SHORT-FORMAT PAPERS

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Structure of $Sr_xBa_{3-x}(B_3O_6)_2$ in a Solid Solution

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Abstract. $Sr_xBa_{3-x}(B_3O_6)_2$ where $x = 1.16$, $M_r = 611.2$, trigonal, $R\bar{3}c$, $a = 7.162\,(1)$, $c = 37.235\,(7)$ Å, $V = 1653.9$ Å^3, $Z = 6$, $D_x = 3.68$, $D_m = 3.67$ g cm^{-3} (using specific gravity bottle and toluene), Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 119.9$ cm^{-1}, $F(000) = 1639$, $T = 296$ K, $R = 0.031$ for 311 unique reflections with $I > 3\sigma(I)$. The structure is isostructural with the high-temperature phase of α-$Ba_3(B_3O_6)_2$. Sr^{2+} ions are located at the 6(a) positions with full occupancy and also share, statistically, the 12(c) positions with Ba^{2+} ions. The solid solution is stable down to room temperature without a phase transition.

Experimental. The crystals of the title compound were obtained by cooling the melt of $3BaB_2O_4 + 2SrB_2O_4$. The starting materials, $BaCO_3$, $SrCO_3$ and H_3BO_3 (analytical purity), were mixed in the molar ratios 0.6:0.4:2 (corresponding to $3BaB_2O_4$:$2SrB_2O_4$) and heated in a Pt crucible to 1363 K for 3 h. The melt was then cooled slowly at a rate of 3 K per day to 1323 K. Colourless crystals, some larger than 2 × 3 × 5 mm, were grown on a Pt wire which was placed on the surface of the melt. A single crystal with dimensions of 0.45 × 0.7 × 0.25 mm was chosen for the structure determination. Unit-cell parameters were derived from a least-squares analysis of 25 reflections in the range $18 < 2\theta < 19°$. A total of 7143 reflections were collected at 296 K on an Enraf–Nonius CAD-4 four-circle diffractometer using monochromatic Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation. Intensity data in the range $2 < 2\theta < 54°$ ($-9 < h < 9$, $-9 < k < 9$, $0 < l < 47$) were collected using the ω–2θ-scan technique with scan speeds ranging from 2 to 7° min^{-1} and a scan width $\omega = (0.40 + 0.35\tan\theta)°$. Three standard reflections were measured during the data collection but only random deviations were observed. However, an anisotropic decay correction was applied and the correction factors on I ranged from 0.989 to 1.031 with an average value of 1.011. Lorentz–polarization corrections were applied to the data. An empirical absorption correction based on a series of ψ scans was applied to the data with relative transmission coefficients between 0.465 and 0.998, average 0.720. After structure refinement with isotropic thermal parameters, a further empirical absorption correction calculated using the program *DIFABS* (Walker & Stuart, 1983) was made with maximum and minimum coefficients of 1.222 and 0.777 respectively, average 0.911. Intensities of equivalent reflections were averaged with an agreement factor R_{int} of 4.3% based on intensity, and a total of 403 unique reflections were obtained. A correction for secondary extinction was required (Zachariasen, 1963). The final R coefficient, refined in least squares, was $R = 2.9 \times 10^{-6}$. From the systematic absences hkl, $-h + k + l = 3n$: hhl $l = 2n$ (or $h = k$, $l = 2n$, $0kl$, $l = 2n$) and combined with the report of X-ray powder diffraction (Wang, Huang & Liang, 1984), the space group was determined to be $R\bar{3}c$ and the solid solution is isostructural with α-BaB_2O_4. By using the positional parameters for α-BaB_2O_4 (Mighell, Perloff & Block, 1966), the structure was refined by full-matrix least-squares techniques. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/[\sigma^2(I) + pF_o^2]^2$ and $p = 0.07$. Final least-squares refinement on F_o with 311 unique reflections having $I > 3\sigma(I)$ and anisotropic thermal factors for each atom resulted in final residuals of R

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Table 1. *Atom coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = 4/3\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j\beta_{ij}.$$

	x	y	z	B_{eq}(Å^2)
B	0.9595 (7)	0.1761 (8)	0.0403 (1)	1.8 (1)
O(1)	1.1704 (5)	0.2075 (4)	0.04161 (9)	2.17 (6)
O(2)	0.9325 (4)	0.3422 (4)	0.03762 (7)	1.85 (6)
Sr	0.6667	0.3333	0.0833 (0)	1.27 (1)
BS*	1.3333	0.6667	0.01831 (1)	1.435 (7)

* BS indicates a 12(*c*) site occupied by Ba^{2+} and Sr^{2+} in the ratio 0.92:0.08.

Table 2. *Important interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

B—O(1)	1.412 (8)	O(2)—Sr	2.531 (4)
B—O(1^{i})	1.392 (9)	O(2)—BS	2.736 (3)
B—O(2)	1.301 (7)	O(2)—BS^{ii}	2.801 (3)
B—Sr	3.255 (6)	Sr—BS	3.7847 (7)
B—BS	3.283 (7)	BS—BS	4.3538 (4)
O(1)—BS	3.015 (4)		

O(1)—B—O(1)	115.9 (5)	O(1)—BS—O(2)	47.8 (2)
O(1)—B—O(2)	119.6 (5)	O(1)—BS—O(2)	107.5 (1)
O(1)—B—Sr	138.7 (4)	O(1)—BS—O(2)	67.1 (2)
O(1)—B—O(2)	124.6 (5)	O(1)—BS—O(2)	67.7 (1)
O(2)—B—BS	54.3 (4)	O(1)—BS—O(2)	146.6 (2)
B—O(1)—B	123.8 (5)	O(1)—BS—O(2)	136.0 (2)
O(2)—Sr—O(2)	79.7 (1)	O(2)—BS—O(2)	76.3 (2)
O(2)—Sr—O(2)	134.3 (1)	O(2)—BS—O(2)	113.35 (6)
O(2)—Sr—O(2)	138.9 (1)	O(2)—BS—O(2)	89.8 (1)
O(2)—Sr—O(2)	84.6 (1)	O(2)—BS—O(2)	145.75 (8)
O(2)—Sr—O(2)	138.9 (1)	O(2)—BS—O(2)	70.8 (1)
O(1)—BS—O(1)	112.07 (6)		

Symmetry code: (i) $1-y, x-y-1, z$; (ii) $\frac{1}{3}-x, \frac{2}{3}-y, \frac{2}{3}-z$.

$= 0.031$ and $wR = 0.038$, largest shift was 0.04σ and $S = 0.859$. Minimum and maximum heights in final difference Fourier synthesis were -2.33 and 1.20 e Å^{-3}, respectively. The scattering factors for the Ba^{2+}, Sr^{2+} and O^- ions were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B). All calculations were performed on a VAX 785 computer with the *SDP/VAX Program Packages* (Frenz, 1978).

Final atomic coordinates and equivalent isotropic thermal parameters for the title compound are listed in Table 1,* in which BS represents a statistical distribution of ions with $0.92Ba^{2+} + 0.08Sr^{2+}$. Selected interatomic distances and angles are given in Table 2. An *ORTEP*II (Johnson, 1976) drawing of the molecular packing in one half of a unit cell is shown in Fig. 1. Fig. 2. shows the $(B_3O_6)^{3-}$ anion ring. Fig. 3 shows the relationship between the $(B_3O_6)^{3-}$ plane ring and the Sr^{2+} and BS^{2+} cations.

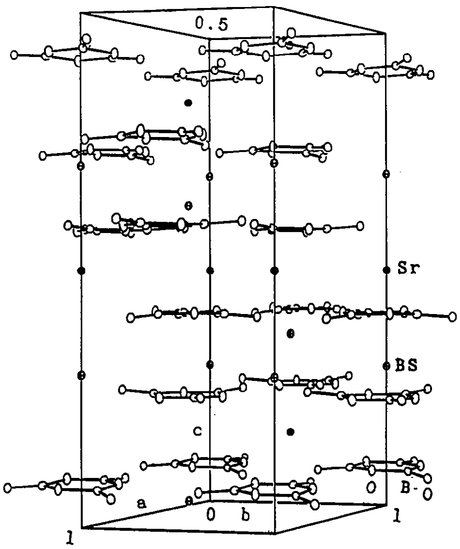

Fig. 1. A view of the molecular packing in one half of the unit cell of $Sr_xBa_{3-x}(B_3O_6)_2$.

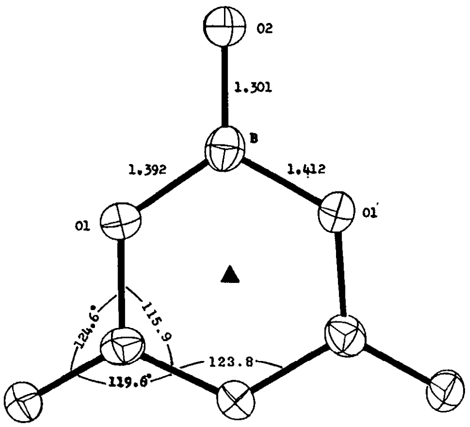

Fig. 2. The $(B_3O_6)^{3-}$ anion ring.

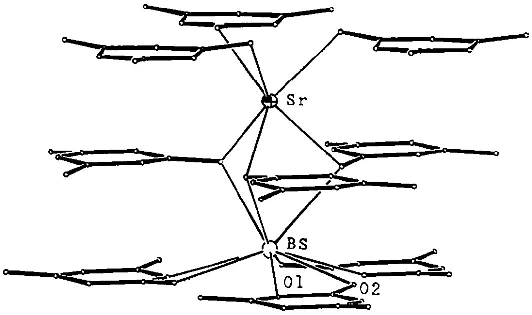

Fig. 3. The relationship between the $(B_3O_6)^{3-}$ plane ring and the cations Sr^{2+} and BS^{2+}.

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* Lists of structure factors, anisotropic thermal parameters and a complete list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54478 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI0063]

Related literature. The solid solution is isostructural with α-BaB_2O_4 (Mighell, Perloff & Block, 1966) and its structure is stable down to room temperature (Block, Perloff & Weir, 1964). Various other compounds $MBa_2[B_3O_6]_2$ where M = Ca, Cd, Co, Ni and Mg have also been found and their structures (Liebertz & Fröhlich, 1984) also shown to be more closely related to α-BaB_2O_4 than to β-BaB_2O_4. The crystal structure of the solid solution of $Sr_xBa_{3-x}(B_3O_6)_2$ (x = 1.16) reported here enables us to define a similar relationship for $MBa_2(B_3O_6)_2$ where M is an alkaline-earth metal.

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New Refinement of $LiCdPO_4$

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Abstract. Cadmium lithium phosphate, M_r = 214.31, orthorhombic, *Pnma*, but previously reported as $Pna2_1$ by the present authors [Elammari, Elouadi & Depmeier (1988). *Acta Cryst.* C**44**, 1357–1359], a = 10.724 (4), b = 6.288 (1), c = 4.804 (1) Å, V = 323.9 (1) Å^3, Z = 4, D_x = 4.40 g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, μ = 70.4 cm^{-1}, $F(000)$ = 392, T = 298 K, R = 0.0207 for 759 independent reflections. The revised structure is less distorted but is otherwise comparable, with discrete PO_4 tetrahedra linked by distorted CdO_6 (c site symmetry m) and LiO_6 (b site symmetry $\bar{1}$) octahedra as described previously.

Experimental. X-ray diffraction data were collected under the conditions reported in Table 1. The refinement of the structure in both space groups, $Pna2_1$ and *Pnma*, gives comparable indicators in each (R = 0.0182 and wR = 0.0172 for $Pna2_1$; R = 0.0207 and wR = 0.0214 for *Pnma*). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Related literature. New results of second-harmonic generation (SHG) tests performed with very sensitive equipment (Dougherty & Kurtz, 1976) on as-grown crystals suggest the centrosymmetric space group *Pnma*, since no SHG signal was detected (Williams, 1989). No significant difference is observed between the values of atomic coordinates and interatomic distances given in our former study (Elammari, Elouadi & Depmeier, 1988) and those shown in Tables 2† and 3. It is however surprising that the SHG test performed earlier gave a positive result. This was probably an artefact not related to $LiCdPO_4$.

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54492 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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