

Structure determination of the novel borate oxide, $\text{SrBi}_2\text{OB}_4\text{O}_9$

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The $\text{SrBi}_2\text{B}_4\text{O}_{10}$ compound was discovered in 2006 during exploratory syntheses of novel bismuth borates for potential applications as nonlinear optical materials. The compound melts incongruently and single crystal growth has not been attempted. Instead, it was decided to attempt an ab-initio structure determination using a combination of high-resolution X-ray and neutron powder diffraction data. The X-ray data were collected on a Panalytical Expert diffractometer at McMaster University and the neutron data were collected on the C2 diffractometer at Chalk River.

A 10-gram powder sample of $\text{SrBi}_2\text{B}_4\text{O}_{10}$ was synthesized by solid-state reaction using a stoichiometric mixture of high-purity SrCO_3 , Bi_2O_3 and ^{11}B -enriched (99.3%) $\text{B}(\text{OH})_3$ powders heated to 650°C over several days with intermediate mixings. The neutron diffraction patterns were measured at room temperature in 0.05° steps at two different wavelengths of 2.37150 and 1.33063 Å. The availability of the longer wavelength was found advantageous during the structure solution step by minimizing the strong peak overlap associated with the unit-cell geometry ($a = 6.86562$ Å, $b = 9.79777$ Å, $c = 6.81478$ Å, $\alpha = 109.126^\circ$, $\beta = 101.89^\circ$, $\gamma = 96.14^\circ$) (Fig. 1).

The direct-space global optimization program FOX [1,2] was used to solve the structure of $\text{SrBi}_2\text{B}_4\text{O}_{10}$ ab initio from the combined X-ray and neutron diffraction data. As expected, the X-ray pattern was insensitive to the B and O atoms in the presence of the heavy Bi and Sr atoms, and the neutron data were essential for a successful structure solution. Initially, several structural models with different combinations of BO_3 and BO_4 groups were found to provide similar fits to the experimental data. The determination of the correct model was made possible by collecting ^{11}B NMR spectra at McMaster University that indicated a 3:1 ratio of BO_3 to BO_4 groups in the structure. FOX then established the presence of one Sr site, two Bi sites, one isolated $\text{B}_4\text{O}_9^{6-}$ borate anion and one additional O^{2-} oxide anion to yield a borate oxide composition of $\text{SrBi}_2\text{B}_4\text{O}_{10}$ with two formula units per unit-cell (P-1 space group). The crystal structure was subsequently refined with the Rietveld program PROF (Table 1) [3]. The large displacement parameters for the S, Bi and O5 atoms suggest some residual disorder or a distortion to P1 symmetry for the crystal structure. This point remains to be elucidated.

The structure of $\text{SrBi}_2\text{B}_4\text{O}_{10}$, or $\text{SrBi}_2\text{OB}_4\text{O}_9$, consist of $\text{SrB}_4\text{O}_9^{4-}$ and Bi_2O^{4+} layers alternating in the [010] direction (Fig. 2). The asymmetric coordination of the Bi atoms and the short Bi-O bonds (2.10 - 2.28 Å) are typical of

the Bi^{3+} ion with a stereoactive lone pair, as also observed in BaBiBO_4 [4] and $\text{SrBi}_2\text{B}_2\text{O}_7$ [5]. The presence of borate and oxide anions distinguishes the structure of $\text{SrBi}_2\text{OB}_4\text{O}_9$ from that of $\text{BaBi}_2\text{B}_4\text{O}_{10}$ which only contains the $\text{B}_4\text{O}_{10}^{8-}$ borate anion⁶.

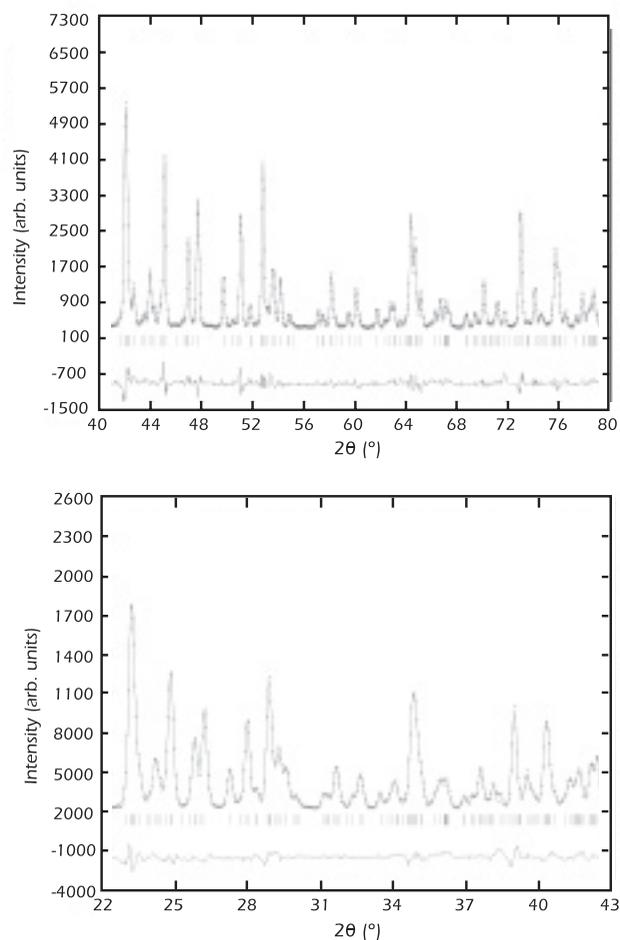


Fig. 1 Selected regions of final Rietveld plots for the structure refinement of $\text{SrBi}_2\text{OB}_4\text{O}_9$, illustrating the much improved peak resolution at higher neutron wavelength, 2.3715 Å (top) vs. 1.3306 Å (bottom).

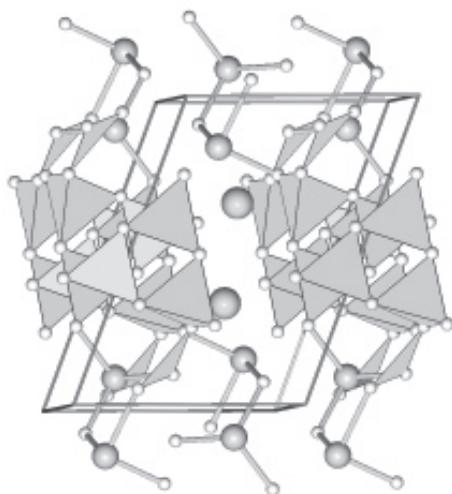


Fig. 2 Drawing of the $\text{SrBi}_2\text{OB}_4\text{O}_9$ structure illustrating the $\text{SrB}_4\text{O}_9^{4+}$ and $\text{Bi}_2\text{O}_4^{4+}$ layers alternating in the [010] direction, and the asymmetric coordination of the Bi^{3+} ions. Large, medium and small spheres represent Sr, Bi and O atoms, respectively. Only the short Bi-O bonds (less than 2.3 Å) are shown.

	x	y	z	B (Å ²)
Sr	0.6503(7)	0.3352(5)	0.4671(7)	1.86(11)
Bi1	0.4802(3)	0.0974(3)	0.8014(4)	2.44(4)
Bi2	0.8640(3)	0.8368(3)	0.7658(4)	2.44(4)
B1	0.2019(12)	0.3258(9)	0.6981(13)	0.66(8)
B2	0.7525(12)	0.4024(9)	0.0894(12)	0.66(8)
B3	0.1051(11)	0.8663(9)	0.3485(13)	0.66(8)
B4	0.2916(13)	0.4275(9)	0.0980(12)	0.66(8)
O11	0.3192(14)	0.2502(10)	0.5553(14)	0.82(6)
O12	0.2841(13)	0.3190(10)	0.9087(13)	0.82(6)
O13	0.2068(14)	0.4834(9)	0.7193(14)	0.82(6)
O14	-0.0121(12)	0.2513(10)	0.6127(15)	0.82(6)
O21	0.7263(14)	0.2612(9)	0.0804(15)	0.82(6)
O23	0.7352(15)	0.4330(10)	-0.0969(14)	0.82(6)
O31	0.3142(12)	0.8963(10)	0.4197(15)	0.82(6)
O32	0.0036(13)	0.9478(10)	0.2528(15)	0.82(6)
O42	0.3372(14)	0.4053(11)	0.2866(14)	0.82(6)
O5	0.3892(15)	0.0849(11)	0.1438(15)	1.29(20)

Table 1 Atomic coordinates and displacement parameters for $\text{SrBi}_2\text{OB}_4\text{O}_9$ from the combined Rietveld refinement of one X-ray and two neutron powder diffraction data sets (combined $\chi^2 = 5.71$). Unit-cell data: $a = 6.86602(1)$ Å, $b = 9.79834(1)$ Å, $c = 6.81524(1)$ Å, $\alpha = 109.1268(1)^\circ$, $\beta = 101.8973(1)^\circ$, $\gamma = 96.1452(1)^\circ$, $Z = 2$, P-1).

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