monochromatic beam)

Temperature dependent X-ray powder diffraction of such metastable phases reveals a phase transition at elevated temperatures which leads to the stable modifications, either represented by long-range ordered superstructures or the cubic high-temperature phase. The diffuse streaks in single-crystal diffraction patterns (cf. Fig. 2) of GeTe-rich single crystals gradually disappear when they are heated to about 300 °C and appear again when recooled (rate approximately 1 °C per second).

4. CONCLUSION

Both reversible and irreversible order-disorder transitions might be interpreted in terms of a correlated diffusion and relaxation process. Although this process is not directly related to the amorphous-to-crystalline transition during the write and erase cycles of phase-change materials, it might affect their performance. As in situ nanostructuring is an intriguing option to alter various physical properties, it is worthwhile to further investigate the effect.

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Biography

Matthias Schneider received his B. Sc degree in Chemistry and Biochemistry in 2006 followed by a M. Sc. degree in Chemistry in 2008 at the Ludwig Maximilian University in Munich. He and his colleagues Tobias Rosenthal and Thorsten Schröder are currently working on their Ph. D. projects in the group of PD Dr. Oliver Oeckler. The research interest of the group is focused on the establishment of structure-property relationships especially regarding the elucidation of real structure phenomena by various methods such as analysis of diffuse scattering and high-resolution electron microscopy.