ESRF	**Experiment title:** Structure determination of ternary rare-earth metal bismuthide tellurides and bismuthide selenides by microfocus diffraction	**Experiment number**: CH-5506
Beamline: ID11	**Date of experiment**: from: 03.10.2018 to: 08.10.2018	**Date of report**: 26.11.2019 *Received at ESRF:*
Shifts: 15	**Local contact(s)**: Jonathan Wright	

Names and affiliations of applicants (* indicates experimentalists):

Dr. Christopher Benndorf* (Leipzig University)

Prof. Dr. Oliver Oeckler (Leipzig University)

M. Sc. Tobias Stollenwerk* (Leipzig University)

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

M. Sc. Daniel Günther* (Leipzig University)

Report:

Note that some samples investigated during this beamtime correspond to projects CH5140.

Aim

Ternary rare-earth metal pnictide chalcogenides are characterized by the absence of bonding interactions between pnictogen and chalcogen atoms. We synthesized ternary rare-earth metal bismuth selenides and bismuthide tellurides which crystallize with the LaSbTe-type or distortion variants of it. LaSbTe itself exhibits a layer-like crystal structure and shows charge density waves (CDW) [1]. Because of the crystal chemical relation to this structure type, it is expected to find similar electronic phenomena in ternary compounds with equiatomic *RE*BiSe and *RE*BiTe (*RE* = La-Nd, Gd, Tb) composition. The samples were synthesized via high-temperature methods in closed niobium ampoules or by the reaction of cold-pressed element mixtures and characterized by means of PXRD, SEM and TEM EDX. While the tellurides seem to crystallize with the LaSbTe type structure, the selenides adopt the CeAsS-type. All pre-investigated rare-earth metal bismuthide chalcogenides occur as microcrystalline substances with plate-like crystals and approximate sizes of 3 μm and less. Since the layer-like structure of the compounds limits the growth of single-crystals suitable for conventional diffraction experiments, the combination of pre-selective methods and microfocused synchrotron radiation is necessary for our aim to determine the crystal structure of these samples. A complicated bonding situation due to distortion effects for the series of *RE*Bi*Ch* compounds is expected to be found within the characteristic sheet-like $[\mathrm{Bi}^-]$ building units in dependence of the relative atomic size and the electronic contribution of the associated rare-earth metal and chalcogen atoms. Results obtained via this technique give the fundamental basis for further experimental and theoretical investigations.

Experimental Details and results

All samples were investigated by TEM EDX and selected area electron diffraction (SAED) experiments to ensure the selection of suitable crystallites, i.e. right composition and good crystallinity. The selected crystallites were fixed on carbon-film-coated TEM finder grids, which were then glued to glass fibers or sample holders in a way that the crystal of choice (or parts of it) was best accessible by the beam. Beamline ID11 is equipped with an optical telescope that was used to align the crystallites in the beam. Additionally, fluorescence scans were performed to achieve final centering. For the experiments with a microfocused beam, the energy was kept at 41 keV ($\lambda = 0.3024$ Å) to ensure minimal absorption for the investigated compounds and maximal brilliance of the beam. The beam size used for these experiments was 1.6 µm vertically and 1.0 µm horizontally. For subsequent investigations of larger crystals, the size of the beam was increased to 50 µm vertically and 30 µm horizontally. All investigations of the beam- and air-resistant samples were implemented under ambient condition. The data sets were analyzed by using the CrysAlis software [2]. Structure solution and refinement was conducted using the SHELX or Jana2006 software package. The following samples were examined:

a) *RE*BiTE

Pre-selected single-crystals of *RE*BiTe (*RE* = La, Pr) were investigated (Fig. 1). The substances containing La and Pr found to crystallize as a ternary variant of the $CaSb_2$ type structure ($P2_1/m$). The compounds are characterized by an alternating stacking of $[RECh]^+$ and $[Bi]^-$ building blocks [3].

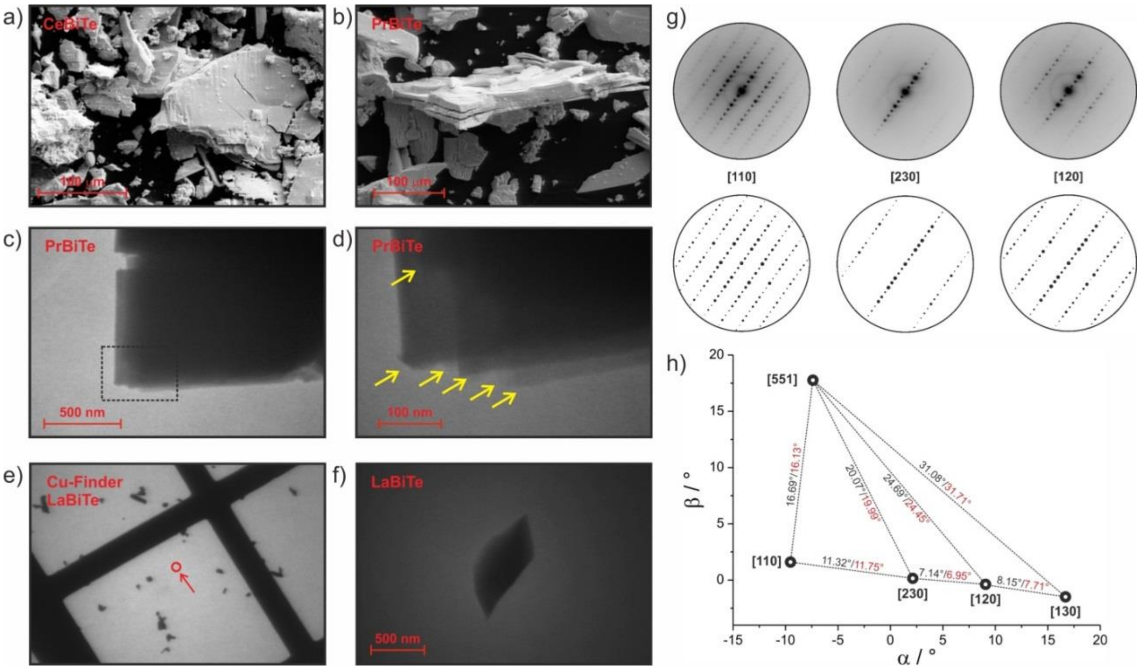

Fig. 1: Secondary electron SEM images of CeBiTe (a) and PrBiTe (b) emphasizing the flaky habit of the crystals accompanying strong intergrowth. c) and d) show TEM bright field images of a large agglomerate of PrBiTe crystals indicated by arrows. A small crystal of LaBiTe investigated at ID11 is shown in e) (STEM-BF image) and f) (TEM-BF image). The pre-selected crystal was investigated by SAED (g and h).

b) $Nd_3VSe_3O_3$

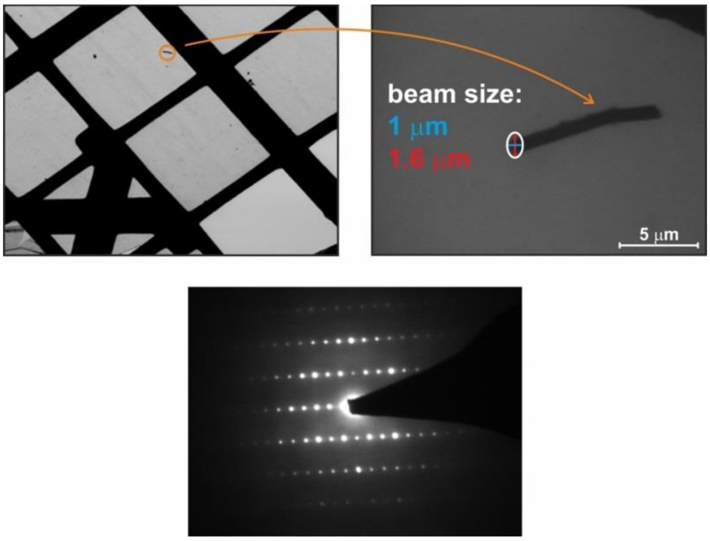

Fig. 2: STEM-BF image of a small $Nd_3VSe_3O_3$ single-crystal investigated at ID11 (left). The area used for data collection is emphasized (right). The crystals quality was pre-investigated by SAED (bottom).

Small needle-like and extremely fragile crystals of a hitherto unknown neodymium vanadium selenide oxide were investigated (Fig. 2). The compound was found to crystallize with its own structure type ($P2_1/m$, a = 9.751(2) Å, b = 3.849(8) Å, c = 10.631(2) Å, β = 94.31(3)°) characertized by chains of edge-sharing [$\mathrm{VSe_4O_2}$] octahedral. The substance can be described electron precisely according to $(3RE^{3+})^{9+}\mathrm{V}^{3+}(3\mathrm{Se}^{2-})^{6-}(3\mathrm{O}^{2-})^{6-}$. On basis of the experiments conducted at ID11, four additional compounds $RE_3\mathrm{V}Ch_3\mathrm{O}_3$ could be find so far [4].

c) ~$\mathrm{Be_{370}Sr_{46}N_{284}}$
A data set of a Be/Sr/N containing microcrystal was collected. The compound crystallizes with space group $I2/m$ and lattice parameters of a = 14.1953(2) Å, b = 26.1903(2) Å, c = 15.1003(2) Å and β = 90.057(1)°. First structure refinement revealed a network of $\mathrm{BeN_4}$-tetrahedra including few triginonal planar coordinated Be atoms. In larger spaces $\mathrm{SrN_{12}}$ cuboctahedra or $\mathrm{Sr_3N_{22}}$ groups of face-shared cuboctahedron-like polyhedra occure. Furthermore, the structure includes mixed Sr/N sites and partially occupied Be sites.

d) $\mathrm{Ca_3P_5N_{10}Cl}$
A dataset of $\mathrm{Ca_3P_5N_{10}Cl}$ was collected and analyzed. The compound crystallizes with the orthorhombic space group $P2_1/n$ and lattice parameters of a =11.955 Å, b = 12.748 Å and c =13.163 Å. The Structure is built up by a network of corner-sharing $\mathrm{PN_4}$ tetrahedra forming large channel-like cavities containing the Ba and Cl atoms. Diffuse diffraction and electron charge residue in these channels indicate a high mobility of the located atoms.

e) $\mathrm{La_{21}P_{40}O_{46}N_{57}}$
The collected data set of $\mathrm{La_{21}P_{40}O_{46}N_{57}}$ was refined in the space group $P2_1/n$ (a = 14.042(4) Å, b = 7.084(3) Å, c = 41.404(10) Å and β = 97.73°). Characteristic for this structure are the hybrid $\mathrm{PN_4}$ tetrahedra chains (symbol: $\mathrm{La}_{21}\{\boldsymbol{hB},1^{1}\infty\}$ [$^{21}\mathrm{P}_{21}(\mathrm{N,O})_{63}(\mathrm{P(N,O)}_2)_{17}(\mathrm{P(N,O)}_3)_2$]). Furthermore, disorder P-P split position and La/N mixed sites lead to 8 different variants of the chain. [5]

f) $\mathrm{Cu_{1.2}Ag_{0.4}Bi_{4.7}Se_8}$
Two datasets of $\mathrm{Cu_{1.2}Ag_{0.4}Bi_{4.7}Se_8}$ were collected for reasons of completeness and merged. The compound crystallizes in the space group $C2/m$ (a = 13.670(3) Å, b = 4.1800(9) Å, c = 15.245(4) Å and β = 99.54(3)°) and is similar to the ^{4}P-type structure of $\mathrm{Cu_{1.3}Ag_{0.8}Bi_{5.3}S_9}$ [6] as a member of the pavonite homologous series [7]. This shows that the substitution of Cu in the ^{3}P-type structure [8] with Ag results in a pavonite-type crystal structure with thicker NaCl-type blocks, because Ag mixes with Bi onto the cation positions within this block.

g) compounds in the system Cu/Fe/S/Se
Six single crystals with different ratios of Cu/Fe and S/Se were measured and resulted in twinned structures or superstructures similar to the temperature-dependent polymorphs of the mineral $\mathrm{Cu_5FeS_4}$ stabilized at room temperature [9-11]. Furthermore, the variation of the cation and anion ratios gave access to new complex and modulated crystal structures. The solutions and refinements of these crystal structures are still under investigation.

Outlook

By combining pre-selective methods like TEM with microfocused synchrotron diffraction we achieved structure determinations, which would have not been possible with conventional electron, x-ray or synchrotron diffraction methods. Through this technique we could elucidated several new structures. The first publications stemming from this project are already written and further papers are following soon. This method has proven to be an essential and reliable tool for the structure determination of micro-sized compounds. We are confident that results of similar quality can be achieved in future research projects. For further enhancement of structural characterizations heat or cooling sources might be beneficial, to make metastable phases or phase transitions accessible for measurement.

References

[1] E. DiMasi, B. J. Foran, M. C. Aronson, S. Lee, *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *54*, 13587-13596.
[2] Agilent Technologies Ltd, *CrysAlis PRO*, Yarnton, Oxfordshire, England, **2015**.

[3] T. Lindemann, T. Block, F. Stegemann, O. Janka, J. P. Wright, C. Benndorf: "*Rare-earth pnictide chalcogenides REBiTe and RESbS (RE = La-Nd): staructure determination by a combination of transmission electron microscopy and microfocused synchrotron radiation*", poster presentation at the 32nd European Crystallographic Meeting, Vienna, Austria, **2019.**

[4] F. Gehlhaar, C. Benndorf: "Structure determination of rare-earth vanadium selenide oxides by combination of transmission electron microscopy and microfocused synchrotron radiation", oral speech at the 27th Annual Conference of the German Crystallographic Society, Leipzig, Germany, **2019**.

[5] M. Nentwig, S. Kloß, L. Neudert, L. Eisenburger, W. Schnick, O. Oeckler, *Chem. Eur. J.* **2019**, *25*, 14382-14387.

[6] D. Topa, E. Makovicky, T. Balic-Zunic, *Can. Mineral.* **2008**, *46*, 515-523.

[7] E. Makovicky, W. G. Mumme, J. A. Watts, *Can. Mineral.* **1977**, *15*, 339-348.

[8] J. Y. Hwang, H. A. Mun, S. I. Kim, K. L. Lee, J. Kim, K. H. Lee, S. W. Kim, *Inorg. Chem.* **2014**, *53*, 12732-12738.

[9] N. Morimoto, *Acta Crystallogr.* **1964**, *17*, 351-360.

[10] Y. Kanazawa, K. Koto, N. Morimoto, *Can. Mineral.* **1978**, *16*, 397-404.

[11] K. Koto, N. Morimoto, *Acta Crystallogr. B* **1975**, *31*, 2268-2273.