

## The Crystal Structure of Highly Nonstoichiometric Potassium $\beta$ -Alumina, $K_{1.50}Al_{11.0}O_{17.25}$

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The crystal structure and cation distribution of highly nonstoichiometric potassium  $\beta$ -alumina  $K_{1.50}Al_{11.0}O_{17.25}$  have been studied by single-crystal X-ray diffraction. The single crystal was obtained by ion exchange from barium  $\beta$ -alumina ( $Ba_{0.75}Al_{11.0}O_{17.25}$ ) and the least-squares refinement was accomplished with a final  $R$  value of 0.029. The occupation of K ion in the mirror plane ( $z = 0.25$ ) was explained by assuming three types of cells: singlet cell ( $KAl_{11}O_{17}$ ), K-K-K triplet cell ( $K_3Al_{11}O_{17}$ ), and K-K-Oi triplet cell ( $K_2O \cdot Al_{11}O_{17}$ ) where Oi stands for interstitial oxygen. This model was shown to be applicable to the ordinary potassium  $\beta$ -alumina ( $K_{1.30}Al_{11.0}O_{17.15}$ ). © 1986 Academic Press, Inc.

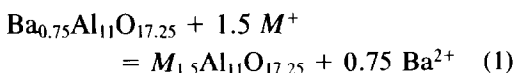
### Introduction

The unit formula of  $\beta$ -alumina can be expressed as  $M_{1+x}Al_{11}O_{17+x/2}$ , where  $M$  is a mono-valent cation, and  $\beta$ -alumina compounds usually show nonstoichiometry with the level of  $x \approx 0.3$ . Up to now, many structural investigations on  $\beta$ -alumina compounds have been published (1-5), and it was revealed that charge compensation was accomplished by the interstitial oxygen in the mirror plane (conduction plane) (6). The specimens were almost always obtained by the ion exchange of sodium  $\beta$ -alumina, which has the composition with  $x \approx 0.3$ . Accordingly, their compositions were determined by the composition of sodium  $\beta$ -alumina used as the starting material for ion exchange. For structural study of  $\beta$ -alumina containing more or less cations than the "usual" composition  $x \approx 0.3$ , new routes of synthesis or elaboration of the customary techniques to prepare  $\beta$ -alu-

mina with various  $x$  levels are needed. The relation between the composition and the cation distribution or configuration in the mirror plane ( $z = 0.25$ ) is one of the important problems in  $\beta$ -alumina system.  $\beta$ -Aluminas of the poorest cation content with  $x = 0.0$ , in other words  $\beta$ -alumina compounds having "ideal" stoichiometric compositions  $MA_{11}O_{17}$ , were prepared by the elegant synthetic route via  $(H_3O)Al_{11}O_{17}$  (7) or  $DA_{11}O_{17}$  (8), and subjected to structural analysis using X-ray single-crystal diffraction or powder neutron diffraction. On the other hand, several reports were also published on the excess cation containing  $\beta$ -alumina compounds beyond  $x \approx 0.3$ . Mg-Doped  $\beta$ -aluminas with excess cation have been extensively investigated by Collin *et al.* (9). However, in these materials, there operates another type of charge compensation mechanism, in which  $Mg^{2+}$  compensates the excess cation in the mirror plane. Indeed nondoped  $\beta$ -alumina compounds

with excess cation have been prepared and reported (12), but enough characterization for discussing the structure are lacking. England *et al.* (13), for the first time, prepared Ag  $\beta$ -alumina and Na  $\beta$ -alumina with  $x \approx 0.45$  composition, and refined the occupancy and positional parameters using powder neutron diffraction data. For determination of cation distribution, it would be preferable to analyze by the single-crystal X-ray diffraction method.

Recently, we prepared the single crystals of  $M_{1.50}Al_{11.0}O_{17.25}$ , where  $M = K, Na$  by the ion-exchange reaction of barium  $\beta$ -alumina ( $Ba_{0.75}Al_{11.0}O_{17.25}$ ) according to the following reaction equation (14);



On the basis of simple ion-ion interaction analysis, Newsam (15) assumed the existence of a triply occupied mirror plane and predicted the upper limit of excess cation to be  $x = 0.571$  per unit formula with interstitial oxygen compensating the charge of excess cations. The compound  $M_{1.50}Al_{11.0}O_{17.25}$  ( $M_{1.50}$   $\beta$ -alumina) is near to the upper limit composition.

The present paper reports the determination of the crystal structure of  $K_{1.50}$   $\beta$ -alumina by the X-ray single-crystal diffraction method, and aims to clarify the cation distribution in the mirror plane and the influence of excess cation on the positional parameters of other atoms.

## Experimental

The single crystal was prepared by the ion exchange from barium  $\beta$ -alumina as previously reported (14). A  $0.4 \times 0.4 \times 0.4$ -mm<sup>3</sup> cube of barium  $\beta$ -alumina single crystal, which was grown by the floating zone method (16), was ground into a tiny sphere. This spherical specimen was buried in a great excess of  $K_2CO_3$  (10 g) contained in a

Pt crucible. The crucible was placed in the muffle furnace at 980°C and held for 20 hr in air. The radius of the specimens was 99  $\mu$ m, and the absorption factor ( $\mu R$ ) for this specimen was 0.162. After examination by the precession method to ascertain the crystallinity and the space group symmetry, the intensity data were measured on the computer-controlled four-circle diffractometer (Rigaku Denki Co. Ltd.) using graphite-monochromatized  $MoK\alpha$  radiation ( $\lambda = 0.71069$  Å). A set of three check reflections, (107), (220) and (00-10), was measured every 50 reflections. The reflections below  $2\theta = 120^\circ$  were collected. After Lorenz polarization and absorption corrections, it provided 558 nonzero independent  $F_0$ 's. Values of neutral atom scattering factors were taken from the "International Table for X-Ray Crystallography" (Vol. IV). For full-matrix refinement, the modified RSFLS-4 program of UNICS system which was originally written by Sakurai *et al.* (17) were used. Fourier syntheses were made using RSSFR-5 (UNICS) (18). The lattice parameters were obtained from a least-squares procedure applied to  $2\theta$ -values of 20 reflections measured on the four-circle diffractometer. The nomenclature of the sites in the mirror plane is taken after Peters *et al.* (1). Crystallographic data are shown in Table I.

A list of the observed and calculated structure factors is available from the authors.

TABLE I  
CRYSTALLOGRAPHIC DATA

Formula	$K_{1.50}Al_{11.0}O_{17.25}$
Symmetry	Hexagonal
Space group	$P6_3/mmc$
	$a = 5.598(1)$ Å
	$c = 22.732(5)$ Å
	$V = 616.9(2)$ Å <sup>3</sup>
	$Z = 2$
	$D_{obs} = 3.39$ g cm <sup>-3</sup>
	$D_{calc} = 3.399$ g cm <sup>-3</sup>

## Refinement

The precession photographs revealed diffuse spots of the superstructure as shown in Fig. 1. In the present paper, the average crystal was investigated using Bragg reflections. The space group was determined to be  $P6_3/mmc$  from the systematic absence of  $l = 2n + 1$  for  $hhl$  reflections, where  $n$  is an integer. As the fundamental structure was assumed to be a  $\beta$ -alumina structure (14), Fourier and difference Fourier syntheses were made by using the positional parameters Al(1) to Al(4) and O(1) to O(5) of potassium  $\beta$ -alumina with  $x = 0.3$  per unit formula ( $K_{1.30}$   $\beta$ -alumina) (4). Potassium was placed at the BR site (Beever-Ross site;  $(\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$ ) and the occupancy was assigned to unity for all atoms. The  $R$  factor ( $= \Sigma ||F_o| -$

$|F_c|/|\Sigma|F_o|$ ) was 0.278 at this stage. The difference Fourier sections show the deficiency of K at the BR site and Al(1) at  $z = 0.10$ . On the other hand, additional electron density was indicated at the mO site (mid-oxygen site;  $(\frac{5}{6}, \frac{2}{3}, \frac{1}{4})$ ) in the mirror plane ( $z = 0.25$ ). In the next refinement, K at the BR site was assigned to K(1) and K was added to the mO site as K(2). With varying the occupancy of K ions and Al(1), the refinement was accomplished on the positional parameters to give an  $R$  value of 0.145. Difference Fourier synthesis at this stage indicated the off-centering of K(1) from the ideal BR site, and O(5) from the  $2c$  site ( $\frac{1}{2}, \frac{2}{3}, \frac{1}{4}$ ). Further addition of K at the mO site nearer to the anti-BR site ( $0, 0, \frac{1}{4}$ ) than K(2) position was indicated, which was referred to as K(3) in the successive refinement. Af-

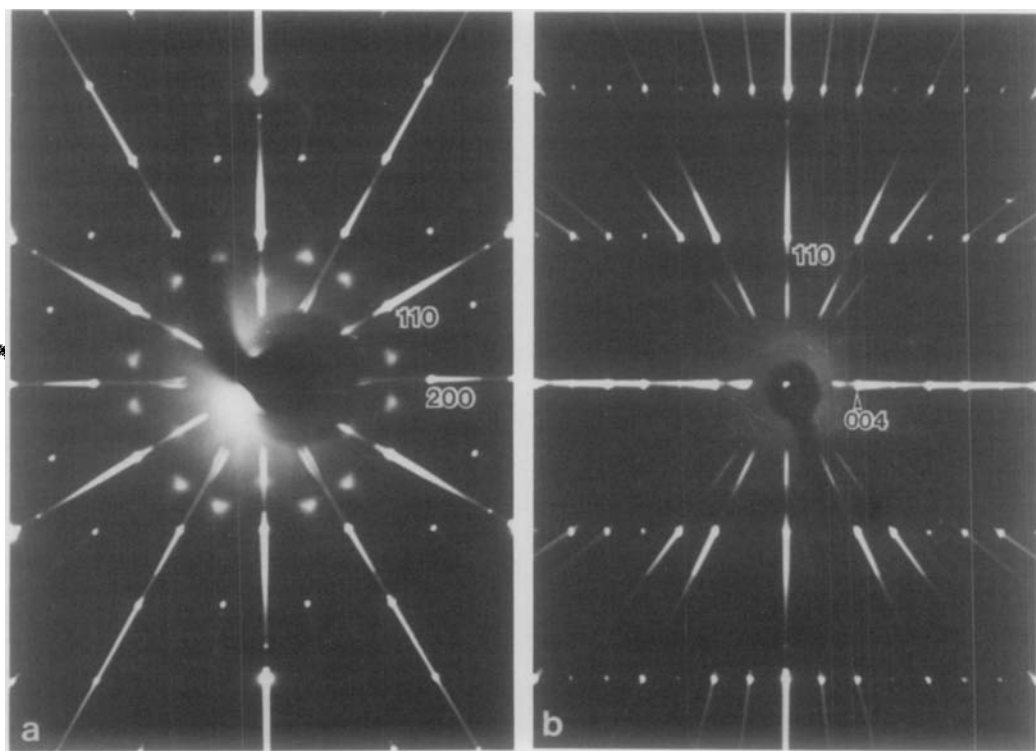


FIG. 1. X-ray diffraction patterns taken by the precession method using  $MoK\alpha$  radiation with Zr filter. The incident X-ray beam is normal to (a) (001) and (b) (100) planes. Diffuse superstructure reflections were shown by the long exposure. The  $hkl$  indices are based on the Bragg reflections.

TABLE II  
 THE POSITIONAL AND THERMAL<sup>a</sup> PARAMETERS

Position	Number per unit cell	<i>x</i>	<i>z</i>	$\beta_{11} \times 10^5$	$\beta_{22} \times 10^5$	$\beta_{33} \times 10^6$	$\beta_{23} \times 10^6$	$B_{eq}^b$	
K(1)	6 <i>h</i>	1.23(2)	0.6786(30)	$\frac{1}{4}$	2083(192)	5705(1125)	384(39)	0	2.3(6)
K(2)	6 <i>h</i>	1.45(5)	0.8830(12)	$\frac{1}{4}$	2364(206)	6073(652)	284(49)	0	2.5(5)
K(3)	6 <i>h</i>	0.26(4)	0.9672(49)	$\frac{1}{4}$	3734(1703)	1949(1907)	723(320)	0	2.5(17)
Al(1)	12 <i>k</i>	10.70(6)	0.8318(1)	0.10426(3)	484(23)	358(29)	165(9)	-96(54)	0.39(7)
Al(2)	4 <i>f</i>	4	$\frac{1}{2}$	0.02430(5)	401(26)	$\beta_{11}$	148(16)	0	0.35(3)
Al(3)	4 <i>f</i>	4	$\frac{1}{2}$	0.17454(6)	954(33)	$\beta_{11}$	145(15)	0	0.70(5)
Al(4)	2 <i>a</i>	2	0	0	452(40)	$\beta_{11}$	227(24)	0	0.44(4)
Al(5) <sup>c</sup>	12 <i>k</i>	0.89(4)	0.8377(14)	0.1748(4)					0.485 <sup>d</sup>
O(1)	12 <i>k</i>	12	0.1575(2)	0.04953(7)	817(45)	456(58)	227(18)	-40(101)	0.59(39)
O(2)	12 <i>k</i>	12	0.5033(3)	0.14626(8)	592(39)	659(59)	477(21)	-401(123)	0.71(10)
O(3)	4 <i>f</i>	4	$\frac{1}{2}$	0.05503(13)	709(63)	$\beta_{11}$	205(33)	0	0.59(7)
O(4)	4 <i>e</i>	4	0	0.14138(13)	471(56)	$\beta_{11}$	243(38)	0	0.46(6)
O(5)	6 <i>h</i>	2	0.318(10)	$\frac{1}{4}$	3060(770)	5905(3536)	121(64)	0	2.6(21)
O(6) <sup>c</sup>	6 <i>h</i>	0.5	0.799(5)	$\frac{1}{4}$					0.485 <sup>d</sup>

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

$$^b B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i a_j (\text{\AA}^2).$$

<sup>c</sup> Interstitials.

<sup>d</sup> Isotropic and fixed.

ter shifting K(1) and O(5) to the 6*h* sites, the refinement with a general temperature factor gave 0.116 as an *R* value. At this stage, secondary extinction effects were observed, so secondary extinction corrections (19) were introduced in the successive refinements. By this treatment the *R* value dropped to 0.080 immediately. Further refinements was accomplished by adding interstitial Al(5) at *z* = 0.17 according to the indications of the difference Fourier maps, yielding an *R* value of 0.068. Subsequent isotropic refinement reduced the *R* factor to 0.053. At this time interstitial O(6) was included in the refinement because the scattering power of 0.5 oxygen per unit cell estimated from the chemical formula could not be neglected as compared with that of potassium atom. The residual electron density just inside K(2) was attributed to interstitial oxygen. Final anisotropic refinement gave *R* = 0.029 and *wR* =  $(\sum w(|F_o| - |F_c|)^2 /$

$\sum w|F_o|^2)^{1/2} = 0.035$  with *w* = 1.0. The *g* value for the secondary extinction was  $2.76(9) \times 10^4$ . Final difference electron maps showed featureless peaks and depressions of electron density not exceeding the range of +0.6 to -0.8 e/Å<sup>3</sup>. The final positional parameters are given in Table II. The data of bond length and angles are shown in Tables III and IV, respectively. Figure 2 shows the electron density at the section of *z* = 0.25.

## Discussion

The present specimen was obtained by ion exchange of barium  $\beta$ -alumina. If Al defect and interstitial oxygen are retained through the ion-exchange reaction, the reaction formula can be written as Eq. (1). As previously reported (14), EPMA (electron-probe microanalysis), cell parameters, and density data support the composition of the

TABLE III  
INTERATOMIC DISTANCES

	Number of bonds	Distance (Å)
Octahedral coordination		
Al(1)–O(1)	2	2.012(2)
–O(2)	2	1.857(2)
–O(3)	1	1.953(2)
–O(4)	1	1.836(2)
Al(4)–O(1)	6	1.897(2)
Tetrahedral coordination		
Al(2)–O(1)	3	1.799(2)
–O(3)	1	1.803(3)
Al(3)–O(2)	3	1.769(3)
–O(5)	1	1.722(9)
Al(5)–O(2)	2	1.747(10)
–O(4)	1	1.747(13)
–O(6)	1	1.750(14)
Polyhedron 9-coordinated		
K(1)–O(2)	4	2.811(13)
–O(2)′	2	2.907(17)
–O(5)	3	3.24(9) (averaged)
Polyhedron 8-coordinated		
K(2)–O(2)	4	3.024(7)
–O(4)	2	2.717(6)
–O(5)	2	2.87(8)
Polyhedron 9-coordinated		
K(3)–O(2)	4	3.456(30)
–O(4)	2	2.490(7)
–O(5)	2	3.09(8) (averaged)
–O(5)′	1	3.40(11)

product. The result of refinement showed the total number of K ion to be 1.47 (4) per unit formula, which is well in accordance with the formula. So we could presume that the ion-exchange reaction proceeded according to the reaction equation (1) without alteration of the host lattice.

From crystallographic point of view, the change of the number of cations in the mirror plane in  $\beta$ -alumina presents two interesting problems. One is the problem of cation distribution among cation sites in the mirror plane. The other is the effect of excess cations on the positional parameters of the other atoms of the host lattice. To re-

TABLE IV  
BOND ANGLES

	Bond angles (deg)
Octahedral coordination	
O(1)–Al(1)–O(1)′	82.18(11)
–O(2)	91.16(10)
–O(3)	89.95(8)
–O(4)	84.34(9)
O(2)–Al(1)–O(2)′	95.25(17)
–O(3)	86.41(11)
–O(4)	98.67(8)
O(1)–Al(4)–O(1)′	88.38(8)
–O(1)″	91.62(8)
Tetrahedral coordination	
O(1)–Al(2)–O(1)′	110.33(6)
–O(3)	108.59(6)
O(2)–Al(3)–O(2)′	107.57(8)
–O(5)	108.8(26)
O(2)–Al(5)–O(2)′	103.45(65)
–O(4)	106.56(44)
–O(6)	104.85(85)
O(4)–Al(5)–O(6)	128.2(17)

veal these problems, a comparison was made with ordinary cation-excess potassium  $\beta$ -alumina ( $K_{1.30}Al_{11.0}O_{17.15}$ ;  $K_{1.30}$   $\beta$ -alumina) reported by Collin *et al.* (4). Some of positional and occupational parameters to be discussed are given in Table V for  $K_{1.30}$   $\beta$ -alumina and  $K_{1.50}$   $\beta$ -alumina.

To explain the cation distribution among various sites in these two potassium  $\beta$ -aluminas, we first considered K(3) site at  $x =$

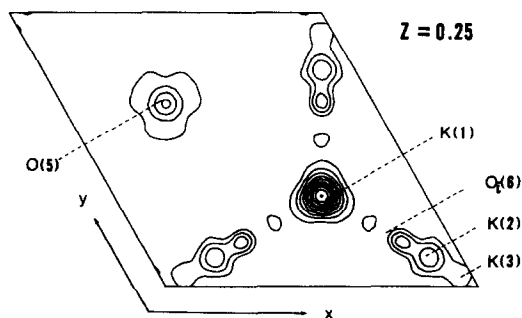


FIG. 2. Fourier section showing the electron density in the mirror plane at  $z = \frac{1}{4}$ . Contour lines are drawn with the interval of  $5 e \text{ \AA}^{-3}$  starting at  $5 e \text{ \AA}^{-3}$ .

TABLE V  
OCCUPANCY AND POSITIONAL PARAMETERS OF  
POTASSIUM  $\beta$ -ALUMINAS

		$K_{1.30-\beta^a}$	$K_{1.50-\beta}$
K(1)	$x$	0.6887(3)	0.6786(30)
	Occup. <sup>b</sup>	1.56(1)	1.23(2)
K(2)	$x$	0.8824(9)	0.8830(12)
	Occup. <sup>b</sup>	0.75(1)	1.45(5)
K(3)	$x$	0.9707(22)	0.9672(49)
	Occup. <sup>b</sup>	0.28(1)	0.26(4)
O(2)	$x$	0.5027(2)	0.5033(3)
	$z$	0.1454(1)	0.14626(8)
O(4)	$x$	0.0	0.0
	$z$	0.1411(2)	0.1414(1)
Lattice parameters			
	$a$	5.602 Å	5.598(1) Å
	$c$	22.734 Å	22.732(5) Å

<sup>a</sup> Ref. (4).

<sup>b</sup> Number of atoms per unit cell.

0.97 as caused by the shift from the mO site due to cation-cation interaction. (We will regard the cation near the BR site which cannot coexist with its symmetrically equivalent cations in the same single mirror plane as the cation situated at "the BR site." The "mO site" is considered to be in the range between the BR and aBR (0, 0,  $\frac{1}{4}$ ) sites.) In the second place, we tried to explore the simplest model in which the smallest number of cell types constitute potassium  $\beta$ -alumina. In the case of divalent  $\beta$ -alumina  $Ba_{0.75}Al_{11.0}O_{17.25}$ ,  $(BaAl_{11}O_{17})^{1+}$  and  $(OAl_{11}O_{17})^{3-}$  were considered to be the cells constituting barium  $\beta$ -alumina (16). Since there were only two types of cells oppositely charged, the composition of barium  $\beta$ -alumina was fixed for attaining charge neutrality. In fact, no solid solution has been found either to the  $Al_2O_3$ -rich or to the BaO-rich side along BaO- $Al_2O_3$  tie-line. To explain the existence of solid solution in the present case, a neutral cell is needed besides the oppositely charged cells. We supposed  $(KAl_{11}O_{17})$  as the basic and neutral cell, in which K is situated at the BR

site. The K ion at the mO with  $x = 0.88$  could not coexist with K at the BR site in the same single mirror plane due to short distance of 2.4 Å between them, and also K ion at the mO site with  $x = 0.97$  (near to aBR site) would not be found in the same single mirror plane with K at the BR site. Besides neutral cells  $(KAl_{11}O_{17})$ , the other cells assumed to constitute potassium  $\beta$ -alumina were triply occupied cells (or "triplet cells")  $(K_3Al_{11}O_{17})^{2+}$  and  $(K_2O \cdot Al_{11}O_{17})^{1-}$  (Fig. 3). The former has three K ions at the mO sites, i.e., K-K-K triplet cluster, in a single mirror plane. The latter has two K ions and one interstitial oxygen at the mO sites, forming K-K-Oi triplet cluster, where Oi stands for interstitial oxygen. For attaining charge neutrality,  $(K_3Al_{11}O_{17})^{2+}$  and  $(K_2O \cdot Al_{11}O_{17})^{1-}$  cells should be 1 to 2 in number. Thus potassium  $\beta$ -alumina could be expressed as  $(KAl_{11}O_{17})_{1-z} \cdot ((K_3Al_{11}O_{17}) \cdot 2(K_2O \cdot Al_{11}O_{17}))_z$ . The number of the mO site cation would be  $7x/4$  and cation at the BR site would be  $1-3x/4$ , when taking  $x$  as the excess cation number per unit formula. These triplet cells were already thought to constitute potassium  $\beta$ -gallate structure by Anderson *et al.* (20), and this concept was used for prediction of the upper limit of cation content by Newsum (15). The calculated occupation number is shown in Table VI. For comparison, the occupancy calculated by the model of Wang *et al.* (21) is also shown. Their model

TABLE VI  
COMPARISON OF THE OCCUPATION NUMBER<sup>a</sup> WITH  
THE MODELS

	$K_{1.30-\beta}$		$K_{1.50-\beta}$	
	BR'	mO'	BR'	mO'
Wang's model	0.700	0.600	0.500	1.000
Triplet model	0.775	0.525	0.625	0.875
The result of refinement	0.78	0.52	0.62	0.86

<sup>a</sup> The number of atoms per unit formula.

is equivalent to considering  $M$ - $M$  doublet cell ( $M_2Al_{11}O_{17}$ )<sup>1+</sup> and  $M$ - $M$ - $O_i$  triplet cell ( $M_2O \cdot Al_{11}O_{17}$ )<sup>1-</sup> besides neutral cell ( $MAl_{11}O_{17}$ ), where  $M$  is monovalent cation. In both cases of potassium  $\beta$ -alumina, the triplet model fits well with the real occupation as can be seen from Table VI.

The cation distribution of other  $\beta$ -alumina compounds can be interpreted by this triplet model. For Na<sub>1.29</sub>  $\beta$ -alumina, Peters *et al.* (1) reported the site occupation number of Na at the BR site and the mO site to be 0.75(4) and 0.52(5) per unit formula. From the triplet model, site occupation would be 0.78 and 0.51, respectively. Furthermore, site occupation number per unit formula in Ag<sub>1.25</sub>  $\beta$ -alumina (7) were assigned to be 0.815 and 0.435 for the "BR site" (BRD(1) + BRD(2)) and the "anti-BR site" (aBR(3)), respectively. If the "anti-BR site" with  $x = 0.976$  is considered as only caused by the shift from the mO site, the triplet model can be also applied and the number would be 0.813 and 0.438, respectively. In this way, the triplet model has a wide applicability to the explanation of the site occupancy in  $\beta$ -alumina compounds.

The conclusions above described were based on the average structure obtained by

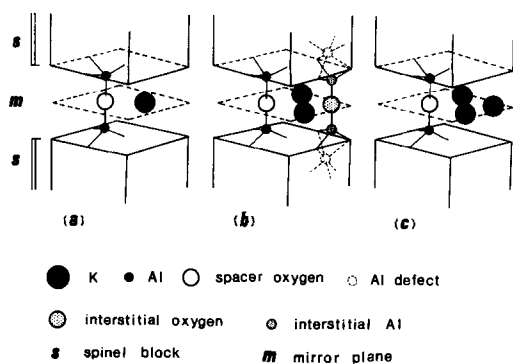


FIG. 3. Schematic depiction of three types of cells assumed to constitute  $K_{1.50}$   $\beta$ -alumina structure. (a) Singlet cell ( $KAl_{11}O_{17}$ ), (b)  $K$ - $K$ - $O_i$  triplet cell ( $K_2O \cdot Al_{11}O_{17}$ )<sup>1-</sup>, and (c)  $K$ - $K$ - $K$  triplet cell ( $K_3Al_{11}O_{17}$ )<sup>2+</sup>. (b) and (c) should be in the ratio of 2 to 1 for attaining charge neutrality.

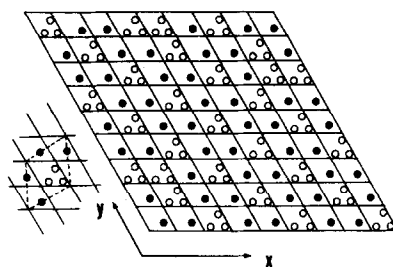


FIG. 4. Representation of the  $z = \frac{1}{4}$  sections of two-dimensional  $a\sqrt{3} \times a\sqrt{3}$  superstructure arrangement in  $K_{1.50}$   $\beta$ -alumina. An  $a\sqrt{3} \times a\sqrt{3}$  superstructure cell is indicated by the dotted line. Filled circles represent K ions at the BR sites and the open circles are K or interstitial oxygens forming triplet cluster. Spacer oxygens are omitted. In this region, three singlet cells are changed into triplet cells, causing the discontinuity of the arrangement. The triplet clusters should be  $K$ - $K$ - $K$  and  $K$ - $K$ - $O_i$  in the ratio of 1 to 2 as a whole.

using the sharp Bragg reflections. As described before (14), there were found somewhat broader superstructure reflections besides Bragg reflections. Here, we have to clarify the causes of superstructure by using above discussed structure model. The precession photographs (Fig. 1) revealed the superstructure to be essentially of  $a\sqrt{3} \times a\sqrt{3} \times c$  type. The diffuseness indicates the presence of small domains. We assumed that two singlet cells and one triplet cell constitute  $a\sqrt{3} \times a\sqrt{3}$  superstructure. Here, the triplet cell part is randomly occupied by  $K$ - $K$ - $K$  triplet or  $K$ - $K$ - $O_i$  triplet cells, in total 1-to-2 ratio. This two-dimensional  $a\sqrt{3} \times a\sqrt{3}$  arrangement would give a composition with  $x$  level of 0.444, which is slightly less than the present composition of  $x = 0.5$ . Accordingly some singlet cells, in the ratio of about 1 to 20 singlet cells, might be converted into  $K$ - $K$ - $K$  triplet cells with causing the partial discontinuity of  $a\sqrt{3} \times a\sqrt{3}$  fundamental superstructure long-range ordering (Fig. 4). The observed slightly broad diffuses can be interpreted by this partial disordering.

The remaining problem is the effect of excess  $K^+$  ion in the mirror plane on the

lattice parameters and the positional parameters of host lattice. As can be seen in Table V, lattice parameters change little in spite of the increment of K ion population in the mirror plane. However, the positional parameters differ slightly from each other. Here, we define the distance between O(2) at the 12k site just up and down the mirror plane ( $z = 0.25$ ) as "the thickness of the mirror plane"  $M_{12k}$  as shown in Fig. 5. If measured from O(4) at the 4e site to its counterpart across the mirror plane, "the thickness of the mirror plane" is referred to as  $M_{4e}$ . In the same way, "the thickness of the spinel block"  $S_{12k}$  and  $S_{4e}$  can be defined. They are measured across the spinel block. These hold the equation  $c/2 = M_{12k} + S_{12k} = M_{4e} + S_{4e}$ .  $M_{12k}$  for  $K_{1.30}$   $\beta$ -alumina and  $K_{1.50}$   $\beta$ -alumina are 4.756 and 4.716 Å, respectively. Here, contraction of the "thickness of the mirror plane" by 0.040 Å can be observed. On the other hand,  $M_{4e}$  are 4.952 and 4.938 Å for  $K_{1.30}$   $\beta$ -alumina and  $K_{1.50}$   $\beta$ -alumina, respectively. The difference of 0.014 Å is little when compared with the difference of  $M_{12k}$ . The excess cation might effect the distance  $M_{12k}$

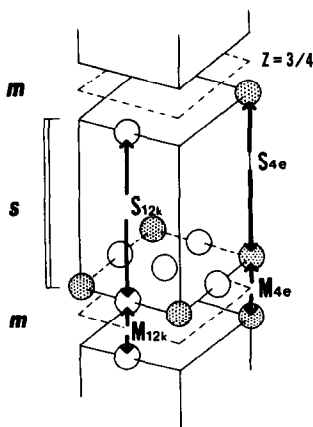


FIG. 5. The simplified  $\beta$ -alumina structure showing the thickness of the mirror plane  $M_{12k}$ ,  $M_{4e}$ , and the thickness of the spinel block  $S_{12k}$ ,  $S_{4e}$ . Open circles represent O(2) at the 12k site and shaded circles are O(4) at the 4e site.  $S$  and  $M$  stand for the spinel block and the mirror plane, respectively.

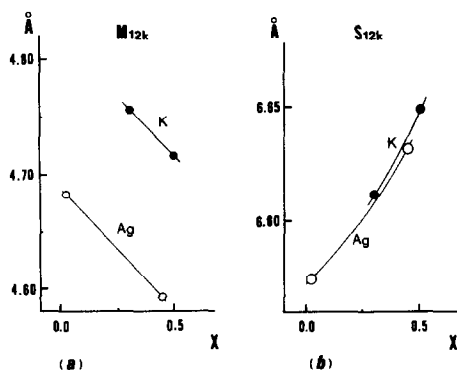


FIG. 6. Relation between  $x$  = excess cation content per unit formula and (a)  $M_{12k}$ , (b)  $S_{12k}$  in the case of K  $\beta$ -alumina and Ag  $\beta$ -alumina compounds.

more than that of  $M_{4e}$ . Furthermore, the distance  $S_{12k}$  for  $K_{1.30}$   $\beta$ -alumina is 6.611 Å and that for  $K_{1.50}$   $\beta$ -alumina is as large as 6.650 Å. Thus, the contraction of  $M_{12k}$  and enlargement of  $S_{12k}$  owing to the excess potassium ion in the mirror plane compensate each other to make little difference of lattice parameter  $c$  between  $K_{1.30}$   $\beta$ -alumina and  $K_{1.50}$   $\beta$ -alumina. This relation is shown in Fig. 6. The increment of  $S_{12k}$  might be attributed to the concentration of Al defect in the spinel block.

Well investigated Ag  $\beta$ -alumina compounds shows the same tendency for  $M_{12k}$  and  $S_{12k}$  (Fig. 6). At the temperature of 4 K, stoichiometric  $AgAl_{11}O_{17}$  (8) has 6.58 Å of  $S_{12k}$  and 4.68 Å of  $M_{12k}$ ; on the other hand, cation excess  $Ag_{1.45}$   $\beta$ -alumina (13) has larger value 6.63 Å of  $S_{12k}$  and smaller value 4.60 Å of  $M_{12k}$ . This relation is also true for  $Ag_{1.0}$   $\beta$ -alumina (7) and  $Ag_{1.33}$   $\beta$ -alumina (2) at room temperature. Surprisingly enough, the values of  $S_{12k}$  of the nondoped monovalent  $\beta$ -alumina compounds (1-5) having an  $x$  level of about 0.3, namely having the same amount of Al defects within the spinel block, are confined to the range of 6.59 ~ 6.61 Å with exception of the slightly smaller value of 6.58 Å in Tl  $\beta$ -alumina (4). On the other hand,  $M_{12k}$  gradually contracts in proportion as the cation radius decreases, with



the lower limit of about 4.6 Å. As far as nondoped monovalent cation containing  $\beta$ -alumina compounds are concerned, we could assume that the mirror plane thickness  $M_{12k}$  might reflect the population and the radius of the cation in the mirror plane, and that the spinel block thickness  $S_{12k}$  might reflect mainly the defect concentration in the spinel block. However, accurate positional parameters of the  $\beta$ -aluminas with various cation content are needed to draw a more precise conclusion.

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