



**Experiment title: Mixed anionic chalcogenide oxides and their redox chemistry**

**Experiment number:**  
CH-5663

<b>Beamline:</b> ID11	<b>Date of experiment:</b> from: 05.10.2020 to: 08.10.2021 from: 27.01.2021 to: 28.01.2021 from: 26.02.2021 to: 28.02.2021	<b>Date of report:</b> 17.09.2021
<b>Shifts: 15</b>	<b>Local contact(s):</b> Carlotta Giacobbe, Carlotta Giacobbe, Jonathan Wright	<i>Received at ESRF:</i>

**Names and affiliations of applicants** (\* indicates experimentalists):

Dr. Christopher Benndorf\* (Universität Leipzig)

Prof. Dr. Oliver Oeckler\* (Universität Leipzig)

M. Sc. Daniel Günther\* (Universität Leipzig)

M. Sc. Monika Pointner\* (LMU München)

Alexander Feige\* (Universität Leipzig)

**Report:**

*Note that some samples investigated during this beamtime correspond to other projects. The beamtime was splitted into three different sessions mentioned above.*

**Aim**

Previous investigations of the mixed-anionic selenide oxide  $\text{Nd}_3\text{VSe}_3\text{O}_3$  were conducted using TEM pre-characterization in combination with diffraction experiments using micro-focused synchrotron radiation at beamline ID11. Further synthetic investigations of the systems  $RE/T/Se/O$  ( $RE$  = rare-earth metal;  $T$  = early transition metal) lead to the discovery of various new compounds, e. g.  $RE_2\text{ZrSe}_2\text{O}_3$ . A major problem of structural investigations is the lack of single-crystals suitable for diffraction experiments on laboratory scale. The selenide oxides appear as thin, needle-like crystals with sizes less than 5  $\mu\text{m}$  which are highly sensitive to mechanical damage. We aimed to investigate small single-crystals selenide oxides with various compositions for structural characterization forming the basis for further characterization of mixed-anionic materials.

**Experimental Details and results**

The samples investigated during the beamtime at beamline ID11 were pre-characterized by TEM investigations including EDX spectroscopy and selected area electron diffraction to ensure high crystal quality. The samples were transferred to conventional carbon-coated TEM finder grids and these were fixed to sample holders at the ESRF. The experiments were conducted by the beamline staff at ID11, data analysis was conducted by the applicants remotely due to the SARS-CoV-2 pandemic. In the third session (26.-28.02.2021) some of the applicants were allowed to conduct the experiments in presence at the ESRF.

a)  $\text{Ce}_7\text{TiSe}_5\text{O}_7$

Needle-like crystals obtained by the reaction of Ce,  $\text{CeO}_2$ , Ti, and Se in NaCl/KCl flux were pre-investigated by TEM-EDX. The chemical composition suggested the presence of an unknown compound. The compound was found to crystallize with the  $\text{La}_7\text{VSe}_5\text{O}_7$  structure type [1] (space group  $Cmcm$ ,  $a = 3.895(3) \text{ \AA}$ ,  $b = 12.5920(13) \text{ \AA}$ ,  $c = 31.747(2) \text{ \AA}$ ) (see Fig. 1).

Electron precise description according to  $7\text{Ce}^{3+}\text{Ti}^{3+}5\text{Se}^{2-}7\text{O}^{2-}$  suggests the presence of  $\text{Ti}^{3+}$  ions. Typical building units of chalcogenide oxides are present in the crystal structure

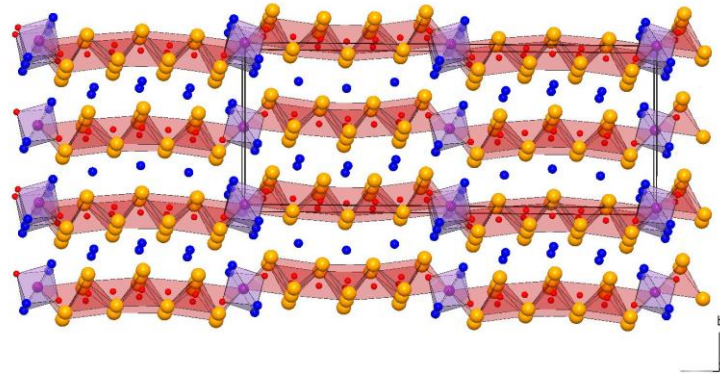


Fig. 1: Crystal structure of  $\text{Ce}_7\text{TiSe}_5\text{O}_7$  projected along  $[100]$ . The cerium, titanium, selenium, and oxygen atoms are depicted in yellow, purple, blue, and red, respectively. The coordination polyhedra of the O and Ti atoms are emphasized.

b)  $\text{BePn}_2$

The structure of the binary beryllium pnictides  $\text{BePn}_2$  ( $Pn = \text{P, As, Sb}$ ) was investigated using microdiffraction on small crystallites. The compounds were synthesized by reaction Be and P, As, and Sb, respectively, in powdered forms at high temperatures under inert conditions resulting in microcrystalline products.  $\text{BeSb}_2$  was found to crystallize with its own structure type, space group  $I4_1/amd$ , and lattice parameters of  $a = 3.5577(2) \text{ \AA}$ , and  $c = 15.071(1) \text{ \AA}$ . The Sb atoms are connected to infinite  $[\text{Sb}]^-$  chains extended in  $a$  and  $b$  direction, respectively. The compound can be described electron precisely according to  $\text{Be}^{2+}2[\text{Sb}]^-$ .

The diffraction patterns of  $\text{BeP}_2$  and  $\text{BeAs}_2$  exhibit strong diffuse scattering suggesting disorder. The crystal structures were found to be isotypic (space group  $C2/c$ ;  $\text{BeAs}_2$ :  $a = 10.659(2) \text{ \AA}$ ,  $b = 10.656(2) \text{ \AA}$ ,  $c = 8.343(1) \text{ \AA}$ ,  $\beta = 108.59(1)^\circ$ ). The compounds are build up by cyclic  $[\text{Pn}_8]^{8-}$  rings and can be written electron precisely according to  $4\text{Be}^{2+}[\text{Pn}_8]^{8-}$ .

c)  $\text{TiPn}_2\text{Te}_4$

The rhombohedral compounds  $\text{TiPn}_2\text{Te}_4$  ( $Tt = \text{Ge, Sn, Pb}$ ;  $Pn = \text{As, Sb, Bi}$ ) feature septuple layers, in which the multiplicity of Wyckoff positions would allow complete cation ordering, which has been postulated in some cases [2]. However, more detailed studies based on single-crystal diffraction data almost always revealed cation disorder [3]. In the case of small scattering contrast, resonant X-ray diffraction corroborated the disorder [4].

d) Cs/In/Sb/S

A novel compound of the system Cs/In/Sb/S obtained by solvothermal synthesis in ethylene diamine was investigated at ID11. It crystallizes in the orthorhombic space group  $Immm$  with the following lattice parameters:  $a = 5.61273(7) \text{ \AA}$ ,  $b = 7.32623(9) \text{ \AA}$ ,  $c = 25.0394(5) \text{ \AA}$ . The data showed strong diffuse scattering along with the  $c^*$  direction, therefore stacking faults are expected to be seen along with  $c^* = [001]^* = [001]$ .

e)  $\text{Ta}_8\text{PN}_{15}$

A single-crystal data set of an approximately  $3.5 \mu\text{m}$  long needle of a tantalum phosphorus nitride was obtained.  $\text{Ta}_8\text{PN}_{15}$  crystallizes in the monoclinic space group  $C2/m$  ( $a = 16.224(3) \text{ \AA}$ ,  $b = 2.9000(6) \text{ \AA}$ ,  $c = 11.100(2) \text{ \AA}$ ,  $\beta = 126.50(3)^\circ$ ) and exhibits rarely seen columns along  $[010]$  of edge-sharing octahedra. A close relationship to the high-pressure phase  $\text{Ta}_3\text{N}_5$  could be obtained, which is evident in a similar  $b$ -lattice, as well as the arrangement of tantalum polyhedra forming channels of Dreier rings along  $[010]$ . Single crystal data in

accordance with STEM HAADF data showed an unusual mixed occupation of the octahedral voids by phosphorous with about 15 % tantalum.

f)  $\text{CaSi}_3\text{P}_4\text{N}_{10}(\text{NH})_2$

From two datasets collected at ID11 the crystal structure of the first nitridic mica  $\text{CaSi}_3\text{P}_4\text{N}_{10}(\text{NH})_2$  could be elucidated. High intensity/high precession data enabled us to combine two datasets in order to increase completeness. Powder-data from isotopic  $\text{AESi}_3\text{P}_4\text{N}_{10}(\text{NH})_2$  ( $AE = \text{Mg}, \text{Sr}, \text{Mg}_{0.9}\text{Ca}_{0.1}$ ) could be analyzed in terms of phase contents following the SCXRD structure model.

g)  $\text{Sr}_2\text{AlP}_8\text{N}_{15}\text{O}:\text{Eu}^{2+}$

A dataset of a 2  $\mu\text{m}$  large crystal of  $\text{Sr}_2\text{AlP}_8\text{N}_{15}\text{O}:\text{Eu}^{2+}$  was collected at ID11. The crystal structure ( $Pnma$ ,  $a = 13.261(3) \text{ \AA}$ ,  $b = 8.061(2) \text{ \AA}$ ,  $c = 11.636(2) \text{ \AA}$ ) contains a network of all-side vertex-sharing  $\text{PN}_4$  tetrahedra forming three-, six- and twelve-membered rings along  $[010]$  as well as six-membered rings along  $[10\bar{1}]$ . Sr atoms occupy the 12er-rings.  $\text{Al}(\text{N/O})_6$  octahedra are located in between the voids created by the six-membered rings running along  $[010]$  and share edges and vertices with  $\text{PN}_4$  tetrahedra. The structure contains triply bridging  $\text{N}^{3-}$  and tetrahedra edge and vertices sharing with octahedra. The condensed network ( $\kappa = 0.56$ ) therefore closes the gap between  $\kappa = 1/2$  and  $3/5$  in previously existing rare-earth nitridophosphates.

h)  $\text{Al}_5\text{P}_{12}\text{N}_{26}$

The structure of  $\text{Al}_5\text{P}_{12}\text{N}_{26}$  was determined based on a dataset from ID11. The compound exhibits cubic metric ( $a = 11.784(12) \text{ \AA}$ ). The crystal structure is characterized by the presence of vertex-sharing  $\text{AlN}_6$ -octahedra and  $\text{PN}_4$ -tetrahedra. However, P/Al split positions occur, which may be resolved by further investigations using lower symmetric space groups.

## Outlook

The combination of TEM investigations as a pre-selective method for structure determination of micro-sized crystals of several different compounds was successful. Publication of the results relating to different projects is in progress and will be done soon. The executed method to investigate micro-sized crystals of a large variety of compound classes is a highly valuable combination of analytical techniques which can only be done by using the high brilliance beam of the ESRF. The applicants are confident that results of similar quality can be achieved in future research projects including new developments like temperature-dependent investigations of micro-sized crystals.

## References

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