The Crystal Structure of Strontium Diborate, SrO·2B$_2$O$_3$

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Strontium diborate, SrO·2B$_2$O$_3$, crystallizes in the space group *Pmn*2$_1$ with unit cell dimensions: $a = 10.711 \pm 0.005$ Å, $b = 4.427 \pm 0.002$ Å, $c = 4.235 \pm 0.002$ Å and two formula units in the cell, corresponding to a calculated density of 4.02 g/cm^3. The crystal structure has been solved with two-dimensional Patterson and three-dimensional Fourier syntheses and refined with the method of least squares. A reliability index $R = 0.126$ was obtained for data from 189 three-dimensional reciprocal lattice points. The structure consists of a three-dimensional network of BO$_4$-tetrahedra. Some of the oxygens in the structure are bonded to three borons.

As part of a general survey of anhydrous polyborate structures, the crystal structure of strontium diborate has been determined. The preceding paper in this series is concerned with the structure of silver tetraborate.[1] This compound obeyed the rule that the number of borons in four-fold coordination is equal to the number of foreign cation charges. The same coordination behaviour of boron was previously observed in a series of alkali borates with a high boron oxide content. Considering the small energy requirement for a coordination change of boron,[2] it cannot be assumed that the rule is of general validity, especially if other cations than alkali atoms are introduced. The present investigation has revealed a new case where the rule breaks down. Here we have a type of anomalous coordination behaviour related to that discovered by Clark [3] in the hydrated borate mineral, tunnellite, SrO·3B$_2$O$_3$·4H$_2$O.

Recently X-ray data for strontium diborate have been published by Stewart and Rindone[4], and by Block, Perloff and Weir.[5] The unit cell dimensions given by the latter authors agree reasonably well with those reported here.

EXPERIMENTAL

Strontium diborate was crystallized around 900°C from a melt with a slight excess of boron oxide.

The following unit cell dimensions were determined with a least squares fit of powder diffraction data from a Hägg—Guinier camera, using lead nitrate as internal standard:

$$a = 10.711 \pm 0.005 \text{ Å}$$
$$b = 4.427 \pm 0.002 \text{ Å}$$
$$c = 4.235 \pm 0.002 \text{ Å}$$

With 2 formula units of $SrO:2B_2O_3$ in the cell, the calculated density becomes 4.02 g/cm^3. This is a relatively large value. However, by floating the sample in Clericis solution it was verified that the density was above 3.9 g/cm^3 and close to 4.0 g/cm.[3]

Single crystal integrated Weissenberg exposures were obtained with $CuK\alpha$-radiation around the two shortest axes for the zeroth to second layer. Systematic extinction were observed for the $h0l$ reflections when $h + l = 2n + 1$, indicating one of the space groups $Pmn2_1$ and $Pmmn$.

The crystal, which was rotated around the b-axis, had a quadratic cross-section 0.005 × 0.005 cm perpendicular to the axis of rotation and the crystal rotated around the c-axis had a corresponding cross-section 0.007 × 0.0085 cm. The linear absorption coefficient is 200 cm^{-1} for $CuK\alpha$-radiation, so that the absorption effects are not entirely negligible. No corrections for absorption were made, but a rough estimate of the effect will be given in the next paragraph.

Intensities were estimated visually from triple film packs by comparing the Weissenberg spots with a calibrated strip. After the Lorentz-polarization corrections, the intensities from the various layers around the two axes were adjusted so as to bring all the values on a common scale. For reciprocal lattice points, where two measurements were available, those from the smaller crystal were given a higher weight.

THE STRUCTURE DETERMINATION

The Patterson projections revealed a strontium—strontium vector incompatible with the special two-fold positions in the space group $Pmmn$. It was therefore concluded that the correct space group is $Pmn2_1$. Based on information from the Patterson functions about the strontium position, a three-dimensional electron density distribution was calculated. The summation contained a false symmetry (since phases were obtained only from strontium positions) but peaks due to the false symmetry could be eliminated by considering interatomic distances. The structure thus obtained was refined to a reliability index of 12.6 % with the method of least squares, using the program written by Åsbrink and Brändén for the Facit computer. Absolute values of the calculated structure factors are given in Table 1 and the final atomic parameters are reported in Table 2. The atoms Sr and O_1 occupy special two-fold positions in the space group. The origin along the z-axis is arbitrarily fixed on the strontium atom.

From the two last columns given in Table 2, the strontium atom appears to have a significant negative temperature factor parameter $B = -0.67$. This is largely accounted for by absorption errors, however. If the crystal with cross-section 0.005 × 0.005 cm (respectively 0.007 × 0.0085 cm) had been a cylinder with the same cross-sectional area, the absorption correction for the equatorial layer would, well within the accuracy of the intensity reading, correspond to multiplying the intensities with an artificial temperature factor with parameter value $2B = 0.4$ (respectively $2B = 0.6$)... Somewhat larger corrections are valid for the upper layers, and larger corrections also apply for certain planes in the equatorial layer of the quadratic or rectangular crystals. It is therefore reasonable to blame the absorption errors for the fact that the temperature factor parameter for strontium becomes negative in the least squares refinement.

Table 1. Observed and calculated structure factors, multiplied by 10.

h k l	F_o	$|F_c|$	h k l	F_o	$|F_c|$	h k l	F_o	$|F_c|$
2 0 0	263	328	3 1 2	469	414	8 2 2	566	483
4 0 0	422	469	4 1 2	384	226	9 2 2	302	296
6 0 0	601	625	5 1 2	530	482	10 2 2	363	395
8 0 0	910	914	6 1 2	106	92	0 2 3	255	165
10 0 0	352	333	7 1 2	501	492	1 2 3	331	301
12 0 0	310	325	8 1 2	79	90	2 2 3	366	375
1 0 1	404	377	9 1 2	390	396	3 2 3	575	494
3 0 1	645	765	10 1 2	129	112	4 2 3	134	182
5 0 1	475	548	11 1 2	351	368	5 2 3	584	459
7 0 1	504	467	0 1 3	554	538	6 2 3	343	319
9 0 1	366	370	1 1 3	255	192	7 2 3	231	267
11 0 1	525	527	2 1 3	736	646	8 2 3	137	162
0 0 2	889	858	4 1 3	457	287	0 2 4	334	416
2 0 2	563	653	5 1 3	128	134	1 2 4	196	255
4 0 2	489	517	6 1 3	513	568	2 2 4	275	396
6 0 2	519	549	7 1 3	116	112	3 2 4	160	208
8 0 2	621	650	8 1 3	443	510	4 2 4	434	428
10 0 2	343	392	9 1 3	181	189	0 3 0	316	283
1 0 3	396	332	1 1 4	557	427	1 3 0	246	214
3 0 3	581	593	2 1 4	149	125	2 3 0	272	225
5 0 3	581	655	3 1 4	351	409	3 3 0	472	434
7 0 3	119	187	4 1 4	114	135	4 3 0	692	728
9 0 3	419	455	5 1 4	466	465	5 3 0	425	437
0 0 4	401	488	6 1 4	81	123	6 3 0	152	165
2 0 4	478	506	0 2 0	778	985	7 3 0	90	120
4 0 4	390	473	1 2 0	178	180	8 3 0	248	219
6 0 4	325	419	2 2 0	434	505	9 3 0	325	337
0 1 0	190	161	3 2 0	434	414	0 3 1	460	431
1 1 0	272	351	4 2 0	422	377	1 3 1	504	428
2 1 0	44	17	5 2 0	76	75	2 3 1	607	472
3 1 0	504	689	6 2 0	583	518	3 3 1	284	232
4 1 0	487	518	7 2 0	334	277	4 3 1	451	367
5 1 0	451	450	8 2 0	675	636	5 3 1	213	206
6 1 0	49	12	9 2 0	166	165	6 3 1	484	413
7 1 0	510	506	10 2 0	369	344	7 3 1	484	431
8 1 0	59	62	11 2 0	316	330	8 3 1	419	367
9 1 0	255	238	0 2 1	580	459	9 3 1	355	309
10 1 0	167	163	1 2 1	475	423	10 3 1	375	330
11 1 0	525	501	2 2 1	313	254	0 3 2	331	269
12 1 0	161	162	3 2 1	486	433	1 3 2	384	317
0 1 1	513	536	4 2 1	211	212	2 3 2	360	344
1 1 1	316	259	5 2 1	443	419	3 3 2	451	341
2 1 1	700	784	6 2 1	434	365	4 3 2	598	477
3 1 1	108	131	7 2 1	463	388	5 3 2	407	293
4 1 1	680	783	8 2 1	243	217	6 3 2	266	257
5 1 1	96	69	9 2 1	346	349	7 3 2	372	337
6 1 1	504	508	10 2 1	164	181	8 3 2	296	258
7 1 1	355	247	11 2 1	357	363	9 3 2	313	277
8 1 1	495	421	0 2 2	645	578	0 4 0	166	114
9 1 1	119	111	1 2 2	266	220	1 4 0	437	414
10 1 1	656	642	2 2 2	545	484	2 4 0	434	424
11 1 1	93	93	3 2 2	360	272	3 4 0	363	333
12 1 1	378	371	4 2 2	496	506	4 4 0	278	239
0 1 2	125	187	5 2 2	272	281	5 4 0	246	277
1 1 2	660	605	6 2 2	507	416	6 4 0	331	312
2 1 2	219	214	7 2 2	193	227	7 4 0	337	402

h k l	F_o	$|F_c|$	h k l	F_o	$|F_c|$	h k l	F_o	$|F_c|$
0 4 1	484	362	7 4 1	360	312	6 4 2	334	248
1 4 1	437	337	0 4 2	210	183	0 5 0	293	345
2 4 1	522	433	1 4 2	437	373	1 5 0	61	83
3 4 1	155	101	2 4 2	396	282	2 5 0	340	433
4 4 1	428	349	3 4 2	407	366	0 5 1	193	229
5 4 1	246	202	4 4 2	413	414	1 5 1	387	401
6 4 1	516	470	5 4 2	360	321	2 5 1	222	151

Table 2. Atomic position parameters (with standard deviations) as fractions, multiplied by 1000, of the unit cell edge. The last two columns give the parameter B (together with its standard deviation) of the temperature factor $\exp[-B(\sin \Theta/\lambda)^2]$.

Atom	x/a	$\sigma_{x/a}$	y/b	$\sigma_{y/b}$	z/c	$\sigma_{z/c}$	B (in Å²)	σ_B
Sr	0		289	1	0		−0.67	0.07
O_1	0		728	12	454	20	1.1	1.1
O_2	359	2	857	7	064	8	−0.6	0.5
O_3	221	3	631	8	335	9	0.0	0.6
O_4	365	4	226	9	335	12	0.6	0.8
B_1	379	4	174	9	976	20	−0.6	0.7
B_2	246	5	671	11	963	19	0.1	0.9

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

A projection of the structure along the a-axis is shown in Fig. 1. The structure consists of a three-dimensional network of BO_4-tetrahedra. The
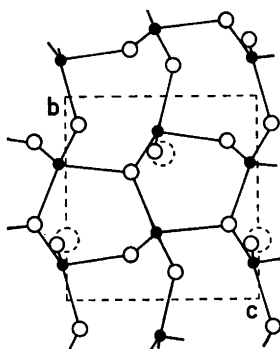

Fig. 1. Projection along the a-axis. Filled circles represent boron, open circles represent oxygen, large dashed circles represent strontium. The unit cell is indicated with dashed lines. Oxygens closest to strontium in projection form bridges with layers below or above, which are mirror images of the layer shown.

layer of BO_4-tetrahedra, shown in the figure, is connected with its own mirror image exactly above or below through the atom O_1. The O_1 atom, seen closest to strontium in the projection, will thus appear in this projection as if it were bonded to only one boron. (O_1 atoms with z-parameters 0.454 connect with layers above, those with z-parameters 0.954 connect with layers below).

Table 3. Boron—oxygen bond distances and shortest strontium—oxygen distances, with standard deviations. Each of the tabulated distances from strontium to O_2, O_3, and O_4 occurs twice, so that strontium has 9 oxygen neighbours below 3 Å.

$B_1 - O_1$	1.37 ± 0.04 Å	$Sr - O_1$	2.73 ± 0.07 Å
$B_1 - O_2$	1.47 ± 0.05		3.02 ± 0.07
$B_1 - O_3$	1.50 ± 0.06		3.14 ± 0.07
$B_1 - O_4$	1.55 ± 0.09		3.39 ± 0.07
$B_2 - O_2$	1.53 ± 0.06	$Sr - O_2$	2.47 ± 0.03
$B_2 - O_3$	1.48 ± 0.06		2.90 ± 0.03
$B_2 - O'_3$	1.61 ± 0.09		
$B_2 - O_4$	1.38 ± 0.06	$Sr - O_3$	3.09 ± 0.03
			3.15 ± 0.03
		$Sr - O_4$	2.68 ± 0.04
			2.79 ± 0.04

It is also seen from Fig. 1 that the structure contains six-membered boron-oxygen rings. Such rings are a very common feature in a wide variety of borate structures. The present structure may even be described as chains along the *c*-axis formed by these six-membered rings sharing edges. The chains are crosslinked with neighbouring chains at regular intervals.

The boron-oxygen bond lengths are given in Table 3. The average value of these bond lenghts, 1.49 Å, is slightly larger than the average value of 1.47 Å found for BO_4-tetrahedra in several structures. The spread of the individual bond lengths about the average value cannot be considered significant (perhaps with the exception of the $B_1 - O_1$ distance). It is not unlikely, however, that the BO_4-tetrahedra could be somewhat distorted.

The atom O_3 is remarkable inasmuch as it is bonded to three boron atoms. This situation is not quite unique, however. Structures with oxygens three-fold coordinated by boron have been reported for hexagonal boron oxide by Berger [6] and recently for the mineral tunellite, $SrO \cdot 3B_2O_3 \cdot 4H_2O$, by Clark.[3] Three-bonding oxygens with two bonds to boron and a third to hydrogen are known from some metaboric acids.[7] In the present structure the average of the three bond distances to O_3 (1.53 Å) seems to be somewhat larger than the average of the remaining boron-oxygen distances (1.46 Å). The available data are not sufficiently accurate to establish this lengthening with certainty, but a similar lengthening of the boron-oxygen bond for three-fold coordinated oxygen has been indicated by the study of tunellite.[3]

The coordination of strontium by oxygen is definitely irregular. An irregular cation coordination has previously been observed in other anhydrous borates.[1] It is therefore difficult to establish a meaningful value for the coordination number of the cation in these phases. Table 3 lists values for the 16 shortest strontium-oxygen distances ranging upwards from 2.74 Å to 3.39 Å. The sum of the ionic radii of strontium and oxygen is 2.35 Å. Setting an arbitrary limit at 2.90 Å for the first coordination sphere of strontium, a coordination number of 9 follows. It is interesting to note that the three-fold coordinated oxygen is comparatively far removed (3.09 Å or more) from strontium.

The structure reported here demonstrates the precarious balance of boron between the coordination numbers three and four. This circumstance has previously been emphasized by the author, *e.g.* it has been proposed that the comparatively low viscosity of molten boron oxide is due to the low energy required for activating states with four-fold coordinated boron and three-fold coordinated oxygen.[8]

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