

The Crystal Structure of Barium Hexaaluminate Phase I (Barium β -Alumina)

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The crystal structure of barium hexaaluminate phase I ($\text{Ba}_{0.79}\text{Al}_{10.9}\text{O}_{17.14}$) was determined by single crystal X-ray reflection data. The refinements were carried out by the least-square method to give a final R -value of 0.023. The structure was revealed to be essentially of a β -alumina type and the Ba ion was detected only at the $6h$ site near the Beavers-Ross site ($2d$ site). The charge compensation for nonstoichiometry was found to be principally effected by the interstitial oxygen due to Frenkel defects of Al ions. From the structural point of view, phase I was referred to as "barium β -alumina."

Introduction

The hexagonal aluminates containing divalent ions ($M\text{Al}_2\text{O}_9$; $M = \text{Ca}, \text{Sr}$) have a crystal structure of the magnetoplumbite type (1, 2). Barium hexaaluminate was supposed to have the same structure though decisive evidence for this assumption was lacking. Recently, however, the idea of stoichiometric " $\text{BaAl}_{12}\text{O}_{19}$ " having a magnetoplumbite structure has been brought into doubt. Stevels *et al.* (3) and Stevels (4), for the first time, considered barium hexaaluminate as having β -alumina structure with the formula $\text{Ba}_{1-x}\text{Al}_{10\frac{1}{2}+x}\text{O}_{17+x}$ ($-0.2 \leq x \leq 0.35$). Afterwards Haberey *et al.* (5) and Kimura *et al.* (6), in the phase investigation on the system $\text{BaO}-\text{Al}_2\text{O}_3$, revealed the existence of two compounds near the $\text{BaO} \cdot 6\text{Al}_2\text{O}_3$ composition, which were tentatively denoted as barium hexaaluminate phase I and phase II by Kimura *et al.* (6). We showed (7) that barium hexaaluminate phase I and phase II

have the composition of $\text{Ba}_{0.79}\text{Al}_{10.9}\text{O}_{17.14}$ and $\text{Ba}_{2.34}\text{Al}_{21.0}\text{O}_{33.84}$, respectively. We also suggested on the basis of the electron diffraction and crystallographic data that these were essentially of β -alumina structure. But, as yet, no refinement of the crystal structure has been achieved, so the detailed structure and charge compensation mechanism for nonstoichiometry are not clearly determined.

The present paper reports the structure determination of barium hexaaluminate phase I using the single-crystal X-ray reflection data and proposes a charge compensation mechanism for nonstoichiometry on the basis of the refined parameters.

Experimental

Several spherical specimens were prepared from the single crystal which was grown by the floating zone (FZ) method as described in the previous paper (7). After examination by precession photographs, a

spherical specimen of radius 92 μm was used for the data collection. The absorption factor for the chosen sample was $\mu R = 0.335$. The intensities were measured below $2\theta = 120^\circ$, using a computer-controlled four-circle diffractometer (Rigaku Denki) with monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). A set of standard reflections (107), (220), and (00 · 10) was measured every 50 reflections. The 836 independent non-zero reflections were corrected for Lorenz-polarization and absorption effects. Atomic scattering factors were taken from the *International Tables for X-ray Crystallography* (Vol. IV) and the values for the anomalous dispersion corrections for Ba were from the same reference (Vol. III). The refinement was carried out using the modified RSFLS-4 program (UNICS) which was originally written by Sakurai *et al.* (8) and Fourier syntheses were done with RSSFR-5 program (UNICS) written by Sakurai (9). The lattice parameters are refined using 2θ -data of 20 reflections collected on the four-circle diffractometer. The refined lattice parameters are slightly different from those using powder diffraction data (7). The nomenclature of the sites in the mirror plane is after that of Peters *et al.* (10). Crystallographic data are shown in Table I, which are partly from our previous work (7). A list of the observed and calculated structure factors is available from the authors.

TABLE I
CRYSTALLOGRAPHIC DATA

Formula	$\text{Ba}_{0.79}\text{Al}_{10.9}\text{O}_{17.14}$
Symmetry	hexagonal
Space group	$P6_3/mmc$
	$a = 5.588(2) \text{ \AA}$
	$c = 22.769(9) \text{ \AA}$
	$V = 615.7(4) \text{ \AA}^3$
	$Z = 2$
	$D_{\text{obs}} = 3.657 \text{ g cm}^{-3}$

Refinement

In the previous study (7) using the electron diffraction method, barium hexaaluminate phase I was considered to be of β -alumina structure. For Fourier and difference Fourier syntheses, the positional parameters of Al(1) to Al(4) and O(1) to O(5) were chosen from the structure of K β -alumina (11), and the Ba ion was placed in the ideal Beevers-Ross site (BR site; $2d$ site; $(2/3, 1/3, 1/4)$). The Fourier sections, which corresponded to an R -value = $\frac{\sum |F_0| - |F_c|}{\sum |F_0|} = 0.218$, revealed that main electron density differences occurred in the mirror plane ($z = 0.25$). The barium site was only partially occupied as anticipated from the formula $\text{Ba}_{0.79}\text{Al}_{10.9}\text{O}_{17.14}$. No unusual electron density variations were observed in the spinel block. Refinements were attempted on the occupation factor of Ba in addition to the general temperature factor and positional parameters, which led to convergence with an R -value = 0.157. In the subsequent refinement individual isotropic temperature factors were introduced. At this stage an R -factor of 0.135 was obtained, but the isotropic temperature factor of oxygen at the $2c$ site ($1/3, 2/3, 1/4$) in the mirror plane increased anomalously to 2.0 as compared to 0.2–0.4 for the oxygen ions at other sites. Further refinements based on this simple β -alumina model in which the Ba ion partially occupies the BR site turned out to be unsatisfactory.

Subsequent difference Fourier maps using the parameters corresponding to an R -value of 0.135 revealed that the electron density distribution of Ba and oxygen in the mirror plane was distorted and triangular. After splitting the Ba and oxygen sites into $6h$, the next refinement of general temperature factor, positional parameters, and the occupation factors of ions in the mirror plane resulted in an R -value of 0.083. Difference Fourier sections suggested additional electron density at the $2c$ site ($z =$

0.25) and the 12*k* site near $z = 0.18$. Electron density around the 2*c* site could not be accounted for only by oxygen at the 6*h* site. The oxygen in the mirror plane would probably be distributed between the 2*c* and 6*h* sites. On the other hand, the atom occupying the 12*k* site near $z = 0.18$ would be interstitial Al. The existence of interstitial Al was already reported in some β -alumina compounds, by Roth *et al.* (14) and Collin *et al.* (11). In the next refinement, occupation factors of Al(1), interstitial Al(5), O(5) at the 2*c* site, and O(6) at the 6*h* site were treated as additional variables. With a type I isotropic secondary extinction correction (13) and individual isotropic temperature factors, the *R*-factor dropped to 0.043. Subsequent anisotropic refinements led to $R = 0.026$ and $wR = (\sum w(|F_0| - |F_c|)^2 / \sum w|F_0|^2)^{1/2} = 0.031$, with unit weights. At this stage the difference Fourier still showed small amount of excess electron density ($2.2 e \text{ \AA}^{-3}$) at the 6*h* site ($x, 2x, 1/4$) with $x = 0.88$.

This was assumed to be due to the interstitial oxygen as was already found in $M^{+1} \beta$ -alumina (11, 14). With the interstitial oxygen as O(7), the last refinement with anomalous dispersion corrections yielded final $R = 0.023$ and $wR = 0.027$, with unit weights. The *g*-value for the secondary extinction was $1.36(6) \times 10^4$. Final difference electron maps showed random peaks and depression, not exceeding the maximum amplitude of $\pm 1 e \text{ \AA}^{-3}$. These final values of the positional and thermal parameters are given in Table II. The interatomic distances and bond angles are presented in Tables III and IV, respectively.

Discussion

β -Alumina and magnetoplumbite structures resemble each other. They consist of spinel blocks separated by intermediate layers containing large cations. The main dif-

TABLE II
THE POSITIONAL AND THERMAL^a PARAMETERS

	Position	Number per unit cell	<i>x</i>	<i>z</i>	$\beta_{11} \times 10^5$	$\beta_{22} \times 10^5$	$\beta_{33} \times 10^6$	$\beta_{23} \times 10^6$	<i>B</i>
Ba	6(<i>h</i>)	1.485(6)	0.6717(6)	1/4	1144(19)	2514(150)	197(4)	0	
Al(1)	12(<i>k</i>)	10.86(4)	0.83256(8)	0.10462(2)	576(15)	461(19)	212(6)	-259(35)	
Al(2)	4(<i>f</i>)	4	1/3	0.02356(4)	381(17)	β_{11}	164(9)	0	
Al(3)	4(<i>f</i>)	4	1/3	0.17537(4)	907(22)	β_{11}	146(10)	0	
Al(4)	2(<i>a</i>)	2	0	0	502(26)	β_{11}	166(14)	0	
Al(5) ^b	12(<i>k</i>)	0.93(3)	0.8426(8)	0.1769(3)	136(141)	110(202)	146(66)	-12(311)	
O(1)	12(<i>k</i>)	12	0.1580(1)	0.04953(5)	822(27)	395(35)	245(10)	80(66)	
O(2)	12(<i>k</i>)	12	0.5039(2)	0.14721(5)	534(23)	670(37)	422(13)	-281(73)	
O(3)	4(<i>f</i>)	4	2/3	0.05574(8)	652(36)	β_{11}	175(19)	0	
O(4)	4(<i>e</i>)	4	0	0.14110(8)	468(32)	β_{11}	211(21)	0	
O(5)	2(<i>c</i>)	0.38(9)	1/3	1/4					0.4(4)
O(6)	6(<i>h</i>)	1.63(10)	0.290(2)	1/4	2601(348)	2451(754)	104(54)	0	
O(7) ^b	6(<i>h</i>)	0.55(4)	0.881(3)	1/4					0.9(6)

^a The thermal parameters are of the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. $\beta_{12} = 1/2 \beta_{22}$; $\beta_{13} = 1/2 \beta_{23}$.

^b Interstitials.

TABLE III
INTERATOMIC DISTANCES

	Number of bonds	Distance (Å)
Octahedral coordination		
Al(1)–O(1)	2	2.015(2)
–O(2)	2	1.863(2)
–O(3)	1	1.954(2)
–O(4)	1	1.821(2)
Al(4)–O(1)	6	1.900(2)
Tetrahedral coordination		
Al(2)–O(1)	3	1.797(2)
–O(3)	1	1.806(3)
Al(3)–O(2)	3	1.771(2)
–O(5)	1	1.699(2)
Al(5)–O(2)	2	1.777(7)
–O(4)	1	1.728(8)
–O(7)	1	1.705(9)
Polyhedron 9-coordinated		
Ba–O(2)	4	2.808(4)
–O(2)′	2	2.849(4)
–O(5)	2	3.202(5)
–O(5)′	1	3.275(6)

TABLE IV
BOND ANGLES

	Bond angles (°)
Octahedral coordination	
O(1)–Al(1)–O(1)′	82.18(9)
O(1)–Al(1)–O(2)	91.68(9)
O(1)–Al(1)–O(3)	89.67(7)
O(1)–Al(1)–O(4)	84.63(7)
O(2)–Al(1)–O(2)′	94.14(13)
O(2)–Al(1)–O(3)	86.31(9)
O(2)–Al(1)–O(4)	98.81(7)
O(1)–Al(4)–O(1)′	88.40(9)
O(1)–Al(4)–O(1)″	91.60(9)
Tetrahedral coordination	
O(1)–Al(2)–O(1)′	109.77(10)
O(1)–Al(2)–O(3)	109.16(10)
O(2)–Al(3)–O(2)′	107.64(11)
O(2)–Al(3)–O(5)	111.25(10)
O(2)–Al(3)–O(6)	103.9(7)
O(2)–Al(3)–O(6)′	125.1(6)
O(2)–Al(5)–O(2)′	100.3(4)
O(2)–Al(5)–O(4)	105.9(4)
O(2)–Al(5)–O(7)	118.9(12)
O(4)–Al(5)–O(7)	105.6(10)

ferences between the two exist in the intermediate layer (mirror plane) as shown in Fig. 1. In the magnetoplumbite structure, the intermediate layer of a single unit cell contains a large cation, an Al ion, and three oxygen ions; in the β -alumina structure it contains only a large cation and an oxygen ion. The hexaaluminates containing a large divalent ion such as Ca or Sr (1, 2) are of a magnetoplumbite type with the general formula $MAl_{12}O_{19}$ (M = large cation). Unlike these hexaaluminates, the barium hexaaluminate phase I completely corresponds to a β -alumina structure in accordance with our preliminary study (7). Accordingly, from the structural point of view, barium hexaaluminate phase I should be referred to as "barium β -alumina." The reason for the β -alumina structure in the case of this hexaaluminate with Ba^{2+} ions is probably because the configuration of the intermedi-

ate layer in a β -alumina structure affords the more space for the large Ba ion (compared to other divalent ions) than that in a magnetoplumbite structure, as pointed out by Stevels *et al.* (3).

The β -alumina structure was originally found in aluminates containing monovalent cations. Up to now, extensive investiga-

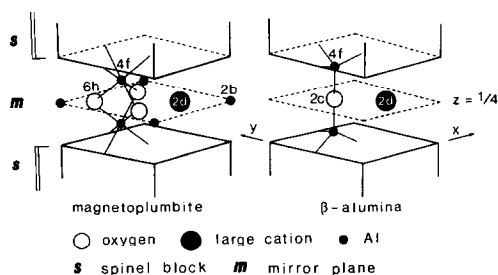


FIG. 1. Schematic representation of a part near the mirror plane ($z = 0.25$) in the structure of the (a) magnetoplumbite type and (b) β -alumina type.

tions on the crystal structure, charge compensation, and ionic conduction mechanism have been made. According to the refinements of M^{+1} β -alumina (14–17), the monovalent cation distributes among the BR, anti-BR, and mO (mid-oxygen) sites, with the ratio of distribution depending on the species of the large cation. In the case of barium β -alumina, however, no significant electron density attributable to the Ba ion was detected at the BR and mO sites. The Ba ion was found to be confined to the area near the BR site.

Another point to be noted is the charge compensation mechanism for nonstoichiometry in this β -alumina containing a divalent cation (Ba^{2+}). Difference Fourier maps clearly indicate additional maxima at the $12k$ site near $z = 0.18$. The electron density section at $z = 0.177$ after refinement is shown in Fig. 2b. This site is consistent with the interstitial Al site as pointed out by Roth *et al.* (14). Our observed site occupancy of interstitial Al(5) is almost equal to the lack of Al(1), which suggests that the Frenkel defect mechanism proposed by Roth *et al.* (14) and Collin *et al.* (11) does operate in barium β -alumina. Furthermore, the difference Fourier at $R = 0.026$ showed small amounts of additional electron density at the $6h$ site ($x, 2x, 1/4$) with $x = 0.88$. These were attributed to the interstitial oxygen bridging a pair of interstitial Al ions as

already reported in M^{+1} β -alumina. In fact, the incorporation of interstitial oxygen as O(7) in the refinement resulted in the significant reduction of the R -factor, and after refinement the number of interstitial Al(5) per unit cell turned out to be nearly twice that of interstitial O(7). These results support the existence of interstitial oxygen in the mirror plane and are well consistent with the defect mechanism in which an interstitial oxygen bridges a pair of interstitial Al, as shown in Fig. 3b. According to this defect mechanism, the Al ions do not directly participate in charge compensation because the number of Al ions in a unit cell does not change. It is the interstitial oxygens that compensate the extra charge due to Ba ions.

On the basis of the atomic parameters and supposed defect mechanism, a possible structure model for barium β -alumina may be proposed. A Ba ion is located near the BR site and an interstitial oxygen is placed near the mO site. Simultaneous occupation by an interstitial oxygen and a barium ion in the same mirror plane of a single cell is, however, unacceptable owing to the large ionic radii of both atoms compared with the distance of 2.0 \AA between the Ba and O(7) sites. Accordingly two kinds of half unit cells with $1/2c$ dimension, which contains one mirror plane and one spinel block, can be supposed as shown in Figs. 3a and b; one

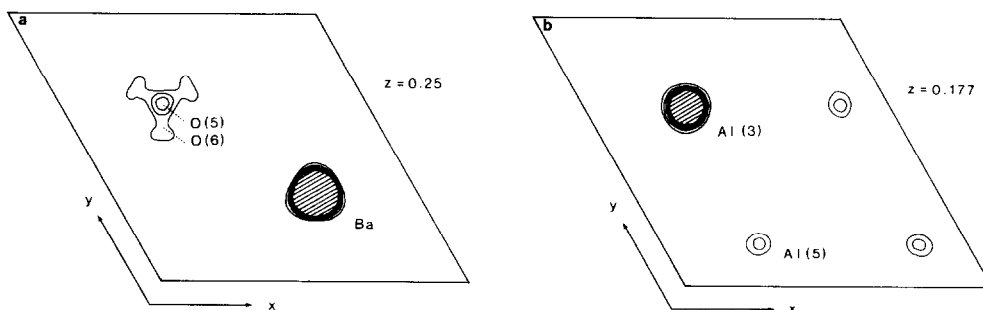


FIG. 2. Electron density at the sections of (a) $z = 0.25$ and (b) $z = 0.177$.

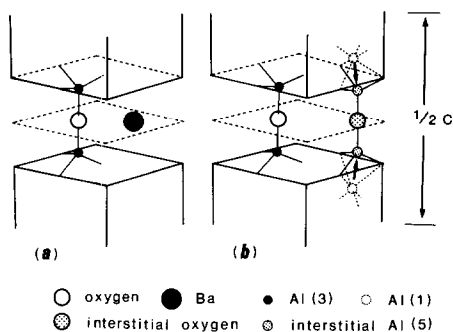


FIG. 3. Two kinds of half unit cell assumed to constitute barium β -alumina. (a) Half unit cell containing a Ba and an oxygen ions in the mirror plane. (b) Half unit cell containing interstitial Al and oxygen ions with the defect of Ba ion. The arrow indicates the shift of Al ions due to Frenkel defect mechanism.

contains a barium ion and has the composition of "BaAl₁₁O₁₇" with a charge of +1, and the other contains an interstitial oxygen with the defect of barium ion in the mirror plane due to Frenkel defect of Al ions, the composition of which is "OAl₁₁O₁₇" with a charge of -3. To attain charge neutrality as a whole, the molar ratio of these two types of half cell should be 3 to 1. Furthermore, the lack of superstructure reflections (7) suggests random distribution of the two kinds of half unit cell throughout a crystal. Thus the formula of barium β -alumina would be necessarily Ba_{0.75}Al_{11.0}O_{17.25}. According to this structure model, it follows that the number per unit cell of Ba, Al(1), Al(5), and O(7) are 1.5, 11.0, 1.0, and 0.5, respectively. These values are consistent with the results obtained by X-ray structure analysis (Table II). In the previous study (7), however, the chemical formula was determined to be Ba_{0.79}Al_{10.9}O_{17.14} from density, cell volume and electron probe microanalysis data. This result is slightly different from the above formula based on the model deduced from the obtained parameters. In addition, there exists inconsistency in the reported composition between the researchers (5, 6). These might origi-

nate in the real compositional variation due to solid solution and/or the observational errors in the technics to obtain the data. As yet, no evidence for compositional variation were found among the specimens examined by electron probe microanalysis, so we attribute the discrepancy to the inaccuracy of the data to derive the composition or chemical formula. At present, we suppose that the formula Ba_{0.79}Al_{10.9}O_{17.14} represents the composition of barium β -alumina best. It is, therefore, possible that other types of Al ion defects occur in order to compensate extra charge due to more barium ion than 1.5 per unit cell. Nevertheless, the discrepancy has little effect on the above outlined structure model for barium β -alumina.

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