	Experiment title: Phase composition of thermoelectric composite materials and structure elucidation of precipitates therein	**Experiment number**: CH-4988
Beamline: ID11	**Date of experiment**: from: 28th of June 2017 to: 3rd of July 2017	**Date of report**: 17.10.2017
Shifts: 15	**Local contact(s)**: Pavel Sedmak	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Prof. Dr. Oliver Oeckler* (Leipzig University)

M. Sc. Stefan Schwarzmüller* (Leipzig University)

M. Sc. Markus Nentwig* (Leipzig University)

M. Sc. Lucien Eisenburger* (Ludwig Maximilian University Munich)

Report

Aim

The phase composition and stability of multinary systems are difficult to predict since many different metastable or thermodynamically stable binary or ternary phases may occur. However, many multinary systems are highly relevant in materials science (e.g. high entropy alloys, steel, superconductors) and often feature unique properties that are related to their complexity. In order to overcome the correlation of thermal and electrical conductivity as well as electrical conductivity and Seebeck coefficient in ideal crystals of thermoelectric materials, doping, alloying and/or the formation of precipitates is required. This enables the design of complex optimized multinary thermoelectric materials as demonstrated for the system $AgPb_mSbTe_{2+m}$ (lead/antimony/silver/tellurium = LAST).[1] Cu-based thermoelectric materials like Cu_2Te,[2] Cu_2Se,[3] or Cu_7PSe_6 [4] exhibit extremely low thermal conductivities due to highly disordered and mobile Cu atoms, which led to the derivation of the phonon-liquid electron-crystal (PLEC)[3] concept, which includes phonon scattering at mobile atoms, from the phonon-glass electron-crystal concept (PGEC),[5] which relates to phonon scattering at defects, grain boundaries and precipitates. However, these materials often lack a high electronic conductivity and are not long-term stable because of copper segregation.[6]

In the system Cu/Ge/Sb/Te, the advantages of Cu_2Te and germanium antimony tellurides (GST materials) are combined and lead to superior thermoelectric performance and ZT values up to at least 1.8. Embedded in a Cu-doped GST matrix phase, copper telluride precipitates occur with dimensions in a length scale from 50 nm to 50 μm. Concerning this element combination, several aspects contribute to the complexity of the quartanery system as illustrated for the composition $Cu_2Ge_{11}Sb_2Te_{15}$: (1) the GST phase shows a phase transition from a layered to a rocksalt-type structure at 230 °C; (2) the binary phase diagram Cu/Te features a plethora of phases around 66 mol% Cu;[7] (3) energy dispersive X-ray spectroscopy (EDX) from transmission electron microscopy (TEM) suggests solubility of Cu in GST of 2-3 atom%, which might change with temperature; (4) powder X-ray diffraction (PXRD) patterns typically exhibit only the three strongest reflections of the precipitates with very low intensity. These are rather similar for at least three polymorphs of $Cu_{2-x}Te$, so that its actual structure remains unclear. While tracing these reflections with temperature, they vanish at 425 °C. This might be either due to dissolution in the main phase, a phase transition to a high-temperature (HT) cubic phase whose lattice parameter is very similar to that of matrix phase or simple melting of the copper telluride. While TEM is well suited at room temperature on a local scale, a synchrotron

beam together with a suitable sample environment provides space-averaged statistical data at various temperatures. Still, they enable spatial resolution by subsequently irradiating different sample volumes.

Thus, one aim of the present study is to elucidate the room temperature structures and temperature dependent behavior of copper tellurides in the GST matrix phase as well as the interaction of matrix and precipitates. In addition, we had planned to elucidate the crystal structure of compounds in the system Mn/Bi/Te and related issues. For these systems, it was impossible to obtain crystals that are large enough for conventional laboratory single crystal X-ray diffraction. Thus, a combined study of TEM and synchrotron microdiffraction[8] was proposed.

Experimental details and results

Sample preparation: Samples of Cu containing GST phases were prepared as extended thin sections (0.5-1 x 15-20 mm^2) with a thickness between 50 and 200 μm. Some of them were additionally polished with a dimple grinder at one edge from the front and the back in order to obtain a wedge-shaped edge. Microstructures were pre-investigated by means of scanning electron microscopy (SEM). Afterwards, samples were glued into glass capillaries with an amorphous high-temperature glue, set under argon atmosphere, sealed and glued into pins fitting into goniometer heads. Samples with potentially new compounds were suspended in ethanol, drop-cast on TEM finder grid and pre-investigated by means of SAED and TEM-EDX.

a) Crystal structure of copper telluride in germanium antimony tellurides at room temperature

The room temperature PXRD pattern of $Cu_2Ge_{11}Sb_2Te_{15}$ shows three reflections with very low intensity in addition to those of the GST matrix phase. These reflections can be attributed to a $Cu_{2-x}Te$ phase. However, due to the low number and intensity of these reflections and the complexity of the binary Cu/Te phase diagram around 66 mol% Cu, different structure types are possible: A phase in space group $P6/mmm$ with lattice parameters $a = 4.19$ Å and $c = 7.29$ Å, reported as high HT phase above 635 K, a twofold superstructure along [100] in spacegroup $P3m1$ with lattice parameters $a = 8.328$ Å and $c = 7.219$ Å reported as RT phase, or an additional threefold superstructure along [001] in spacegroup $P3m1$ with lattice parameters $a = 8.453$ Å and $c = 21.793$ Å reported as HT phase between 550 and 615 K.[9] In the data obtained at ID11, the main phase exhibits hexagonal metrics related to that of $Ge_{12}Sb_2Te_{15}$ [10] with $a = 4.2128(1)$ Å and $c = 10.3971(7)$ Å. For the copper telluride phase, hexagonal metrics with lattice parameters of $a = 4.2128(4)$ Å and $c = 21.8300(14)$ Å was found (Fig. 1 a) and b)) from single-crystal data acquired with microfocus diffraction. With a ($Ge_{12}Sb_2Te_{15}$) ≈ a (Cu_2Te) and $2c$ ($Ge_{12}Sb_2Te_{15}$) ≈ c (Cu_2Te), the occurrence of endotaxial intergrowth, which was also confirmed by means of HRTEM, can be explained. The intensity of the reflections originating from Cu_2Te is still weak compared to those from the GST matrix and the volume of the whole thin section sample being exposed is different for every frame. In combination with the overlap of reflections, the challenge to obtain a sufficient structural model will be addressed in the near future.
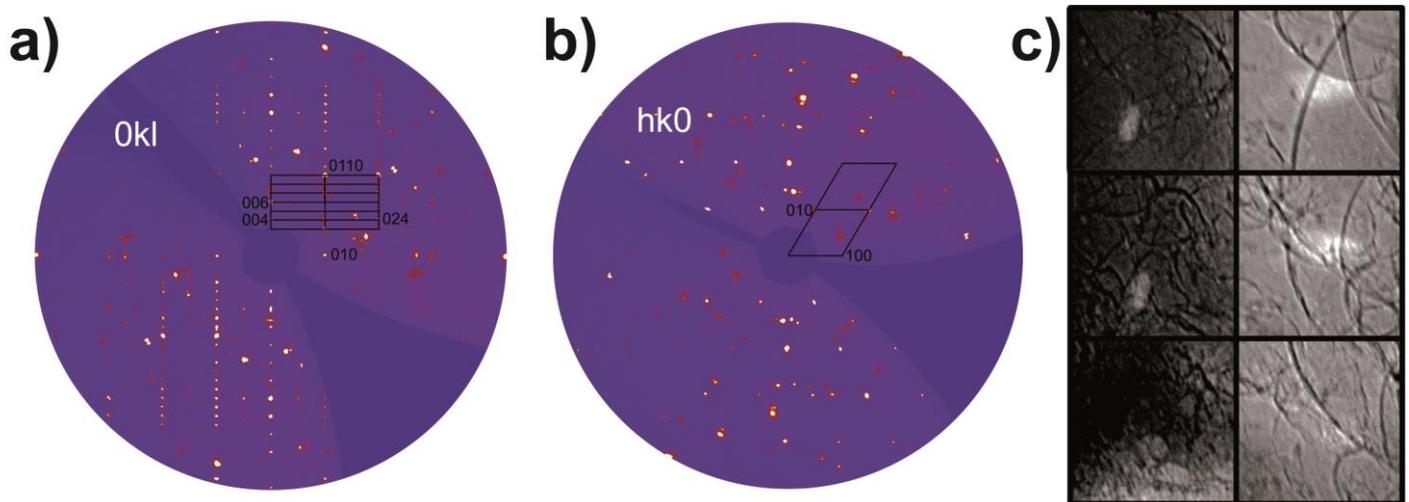
Figure 1: a) and b) Reciprocal lattice sections 0kl and hk0 of a Cu_2Te crystallite embedded in a GST matrix at RT. **c)** X-ray absorption contrast imaging of two copper telluride precipitates (left and right), increasing temperature from top to bottom .

b) Temperature dependent dissolution of copper telluride in germanium antimony tellurides

Copper telluride precipitates were observed during increasing temperature by means of X-ray absorption contrast imaging (Fig. 1c)) and X-ray diffraction. At 425 °C, i.e. the temperature where the reflections attributed to copper telluride vanish in a temperature dependent PXRD study carried out at ID11 at a previous beam time (CH-4020), the size and shape of the precipitates does not change in the absorption contrast imaging. The disappearance of the reflections can now be attributed to a phase transition of the copper telluride precipitates to a cubic HT phase with a very similar lattice parameter as cubic GST. Shoulders with low intensity at some GST reflections at HT support this finding. Upon further heating, the precipitates eventually dissolve in the matrix at ~580 °C, which coincides with a change of the slope of the lattice parameter of the GST matrix phase as a function of temperature. Further data evaluation might show the same trend in lattice parameters of single crystal data. Reflection splitting attributed to the simultaneous presence of a cubic HT phase of GST and a cubic HT phase of Cu_2Te with similar lattice parameters is expected.

c) Structure of copper telluride nanoprecipitates

In addition to the precipitates of Cu_2Te of 1-50 μm described in paragraph a), smaller precipitates could be observed by means of TEM. They have sizes between 50 and 500 nm. SAED patterns as well as HRTEM images indicate crystal structures different from those mentioned in paragraph a). Although some of these precipitates could also be observed in wedge-shaped thinned sections at the very thin end by means of X-ray absorption contrast during the beam time, it was impossible to extract information about their structure from X-ray diffraction data. This is due to the fact that the synchrotron beam could not be focused down to 1-3 μm but was 30 – 40 μm. (The beamsize was estimated via the fluorescence and diffraction signal of a single crystal needle of boulangerite with a few μm in diameter) Hence, only the known structure of the matrix material was observed.

d) Crystal structure of microcrystallites on TEM grids

Crystals with the element combinations Mn/Bi/Te and, as a further test, Ba/Lu/Si/O/N prepared on TEM grids had an extension of 1-10 μm and a thickness of a few micrometers. However, with a beam size of 30-40 μm it was not possible to obtain reasonable diffraction data of the microcrystals, since only background but no reflections was present.

Outlook

Although part c) and d) could not be carried out as planned because of the too large beam size, the beam time was, in general, successful and several useful datasets were obtained. The beamline staff were helpful and contributed to the success of this study with the idea of using X-ray absorption imaging in addition to X-ray diffraction. Concluding from this temperature-dependent study with a small beam pointed on different areas of a polycrystalline sample, previously obtained HT powder data can be perfectly complemented and extended. Due to contributions of a few crystallites with different orientations and very different absorption depending on the angle of incidence of the beam further data handling is required. Better absorption correction and/or neglecting the frames which are affected by high absorption is necessary. After addressing these issues, crystal structure of copper tellurides in GST materials at RT and at high temperature as well as the influence of both phases on each other's phase transition, composition and grain size can be clarified and linked to their thermoelectric properties. The results will be published in scientific journals.

References

[1] K. F. Hsu, S. Loo, F. Guo, W. Chen, J. S. Dyck, C. Uher, T. Hogan, E. Polychroniadis, M. G. Kanatzidis, *Science* **2004**, *303*, 818. [2] D. R. Brown, T. Day, T. Caillat, G. J. Snyder, *J. Electr. Mater.* **2013**, *42*, 2014. [3] Y. He, T. Zhang, X. Shi, S.-H. Wei, L. Chen, *NPG Asia Mater.* **2015**, *7*, e210-1. [4] H. Liu, X. Shi, F. Xu, L. Zhang, W. Zhang, L. Chen, Q. Li, C. Uher, T. Day, G. J. Snyder, *Nat. Mater.* **2012**, *11*, 422. [5] K. S. Weldert, W. G. Zeier, T. W. Day, M. Panthöfer, G. J. Snyder, W. Tremel, *J. Am. Chem. Soc.* **2014**, *136*, 12035. [6] G. A. Slack in: *CRC Handbook of Thermoelectrics* (Ed.: D. M. Rowe), CRC Press, Boca Raton **1995**, p. 407. [7] T. B. Massalski, *Binary alloy phase diagrams*, 2nd ed., ASM international, Ohio **2007**, p. 1490. [8] F. Fahrnbauer, T. Rosenthal, T. Schmutzler, G. Wagner, G. B. M. Vaughan, J. P. Wright, O. Oeckler, *Angew. Chem. Int. Ed.* **2015**, *54*, 10020. [9] R. Blachnik, M. Lasocka, U. Walbrecht, *J. Solid State Chem.* **1983**, *48*, 431. [10] T. Rosenthal, S. Welzmiller, O.Oeckler, *Solid State Sci.* **2013**, *25*, 118.