



	Experiment title: Cu and Ag dynamics in phonon-liquid electron-crystal thermoelectric chalcogenides at elevated temperatures	Experiment number: CH-4698
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Report

Aim

Phonon-liquid electron-crystal (PLEC) compounds are emerging materials for thermoelectric applications that combine a low phononic thermal conductivity with reasonable electrical conductivity.^[1,2] This is possible due to mobile atoms such as Ag or Cu that move dynamically on more or less distinct diffusion pathways defined by a rigid substructure. Such diffusion requires partially occupied atom sites which are closely interconnected. This holds, for instance, for argyrodite-type and lillianite-type structures. The room temperature structure of one example of the latter ($\text{Ag}_3\text{Pb}_4\text{Bi}_{11}\text{Se}_{22}$) has been investigated previously in our group.^[3]

Now, single crystals from lillianite-type compounds $\text{Ag}_2\text{Pb}_3\text{Bi}_4\text{Se}_{10}$, $\text{Cu}_3\text{Pb}_6\text{Bi}_{11}\text{Se}_{24}$ and $\text{Cu}_2\text{Pb}_8\text{Bi}_{10}\text{Se}_{24}$ as well as from argyrodite-type $\text{Cu}_8\text{GeSe}_4\text{Te}_2$ could be synthesized. Thermoelectric measurements showed a low thermal conductivity for all of these materials. Concluding from their atomic structure obtained from room temperature single-crystal X-ray diffraction (SCXRD), this suggests that they are probably among the rather few known PLEC materials. The aim of the study is to obtain temperature-dependent (from room temperature to 500 °C) SCXRD data in order to investigate Cu or Ag mobility or pathways, respectively, in the same temperature regime as the one applied during thermoelectric measurements. The refinement of split-atom models or anharmonic displacement parameters and calculation of joint probability density functions (j.p.d.f.) allows one to visualize diffusion pathways and, in favorable cases, to calculate activation energies.

Experimental details and results

Single crystals of the mentioned (and some additional) compounds were mounted on glass fibers and precharacterized by means of energy dispersive X-ray (EDX) spectroscopy and SCXRD at room temperature on a Stoe IPDS laboratory diffractometer. At the Swiss-Norwegian Beamline (SNBL, BM01), samples were mounted on goniometer heads and diffraction data between room temperature and 550 °C were obtained with a Pilatus detector. For the refinement of anharmonic displacement parameters, the reflection / parameter ratio is often crucial. Hence, the wavelength was chosen as short as possible ($\lambda = 0.68010 \text{ \AA}$) and, in addition, diffraction data with different detector offsets were collected, yielding an overall resolution of 0.6 Å. The settings of the detector were optimized to reduce the detection of fluorescence. At first glance, the temperature dependence of lattice parameters and isotropic atomic displacement parameters (U_{iso}) indicated pronounced changes within the mobile substructure. Eventually, anharmonic displacement parameters and joint probability density functions (j.p.d.f.) are to be obtained in order to visualize diffusion pathways and calculate activation energies as a function of temperature.

In addition to the proposed experiments, room temperature data sets of two further new compounds ($\text{Ge}_7\text{As}_2\text{Te}_{10}$ and $\text{Ce}_{4-x}\text{Li}_3\text{P}_{18}\text{N}_{35-1.5x}\text{O}_{1.5x}$) with extremely weak diffraction phenomena were collected successfully in remaining beamtime.

a) $\text{Ag}_2\text{Pb}_3\text{Bi}_4\text{Se}_{10}$, $\text{Cu}_3\text{Pb}_6\text{Bi}_{11}\text{Se}_{24}$ and $\text{Cu}_2\text{Pb}_8\text{Bi}_{10}\text{Se}_{24}$

The complex selenides $\text{Ag}_2\text{Pb}_3\text{Bi}_4\text{Se}_{10}$, $\text{Cu}_3\text{Pb}_6\text{Bi}_{11}\text{Se}_{24}$ and $\text{Cu}_2\text{Pb}_8\text{Bi}_{10}\text{Se}_{24}$ were investigated with respect to possible mobility of Ag and Cu, respectively. One crystal of each compound was investigated in a temperature-programmed SCXRD experiment. Data were acquired every 25 °C up to the point of irreversible decomposition of the samples. This was elucidated by Le Bail fits on powder data calculated from the superposition of all frames for one temperature. The progression of the unit-cell parameters for $\text{Ag}_2\text{Pb}_3\text{Bi}_4\text{Se}_{10}$ is almost linear with a plateau at temperatures close to decomposition. Subsequently, SCXRD measurements of another single crystal with multiple detector offsets were carried out to ensure a maximal coverage of reciprocal space. Measurements took place at defined temperatures according to the stability range of the corresponding sample as analyzed beforehand. First evaluation of the equivalent isotropic displacement parameters U_{eq} for $\text{Cu}_2\text{Pb}_8\text{Bi}_{10}\text{Se}_{24}$ revealed differences in the temperature-dependent progression for different atom positions. The U_{eq} value for the cation position interconnecting the characteristic NaCl-type slabs of the structure (Bi3/Cu3) shows a linear progression while U_{eq} values for the other positions depict a step-like progression (cf. Figure 1d).

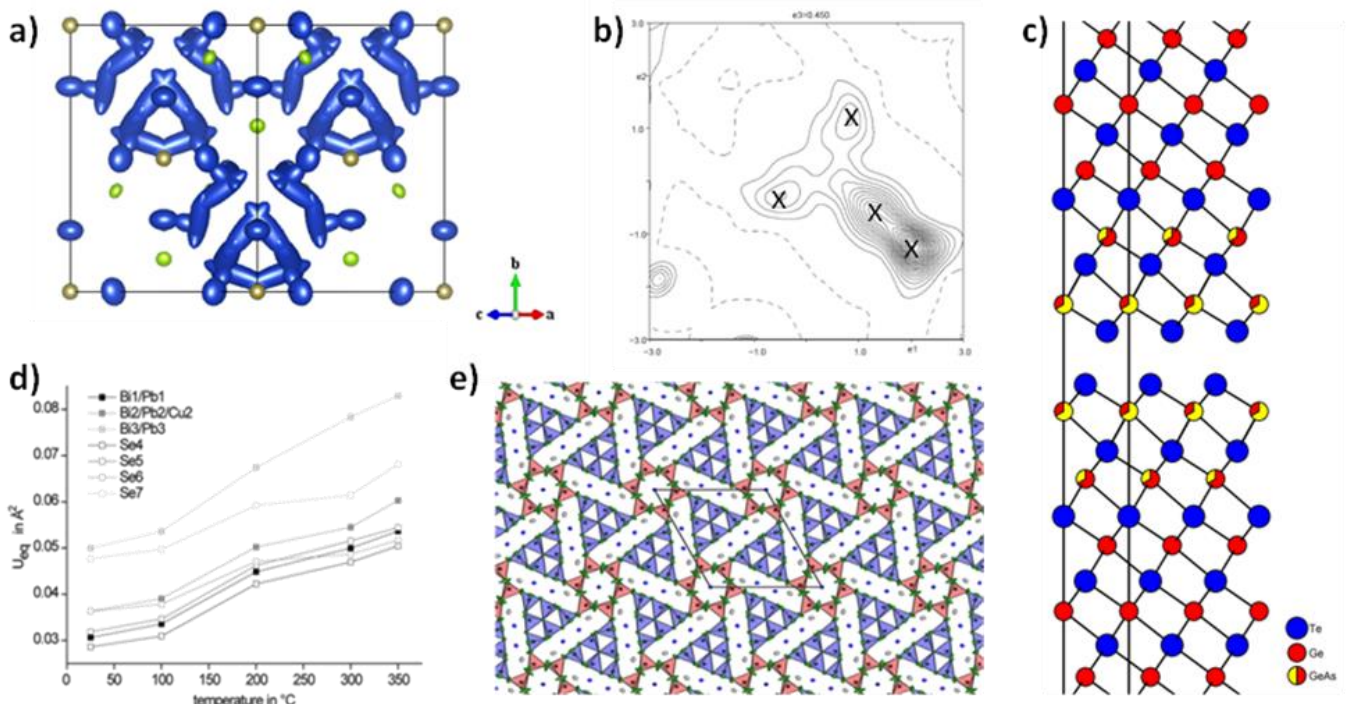


Figure 1: a) Crystal structure of $\text{Cu}_8\text{GeSe}_4\text{Te}_2$ at 450 °C with anharmonically refined Cu atom positions in blue; b) corresponding joint probability density function (j.p.d.f.) at 450 °C with Cu positions marked by “x”; c) crystal structure of $\text{Ge}_7\text{As}_2\text{Te}_{10}$; d) temperature-dependent progression of U_{eq} values of $\text{Cu}_2\text{Pb}_8\text{Bi}_{10}\text{Se}_{24}$; e) crystal structure of $\text{Ce}_{4-x}\text{Li}_3\text{P}_{18}\text{N}_{35-1.5x}\text{O}_{1.5x}$

b) $\text{Cu}_8\text{GeSe}_4\text{Te}_2$

$\text{Cu}_8\text{GeSe}_4\text{Te}_2$ crystallizes in a cubic argyrodite-type structure (space group $F\bar{4}3m$) with $a = 10.46053(6)$ Å. The anion substructure is comparable to other cubic argyrodites except for the anion ordering in $\text{Cu}_8\text{GeSe}_4\text{Te}_2$. Se^{2-} with its smaller ionic radius of 198 pm prefers the $16e$ position, which is part of the characteristic GeSe_4^{4-} tetrahedra. Te^{2-} with an ionic radius of 221 pm occupies the $4a$ and $4c$ positions. Site occupancy factors and positions of Cu atoms change during heating, which is also visible in a step-like increase of the lattice parameter. For all temperatures, the displacement parameters of Cu were refined with a Gram-Charlier expansion (3rd order, cf. Figure 1a). J.p.d.f. plots visualize the displacement of Cu-atom positions (cf. Figure 1b).

c) $\text{Ge}_7\text{As}_2\text{Te}_{10}$

High-quality single crystal data of a new germanium arsenic telluride could be collected. $(\text{GeTe})_7\text{As}_2\text{Te}_3$ crystallizes in the space group $R\bar{3}m$ with lattice parameters $a = 4.1155(6)$ and $c = 103.41(2)$ Å. The $57R$ -type stacking sequence consists of an ordered arrangement of rocksalt-type slabs. Each is 34.5 Å thick and consists of 10 Te-atom layers alternating with 9 Ge- and As-atom layers. The excellent counting statistics of the high-resolution synchrotron data enabled the refinement of the Ge/As ratio on all cation sites despite the similar scattering factors. This was not possible with standard laboratory SCXRD data. However, only two sites near the van der Waals gap exhibit a significant concentration of As (cf. Figure 1c). The results were published in the *Journal of Alloys and Compounds*.^[4]

d) $\text{Ce}_{4-x}\text{Li}_3\text{P}_{18}\text{N}_{35-1.5x}\text{O}_{1.5x}$

$\text{Ce}_{4-x}\text{Li}_3\text{P}_{18}\text{N}_{35-1.5x}\text{O}_{1.5x}$ crystallizes in the space group $P6_3/m$ ($a = 13.9318(1)$ Å, $c = 8.1355(1)$ Å, $R_1 = 0.0188$, $R_{\text{int}} = 0.0192$) in a network of all-side vertex-sharing PN_4 tetrahedra. The P/N network is highly-condensed due to triply bridging N; the degree of condensation is 0.514. Metal cations are located in 6- and 10-ring channels (cf Figure 1e). The synchrotron data revealed an extremely weak superstructure that is currently being analyzed.

Outlook

This beamtime was extremely productive and very successful – more and better data than expected were obtained. Beamline staff were very helpful! In this study the Cu and Ag mobility of thermoelectric materials was investigated in the temperature range of good thermoelectric performance. The anharmonic and enlarged displacement parameters as well as the smeared out electron density in the joint probability density functions (j.p.d.f.) proves the atom mobility and enables the classification of those materials as phonon-liquid electron-crystal (PLEC) materials. Due to the temperature dependent change in lattice parameter and displacement parameters, phase transitions of the mobile substructure can be detected. This will lead to a better understanding of PLEC materials and enable the improvement of known as well as the development of new materials. The results are going to be published in several articles.

The temperature dependent structural investigation of compounds exhibiting mobile atoms requires high quality data, both in low background and high angular resolution. All this was possible at the Swiss norwegian beamline with the necessary equipment and a well experienced staff.

References

- [1] 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.
- [2] K. S. Weldert, W. G. Zeier, T. W. Day, M. Panthöfer, G. J. Snyder, W. Tremel, *J. Am. Chem. Soc.* **2014**, *136*, 12035.
- [3] F. Heinke, R. Meyer, G. Wagner, O. Oeckler, *Z. Anorg. Allg. Chem.* **2015**, *641*, 192.
- [4] M. Nentwig, F. Fahrnbauer, M. Kasprick, O. Oeckler, *J. Alloys Compd.* **2017**, *694*, 1160.