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The Crystal Structure and Cation Distribution of Highly Nonstoichiometric Magnesium-Doped Potassium β-Alumina

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The crystal structure of Mg-doped potassium β-alumina $K_{1.875}Ba_{0.022}Mg_{0.919}Al_{10.081}O_{17.0}$ ($K_{1.875}$ · Mg β-alumina), obtained by ion exchange from $Ba_{0.956}Mg_{0.912}Al_{10.088}O_{17.0}$ ($Ba_{0.956}$ · Mg β-alumina), has been refined from single-crystal X-ray data with a final R-value of 0.034. $K_{1.875}$ · Mg β-Alumina contains an extremely large number of K ions while retaining the fundamental β-alumina structure and space group symmetry $P6_3/mmc$. The structure was found to be consistent with a model composed of singly occupied cells containing a K ion at the Beevers–Ross (BR) site and triplet cells containing three K ions at the mid-oxygen (mO) sites, as in the case of $K_{1+y}Mg_yAl_{11-y}O_{17}$ with $y = 0.62$. The extra cations were assumed to be accommodated in the anti-BR (aBR) sites created by clustering of three triplet cells. The occupancies of K ion sites calculated by this model agree well with those obtained by the refinement. The structure of $Ba_{0.956}$ · Mg β-alumina was also refined, yielding $R = 0.031$.

Introduction

β-Alumina compounds usually exhibit nonstoichiometric compositions with the formula $M_{1+x}Al_{11.0}O_{17+x/2}$ (M: monovalent cation) where $x \approx 0.3$. In these nondoped β-alumina compounds, the extra charge due to excess cations is known to be compensated by interstitial oxygen in the conduction plane (mirror plane; $z = 0.25$) (*1*). The cation distribution in nonstoichiometric β-alumina containing more than the ordinary composition $x \approx 0.3$ is an interesting problem. For the preparation of such a highly nonstoichiometric β-alumina, we (*2*) found a new synthetic route using the ion-exchange reaction of barium β-alumina ($Ba_{0.75}Al_{11.0}O_{17.25}$) (*3*), and, recently, we (*4*) reported the cation distribution of highly nonstoichiometric potassium β-alumina ($K_{1.50}Al_{11.0}O_{17.25}$). It was assumed that the triply occupied cells (triplet cells; half unit cells with $c/2$ dimension), in which K or interstitial oxygen occupy the mO site [mid-oxygen site, $(\frac{5}{6},\frac{2}{3},\frac{1}{4})$] of a single mirror plane, such as ($K_3Al_{11}O_{17}$) and (K_2O · $Al_{11}O_{17}$) in addition to the singly occupied cells containing K at the BR site [Beevers–Ross site; $(\frac{2}{3},\frac{1}{3},\frac{1}{4})$] make up the structure. Furthermore, we showed that the ion-exchange method was applicable to Mg-doped barium β-alumina having composition $Ba_{0.956}Mg_{0.912}Al_{10.088}O_{17.0}$ ($Ba_{0.956}$ · Mg β-alumina), and that equimolar exchange between Ba and K_2 took place (*2*). Aside from nondoped β-alumina, Mg-doped β-alumina constitutes one of the important series of β-aluminas. The charge compensation is supposedly due to Mg^{2+} substitution for Al^{3+} in the spinel block, in contrast to undoped β-

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alumina. Collin *et al.* (*5*) have studied Mg-doped β-alumina and prepared $M_{1+y}Mg_y Al_{11-y}O_{17}$ with $y = 0.62$ by cooling the melt of a given composition. By this direct reaction, β″-alumina formation was reported (*6*) starting with compositions beyond $y = 0.667$. The ion-exchanged product which we have prepared yielded a large excess cation content, greater than $y = 0.667$, while maintaining the fundamental structure of a β-alumina type. Newsam (*7*) has predicted the upper limit of the cation content in Mg-doped β-alumina to be $y = 0.667$, if there occurs no occupation of the aBR sites [anti-Beevers-Ross sites, $(0,0,\frac{1}{4})$]. It is, therefore, of great interest to determine how excess cations can be accommodated in the mirror plane of the Mg-doped β-alumina host lattice.

The purposes of the present study are to report the structure determination of $K_{1.875}$ · Mg β-alumina by using X-ray single-crystal diffraction data, and to explain the cation distribution in terms of a reasonable structure model. We also present the positional parameters and other data of $Ba_{0.956}$ · Mg β-alumina used for ion exchange.

Experimental

Nonstoichiometric Mg-doped potassium β-alumina, $K_{1.875}$ · Mg β-alumina, was prepared by ion exchange from $Ba_{0.956}$ · Mg β-alumina as previously reported (*2*). The single crystal of the starting material $Ba_{0.956}$ · Mg β-alumina was grown by the floating zone (FZ) method using a xenon arc lamp as the heat source (*8*). The growth rate was 1 mm/hr and nitrogen was used as the growth atmosphere. The grown boule was largely $Ba_{0.956}$ · Mg β-alumina, but a small amount of $BaMg_3Al_{14}O_{25}$ coexisted in the center of the boule. Part of the $Ba_{0.956}$ · Mg β-alumina was analyzed by EPMA (electron probe microanalyzer), which showed a small Ba deficiency relative to the expected composition $BaMgAl_{10}O_{17}$ (*2*). The crystalline part of $Ba_{0.956}$ · Mg β-alumina was cut into cubes with dimension approximately $0.4 \times 0.4 \times 0.4$ mm^3 and was used as the starting material for ion exchange. Several specimens were placed in a Pt crucible and a great excess of K_2CO_3 powder (about 10 g) was added. The crucible was placed in a Muffle furnace and heated at 980°C for 20 hr in an air atmosphere. The resulting crystal was further cut into a $200 \times 200 \times 100$ μm cube and directly examined by EPMA. The composition was almost the same as previously reported (*2*), showing that the mole fraction of the remaining Ba was 0.0118 relative to the K content. The specimen was checked for crystallinity and space group by the precession method. The space group was determined to be $P6_3/mmc$; we found no superstructure spots or diffuse scattering. For intensity data collection, the crystal was mounted on an automatic four circle diffractometer (Rigaku Denki Co. Ltd.) with monochromatized Mo*Kα* radiation ($\lambda = 0.71069$ Å). Reflections below $2\theta = 120°$ were collected by checking against a set of reflections (107) and (00 · 10), measured ever 50 reflections. After Lorenz polarization and absorption corrections, we obtained 775 nonzero independent intensities. The linear absorption coefficient (μ) was calculated as 17.7 cm^{-1} and the intensity data were further subjected to an absorption correction (*9*) producing a final set of F_0's. The neutral atom scattering factors were taken from the International Tables for X-Ray Crystallography (Vol. IV). Of the UNICS system, we used RSFLS-4 (*10*) and RSSFR-5 (*11*) programs, which were modified by the authors, for least-squares refinement and Fourier syntheses, respectively. The lattice parameters were refined by using data collected on the four-circle diffractometer with Mo*Kα* radiation. The structure of $Ba_{0.956}$ · Mg β-alumina was similarly refined. The specimen was a sphere of radius of 70 μm, the collected nonzero unique intensity data amounted to 677. Ab-

TABLE I

CRYSTALLOGRAPHIC DATA

Formula	$K_{1.875}Ba_{0.022}Mg_{0.919}Al_{10.081}O_{17.0}$	$Ba_{0.956}Mg_{0.912}Al_{10.088}O_{17.0}$
Symmetry	Hexagonal	Hexagonal
Space group	$P6_3/mmc$	$P6_3/mmc$
	a = 5.6408(5) Å	5.6275(7) Å
	c = 22.645(3) Å	22.658(7) Å
	V = 623.98(9) Å^3	621.42(21) Å^3
	Z = 2	2
	D_{calc} = 3.420 g cm^{-3}	3.728 g cm^{-3}

sorption corrections were also applied in this case, as the linear absorption coefficient was 42.7 cm^{-1}. The nomenclature of the cation sites in the mirror plane was taken from that of Peters *et al.* (*12*), but in a wider sense. We define the BR site as the site near $(\frac{2}{3},\frac{1}{3},\frac{1}{4})$. This cannot be occupied at the same time as the symmetrical equivalent and mO cation sites in the same single mirror plane. Similarly, the mO site can be defined as the site near $(\frac{5}{6},\frac{2}{3},\frac{1}{4})$ which is able to coexist with the symmetrical equivalents or other mO sites. The aBR site is $(0,0,\frac{1}{4})$. Table I contains crystallographic data of $K_{1.875}$ · Mg β-alumina and $Ba_{0.956}$ · Mg β-alumina.

Tables of the calculated and observed structure factors can be obtained from the authors on request.

Refinement

The fundamental structure of $K_{1.875}$ · Mg β-alumina was supposed to be the β-alumina type. Fourier and difference Fourier syntheses were, at first, carried out using the positional parameters of Al(1) to Al(4) and O(1) to O(5) of potassium β-alumina as refined by Collin *et al.* (*13*). K was placed as K(1) at the ideal BR site $(\frac{2}{3},\frac{1}{3},\frac{1}{4})$ with full occupancy. The Fourier synthesis of this model with an R-value $= \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.270$ indicated a slight deficiency at K(1), and additional electron density at the mO site. After addition of K(2) at the mO site, further refinement was made varing the occupancy of K(1), yielding an R-factor of 0.136. At this stage, there was residual electron density around the BR site; therefore, K(1) was split into the 6h site near the BR site. After addition of K(3) at the aBR site $(0,0,\frac{1}{4})$ as indicated by the difference Fourier maps, the R-value was reduced to 0.105 using a general temperature factor. Successive refinements using individual isotropic temperature factors further reduced the R-value to 0.077. Still, there remained electron density probably due to K ions at the mO site ($x = 0.82$) just inside the K(2) position; thus, we added K as K(4). The final isotropic refinement yielded $R = 0.065$. As next anisotropic refinement indicated a tendency of K(1) at the 6h site to shift back to the BR site, further refinements were accomplished with K(1) being situated at the BR site. In this manner, an anisotropic refinement was successfully conducted, yielding an R-value of 0.034 ($wR = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2} = 0.045 : w = 1.0$). As pointed out earlier, EPMA revealed that Ba still remained at a molar ratio of 0.0118 relative to K, so Ba was included in the successive anisotropic refinement by assuming Ba to be situated at the same site having the same temperature factor (in the form $B_{eq.}$) as in barium β-alumina ($Ba_{0.75}Al_{11.0}O_{17.25}$) (*3*). In the refinement the Ba occupancy was specified by

TABLE II

THE POSITIONAL AND THERMAL[a] PARAMETERS OF $K_{1.875} \cdot Mg$ β-ALUMINA

Position		Number per unit cell	x	z	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^5$	$\beta_{23} \times 10^5$	$B_{eq.}$[b]
K(1)	2*d*	1.34(3)	$\frac{2}{3}$	$\frac{1}{4}$	333(15)	β_{11}	35(4)	0	2.4(2)
K(2)	6*h*	1.32(22)	0.9112(39)	$\frac{1}{4}$	276(56)	726(205)	38(8)	0	3.0(12)
K(3)	2*b*	0.39(8)	0	$\frac{1}{4}$	685(148)	β_{11}	33(18)	0	4.6(19)
K(4)	6*h*	0.70(19)	0.821(12)	$\frac{1}{4}$	372(148)	1212(565)	29(12)	0	4.3(33)
Ba	6*h*	0.044[c]	0.617[d]	$\frac{1}{4}$					1.14[e]
Al(1)	12*k*	12	0.8330(1)	0.10521(3)	30(2)	31(2)	21(1)	−4(5)	0.34(16)
Al(2)	4*f*	4	$\frac{1}{3}$	0.02481(6)	42(3)	β_{11}	23(2)	0	0.42(3)
Al(3)	4*f*	4	$\frac{1}{3}$	0.17345(6)	40(3)	β_{11}	13(2)	0	0.34(4)
Al(4)	2*a*	2	0	0	32(4)	β_{11}	19(3)	0	0.33(4)
O(1)	12*k*	12	0.1533(2)	0.05150(7)	58(4)	73(7)	27(2)	−51(10)	0.59(6)
O(2)	12*k*	12	0.5035(3)	0.14714(7)	39(3)	42(5)	28(2)	16(11)	0.45(12)
O(3)	4*f*	4	$\frac{2}{3}$	0.05815(16)	37(5)	β_{11}	38(4)	0	0.50(5)
O(4)	4*e*	4	0	0.14389(15)	42(6)	β_{11}	32(4)	0	0.49(6)
O(5)	2*c*	2	$\frac{1}{3}$	$\frac{1}{4}$	137(13)	β_{11}	12(5)	0	0.95(27)

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

[b] $B_{eq.} = \frac{4}{3}\Sigma_i\Sigma_j B_{ij}a_i a_j$ (Å^2).

[c] Contrained $n(K(1) + K(2) + K(3) + K(4)) \times 0.0118 = n(\mathrm{Ba})$, n; occupation number.

[d] Fixed.

[e] Fixed isotropic temperature factor.

the total potassium occupation multiplied by the factor 0.0118, while the positional parameters and temperature factor of Ba were held fixed. With this treatment, only the K(1) occupation changed, without affecting the other parameters beyond the

TABLE III

THE POSITIONAL AND THERMAL[a] PARAMETERS OF $Ba_{0.956} \cdot Mg$ β-ALUMINA

Position		Number per unit cell	x	z	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^5$	$\beta_{23} \times 10^5$	$B_{eq.}$[b]
Ba	2*d*	1.912(9)	0.6678(11)	$\frac{1}{4}$	80(9)	89(19)	26(1)	0	0.70(6)
Al(1)	12*k*	12	0.8343(1)	0.10544(4)	32(2)	33(3)	24(1)	−3(6)	0.37(22)
Al(2)	4*f*	4	$\frac{1}{3}$	0.02400(7)	50(4)	β_{11}	25(2)	0	0.49(3)
Al(3)	4*f*	4	$\frac{1}{3}$	0.17416(7)	33(3)	β_{11}	18(2)	0	0.33(3)
Al(4)	2*a*	2	0	0	29(5)	β_{11}	18(3)	0	0.31(5)
O(1)	12*k*	12	0.1534(3)	0.05152(9)	55(5)	67(9)	27(2)	−31(12)	0.56(9)
O(2)	12*k*	12	0.5042(3)	0.14799(9)	43(5)	41(6)	30(3)	7(13)	0.47(34)
O(3)	4*f*	4	$\frac{2}{3}$	0.05901(17)	39(7)	β_{11}	45(5)	0	0.56(7)
O(4)	4*e*	4	0	0.14437(16)	42(7)	β_{11}	27(4)	0	0.45(6)
O(5)	2*c*	2	$\frac{1}{3}$	$\frac{1}{4}$	198(19)	β_{11}	28(7)	0	1.4(3)

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

[b] $B_{eq.} = \frac{4}{3}\Sigma_i\Sigma_j B_{ij}a_i a_j$ (Å^2).

esd's. The R-value also remained unchanged. As a check, difference Fourier sections were taken, which showed a slight depression of $-1.7\ e/\text{Å}^3$ at (0,0,0.21), with a noise level not exceeding the range of -1.0 to $+0.8\ e/\text{Å}^3$.

The structure of $Ba_{0.956} \cdot Mg$ β-alumina was similarly refined. We started with the positional parameters of barium β-alumina (*3*), not including interstitials ($R = 0.122$). The refinement, using a general temperature factor, yielded $R = 0.045$ when varing the occupancy of Ba. Further individual isotropic refinement reduced the R-factor to 0.035. The final anisotropic refinement converged to yield $R = 0.031$ ($wR = 0.035$, $w = 1.0$). Difference Fourier synthesis at the last stage showed featureless depressions and peaks within the limit of $+1.1$ to $-1.2\ e/\text{Å}^3$, with the exception of a slight large peak of $2.9\ e/\text{Å}^3$ at $(\frac{1}{3},\frac{2}{3},0.23)$.

TABLE IV

INTERATOMIC DISTANCES

	Number of bonds	Distance (Å)	
		$K_{1.875} \cdot Mg$-β	$Ba_{0.956} \cdot Mg$-β
	Octahedral coordination		
Al(1)–O(1)	2	1.985(2)	1.980(3)
–O(2)	2	1.869(2)	1.876(3)
–O(3)	1	1.943(2)	1.943(3)
–O(4)	1	1.851(2)	1.841(2)
Al(4)–O(1)	6	1.898(2)	1.897(3)
	Tetrahedral coordination		
Al(2)–O(1)	3	1.860(2)	1.862(3)
–O(3)	1	1.879(4)	1.881(4)
Al(3)–O(2)	3	1.766(3)	1.768(3)
–O(5)	1	1.733(2)	1.718(2)
	Polyhedron 9-coordinated		
K(1) –O(2)	6	2.822(2)	
–O(5)	3	3.2568(3)	
	Polyhedron 8-coordinated		
K(2) –O(2)	4	3.14(2)	
–O(4)	2	2.555(14)	
–O(5)	2	2.921(30)	
	Polyhedron 9-coordinated		
K(3) –O(2)	4	3.658(2)	
–O(4)	2	2.403(4)	
–O(5)	3	3.2567(3)	
	Polyhedron 8-coordinated		
K(4) –O(2)	4	2.80(5)	
–O(4)	2	2.97(7)	
–O(5)	2	2.82(9)	
	Polyhedron 9-coordinated		
Ba –O(2)	4		2.773(6)
–O(2)′	2		2.865(7)
–O(5)	2		3.196(9)
–O(5)′	1		3.358(11)

TABLE V

BOND ANGLES

	Bond angles (°)	
	$K_{1.875} \cdot Mg$-β	$Ba_{0.956} \cdot Mg$-β
Octahedral coordination		
O(1)–Al(1)–O(1)′	81.59(12)	81.63(15)
–O(2)	91.48(10)	92.06(12)
–O(3)	92.06(10)	91.98(11)
–O(4)	84.14(10)	84.89(13)
O(2)–Al(1)–O(2)′	95.22(14)	93.96(17)
–O(3)	84.72(11)	84.32(13)
–O(4)	98.64(10)	98.48(12)
O(1)–Al(4)–O(1)′	86.20(8)	86.08(10)
–O(1)″	93.80(8)	93.92(10)
Tetrahedral coordination		
O(1)–Al(2)–O(1)′	109.98(6)	109.38(8)
–O(3)	108.96(6)	109.57(8)
O(2)–Al(3)–O(2)′	109.23(7)	109.34(9)
–O(5)	109.71(7)	109.60(8)

The positional parameters of $K_{1.875} \cdot Mg$ β-alumina and $Ba_{0.956} \cdot Mg$ β-alumina are given in Tables II and III, respectively. Interatomic distances and angles for both compounds are shown in Tables IV and V. Figure 1 shows the Fourier section at $z = 0.25$ of $K_{1.875} \cdot Mg$ β-alumina.

Discussion

The refinement showed $Ba_{0.956} \cdot Mg$ β-alumina to be a typical β-alumina, having Ba at the BR site, without any interstitial ions. From the bond lengths in both compounds, Mg might be situated at the Al(2) tetrahedral site within the spinel block, as

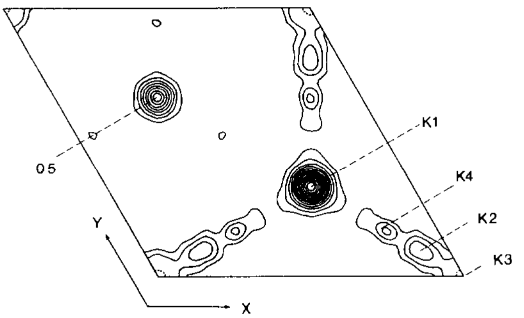

FIG. 1. The electron density map for the section z = 0.25. Contour lines are drawn at the interval of 5 e/Å^3 at the minimum value of 5 e/Å^3.

was found in other Mg-doped β-alumina compounds (*5*). The $Ba_{0.956}$ · Mg β-alumina used as the starting material contained slightly less Ba than corresponds to the ideal formula $BaMgAl_{10}O_{17}$, so the resulting Mg-doped potassium β-alumina also exhibited a somewhat smaller K-content than expected for the reaction previously described (*2*);

$$BaMgAl_{10}O_{17} + 2K^+ = K_2MgAl_{10}O_{17} + Ba^{2+}$$

Table I specifies the composition of both Mg-doped compounds calculated from the occupancy obtained in the refinements. From EPMA data, we obtained the formulae, $Ba_{0.955}Mg_{0.962}Al_{10.056}O_{17.0}$ and $K_{1.872}Ba_{0.022}Mg_{0.921}Al_{10.08}O_{17.0}$. In these calculations the number of oxygen per unit formula was specified as 17.0. The formulae derived from X-ray data and from EPMA data agreed very well with each other and the result clearly shows that the reaction proceeded with equimolar exchange, as in the case of $K_{1.50}$ β-alumina (*4*).

The cation distribution of $K_{1.875}$ · Mg β-alumina represents a very interesting problem, as there are more cations than the upper limit of y = 0.667 in $K_{1+y}Mg_yAl_{11-y}O_{17}$ which Newsam predicted on the basis of the "triply occupied mirror plane" concept (*7*). Furthermore, Collin *et al.* (*5*) studied the cation distribution of Mg-doped potassium β-alumina up to y = 0.62. Using the standard preparative method they were unable to extend the synthesis of β-alumina compounds beyond y = 0.667; instead, β″-alumina having rhombohedral symmetry was obtained. The present compound $K_{1.875}$ · Mg β-alumina is one of the compounds of the series $K_{1+y}Mg_yAl_{11-y}O_{17}$, with y = 0.875 far beyond 0.667, which retains the fundamental β-alumina structure. In $K_{1.667}$ · Mg β-alumina, it is assumed that K–K–K triply occupied cells (triplet cells; K ions are situated at the three mO sites) and K singly occupied cells (K ion is situated at the BR site) make up the structure in the ratio of 1 to 2 (*6, 7*). For y = 0.667, the occupation numbers per unit formula were calculated to be 0.667 and 1.00 for the BR and mO sites, respectively. The composition y = 0.667 was considered to be the upper limit of K-content in Mg-doped potassium β-alumina because there was no room for accommodating the K–K–K triplet cells without coming in contact with other nearest neighbor triplet cells. The distance between K at the mO site of one cell and the nearest K at the mO of the neighboring cell was considered by Newsam (*7*) to be too short. In the present compound, there are more cations than in the compound with y = 0.667, so the excess cation might occupy the aBR site. However, there are no aBR sites far enough apart to avoid K–K interaction: all aBR sites are too close to the occupied mO sites, at a distance of only about 1.75 Å, even at the composition y = 0.667. Accordingly it is appropriate to consider that triplet cells could change into cells of an aBR–BR arrangement for accommodating excess cations, as shown in Fig. 4b. According to this model, the occupancy at the mO site would decrease and that at the BR site would increase in proportion to the increment of cation content beyond y = 0.667. However, the results of refinement of $K_{1.875}$ · Mg β-alumina clearly

TABLE VI

OCCUPANCY AND POSITIONAL PARAMETERS OF Mg-DOPED POTASSIUM β-ALUMINAS

		Site	$K_{1.62} \cdot$ Mg-β[a]	$K_{1.875} \cdot$ Mg-β
K(1)	x	BR	0.6716(10)	0.6667
	Occup.[b]		1.37(1)	1.34(3)
K(2)	x	mO	0.8844(6)	0.9112(39)
	Occup.[b]		1.88(1)	1.32(22)
K(3)	x	aBR	—	1.000
	Occup.[b]		—	0.39(8)
K(4)	x	mO	—	0.821(12)
	Occup.[b]		—	0.70(19)
Lattice parameters				
	a		5.608(2) Å	5.6408(5) Å
	c		22.56(1) Å	22.645(3) Å

[a] Ref. (5).

[b] Numbers of atoms per unit cell.

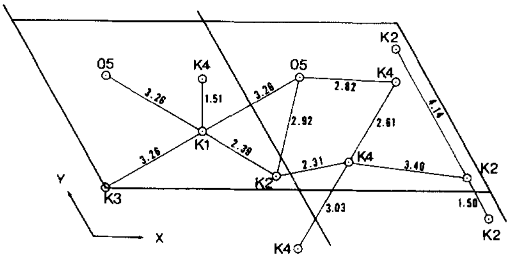

FIG. 2. The distances between the sites in the z = 0.25 mirror planes in Ångstrom (Å) units.

show that this model is not correct. Surprisingly, the BR and mO occupancies changed little compared with that of $K_{1.62} \cdot$ Mg β-alumina, as shown in Table VI, and also showed nearly the same values as the expected occupancies for $K_{1.667} \cdot$ Mg β-alumina. The fact indicates that there are triplet cells in contact with other triplet cells. The difference in cation arrangement between $K_{1.62} \cdot$ Mg β-alumina and $K_{1.875} \cdot$ Mg β-alumina may be reflected in the positional parameters of the mO sites. As shown in Table VI, there are two mO sites in $K_{1.875} \cdot$ Mg β-alumina. One of the mO sites, x = 0.82, is inside the usual mO site, but shifted toward the BR site, which is not observed in $K_{1.62} \cdot$ Mg β-alumina. This mO position, which K(4) occupies, seems to play an important role. The distances between various sites in the same and adjacent cells are given in Fig. 2. The mO site at x = 0.82 (K(4) position) could coexist with the mO site at x = 0.82 of the next cell because the 3.03 Å separation is not too short as a K–K distance. The K(4) position may be interpreted as the shift of K(2) to avoid a very short separation from the nearest mO site. K(4) at x = 0.82 itself cannot coexist with the symmetric equivalent K(4) in the same single mirror plane, owing to the short distance of 2.61 Å between them. So it is reasonable, considering the radius of the K ion, to assume the existence of a K(4)–K(2)–K(2) triplet in contact with another K(4)–K(2)–K(2) triplet via K(4) cations. Furthermore, from this K–K–K triplet arrangement in a mirror plane, the triple triplet-cells cluster shown in Fig. 3 may be supposed to be produced, because there a chain-like concentration of the K–K–K triplet can not exist, in sofar as the triplet is in a K(4)–K(2)–K(2) arrangement. The triple triplet-cell clusters thus formed, referred to as TTC-clusters below, enable some aBR sites to accommodate the extra K ions as shown in Fig. 4a. As TTC-cluster

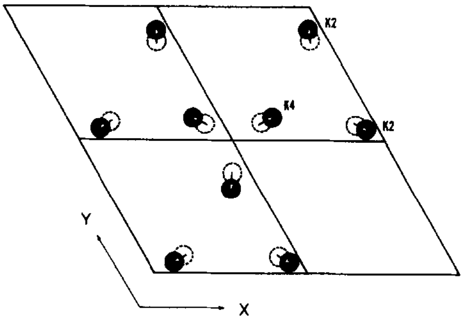

FIG. 3. Schematic representation of the triple triplet-cell cluster in the mirror planes, showing the shift of K ions in order to avoid the cation–cation interaction. In a single mirror plane, K(2)–K(2)–K(4) triplets are formed. Dotted circles indicate K ion at the mO position of $K_{1.62} \cdot$ Mg β-alumina.

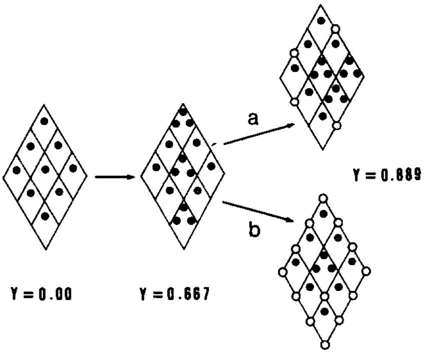

FIG. 4. The change of cation configuration in the mirror planes of Mg-doped potassium β-alumina as y (= excess cation per unit formula) increases. In addition to path (a), there is an alternative path (b), but the results of the refinement agree with the path (a). Closed circles stand for mO cations, shaded ones represent BR cations, and open circles represent aBR cations.

formation occurs beyond the $y = 0.667$ composition, the occupation numbers at the mO and BR sites remain unchanged in spite of the cation content increment beyond $y = 0.667$. Table VII presents the occupancy as obtained from the refinement process and that calculated from the TTC-cluster model for comparison; there is good agreement between them. The maximum K-content by this TTC-cluster mechanism would be $y = 0.889$. Unexpectedly, the present compound $K_{1.875}$ · Mg β-alumina is very close to this upper limit of $y = 0.889$.

TABLE VII

COMPARISON OF THE OCCUPANCY[a] WITH THE MODEL

Site	Result of refinement	TTC-Cluster model
BR	0.67	0.667
mO(1)[b]	0.35	0.313
mO(2)	0.66	0.687
aBR	0.195	0.208
Total	1.875	1.875

[a] Number per unit formula.

[b] Inner mO site.

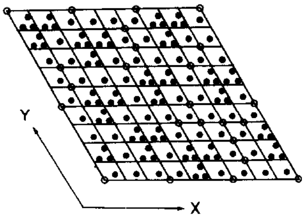

FIG. 5. Potassium ion distribution in the $z = 0.25$ mirror planes of Mg-doped potassium β-alumina yielding the composition $y = 0.889$, which is a little larger than that of the present compound, $K_{1.875}$ · Mg β-alumina. Closed circles indicate BR and mO positions, while open circles show aBR positions.

Figure 5 schematically shows the supposed K ion arrangement in the mirror plane for the composition $y = 0.889$, close to the composition of the present compound. In the figure, TTC-clusters are arranged so as to avoid the contact with each other, and no superstructure domains are formed. Beyond the $y = 0.889$ composition, TTC-clusters would change into BR–aBR arrangement of cations. This could be confirmed by preparing a specimen obtained by the ion exchange of $BaMgAl_{10}O_{17}$ having no Ba-defects. In the Mg-doped potassium β-alumina system, it seems that the K ion resists the formation of the BR–aBR configuration, judging from the formation of the TTC-cluster.

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