ESRF	**Experiment title:** Structure determination of (sub-) microcrystals of luminescent nitrides by microfocus diffraction in combination with TEM	**Experiment number**: CH-4318
Beamline: ID11	**Date of experiment**: from: 17.06.2015 to: 23.06.2015	**Date of report**: 21.10.2015
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Report:

Aim

Oxonitridosilicates are a highly important class of compounds in the field of luminescent materials for phosphor-converted LEDs and porous materials.[1] Extreme reaction conditions are required for the synthesis of such nitrides; and as aconsequence, inhomogeneous and microcrystalline samples are often obtained. Thus structure determination with routine X-ray methods is often not successful, whereas electron crystallography is not precise enough for detailed discussions. Therefore, we aimed at the characterization of microcrystals of new compounds in heterogeneous samples by means of micofocussed synchrotron radiation. Samples were pre-characterized by transmission electron microscopy (TEM) and EDX spectroscopy and in some more straightforward cases by SEM. The structure elucidation of novel compounds can be expected to extend the structural diversity of complex silicate network structures. The close analogy between (oxo-)nitridosilicates and nitridophosphates inspired the application of the method to the latter class of compounds which may also yield intriguing host lattices for dopes luminescent materials. In addition, these investigations contribute to the advancement and improvement of structure analyses that exploit the synergism of electron and microcrystal diffraction.

Experimental details and results

Prior to the beamtime, we examined most of the samples by means of TEM or SEM in combination with EDX in order to be sure to select crystallites of new compounds. The respective crystallites were mounted either on Kapton micromounts or a carbon-film-coated TEM finder grids. The latter were fixed on glass fibers in a way that the crystal of choice (or parts of it) was best accessible by the beam. At beamline ID11, an optical telescope was used to approximately center the crystallites in the beam and X-ray fluorescence scans provided an exact final alignment. For the microfocus experiments the energy was kept at 30 keV to ensure minimal absorption for the investigated compounds with a beam of maximal brilliance, utilizing beam

sizes down to ca. 2 µm. High-angle data were collected by additional measurements with detector offset. In addition, we had obtained an additional day of beamtime in order to compensate for technical problems during the previous experiment CH-4131. This was used for resonant scattering experiments at the K-edges of Bi, Pb, Sn, Ag and an additional off-edge energy of 81.7 keV. The following samples were examined in our experiments:

a) Novel PON tetrahedral network structure

High-quality data of a microcrystal of an unknown high-pressure modification of phosphorus oxide nitride could be collected. The composition obviously deviates from the expected composition PON. Preliminary structure solution and refinenents revealed an unusual silicate analogon. Reconstructed reciprocal lattice section are rather complex and most likely indicate an incommensurate modulation, which is currently under investigation. We believe that this will become an intriguing investigation and expect that it will result in a publication in high-impact journal.

b) Lanthanum strontium sialon

An extremely thin needle of a lanthanum strontion sialon was investigated and yielded brilliant diffracted intensities. The trigonal structure (probably *P*31*c*, *a* = 16.239(2) Å, *c* = 9.436(2) Å) could be refined to reasonable R values, the approximate composition is "$La_{25}Sr_{11}Si_{36}N_{78}O_6F_2$", which requires further chemical analysis in order to quantify and assign the light atoms' types. However, it is clear that the compound exhibits a new and unusual network structure. The results also hint at strategies for synthesis optimization.

c) New complex network structures in the La/Ba/Si/N system

Preliminary TEM investigations and earlier data obtained at ID11 had shown unusual diffraction patterns (e.g. SAED pattern in Figure 1b) that hinted at an intergrowth of two slightly different structures with a common subcell, and twinning was also likely. Thorough and detailed TEM investigation could successfully identify single crystals of both structure types that exhibited only one part of the previous diffraction patterns each. High-quality X-ray data of both these new nitridosilicate network structures could be obtained using very small microfocussed beam. Probably both compounds crystallize in the space group: $P\bar{6}$, one wi th *a* = 20.19 Å and *c* = 22.68 Å and the other one with *a* = 17.48 Å and *c* = 22.68 Å. The corresponding reciprocal lattice sections reconstructed from data measured at ID11 are depicted in Figures 1c and 1d. The tetrahedral networks shown in Figure 1a consist of edge- and corner-sharing SiN_4 tetrahedra, the cavities are occupied by La. Doped with Eu^{2+}, these compounds show a narrow green luminescens and are potential LED phosphors due to their high temperature stability and inertness towards moisture and oxidation at ambient conditions.

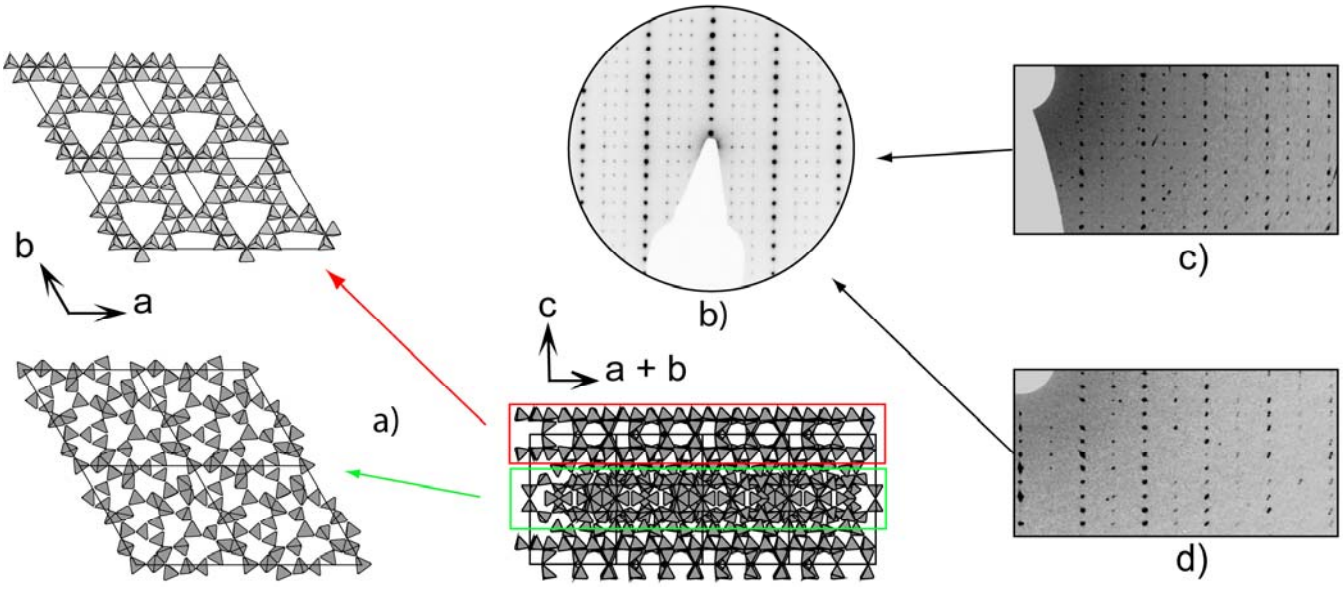

Figure 1: a) Silicate network structure (a = 17.48 Å, c = 22.68 Å) corresponding to the *hhl* diffraction pattern (shown in c), view of slabs extending along (001) (only tetrahedra are drawn); b) SAED pattern of an intergrown sample (superposition, zone axis [010] / [1$\bar{1}$0]); c) and d): corresponding reciprocal lattice sections *hhl* and *h0l* from single crystal synchrotron data.

d) Chalcogenides

An additional task left from experiment CH4131 (see above and corresponding experimental report) was the determination of the the cation distribution in chalcogenides that contain elements with similar electron counts using resonant X-ray scattering at *K* edges with high energies (e.g. Pb / Bi).

In the system Sn/Bi/Se, datasets for 3 samples were collected, each at the Sn-*K* edge (~29.1 keV), Bi-*K* edge (~90.5 keV) and off-edge. The refined compositions of all samples agreed well with preliminary EDX analysis. In addition, the presence of vacancies on each cation position could be confirmed. The structure of $SnBi_4Se_7$ consists of NaCl type-like slabs and ribbon-like elements related to those in the Sb_2S_3 structure (space group: *C*2/*m*, *a* = 27.128 Å, *b* = 4.1805 Å, *c* = 21.375 Å, β = 131.70°). The compound is isostructural to $K_{0.66}Sn_{4.82}Bi_{11.18}Se_{22}$.[2] Between the ribbon-like entities, there are strands of empty edge-sharing Se_6 octahedra. Vacancies on each cation position render this material promising with respect to further optimization of its thermoelectric properties. $Sn_{13}Bi_{14}Se_{34}$ (space group: *C*2/*m*, *a* = 13.812 Å, *b* = 4.188 Å, *c* = 26.636 Å, β = 95.76°) and $Sn_2Bi_2Se_5$ (space group: *Cmcm*, *a* = 4.173 Å, *b* = 13.811 Å, *c* = 31.844 Å) crystallize in structure types related to that of the multinary sulfide lillianite.[3] Both structures consist of tilted NaCl type-like slabs interconnected by trigonal prismatically coordinated cations. The structural data provide new insight into the defect chemistry of multinary chalcogenides.

In each of the systems Cu/Pb/Bi/Se and Ag/Pb/Bi/Se, two compounds were investigated by collecting datasets at the Pb-*K* edge (~87.9 keV), Bi-*K* edge (~90.5 keV) and off-edge. For the silver containing samples an additional dataset was collected at the Ag-*K* edge (~25.4 keV). The further evaluation of the datasets is still ongoing; however, concluding from the results for the Sn/Bi/Se system, we expect successful structure analyses.

Resonant scattering at the Bi- and Pb *K*-edges of tetradymite-like compounds $(PbS)_nBi_2Te_2S$ (n = 0, 0.5, 1, 2) shows that all cations are completely ordered, which is quite rare for such layered structures, e.g. in comparison with the well known Ge/Sb/Te system.[4] So far, only very few (if any) successful resonant experients at the Pb/Bi K-edges had been reported, and none for tetradymite-like systems.

Outlook

The combination of TEM and microfocus synchrotron diffraction is an excellent tool for challenging structure determinations where electron diffraction and conventional (or microfocus) X-ray diffraction alone are not sufficient. With the experience gained from this experiment, we are able to further optimize the procedure described, which should enable us to go to even more complex systems and more demanding experimental setups during our next beamtime. The use of microfocused beams in high-temperature measurements is one of upcoming challenges. The resonant scattering esperiments show that high-energy K-edges (Pb, Bi) are well suitable to elucidate the distribution of such elements (and others like Tl, Hg, Au, etc.). Even if there are no scattering contrast problems, single elements can reliably be highlighted and vacancies that occur on mices cation positions can be detected unequivocally. In the whole area of “energy materials” such as thermoelectric or luminecent materials, ID11 provides excellent opportunities for accurate structure analyses that contribute significantly to the unterstanding and optimization of such copmpounds.

References

[1] M. Zeuner, S. Pagano, W. Schnick, *Angew. Chem. Int. Ed.* **2011**, *50*, 7754.
[2] A. Mrotzek, D.Y. Chung, T. Hogan, M. G. Kanatzidis, *J. Mater. Chem.* **2000**, *10*, 1667.
[3] J. Takagi,Y. Takéuchi, *Acta Crystallogr. Sect. B* **1972**, *28*, 651.
[4] M. N. Schneider, M. Seibald, P. Lagally, O. Oeckler, *J. Appl. Crystallogr.* **2010**, *43*, 1012.