Refinement of the crystal structure of praseodymium trithioborate, $Pr[BS_3]$, *single crystal data*

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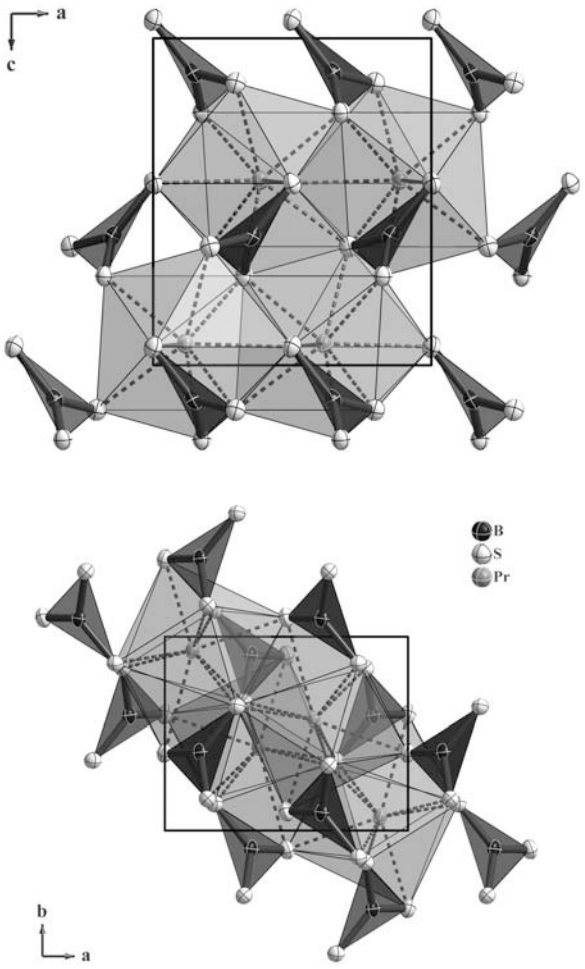

Abstract

$BPrS_3$, orthorhombic, $Pna2_1$ (no. 33), a = 7.5434(8) Å, b = 6.0130(5) Å, c = 8.886(1) Å, V = 403.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.025, $wR_{ref}(F^2)$ = 0.060, T = 295 K.

Source of material

A mixture of 779.01 mg (5.528 mmol) praseodymium powder (ChemPur, 99.9 %), 298.90 mg (27.648 mmol) amorphous boron (powder, ABCR, 99 %) and 1595.66 mg (49.762 mmol) sulfur (Alfa Aesar, 99.9995 %, sublimed under vacuum to reduce oxygen contamination below 1 %) was ground, cold pressed, again ground and filled in a boron nitride crucible (diameter 16/10 mm, height 50 mm). The crucible was deposited in a sealed tantalum ampoule (diameter 18 mm, height 100 mm) under ambient argon pressure. Due to the side reaction of B_2S_3 with tantalum some excess boron and sulfur were used. By this, the educts sum up to the total chemical composition PrB_5S_9. The complete reaction container was deposited in a quartz glass reactor with connections to argon supply and a relief pressure valve. The reaction was performed by using a vertical tube furnace. The following temperature program was applied under constant argon flow: 298 K → 4 h → 673 K (5 h) → 10 h → 1023 K (10 h) → 20 h → 1323 K (300 h) → 500 h → 473 K → 10 h → 298 K. Green needle-shaped crystals up to 3mm in length were grown on the top of the surface of the single-phase product pellet. For single crystal structure determinations the crystals were cut into prismatic pieces.

Discussion

During our investigations in the systems *RE*-B-S (*RE* = Ce, Pr, Nd) we prepared the isotypic series of compounds *RE*$[BS_3]$ (*RE* = Ce, Pr, Nd) [1]. The crystal structures were determined from X-ray powder diffraction data. However, because of the data limitations the boron atoms could not be refined without restraints. Furthermore, all displacement parameters had to be treated isotropically and the absolute configuration could not be determined. Here, we report an improved refinement of the crystal structure of $Pr[BS_3]$ using single crystal diffraction data with anisotropic displacement parameters for all the atom sites (including boron). As to be expected, the result of the Rietveld refinement is generally confirmed.

In the crystal structure of $Pr[BS_3]$ the sulfur atoms form the vertices of corrugated kagome nets. Within these nets every second triangle is occupied by boron and the large hexagons are centered by Pr cations. The layers are stacked along [100] according to the sequence ABAB. The Pr cations are surrounded by nine sulfur species originating from six neighboring thioborate units and forming a heavily distorted tricapped trigonal prism. The Pr-S distances range from 2.872(2) Å to 3.294(1) Å. The bond lengths and angles within the thioborate units (distances B—S: 1.800(7) Å, 1.828(6) Å and 1.830(6) Å; angles S–B–S: 116.0(4)°, 120.7(3)° and 122.8(3)°) are more closer related to the - soft restrained - values obtained from the Rietveld refinements. The observation of the more distorted $[BS_3]^{3-}$ groups in comparison with related compounds of alkali and alkaline earth metals was assumed to be caused by the higher charge of the cations and the decrease of the cation/anion ratio and is herewith confirmed. Boron takes a position slightly shifted out of the plane defined by the three sulfur atoms (0.081(6) Å).

In conclusion, it can be stated that long-time annealing at temperatures above the melting point of the *RE* metal in combination with small cooling rates is an appropriate method to grow single

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crystals of *RE*[BS_3]. At the same time, Rietveld refinements are proven to be a feasible approach for crystal structure determinations of ternary phases in the systems *RE*-B-S.

Table 1. Data collection and handling.

Crystal:	green prism, size 0.05 × 0.06 × 0.12 mm
Wavelength:	Mo K_α radiation (0.71074 Å)
μ:	134.00 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7 with Saturn724, φ
$2\theta_{max}$:	66.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3068, 1410
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1365
$N(param)_{refined}$:	47
Programs:	SHELXS-97 [2], SHELXL-97 [2], DIAMOND [3]

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

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pr(1)	4*a*	0.88556(3)	0.06989(3)	0.4335(1)	0.0115(1)	0.0155(1)	0.0156(1)	0.00123(6)	0.0004(2)	0.0006(1)
B(1)	4*a*	0.8551(8)	–0.4042(9)	0.6045(8)	0.012(2)	0.017(2)	0.016(3)	–0.000(2)	–0.003(2)	–0.000(2)
S(1)	4*a*	1.0002(2)	–0.4018(2)	0.4437(3)	0.0132(4)	0.0199(4)	0.0191(6)	0.0025(3)	0.0017(7)	–0.0012(6)
S(2)	4*a*	1.2039(2)	0.1374(2)	0.6370(2)	0.0152(6)	0.0140(5)	0.0180(7)	0.0004(4)	0.0008(5)	0.0013(5)
S(3)	4*a*	0.8255(2)	–0.1631(2)	0.7272(2)	0.0138(6)	0.0139(4)	0.0168(7)	–0.0009(4)	–0.0003(5)	–0.0004(4)

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