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![ESRF logo]	**Experiment title: Determination of the elemental distribution in long-periodically ordered multinary tellurides by resonant X-ray diffraction**	**Experiment number**: **HS-4826**
Beamline: ID31	**Date of experiment**: from: 03.04.2013 to: 09.04.2013	**Date of report**: 05.09.2013
Shifts: 18	**Local contact(s)**: Andy Fitch	*Received at ESRF:*

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Report:

Aim

Multinary tellurides containing germanium and antimony show promising thermoelectric properties which can be influenced by a broad range of substitutions.[1-3] As these properties strongly depend on the dopant concentration and its homogeneous distribution,[2] the analysis of powder samples is mandatory as controlling the exact composition during single-crystal growth is almost impossible in these systems. Such compounds contain elements with similar electron counts such as Ag, In, Sn, Sb or Te, whose scattering contrast does not allow one to differentiate them in conventional X-ray experiments (their neutron scattering cross-sections are also similar). The present experiment aimed at solving this problem by resonant scattering at absorption edges of elements involved.[4-6] In order to understand the influence of the element distribution on the thermoelectric properties, multi-dataset refinements were to be carried out for doped germanium antimony tellurides (GST materials). Their layered structures consist of rocksalt-like slabs divided by van der Waals gaps. Furthermore, chalcopyrite-type and related materials were investigated with the aim of obtaining reliable information on their space groups and cation ordering.

The temperature-dependent investigation of long-range ordered doped GST materials like $Ge_3SnSb_2Te_7$ with resonant scattering was an attempt to track the changes of the element distribution before and during phase transitions and possible decomposition reactions that occur at about 400 °C, where the trigonal layered phase transforms to a rocksalt-type high-temperature phase.

Experiments and Results

As a first part of the experiment, precise high-resolution powder diffraction data were collected at the K absorption edges of the respective elements (Sb, Te, Sn, In, Cd) and at 35.00 keV for 7 layered GST materials doped with Sn, In and Cd. Each pattern was measured with an individual energy for the respective compound directly at the edge which was determined by precisely recording the absorption edge of the respective elements with an energy-dispersive fluorescence detector (detecting interval around the specific emission line). The dispersion correction terms Δf' and Δf" were calculated via the Kramers-Kronig transform from these fluorescence data using CHOOCH.[7] The element distribution was refined using the Rietveld method in multidataset refinements [8] with TOPAS.[9] The sum formula of the phase pure samples was fixed, no further constraints were required. The refinements showed no problems (e. g. no tendency to diverge), the data proved to be excellent. This way it was possible to refine the element distribution in GST

materials like $Cd_{0.2}Ge_{0.8}Sb_2Te_4$, $Cd_{0.2}Sn_{0.8}Sb_2Te_4$, $Ge_{0.5}Sn_{0.5}Sb_2Te_4$ $GeSnSbInTe_5$, $GeSbInTe_4$, $Ge_2SbInTe_5$ and $Ge_3SnSb_2Te_7$ (Fig. 1 shows two examples: $Cd_{0.2}Ge_{0.8}Sb_2Te_4$ and $Cd_{0.2}Sn_{0.8}Sb_2Te_4$). In $Cd_{0.2}Ge_{0.8}Sb_2Te_4$, for isntance, Cd is rather uniformly distributed over both cation positions – in contrast to $Cd_{0.2}Sn_{0.8}Sb_2Te_4$ were Cd concentrates in the centre of the distorted rocksalt-type slab.

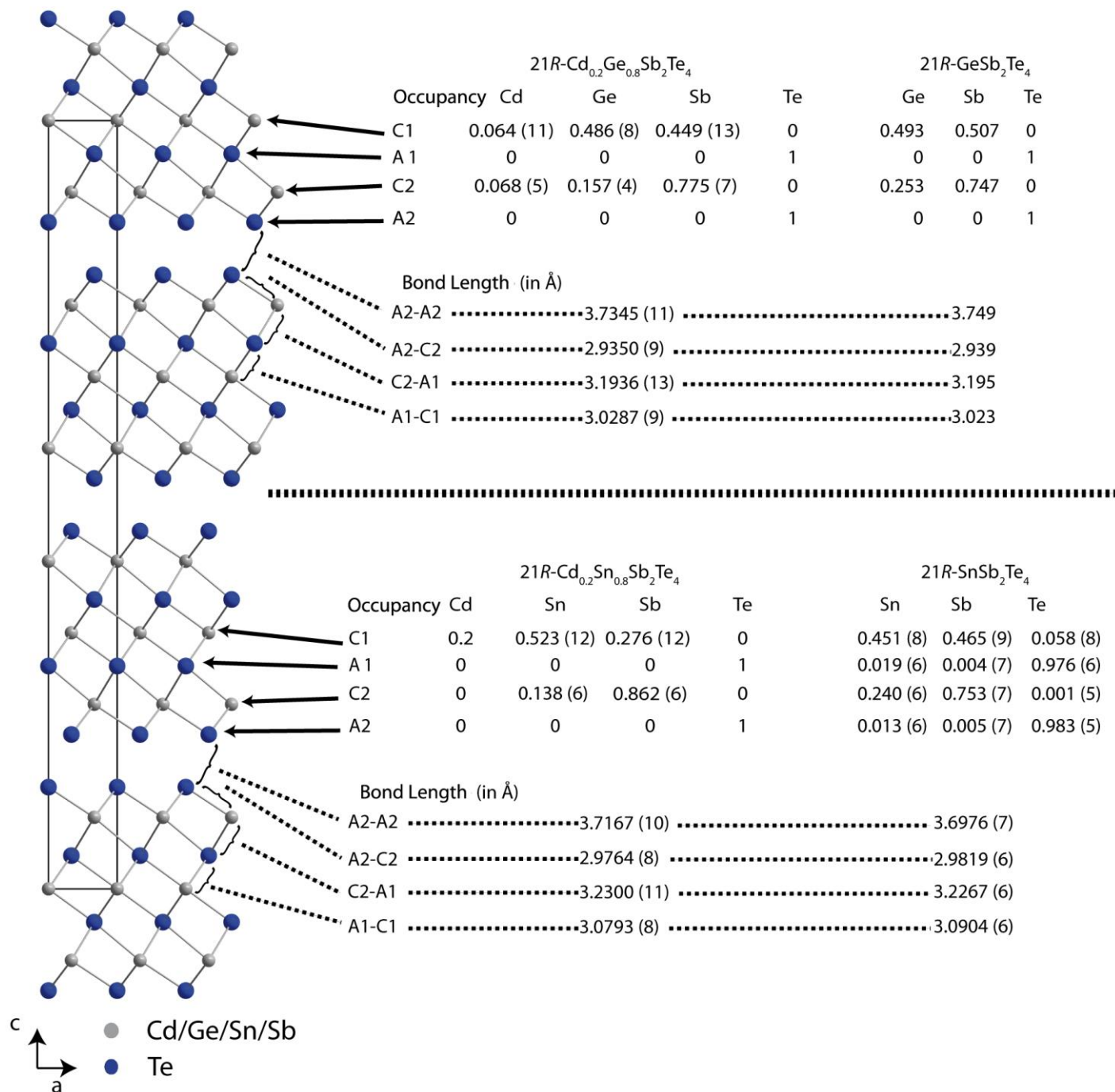|	21R-$Cd_{0.2}Ge_{0.8}Sb_2Te_4$				21R-$GeSb_2Te_4$		
Occupancy	Cd	Ge	Sb	Te	Ge	Sb	Te
C1	0.064 (11)	0.486 (8)	0.449 (13)	0	0.493	0.507	0
A1	0	0	0	1	0	0	1
C2	0.068 (5)	0.157 (4)	0.775 (7)	0	0.253	0.747	0
A2	0	0	0	1	0	0	1

Bond Length (in Å)

	21R-$Cd_{0.2}Ge_{0.8}Sb_2Te_4$	21R-$GeSb_2Te_4$
A2-A2	3.7345 (11)	3.749
A2-C2	2.9350 (9)	2.939
C2-A1	3.1936 (13)	3.195
A1-C1	3.0287 (9)	3.023

	21R-$Cd_{0.2}Sn_{0.8}Sb_2Te_4$				21R-$SnSb_2Te_4$		
Occupancy	Cd	Sn	Sb	Te	Sn	Sb	Te
C1	0.2	0.523 (12)	0.276 (12)	0	0.451 (8)	0.465 (9)	0.058 (8)
A1	0	0	0	1	0.019 (6)	0.004 (7)	0.976 (6)
C2	0	0.138 (6)	0.862 (6)	0	0.240 (6)	0.753 (7)	0.001 (5)
A2	0	0	0	1	0.013 (6)	0.005 (7)	0.983 (5)

Bond Length (in Å)

	21R-$Cd_{0.2}Sn_{0.8}Sb_2Te_4$	21R-$SnSb_2Te_4$
A2-A2	3.7167 (10)	3.6976 (7)
A2-C2	2.9764 (8)	2.9819 (6)
C2-A1	3.2300 (11)	3.2267 (6)
A1-C1	3.0793 (8)	3.0904 (6)

● Cd/Ge/Sn/Sb
● Te

Fig. 1: Results of the Rietveld refinements for $Ge_{0.8}Cd_{0.2}Sb_2Te_4$ (R_p: 0.0589, R_{wp}: 0.0854) and $Sn_{0.8}Cd_{0.2}Sb_2Te_4$ (R_p: 0.0667, R_{wp}: 0.0944) in comparison with unsubstituted compounds [10, 11] (as the compounds are isostructural, a common structure representation is used - the different compositions are shown for different slabs).

For the second part of the experiment, i. e. chalcopyrite-like compounds, the data quality was even better and the refinements (done as described above, additional data at the Ag-K edge) yield the element distribution unambiguously. Furthermore, the element distribution and vacancy ordering in solid-solution series between $CdIn_2Te_4$ and $AgInTe_2$, $AgIn_3Te_5$ or $AgIn_5Te_8$ was investigated successfully. For comparison, all end members except $AgInTe_2$ were also analyzed. This allowed us to assign the correct space groups in several cases where there had been some debate in the literature (e.g. $AgIn_5Te_8$).[12]
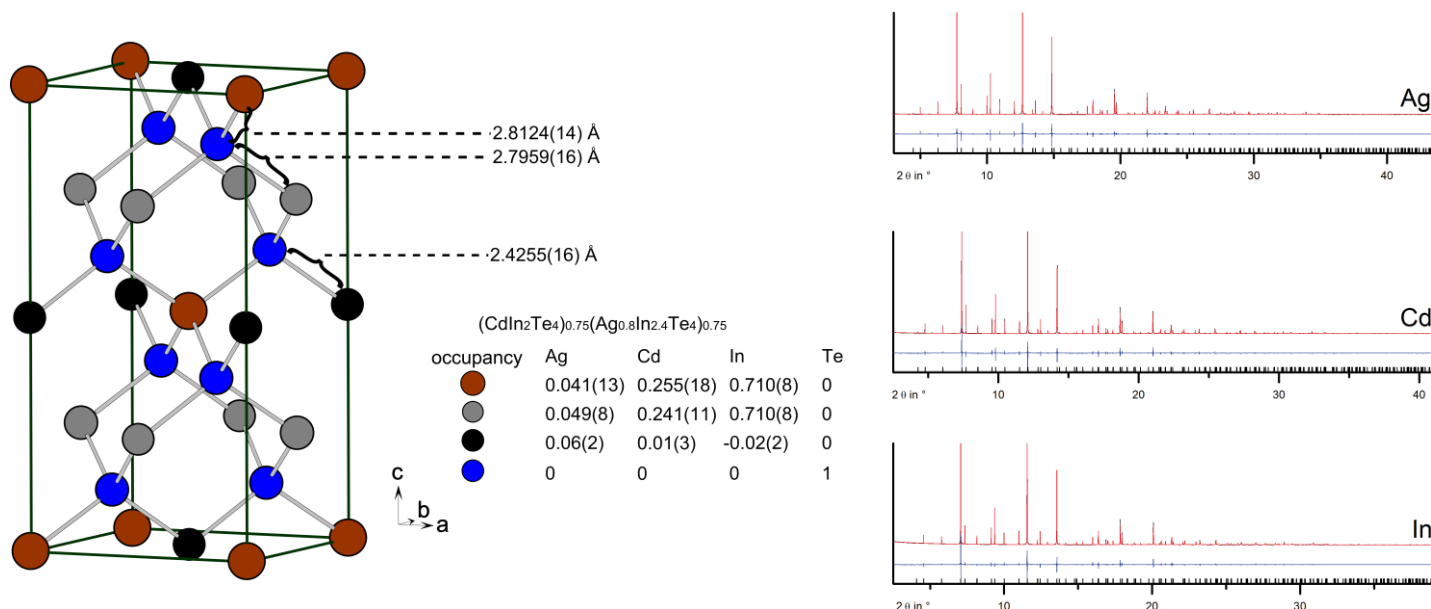
Fig. 2: Crystal structure of $(CdIn_2Te_4)_{0.75}(Ag_{0.8}In_{2.4}Te_4)_{0.25}$ refined from resonant scattering data (R_p: 0.0943, R_{wp}: 0.1273, left); calculated intensities (Rietveld refinement; red curve) compared with measured intensities (black curve) and difference plot (blue curve), only datasets for resonant scattering cations are shown (right).

For example, the refinement of $(CdIn_2Te_4)_{0.75}(Ag_{0.8}In_{2.4}Te_4)_{0.25}$ (Fig. 2) shows a more or less uniform cation distribution with one almost unoccupied Wyckoff position (due to vacancies; cation / anion ratio 3.05 / 4). This corresponds to the $HgCu_2I_4$ structure type observed for the end member $CdIn_2Te_4$.[13] Datasets for all other compounds investigated unambiguously yielded the element distribution in the same way.

Heating experiments, the third part of the experiment, were carried out for the layered compound $Ge_3SnSb_2Te_7$ at temperatures between 300 °C and 550 °C. They indicate a series of phase transition passing different layered structure types. This phase transition seems both temperature- and time-dependent; exsolution effects cannot yet be excluded. Further data evaluation and additional investigations are currently being carried out to fully understand the process; however, the data quality from ID31 will not be a bottleneck.

Outlook

The experiments at ID31 were extraordinarily successful. The method used allowed us to easily deal with compounds with scattering contrast problems like substituted GST materials or chalcopyrite-like materials. As these materials are promising thermoelectrics, the data obtained are important to correlate their structure with the physical properties. The results will be published soon in several papers. *In-situ* heating experiments provided a deeper insight in structure-property relationships at elevated temperatures. So far, only one example could be studied, yet the method would be a promising opportunity for a plethora of related investigations on a broad range of very interesting compounds.

References

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