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ESRF

Experiment Report Form

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- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** **"Temperature dependent synchrotron study of order-disorder transitions in multinary antimony telluride phase-change and thermoelectric materials by Laue diffraction techniques"**	**Experiment number**: MA-1194
Beamline: ID11	**Date of experiment**: from: 03.12.2010 to: 11.12.2010	**Date of report**: 01.04.2012
Shifts: **15**	**Local contact(s)**: Xavier Biquard	*Received at ESRF:*

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Report:

Aim

GeTe-rich compounds $(GeTe)_nSb_2Te_3$ ($n > 3$) exhibit cubic rocksalt-type high-temperature phases with a random distribution of 1/(n+3) cation vacancies per anion. The corresponding thermodynamically stable room-temperature phases, crystallize in trigonal long-periodically layered structures. These consist of distorted rocksalt-type slabs without cation defects which are separated by van der Waals gaps. Cubic and trigonal modifications are related by a phase transition that involves diffusion. Formally, cation defects form 2D extented layers at low temperature, which is accompanied by a rearrangement of the stacking sequence of the Te atom layers so that van der Waals gaps are formed. Metastable modifications obtained by quenching the HT phases represent an "intermediate state" of this phase transition and exhibit diffraction patterns with pseudo-cubic symmetry that correspond to the superposition of intensities from individual trigonal domains of the multiply twinned crystals. Short-range ordering of defects in interesecting vacancy layers perpendicular to the pseudo-cubic <111> directions produces pronounced nanostructures as indicated by diffuse scattering and electron microscopy.[1,2] The metastable modifications play an essential role in write-erase cycles of phase-change data storage media. In addition, compounds with the same compositions exhibit thermoelectric figures of merit ZT up to 1.3 which strongly depend on real-structure effects.[3,4] The thermoelectric properties depend significantly on the temperature. Hence, the aim of our experiments at the ESRF beamline BM32 was to study the temperature-dependent diffusion processes associated with the formation of different nanostructures. This should provide a basis for the understanding of the corresponding physical properties. Micro-focused white beam diffraction allows one to partially exclude space-averaging effects typical for conventional X-ray diffraction experiments while it simultanuously enables one to record large areas of reciprocal space in a single frame. Furthermore, a single image is representative for the whole diffraction patterns so that the change of diffuse scattering can be monitored quickly. Therefore, the in situ real-time observation of diffusion processes becomes possible.

Experiments and Results

Laue diffraction patterns of various GeTe-rich crystals $(GeTe)_n(Sb_2Te_3)$ ($6 > n > 15$) grown by chemical transport reactions were collected using a micro-beam (focus < 1 x 1 μm^2) with energies between 5 and 25 keV. Due to the excellent spatial resolution corresponding to the small beam size, diffraction patterns showing Bragg reflections as well as diffuse intensities could be obtained from various positions on the samples. Temperature-dependent investigations were performed in a temperature range from room temperature to ~ 600 °C using a domed hot stage (Anton Paar) calibrated with a thermocouple at the sample position (with estimated temperature error of about ± 10 °C). At a heating rate of 10 °C/min and exposure times of 1 second with read-out times of 5 seconds an approximate temperature resolution of 1 °C was realized. Data evaluation and treatment were performed using the software packages X-ray Microdiffraction Analysis Software (X-MAS) and the Daresbury Laue Software Suite.[5,6]

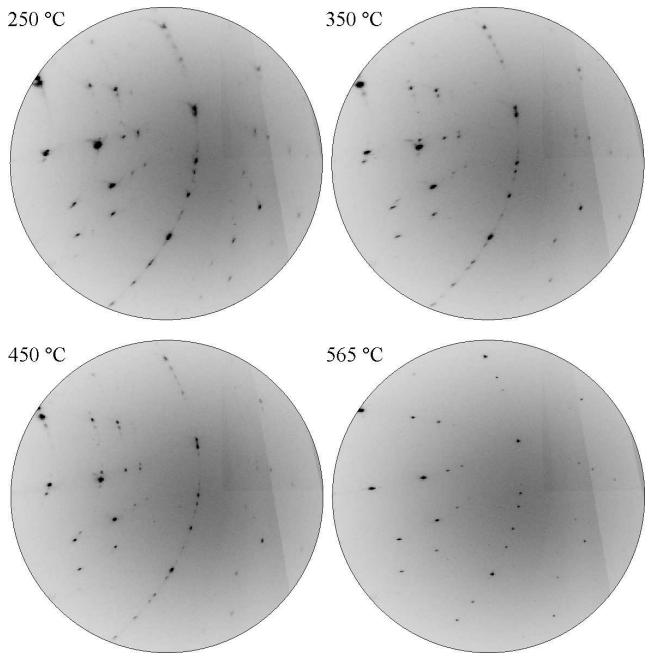

Fig 1: Experimental Laue diffraction patterns collected during heating $Ge_{0.65(3)}Sb_{0.22(1)}Te$ = $(GeTe)_{5\text{-}6}Sb_2Te_3$; the temperatures at which the selected diffraction patterns were collected are depicted over the diffraction patterns

For a crystal of $(GeTe)_6Sb_2Te_3$, asymmetrically broadened Bragg reflections interconnected by diffuse streaks indicate 1D disorder of planar defects in trigonal domains at least as large as the area illuminated. Upon heating this crystal, diffuse streaks gradually transform into sharp reflections characteristic for a long-periodically layered structure at 250 - 300 °C. At ~ 550 °C the cubic HT modification is formed (cf. Fig. 1) .

For a crystal of $(GeTe)_{12}Sb_2Te_3$, broadened Bragg reflections and only weak diffuse scattering without preferred orientation of streaks indicates twinning on the nanoscale. Upon heating the crystal the diffuse scattering transforms into streaks that interconnect sharp Bragg reflections at 400 °C. No long-periodically ordered layered phase is formed before the transition to the HT rocksalt-type phase occurs at ~ 500 °C.

In contrast to these samples, a GeTe-rich crystal $(GeTe)_{15}Sb_2Te_3$ grown at lower temperatures (i.e. not in the stability range of the high-temperature phase) did not exhibit broadened Bragg positions at RT as its individual domains are not (pseudo-)cubic. Laue frames revealed groups of reflections characteristic for trigonal twin domains with unit cells significantly deviating from cubic metrics. These groups are interconnected by weak streaks due to domain-wall scattering. No diffuse scattering corresponding to pronounced short-range ordering of cation defects was present. As shown in Figure 2, heating the crystal above 330 °C leads to additional reflections corresponding to the rocksalt-type high-temperature phase between the reflections of each group. The additional reflections gain intensity as the metric distortion decreases with incresing temperature. At 400 °C, only intensities of the cubic HT modification were observed. Upon cooling this sample below 330 °C, the sharp reflections of the HT phase significantly broaden and indicate the formation of a nano-domain transformation twin whereas before heating a growth twin was present.

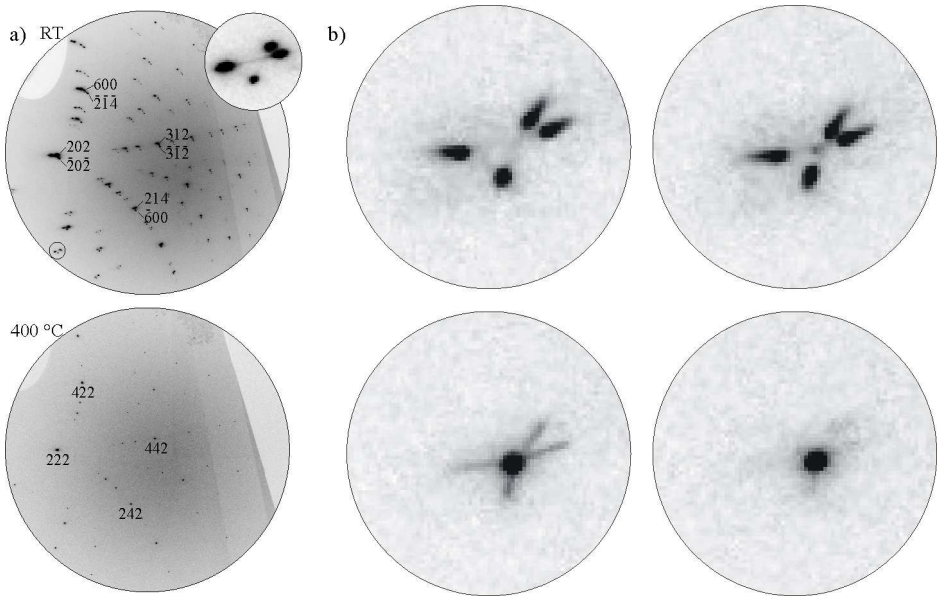

Fig. 2 a) Laue diffraction patterns of $(GeTe)_{15}(Sb_2Te_3)$ collected at room and at 415 °C (the inset shows an enlarged group of reflections belonging to different domains, indices of some reflections of the room temperature as well as high-temperature modification are depicted); b) enlarged sections of the reflection group indicated in a) showing the changing intensity distribution between 330 and 340 °C during heating.

Several conclusions can be drawn from these experiments: the real structures at room temperature and cation defect arrangements upon heating depend on the composition, which determines defect concentration. However, in all cases cation defect diffusion associated with the observed phase transitions is activated at approximately 300 °C. As the thermoelectric properties of such phases have been measured and show discontinuities in a similiar temperature range, our experiments at station BM32 allowed us to detect in situ diffraction patterns associated with this temperature dependent order-disorder transition and correlate it with the materials properties. These valuable results have already been published in *Chemical Communications* including the possibility to present them on the cover of the journal.[7] The excellent experimental conditions, e.g. perfect beam stability, high spatial resolution and the possibility for fast data collection in combination with the very helpful beamline staff made it possible to optimally use the allocated beamtime.

Outlook

The data obtained demonstrate the possibilities of the method compared to X-ray diffraction techniques using a monochromatic beam. Our results initiated new ideas for further experiments: the observation of phase transitions of small crystalline grains in a surrounding matrix, e.g. in polished samples from high-pressure syntheses or even in actual recording media based on phase-change materials. Even if the data evaluation is so far restricted to qualitative considerations, these would be intriguing experiments. Furthermore, we think it would be a demanding but worthwhile task to extract intensities for structure solution and refinement from microfocused Laue diffraction data of single grains of unknown phases. We are considering to apply for beamtime again and would like to further optimize the technique with respect to aspects of real structure elucidation.

References

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