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Crystal Structure of High Pressure SrB_2O_4(IV)

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Single crystals of SrB_2O_4(IV) were synthesised at 1250°C and 5.0 GPa in a multianvil press: Space group $Pa\bar{3}$, $Z = 12$, $a = 9.2123(7)$ Å. Structure refinement of 18 parameters to 245 unique data gave $R = 0.036$, $R_w = 0.021$. It was confirmed to be isostructural with CaB_2O_4, with BO_4 tetrahedra forming a three-dimensional framework.

Introduction

During an investigation of the high pressure phase relations of $SrGeO_3$ one of the experimental charges reacted with the boron nitride sample container and produced, among other phases, single crystals of a strontium borate phase. Examination by X-ray diffraction identified this as SrB_2O_4(IV), for which a powder pattern has been reported (*1*). Due to its similarity to the powder pattern of CaB_2O_4(IV) (*2*), SrB_2O_4(IV) was inferred (*1*) to have the same structure. We report the confirmation of this inference by single-crystal X-ray diffraction and structure refinement.

Experimental

The high pressure, high temperature runs were carried out in a tetrahedral-anvil press at the SERC High Pressure Laboratory at STC, Harlow, UK. Starting material for the runs was $SrGeO_3$ prepared from a 1 : 1 mixture of reagent grade $SrCO_3$ and GeO_2 heated at 1050°C for 24 hr. The product examined by powder X-ray diffraction showed good agreement with $SrGeO_3$(I) (*3*). The starting material was loaded in a cell assemblage consisting of a pyrophyllite tetrahedron, inside of which a cylindrical graphite furnace was fitted with a sleeve and two inserts of boron nitride that served as a capsule for the sample. The run temperatures were measured in the central part of the sample with a Pt–$Pt_{87}Rh_{13}$ thermocouple. Sample pressure versus ram load had been calibrated at room temperature with the Bi I–II, Th I–II, and Ba I–II transitions.

Single crystals were obtained from reaction between the experimental charge of Sr GeO_3 and its BN container, which had been held for 2 hr at 1250°C and 5.0 GPa, followed by slow cooling, in the tetrahedral-anvil press. It should be noted that this pressure is higher than the previously proposed stability limit of 4 GPa (*1*), although the microstructure of the recovered charge suggests nonequilibrium behavior. Energy dispersive electron microprobe analysis of the crystals indicated that Sr was the major cation present, with Ca as a variable (<5 mol%) con-

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taminant; B and O cannot be analyzed directly, but oxide totals were consistent with a composition SrB_2O_4.

A colorless transparent crystal was selected for X-ray diffraction experiments. Precession photographs confirmed cubic symmetry and absences $k = 2n + 1$ in $0kl$ (cyclically permutable). Data collection with a Krisel-automated Picker four-circle diffractometer, and subsequent data reduction, confirmed the Laue class as $m\bar{3}$, uniquely identifying the space group as $Pa\bar{3}$. Further experimental details are given in Table I. Structure refinements were carried out with RFINE88, a development version of RFINE4 (*4*); function minimized was $\Sigma w (|F_o| - |F_c|)^2$. Complex atomic scattering factors for neutral atoms were taken from *International Tables for X-Ray Crystallography* (*5*). A secondary extinction coefficient (*6*) refined to less than its *esd* and was therefore omitted. Refined atomic coordinates are given in Table II, tables of anisotropic thermal parameters (for Sr sites) and observed and calculated structure factors have been deposited.[1]

Discussion

SrB_2O_4 is confirmed to be isostructural with CaB_2O_4, as previously proposed (*1*): Bond lengths and angles for the two compounds are presented in Table III. The structure of both compounds consists of a fully connected three-dimensional framework of BO_4 corner-sharing tetrahedra with the large cations occupying voids within the

TABLE I

DATA COLLECTION AND REFINEMENT PARAMETERS

Crystal data	
Space group	$Pa\bar{3}$ (No. 205)
Cell dimensions	a = 9.2123(7) Å from 20 reflns 34 < 2θ < 39 centered by method of King and Finger (*8*)
Composition	SrB_2O_4
Z	12
Density (calcd)	4.41 g cm^{-1}
Crystal size	0.085 × 0.085 × 0.040 mm
$\mu_l(MoK\alpha)$	198.64 cm − 1
Data collection and reduction	
T	24°C
Radiation	$MoK\alpha$ (Nb filter; λ = 0.7093 Å)
ω-scan width	1°; 40 steps per scan
$2\theta_{max}$	60°
Standards	Two measured every 3 hr
Data limits	$-12 < h < 12$ $0 < k, l < 12$
Data collected	2209 symmetry allowed
Unique data	385
Absorption corrections	Method of Burnham (*9*)
Transmission coefficients	0.242–0.465
R_{int}	0.043 for 245 $F > 3\sigma(F)$
Structure refinement	
Data	245 $F > 3\sigma(F)$
Parameters	18
Weighting scheme	$w = \sigma^{-2}(F)$
Final R, R_w, G_{fit}	0.036, 0.021, 1.32
$\lvert\Delta\rho\rvert_{max}$	1.7 e · $Å^{-3}$

TABLE II

POSITIONAL PARAMETERS

	x	y	z	B_{eq}/B_{iso}
Sr1	0.0000	0.0000	0.0000	0.61
Sr2	0.37098(6)	0.37098	0.37098	0.33
B	0.1143(8)	0.1898(7)	0.3387(7)	0.4(1)
O1	0.3257(3)	0.2602(4)	0.1151(5)	0.14(6)
O2	0.0931(4)	0.2817(4)	−0.0022(5)	0.29(7)

Note. For Tables II and III, numbers in parentheses represent estimated standard deviations in the last decimal place quoted. Anisotropic thermal parameters refined for Sr1, Sr2, isotropic for B, O1, and O2.

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[1] See NAPS Document No.04800 for 4 pages of supplementary material. Order from ASIS/NAPS. Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, $1.50 for postage of microfiche orders.

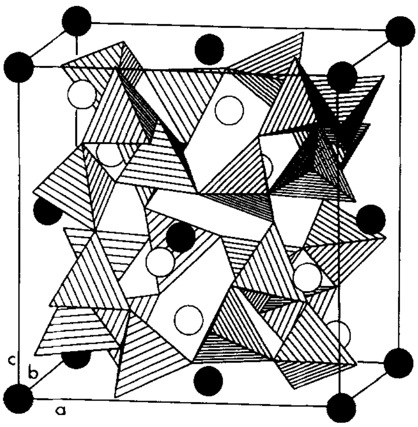

FIG. 1. A polyhedral (*7*) representation of the structure of SrB_2O_4. Filled circles are Sr1 sites, open circles Sr2.

framework (Fig. 1). The borate framework may be subdivided into 3-rings of BO_4 tetrahedra with point symmetry 3, which lie parallel to {111} planes, and which are connected into larger rings by sharing O2 oxygens. The 3-ring oxygen site, O1, is displaced slightly from the {111} plane of the three boron atoms by 0.31 Å in SrB_2O_4 and 0.36 Å in CaB_2O_4. Otherwise the substitution of Sr for Ca results in very little distortion of the 3-rings, with average B–O1 distances being identical, and the B–B distance within the ring being increased from 2.56 Å in CaB_2O_4 to 2.58 Å in SrB_2O_4. By contrast, the distance between B atoms linked by an O2 oxygen (i.e., outside of the 3-rings) in-

TABLE III

INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR SrB_2O_4 AND CaB_2O_4

Sr1—O1	6×	2.930(4)	Ca1—O1	6×	2.785(3)
Sr1—O2	6×	2.733(4)	Ca1—O2	6×	2.671(2)
Average		2.832	Average		2.728
Volume		53.5 Å^3	Volume		48.9 Å^3
Sr2—O1	3×	2.587(4)	Ca2—O1	3×	2.483(3)
Sr2—O1	3×	2.603(4)	Ca2—O1	3×	2.598(3)
Sr2—O2	3×	2.515(4)	Ca2—O2	3×	2.385(3)
Sr2—O2	3×	3.146(4)	Ca2—O2	3×	3.142(3)
Average (12)		2.713	Average (12)		2.652
Volume (12)		43.5 Å^3	Volume (12)		40.6 Å^3
Average (9)		2.568	Average (9)		2.489
B—O1		1.446(6)	B—O1		1.465(4)
B—O1′		1.515(8)	B—O1′		1.495(4)
B—O2		1.502(8)	B—O2		1.491(4)
B—O2′		1.491(8)	B—O2′		1.468(4)
Average		1.489	Average		1.480
Volume		1.69 Å^3	Volume		1.66 Å^3
Q.E.		1.001	Q.E.		1.001
A.V.		3.56	A.V.		3.00

Framework angles

O1—B—O1′	110.5(6)	O1—B—O1′	108.9
O1—B—O2	109.7(5)	O1—B—O2	108.2
O1—B—O2′	110.2(5)	O1—B—O2′	111.3
O1′—B—O2	105.8(4)	O1′—B—O2	107.2
O1′—B—O2′	109.8(5)	O1′—B—O2′	110.0
O2—B—O2′	110.8(5)	O2—B—O2′	111.2
B—O1—B	121.0(6)	B—O1—B	119.7
B—O2—B	124.3(3)	B—O2—B	120.1

Note. Data for CaB_2O_4 is from (*2*). Q.E. is the quadratic elongation of the polyhedron, A.V. the angle variance (*10*).

creases from 2.56 Å in CaB_2O_4 to 2.65 Å in SrB_2O_4. This expansion is generated by a simultaneous increase in both the B–O2–B angle by 4.2° and the mean B–O2 distance by 0.017 Å (Table III).

We therefore see that the expansion of the lattice from a = 9.008(1) Å (*2*) to a = 9.2123(7) Å, arising from the substitution of Sr for Ca is accommodated within the larger rings of the borate tetrahedral framework.

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