Structure of $Sr_3Sc(BO_3)_3$

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The structure of the compound $Sr_3Sc(BO_3)_3$ is described. Crystal data: FW = 484.24 amu, $R\bar{3}$ (No. 148), hexagonal axes, $a = 12.135(1)$, $c = 9.184(1)$ Å, $V = 1171.3(2)$ Å^3, $Z = 6$, Mo Kα ($\lambda = 0.710\ 69$ Å), $\mu = 206.38$ cm^{-1}, $F(000) = 1332$, $T = 296$ K, $R = 0.018$, $R_w = 0.022$ for 725 averaged reflections. The structure exhibits chains comprised of Sc-centered O octahedra and BO_3 triangles that are bridged by 9-coordinate Sr atoms. Each chain contains two crystallographically independent Sc atoms; the distorted octahedral environment about atom Sc1 is compressed along the trigonal axis, O1−Sc1−O1 = 85.20(7)°, while the environment about atom Sc2 is elongated along the same axis, O2−Sc2−O2 = 92.28(7)°. These angles are consistent with the chemical inequivalence of the environments as determined by their associations with neighboring Sr atoms.

Introduction

This report is the first in a series detailing the crystal chemistry of borates derived from the general formula $A_3M(BO_3)_3$ and represented by the structural types of the parent compounds $Sr_3Sc(BO_3)_3$ and $Ba_3Sc(BO_3)_3$. As we have reported,[1] derivatives of the Sr compound now comprise one of the larger structural families of solid-state oxide discovered to date. A detailed discussion of these derivatives is given in the third paper of this series.

Here, following, we describe the structure of the compound $Sr_3Sc(BO_3)_3$, a material that exhibits potentially useful optical characteristics when doped with the ion Cr^{3+}.[2] In the ensuing papers we discuss the structure of the compound $Ba_3Sc(BO_3)_3$, the derivatives of both structural types, and the interrelationships between them.

Experimental Section

Single crystals of the title compound were grown in a Pt crucible from a melt of composition 40 mol % SrO, 10 mol % Sc_2O_3, 40 mol % B_2O_3, and 10 mol % Li_2O that was cooled from 1313 to 773 K at 6 K/h. The crystals were isolated by treating the solidified melt with dilute HNO_3(aq). Unit-cell parameters were determined from least-squares refinement of 20 reflections in the range $17 \leq 2\theta \leq 35°$ that had been automatically centered on a Rigaku AFC6R diffractometer. A check of the Laue symmetry on the diffractometer revealed that the material crystallized in group $\bar{3}$. Crystal data and experimental conditions for the X-ray measurements are given in Table 1. Three standard reflections that were measured after each block of 200 data exhibited an overall average excursion of 1.6%.

Calculations were performed on a μVAX-II computer with programs from the TEXSAN system of programs.[3] Final least-squares refinement on F_o included 725 averaged data, 51 variables, and anisotropic displacement coefficients on each atom. The largest peak in the final difference electron density map corresponds to 1.3% of a Sr atom. Analysis of the residuals as a function of Miller indices and $|F_o|$ reveals no unusual trends. Final atomic parameters are listed in Table 2.

Table 1. Crystal Data and Experimental Conditions for $Sr_3Sc(BO_3)_3$

formula	$Sr_3Sc(BO_3)_3$
FW, amu	484.24
space group	$R\bar{3}$
a, Å	12.135(1)
c, Å	9.184(1)
V, Å^3	1171.3(2)
Z	6
T of data collection, K	296
ϱ_{calcd}, g cm^{-3}	4.12
radiation	graphite monochromated Mo Kα (λ(Kα) = 0.710 69 Å)
μ cm^{-1}	206.38
transmission factors	0.932−1.089
R_{int}	0.032
$R_w(F_o)$	0.022
$R(F_o)$ for $F_o^2 > 3\sigma(F_o^2)$	0.018

Table 2. Atomic Parameters for $Sr_3Sc(BO_3)_3$[a]

atom	x	y	z	B_{eq}
Sr	0.03998(2)	0.46988(2)	0.30855(2)	0.636(9)
Sc1	0	0	$^1/_2$	0.45(2)
Sc2	0	0	0	0.46(2)
B	0.1406(3)	0.4699(3)	0.0994(3)	0.65(8)
O1	0.0522(2)	0.1644(2)	0.3809(2)	0.79(6)
O2	−0.1779(2)	0.3683(2)	0.1934(2)	0.72(5)
O3	0.0047(2)	0.2637(2)	0.1865(2)	0.81(6)

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

Results and Discussion

A labeled drawing of the contents of the unit cell is given in Figure 1. The structure is simple and readily described as a collection of one-dimensional chains (Figure 2) extending along the c axis. Each chain contains Sc-centered distorted octahedra that are linked by triangular BO_3 groups. Two nonequivalent Sc sites are present in each chain, and they alternate in their lodgments along the chain axis. The chains, packing

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(2) Thompson. P. D.; Keszler, D. A. *Chem. Mater.* **1989,** *1,* 292.

(3) TEXSAN: Single Crystal Structure Analysis Software, Version 5.0, 1989. Molecular Structure Corporation, The Woodlands, TX 77381.

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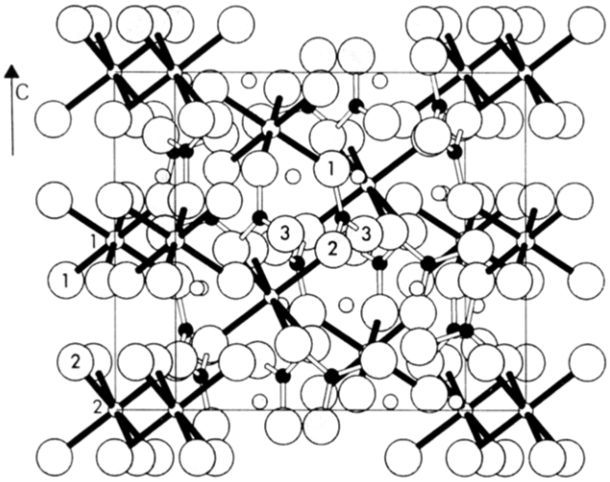

Figure 1. Sketch of the contents of the unit cell for the compound $Sr_3Sc(BO_3)_3$. Sr atoms are indicated as small lined circles, Sc atoms as small open circles, B atoms as small filled circles, and O atoms as large shaded circles, here and in all subsequent figures.

Table 3. Interatomic Distances (Å) and Angles (deg) for $Sr_3Sc(BO_3)_3$

Sr−O3	2.500(2)	O1−Sr−O2	51.20(6)
Sr−O2	2.524(2)	O1−Sr−O1	61.19(7)
Sr−O3	2.574(2)	O2−Sr−O3	70.12(5)
Sr−O1	2.714(2)	O2−Sr−O3	84.48(6)
Sr−O1	2.758(2)	O1−Sr−O2	94.50(6)
Sr−O3	2.760(2)	O2−Sr−O3	109.20(6)
Sr−O2	2.760(2)	O1−Sr−O2	125.40(6)
Sr−O1	2.765(2)	O1−Sr−O2	144.64(6)
Sr−O3	2.857(2)		
Sr−O(av)	2.69(13)		
Sc1−O1	2.077(2)	O1−Sc1−O1	85.20(7)
Sc2−O2	2.142(2)	O2−Sc2−O2	92.28(7)
B−O1	1.388(3)	O3−B−O2	121.2(2)
B−O2	1.383(3)	O3−B−O1	119.9(2)
B−O3	1.364(3)	O2−B−O1	118.7(2)
B−O(av)	1.38(1)		

according to the rhombohedral centering conditions of the cell, are bridged by Sr atoms occupying 9-coordinate environments. Linkage of these Sr-centered polyhedra in all directions, however, mitigates the anisotropy to be expected from the chain description, affording instead a dense, pure three-dimensional structure.

Selected interatomic distances and angles are listed in Table 3. Atoms Sc1 and Sc2 occupy distorted octahedral sites having S_6 ($\bar{3}$) point-group symmetry. The Sc1−O1 distance is 2.077(2) Å and the O1 octahedron is slightly compressed along the trigonal axis, O1−Sc1−O1 = 85.20(7)°. The Sc2−O2 distance, 2.142(2) Å, is longer and the O2 octahedron is now trigonally elongated, O2−Sc2−O2 = 92.28(7)°. These interatomic distances and angles may be compared to the Sc−O distance 2.120(2) Å and the trigonal elongation O−Sc−O = 92.28(1)° observed in the compound $ScBO_3$.[4]

These distances and angles are consistent with the chemical nonequivalence of the two Sc sites. The origin of this nonequivalence is best appreciated by considering the associations between the Sc and Sr environments as depicted in Figure 3. The O1 octahedron shares triangular faces with Sr-centered polyhedra, while the O2 octahedron shares only vertices. Because the symmetry of the O octahedra is S_6, each of the six triangular faces of the O1 polyhedron (related by the improper rotation axis) is shared by a Sr-centered polyhedron, and each vertex of the O2 polyhedron is shared by two Sr-centered environments. This results in placement of a distorted octahedron of Sr atoms about the coordination environment of atom Sc1 and a distorted icosahedron about Sc2. The trigonal compression of the O1 octahedron results from the decrease in its edge lengths from face sharing. The trigonal height of the O2 octahedron is determined by the span Sr−(O3⋯O3)−Sr in conjunction with the metrical and electrostatic requirements of the Sr and Sc atoms; the disposition of atom O3 is largely fixed through its interaction with the B atom to form the triangular planar BO_3 group.

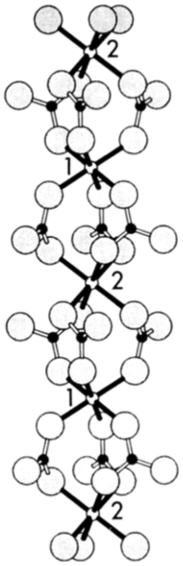

Figure 2. Drawing of an individual chain containing Sc1- and Sc2-centered distorted octahedra bridged by BO_3 groups.

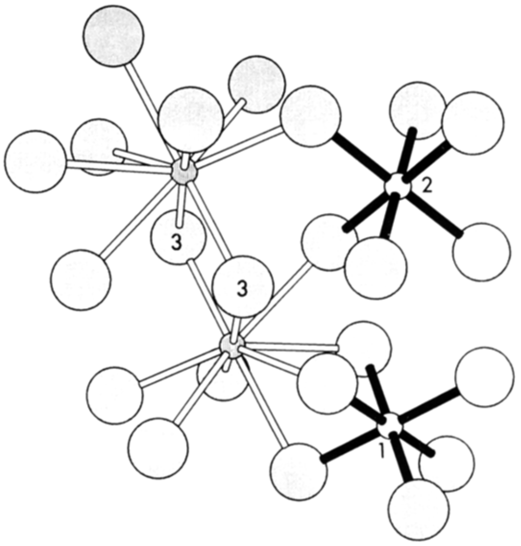

Figure 3. Drawing of a portion of the structure of $Sr_3Sc(BO_3)_3$ emphasizing linkages between the Sr- and Sc-centered polyhedra.

Sr−O distances, 2.500(2)−2.857(2) Å, are normal with the average length 2.69(12) Å comparing well to the value 2.71 Å computed from empirically derived radii.[5] The O environment about the Sr atom may be described as a highly distorted, capped square antiprism. By sharing vertexes, edges, and faces, each Sr-centered

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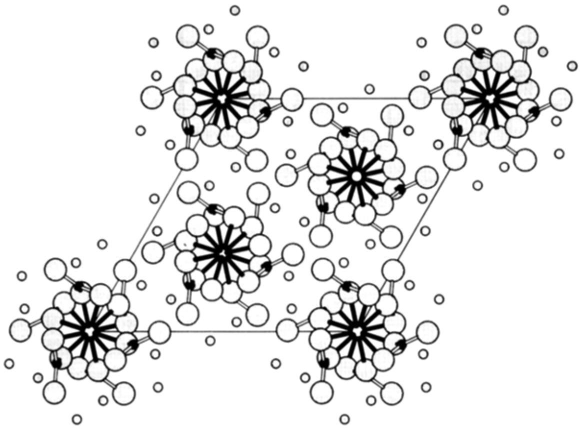

Figure 4. View of the structure of $Sr_3Sc(BO_3)_3$ along the *c* axis.

polyhedron associates with 11 others of the same type to form a complete three-dimensional framework.

The borate group is regular with the average B−O distance 1.38(1) Å comparing well to the 1.379 Å value deduced from crystal radii. The packing of the borate groups, however, is unique, affording the pinwheel pattern as seen in the view along the *c* axis (Figure 4). This contrasts to the more common packings of orthoborate groups that are typically found in layered-type structures related to those of the minerals calcite, dolomite, and huntite.

Atoms O1 and O3 occupy 5-coordinate sites that are best described as highly distorted triangular bipyramids; atom O1 binds 3 Sr, 1 Sc, and 1 B (Sc−O1−B = 135.0(2)°), while atom O3 binds 4 Sr and 1 B. Atom O2 resides in a distorted tetrahedral site comprised of 2 Sr, 1 Sc, and 1 B (B−O2−Sc2 = 114.5(2)°). All of these coordination numbers are greater than the 3-coordination of the O atom in the calcite derivative $ScBO_3$. This feature contributes to the high density of the title compound and its thermodynamic stability with respect to a simple mixture of the phases $Sr_3(BO_3)_2$ and $ScBO_3$. The formula volume of the compound $Sr_3Sc(BO_3)_3$—195.2 Å^3—is smaller than that computed for the mixture $Sr_3(BO_3)_2$ + $ScBO_3$—198.1 Å^3—indicating a greater lattice energy and stability for $Sr_3Sc(BO_3)_3$ should be observed, even though the Sr atom is 9-coordinate and the Sc atom is 6-coordinate in each compound.

We conclude by noting that the results indicate the structure to be highly ordered. In particular, there is no evidence for extensive disorder among the Sr and Sc sites.

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Supplementary Material Available: Listing of complete crystal data and anisotropic displacement coefficients (2 pages). Ordering information is given on any current masthead page.