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Strontium Metaborate, SrB_2O_4

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Abstract

Single crystals of strontium metaborate, SrB_2O_4, were grown for the first time from the melt by the Czochralski method and a detailed structure analysis was carried out. The Sr atom is dodecahedrally coordinated by eight O atoms from the neighbouring infinite planes of borate molecules so that all O atoms in the borate molecules participate in the coordination with Sr···O distances ranging from 2.522 (7) to 2.728 (5) Å.

Comment

Strontium borate has become a focus of interest in recent years due to the possibility of it being a new non-linear optical material such as lithium borate or barium borate. Optical properties for the system $SrO–B_2O_3$ have been reported for the five compounds (3:1, 2:1, 1:1, 1:2 and 1:3) in this system (Weir & Schroeder, 1964; Hart & Smallwood, 1962; Koskentalo, Leskelä & Niinistö, 1985) and a phase-equilibrium diagram as determined by DTA has been reported (Witzmann & Herzog, 1964). However, with the exception of luminescence studies of the tetraborate SrB_4O_7 (Meijerink, Nuyten & Blasse, 1989; Blasse, Dirksen & Meijerink, 1990), studies of the physical properties of the strontium borates are rare.

In our laboratory, single crystals of the metaborate (SrB_2O_4), tetraborate and triborate (SrB_6O_{10}) were successfully grown from the melt by the Czochralski method. In this work, we report the detailed crystal structure of SrB_2O_4. The cell parameters, the space group and the probable structure of this compound have been described previously (Block, Perloff & Weir, 1964).

As shown in Fig. 1, each B atom in the infinite chains of BO_3 groups is surrounded by three O atoms. The bond lengths of the trigonal B—O bonds vary over the range 1.328 (10)–1.395 (12) Å with a mean value of 1.370 Å. The B—O—B angles are in the range 115.8 (7)–126.9 (8)° with a mean value of 120.0°. The BO_3 groups have an almost perfectly planar structure. The dihedral angle between the neighbouring planes of BO_3 groups is 163.1 (3)°, so the layers consisting of these groups are slightly puckered; these layers lie almost parallel to the (204) plane (Fig. 2). The Sr atom is coordinated by eight O atoms at distances ranging from 2.522 (7) to 2.728 (5) Å and the smallest O—Sr—O angle is 50.9 (2)° (see Table 2). All the geometric data are very similar to those of CaB_2O_4 (Marezio, Plettinger & Zachariasen, 1963).

To conclude, the strontium metaborate structure consists of slightly puckered layers with the composition $(B_2O_4)_n^{2n-}$ and Sr^{2+} atoms each coordinated by eight O atoms from neighbouring $(B_2O_4)_n^{2n-}$ layers. The shortest Sr···Sr(x, $1-y$, $\frac{1}{2}+z$) distance is 3.8864 (7) Å.

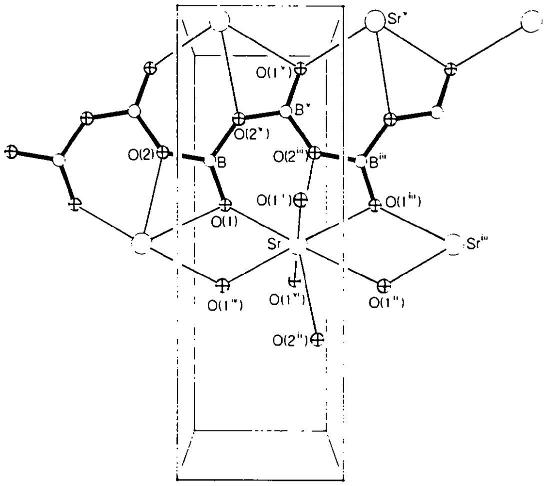

Fig. 1. The structure of SrB_2O_4 showing the infinite $(BO_2)_n^{2n-}$ chain and the labelling scheme. The Sr atom is coordinated by eight O atoms. (Symmetry codes are as given in Table 2.)

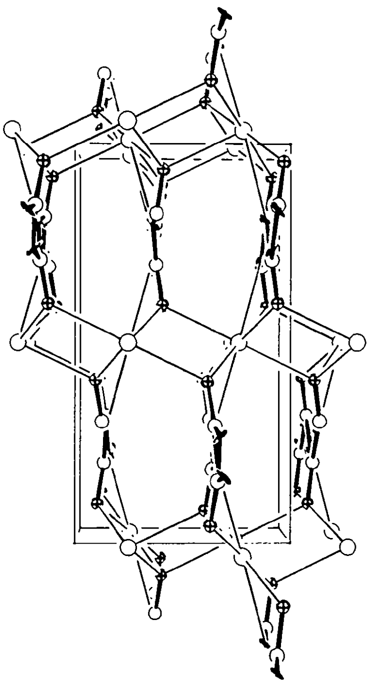

Fig. 2. A unit-cell packing diagram for SrB_2O_4. The origin is at the lower left, the c axis is horizontal and the a axis is vertical.

Experimental

The starting materials used to prepare the single crystals of SrB_2O_4 were 99.99% $SrCO_3$ and B_2O_3 dried at 473 K for 20 h. They were mixed together in the appropriate stoichiometric ratio and ball-milled for 10 h. The raw mixture was RF-heated at 1173 K for 10 h, and then melted at 1428 K in a 150 ml platinum crucible. Seed crystals were obtained by pulling the platinum rod from the melt. A personal computer was used to control the furnace to within ±0.3 K at the running temperature. Typical growth conditions were as follows: seed crystal direction = *b* axis; pulling speed = 0.1–0.3 mm h^{-1}; rotation speed = 15–25 r.p.m.; temperature gradient above solid–liquid interface = 60° cm^{-1}. The as-grown crystals were colourless and transparent, and had twofold symmetry along the *b* axis. The typical diameter and length of the crystals were 20 and 40 mm, respectively. The density D_m was measured using a densitometer.

Crystal data

SrB_2O_4
$M_r = 173.24$
Orthorhombic
Pbcn
$a = 12.0135\,(7)$ Å
$b = 4.339\,(2)$ Å
$c = 6.5864\,(4)$ Å
$V = 343.3\,(4)$ Å^3
$Z = 4$
$D_x = 3.35$ Mg m^{-3}
$D_m = 3.35$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 15.95$–$20.12°$
$\mu = 15.08$ mm^{-1}
$T = 293$ K
Rectangular plate
0.2 × 0.2 × 0.03 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*SDP*; Enraf–Nonius, 1985)
$T_{\min} = 0.1754$, $T_{\max} = 0.9652$
363 measured reflections
354 independent reflections

211 observed reflections $[F > 3\sigma(F)]$
$\theta_{\max} = 24°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 4$
$l = 0 \rightarrow 7$
3 standard reflections
frequency: 100 min
intensity decay: 1%

Refinement

Refinement on *F*
$R = 0.0504$
$wR = 0.0551$
$S = 1.5271$
211 reflections
33 parameters
$w = 1/[\sigma^2(F) + 0.001588F^2]$
$(\Delta/\sigma)_{\max} = 0.007$

$\Delta\rho_{\max} = 1.89$ e Å^{-3}
$\Delta\rho_{\min} = -1.43$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Sr	1/2	0.7378 (2)	1/4	0.007 (1)
O(1)	0.5906 (4)	0.2643 (10)	0.4046 (11)	0.007 (4)
O(2)	0.7116 (4)	−0.1471 (14)	0.3548 (11)	0.013 (3)
B	0.6942 (7)	0.170 (2)	0.3726 (19)	0.009 (5)

Table 2. *Selected geometric parameters (Å, °)*

Sr—O(1)	2.538 (5)	Sr—O(2^{ii})	2.681 (5)
Sr—O(1^{i})	2.522 (7)	B—O(2^{v})	1.388 (11)
Sr—O(1^{ii})	2.728 (5)	Sr—O(2^{iii})	2.681 (5)
O(2)—B	1.395 (12)	Sr—O(1^{vi})	2.522 (7)
Sr—O(1^{iii})	2.728 (5)	O(1)—B	1.328 (10)
Sr—O(1^{iv})	2.538 (5)		
O(1)—Sr—O(1^{iii})	110.9 (2)	O(1)—Sr—O(2^{iii})	69.0 (2)
O(1)—Sr—O(1^{i})	100.0 (2)	O(1)—Sr—O(1^{iv})	71.9 (2)
O(1)—Sr—O(1^{vi})	79.7 (2)	O(1)—Sr—O(1^{ii})	177.2 (2)
O(1)—Sr—O(2^{ii})	131.4 (2)	O(1^{iii})—Sr—O(2^{iii})	50.9 (2)
O(1^{iii})—Sr—O(1^{i})	99.7 (2)	O(1^{iii})—Sr—O(1^{iv})	177.2 (2)
O(1^{iii})—Sr—O(1^{vi})	80.7 (2)	O(1^{iii})—Sr—O(1^{ii})	66.2 (2)
O(1^{iii})—Sr—O(2^{ii})	108.6 (2)	O(2^{iii})—Sr—O(1^{i})	79.8 (2)
O(2^{iii})—Sr—O(1^{iv})	131.4 (2)	O(2^{iii})—Sr—O(1^{vi})	100.2 (2)
O(2^{iii})—Sr—O(1^{ii})	108.6 (2)	O(2^{iii})—Sr—O(2^{ii})	158.5 (2)
O(1^{i})—Sr—O(1^{iv})	79.7 (2)	O(1^{i})—Sr—O(1^{vi})	179.6 (1)
O(1^{i})—Sr—O(1^{ii})	80.7 (2)	O(1^{i})—Sr—O(2^{ii})	100.2 (2)
O(1^{iv})—Sr—O(1^{vi})	100.0 (2)	O(1^{iv})—Sr—O(1^{ii})	110.9 (2)
O(1^{iv})—Sr—O(2^{ii})	69.0 (2)	O(1^{vi})—Sr—O(1^{ii})	99.6 (2)
O(1^{vi})—Sr—O(2^{ii})	79.8 (2)	O(1^{ii})—Sr—O(2^{ii})	50.9 (2)
Sr—O(1)—B	126.1 (6)	O(1)—B—O(2)	117.3 (7)
O(1)—B—O(2^{v})	126.9 (8)	O(2)—B—O(2^{v})	115.8 (7)
B—O(2^{v})—B^{v}	132.8 (7)		

Symmetry codes: (i) $x, 1-y, z-\frac{1}{2}$; (ii) $1-x, 1+y, \frac{1}{2}-z$; (iii) $x, 1+y, z$; (iv) $1-x, y, \frac{1}{2}-z$; (v) $\frac{3}{2}-x, \frac{1}{2}+y, z$; (vi) $1-x, 1-y, 1-z$.

Preliminary photographic studies (Suh, Suh, Ko, Aoki & Yamazaki, 1988; Suh, Lee, Lim, Ryu & Park, 1994) of the crystal using rotation, Weissenberg and precession cameras revealed the approximate unit-cell dimensions and the reflection conditions $0kl$: $k = 2n$, $h0l$: $l = 2n$, $hk0$: $h + k = 2n$, indicating a uniquely defined centrosymmetric orthorhombic space group (D_{2h}^{14}). Data were collected using an ω-scan width of $(0.8 + 0.35\tan\theta)°$ (Suh *et al.*, 1993). Intensity data were corrected for Lp factors. Anomalous-dispersion terms were taken from the usual sources (Ibers & Hamilton, 1974).

Data collection: *SDP* (Enraf–Nonius, 1985). Cell refinement: *SDP*. Data reduction: *SDP*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP* (Johnson, 1971). Software used to prepare material for publication: *GEOM* (Shin, 1978).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: OH1085). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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La_2LiMoO_6

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Abstract

Dilanthanum lithium molybdenum(V) oxide has a monoclinically distorted perovskite-type structure with an ordered distribution of the Mo^{5+} and Li^+ ions over the octahedral sites. The Mo—O distances within the slightly distorted MoO_6 octahedra range between 1.959 (2) and 1.970 (2) Å with an average value of 1.965 Å. The LiO_6 octahedra are more distorted with Li—O distances in the range 2.099 (2)–2.155 (2) Å (average distance 2.132 Å). The La^{3+} ions are surrounded by eight O atoms at distances ranging from 2.409 (3) to 2.776 (2) Å with the four nearest O atoms forming a distorted tetrahedron and the remaining O atoms roughly capping two faces or bridging two edges of this tetrahedron.

Comment

The $AMoO_3$ (A = Ca, Sr and Ba) (Scholder & Brixner, 1955) compounds are the only ternary reduced molybdenum oxides which crystallize with the perovskite structure. Replacement of half of the Mo^{4+} ions by a $3d$ element (Sc, Cr, Fe) (Patterson, Moeller & Ward, 1963) or a rare earth element (La → Lu) (Brandle & Steinfink, 1971) leads to reduced Mo compounds with general formula A_2BMoO_6. The differences in radius and valence between the B^{3+} and Mo^{5+} ions lead to the ordering of the latter. As a consequence, these quaternary oxides crystallize in cubic, tetragonal or orthorhombic perovskite supercells, closely related to the cryolite structure, depending upon the sizes of the A and B ions. More complex quadruple oxides containing Mo^{5+} ions and having perovskite-related structures are also known, such as $ALaMnMoO_6$ (A = Ca, Sr and Ba) (Nakamura & Choy, 1977) and $La_2M_{4/3}Mo_{2/3}O_6$ (M = Mg and Mn) (Bazuev, Makarova & Shveikin, 1987). However, with the exception of Ba_2NdMoO_6, the structure of which was determined at 473 K (Brandle & Steinfink, 1971), none of the above compounds has been the subject of accurate single-crystal or powder structure determinations.

We present here the crystal structure of a new ordered A_2BMoO_6 compound containing Mo^{5+} ions: La_2LiMoO_6. This compound belongs to the large family of analogous phases La_2LiMO_6 (M = V, Fe, Nb, Ru, Ta, Re, Os and Ir) and was mentioned by Demazeau, Oh-Kim, Choy & Hagenmuller in 1987, though no details of the synthesis or the structural parameters were given. La_2LiMoO_6 crystallizes in a monoclinically distorted variant (space group $P2_1/n$) of the perovskite structure with unit-cell parameters of ca $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$ where a_p is the unit-cell parameter of an ideal cubic

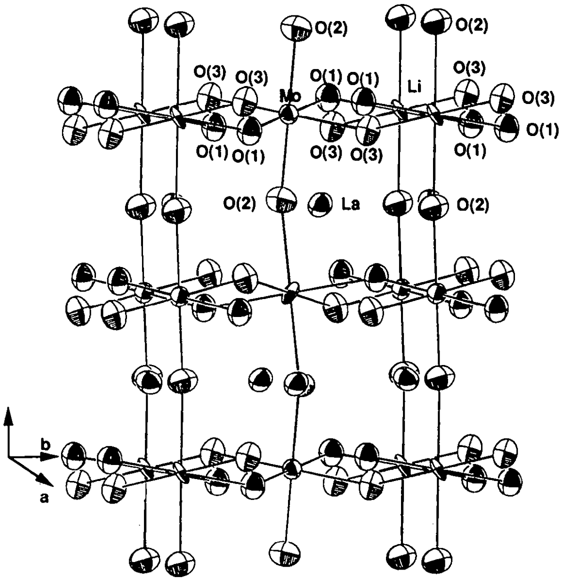

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the structure of La_2LiMoO_6. Displacement ellipsoids are drawn at the 95% probability level.