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Synthesis and crystal structure of the isotypic rare earth thioborates Ce[BS₃], Pr[BS₃], and Nd[BS₃]

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ABSTRACT

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Keywords: Rare earth compounds Thioborates Preparation Crystal structure The orthothioborates Ce[BS₃], Pr[BS₃] and Nd[BS₃] were prepared from mixtures of the rare earth (*RE*) metals together with amorphous boron and sulfur summing up to the compositions CeB₃S₆, PrB₅S₉ and NdB₃S₆. The following preparation routes were used: solid state reactions with maximum temperatures of 1323 K and high-pressure high-temperature syntheses at 1173 K and 3 GPa. Pr[BS₃] and Nd[BS₃] were also obtained from rare earth chlorides *RE*Cl₃ and sodium thioborate Na₂B₂S₅ by metathesis type reactions at maximum temperatures of 1073 K. The crystal structure of the title compounds was determined from X-ray powder diffraction data. The thioborates are isotypic and crystallize in the orthorhombic spacegroup Pna2₁ (No. 33; *Z* = 4; Ce: *a* = 7.60738(6) Å, *b* = 6.01720(4) Å, *c* = 8.93016(6) Å; Pr: *a* = 7.56223(4) Å, *b* = 6.00876(2) Å, *c* = 8.89747(4) Å; Nd: *a* = 7.49180(3) Å, *b* = 6.00823(2) Å, *c* = 8.86197(3) Å). The crystal structures contain isolated [BS₃]³⁻ groups with boron in trigonal-planar coordination. The sulfur atoms form the vertices of undulated kagome nets, which are stacked along [100] according to the sequence ABAB. Within these nets every second triangle is occupied by boron and the large hexagons are centered by rare earth ions, which are surrounded by overall nine sulfur species.

1. Introduction

Borates represent a well known class of compounds with a wide range of applications. Especially in the field of optical materials, *RE* oxoborates play a major role. Although a huge number of crystal structures of oxoborates is known, the crystal chemistry of thioborates is less investigated. Thus, we started to prepare thioborates of the rare earth metals, where the driving idea behind was the preparation of low-dimensional materials which might have interesting (*RE*-dominated) physical properties. So far, there is only one report on a crystal structure of a *RE* thioborate (Eu[B₂S₄] [1]). Obviously, this is mainly due to the lack of improved preparation techniques for thioborate syntheses. Therefore, we started to develop and optimize useful preparation routes.

Binary boron sulfides as well as ternary and quaternary thioborates contain boron in trigonal-planar and/or tetrahedral coordination, forming various types of chalcogenoborate complexes [2]. Small, highly charged ions such as $[BS_3]^{3-}$ [3–5], $[B_2S_4]^{2-}$ [6], $[B_2S_5]^{2^-}$ [7], and $[B_3S_6]^{3-}$ [5,8–10] are typical for systems with trigonal-planar coordinated boron. Structures with boron in tetrahedral coordination tend to form larger complex anions [11–14].

Here, we report on different preparation routes and describe the crystal structures of $RE[BS_3]$ (RE = Ce, Pr, Nd) as first examples of ternary thioborates containing trivalent cations. 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. Silica glass tubes are attacked by boron chalcogenides at temperatures above 700 K (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 1200 K. 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 moisture and, hence, they have to be handled in an inert environment.

It is well known that *RE* polychalcogenides [15] and nitridoborates [16] can be obtained by metathesis reactions at moderate temperatures. Employing this method we carried out similar experiments for the preparation of *RE* thioborates [17] which indeed appeared to be a promising route.

2. Materials and methods

Our attempts to optimize the high-temperature routes (beyond the melting points of the *RE* metals) led to the

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development of specially designed crucibles made of sintered boron nitride (without any binder component) 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 1200 K. However, a stable, protective layer of tantalum sulfide that prevents further reaction of the sample with 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 1450 K. The development of closed (pressure-resistant) boron nitride lined reactors operating at even higher temperatures is in progress.

For evaluation purposes we reinvestigated the only known RE thioborate, EuB_2S_4 [1], which is an isotype of SrB_2S_4 [18]. Starting from the elements, the syntheses were successful, and the purity of the reaction products was higher than the values reported for the samples originally prepared in carbon-coated quartz glass ampoules. Attempts to grow single crystals by chemical transport reaction with iodine failed so far. Subsequently, the ternary systems Ce-B-S, Nd-B-S and Pr-B-S were investigated. At temperatures below the melting points of the respective RE metals, only binary phases are formed as the major components together with small amounts of unknown phases (depending on the composition, sample loading, and temperature). At temperatures above 1323 K and with high sample loadings nearly single phase products of Pr[BS₃] and Nd[BS₃] as well as Ce[BS₃] contaminated with small amounts ($\approx 8\%$) of CeS₂, were obtained. Furthermore, Pr[BS₃] and Nd[BS₃] were prepared by application of external pressure (3 GPa, 1173 K, 30 min) by means of a multianvil press as described in [19] and by metathesis type reactions, respectively.

The reaction products were characterized by means of X-ray powder diffraction, scanning electron-microscopy and energydispersive X-ray spectroscopy (EDXS).

2.1. Materials

For the preparations from the elements neodymium (powder, ChemPur, 99.9%), praseodymium (powder, ChemPur, 99.9%), cerium (chips, ChemPur, 99.9%) and amorphous boron (powder, ABCR, 99%) were used as purchased without further purification. Sulfur (Alfa Aesar, 99.9995%) was sublimed under vacuum to reduce oxygen contamination below 1%. Na₂B₂S₅, used for metathesis reactions, was prepared from Na₂S (Strem, 95%), amorphous boron and sulfur according to literature data [7]. NdCl₃ (Aldrich, 99.99%) and PrCl₃ (Aldrich, 99.99%) were used without any further purification. All educts were checked by means of elemental analysis using a LECO RH 404 analyzer (H), LECO TC 436 DR/5 analyzer (N/O), LECO C-200 CHLH analyzer (C) and a simultanious inductively coupled plasma-optical emission (ICP-OES) Echelle spectrometer (other elements), respectively.

2.2. Syntheses

2.2.1. High-temperature routes

Mixtures of rare earth metal powders, amorphous boron and sulfur were ground, cold pressed and again ground. Due to the side reaction of B₂S₃ with tantalum some excess boron and sulfur were used. By this, the educts sum up to the total compositions CeB₃S₆, PrB₅S₉ and NdB₃S₆, respectively. Molar ratios corresponding to the compositions CeBS₃, CeB₂S₅, CeB₄S₈, CeB₅S₉, PrBS₃, PrB₃S₆, NdBS₃ and NdB₅S₉ did not yield sufficiently pure reaction products. The resulting powders were filled in boron nitride crucibles (diameter 16/10 mm, height 50 mm), which were deposited in sealed tantalum ampoules (diameter 18 mm) under ambient argon pressure. The complete reaction containers were deposited in quartz reactors with connections to argon supply and relief pressure valve and tempered using an one-zone vertical tube furnace. The reactions were carried out under constant argon flow by applying the following temperature program: $298 \text{ K} \xrightarrow{5 \text{ h}} 673 \text{ K}(5 \text{ h}) \xrightarrow{10 \text{ h}} 1023 \text{ K}(10 \text{ h}) \xrightarrow{20 \text{ h}} 1323 \text{ K}(300 \text{ h}) \xrightarrow{150 \text{ h}}$

 $473 \text{ K} \xrightarrow{5 \text{ h}} 298 \text{ K}.$

2.2.2. High-pressure high-temperature routes

Pressure transmission was realized by octahedra made of MgO with an edge length of 18 mm. Reaction temperatures were adjusted by resistance heating using graphite tubes. Pressure and temperature calibration was performed prior to the experiments by *in situ* monitoring of the resistance changes of elemental bismuth and by performing runs using a thermocouple. Hexagonal boron nitride was used as the crucible material. The syntheses were accomplished at 1173 K and 3 GPa for 30 min. No indications of reactions between the container material and the sample were observed, and the reaction products could easily be removed from the crucibles.

2.2.3. Metathesis reactions

Our first attempts in running metathesis reactions in carbon crucibles inserted in silica ampoules revealed that significant reactions between the container material and gaseous B-S species take place yielding in quaternary sulfides, such as $RE_9AlSi_3S_{21}$. Therefore, tantalum was used instead of silica. $RE[BS_3]$ was obtained from mixtures of Na₂B₂S₅ [7] and $RECl_3$ in the molar ratio 3:2. The reactions were carried out in an one-zone vertical tube furnace by applying the following temperature program: 298 K $\xrightarrow{8 h}$ 1073 K(16 h) $\xrightarrow{60 h}$ 298 K. Subsequent separation of the reaction products ($RE[BS_3]$ and NaCl) by sublimation at

Table 1

Crystallographic data of the isotypic phases $RE[BS_3]$ (RE = Ce, Pr, Nd). See also Table S1 in the supporting information.

	Ce[BS ₃]	Pr[BS ₃]	Nd[BS ₃]
Color Space group, Z Formula mass [g mol ⁻¹]	Yellow-green Pna2 ₁ , 4 247.11	Emerald green Pna2 ₁ , 4 247.90	Light green Pna2 ₁ , 4 251.23
Radiation, λ [Å]	Cu Kα ₁ , 1.540562	Cu Kα ₁ , 1.540562	Cu Kα ₁ , 1.540562
Temperature [K]	298	298	298
Diffractometer	G670	G670	G670
a [Å]	7.60873(4)	7.55960(5)	7.48692(3)
b [Å]	6.01685(2)	6.00673(3)	6.00551(2)
c [Å]	8.93188(4)	8.89435(5)	8.85815(3)
Cell volume [Å ³]	408.906(3)	403.879(4)	398.287(2)
Density [g cm ⁻³]	4.014	4.077	4.190
Weighted profile <i>R</i> - factor <i>R</i> _{wp}	0.023	0.044	0.022
Profile R-factor Rp	0.015	0.028	0.016
Structure R-factor R _F	0.051	0.098	0.056
Expected R-factor R_{exp}	0.019	0.017	0.018

Rietveld refinement was used to minimize $\sum w_i(I_{o,i}-I_{c,i})^2$ where $I_{o,i}$ and $I_{c,i}$ are the observed and calculated powder diffraction intensities for the *i* th point, respectively. Weights, w_i , are $1/I_{o,i}$. Weighted and unweighted profile *R*-factors are defined as $R_{wp} = \sqrt{\sum w_i(I_{o,i}-I_{c,i})^2 / \sum w_i(I_{o,i})^2}$ and $R_p = \sum |(I_{o,i}-I_{c,i})| / \sum I_{o,i}$. The structure factor R_F is defined as $R_F = \sum (F_o-F_c)^2 / \sum (F_o)^2$. The expected *R*-factor (the statistically best possible value for R_{wp}) is defined as $R_{exp} = \sqrt{N-P/\sum w_i(I_{o,i})^2}$ where *N* is the number of observed powder diffraction data points and *P* is the number of refined parameters.

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