Supporting Information

From metastable to stable modifications – *in situ* Laue diffraction investigation of diffusion processes during the phase transitions of $(GeTe)_nSb_2Te_3$ (6 < n < 15) crystals

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Experimental

Synthesis of crystalline samples

GeTe-rich metastable $(GeTe)_nSb_2Te_3$ bulk samples with $n \geq 3$ were prepared by melting stoichiometric amounts of the elements Ge (99.999%, Sigma Aldrich), Sb (99.999%, Smart Elements) and Te (99.999%, Alfa Aesar) in sealed silica glass ampoules under Ar atmosphere. After melting the mixtures at 950 °C, the ampoules were quenched in air. From samples obtained this way, octahedral crystals $(GeTe)_nSb_2Te_3$ $n \geq 3$ with sizes of about 0.5x0.5x0.5 mm^3 were grown by chemical transport reactions. The crystal $Ge_{0.65(3)}Sb_{0.22(1)}Te = (GeTe)_6Sb_2Te_3$ was grown from approximately 100 mg of powdered material with initial element ratio of Ge:Sb:Te = 1.44:2:5 in a silica glass ampoule (length 10 cm, diameter 10 mm) under Ar atmosphere. The material was 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 sample was quenched in air. This way GeTe-poor crystals are obtained, n varies between 3 and 12. For GeTe-rich crystals such as $Ge_{0.83(4)}Sb_{0.14(1)}Te = (GeTe)_{12}Sb_2Te_3$ and $Ge_{0.84(1)}Sb_{0.12(1)}Te = (GeTe)_{15}Sb_2Te_3$ different procedures were used. Powdered starting material (ca. 100 mg, initial element ratio for both crystals Ge:Sb:Te = 12:2:15) was sealed in evacuated silica glass ampoules (length 15-20 cm, diameter 10-15 mm). SbI_3 (< 10 weight%) was added to generate the transport agent I_2 by decomposition at elevated temperatures. Octahedral single crystals $Ge_{0.83(4)}Sb_{0.14(1)}Te = (GeTe)_{12}Sb_2Te_3$ grew in a two-zone furnace (temperature gradient from 600 to 500°C, 24 h) and were subsequently quenched to room temperature by removing the ampoule from the furnace. Growth twinned crystals $Ge_{0.84(1)}Sb_{0.12(1)}Te = (GeTe)_{15}Sb_2Te_3$ where obtained in a standard tube furnace by heating the side of the silica glass ampoule containing the starting material to 615 °C (10 days) whereas the other side was situated outside the furnace. Both these techniques allow to reproducibly synthesize single crystal used for the investigations.

For the measurement of thermoelectric properties, stoichiometric melts of the elements were solidified in silica ampoules with flat bottom to obtain disc-shaped ingots with diameters of approximately 15 mm and thicknesses of 3-6 mm. The ingots were heated to the stability range of the high temperature modification and subsequently quenched to room temperature in water to obtain metastable samples. For thermoelectric measurements, they were polished to flat plates.

X-ray diffraction and EDX spectroscopy

Laboratory single-crystal intensity data were collected on a STOE IPDS-I diffractometer with imaging plate detector using Mo-K_α or Ag-K_α radiation (graphite monochromator, λ = 0.71073 Å and 0.56087 Å) to check the crystal quality before selecting appropriate samples for the synchrotron investigations. This way single crystals of the given compositions and with the characteristic diffraction patterns described in the text can be reproduced. The compositions of the crystals used for the experiments were checked by energy dispersive X-ray spectroscopy (EDX). EDX analysis were performed using a JSM-6500F (Jeol, USA) scanning electron microscope with EDX detector (model 7418, Oxford Instruments, Great Britain). The averaged values of 3-7 point analyses on the single crystals used for X-ray data collection at BM32 (ESRF, Grenoble) correspond to the formulae $Ge_{0.65(3)}Sb_{0.22(1)}Te = (GeTe)_6Sb_2Te_3$, $Ge_{0.83(4)}Sb_{0.14(1)}Te = (GeTe)_{12}Sb_2Te_3$ and $Ge_{0.84(1)}Sb_{0.12(1)}Te = (GeTe)_{15}Sb_2Te_3$, respectively.

Laue diffraction at BM32

The Laue diffraction patterns were collected at ESRF on BM32 with a white beam (energies from 5 keV to 25 keV) focused via KB mirrors to a size of about 1 x 1 µm^2 on the sample (http://www.esrf.eu/UsersAndScience/Experiments/CRG/BM32/). The sample was inclined 40° with respect to the beam and the CCD camera (165 x 165 mm) was placed approximately 70 mm above the samples, which were fixed in silica capillaries filled with argon attached to silica glass or silicon holders with high-temperature cement. A domed hot stage (Anton Paar) was used for heating the samples. Its temperature was calibrated using a thermocouple fixed to the furnace in the same fashion as the samples (with an estimated error for the temperature of about ± 10 °C). At exposure times of about 1 second per image and read-out times of about 5 seconds, about ten diffraction images per minute can be collected yielding an approximate temperature resolution of 1°C using a heating rate of approximately 10 °C/min. As a microfocused beam was used for the experiments, so that only small volumes diffracted in a single exposure. Therefore even small samples shifts resulting from the dilation of the heating stage affect the diffraction pattern and the sample position had to be optimized repeatedly during the heating process. Data evaluation and treatment was performed using the software packages X-ray Microdiffraction Analysis Software (X-MAS; N. Tamura, R. S. Celestre, A. A. MacDowell, H. A. Padmore, R. Spolenak, B. C. Valek, N. Meier Chang, *J. Synchrotron Rad.* **2003**, *10*, 137) and the Laue Daresbury Software Suite (modified for the CCD-detector data, J. R. Helliwell, J. Habash, D. W. J. Cruickshank, M. M. Harding, T. J. Greenhough, J. W. Campbell, I. J. Clifton, M. Elder, P. A. Machin, M. Z. Papiz, and S. Zurek, *J. Appl. Crystallogr.* **1989**, *22*, 483). For indexing exemplary diffraction patterns, the (approximate) sample-detector distance for room temperature as well as high temperature diffraction patterns was determined from a silicon or germanium reference fixed on the sample holders using X-MAS. For further indexing, the Laue Daresbury Software Suite was used. Initially, a cubic cell with a_{cubic} = 6.00 Å in trigonal setting ($a_{\text{trigonal}} = (1/\sqrt{2})a_{\text{cubic}}$; $c_{\text{trigonal}} = (\sqrt{3})a_{\text{cubic}}$) was used for indexing the diffraction patterns of the high-temperature modifications. Although a white beam diffraction experiment does not allow one to obtain the absolute lattice parameters, the unit cell parameters (i.e. *c*, with *a* fixed) were refined to determine the deviation from the axis ratio $a_{\text{trigonal}}/c_{\text{trigonal}} = (1/\sqrt{2})/(\sqrt{3})$. For the high-temperature modifications, there was no significant deviation, hence the patterns were indexed based on a c*F*-lattice a_{cubic} = 6.00 Å. Simulated spot positions match well with the observed ones (cf. Fig. S2). To index the diffraction patterns of other not long-periodically ordered structures, the axis ratio of the trigonal average structure $a_{\text{trigonal}}/c_{\text{trigonal}}$ was manually varied in between 0.408 (cubic, β-GeTe) and = 0.389 (rhombohedral, α-GeTe) to find the best match between observed and predicted spot positions (cF. Fig. S3 and S4). For the diffraction patterns indicative of a long-periodically ordered structure, an initial cell can be derived from a structural prediction based on the composition described in detail elsewhere (L. E. Shelimova, O. G. Karpinsky, M. A. Kretova, V. I. Kosyakov, V. A. Shestakov, V. S. Zemskov, F. A. Kuznetsov, *Inorg. Mater.* **2000**, *36*, 768; M. N. Schneider, O. Oeckler, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2557). For the composition $(GeTe)_6Sb_2Te_3$ a 51*R*-type ($a \approx 4.2$ Å, $c \approx 93.8$ Å) layered structure is expected. This cell allows one approximately index the Bragg reflections characteristic for the long-periodically ordered structure. However, they are rather broad so that the indexing is not unequivocal with respect to closely related stacking sequences. All lattice parameters given in the text contain two digits as given by the Laue Daresbury Software Suite and with an estimated error < 0.03. For the trigonal phases, the axis ratios $a_{\text{trigonal}}/c_{\text{trigonal}}$ which are not affected by detector distance errors are given in addition.

Thermoelectric characterization

To determine the temperature dependency of the thermoelectric properties, both commercial and in-house built facilities were used to characterize the electrical and the thermal conductivities as well as the Seebeck coefficient in the range from room temperature to approx. 500 °C under vacuum. In order to avoid Peltier influences on the measurement a four point-probe setup above room temperature using an AC method was used to measure the eletrical conductivity. The Seebeck coefficient was determined using a small temperature gradient across the sample while slowly changing the environmental temperature, in order to the values for each mean temperature. The thermal conductivity was calculated from measurements of the thermal diffusivity by a Laser Flash Apparatus (Netzsch LFA 427) and heat capacity determined by Differential Scanning Calorimetry (Netzsch DSC 404). The samples' density was measured using a Mohr's balance.

Additional Figures

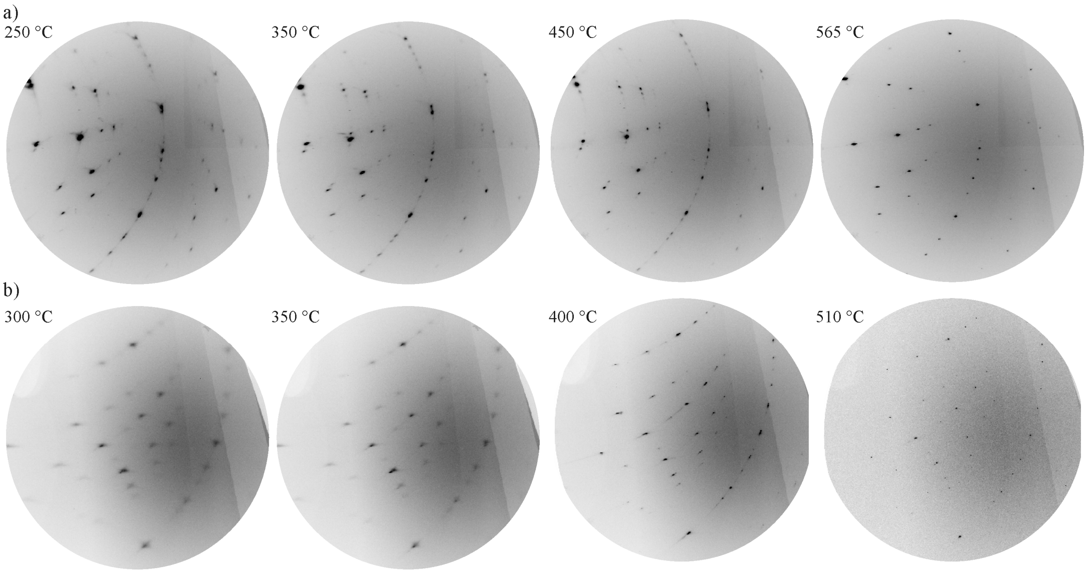

Fig. S1: Enlarged sections of the experimental Laue diffraction patterns collected during heating a) $Ge_{0.65(3)}Sb_{0.22(1)}Te = (GeTe)_6Sb_2Te_3$, and b) $Ge_{0.83(4)}Sb_{0.14(1)}Te = (GeTe)_{12}Sb_2Te_3$; the temperatures at which the selected diffraction patterns were collected are depicted next to the diffraction patterns

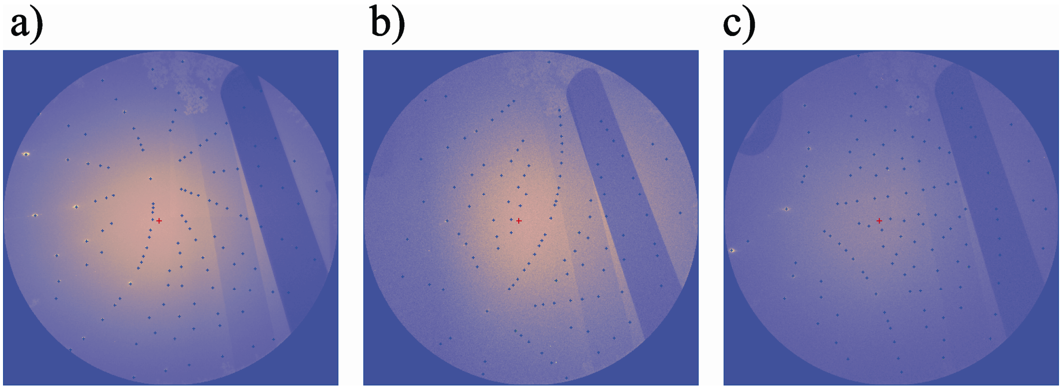

Fig. S2: Experimental Laue diffraction patterns of the high-temperature modifications of a) $Ge_{0.65(3)}Sb_{0.22(1)}Te$ = $(GeTe)_6Sb_2Te_3$ (565 °C), b) $Ge_{0.83(4)}Sb_{0.14(1)}Te$ = $(GeTe)_{12}Sb_2Te_3$ (515 °C), and c) $Ge_{0.84(1)}Sb_{0.12(1)}Te$ = $(GeTe)_{15}Sb_2Te_3$ (415 °C) with simulated reflection positions corresponding to a cubic cell (a = 6.00 Å) derived from a combined approach using the software packages X-MAS and the Laue Daresbury Software suite which allow one to index the reflections of the crystal in the corresponding orientation.

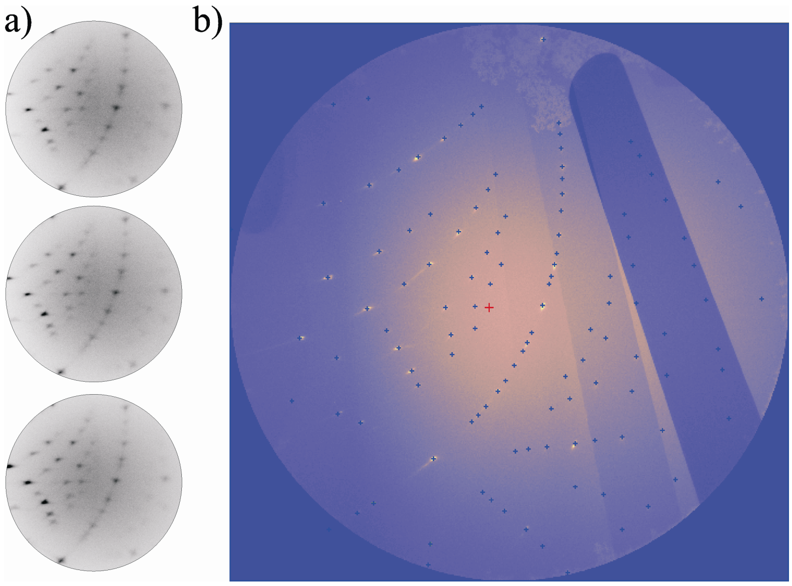

Fig S3: a) Laue diffraction patterns of $Ge_{0.83(4)}Sb_{0.14(1)}Te$ = $(GeTe)_{12}Sb_2Te_3$ collected from different positions on the sample at room temperature; b) Experimental diffraction pattern from the same crystal collected at 400 °C overlayed with reflection positions simulated by the Laue Daresbury Software suite which index the reflections (hR a = 4.25 Å, c = 10.52 Å a/c = 0.404)

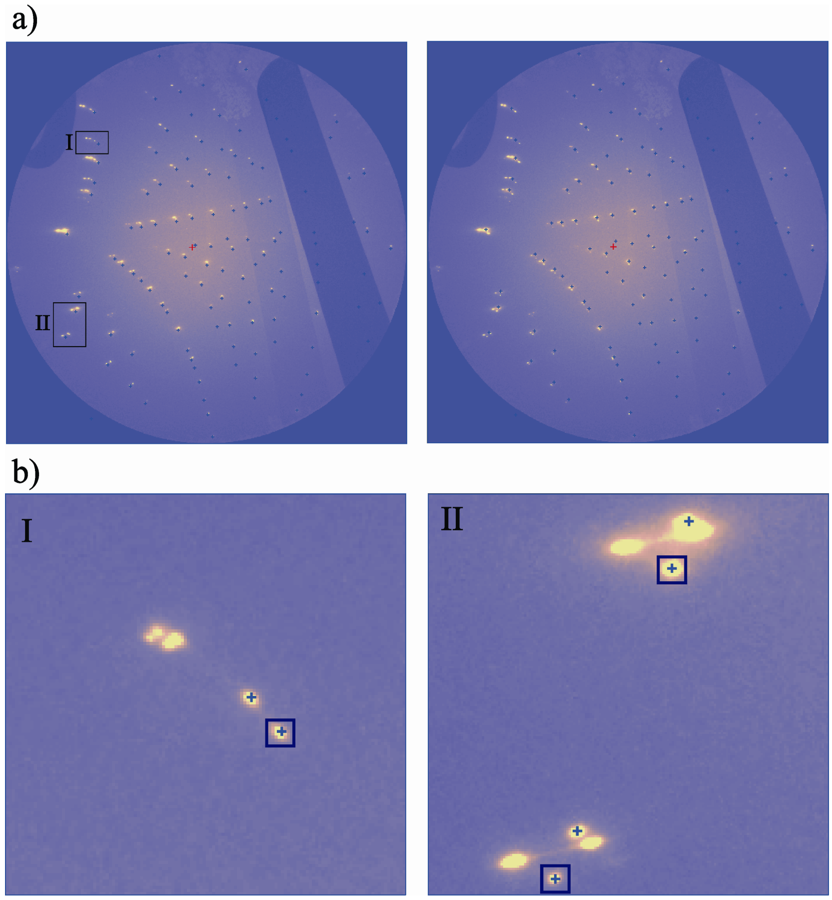

Fig S4: a) Laue diffraction pattern of $Ge_{0.84(1)}Sb_{0.12(1)}Te$ = $(GeTe)_{15}Sb_2Te_3$ collected at room temperature; the pattern is depicted twice as the individual patterns are overlayed with the reflection positions of one domain each which can be individually indexed (hR a = 4.22 Å, c = 10.57 Å a/c = 0.399) b) enlarged sections indicated in a); (I) a group of reflections which shows that all domain orientations expected for a fourfold twin according to the group-subgroup scheme $Fm\bar{3}m$ – $R\bar{3}m$ – $R3m$ contribute to the diffraction patterns (two orientations are indexed as indicated by crosses only and a cross-square combination); (II) Groups of several reflections belonging to different domain orientations which are interconnected by six diffuse streaks as expected for six different domain wall orientation possible in a fourfold twin.

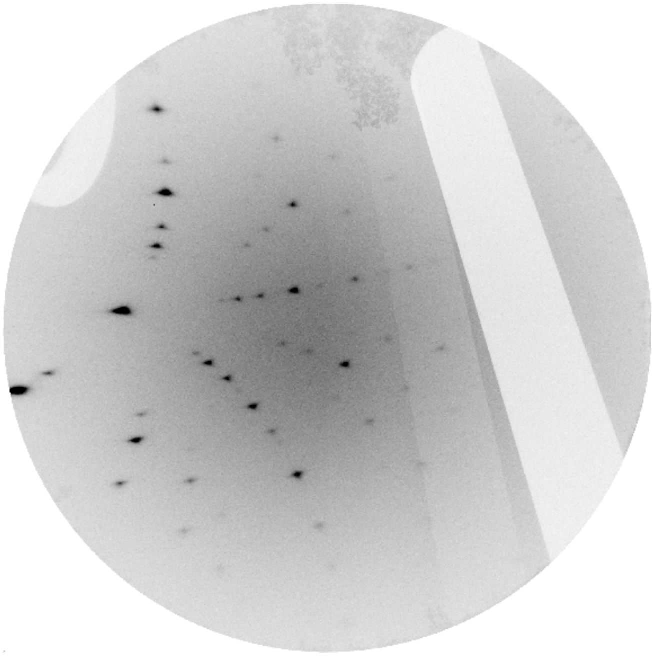

Fig. S5. Diffraction pattern of a $Ge_{0.84(1)}Sb_{0.12(1)}Te$ = $(GeTe)_{15}Sb_2Te_3$ crystal after cooling from the cubic high-temperature phase (see text and compare with Fig. 3a) at 260 °C.