Refinement

Refinement on F
$R = 0.0398$
$wR = 0.0576$
$S = 0.54$
1382 reflections
73 parameters
Calculated weights
$w = 1/[\sigma^2(F) + 0.0096F^2]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 6.41$ e Å^{-3}
$\Delta\rho_{\min} = -5.37$ e Å^{-3}

Extinction correction: modified Larson (1970) method (*SHELXTL-Plus*; Sheldrick, 1991)
Extinction coefficient: 0.0045 (3)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.3.1 and 2.2B)

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

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

	x	y	z	$U_{\rm eq}$
Bi1	0.10793 (9)	−0.20460 (6)	0.69944 (6)	0.0096 (2)
Bi2	0.42486 (10)	0.15405 (7)	0.63975 (6)	0.0106 (2)
Cu1	−0.3625 (3)	−0.2236 (2)	−0.0257 (2)	0.0086 (5)
Cu2	0	0	0	0.0078 (7)
V	0.2506 (5)	−0.4285 (3)	0.2456 (3)	0.0087 (7)
O1	0.2904 (19)	−0.0696 (13)	−0.1488 (12)	0.008 (2)
O2	0.2261 (18)	0.0437 (13)	0.1669 (12)	0.010 (2)
O3	−0.0010 (30)	−0.3373 (22)	0.0868 (19)	0.040 (3)
O4	−0.4742 (23)	−0.3906 (17)	0.1548 (15)	0.022 (2)
O5	0.1811 (24)	−0.3213 (18)	0.4045 (16)	0.024 (2)
O6	0.3302 (20)	0.3292 (14)	0.3250 (13)	0.013 (2)
O7	0.2474 (17)	−0.0025 (13)	0.5043 (11)	0.006 (2)

Table 2. *Selected geometric parameters* (Å)

Bi1—O1$^{\rm i}$	2.239 (12)	Cu1—O2$^{\rm v}$	1.916 (11)
Bi1—O7	2.243 (10)	Cu1—O4	1.928 (12)
Bi1—O2$^{\rm ii}$	2.263 (10)	Cu1—O3	1.943 (15)
Bi1—O7$^{\rm ii}$	2.351 (8)	Cu1—O1$^{\rm vi}$	1.942 (8)
Bi1—O5	2.760 (14)	Cu1—O6$^{\rm v}$	2.752 (12)
Bi1—O6$^{\rm iii}$	2.837 (10)	Cu1—Cu2	3.063 (3)
Bi1—O6$^{\rm ii}$	2.845 (13)	Cu2—O1	1.970 (9)
Bi1—O4$^{\rm iv}$	3.050 (11)	Cu2—O1$^{\rm v}$	1.970 (9)
Bi2—O7$^{\rm iii}$	2.266 (9)	Cu2—O2	1.988 (11)
Bi2—O2$^{\rm iii}$	2.271 (8)	Cu2—O2$^{\rm v}$	1.988 (11)
Bi2—O7	2.271 (12)	Cu2—O3	2.576 (18)
Bi2—O1$^{\rm i}$	2.405 (10)	Cu2—O3$^{\rm v}$	2.576 (18)
Bi2—O6	2.519 (10)	V—O3	1.691 (15)
Bi2—O5$^{\rm iii}$	2.804 (15)	V—O4$^{\rm vii}$	1.711 (13)
Bi2—O4$^{\rm ii}$	2.887 (15)	V—O6$^{\rm viii}$	1.754 (11)
Bi2—O5$^{\rm ii}$	3.028 (12)	V—O5	1.694 (15)

Symmetry codes: (i) $x, y, 1+z$; (ii) $-x, -y, 1-z$; (iii) $1-x, -y, 1-z$; (iv) $-x, -1-y, 1-z$; (v) $-x, -y, -z$; (vi) $x-1, y, z$; (vii) $1+x, y, z$; (viii) $x, y-1, z$.

Data collection, cell refinement and data reduction were performed with Nicolet *R3m/V* software. Structure solution, structure refinement, preparation of molecular graphics and generation of material for publication were performed using *SHELXTL-Plus* (Sheldrick, 1991).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1063). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Li_3BS_3

P. VINATIER, P. GRAVEREAU, M. MÉNÉTRIER, L. TRUT AND A. LEVASSEUR

Laboratoire de Chimie du Solide du CNRS and Ecole Nationale Supérieure de Chimie et Physique de Bordeaux, 351, cours de la Libération, 33405 Talence CEDEX, France

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Abstract

The structure of lithium orthothioborate, Li_3BS_3, obtained by crystallizing the corresponding glass, consists of quasi-planar Li_3BS_3 entities in which B atoms are tricoordinated by S atoms. Tetrahedra of S atoms around Li are linked to one another *via* corners and/or edges. This structure, which exhibits a higher symmetry than other $M_3B(O,S)_3$ structures, such as Li_3BO_3 or Tl_3BS_3, appears to be a new member of the M_3AX_3 group of compounds.

Comment

Lithium thioborate compounds, designated as $(1-x)B_2S_3 - xLi_2S$, have been found to give homogeneous glasses for $0.5 \leq x \leq 0.75$ and $x = 0.375$. These glasses exhibit a very high Li^+ ion conductivity ($\simeq 0.1\,\Omega^{-1}\,m^{-1}$ at room temperature). Some of the authors have undertaken an extensive study of their structure to discover its relation to their ionic conductivity (Ménétrier, Estournès & Levasseur, 1992). Among the crystalline phases of this system, $Li_{6+2n}(B_{10}S_{18})S_n$, $n \simeq 2$ (corresponding to $x = 0.5$), is the only one for which the crystal structure has been determined (Zum Hebel, Krebs, Grüne

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& Müller-Warmuth, 1990). By crystallizing the glasses, we have isolated Li_3BS_3 (corresponding to $x = 0.75$) and grown a single crystal. This paper reports the structure determination of Li_3BS_3, which was investigated in connection with the structural study of the corresponding glass.

Since Li_3BS_3, like the other thioborates, is extremely sensitive to moisture, all preparations were performed in a glove box filled with dry Ar, containing less than 5 p.p.m. of water. The first step involved the synthesis of Li_3BS_3 according to the procedure already employed for the glasses (Ménétrier, Estournès, Levasseur & Rao, 1992); the crystallization was achieved in a second step by the Bridgman method.

Approximately 2 g of a mixture of amorphous B, S and Li_2S was melted in a silica ampoule sealed under vacuum. In order to avoid reaction with SiO_2, the mixture was placed in a vitreous carbon crucible inserted in the silica ampoule. The sample was heated to 775 K for 12 h, to 1075 K for 6 h and then air quenched; it was then partially crystallized. The single crystal was obtained by placing the ground sample in a graphite crucible inserted in an evacuated silica tube. The sample was melted at 825 K and cooled to 675 K at 0.8 K h^{-1} using the Bridgman technique. This process yielded an aggregate of crystals, some of them single. One was selected for the structural investigations.

Density measurements and chemical analysis were performed on a part of the aggregate. Chemical analysis results led to S/B and Li/B ratios close to 3. Nevertheless, X-ray powder diffraction on the aggregate revealed the presence of traces of unreacted Li_2S, which could arise from a lack of boron as a result of its slight oxygen contamination (4.6 wt% of oxygen). However, the composition of the single crystal utilized has been confirmed *a posteriori* by the structure determination itself.

The main result for glassy Li_3BS_3 (Suh, Hojjaji, Villeneuve, Ménétrier & Levasseur, 1991) is confirmed: B is tricoordinated by S, with a B—S distance of 1.83 Å, as in Tl_3BS_3 (Krebs & Hamann, 1988). In fact, the crystal structure can be depicted as an arrangement of Li_3BS_3 entities, each unit cell containing two pairs as shown in Fig. 1. These entities are quasi planar and very regular with six LiBS angles very close to 60°. They are located perpendicular to the (010) plane. Each includes one B, one S(1) and one Li(1) in the mirror plane, and the two remaining S(2) and Li(2) outside the mirror plane.

From the cation-coordination point of view, the structure is quite original. Each Li is surrounded by four S, two of which belong to the same BS_3^{3-} unit. Each S connects four tetrahedra to one another. Tetrahedra around Li(1) share only corners, whereas tetrahedra around Li(2) also share edges to form pairs. The common edge is formed by two S belonging to separate BS_3^{3-} triangles. This arrangement is partially shown in Fig. 2.

This structure contains rather large empty sites, which are difficult to visualize. Indeed, the corresponding glass exhibits a remarkably more compact 'structure' with a higher density (1.76 compared to 1.68 Mg m^{-3} for the crystal).

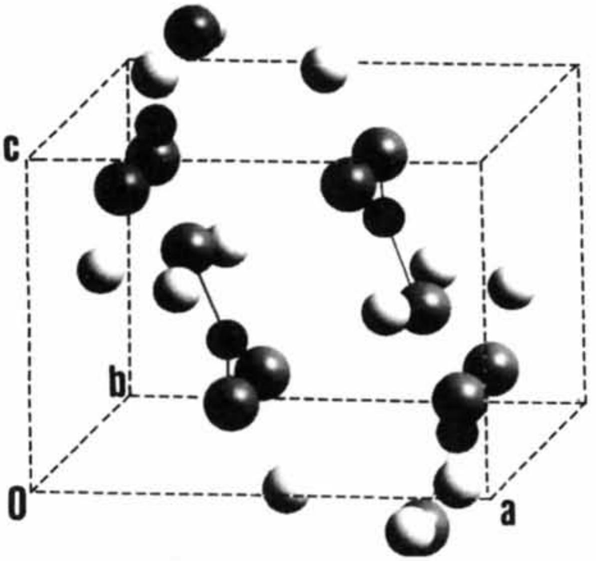

Fig. 1. Representation of one unit cell of Li_3BS_3 showing Li_3BS_3 planar entities (arbitrary atomic sizes; small circles represent B, medium Li and large S).

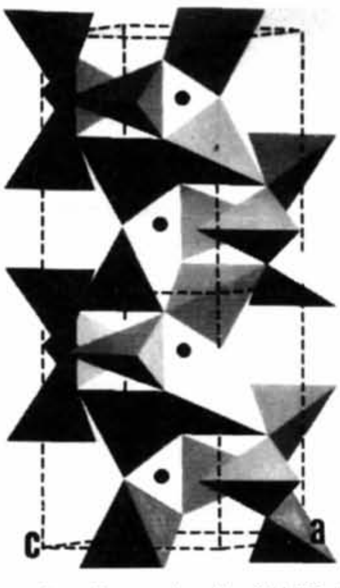

Fig. 2. Representation of two unit cells of Li_3BS_3 showing corner and/or edge-sharing LiS_4 tetrahedra (arbitrary atomic size; small circles represent B).

Experimental

As Li_3BS_3 is highly sensitive towards moisture, both single crystal and powder studies were performed using glass capillaries, filled in a glove box under a dry Ar atmosphere.

Crystal data

Li_3BS_3
$M_r = 127.83$
Orthorhombic
Pnma
$a = 8.150$ (3) Å
$b = 10.070$ (3) Å
$c = 6.159$ (2) Å
$V = 505.5$ (3) Å^3
$Z = 4$
$D_x = 1.680$ Mg m^{-3}
$D_m = 1.69$ Mg m^{-3}
D_m measured by flotation in bromobenzene

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 14 reflections (from powder Co $K\alpha_1$, $\lambda = 1.7890$ Å)
$\theta = 18.5–46°$
$\mu = 1.23$ mm^{-1}
$T = 293$ K
Irregular fragment
0.25 × 0.25 × 0.20 mm
Yellowish white
Crystal source: Bridgman method

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical (*ABSORB*; Ugozzoli, 1987)
$T_{\min} = 0.675$, $T_{\max} = 1.409$
4593 measured reflections
670 independent reflections $[\langle F_o^2\rangle \geq 3.0\sigma(\langle F_o^2\rangle)]$

2079 observed reflections $[I \geq 3.0\sigma(I)]$
$R_{\rm int} = 0.050$ (after absorption correction)
$\theta_{\max} = 35°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 16$
$l = -9 \rightarrow 9$
3 standard reflections frequency: 240 min intensity variation: −2.5%

Refinement

Refinement on F
$R = 0.069$
$wR = 0.058$
$S = 3.795$
670 reflections
37 parameters
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.19$ e Å^{-3}
$\Delta\rho_{\min} = -1.22$ 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)

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	Wyckoff position	Site symmetry	x	y	z	$B_{\rm eq}$
S(1)	4(*c*)	*.m.*	0.2993 (2)	1/4	0.6577 (4)	1.24 (5)
S(2)	8(*d*)	1	0.4232 (2)	0.0934 (1)	0.2396 (4)	1.36 (4)
B	4(*c*)	*.m.*	0.3812 (9)	1/4	0.383 (2)	1.1 (2)
Li(1)	4(*c*)	*.m.*	0.006 (3)	1/4	0.553 (3)	2.5 (5)
Li(2)	8(*d*)	1	0.327 (2)	0.007 (2)	0.602 (3)	2.7 (4)

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *in* Li_3BS_3

Li_3BS_3 entities

B—S(1)	1.82 (2)	S(1)—B—S(2)	120.9 (3)
B—S(2) (× 2)	1.838 (5)	S(2)—B—S($2^{\rm vii}$)	118.2 (6)
B—Li($1^{\rm i}$)	2.87 (3)	Li($1^{\rm i}$)—B—Li(2)	120.1 (3)
B—Li(2) (× 2)	2.84 (2)	Li(2)—B—Li($2^{\rm vii}$)	119.8 (8)

Li(1)S_4 tetrahedron

Li(1)	S(1)	S($1^{\rm ii}$)	S($2^{\rm iii}$)	S($2^{\rm iv}$)
S(1)	2.47 (2)	4.230 (1)	4.228 (3)	4.228 (3)
S($1^{\rm ii}$)	118.4 (4)	2.45 (2)	4.043 (3)	4.043 (3)
S($2^{\rm iii}$)	116.8 (5)	109.8 (5)	2.49 (2)	3.154 (3)
S($2^{\rm iv}$)	116.8 (5)	109.8 (5)	78.6 (5)	2.49 (2)

Li(2)S_4 tetrahedron

Li(2)	S(1)	S(2)	S($2^{\rm v}$)	S($2^{\rm vi}$)
S(1)	2.49 (2)	3.184 (3)	4.180 (2)	3.937 (2)
S(2)	78.9 (3)	2.52 (2)	3.717 (4)	4.581 (2)
S($2^{\rm v}$)	115.0 (4)	103.5 (5)	2.47 (2)	4.077 (1)
S($2^{\rm vi}$)	106.6 (4)	135.6 (5)	112.7 (5)	2.43 (2)

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

Symmetry and space group were determined by Weissenberg photographs. The films revealed the relatively poor quality of the single crystal, with quite large and diffuse diffracted spots. Moreover, it was difficult to refine a good orientation matrix on the CAD-4 diffractometer. More accurate cell parameters were obtained from a powder spectrum recorded on an Inel CPS120. The spectrum showed the presence of traces of Li_2S, one of the starting products, which had been used as an internal standard (Powder Diffraction File 23-369, International Center for Diffraction Data, Swarthmore, PA).

The absorption resulting from the glass capillary explains the high value of the internal coherence coefficient before absorption correction ($R_{\rm int} \approx 0.10$). The structure was solved in the *Pnma* space group by Patterson function deconvolution and B and Li atoms were located with several difference Fourier syntheses.

Calculations were performed on an IBM 3090-400 computer at the computing center of Montpellier using *SHELX76* (Sheldrick, 1976). Absorption correction was performed with an empirical algorithm (Walker & Stuart, 1983) using *ABSORB* (Ugozzoli, 1987). Molecular graphics were obtained using *CERIUS* (Molecular Simulations, 1993).

The authors wish to thank Dr J. P. Chaminade for providing the single crystal, and the EC Commission for financial assistance.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: DU1068). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Redetermination of the Structure of $LaMo_5O_8$ by Single-Crystal X-ray Diffraction

P. Gall and P. Gougeon

Université de Rennes I, Laboratoire de
Chimie du Solide et Inorganique Moléculaire,
URA CNRS No 1495, Avenue du Général Leclerc,
35042 Rennes CEDEX, France

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Abstract

We have redetermined the structure of $LaMo_5O_8$ by single-crystal X-ray diffraction. Its structure has been determined previously by powder X-ray and neutron diffraction with rather high *R* factors resulting from impurities in the sample. The crystal structure of $LaMo_5O_8$ is based on $Mo_{10}O_{18}$ cluster units, the Mo cores of which are Mo_{10} bioctahedra resulting from the edge-sharing of two Mo_6 octahedra. These bioctahedral $Mo_{10}O_{18}$ cluster units share opposite O atoms to form infinite molybdenum oxide chains in which the Mo_{10} clusters are strongly linked through short Mo—Mo intercluster bonds of 2.6890 (7) Å and two weaker Mo—Mo bonds of 2.9108 (5) and 3.0911 (5) Å. These chains are then interconnected through Mo—O—Mo bonds to create four-sided channels in which the La^{3+} cations reside. The Mo—Mo distances within the Mo_{10} cluster range from 2.6102 (5) to 2.8279 (5) Å (average 2.749 Å). The Mo—O distances are in the range 1.990 (3)–2.146 (3) Å (average 2.076 Å). The La^{3+} cation is surrounded by ten O atoms at distances ranging from 2.443 (3) to 2.919 (3) Å with an eleventh O atom at 3.232 (3) Å.

Comment

The present work constitutes part of our program on the study of the structural and physical properties of the compounds MMo_5O_8 (M = Ca, Sr, Ba, Sn, Pb, La, Ce, Pr, Nd, Sm, Eu and Gd) containing chains of bioctahedral Mo_{10} clusters. The first member to have its structure established was $LaMo_5O_8$. The structure was determined *ab initio* from X-ray and neutron powder diffraction data by Hibble, Cheetham, Bogle, Wakerley & Cox (1988). However, in both cases the *R* values were rather high (0.11 and 0.114, respectively) as a result of impurities in the sample. Thus, the present work deals with the refinement of the crystal structure from new data collected from a single crystal in order to improve the accuracy of the structure and to enable a precise comparison between the structure of this compound and those of the others in the series.

The basic structural building block of $LaMo_5O_8$ is the bioctahedral cluster unit $Mo_{10}O_{18}$ which results from the metal-edge condensation of two Mo_6O_{12}-type cluster units (Fig. 1). The $Mo_{10}O_{18}$ cluster units are then linked on opposite edges *via* common O atoms to form infinite chains in which the Mo_{10} clusters are strongly linked through intercluster Mo—Mo bonds (Fig. 2*a*). These chains, which run parallel to the *a* axis, are then interlinked through O atoms to create one-dimensional four-sided channels where the cations reside (Fig. 2*b*).

Examination of Table 2 shows that the Mo—Mo distances are roughly the same as those established previously from powder samples while the Mo—O and La—O distances are very different. The Mo—Mo distances within the Mo_{10} double octahedron range between 2.6102 (5) and 2.8279 (5) Å with the shortest of these occurring between the apical atoms Mo(3) and Mo(4). The average value is 2.749 Å and does not differ significantly from those observed for the compounds with divalent [$SnMo_5O_8$ 2.746 Å and $PbMo_5O_8$ 2.745 Å (Gougeon, Potel & Sergent, 1990; Dronskowski & Simon, 1989; Dronskowski, Simon & Mertin, 1991)] or trivalent cations [$RE^{3+}Mo_5O_8$ 2.746–2.750 Å (Gougeon, Gall & Sergent, 1991; Gall, 1990, 1993)]. The intercluster distances are 2.6890 (7) (1 ×), 2.9108 (5) (2 ×) and 3.0911 (5) Å (2 ×) and are in the order of corresponding distances in the other compounds containing trivalent rare earth ions. In the $M^{2+}Mo_5O_8$ compounds (M = Ca, Sr, Sn, Pb and Eu) the two shortest intercluster distances Mo(1)—Mo(1) and Mo(1)—Mo(2) are much longer (*ca* 2.77 and 3.04 Å, respectively) while the third intercluster distance Mo(1)—Mo(3) remains about the same as that observed for the $RE^{3+}Mo_5O_8$ compounds. The range of the Mo—O distances in $LaMo_5O_8$ is 1.990 (3)–2.146 (3) Å with an average distance of 2.076 Å, which also corresponds with the data for the remaining $RE^{3+}Mo_5O_8$ compounds (2.074–2.078 Å).

The La^{3+} ions, which are in general positions, are surrounded by ten O atoms at distances ranging from 2.443 (3) to 2.919 (3) Å with an eleventh O atom at 3.232 (3) Å.

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