

The Crystal Structure of SrBe₃O₄*

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The crystal structure of SrBe₃O₄ has been derived and refined from X-ray diffraction data. The hexagonal unit cell with $a_0 = 4.5961$, $c_0 = 8.9300$ Å contains two formula weights and conforms to the space group $P\bar{6}2c$. The basic structure is composed of nearly close-packed layers of oxygen and strontium atoms in which strontium atoms occupy sites of ninefold anion coordination. Four of the beryllium atoms in each cell have normal tetrahedral oxygen-atom environments but the other two are trigonally coordinated to oxygen.

Introduction

Previously reported determinations of crystal structures of Ca₁₂Be₁₇O₂₉, Y₂BeO₄, and La₂Be₂O₅ (Harris & Yakel, 1966, 1967, 1968) show that beryllium-oxygen atom coordinations may occur as either planar trigonal BeO₃ groupings or as the more usual tetrahedral BeO₄ groupings. While the problems besetting experimental verification of thermodynamic stability in these systems are by no means resolved, we believe that trigonal coordinations occur in unstable or metastable phases.

We describe here the crystal structure of a strontium beryllium oxide compound whose composition was fixed by the structural analysis as SrBe₃O₄. Good agreement is found between our X-ray diffraction data for SrBe₃O₄ and powder diffraction data for a compound called Sr₂Be₉O₁₁, reported by Mercer & Miller (1964, 1966). The SrO-BeO equilibrium diagram (Levin, Robbins & McMurdie, 1964) shows only one phase, called SrBe₄O₅, lying between Sr₂Be₃O₅ and BeO. The diagram indicates a peritectic decomposition of this phase at 1380°C.

Experimental

Single crystals of SrBe₃O₄ were grown from a mixture of 1SrO (as SrCO₃):4BeO which was heated on the platinum strip of a resistance furnace to about 1400°C, in air. The mass appeared essentially molten at this temperature. The mixture was cooled to 1000°C at an average rate of 10°C min⁻¹ and then rapidly brought to room temperature by cutting off power to the strip heater. The resulting material consisted of colorless, clear crystals of SrBe₃O₄ as the major phase and BeO as a minor phase. We were not able to form SrBe₃O₄ by solid state reactions, and we observed partial decomposition of the compound on heating to 1100°C.

The SrBe₃O₄ crystals had a plate-like morphology and were optically isotropic when viewed normal to

the plate faces, but birefringent when viewed in other directions. A uniaxial positive optic figure was observed. Refractive indices measured parallel and perpendicular to plate face normals were $n_e = 1.72 \pm 0.01$ and $n_o = 1.71 \pm 0.01$, respectively. Occasional cleavages normal to the plate faces intersected at 120° angles, suggestive of hexagonal or trigonal symmetry.

The single crystal selected for X-ray diffraction experiments can be described as a halved hexagonal prism. The halving occurred normal to basal pinacoid faces {0001} and parallel to a trigonal prism face {10 $\bar{1}$ 0}. The crystal dimensions were 0.025 mm between pinacoid faces and 0.100–0.150 mm between prism faces. The mounting fiber's direction was close to what was later shown to be an hexagonal a axis.

Film data collected using Cu $K\alpha$ ($\lambda = 1.54178$ Å) and Mo $K\alpha$ ($\lambda = 0.71069$ Å) X-radiations confirmed the hexagonal crystal system and showed 6/ mmm Laue symmetry. The only observed systematic space group absences occurred for reflections $hh.l$ with l odd. Possible space groups were therefore $P6_3/mmc$, $P\bar{6}2c$, and $P6_3mc$. Since the crystals showed a pyroelectric effect normal to the c axis, the space group $P\bar{6}2c$, D_{3h}^4 was selected as most probable. Absences were also noted for reflections $hk.l$ with $h-k = 3n$ and l odd.

The crystal was mounted on a computer-controlled four-circle diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968) for the measurement of reflection scattering angles and the collection of intensity data. Cu $K\alpha$ X-radiation was used for the former measurements. Lattice parameters derived from them were $a_0 = 4.5961 \pm 0.0002$ and $c_0 = 8.9300 \pm 0.0004$ Å. The theoretical density, computed with two formula weights of SrBe₃O₄ per cell, is 3.6306 ± 0.0005 g.cm⁻³, which may be compared with an observed density of 3.4 ± 0.1 g.cm⁻³ measured with an 0.014 g. sample weighed in a Berman balance. Prior to definition of the stoichiometry by the structural analysis, the observed density and unit cell volume indicated that the number of strontium atoms per cell is probably two.

Intensity data were initially collected with Cu $K\alpha$ X-radiation. This set included a total of 486 measured reflections of which 117 were non-equivalent and al-

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lowed by the space group. The data were corrected for Lorentz, polarization, and absorption effects. In the latter correction, the crystal shape was approximated by seven bounding planes and the *ORABS program* (Wehe, Busing & Levy, 1962) was used to generate transmission coefficients. A linear absorption coefficient corresponding to the stoichiometry Sr₂Be₉O₁₁ was assumed; this small error was later rectified when the true composition became apparent. Relative $|F|^2$ values were placed on an approximate absolute scale following the method of Wilson (1942). Again, a small error was introduced in this scale factor owing to uncertainty regarding composition.

A second intensity data set was collected with Mo $K\alpha$ X-radiation after we had obtained the trial structure. This set included 520 nonequivalent, space-group-allowed reflections. Corrections were applied as described above, except that the linear absorption coefficient for SrBe₃O₄ was used in the absorption correction. In the final stages of refinement, we corrected these data for secondary extinction by the method of Zachariasen (1963).

Structure derivation and refinement

A three-dimensional Patterson function, computed from the Cu $K\alpha$ data set, showed peaks consistent with atoms in the following positions of space group $P\bar{6}2c$: 2 strontium atoms in 2(c) ($\frac{1}{3}, \frac{2}{3}, \frac{1}{4}; \frac{2}{3}, \frac{1}{3}, \frac{3}{4}$); 6 oxygen atoms in 6(g)($x, 0, 0$; *etc.* with $x \approx \frac{2}{3}$); 2 oxygen atoms in 2(d)($\frac{2}{3}, \frac{1}{3}, \frac{1}{4}; \frac{1}{3}, \frac{2}{3}, \frac{3}{4}$). The presence of 4Be atoms in 4(f)($\frac{1}{3}, \frac{2}{3}, z$; *etc.* with $z \approx 0.58$) was also suggested.

Atom form factors used in structure factor calculations were those given by Cromer & Waber (1965) for Be²⁺ and Sr²⁺, and by *International Tables for X-ray Crystallography* (1962) for O⁻. Anomalous dispersion

corrections to the strontium atom form factors were taken from the latter source. A structure factor calculation including only strontium atoms was used to obtain approximate phases for an electron density map of the structure. In this synthesis we found the 2 strontium, 6 oxygen, and 4 beryllium atoms located with the Patterson function and also found 2 beryllium atoms in positions 2(a)(0,0,0; 0,0, $\frac{1}{2}$). No other significant peaks appeared in the map, and it was at this point in the analysis that the 1SrO:3BeO stoichiometry was tentatively accepted.*

The Mo $K\alpha$ intensity data set was then collected, corrected, and used to refine the trial structure by iterative least-squares calculations. The weighting scheme used in previous analyses (Harris & Yakel, 1967, 1968) was adopted. The final least-squares cycles were computed with anisotropic atom temperature factors and resulted in measures of agreement $R_1 = 0.047$, $R_2 = 0.052$, and $\sigma = 0.80$, where $R_1 = \Sigma (||F|_o - |F|_c|) / \Sigma |F|_o$, $R_2 = \Sigma (||F|_o^2 - |F|_c^2|) / \Sigma |F|_o^2$, and $\sigma = \sqrt{\Sigma w (|F|_o^2 - |F|_c^2)^2} / \sqrt{n - m}$. In the definition of σ , w is a weight, n is the number of observations, and m is the number of variable parameters. Sums were taken over all 520 nonequivalent reflections. A difference map, computed from the final values of F_c and with all atoms removed, showed no peaks containing more than 0.5 electron.

Atomic positions and thermal parameters from the final least-squares cycle are listed in Table 1. These parameters yield $|F|_c$ values that are compared with observed $|F|_o$ values in Table 2.

* *Note added in proof*: - The compound is most probably identical with that studied by Mercer & Miller (1964, 1966) and possibly identical with that reported by Levin, Robbins & McMurdie (1964); we would ascribe the differences in formula to inaccuracies in chemical analysis.

Table 1. Atomic parameters for SrBe₃O₄

Least-squares standard errors are given in parentheses.

| | Fractional position parameters | | | Thermal vibration parameters* | | | | | |
|-------|--------------------------------|---------------|---------------|-------------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> ₁₁ | <i>B</i> ₂₂ | <i>B</i> ₃₃ | <i>B</i> ₁₂ | <i>B</i> ₁₃ | <i>B</i> ₂₃ |
| Sr | $\frac{1}{3}$ | $\frac{2}{3}$ | $\frac{1}{4}$ | | | | | | |
| Be(1) | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.57075 (37) | | | | | | |
| Be(2) | 0 | 0 | 0 | | | | | | |
| O(1) | $\frac{2}{3}$ | $\frac{1}{3}$ | $\frac{1}{4}$ | | | | | | |
| O(2) | -0.33371 (43) | 0 | 0 | | | | | | |
| | | | | | | | | | |
| Sr | 0.00790 (11) | 0.00790 | 0.00114 (2) | 0.00395 | 0 | 0 | | | |
| Be(1) | 0.00767 (87) | 0.00767 | 0.00102 (24) | 0.00383 | 0 | 0 | | | |
| Be(2) | 0.00542 (122) | 0.00542 | 0.00181 (40) | 0.00271 | 0 | 0 | | | |
| O(1) | 0.01381 (85) | 0.01381 | 0.00105 (19) | 0.00690 | 0 | 0 | | | |
| O(2) | 0.00427 (50) | 0.00517 (79) | 0.00212 (11) | 0.00258 | -0.00032 | -0.00063 (30) | | | |

* Coefficients in the expression $B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl$. For atoms Sr, Be(1), Be(2), and O(1), $B_{22} = B_{11}$, $B_{12} = B_{11}/2$, $B_{13} = B_{23} = 0$. For atoms O(2), $B_{12} = B_{22}/2$, $B_{13} = B_{23}/2$.

Table 2. Comparison of observed and calculated |F| Values

FC=10. |F|calc, FO=10. |F|obs. SIG=10. sigma(|F|obs), where sigma(|F|obs) is defined as sigma(Fobs^2)/2|F|obs unless Fobs^2 is less than 1 (indicated by a W to the right of the entry for SIG in the Table), in which case SIG=sigma(Fobs^2). PH=tan^-1(Bcalc/Acalc) to the nearest degree.

A large grid of numerical data organized into columns and rows, with headers FC, FO, SIG, PH for each column group. The data includes various numerical values and symbols like 'H' and 'W' indicating specific conditions or observations.

Description of the structure

Important interatomic distances and angles were computed from the parameters of Table 1 with the *ORFFE* program of Busing, Martin & Levy (1964). They are given in Table 3.

Table 3. *Interatomic distances and angles in SrBe_3O_4*

| Distances | | |
|---------------------|----------|---------------------|
| | <i>D</i> | Standard deviations |
| (3)* Sr—O(1) | 2.6536 Å | 0.0001 Å |
| (6) Sr—O(2) | 2.7071 | 0.0006 |
| (1) Be(1)—O(1) | 1.601 | 0.003 |
| (3) Be(1)—O(2) | 1.656 | 0.002 |
| (3) Be(2)—O(2) | 1.534 | 0.002 |
| Angles | | |
| | Angle | Standard deviations |
| (2)* O(1)—Sr —O(1) | 120° | — |
| (2) O(1)—Sr —O(2) | 60.652 | 0.07° |
| (2) O(1)—Sr —O(2) | 90.03 | 0.04 |
| (2) O(1)—Sr —O(2) | 119.31 | 0.03 |
| (1) O(2)—Sr —O(2) | 111.11 | 0.03 |
| (2) O(2)—Sr —O(2) | 58.66 | 0.03 |
| (2) O(2)—Sr —O(2) | 147.14 | 0.01 |
| (3) O(1)—Be(1)—O(2) | 112.4 | 0.1 |
| (2) O(2)—Be(1)—O(2) | 106.4 | 0.1 |
| (2) O(2)—Be(2)—O(2) | 120 | — |

* Numbers in parentheses preceding interatomic distances indicate the number of symmetrically equivalent distances about the metal atom named. Those preceding angles indicate the number of symmetrically equivalent angles about the vector from one of the set of oxygen atoms named first to the metal named.

The structure contains pseudo-close-packed layers of atoms in a hexagonal sequence $AB_1AB_2AB_1\dots$. *A* layers consist only of oxygen atoms with no vacancies; *B* layers have an equal and ordered distribution of

oxygen atoms, strontium atoms, and vacancies. The latter are at positions $2(b)$ $(0,0,\frac{1}{4}; 0,0,\frac{3}{4})$, and the location of strontium or oxygen atoms at $x=\frac{1}{3}$, $y=\frac{2}{3}$ distinguishes the B_1 and B_2 layers. The deviation from close-packing is apparent in the deviation of the axial ratio $(c/2)/(a/\sqrt{3})=1.683$ from the ideal value of 1.633. Finally, beryllium atoms $4(f)$ are located in tetrahedral interstices between *A* and *B* layers, while beryllium atoms $2(a)$ are trigonally coordinated with *A*-layer-oxygen atoms.

These arrangements are shown in Fig. 1, a stereoscopic drawing prepared with the *ORTEP* program (Johnson, 1965). The ninefold coordination of oxygen atoms about a strontium atom forms a trigonal prism with three additional coordinating oxygen atoms in the prism midplane, but skewed with respect to the prism face centers. The average strontium–oxygen separation in this group is 2.69 Å, which may be compared with separations of 2.57 and 2.75 Å for Sr–O separations in sixfold [*e.g.* SrO (Gerlach, 1922)] and twelffold [*e.g.* SrTiO₃ (Goldschmidt, 1926)] coordinations, respectively.

The trigonally coordinated beryllium atom is at the center of an equilateral triangle of oxygen atoms with all Be–O distances equivalent by symmetry and 1.535 Å in length. This value is consistent with previous observations of similar groups in Y₂BeO₄ and Ca₁₂Be₁₇O₂₉ (Harris & Yakel, 1966, 1967, 1968). The tetrahedra of oxygen atoms about the four-coordinated beryllium atoms form end caps on the trigonal prisms of strontium–oxygen coordination polyhedra. These tetrahedra contain three symmetrically equivalent Be–O separations of 1.656 Å and one shorter 1.600 Å contact. The short separation occurs in a line parallel with the *c* axis and is probably the result of repulsion by the strontium atom lying on that same line and screened from a $4(f)$ beryllium atom by three oxygen atoms of a trigonal prism (or tetrahedron) base.

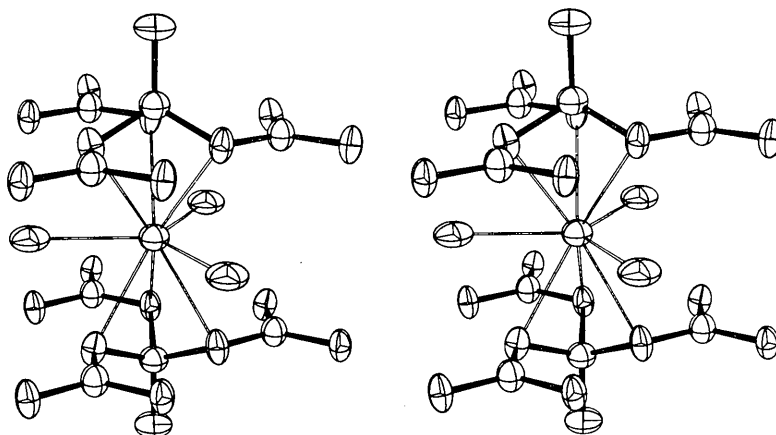


Fig. 1. Stereoscopic drawings of the environs of the strontium atom in SrBe_3O_4 . The *c* axis is approximately vertical while an *a* axis is almost normal to the plane of view. The strontium atom is central in each drawing. Atoms are represented by thermal displacement ellipsoids including 99.7% probability ($4 \times$ r.m.s. displacement). Bounding and principal ellipses only are shown for strontium and beryllium atoms; forward principal axes are added for oxygen.

Results of this analysis, together with the previous work cited in the introduction, again illustrate the occurrence of unusual trigonal beryllium oxygen coordinations in oxides lacking clear thermodynamic stability.

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The Crystal Structure of Sparteine-N(16)-oxide Sesquiperchlorate

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Sparteine-N(16)-oxide sesquiperchlorate, $2C_{15}H_{26}N_2O \cdot 3HClO_4$, crystallizes in the space group $P2_12_12$. The unit-cell dimensions are $a=18.01$, $b=12.47$, $c=8.14$ Å and $Z=2$. The structure has been refined by block-diagonal least squares to the R value of 0.096 with use of photographic data for 1894 observed reflexions. All four rings of this compound are in the chair conformation and the oxygen atom is attached to the nitrogen atom of the *cis*-quinolizidine system. The crystallographically symmetrical hydrogen bond between the oxygen atoms of two neighbouring molecules of the alkaloid was found to be 2.479 ± 0.008 Å.

Introduction

The X-ray analysis of α -isosparteine monohydrate, (Przybylska & Barnes, 1953) confirmed the *cis-cis* configuration proposed for α -isosparteine by Marion & Leonard (1951), as the two hydrogen atoms, at C(6) and C(11), were found to be *cis* with respect to the methylene bridge. The molecule consists of two *trans*-quinolizidine systems (see Fig. 1). The results of the molecular and crystal structure determination of 7-hydroxy- β -isosparteine perchlorate, which is the *trans-trans* compound and has two *cis*-quinolizidine systems, were

published by Pinkerton & Steinrauf (1967) when this investigation was in its final stages. Sparteine-N(16)-oxide sesquiperchlorate is the first *cis-trans* C_{15} lupine alkaloid studied by X-ray analytical methods.

On the basis of chemical and physico-chemical evidence the oxygen atom was expected to be attached to N(16) of the *cis*-quinolizidine system; however, a confirmation of this fact by a structural determination was considered useful, as both types of evidence had weak points.

The conformation of the rings was also of interest because the inversion of N(16) can apparently readily take place in solution, transforming the ring C into a boat form (Bohlmann, Schumann & Arndt, 1965; Wiewiorowski, Edwards & Bratek-Wiewiorowska, 1967).

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