



	<b>Experiment title:</b> Structure determination of luminescent nitridoaluminates and nitridoberyllates by microfocus diffraction	<b>Experiment number:</b> CH-5140
<b>Beamline:</b> ID11	<b>Date of experiment:</b> from: 04.12.2017 to: 11.12.2017	<b>Date of report:</b>
<b>Shifts:</b> 15	<b>Local contact(s):</b> Jon Wright	<i>Received at ESRF:</i>
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## Report

*Note that some samples investigated during this beamtime correspond to project CH5142, whereas some samples from CH5140 were investigated during beamtime CH5142*

## Aim

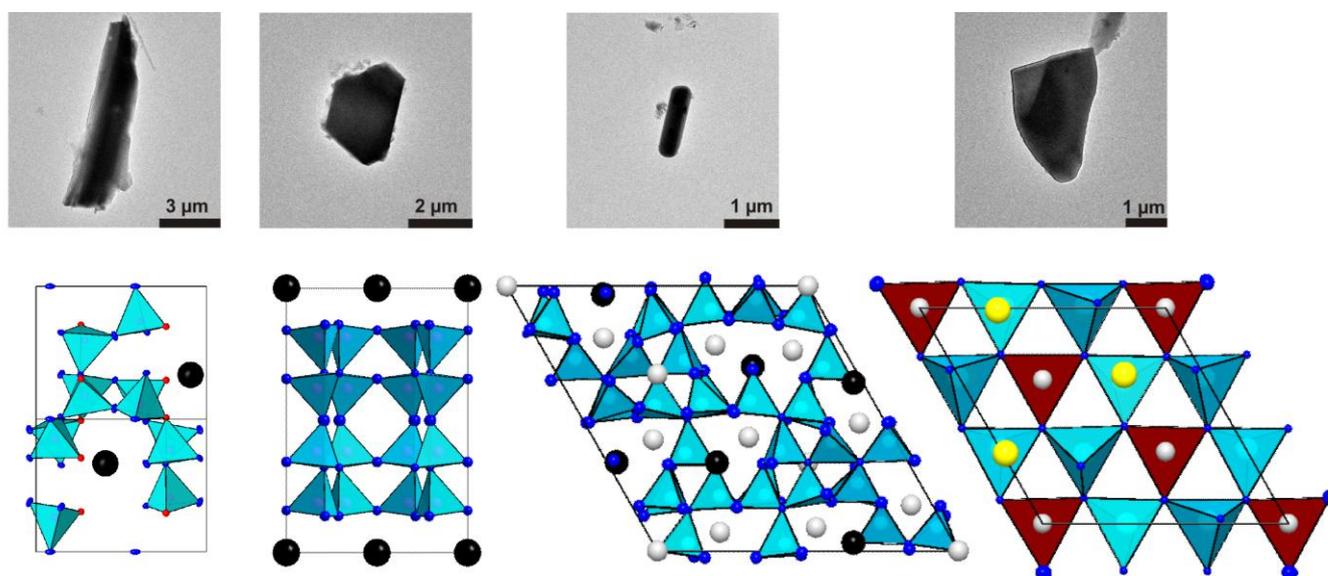
The development of efficient luminescence materials is an important task in terms of energy saving. Therefore, the most promising way to achieve less power consumption in LED lighting per lumen is the reduction of infrared light emission.<sup>[1]</sup> This goal is not only achieved by co-doping of known host lattices but even more by the exploration of new classes of compounds. The luminescence properties of rare earth metal doped nitridoberyllates, nitridosilicates and nitridophosphates strongly depend on the coordination sphere, ligand field and symmetry of the activator ion site. That information can only be correlated with luminescence if accurate structural data are available. New materials are often found by explorative syntheses that often yield microcrystalline samples. This impedes structure elucidation by laboratory single-crystal X-ray diffraction. The project focussed on nitridoberyllates, nitridosilicates and nitridophosphates, compound classes of special interest because of their structural variety. Their dense tetrahedral networks show multiple ways of possible interconnection between  $\text{SiN}_4$ ,  $\text{PN}_4$  and  $\text{BeN}_3$  units owing to N atoms' flexibility concerning terminal, two-, three- or fourfold interconnecting positions.<sup>[2,3]</sup> These possible motifs can be further expanded by the formation of  $\text{PN}_5$  trigonal bipyramids under high pressure.<sup>[4]</sup> Such dense frameworks often fulfill the essential requirements of possible host lattices for activator ions, e.g. optical transparency and high thermal stability. Beryllium, despite being infamously known as a toxic element, will not pose any hazard once incorporated in dense silicate frameworks as well-known from emerald jewelery. In order to elucidate the structures of new compounds from microcrystalline samples and to distinguish between multiple phases, transmission electron microscopy (TEM) is well suited. These studies yield information about the unit cell metrics from selected area electron diffraction (SAED) and about the elemental composition from energy dispersive X-ray spectroscopy (EDX). Careful pre-characterization enables the re-location of microcrystals

on TEM grids at ID11 by fluorescence scans. Subsequent data collection from single crystallites are possible with a microfocused synchrotron beam.<sup>[5,6]</sup>

## Experimental details and results

**Sample preparation:** Samples from the compound classes mentioned above were synthesized using high-pressure and/or high-temperature methods. Small amounts of the products were thoroughly ground in an agate mortar, suspended in ethanol and this suspension then dropped on TEM finder grids. Crystallites to be measured were chosen by size and thickness contrast (~500 x500 nm at least), SAED patterns were taken at different areas of the crystallites in order to avoid aggregates of crystals. Elemental compositions were derived from EDX. Prepared TEM grids were mounted on the hexapod “nanoscope” and crystals on the grids were re-located optically with a microscope and centered by fluorescence scans.

Several single-crystal datasets were obtained and most structures could be immediately solved and refined (see Fig.1):



**Figure 1:** Investigated crystallites (top) and corresponding crystal structures for a-d from left to right (bottom); a)  $\text{PO}_2\text{N}_2$  tetrahedra (blue) and Ba atoms (black), b)  $\text{PN}_4$  tetrahedra (blue) and Ba atoms (black), c)  $\text{Si}(\text{C},\text{N})_4$  tetrahedra (blue), Ba atoms (black) and Lu atoms (gray), d)  $\text{SiN}_4$  tetrahedra (blue),  $\text{BeN}_3$  units (red) and Ca atoms (yellow)

### a) a new Sr containing nitridoberyllate doped with $\text{Eu}^{2+}$

We collected a dataset of a new Sr containing nitridoberyllate which possesses tetragonal metrics with lattice parameters probably corresponding to  $a = 5.727(1) \text{ \AA}$ , and  $c = 19.809(4) \text{ \AA}$ . Twinning by reticular pseudo-merohedry is present. This compound shows white luminescence under irradiation with UV-light. The structure elucidation will be completed in the near future.

### b) $\text{CaBeSi}_2\text{N}_4$

The structure was elucidated based on the dataset from ID11. The compound crystallizes in space group  $P\bar{6}$  with lattice parameters  $a = 8.374(2) \text{ \AA}$  and  $c = 9.184(2) \text{ \AA}$  ( $R_{\text{int}} = 0.0523$ ,  $R1(\text{obs}) = 0.0274$ ). It is so far the sixth compound in the family of nitridoberyllates.

### c) $\text{BaP}_6\text{N}_8\text{O}_3$

This structure was also elucidated based on the dataset from ID11: space group  $P6_3$  with lattice parameters  $a = 7.5766(1) \text{ \AA}$  and  $c = 8.5260(1) \text{ \AA}$  ( $R_{\text{int}} = 0.0309$ ,  $R1(\text{obs}) = 0.0315$ ). This compound constitutes the second example of barium oxonitridophosphates so far.

### d) $\text{BaP}_8\text{N}_{14}$

The dataset from ID11 enabled straightforward structure solution and refinement. The compound crystallizes in space group  $Amm2$  with lattice parameters  $a = 12.477(3)$  Å,  $b = 8.6619(17)$  Å and  $c = 5.135(1)$  Å ( $R_{int} = 0.0252$ ,  $R1(obs) = 0.0270$ ). It is closely related to an isostructural Sr compound. However, it shows a slightly different structure with only half of the unit-cell volume as a consequence of a different orientation of the  $PN_4$  tetrahedra in both compounds.

**e)  $Lu_{12}Ba_6Si_{36}N_{60}C_3:Eu^{2+}$**

This new carbidonitridosilicate crystallizes in space group  $P3$  with lattice parameters  $a = 16.3153(4)$  Å and  $c = 6.0077(1)$  Å ( $R_{int} = 0.0252$ ,  $R1(obs) = 0.0491$ ). There is some structural disorder that can well be discussed on the basis of the data obtained at ID11. The compound shows green luminescence under irradiation with UV light.

**f)  $Mn_{0.81}Bi_{6.13}Te_{10}$**

In addition to and beyond the original scope of the project, this compound from project CH-5142 was investigated as the experimental conditions were optimal for it. TEM pre-characterization and collecting synchrotron data directly from crystallites on TEM grids is also an excellent approach towards new compounds in the system Bi/Mn/Te. The data from ID11 show that the compound crystallizes in space group  $R\bar{3}m$  with lattice parameters  $a = 4.3700(6)$  Å and  $c = 101.81(2)$  Å ( $R_{int} = 0.0708$ ,  $R1(obs) = 0.0302$ ). Manganese bismuth tellurides are a promising new class of materials possibly combining topological properties of bismuth telluride, magnetism of transition-metal ions and thermoelectric (TE) properties. Corresponding structure-property relations can only be understood by structure elucidation from precise X-ray data. The TE figure of merit of  $Mn_{0.81}Bi_{6.13}Te_{10}$  peaks at  $ZT = 0.28$  at  $325$  °C.

**g)  $Eu_{12}Ta_8O_{12}N_{16}$**

Data collected during this beamtime revealed a new oxide nitride of europium and tantalum with  $Eu^{2+}$  and  $Eu^{3+}$  as shown by Mössbauer spectroscopy.  $Eu_{12}Ta_8(O,N)_{24}$  with (pseudo?)-tetragonal metrics  $a = 5.727(1)$  Å and  $c = 19.809(4)$  Å. Detailed structure refinements are needed to differentiate between orthorhombic or tetragonal symmetry. Once this obstacle is overcome, structure elucidation will be straightforward.

## Outlook

The combination of TEM and synchrotron microfocus diffraction is an ideal approach towards otherwise inaccessible crystal structures of new compounds in microcrystalline, heterogenous samples. After being developed during our past beamtimes at ID11 and optimizing the strategy of re-locating pre-characterized crystallites and centering them in microfocused beams this method can now be applied almost in a routine fashion. A broad range of different structures were elucidated. This will lead to several publications. A next step that would exploit the full potential of this procedure would be the elucidation of reaction mechanisms in solid state chemistry both on micro- to nanometer-sized crystallites. This will avoid the disadvantages of powder diffraction in case of severe reflection overlap present in inhomogeneous samples. After the successful structure determination of two microcrystalline (oxo)nitridophosphates,  $BaP_6N_8O_3$  and  $BaP_8N_{14}$ , we also plan to continue this work at ID11 on other (oxo)nitridophosphates and imidonitridophosphates. These samples will result from quenched high pressure / high temperature reactions and from decomposition reactions of imidophosphates. This will enable us to follow the change of degree of condensation in  $P(O,N)_4$  tetrahedra. In addition, intermediate compounds may be found that would be overlooked otherwise.

## References

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