Crystal structure of monoterbium trithioborate, $Tb[BS_3]$

Marija Borna, Jens Hunger and Rüdiger Kniep*

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

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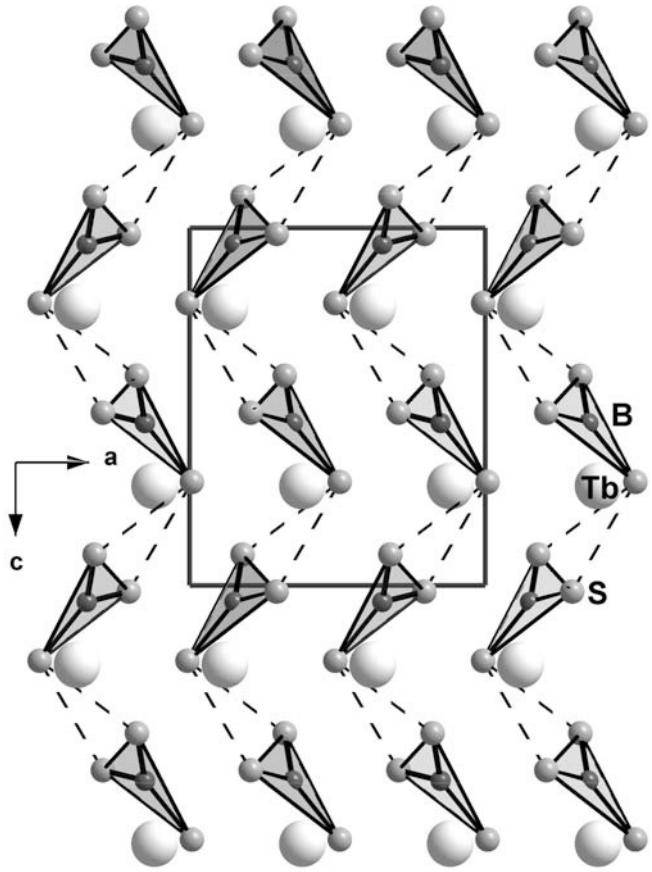

Abstract

BS_3Tb, orthorhombic, $Pna2_1$ (no. 33), a = 7.2053(9) Å, b = 6.0784(9) Å, c = 8.719(1) Å, V = 381.88 Å^3, Z = 4, $R(F^2)$ = 0.043, $R(P)$ = 0.015, T = 295 K.

Source of material

$Tb[BS_3]$ was prepared by high-pressure high-temperature synthesis starting from 1 : 3 : 6 molar ratios of terbium (powder, ChemPur, 99.9 %), amorphous boron (ABCR, 99 %) and sulfur (Alfa Aesar, 99.9995 %, sublimed under vacuum to reduce contamination by oxygen below 1 %). 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 $Tb[BS_3]$, the assembly was heated to 1673 K and compressed to 3 GPa for 5h. After the pressure and heating cycle, the arrangement was instantaneously 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 $Tb[BS_3]$ was obtained as a yellow polycrystalline material.

Experimental details

X-ray powder diffraction data were collected on a STOE StadiP-MP diffractometer in Debye-Scherrer setup. 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 LaB_6 (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 near the centre of gravity of the sulfur atoms of the $[BS_3]^{3-}$ unit. The isotropic displacement parameters of the sulfur and boron atoms were constrained to be equal.

Discussion

The new RE thioborate $Tb[BS_3]$, obtained by a high-pressure high-temperature route, is an isotype of $RE[BS_3]$ series (RE = Ce, Pr, Nd, Sm) [5-7]. The X-ray powder diffraction data were used for the refinement of the crystal structure by application of the Rietveld refinement method [8]. In the crystal structure of $Tb[BS_3]$, the atoms form layers which are stacked along [100] according to the sequence *ABAB*. Tb cations center the large hexagons of corrugated kagome nets formed by the sulfur atoms, while boron atoms occupy every second triangle. The coordination sphere of Tb is generated by nine sulfur species (Tb—S: 2.783(5) Å to 3.547(3) Å) originating from six neighboring thioborate units. Three units act as bidentate ligands, while the other three act as monodentate ones. The thioborate units are surrounded by six Tb cations, three from the same kagome net and three from the two neighboring nets. The planar thioborate unit in $Tb[BS_3]$ is similar to those found in related compounds of alkali and alkaline earth metals [9]. Bond distances (B—S) in the planar thioborate units are 1.837(5) Å, 1.838(6) Å, 1.839(5) Å and the angles (S–B–S) are 120.5(3)°, 118.9(3)° and 120.4(3)°, respectively.

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

Table 1. Data collection and handling.

Powder:	yellow, size < 40 μm
Wavelength:	Cu $K_{\alpha 1}$ radiation (1.54056 Å)
μ:	104.55 cm^{-1}
Diffractometer, scan mode:	Stoe STADIP-MP, Debye-Scherrer
$2\theta_{max}$, stepwidth:	109.98°, 0.02
$N(points)_{measured}$:	5000
$N(hkl)_{measured}$:	257
$N(parameter)_{refined}$:	19
Programs:	GSAS [3], WinCSD [4], DIAMOND [10]

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

Atom	Site	x	y	z	U_{iso}
Tb(1)	4*a*	0.11887(9)	0.4423(1)	0.2228(7)	0.0137(2)
S(1)	4*a*	0.5072(3)	0.3782(4)	0.7108(4)	0.0123(5)
S(2)	4*a*	0.2051(5)	0.6448(6)	0.5169(3)	0.0123
S(3)	4*a*	0.3211(6)	0.1641(5)	0.4137(3)	0.0123
B(1)	4*a*	0.3478(7)	0.3972(8)	0.5467(4)	0.0123

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