



Temperature-dependent ordering phenomena in single crystals of germanium antimony tellurides



Philipp Urban^a, Matthias N. Schneider^b, Oliver Oeckler^{a,*}

^a Faculty of Chemistry and Mineralogy, Leipzig University, Scharnhorststr. 20, 04275 Leipzig, Germany

^b Department of Chemistry, LMU Munich, Butenandtstr. 5-13 (D), 81377 Munich, Germany

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ABSTRACT

The temperature-dependent behavior of quenched single-crystalline $(\text{GeTe})_n\text{Sb}_2\text{Te}_3$ ($n \sim 2.8$, $n \sim 5$ and $n \sim 11$) was investigated by semiquantitative modeling of diffuse X-ray scattering. The structure at room temperature exhibits trigonal twin domains, each comprising a stacking-disordered sequence of distorted rocksalt-type slabs with variable thicknesses. Ge and Sb share the cation position and vacancies are partially ordered in defect layers (van der Waals gaps) between the slabs. The average structure determined with resonant diffraction data corresponds to a rocksalt-type structure whose cation position is split along the stacking direction. Upon heating, cation ordering leads to a metastable superstructure of the rocksalt type at ~ 400 °C, which transforms to a rocksalt-type high-temperature phase with randomly distributed cations and vacancies at ~ 500 °C; this structure was also refined using resonant diffraction. Cooling at high or intermediate rates does not yield the long-range ordered phase, but directly leads to the twinned disordered phase.

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1. Introduction

Germanium antimony tellurides (GST materials) are important phase change materials (PCMs) for data storage [1–3]. In thin films, a phase change between an amorphous and a metastable crystalline phase can be induced by laser irradiation (for optical phase change memory) or resistance heating (for phase change random access memory, PCRAM) [4]. The crystalline cubic phase of GST PCMs exhibits a rocksalt-type structure with Ge and Sb atoms as well as vacancies randomly distributed on the cation site, whereas Te occupies the anion site [5]. $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ are the most important compounds which are used in DVD-RAM and Blu-ray Discs, respectively. In PCRAM devices, nitrogen-doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$ as well as doped Sb_2Te and $\text{Ge}_{15}\text{Te}_{85}$ are used [6]. Detailed investigations of the crystalline cubic phase in thin films revealed deviations from an ideal rocksalt-type structure. For thin films with the composition $(\text{GeTe})_n\text{Sb}_2\text{Te}_3$, distortions of the rocksalt-type structure towards rhombohedral GeTe were observed for $n \geq 8$ at room temperature (RT) [7]. In addition, partial ordering of vacancies in defect layers was observed in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films with transmission electron microscopy (TEM) [8]. Some requirements concerning the physical properties, such as low thermal conductivity, are similar for

thin-film PCMs and bulk thermoelectric materials [9]. Quenched GST bulk material thus exhibits promising thermoelectric properties [10]. Substitution with e.g. Se [11] or Sn [12] further improves those properties. The metastable cubic phase occurring in thin films in PCMs at RT is thermodynamically stable at above 400–500 °C (depending on n) in bulk compounds $(\text{GeTe})_n\text{Sb}_2\text{Te}_3$ for $n \geq 3$ [10,13]. At RT, the corresponding phases crystallize in long-range ordered trigonal layered structures [14–16] which are stable up to incongruent melting ($n=1, 2$) or up to the temperature where the HT phase is formed [17–20]. Due to the low scattering contrast between Sb and Te (and Sn as well) for both laboratory X-rays and neutrons, resonant diffraction using wavelengths at the respective absorption edges is the method of choice for the determination the element distribution in such phases [21].

Quenching the rocksalt-type high-temperature (HT) phase of $(\text{GeTe})_n\text{Sb}_2\text{Te}_3$ with $n > 2$ yields highly disordered twinned phases. Partial layer-like vacancy ordering leads to a symmetry reduction and involves stacking disorder. The structure of these phases is described in more detail in Section 3.1.1. As the thermoelectric figures of merit of such quenched phases are significantly higher than those of the stable long-range ordered phases [10], the structural changes occurring upon heating as well as the thermal stability of the disordered phase are of great interest. Earlier temperature-dependent investigations of single-crystalline $(\text{GeTe})_n\text{Sb}_2\text{Te}_3$ ($6 < n < 15$) by means of Laue diffraction revealed that upon heating defect-layer rearrangement from a modification with a pronounced variance of spacings

* Corresponding author. Tel.: +49 (0)341 9736251; fax: +49 (0)341 9736299.
E-mail address: oliver.oeckler@gmx.de (O. Oeckler).

between defect layers towards equidistantly spaced defect layers starts at ~ 300 °C, before the cubic HT phase forms above ~ 500 °C [22]. Yet, detailed information about local atom environments (i.e. stacking sequence around the defect layer, interatomic distances) as well as the probability distribution of building block thicknesses in disordered phases could not be retrieved. New ordered structures as detected for $(\text{GeTe})_6\text{Sb}_2\text{Te}_3$ at intermediate temperatures [22] could not be elucidated reliably from white-beam data. Thus, the temperature-dependent behavior of quenched GST is not yet fully understood. Therefore, this study uses quenched single crystals grown in the stability range of the HT phase, whose structures resemble those that are typical for high-ZT thermoelectrics in order to track structural changes that occur upon heating. Crystals of selected compounds with $n=2.8$ and 11 cover a broad compositional range and serve as examples for the investigation of temperature-dependent phase changes. The real structures of the RT phases have recently been described with a stacking fault approach [23] using *DIFFaX* [24], as well as refined for $\text{Ge}_4\text{Bi}_2\text{Te}_7$ [25] with *Yell* [26] utilizing a 3D- Δ PDF-approach [27]. In the present study, diffuse X-ray scattering and its change upon heating is matched semiquantitatively with *DIFFaX*. This enables straightforward access to the most important structure motifs in single-crystalline GST phases as described in detail in the Sections 3.1.1 and 3.1.3.

2. Experimental

2.1. Synthesis and chemical analysis

Crystals of $(\text{GeTe})_n\text{Sb}_2\text{Te}_3$ with variable n in the range between ~ 2.8 and ~ 12 were obtained via the gas phase. Ge (99.999%, Sigma Aldrich), Sb (99.999%, Smart Elements) and Te (99.999%, Alfa Aesar) were fused at 950 °C with the elemental ratio Ge:Sb:Te = 1.44:2:5 and subsequently quenched by cooling the ampoule in water. About 200 mg of the powdered product were sealed in a silica glass ampoule (length ~ 10 cm, diameter ~ 10 mm, Ar atmosphere), kept at 628 °C for 4 h and then slowly cooled to 618 °C (within 6 h). After holding this temperature for 75 h, the ampoule was quenched in air. Among other octahedral crystals, it contained single crystals of $(\text{GeTe})_{\sim 11}\text{Sb}_2\text{Te}_3 = \text{Ge}_{0.79}\text{Sb}_{0.14}\text{Te}$. A second synthesis starting from a melt with the same elemental ratio (total weight 246.4 mg), which was quenched in water and subsequently cooled from 628 °C to 618 °C without further annealing, yielded – among others – crystals of $(\text{GeTe})_{\sim 2.8}\text{Sb}_2\text{Te}_3 = \text{Ge}_{0.48}\text{Sb}_{0.34}\text{Te}$. In addition to the slow cooling, the natural temperature gradient of the tube furnace was probably beneficial for crystal growth.

Crystals of $(\text{GeTe})_{\sim 5}\text{Sb}_2\text{Te}_3 = \text{Ge}_{0.63}\text{Sb}_{0.25}\text{Te}$ were grown in the stability ranges of their HT phases by a chemical transport reaction. Quenched and powdered $(\text{GeTe})_{12}\text{Sb}_2\text{Te}_3$ (typically 120 mg, obtained by quenching a melt with stoichiometric composition) and SbI_3 (ca. 50 mg, prepared according to refs. [28,29]) as transport agent and Sb source were sealed in silica glass ampoules (length ~ 15 – 20 cm, diameter 15 mm). Chemical transport was carried out from 600 °C to 520 °C within 1 d. Subsequently, the ampoule was quenched in air.

All methods yielded octahedral crystals with sizes of up to $0.5 \cdot 0.5 \cdot 0.5$ mm³. The chemical composition of selected crystals for diffraction experiments was confirmed by energy dispersive X-ray spectroscopy (EDX) on crystal faces oriented approximately perpendicular to the electron beam using JSM-6500F (Jeol, USA) or VEGA (Tescan, Czech Republic) scanning electron microscopes, both equipped with EDX detector (model 7418, Oxford Instruments, Great Britain). The results from the EDX analyses are summarized in Table 1. The sum formulae were derived to both satisfy the EDX result as well as electroneutrality.

Table 1

Results of EDX analyses of single crystals of $(\text{GeTe})_n\text{Sb}_2\text{Te}_3$ (at least 3 point analyses were averaged, standard deviations calculated from the variance between single point analyses).

Composition	Measured	Calculated
$(\text{GeTe})_{\sim 2.8}\text{Sb}_2\text{Te}_3$	$\text{Ge}_{24.4(6)}\text{Sb}_{22.5(3)}\text{Te}_{53.1(9)}$	$\text{Ge}_{26.4}\text{Sb}_{18.9}\text{Te}_{54.7}$
$(\text{GeTe})_{\sim 5}\text{Sb}_2\text{Te}_3$	$\text{Ge}_{35.8(6)}\text{Sb}_{11.3(4)}\text{Te}_{52.9(5)}$	$\text{Ge}_{33.3}\text{Sb}_{13.3}\text{Te}_{53.4}$
$(\text{GeTe})_{\sim 11}\text{Sb}_2\text{Te}_3$	$\text{Ge}_{40.4(5)}\text{Sb}_{6.8(3)}\text{Te}_{52.8(2)}$	$\text{Ge}_{40.7}\text{Sb}_{7.4}\text{Te}_{51.9}$

2.2. Single-crystal data collection and processing

The crystal quality was checked with a STOE IPDS-I diffractometer with imaging plate detector using Mo- $K\alpha$ or Ag- $K\alpha$ radiation (graphite monochromator, $\lambda=0.71073$ Å or $\lambda=0.56087$ Å, respectively). Synchrotron data of selected single crystals were collected at the undulator beamline ID11 of the ESRF (Grenoble) [30], whose X-ray optics produce a stable beam with small band pass as required for high-resolution single-crystal diffraction. A heavy-duty Huber diffractometer with vertical rotation axis equipped with a FReLoN2K (for the crystals with $n=\sim 5$ and ~ 10) or a FReLoN4M (for the crystal with $n=\sim 2.8$) CCD detector [31] was used for data acquisition. For heating experiments, a gas blower GSB 1300 (Cyberstar, Echirrolles, France) controlled by a Eurotherm controller (Eurotherm/Invensys, Great Britain) was installed at the beamline. The temperature was calibrated by melting and recrystallizing samples of Bi, Te and KI (melting points 271 °C, 450 °C and 681 °C, respectively). Data for average structure determination of $(\text{GeTe})_{\sim 11}\text{Sb}_2\text{Te}_3$ at RT as well as $(\text{GeTe})_{\sim 2.8}\text{Sb}_2\text{Te}_3$ at 535 °C were collected near the absorption edges of Sb and Te, as well as with a wavelength off the edges. The wavelengths used for data acquisition are listed in Tables 2 and 5 for $(\text{GeTe})_{\sim 11}\text{Sb}_2\text{Te}_3$ and $(\text{GeTe})_{\sim 2.8}\text{Sb}_2\text{Te}_3$, respectively. For $(\text{GeTe})_{\sim 11}\text{Sb}_2\text{Te}_3$, a detector offset was used in order to obtain additional high-angle data. After conversion of the frames, the data were indexed using SMART [32] and integrated with SAINT [33]. They were scaled, combined and corrected for absorption using SADABS [34]. Joint structure refinements were performed on three datasets with JANA2006 [35] using dispersion correction terms as implemented in the program, i.e., derived according to ref. [36] (cf. Table S1 in the Supplementary Information). Further information on the determination of the average structures of $(\text{GeTe})_{\sim 11}\text{Sb}_2\text{Te}_3$ (cf. Section 3.1.2) and $(\text{GeTe})_{\sim 2.8}\text{Sb}_2\text{Te}_3$ (cf. Section 3.2) may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (Germany), by quoting the deposition numbers CSD-429034 and CSD-429033 for $(\text{GeTe})_{\sim 11}\text{Sb}_2\text{Te}_3$ and $(\text{GeTe})_{\sim 2.8}\text{Sb}_2\text{Te}_3$, respectively, the names of the authors, and the citation of the paper. Crystal data and refinement details are summarized in Tables 2, 3, 5 and 6.

For the evaluation of diffuse scattering, additional datasets were collected far off the absorption edges so that absorption effects and fluorescence background are minimized, with wavelengths of 0.47686 Å (26.000 keV) for $(\text{GeTe})_{\sim 11}\text{Sb}_2\text{Te}_3$ above RT, 0.43275 Å for $(\text{GeTe})_{\sim 2.8}\text{Sb}_2\text{Te}_3$ (28.650 keV) and 0.56356 Å (22.000 keV) for $(\text{GeTe})_{\sim 10}\text{Sb}_2\text{Te}_3$ as well as $(\text{GeTe})_{\sim 5}\text{Sb}_2\text{Te}_3$ at RT. Reciprocal lattice sections $h\bar{h}l_c$ and the intensity distribution along streaks parallel $\langle 111 \rangle_c = [001]_t$ were reconstructed with the *ImageD11* program suite [37]. Corresponding to individual domain orientations, the subscripts c and t refer to the cubic and trigonal setting of the rocksalt type, respectively, the latter obtained by transformation according to the matrix $(0.5 \ 0 \ -0.5 \ | \ -0.5 \ 0.5 \ 0 \ | \ 1 \ 1 \ 1)$ and the three equivalent ones. Intensities were extracted from the resulting volume files with *HDFextractor* [23]. The program *DIFFaX* [24] was used for the simulation of diffraction patterns of disordered structures as described in detail before [23]. The disorder model is described in Section 3.1.3.

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