

The Crystal Structure of β -Beryllia*

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The crystal structure of β -beryllia has been determined from X-ray powder data collected at 2100 °C. The structure is tetragonal with $a=4.75$ and $c=2.74$ Å, and contains four molecules of BeO in the unit cell. The density is 2.69 g.cm⁻³. The structure is related to rutile, TiO₂, in that the oxygen arrangement is identical. Beryllium atoms are in tetrahedral sites. The space group is $P4_2/mnm$, and the oxygen and beryllium atoms are in sites 4(*f*) and 4(*g*) respectively with $x_O=0.310$ and $x_{Be}=0.336$.

Introduction

A phase inversion has been shown to exist in beryllium oxide in the temperature range 2050–2150 °C. The high temperature phase cannot be quenched and its existence was implied by the physical degradation induced in samples heated through the temperature range. The verification of the high temperature form was obtained by high-temperature X-ray diffractometry by Smith, Cline & Frechette (1962) and Baker & Baldock (1962). Differential thermal analysis by Austerman (1962*a*, 1963*a*) showed a heat of transformation of 1.2 kcal.mole⁻¹, a value which is low when compared with other similar transformations. The crystal structure of β -beryllia† was not evident from the high-temperature X-ray patterns. Evidently, the structure had no room temperature counterpart among the AB-type compounds.

The low heat of transformation suggests that the inversion does not require significant atomic rearrangements. Petrographic studies of single crystals which were heated through the transformation and cooled showed varied results. Smith, Cline & Frechette (1962), using prismatic crystals, observed that the external structure of the crystal was unchanged. An internal domain structure was present but without evident crystallographic relationship among the domains. On the other hand, Austerman (1962*b*), using thin platelets and prismatic crystals, observed a domain structure in which many of the new domains had their *c*-axes rotated 90° from the direction in the original crystal. Fig. 1 shows one of the platelet crystals containing oriented domains.

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† The terms β -beryllia and α -beryllia will be used throughout the paper to distinguish the high-temperature form from the normal form of BeO.

For reference it should be noted that the crystal structure (Smith, Newkirk & Kahn, 1964) of α -beryllia is hexagonal closest-packed (wurtzite type) with lattice constants $a=2.698$, $c=4.377$ Å at room temperature and $a=2.76$, $c=4.47$ Å at 2000 °C (Baldock, Spindler & Baker, 1963). The structure can be regarded conveniently as composed of interpenetrating h.c.p. substructures of oxygen and of beryllium atoms.

The present paper describes further studies which define the general features of the crystal structure of β -beryllia; and finally the most probable positions of the oxygen and beryllium atoms in the unit cell are determined from X-ray diffraction intensities.

Structural features

The various authors have indexed the high-temperature X-ray data in different ways. Smith, Cline & Frechette (1962) and Baker & Baldock (1962) suggested that the diffraction patterns could be indexed to cubic unit cells. Austerman (1963*b*) showed that the pattern can be indexed completely by a hexagonal cell with $a=5.487$, $c=4.752$ Å and $c/a=\sqrt{3}/2$. This cell is related to the α -beryllia cell by increasing the *c* axis by approximately 6% at the inversion and doubling the *a* axis. Cathetometer measurements (Austerman, 1964) of single crystals showed approximately this same amount of expansion in the *c*-axis direction and nil expansion normal to the *c*-axis.

The implication of this hexagonal cell and its relationship to the structure of low beryllia gives a very strong clue to the structure of β -beryllia. The relationship is shown in Fig. 2. The upper half of the figure shows two views of the α -beryllia oxygen h.c.p. arrangement. If alternate oxygen layers were to shift as indicated by the arrows in the figure, the layers would move apart and the arrangement shown in the bottom half of the figure would result. The *c* axis is



Fig. 1. Photomicrograph of a hexagonal platelet of BeO which has been heated through the transformation temperature and cooled. The domain structure which has developed has the c axes parallel to the axes intermediate between a axes of the host crystal. The crystal is about 2 mm across.

expanded 6%, while the a axis is virtually unchanged. Doubling the a axis would give the cell used by Austerman (1962*a*). The true symmetry is not hexagonal but rather tetragonal with the tetragonal c axis 90° from the c axis of α -beryllia. The lattice constants are $a=4.75$, $c=2.74$ Å, and $c/a=1/\sqrt{3}$. Using this cell the powder pattern can be indexed as shown in Fig. 3. This diagram shows the patterns of both β - and α -beryllia and shows the correlation of reflections assuming the cell relationships are as shown in Fig. 2. It is interesting to note that the tetragonal and hexagonal cells will yield powder patterns which are identical; so it is not possible to decide which cell is correct based on the pattern alone.

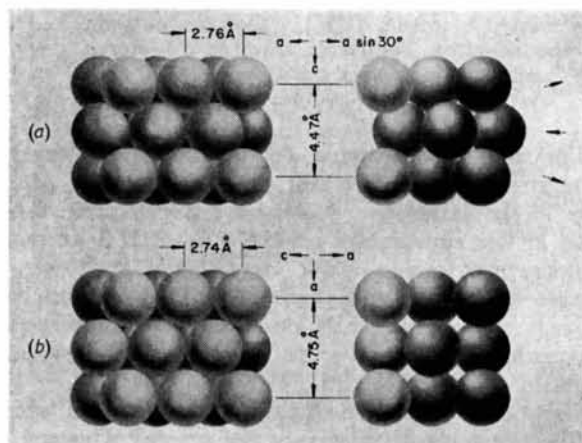


Fig. 2. Relationship of the structure cells of α - and β -beryllia. The oxygen arrangement of α -beryllia is shown in (a). In (b) is shown the oxygen arrangement resulting from shifting the layers in α -beryllia as shown by the arrows; the tetragonal structure cell of β -beryllia is shown.

Another piece of evidence suggesting the tetragonal structure cell was the appearance of some small euhedral crystals which grew on the surface of a BeO sample in the diffractometer furnace. These crystals evidently grew at temperatures above 2100°C

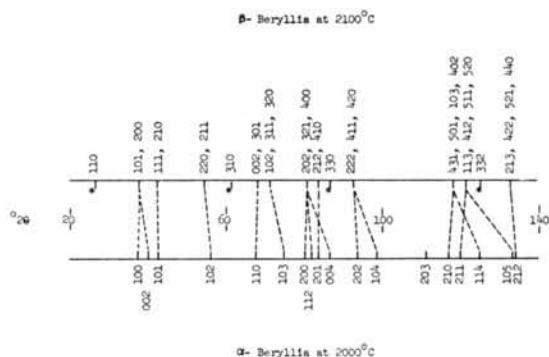


Fig. 3. The powder patterns of α - and β -beryllia for $\text{Cu } K\alpha$. The dashed lines correlate related reflections corresponding to the interpretation shown in Fig. 2. The β -beryllia reflection corresponding to the hexagonal 203 was not observed.

in the form of β -beryllia. Morphologically they are prismatic with a square cross section. All the prism faces are striated normal to the direction of elongation. These striations are caused by alternations of the prism face and a pyramidal face which define a 57° angle. Some 90° angles are also observed. Several of these crystals, examined by X-rays, showed the α -beryllia structure with c axis normal to a prism face as defined above. It is difficult to explain the striations with respect to the α -beryllia structure. If the crystals are pseudomorphs after β -beryllia, both the striations and crystallographic orientations are compatible with the structural picture developed above.

The orientational relationship between the crystal structures of α - and β -beryllia also was checked using single crystals of α -beryllia cut into thin wafers parallel to (10-0), (11-0), (10-1), (00-2), or (10-2) planes. In each of these crystals, the reflections observed at temperatures above that for transformation were those indicated by the correlation diagram in Fig. 3. Transformation of the (10-2) cut is of particular interest, since the family of planes giving rise to the β -beryllia 220 reflection is also responsible for the 110, 330, and 440 reflections. All four of these reflections were observed as predicted, with satisfactory agreement of relative intensities. This agreement is regarded as fairly conclusive evidence that the structural relationships are correctly identified. All other observations described in this paper further confirm this conclusion.

Thus, the crystal structure of β -beryllia at 2100°C is tetragonal, with $a=b=4.75$, $c=2.74$ Å, and $c/a=1/\sqrt{3}$. The calculated density, 2.69 g.cm $^{-3}$, is to be compared with the density, 2.82 g.cm $^{-3}$, of normal BeO at 2000°C . The transformation of axes from hexagonal α -BeO to tetragonal β -BeO follows the rules:

$$\begin{aligned} \mathbf{a}_1^H &\rightarrow \mathbf{c}^T \\ \mathbf{c}^H &\rightarrow \mathbf{a}_1^T \\ \mathbf{a}_3^H - \mathbf{a}_2^H &\rightarrow \mathbf{a}_2^T \end{aligned}$$

The superscripts H and T designate the hexagonal and tetragonal forms, respectively.

Determination of atomic positions

The positions of the beryllium and oxygen atoms were determined from measured intensities of the diffraction peaks. Reliability of the intensity data at high temperature is open to some question. Some of the initial data obtained by Smith, Cline & Frechette (1962) were obtained from polycrystalline beryllia which contained significant preferred orientation. Recent use of samples with more ideally random grain orientation yielded more reliable data. In addition, intensity data have been obtained from Baker & Baldock (1963). Table 1 lists the best data obtained

Table 1. *Diffraction pattern for β -beryllia*

Indices	d (obs.)* (Å)	d (calc.)† (Å)	I (obs.)	I (calc.)‡
110	3.348	3.360	5	11
101, 020	2.375 (2.370)	2.376	100	100
120, 111	2.125 (2.120)	2.125	60	50
121, 220	1.679 (1.676)	1.680	15	14
130	1.501 (1.500)	1.502	4	5
221	—	1.433	—	0.3
031, 002	1.376 (1.370)	1.372	26	24
012, 131, 230	1.317 (1.316)	1.318	2.8	4
112	—	1.270	—	0.4
022, 231, 040	1.187 (1.187)	1.188	12.2	12
122, 410	1.151 (1.152)	1.152	1.2	2
330	1.118 (1.118)	1.120	1.6	3
141, 240, 222	(1.062)	1.062	0.8	1
0.32	—	1.037	—	0.1
132	—	1.013	—‡	1
241	—	0.991	—	0.5
232, 340, 050	—	0.950	—	0.7
150	—	0.931	—	0.3
341, 013, 051, 042	(0.897)	0.898	2	3
151, 142, 250, 113	(0.882)	0.882	0.4	2
332	(0.868)	0.868	0.7	2
251, 123, 440, 242	(0.840)	0.840	2	2

* Values listed are from Smith, Cline & Frechette (1962), except values in parentheses, which are from Baker & Baldock (1963).

† Calculations made for tetragonal unit cell, $P4_2/mnm$, with oxygen in positions 4(f), $x=0.310$, and beryllium in positions 4(g), $x=0.336$. $a=4.75$, $c=2.74$ Å, $c/a=1/\sqrt{3}$.

‡ Obscured by line from tungsten heater.

to date, and these data have been accepted as reasonably reliable.

Because of the abundance of superimposed reflections in the diffraction pattern, the intensity data could not be reduced to determine structure factors. Consequently, to test trial structures quickly by comparing calculated and combined intensities with measured intensities, an IBM 7094 computer program (Smith, 1963) was written. With this program, many trial structures could be quickly tested. Scattering factors for neutral Be and O were used and were taken from the self-consistent model as listed in *International Tables for X-ray Crystallography* (1962).

The structure described in Fig. 2 was found to be oversimplified because it shows the oxygen substructure to have a face-centered unit cell, whereas the X-ray data indicated the unit cell to be primitive. No arrangement of the beryllium atoms was found which could yield intensity contributions strong enough to account for the reflections corresponding to the primitive unit cell. Therefore it was concluded that the oxygen arrangement does not form an exact face-centered unit cell, although packing considerations indicated that only minor distortions of the arrangement would be possible.

The similarity of the c/a ratio, 0.5778, to that of rutile (TiO_2), 0.6442 (Baur, 1961), as well as a similarity of cell size, suggested that the true oxygen arrangement was related to that in rutile. This arrangement was only slightly different from the f.c.t. arrangement already mentioned. The space group, $P4_2/mnm$, was compatible with the data. The only systematic reflection condition, $0kl$ with $k+l=2n$, is possible

because of the superposition of reflections. No other systematic absences could be deduced from the data. Using the slight distortions of oxygen atom positions, as in the rutile structure, those diffraction peaks not allowed by the face-centered structure have reasonable intensities. The problem was to determine the degree of distortion of the oxygen substructure and the location of the beryllium atoms in the unit cell.

The crystal structure of β -beryllia chosen as the most probable is shown in Fig. 4(a) as a projection onto the (001) plane. The space group is $P4_2/mnm$. Oxygen atoms are in positions 4(f) ($x, x, 0$; $\bar{x}, \bar{x}, 0$; $\frac{1}{2}+x, \frac{1}{2}-x, \frac{1}{2}$; $\frac{1}{2}-x, \frac{1}{2}+x, \frac{1}{2}$) with $x=0.310$; the beryllium atoms are in 4(g) ($x, \bar{x}, 0$; $\bar{x}, x, 0$; $\frac{1}{2}+x, \frac{1}{2}+x, \frac{1}{2}$; $\frac{1}{2}-x, \frac{1}{2}-x, \frac{1}{2}$) with $x=0.336$.

Calculated and measured intensities are given in Table 1. The temperature factors $B_{\text{Be}} = 3.0$ and $B_{\text{O}} = 2.0$ were used; accuracy of the experimental data did not justify further refinement of the temperature factors. While maintaining equal bond lengths between all closest oxygen-beryllium neighbors, the atomic position parameters were adjusted to yield the best agreement between calculated and measured intensities. All other trial structures tested yielded gross intensity disagreement, hence were unacceptable. The value of x for oxygen is fortuitously the same as reported for rutile (Baur, 1961).

Discussion

As shown above, the β -beryllia crystal structure is closely related to that of α -beryllia. This relationship is worthy of further comment. The transformation

can be conveniently described by a sequence of steps illustrated in Fig. 4. The $\langle 10\cdot0 \rangle$ projection of α -beryllia is shown in Fig. 4(c). At the transformation, alternate layers of close-packed oxygen atoms shift slightly in a shearing motion relative to the adjoining layers, toward the final rutile-like arrangement. Half the beryllium atoms remain within their original tetrahedral configuration, which is now distorted, while the other half jump to adjacent tetrahedral sites as shown by the dashed arrows in Fig. 4(b). This final arrangement corresponds to the structure as shown in Fig. 4(a). Considering the relative sizes of the atoms (radii of 0.31 Å for Be^{2+} and 1.40 Å for O^{2-}) it is believed that the rate determining step is probably the movement of oxygen atom planes. The measured transformation energy of 1.2 kcal.mole⁻¹

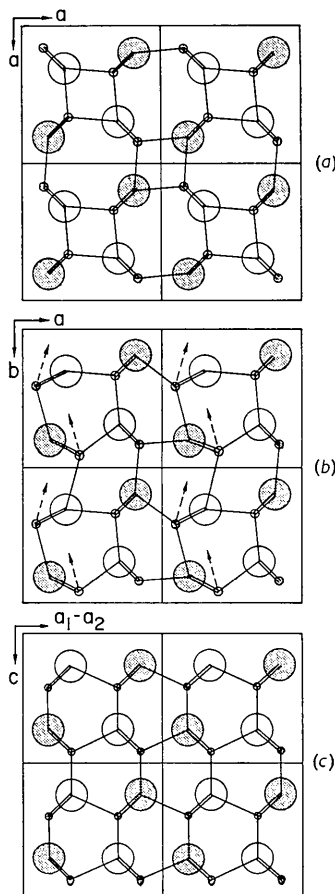


Fig. 4. Conceptual sequence of stages in transformation with structures projected in direction corresponding to tetragonal c axis. The shaded balls represent atoms with $z=0.500$, the others, atoms with $z=0$. The small and large circles represent beryllium and oxygen atoms respectively. Four unit cells are shown. (a) Structure of β -beryllia. (b) Transitional structure between α - and β -beryllia. The oxygen atoms are shown in positions corresponding to β -beryllia; the beryllium atoms are shown in their original but now distorted tetrahedrons. To achieve the transformation, two beryllium atoms must move as shown by the dashed arrows. (c) Structure of α -beryllia.

and the rapid rate of transformation are qualitatively in accord with the above description.

It is interesting to note that the beryllium atoms which shift to alternate tetrahedral sites, as shown in Fig. 4(b), define puckered planes which are perpendicular to the planes of initial movement of the oxygen atoms. These planes of beryllium atoms alternate with planes of atoms which remain essentially in their original relative positions. Because of the tetragonal symmetry of the high temperature form, in particular the existence of (110) mirror planes, the atomic shifts which take place on cooling may be 90 degrees from the original shifts.

The crystal structure for β -beryllia has no known counterpart among AB-type compounds. The relationship of the oxygen arrangement to that found in rutile is noteworthy even though the cations are in tetrahedral rather than octahedral interstices, as in the rutile-type compounds. The arrangement of tetrahedral coordination groups results in the edge sharing of pairs of tetrahedra. Such a configuration also has been recently reported for $\text{Al}_4\text{O}_4\text{C}$ by Jeffrey & Slaughter (1963). The closest neighbor Be-Be distance is relatively small at 2.20 Å, but evidently the oxygen atoms, which are fairly tightly packed, effectively screen any repulsion effects of the close proximity of the beryllium atoms.

In addition to rearrangements which occur at the transformation, there are other smaller distortions which take place in the α -beryllia structure between room temperature and 2050 °C. In the ideal wurtzite, the c/a ratio is 1.633. For α -beryllia the c/a ratio at room temperature is 1.622 and this value decreases steadily to 1.619 (Baldock, Spindler & Baker, 1963) at 2000 °C. The a axis is expanding at the more rapid rate. It has been well substantiated by Jeffrey, Parry & Mozzi (1956), Smith, Newkirk & Kahn (1964), and Sabine & Dawson (1963) that the Be-O bonds in α -beryllia at room temperature are not equal. The bond parallel to the c -axis is longer than the other three. Pryor & Sabine (1963) have shown that this inequality of bonds increases slightly with increasing temperature and with the decreasing c/a ratio. In other words the beryllium atom makes a slight shift toward the base of its tetrahedral coordination. At the transformation, half of the beryllium atoms pass through this base into the adjacent tetrahedron. Thus the reason for the instability of the α -beryllia structure above 2050 °C may be related to the cause of the deviation of the c/a ratio from ideality with increasing temperature.

At the transformation there is a significant dimensional change. The lattice dimension corresponding to the α -beryllia c axis increases 6.3%, whereas the lattice dimension corresponding to the a axis decreases 0.8%. Thus the direction which showed the largest expansion rate actually shows a contraction at the phase change. In the α -beryllia structure just before the transformation the BeO distances are 1.70₀ Å and 1.68₅ Å

(three bonds). In the β -beryllia structure, the point symmetry at both beryllium and oxygen sites is 2 mm. Thus in each BeO_4 group only pairs of BeO distances related by a mirror plane must be equal. However, using the current set of intensity data it is not possible to say that all four lengths are not identical even though the best data fit was obtained from the arrangement with equal distances. This Be-O distance is 1.68 $\frac{1}{2}$ Å. Evidently, at the transformation the relaxation in bond lengths is small, in spite of the decrease in atomic packing.

The temperature factors used in the calculations have been chosen somewhat arbitrarily. The only study of the change of temperature factors with temperature was by Pryor & Sabine (1963) who show B_{Be} changes from 0.36 to 0.89 Å⁻² from room temperature to over 900 °C with a corresponding increase in B_{O} from 0.33 to 0.70 Å⁻². The values of $B_{\text{Be}} = 3.0$ Å⁻² and $B_{\text{O}} = 2.0$ Å⁻² for the structure calculations are not unreasonable compared with these values. The only other set of values tried, $B_{\text{Be}} = 2.0$ Å⁻² and $B_{\text{O}} = 1.0$ Å⁻², did not give as good a fit of calculated *versus* observed data.

The structure of β -beryllia is centrosymmetric, whereas the structure of α -beryllia is polar. The relationship of the crystallographic axes already discussed indicates that the high temperature phase has its c axis along any of the a directions of the low form. One of the a axes corresponds to the old c axis. On cooling, several possibilities may occur. The crystal may revert back to the original orientation; however, the polar direction could be reversed. In addition, the final c direction could correspond to any of the six $\langle 11\bar{2}0 \rangle^*$ directions, depending on the crystal polarity. Thus a crystal of α -beryllia which is initially single and untwinned may yield as many as eight different crystal orientations in the domain structure produced by cycling the crystal through the transformation temperature. All these orientations may be present in the crystal shown in Fig. 1, although it is not possible by X-rays to differentiate regions which

differ only by a reversal of polarity. The physical degradation observed in BeO is due to the combined influence of these multiple atomic reorientations and the anisotropic dimensional changes accompanying the phase transformation.

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