Towards Rare Earth (*RE*) Thio- and Selenoborates

Jens Hunger, Marija Borna, Susann Leipe, and Rüdiger Kniep

Introduction

Borates represent a well known class of compounds with a wide range of applications. Especially in the fields of optical materials, *RE* oxoborates play a major role. Although a huge number of crystal structures of oxoborates is known, the crystal chemistry of thio- and selenoborates is less investigated. So far, there is only one report on the crystal structure of a *RE* thioborate [1] but none on any selenoborate. The situation is schematically presented in Fig. 1.

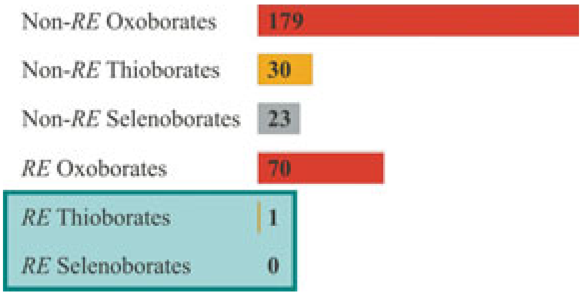

Fig. 1: Numbers of known crystal structures of ternary chalcogenoborates (ICSD 2008-2).

Our interests in the preparation and the crystal chemistry of *RE* compounds were initially focused on *RE* borophosphates [2]. The driving idea behind was the preparation of low-dimensional materials which might have interesting (*RE*-dominated) physical properties. Unfortunately, we did not succeed in these attempts, and we were not even able to prepare any *RE* borophosphate (with the exception of some Sc compounds). However, in our search for new and challenging *RE* containing systems we came across the *RE* thio- and selenoborates which, in fact, are nearly unexplored (see Fig. 1, outlined area).

The synthesis of *RE* thio- and selenoborates from the elements (and/or binary compounds) is fairly problematic because of the high reactivity of the *in situ* formed boron chalcogenides towards most of the common container materials at elevated temperatures. Fused silica tubes are attacked by boron chalcogenides at temperatures above 400 °C (B/Si exchange). Carbon-coated silica tubes, often used for the synthesis of alkali and alkaline earth chalcogenoborates, are disadvantageous with respect to longer reaction times and temperatures above 900 °C. For such kind of reactions the vessels must be made of either boron nitride or glassy carbon. The chalcogenoborates of the heavier chalcogens are sensitive against oxidation and hydrolysis and, hence, they have to be handled in an inert environment. Once the required laboratory equipment was arranged, we started to develop and investigate appropriate routes for the preparation of pure and crystalline *RE* thio- and selenoborates.

Experimental

The optimization of high temperature synthesis routes (beyond the melting points of the *RE* metals) led to the development of specially designed crucibles made of sintered boron nitride (without any binder component) which were enclosed in tantalum ampoules. These ampoules were placed in quartz glass reactors under flowing argon and heated in a tube furnace. Nevertheless, this equipment has still some disadvantages caused by the reaction of the boron chalcogenide gas phase with tantalum at temperatures above 900 °C. However, a stable, protective layer of tantalum sulfide that prevents further reaction between the sample and the ampoule material can be generated by means of excess boron and chalcogen in the reaction mixture. For the time being, the maximum temperature of this equipment is limited to 1150 °C. The development of closed (pressure-resistant) boron nitride lined reactors for even higher operating temperatures is in progress.

In addition, we performed experiments under external pressure by means of a multianvil press as described in [3]. Hexagonal boron nitride is used as the crucible material, while the pressure transmission is realized by MgO octahedra. No indication of a reaction between the container material and the sample was observed, and the reaction products could easily be removed from the crucibles.

Alternatively, we employed the hot isostatic pressing technique within an apparatus originally designed for spark plasma sintering [4]. Sintering dies and punches are made of graphite while different foil materials can be utilized to prevent reactions with the sample.

It is known that *RE* polychalcogenides [5] and nitridoborates [6] can be obtained by metathesis reactions at moderate temperatures. Employing the same method we carried out similar experiments for the preparation of *RE* chalcogenoborates [7] which indeed appears to be a promising route.

The reaction products were characterized by means of X-ray powder diffraction, scanning electron-microscopy, energy-dispersive X-ray spectroscopy (EDXS), chemical analysis (ICP-OES), thermal analysis (DTA), and single crystal X-ray structure analysis.

Based on their melting points we subdivide the *RE* metals into the early ones, La-Eu, with melting points below 1100 °C and the late *RE* elements (Gd-Tm and Lu) with melting points higher than 1300 °C. These two groups require different experimental designs for preparation of chalcogenoborates, and the results will, therefore, be presented separately.

Thioborates of early *RE* metals

The reactions can be performed in standard BN/Ta containers. For evaluation purposes the only known *RE* thioborate, EuB_2S_4 [1], isotypic to SrB_2S_4 [8], was reinvestigated. Starting from the elements, the syntheses were successful, and the purity of the reaction products was higher than the values reported for the samples obtained in carbon-coated quartz glass ampoules. Attempts to grow single crystals by chemical transport reaction with iodine failed so far.

Subsequently, the systems Nd–B–S, Pr–B–S, and Sm–B–S were investigated. At temperatures below the melting points of the respective *RE* metals, only binary phases as the major components and small amounts of unknown phases (depending on the composition, sample loading, and temperature) were formed. At temperatures above 1040 °C and with high sample loadings or by application of external pressure (3 GPa, 900 °C, 30 min) nearly single phase samples of the *RE* thioborates, $Nd[BS_3]$ and $Pr[BS_3]$, were obtained.

Table 1: Crystallographic data of $RE[BS_3]$ (RE = Nd, Pr).

	$Nd[BS_3]$	$Pr[BS_3]$
Color	light green	emerald green
a (Å)	7.48978(3)	7.56051(3)
b (Å)	6.00836(2)	6.00847(2)
c (Å)	8.86197(3)	8.89567(3)
wR_p	0.030 (Co $K\alpha_1$) 0.060 (Cr $K\alpha_1$)	0.061 (Cu $K\alpha_1$)
R_p	0.022 (Co $K\alpha_1$) 0.040 (Cr $K\alpha_1$)	0.040 (Cu $K\alpha_1$)

EDXS confirmed the presence of boron and a *RE*/S molar ratio of 1:3.

The crystal structures of the mentioned RE^{3+} thioborates were solved from X-ray powder diffraction data (Huber G670 Guinier-Camera equipped with a Ge monochromator) by direct space structure solution methods. Subsequently, the Rietveld refinement method was applied (Table 1). The crystal structures were found to be isotypic.

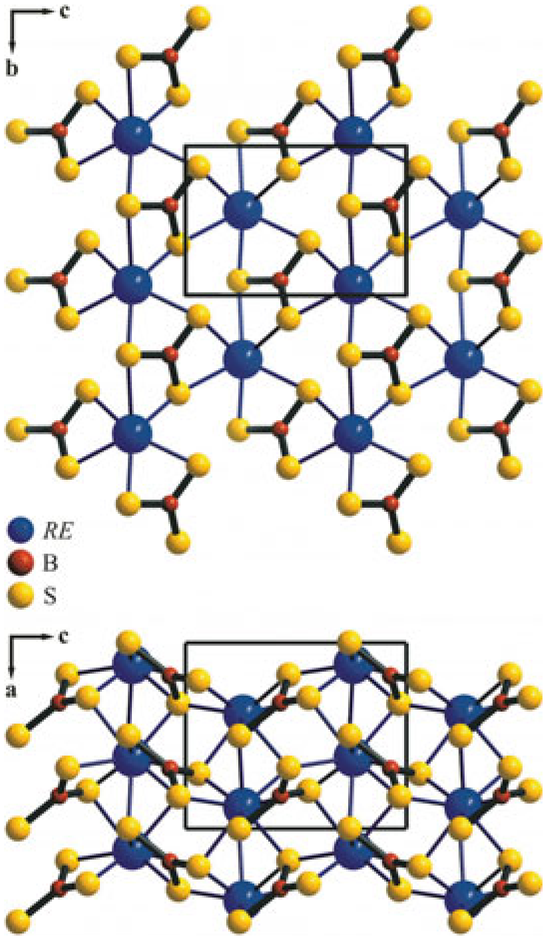

Fig. 2: Crystal structure of $RE[BS_3]$ (RE = Nd, Pr).

In the crystal structure of $RE[BS_3]$ (RE = Nd, Pr) (orthorhombic, $Pna2_1$, No. 33; $Z = 4$) the atoms occupy only general positions (Fig. 2). The sulfur atoms form the vertices of undulated kagome nets. Within these nets every second triangle is occupied by boron and the large hexagons are centered by *RE* cations. The layers are stacked along [100] according to the sequence ABAB.

The *RE* cations are surrounded by 8+1 sulfur species (distances Nd–S: 2.833 Å - 3.051 Å and 3.293 Å; distances Pr–S: 2.833 Å - 3.094 Å and 3.269 Å) which originate from six neighboring thioborate units. Three of these units act as bidentate ligands whereas the remaining three are in a monodentate function. The trigonal planar thioborate units (distances B–S: 1.933 Å- 2.149 Å) are surrounded by *RE* cations, three from the same kagome net (bidentate) and the other three from the two neighboring nets (monodentate). This situation reflects the significant difference to the crystal structure of λ-$Nd[BO_3]$ (Aragonite type) [9] in which the three out-of-net *RE* ions that contribute to the coordination sphere come from only one neighboring layer (Fig. 3).

Attempts to grow single crystals of $RE[BS_3]$ by long-time annealing or by chemical transport reaction were not successful, yet large single crystals of α-Nd_2S_3 with a new three-dimensional superstructure were grown by the transport reactions.

In the corresponding systems *RE*–B–Se and *RE*–B–Te we could so far only obtain binary phases including a new cubic modification of Nd_2Se_3.

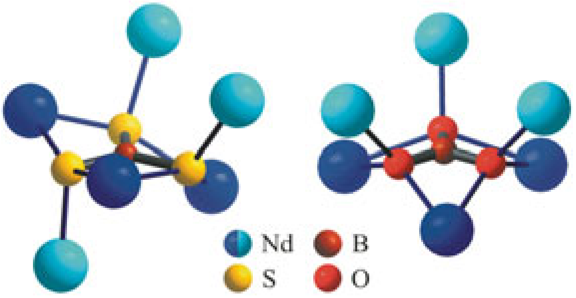

Fig. 3: Comparison of the environments of the $[BS_3]^{3-}$ unit in $RE[BS_3]$ (RE = Nd, Pr) (left) with the coordination of $[BO_3]^{3-}$ in λ-$Nd[BO_3]$ [9] (right). RE cations from the same and the neighboring kagome nets are shown in dark blue and light blue, respectively.

Thioborates of late *RE* metals

Due to the fact that the formation of *RE* chalcogenoborates at autogenous pressure obviously takes place only above the melting point of the *RE* metal, the synthesis of these compounds with the late *RE* metals is rather a difficult task. Nevertheless, by use of our “conventional” preparation method, unknown crystalline phases in the system Lu–B–S were obtained, although not as single phase material. Purification of the samples by means of chemical transport reactions, using iodine as transporting agent, yielded single crystals of ε-Lu_2S_3 with a hitherto unknown three-dimensional superstructure. In an effort to increase purity and crystallinity of these samples, reactions under hot isostatic pressure as well as high pressure syntheses were performed. A series of high-temperature high-pressure experiments was conducted in the system Lu–B–S ($T = 1400$ °C, $p = 3$ GPa, 4.5 GPa and 6 GPa). As a first result, a new ternary phase was obtained. The reaction product obtained at 3 GPa (5 h) was suitable for solution and refinement of the crystal structure of $Lu_6B_{3.33}S_{14}$ (yellow) from X-ray powder diffraction data (STOE StadiP-MP) (Fig. 4).

$Lu_6B_{3.33}S_{14}$ (hexagonal, space group $P6_3$, No. 173; $a = 9.21257(1)$ Å, $c = 5.88680(2)$ Å; $Z = 1$) adopts the $Ce_6Al_{3.33}S_{14}$ structure type [10] (Fig. 5). The boron atoms occupy two different sites with tetrahedral and trigonal planar coordination by sulfur. Isolated $[BS_4]^{5-}$ tetrahedra (distances B–S: 1.946 Å and 1.857 Å), all pointing in the [001] direction, are stacked along the three-fold axis.

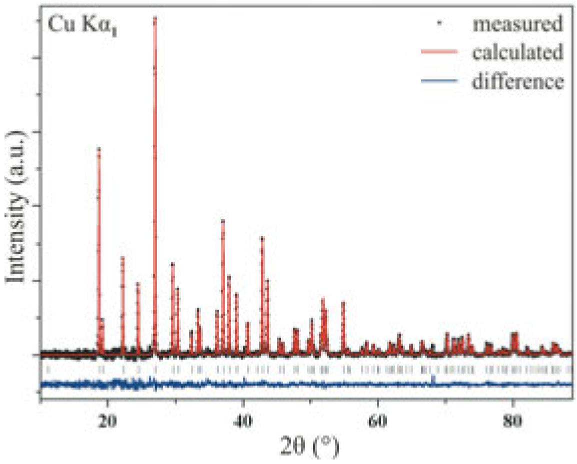

Fig. 4: Rietveld refinement of $Lu_6B_{3.33}S_{14}$ ($wR_p = 0.029$, $R_p = 0.019$).

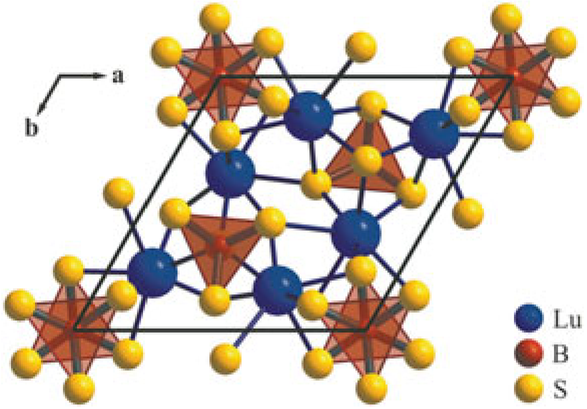

Fig. 5: Crystal structure of $Lu_6B_{3.33}S_{14}$, viewed along [001].

The $[BS_3]^{3-}$ triangles (distance B–S: 1.883 Å) in which boron atoms are slightly shifted out of the trigonal plane propagate along the 6_3 axis.

The sulfur ligands are coordinated by three *RE* cations. Altogether, the S-positions of the $[BS_3]^{3-}$ units and those of the $[BS_4]^{5-}$ tetrahedra that form a triangle parallel to (001), adopt the pattern of the oxygen atoms in the crystal structure of λ-$Nd[BO_3]$. On the other hand, the sulfur atoms located on the three-fold axis act as monodentate ligand towards the three neighboring *RE* cations.

Lutetium is surrounded by two $[BS_3]^{3-}$ and three $[BS_4]^{5-}$ units resulting in an overall 6+1 coordination by sulfur (distances Lu–S: 2.624 Å -2.751 Å and 2.998 Å) thereby forming a mono-capped trigonal prism.

In contrast to the $Ce_6Al_{3.33}S_{14}$ structure, in which vacancies are located on the octahedrally coordinated aluminum site, the vacancies in $Lu_6B_{3.33}S_{14}$ occur most likely on the tetrahedrally coordinated boron site. Therefore, the chemical formula can be written as $Lu_3[BS_3][B_{2/3}S_4]$.

EDXS investigations confirmed the presence of boron and a Lu/S molar ratio of 3:7.

Metathesis reactions

The first attempts with metathesis reactions showed that reactions with the container material take place yielding in new quaternary sulfides, such as $RE_9AlSi_3S_{21}$. Nevertheless, similar experiments involving metathesis reactions starting from different alkali chalcogenoborates, namely Li thio- and selenoborates [11-14] and *RE* chlorides at maximum temperatures of 800 °C, followed by vacuum sublimation of LiCl will be continued. The reaction products of this preparation route have to be investigated in more detail and further optimization of the reaction conditions is required.

Conclusion

After optimization of various preparation routes we succeeded in the synthesis of the RE^{3+} thioborates, $Nd[BS_3]$ and $Pr[BS_3]$, as well as the more intricate thioborate $Lu_6B_{3.33}S_{14}$. Their crystal structures were solved and refined from X-ray powder diffraction data. Metathesis reactions as well as reactions in hot isostatic pressing equipment appear to be promising routes for the preparation of other chalcogenoborates. Moreover, these reactions may open the way for the preparation of *RE* selenoborates after optimization of the reaction conditions.

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