O(bridging)—P—O(terminal) bond angle is 106.2 (3)° and that of O(terminal)—P—O(terminal) is 112.5 (3)°. The PO_3 groups are approximately eclipsed as shown by the O(terminal)—P—P—O(terminal) torsion angles reported in Table 2. In the present instance, the variations in the P—O(terminal) bond distances do not appear to correlate with the number and strength of the Cu—O and Li—O interactions. The terminal O atoms are each bonded either to two Li cations or to one Li and one Cu cation (Table 2). The four close oxygen neighbours of the Cu ion [which lies on a centre of symmetry, 4(c)1] are at distances of 1.926 (5) and 1.923 (5) Å for

O(2) and O(3), respectively, in a square-planar configuration. The Li ion is tetracoordinated in a distorted tetrahedral environment with Li—O distances ranging from 1.87 (1) to 1.98 (1) Å (Table 2).

References

CHENG, P. T., PRITZKER, K. P. H. & NYBURG, S. C. (1980). *Acta Cryst.* B36, 921–924.
Enraf-Nonius (1986). *Structure Determination Package.* Version 18. Enraf-Nonius, Delft, The Netherlands.
FAGGIANI, R. & CALVO, C. (1976). *Can. J. Chem.* 54, 3319–3324.
JOHNSON, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Structure of Strontium Lithium Indium Pyroborate, Sr₂LiInB₄O₁₀

BY KATHLEEN I. SCHAFFERS AND DOUGLAS A. KESZLER*

Department of Chemistry and Center for Advanced Materials Research, Oregon State University, Gilbert Hall 153, Corvallis, Oregon 97330-4003, USA

Abstract. Indium lithium distrontium decaoxotetraborate, $InLiSr_2B_4O_{10}$, $M_r = 500.23$, monoclinic, $P2_1/n$, $a = 12.637$ (1), $b = 5.251$ (1), $c = 13.748$ (1) Å, $\beta = 116.94$ (1)°, $V = 813.2$ (4) Å^3, $Z = 4$, $D_x = 4.085$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 154.94$ cm^{-1}, $F(000) = 912$, $T = 298$ K, $R = 0.060$ for 1731 reflections having $F_o^2 \geq 3\sigma(F_o^2)$. The structure is composed of a three-dimensional SrO_7 polyhedral framework with hexacoordinated In and pentacoordinated Li atoms in interstitial sites. Marked deviations from orthogonality in the distorted octahedral InO_6 group include O3—In—O9, 80.8 (3), O1—In—O9, 80.8 (3), O1—In—O9, 84.6 (3) and O2—In—O9, 97.0 (3)°. Pyroborate groups form layers extending in the plane (101̄).

Introduction. While searching for a suitable lithium borate flux for crystal growth of the compound $Sr_3In(BO_3)_3$ (Cox, Schaffers & Keszler, 1992), we discovered an interaction of the In compound with the metaborate $LiBO_2$ to form the new material $Sr_2LiInB_4O_{10}$. Here, we describe the structure of this material which is a derivative of the Sc analog $Sr_2LiScB_4O_{10}$ (Thompson & Keszler, 1989).

Experimental. Crystals of the title compound were grown from a melt containing 40 mol % SrO made

by heating $Sr(NO_3)_2$ (AESAR, ACS) in air, 6 mol % In_2O_3 (Alfa, ultrapure), 28 mol % $LiBO_2$ (AESAR, 99.9%), and 26 mol % B_2O_3 (Alfa, 99.98%). The sample was melted in a Pt crucible at 1303 K and slowly cooled at 10 K h⁻¹ to 1003 K then 88 K h⁻¹ to 300 K. The resulting crystals were washed in hot distilled water to remove any excess $LiBO_2$. A clear, colorless plate of dimensions 0.15 (1) × 0.07 (1) × 0.25 (1) mm was selected for X-ray structure analysis, and data were collected on a Rigaku AFC-6*R* single-crystal diffractmeter equipped with Mo *Kα* radiation. Accurate unit-cell parameters were derived by automatic centering and least-squares analysis of 20 peaks collected in the range $30 \leq 2\theta \leq 36°$. The ω–2θ scan technique was used to collect 2627 data in the range of indices $0 \leq h \leq 17$, $0 \leq k \leq 7$ and $-19 \leq l \leq 19$. From these measurements, 1731 unique reflections having $F_o^2 \geq 3\sigma(F_o^2)$ were obtained to $\sin\theta/\lambda = 1.36$ Å^{-1}. The intensities of three standard reflections measured after each segment of 200 data exhibited no significant decay during the collection.

The structure was refined with the *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1989). All atomic coordinates were determined by comparison with the isostructural compound $Sr_2LiScB_4O_{10}$. Positional parameters and isotropic thermal factors were refined for each atom, followed by averaging the data ($R_{int} = 0.083$), correction for absorption (transmission coefficients = 0.74–

* Author to whom correspondence should be addressed.

Table 1. *Positional parameters and equivalent isotropic temperature factors for* $Sr_2LiInB_4O_{10}$

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

	x	y	z	B_{eq} (Å^2)
Sr1	0.6849 (1)	0.3752 (2)	0.35420 (9)	0.84 (3)
Sr2	0.64955 (9)	0.4304 (2)	0.62330 (8)	0.79 (3)
In	0.63264 (6)	0.4272 (2)	0.88365 (6)	0.60 (2)
Li	0.116 (2)	0.110 (5)	0.600 (1)	1.5 (8)
B1	0.913 (1)	0.435 (3)	0.771 (1)	0.7 (4)
B2	0.603 (1)	0.861 (3)	0.209 (1)	0.9 (4)
B3	0.594 (1)	−0.100 (3)	0.448 (1)	0.8 (4)
B4	0.927 (1)	0.415 (2)	0.551 (1)	0.6 (4)
O1	0.6469 (7)	0.157 (2	0.7712 (6)	0.8 (3)
O2	0.8902 (7)	0.186 (2)	0.5047 (6)	1.0 (3)
O3	0.6830 (7)	0.024 (2)	0.5326 (6)	1.2 (3)
O4	0.5528 (6)	0.622 (2)	0.1914 (7)	0.9 (3)
O5	0.5710 (7)	0.649 (2)	0.4420 (6)	0.9 (3)
O6	0.8548 (7)	0.627 (3)	0.5091 (6)	1.1 (3)
O7	0.5203 (6)	0.074 (2)	0.3658 (6)	1.0 (3)
O8	0.5370 (7)	0.072 (2)	0.1463 (7)	1.2 (3)
O9	0.8619 (7)	0.209 (2)	0.7261 (6)	0.7 (3)
O10	0.7114 (7)	−0.089 (2)	0.2875 (7)	1.1 (3)

1.44) with the program *DIFABS* (Walker & Stuart, 1983) and full refinement with anisotropic thermal parameters on each atom. Final least-squares minimization on F_o with those 1731 reflections having $F_o{}^2 \geq 3\sigma(F_o{}^2)$ and 163 variables gave the residuals $R = 0.060$ and $wR = 0.067$ where the function $\Sigma w(|F_o| - |F_c|)^2$ is minimized with weights derived from counting statistics $[w = 1/\sigma^2(F_o)]$. Atomic form factors are from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final refinement afforded values of $S = 2.11$ and $\Delta/\sigma = 0.01$. Analysis of the final difference electron density map revealed maximum and minimum peaks corresponding to 1.05 and 0.81% of an Sr atom (220.3 e Å^{-3}), respectively. Atomic parameters are given in Table 1.*

A powder sample was made by grinding a stoichiometric combination of the reagents $Sr(NO_3)_2$ (AESAR, ACS), In_2O_2 (Alfa, ultrapure), $LiNO_3$ (Mallinckrodt, reagent grade) and B_2O_3 (Alfa, 99.98%) and heating in a Pt crucible at 923 K for 30 min. The sample was reground and heated at 1123 K for 16 h to give a single phase as identified by X-ray powder diffraction.

Discussion. The O-atom environment about each cation may be discerned by examination of the labeled sketch of the unit cell provided in Fig. 1. The compound contains heptacoordinated Sr, hexacoordinated In, pentacoordinated Li and tricoordinated B atoms. The integrity of the structure may be viewed as arising from a three-dimensional SrO_7 polyhedral framework (Fig. 2). The remaining

cations occupy sites associated with oblong tunnels that extend along the b axis. As indicated by the descriptive formula $Sr_2LiIn(B_2O_5)_2$, the compound contains a pyroborate group; the group is essentially flat in the principal atomic plane ($\bar{1}01$). Cations of similar type form sheets parallel to this plane so the structure adopts a common trait of borate and carbonate structures where cations are interleaved between layers of planar oxoanions.

Two chemically and crystallographically distinct Sr atoms are present in the structure. The Sr2 atom is heptacoordinated, occupying a distorted tetragonal base–trigonal base environment having an average Sr2—O bond length of 2.57 (6) Å. This length is equal within uncertainty to the average bond length of 2.58 (7) Å for Sr2—O in the compound $Sr_2LiScB_4O_{10}$ and 2.59 (6) Å for heptacoordinated Sr in $Sr_2Cu(BO_3)_2$ (Smith & Keszler, 1989). All of the $Sr2O_7$ polyhedra share edges with three neighboring $Sr2O_7$ polyhedra in the plane orthogonal to ($\bar{1}01$) to form a two-dimensional network as shown in Fig. 3; shared edges include one O5···O5 and two O1···O9 pairs. These layers repeat at intervals of half a unit cell. The Sr1 atom is bound to seven O atoms at lengths ranging from 2.468 (8)– 2.805 (9) Å with three additional O atoms, O3, O8
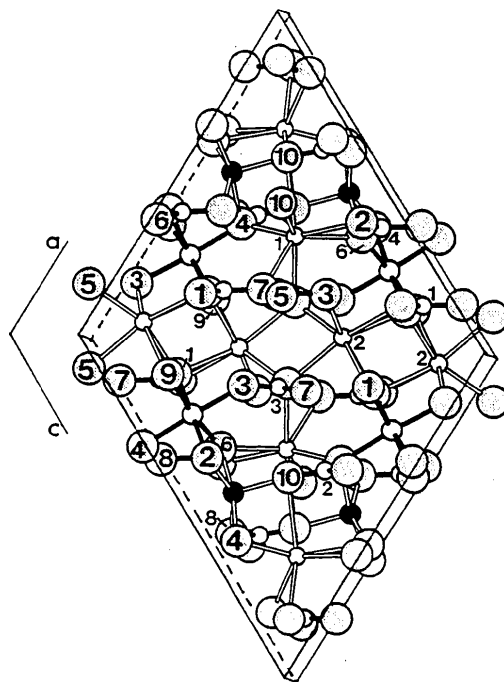

Fig. 1. Labeled drawing of the unit cell of $Sr_2LiInB_4O_{10}$ as viewed down the b axis where the small open circles with open bonds are Sr atoms, the larger shaded circles with open bonds are Li atoms, the larger open cirlces with shaded bonds are In atoms, the small open circles with shaded bonds are B atoms, and the largest shaded circles are O atoms.

and O10, at distances of 3.078 (9), 3.059 (8) and 3.023 (9) Å, respectively. In the material $Sr_2LiScB_4O_{10}$, the Sr1—O bond-length range is 2.478 (3)–2.745 (4) Å, comparing closely to the bond lengths observed for the In derivative. Adjacent Sr1 atoms link through atom O10 creating double chains that propagate in the **b** direction. The chains of Sr1 environments bridge two layers of $Sr2O_7$ polyhedra through their O5 atoms to form the three-dimensional Sr—O polyhedral framework (Fig. 2).

The five O atoms about the Li atom form a distorted square pyramid. Li—O distances range from 2.02 (2) to 2.19 (3) Å and compare well to a distance of 2.06 Å calculated from crystal radii (Shannon, 1976). A long Li—O2 interaction of 2.58 (2) Å would provide a distorted octahedral environment for the Li atom. From a bond-valence calculation (Brown, 1981), this interaction contributes approximately 7% of the univalent charge to
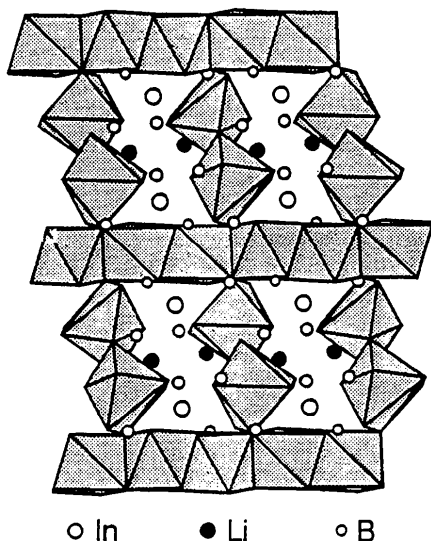

o In   ● Li   o B

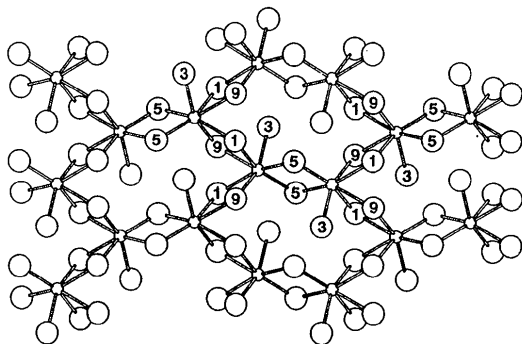Fig. 2. Perspective view of the SrO_7 polyhedral framework along [010].

Fig. 3. Sketch of the two-dimensional Sr2—O network extending in the plane (Ī01).

Table 2. *Selected bond distances* (Å) *and angles* (°) *for* $Sr_2LiInB_4O_{10}$

Sr1—O2	2.671 (8)	Sr2—O1	2.502 (8)
—O4	2.468 (8)	—O1	2.600 (8)
—O5	2.678 (9)	—O3	2.602 (9)
—O6	2.599 (8)	—O5	2.505 (8)
—O7	2.675 (8)	—O5	2.546 (8)
—O10	2.679 (9)	—O9	2.666 (8)
—O10	2.805 (9)	—O9	2.593 (8)
—O3	3.078 (9)		
—O8	3.059 (8)	B1—O1	1.37 (1)
—O10	3.023 (9)	—O7	1.39 (1)
		—O9	1.36 (2)
Li—O2	2.09 (3)		
—O4	2.15 (2)	B2—O4	1.37 (2)
—O6	2.18 (2)	—O8	1.42 (2)
—O8	2.19 (3)	—O10	1.33 (2)
—O10	2.02 (2)		
—O2	2.58 (2)	B3—O3	1.37 (2)
		—O5	1.34 (2)
In—O1	2.165 (8)	—O7	1.42 (1)
—O2	2.165 (9)		
—O3	2.140 (8)	B4—O2	1.34 (1)
—O4	2.105 (7)	—O6	1.39 (1)
—O6	2.114 (9)	—O8	1.42 (1)
—O9	2.139 (8)		

O2—Sr1—O3	61.0 (2)	O8—Sr1—O10	47.5 (2)
O2—Sr1—O5	112.5 (2)	O10—Sr1—O10	69.7 (2)
O2—Sr1—O6	53.3 (3)	O1—Sr2—O1	100.6 (2)
O2—Sr1—O10	72.5 (2)	O1—Sr2—O3	89.1 (3)
O4—Sr1—O5	81.1 (3)	O1—Sr2—O5	77.1 (3)
O4—Sr1—O8	63.3 (3)	O1—Sr2—O9	69.5 (3)
O4—Sr1—O10	50.1 (2)	O1—Sr2—O9	53.1 (3)
O5—Sr1—O6	76.7 (3)	O3—Sr2—O5	94.9 (3)
O5—Sr1—O7	72.6 (3)	O3—Sr2—O9	63.5 (2)
O6—Sr1—O7	128.9 (3)	O5—Sr2—O5	81.2 (3)
O7—Sr1—O10	72.7 (3)	O5—Sr2—O9	113.3 (3)
		O9—Sr2—O9	103.3 (2)

O1—In—O2	176.8 (3)	O1—B1—O7	123 (1)
O1—In—O3	96.7 (3)	O1—B1—O9	119 (1)
O1—In—O4	90.2 (3)	O7—B1—O9	117 (1)
O1—in—O6	90.3 (3)	O4—B2—O8	121 (1)
O1—In—O9	84.6 (3)	O4—B2—O10	123 (1)
O2—In—O3	86.1 (3)	O8—B2—O10	116 (1)
O2—In—O4	87.1 (3)	O3—B3—O5	126 (1)
O2—In—O6	88.0 (3)	O3—B3—O7	111 (1)
O2—In—O9	97.0 (3)	O5—B3—O7	123 (1)
O3—In—O4	172.6 (3)	O2—B4—O6	120.0 (9)
O3—In—O6	94.7 (3)	O2—B4—O8	118 (1)
O3—In—O9	80.3 (3)	O6—B4—O8	122 (1)
O4—In—O6	88.0 (3)	B1—O7—B3	137 (1)
O4—In—O9	97.1 (3)	B2—O8—B4	131 (1)
O6—In—O9	172.9 (3)		

O2—Li—O4	94 (1)	O4—Li—O10	94.5 (8)
O2—Li—O6	88.0 (8)	O6—Li—O8	88 (1)
O2—Li—O	152 (1)	O6—Li—O10	95.9 (8)
O2—Li—O10	100 (1)	O8—Li—O10	107 (1)
O4—Li—O6	169 (1)	O2—Li—O2	94.5 (8)
O4—Li—O8	85.4 (8)		

the Li atom. Through this interaction, a link is formed between adjacent LiO_5 polyhedra thereby creating edge-sharing Li_2O_{10} dimers with an Li···Li separation of 3.19 (4) Å. The corresponding long Li—O2 interaction in the Sc analog is 2.67 (1) Å.

The In atoms occupy distorted octahedral environments aligned in discrete rows along the *b* axis. The octahedra are separated in these rows by B_2O_5 groups so that the In atoms are completely isolated

from one another. The average In—O distance of 2.14 (3) Å is comparable to lengths of 2.18 (5) Å (Marezio, 1966) in In_2O_3, 2.127 (4) and 2.186 (4) Å in $Sr_3In(BO_3)_3$ (Cox, Schaffers & Keszler, 1992) and 2.17 Å calculated with crystal radii for a hexa-coordinated In atom. Each pyroborate layer is formed from one type of group with sheets of B1B3O$_5$ units and B2B4O$_5$ units stacking alternately along (101). B—O bond lengths range from 1.33 (2) to 1.42 (1) Å and compare to 1.342 (7)–1.432 (7) Å for $Sr_2LiScB_4O_{10}$, 1.33–1.38 Å for $Mg_2B_2O_5$ (Takéuchi, 1952) and 1.353 (3)–1.438 (3) Å for $Na_4B_2O_5$ (König, Hoppe & Jansen, 1979). The angles across the bridging O atoms, B1—O7—B3, 137 (1), B2—O8—B4, 131 (1)°, are similar to those in the compound $Sr_2LiScB_4O_{10}$, 133.8 (4) and 129.2 (4)°, respectively. Terminal BO$_2$ groups for each pyroborate anion are twisted from coplanarity by 10.5° for the B1B3O$_5$ unit and 3.1° for the B2B4O$_5$ unit compared to 13.8 and 1.1° for the corresponding anions in the Sc analog. Similar calculations have been performed on pyroborate anions for a variety of compounds (Thompson, Huang, Smith & Keszler, 1991) and deviations from planarity have been found to range from 0 to 76.8°. The ten crystallographically distinct O atoms in the structure have coordination numbers of three or four. Corresponding environments may be discerned from examination of Table 2.

References

BROWN, I. D. (1981). *The Bond Valence Method: an Empirical Approach to Chemical Structure and Bonding. Structure and Bonding in Crystals* II, edited by M. O'KEEFFE & A. NAVROTSKY, pp.1–30. New York: Academic Press.

COX, J. R., SCHAFFERS, K. I. & KESZLER, D. A. (1992). In preparation.

KÖNIG, V. H., HOPPE, R. & JANSEN, M. (1979). *Z. Anorg. Allg. Chem.* **449**, 91–101.

MAREZIO, M. (1966). *Acta Cryst.* **20**, 723–728.

Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Package.* Version 5.0. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.

SHANNON, R. D. (1976). *Acta Cryst.* **A32**, 751–767.

SMITH, R. W. & KESZLER, D. A. (1989). *J. Solid State Chem.* **81**, 305–313.

TAKÉUCHI, Y. (1952). *Acta Cryst.* **5**, 574–581.

THOMPSON, P. D., HUANG, J., SMITH, R. W. & KESZLER, D. A. (1991). *J. Solid State Chem.* **95**, 126–135.

THOMPSON, P. D. & KESZLER, D. A. (1989). *Solid State Ion.* **32/33**, 521–527.

WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

Thermal Effects in the Structure of Potassium Perrhenate

BY R. JULIAN C. BROWN

Chemistry Department, Queen's University, Kingston, Ontario K7L 3N6, Canada

BRIAN M. POWELL

AECL Research, Chalk River Laboratories, Chalk River, Ontario K0J 1J0, Canada

AND STEPHEN N. STUART

Division of Materials Science and Technology, CSIRO, Clayton, Victoria 3168, Australia

Abstract. The structure of $KReO_4$ has been determined by neutron powder diffraction at 298, 150 and 15 K. The structural parameters at room temperature are consistent with the results of Lock & Turner [*Acta Cryst.* (1975), B31, 1764–1765] and their temperature dependences are normal. The orientation of the anion changes by 1.20 (13)° over this temperature range.

Table 1. *Cell dimensions*

These data were obtained from the neutron diffraction profiles assuming a neutron wavelength of 1.49978 (9) Å. E.s.d.'s are given in parentheses and are taken from the Rietveld-program output. The space group is $I4_1/a$.

T (K)	a (Å)	c (Å)	c/a	V (Å^3)
15	5.65029 (8)	12.55557 (24)	2.22211 (5)	400.85 (1)
150	5.66115 (11)	12.61100 (32)	2.22764 (7)	404.16 (2)
298	5.68174 (15)	12.71178 (44)	2.23730 (10)	410.36 (3)