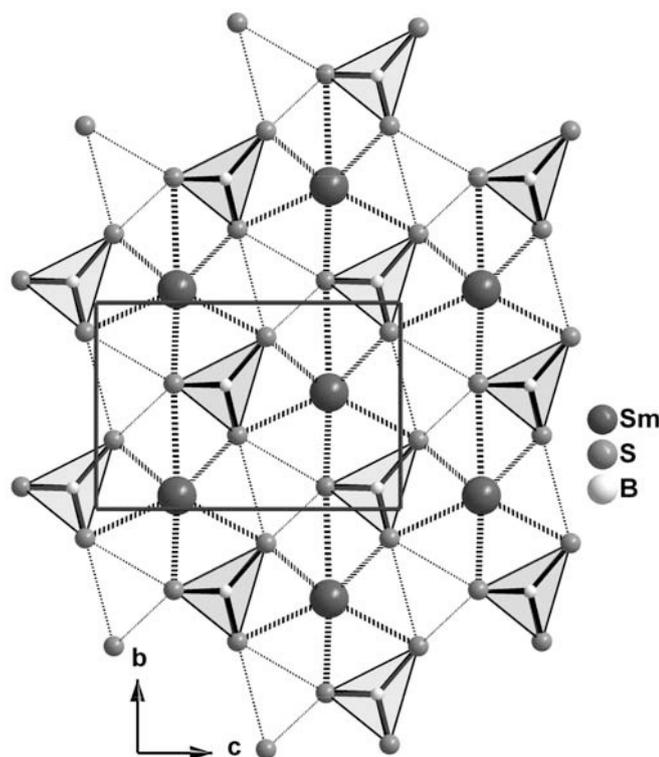


Crystal structure of monosamarium trithioborate, Sm[BS₃]

Marija Borna, Jens Hunger and Rüdiger Kniep*

Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, 01187 Dresden, Germany

Received February 15, 2010, accepted and available on-line April 19, 2010; CSD nos. 710041



Abstract

BS₃Sm, orthorhombic, *Pna*2₁ (no. 33), $a = 7.3657(5)$ Å, $b = 6.0272(2)$ Å, $c = 8.8004(6)$ Å, $V = 390.69$ Å³, $Z = 4$, $R(F^2) = 0.068$, $R(P) = 0.013$, $T = 295$ K.

Source of material

Sm[BS₃] was prepared by using a high-temperature high-pressure route. Molar ratios of 1 : 3 : 6 of samarium (powder, ChemPur, 99.9 %), amorphous boron (ABCR, 99 %) and sulfur (Alfa Aesar, 99.9995 %, sublimed under vacuum to reduce contamination by oxygen below 1 %) were used. Molar ratios corresponding to the chemical composition of the title compound did not yield sufficiently pure materials. The educts were ground and filled into the assembly of the octahedral high pressure setup, under argon atmosphere of a glove box. Hexagonal boron nitride was used as the crucible material. High pressure conditions were achieved by using a hydraulic uniaxial press [1]. Force redistribution was accomplished by a Walker-type module and MgO octahedra with an edge length of 18 mm [2]. Elevated temperatures were realized by resistive heating of graphite tubes enclosing the sample crucible. For the synthesis of Sm[BS₃], the assembly was heated to 1673 K and compressed to 3 GPa for 5 h. After the pressure and heating cycle, the arrangement was instan-

taneously removed and transferred into a glove box where the sample was isolated from the crucible. No indications of a reaction between the sample and the crucible material were observed. The air- and humidity-sensitive compound Sm[BS₃] was obtained as a red-brown polycrystalline material.

Experimental details

X-ray powder diffraction data were collected on a STOE StadiP-MP diffractometer in Debye-Scherrer geometry. The GSAS software package [3] was used for the Rietveld refinements. The unit cell parameters at room temperature were determined from X-ray powder diffraction data (Cu $K\alpha_1$), using LaB₆ ($a = 4.15692(1)$ Å) as internal standard, and refined by least squares refinements using the WinCSD program [4]. The position of the boron atom was restrained to be near the centre of gravity of the sulfur atoms of the [BS₃]³⁻ unit. The isotropic displacement parameters of the sulfur atoms were constrained to be equal and the corresponding parameter of the boron site was constrained to be equal to that of the attached sulfur atoms.

Discussion

The new RE thioborate Sm[BS₃], obtained as a product of the high-pressure high-temperature experiments, is an isotype of the RE[BS₃] series ($RE = Ce, Pr, Nd$) [5,6]. The crystal structure was refined from X-ray powder diffraction data using the Rietveld refinement method [7]. The crystal structure of Sm[BS₃] is characterized by corrugated kagome nets formed by sulfur atoms, with the boron atoms occupying every second triangle, while Sm cations center the large hexagons. The corrugated nets are stacked along [100] according to the sequence ABAB. The coordination sphere of Sm is formed by nine sulfur species originating from six neighboring thioborate units. Three of the [BS₃]³⁻ units act as bidentate ligands, while the other three are in monodentate function. The Sm—S bond distances range from 2.81(2) Å to 3.385(8) Å. The planar thioborate unit in Sm[BS₃] is similar to those found in related compounds of alkali and alkaline earth metals [8], but more distorted. As reasons for the distortion the higher charge of the cations and the decrease of the cation/anion ratio can be assumed. Bond distances (B—S) in the planar thioborate unit are 1.85(2) Å, 1.85(2) Å and 1.86(2) Å and the angles (S—B—S) are 114.3(9)°, 121.1(8)° and 124(1)°. The thioborate units are surrounded by six Sm cations, three from the same kagome net and three from the two neighboring nets.

* Correspondence author (e-mail: kniep@cphys.mpg.de)

Table 1. Data collection and handling.

Powder:	red-brown, size < 40 μm
Wavelength:	Cu $K_{\alpha 1}$ radiation (1.54056 \AA)
μ :	125.51 cm^{-1}
Diffractometer, scan mode:	Stoe STADIP-MP, Debye-Scherrer
$2\theta_{\text{max}}$, stepwidth:	109.98°, 0.02
$N(\text{points})_{\text{measured}}$:	5000
$N(hkl)_{\text{measured}}$:	265
$N(\text{parameter})_{\text{refined}}$:	19
Programs:	GSAS [3], WinCSD [4], DIAMOND [9]

Acknowledgments. The authors would like to thank S. Leipe for supporting high-pressure syntheses and R. Cardoso-Gil for the powder data collection.

References

1. Wosylus, A.; Prots Yu.; Burkhardt, U.; Schnelle, W.; Schwarz, U.: High-pressure synthesis of the electron-excess compound CaSi₆. *Sci. Techno. Adv. Mater.* **8** (2007) 383-388.
2. Walker, D.; Carpenter, M. A.; Hitch, C. M.: Some simplifications to multi-anvil devices for high pressure experiments. *Am. Mineral.* **75** (1990) 1020-1028.
3. Larson, A.; Dreele, R. V.: Los Alamos National Library Report LAUR, 86-748.
4. Akselrud, L. G.; Zavalij, P. Yu.; Grin, Yu.; Pecharsky, V. K.; Baumgartner, B.; Wölfel, E.: Use of the CSD program package for structure determination from powder data. *Mater. Sci. Forum* **133-136** (1993) 335-340.
5. Hunger, J.; Borna, M.; Kniep, R.: Synthesis and crystal structure of the isotopic rare earth thioborates Ce[BS₃], Pr[BS₃], and Nd[BS₃]. *J. Solid State Chem.* **183** (2010) 702-706.
6. Hunger, J.; Borna, M.; Kniep, R.: Single crystal structure determination of monopraseodymium trithioborate, Pr[BS₃]. *Z. Kristallogr. NCS* **225** (2010) 217-218.
7. Rietveld, H. M.: A profile refinement method for nuclear and magnetic structures. *J. Appl. Crystallogr.* **2** (1969) 65-71.
8. Conrad, O.; Jansen, C.; Krebs, B.: Boron-Sulfur and Boron-Selenium Compounds - From Unique Molecular Structural Principles to Novel Polymeric Materials. *Angew. Chem., Int. Ed.* **37** (1998) 3208-3218.
9. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 3.2c. Crystal Impact, Bonn, Germany 1997-2009.

Table 2. Atomic coordinates and displacement parameters (in \AA^2).

Atom	Site	x	y	z	U_{iso}
Sm(1)	4a	0.8834(2)	0.5643(3)	0.765(2)	0.0015(3)
S(1)	4a	0.9992(8)	0.893(1)	0.255(1)	0.005(1)
S(2)	4a	0.177(1)	0.666(2)	0.5582(9)	0.005
S(3)	4a	0.295(1)	0.142(2)	0.4637(8)	0.005
B(1)	4a	0.352(3)	0.401(3)	0.924(1)	0.005