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Crystal Structure and Charge Compensation Mechanism of β''-Alumina Type R^+-Gallate ($R = K^+, NH_4^+$)

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Single crystals of gallium analogs of K^+- and NH_4^+-β''-alumina (K^+- and NH_4^+-β''-gallate) were synthesized by ion exchanging Na^+-β''-gallate. Crystal structures of the two gallates were refined using a single-crystal X-ray diffraction method. The positive charges due to excess K^+ ions over the stoichiometric β-alumina composition in K^+-β''-gallate were compensated by substituting Na^+ ions for Ga^{3+} ions at the middle of spinel block. These Na^+ ions were expelled from the crystals by ion exchange for NH_4^+ ions with considerable changes in crystal structure. The excess positive charges in NH_4^+-β''-gallate were neutralized by O^{2-} ions at the *mO* site associating with a new type of Frenkel defects around the conduction plane. The charge-compensation mechanism of these gallates were discussed from the crystal chemical point of view.

Introduction

Sodium β''-alumina is one of the most widely studied solid electrolytes and many crystal structural studies have been performed on this material. Yamaguchi and Suzuki (*1*) first determined the crystal structure of Na^+-β''-alumina and found that its unit cell consisted of three spinel blocks related by a threefold screw axis parallel to the *c*-axis; the two Na^+ ion sites which corresponded to the *BR* and *aBR* sites in the β-alumina structure were equivalent crystallographically. The electrical neutrality is not satisfied in its ideal structure; i.e., excess alkali ions over the stoichiometric composition of β-alumina give additional positive charges in the crystal. Some divalent ions (Mg^{2+}, Zn^{2+}, Co^{2+}, etc.) or Li^+ ions are usually added as a stabilizer for the synthesis of β''-alumina. The excess positive charges are compensated by the substitution of these stabilizing ions for Al^{3+} ions at the middle of the spinel block (*2–11*).

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Single crystals of gallium analogs of β''-alumina (Na^+-β''-gallate) were synthesized without additives (*12*). Anderson *et al.* (*13*) refined the crystal structure of Na^+-β''-gallate and showed that the charge neutrality of Na^+-β''-alumina was formed by an incorporation of Na^+ ions into spinel blocks. However, Na^+-β''-gallate does not seem to be very suitable for such studies because it has a strong hygroscopic property (*14*).

NH_4^+- and H_3O^+-β''-alumina and gallate have attracted much interest because of high protonic conductivities (*15–21*). The crystal structures of NH_4^+- and H_3O^+-β''-alumina were refined by Thomas and coworkers (*22, 23*) and Roth *et al.* (24) but studies on protonic β''-gallates have not been done so far.

In the present study, the crystal structures of K^+- and NH_4^+-β''-gallate were refined using a single-crystal X-ray diffraction method, and it was found that the charge-compensation mechanisms of these two gallates were completely different.

Experimental

(*1*) Preparation of Specimens

Single crystals of Na^+-β''-gallate were synthesized by an alkali evaporation method reported by Foster and Scadefield (*12*): the mixture of Ga_2O_3 and Na_2CO_3 with 1 : 2 molar ratio was packed in a platinum boat and heated in a gradient temperature furnace for about 3 days. Single crystals thus obtained were converted to K^+-β''-gallate by immersion in molten KNO_3, because Na^+-β''-gallate had a strong tendency to absorb water. The K^+-β''-gallate crystals were subsequently ion exchanged to prepare NH_4^+-β''-gallate. The crystals were immersed in molten NH_4NO_3 at about 200°C for 20 hr, washed with ammonia water, and dried at 60°C. This treatment was repeated more than 20 times.

Chemical compositions of Na^+-, K^+-, and NH_4^+-β''-gallate crystals were analyzed on crystals that were selected under a binocular microscope. They were dissolved in concentrated HCl and the content of alkali ions and Ga^{3+} ions was determined using a flame spectrochemical analyzer (Hiranuma, FPF-2) and an atomic absorption spectrochemical analyzer (Shimazu, AA-610), respectively.

(*2*) Intensity Data Collection

Structure refinements were carried out for K^+- and NH_4^+-β''-gallate crystals. The space group of these crystals was confirmed to be $R\bar{3}m$ from the systematic extinctions ($-h + k + l = 3n$ in hexagonal reciprocal lattice) on Weissenberg photographs, which is consistent with that reported previously (*3*). X-ray intensity data were collected with a four-circle diffractometer (Philips Co., PW1100) using Mo$K\alpha$ radiation with a graphite monochromator. The $\theta - 2\theta$ scanning was done for intensity data collections up to $2\theta = 100°$ in a section of the reciprocal space where all $(h - k) > 0$ and $k, l > 0$. Three standard reflections were measured at intervals of 2 hr to monitor the drifts of beam intensity as well as geometric setting conditions. For weak intensity reflections, measurements were repeated three times until the total intensity counts exceeded 10,000. The structure factor (F_0) was calculated for each reflection, and then, anisotropic absorption corrections were performed with the program FDINCOR (*25*). Equivalent reflections were averaged and each parameter was refined with the full-matrix least-squares program LINUS (*26*).[1] Table I shows pertinent data for each crystal.

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[1] See NAPS Document No. 04490 for 11 pages of supplementary materials from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, New York 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid.

Results

(*1*) *Chemical Compositions of Crystals*

The chemical compositions of the crystals are listed in Table II. The Na content in Na^+-β''-gallate crystals ($Na_2O \cdot 6.11Ga_2O_3$) is slightly less than that reported by Foster and co-workers ($Na_2O \cdot 5.7Ga_2O_3$) (*14*, *27*). The chemical formula of Na^+-β''-gallate is represented by $Na_{1.50}Ga_{10.75}Na_{0.25}O_{17.0}$, assuming that the positive charges of excess Na^+ ions ($0.5 \times 3 \doteq 1.5$ per unit cell) are compensated by the substitution of Na^+ ion ($0.25 \times 3 = 0.75$) for Ga^{3+} ion in the spinel block.

A considerable amount of Na^+ ions was detected in K^+-β''-gallate, showing that Na^+ ions in the spinel block were not ion exchanged for K^+ ions. The Na^+ content in the spinel blocks ($0.23 \times 3 = 0.69$) almost agrees with the chemical formula estimated for Na^+-β''-gallate. The K^+ content ($1.27 \times 3 = 3.81$) is less than that observed for usual β''-alumina-type compounds. This might be due to a partial replacement of K^+ ions by H_3O^+ ions in the ion exchange process (*22*, *23*).

In the case of NH_4^+-β''-gallate, only Ga^{3+} ions were detected by the chemical analysis (Table II), which indicated that Na^+ ions in the spinel block were expelled from the crystal during ion exchange for NH_4^+ ions. This remarkable phenomenon will be discussed later. Tsurumi and co-workers (*18*, *19*) have studied the thermal decomposition of NH_4^+-β''-gallate and found that its thermal decomposition process was complicated; i.e., N_2O, H_2O, and NH_3 were simultaneously liberated at 200–300°C. The definite determination of the chemical formula is therefore difficult, but a tentative formula may be given: $1.33H_2O \cdot (aH_2O, bNH_3, cN_2O) \cdot 5.5Ga_2O_3$, where $a < 1.21$, $b < 1.14$, $c < 0.47$, and $1.21 < a + b + c < 1.41$.

TABLE I

SOME DATA OF CRYSTAL STRUCTURE REFINEMENTS ON K^+- AND NH_4^+-β''-GALLATE PREPARED FROM Na^+-β''-GALLATE

	K^+-β''-gallate	NH_4^+-β''-gallate
Size of crystal (mm)	0.1 × 0.1 × 0.04	0.15 × 0.11 × 0.02
Lattice constants (Å)	$a = 5.856(2)$	5.836(1)
	$c = 35.34(4)$	35.57(1)
Number of independent reflections	861	696
Number of parameters	46	65

TABLE II

CHEMICAL COMPOSITIONS IN wt% AND CHEMICAL FORMULAS OF Na^+-, K^+-, AND NH_4^+-β''-GALLATE[a]

	Ga_2O	Na_2O	K_2O	Ig · loss	Total (wt%)
Na^+-β''-gallate	93.24	5.03		0.51	98.78
$0.90Na_2O \cdot 5.5Ga_2O_3$ ($Na_{1.50}Ga_{10.75}Na_{0.25}O_{17.0}$)					
K^+-β''-gallate	92.81	0.69	5.49	0.47	99.46
$0.65K_2O \cdot 0.12Na_2O \cdot 5.5Ga_2O_3$ ($K_{1.27}Ga_{10.77}Na_{0.23}O_{16.91}$)					
NH_4^+-β''-gallate	95.94	0.0	0.0	4.01	99.95

[a] K^+- and NH_4^+-β''-gallate were prepared from Na^+-β''-gallate.

(*2*) *Refinements of Crystal Structures*

(*a*) *K^+-β''-gallate.* Starting positional parameters used for the refinement were taken from the literature (*3*). The positional parameters and anisotropic temperature factors were refined for all atoms ($R = 0.0425$).[2] Figure 1B shows a difference Fourier map on the (110) plane at this stage. Negative peaks of electron density are observed at Ga(2). Figure 1A is a difference Fourier map of the conduction plane after the refinement of the occupancy of the *BR*(*aBR*) site ($R = 0.0393$). Three notable peaks are observed around the *BR*(*aBR*) site. K^+ ions were then introduced into the positions equivalent to these three peaks and all parameters were refined ($R =$

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[2] The value of the reliability factor (*R* factor) at each stage of the refinement is noted in parentheses in the following descriptions.

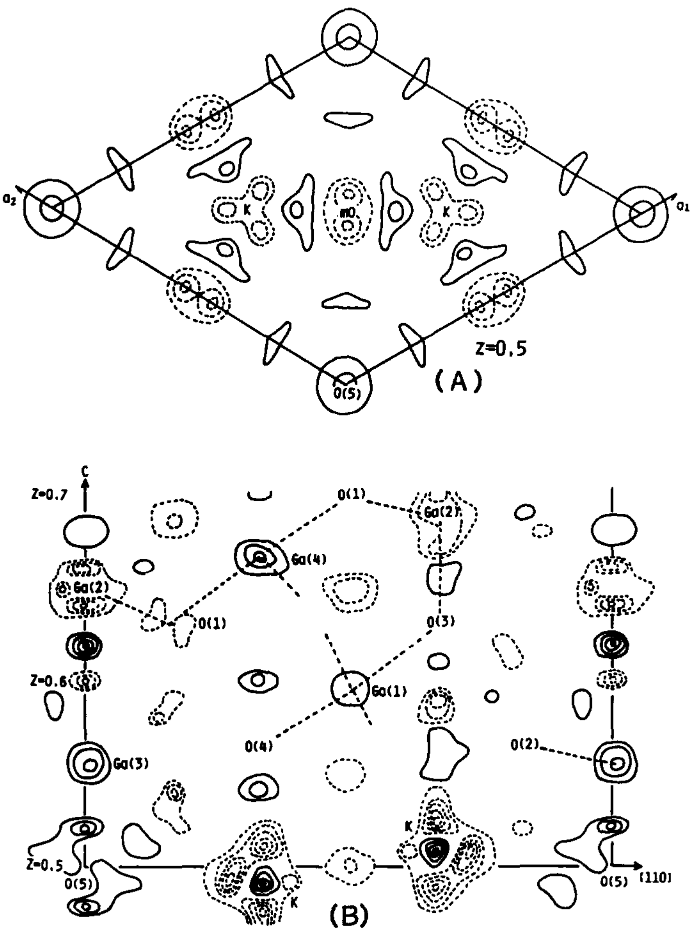

FIG. 1. Difference Fourier maps of K^+-β''-gallate prepared from Na^+-β''-gallate. (A) Conduction plane at $z = 0.5$ when R factor is 0.0393. (B) (110) plane when factor is 0.0425. Solid contours are drawn at intervals of 1 eÅ^{-3}, and dashed contours at intervals of -1 eÅ^{-3}.

0.0380). Since a negative peak at the Ga(2) site indicated partial substitution by Na^+ ions, Na atoms were introduced into the Ga(2) site and occupancies of Na and Ga atoms were refined under the restriction that the total occupancy in the unit cell was fixed at 6 atoms ($R = 0.0374$). Final parameters such as numbers of atoms in the unit cell, positional parameters, and anisotropic temperature factors are listed in Table III.

(*b*) *NH_4^+-β''-gallate.* Starting positional parameters were the same as for K^+-β''-gallate. Positional parameters and isotropic temperature factors were refined for all atoms ($R = 0.0711$). Anisotropic temperature factors and the occupancy of the N atom, not the NH_4^+ ion, were refined ($R = 0.0652$). The difference Fourier maps on the conduction plane and the (110) plane at this stage are shown in Figs. 2A and 2B. In the map of the (110) plane, positive peaks are observed at the Ga(2) sites, instead of negative peaks in K^+-β''-gallate, and some positive peaks are observed at interstitial sites near the conduction plane (Ga(5), Ga(6),

TABLE III

Positional,[a] Thermal, and Occupation Parameters

	Position	Number of atoms per unit cell	X	Z	Thermal Parameters $\times 10^{-4}$			
					β_{11}	β_{33}	β_{12}	β_{13}
K^+-β''-Gallate								
Ga(1)	18(*h*)	18	0.16780(8)	−0.07036(2)	43(1)	62(2)	23(2)	0(1)
Ga(2)	6(*c*)	5.48(3)	0	0.34976(4)	32(1)	43(3)	$= \frac{1}{2}\beta_{11}$	0
Ga(3)	6(*c*)	6	0	0.44966(3)	46(2)	47(3)	$= \frac{1}{2}\beta_{11}$	0
Ga(4)	3(*a*)	3	0	0	48(2)	34(5)	$= \frac{1}{2}\beta_{11}$	0
O(1)	18(*h*)	18	0.1557(4)	0.0339(1)	95(12)	74(23)	53(14)	−4(7)
O(2)	18(*h*)	18	0.1630(5)	0.2360(1)	50(9)	116(15)	24(12)	13(7)
O(3)	6(*c*)	6	0	0.2962(2)	11(10)	138(30)	$= \frac{1}{2}\beta_{11}$	0
O(4)	6(*c*)	6	0	0.0948(2)	82(12)	32(23)	$= \frac{1}{2}\beta_{11}$	0
O(5)	3(*b*)	3	0	$\frac{1}{2}$	828(100)	15(44)	$= \frac{1}{2}\beta_{11}$	0
K(1)	6(*c*)	3.28(18)	0	0.1712(2)	685(37)	112(27)	$= \frac{1}{2}\beta_{11}$	0
K(2)	18(*h*)	1.26(25)	0.5961(52)	0.4976(11)	1950(730)	160(120)	1800(750)	49(73)
Na	6(*c*)	0.52(3)	0	0.34976(4)	32(1)	43(3)	$= \frac{1}{2}\beta_{11}$	0
NH_4^+-β''-Gallate								
Ga(1)	18(*h*)	16.22(10)	0.1684(1)	−0.06940(2)	93(2)	80(2)	60(3)	4(1)
Ga(2)	6(*c*)	5.90(5)	0	0.34956(4)	55(2)	63(4)	$= \frac{1}{2}\beta_{11}$	0
Ga(3)	6(*c*)	5.53(6)	0	0.44960(4)	145(3)	70(4)	$= \frac{1}{2}\beta_{11}$	0
Ga(4)	3(*a*)	3	0	0	68(3)	88(6)	$= \frac{1}{2}\beta_{11}$	0
Ga(5)	18(*h*)	1.11(6)	0.8312(13)	0.2190(2)	11(22)	47(26)	23(26)	0(13)
Ga(6)	6(*c*)	0.26(6)	0	0.1959(12)	290(120)	126(150)	$= \frac{1}{2}\beta_{11}$	0
Ga(7)	18(*h*)	0.37(7)	0.8278(30)	0.4682(8)	100(107)	84(105)	140(110)	14(40)
O(1)	18(*h*)	18	0.1585(5)	0.0333(1)	77(12)	76(13)	41(14)	20(18)
O(2)	18(*h*)	18	0.1633(6)	0.2358(1)	100(11)	131(16)	30(16)	7(18)
O(3)	6(*c*)	6	0	0.2965(2)	60(14)	72(26)	$= \frac{1}{2}\beta_{11}$	0
O(4)	6(*c*)	6	0	0.0942(2)	65(12)	98(29)	$= \frac{1}{2}\beta_{11}$	0
O(5)	3(*b*)	3	0	$\frac{1}{2}$	659(2)	50(48)	$= \frac{1}{2}\beta_{11}$	0
O(6)	9(*d*)	1.20(22)	$X = \frac{1}{2}$ $Y = 0.0$	$\frac{1}{2}$	$\beta_{11} = 1200(600)$ $\beta_{33} = 90(180)$ $\beta_{13} = -520(300)$	$\beta_{22} = 320(290)$ $\beta_{12} = \frac{1}{2}\beta_{11}$ $\beta_{23} = \frac{1}{2}\beta_{11}$		
N	6(*c*)	4.74(5)	0	0.1674(10)	1579(280)	300(150)	$= \frac{1}{2}\beta_{11}$	0

[a] For all atoms $Y = -X$, numbers in parentheses correspond to estimated errors in the last digits.

and Ga(7), Table III). Since these peaks related to interstitial Ga atoms, the occupancy of the Ga(5) site, having highest scattering power, was refined ($R = 0.0501$). In the map of the conduction plane, positive peaks are observed at the *mO* sites. These peaks were attributed to the O^{2-} ions coordinating with the interstitial Ga^{3+} ions, so that the occupancy of the O atom at this site was refined ($R = 0.0445$). Finally, Ga atoms were introduced into the Ga(6) and Ga(7) sites and their occupancies were refined ($R = 0.0392$). The final parameters are listed in Table III.

Ga–O distances of K^+- and NH_4^+-β''-gallate, calculated from the positional parameters and lattice constants, are listed in Table IV.

Discussion

(*1*) *Charge-Compensation Mechanisms*

β''-Alumina contains a substantial excess of Na^+ ions and their positive charges

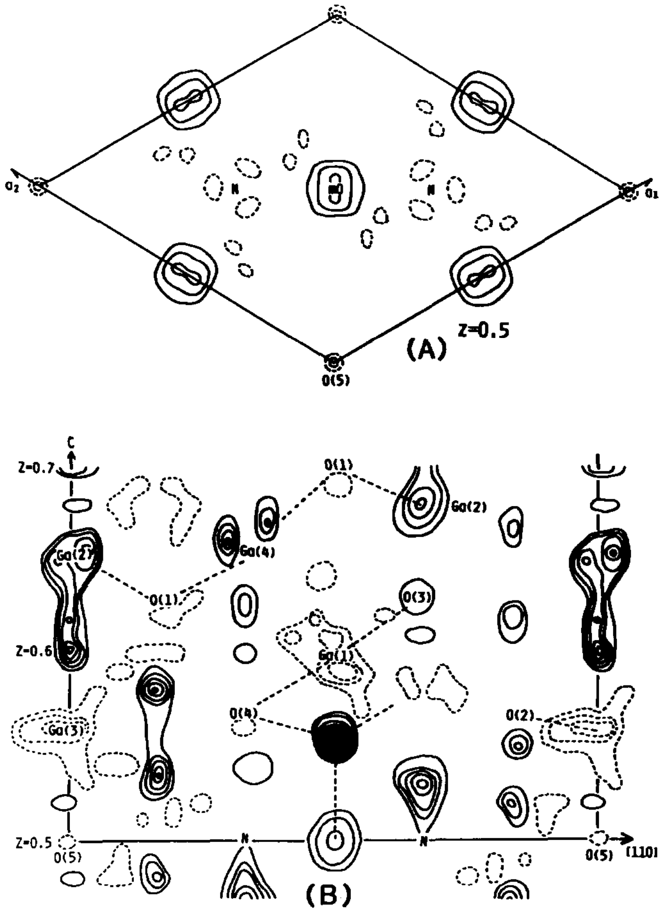

FIG. 2. Difference Fourier maps of NH_4^+-β''-gallate when R factor is 0.0652. (A) Conduction plane at $z = 0.5$. (B) (110) plane. Solid contours are drawn at intervals of 1 $eÅ^{-3}$, and dashed contours at intervals of -1 $eÅ^{-3}$.

should be electrically neutralized. In K^+-β''-gallate, the excess charges are compensated by Na^+ ion substitution for Ga^{3+} ion at the Ga(2) site in the spinel block. This is verified by the following experimental results: (1) a substantial amount of Na^+ ion was detected by chemical analysis, (2) the a-parameter of K^+-β''-gallate was much larger than those of other β- (*28*) and β''-gallates, indicating that large ions such as Na^+ replaced Ga^{3+} ions in the spinel block, (3) a negative peak of electron density was observed at the Ga(2) site when the occupancy of Ga atom at this site was fixed at that of stoichiometric composition (Fig. 1), and (4) the Ga(2)–O bonding distances (Table IV) were larger than those of K^+-, NH_4^+-β-gallate (*28*) and NH_4^+-β''-gallate. However, a tetrahedral coordination of Na^+ ions is not known in oxides with close-packed oxygen structures because the Na^+ ion is too large for such a small site. Anderson *et al.* (*13*) reported the same charge-compensation mechanism for Na^+-β''-gallate. More direct evidence for the tetrahedral coordination of Na^+ ions has been obtained by MAS–NMR measurements (*29*). This suggests the probability of such a compen-

TABLE IV

INTERATOMIC DISTANCES (Å) OF K^+- AND NH_4^+-β''-GALLATE PREPARED FROM Na^+-β''-GALLATE

	Multiplicity	K^+-β''-Gallate	NH_4^+-β''-Gallate
Ga(1)–O(1)	2	2.090(3)	2.094(3)
–O(2)	2	1.920(2)	1.937(3)
–O(3)	1	2.049(5)	2.030(4)
–O(4)	1	1.908(3)	1.917(3)
Ga(1)–O	Mean	1.996	2.002
Ga(2)–O(1)	3	1.904(3)	1.869(4)
–O(3)	1	1.894(9)	1.887(7)
Ga(2)–O	Mean	1.902	1.874
Ga(3)–O(2)	3	1.854(3)	1.843(4)
–O(5)	1	1.779(2)	1.793(2)
Ga(3)–O	Mean	1.835	1.831
Ga(4)–O(1)	6	1.981(3)	1.992(4)
Ga(5)–O(2)	2		1.782(7)
–O(4)	1		1.811(9)
–O(6)	1		1.862(7)
Ga(5)–O	Mean		1.809
Ga(6)–O(2)	3		2.177(28)
–O(6)	3		1.980(22)
Ga(6)–O	Mean		2.079
Ga(7)–O(2)	2		2.181(21)
–O(4)	1		2.178(25)
–O(5)	1		2.076(24)
–O(6)	2		2.007(20)
Ga(7)–O	Mean		2.105
K(1),N–O(2)	3	2.823(8)	2.940(30)
–O(4)	1	2.701(12)	2.604(36)
–O(5)	3	3.385(1)	3.370(1)

sation mechanism. West (*30*) and other investigators (*6, 31, 32*) reported that β- and β''-alumina structures showed a large departure from local electroneutrality and it was improved by adding positive charges into the conduction plane, and removing them from the spinel block. Wang (*33*) reported that the Ga(2) site is electrostatically the best position to substitute for stabilizing ions. The Na^+ ion substitution at the Ga(2) site certainly stabilizes the β''-alumina structure. Ikawa *et al.* (*34*) found that the crystal structure of Na^+-β''-gallate was stable up to 1400°C, the crystal structures of K^+- and Rb^+-β''-gallate were transformed into β-gallate at lower temperatures, and the addition of stabilizing ions, such as Mg^{2+} and Zn^{2+} ions, did not enlarge the stability field of Na^+-β''-gallate. These facts clearly showed the effect of Na^+ ions on the stabilization of Na^+-β''-gallate. No β''-alumina compounds seem to exist without excess positive ions in the conduction plane; i.e., β''-alumina with a stoichiometric composition of β-alumina ($Na_2O \cdot 11Al_2O_3$) may not exist. Without stabilizing ions the charge neutrality is achieved by making Frenkel-type defects (*35–37*). In the Ga_2O_3–Na_2O system large spinel blocks may enable Na^+ ions to enter into them. In the case of Na^+-β''-alumina, Na^+ ions cannot replace Al^{3+} ions at the Al(2) site because of the small spinel block size, and K^+ and Rb^+ ions do not incorporate into the spinel block of gallates because of their large ionic sizes. The occupancy of the Na^+ ion at the Ga(2) site (0.52(3)) is somewhat less than that determined by the chemical analysis (0.69); however, we consider that Na^+ ions are incorporated only into the Ga(2) site because the bonding distances in the other coordinating polyhedra are almost identical to those of other gallates (*28*).

Na^+ ions at the Ga(2) site of K^+-β''-gallate were expelled from the crystal in the process of the ion exchange for NH_4^+ ions. This remarkable phenomenon was verified by the following experimental results: (1) no Na^+ ions were detected in NH_4^+-β''-gallate by chemical analysis, (2) the *a*-parameter of K^+-β''-gallate was decreased by ion exchange (Table I), (3) a negative electron density peak was no longer observed at the Ga(2) site in the difference Fourier map of NH_4^+-β''-gallate (Fig. 2B) and (4) the Ga(2)–O bonding distance (Table IV) decreased significantly after ion exchange and became almost identical to that of other gallates (*28*). In the Fourier map of NH_4^+-β''-gallate (Fig. 2B), some additional peaks of electron density were observed (Ga(5), Ga(6), and Ga(7), Table III and Fig. 3). These positive peaks were attributed to Ga atoms by crystal chemical considerations: the Ga(5) site is at the center of the tetrahedron composed of O(2), O(4), and *mO* sites, while the Ga(6) and Ga(7) sites are at centers of octahedra composed of *mO*, O(2), O(4), and

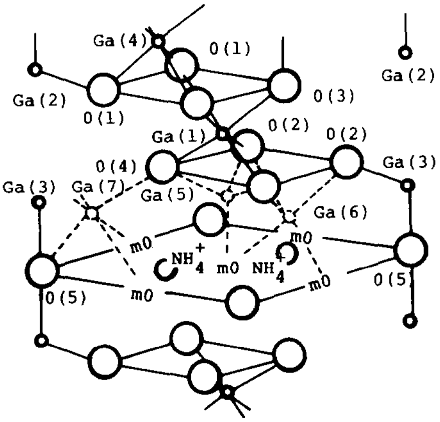

FIG. 3. Frenkel defects in NH_4^+-β''-gallate.

O(5) sites (Fig. 3). Since the Ga(6) site is very close to the *BR*(*aBR*) site, this site might be vacant when the neighboring *BR*(*aBR*) site is occupied by NH_4^+ ion. The positive peaks observed at the *mO* sites in Fig. 2A are due to O^{2-} ions. It is notable that the occupancies of Ga(1) and Ga(3) sites (16.22(10) and 5.53(6), Table III are smaller than those of ideal composition (18 and 6), indicating that the Ga atoms at Ga(5), Ga(6), and Ga(7) sites are those migrating from Ga(1) and Ga(3) sites, to form Frenkel defects. Similar Frenkel defects were observed at the Ga(5) site in β-gallate (*28*). Harbach (*35, 36*) considered that the excess Na^+ ions of partially Mg^{2+}-stabilized β''-alumina were charge compensated by interstitial O^{2-} ions on the conduction plane as well as by the substitution of Mg^{2+} ions. Though the former mechanism has never been confirmed, the present study gives conclusive evidence for a new charge-compensation mechanism in β''-alumina-type compounds—the interstitial O^{2-} ions at *mO* sites associated with the Frenkel defects at the Ga(1) and Ga(3) sites.

The way in which Na^+ ions are expelled from the spinel block or the reason for the structural changes is not completely clear at the present time, but we think Na^+ ions migrate via the conductance plane, and that ion exchange with protonic ions and the instability of the tetrahedrally coordinated Na^+ ions cause the change in defect structure. If Zn^{2+} ions are substituted for Ga^{3+} ions, the change in defect structure does not occur (*18*), i.e., ion exchange for NH_4^+ ions does not decrease the *a*-parameter of Zn^{2+}-doped K^+-β''-gallate prepared from Na^+-β''-gallate, and no Na^+ ions were detected by chemical analysis. On the other hand, ion exchange for H_3O^+ ions as well as for NH_4^+ ions removes Na^+ ions from the spinel block of K^+-β''-gallate (*37*). The results of the present study and those of previous reports (*18, 28*) suggest that ion exchange for protonic ions gives rise to the change of the charge-compensation mechanisms in β- and β''-alumina-type compounds. For example, Frenkel defects in K^+-β''-gallate disappeared in NH_4^+-β-gallate to make a stoichiometric composition and the charge-compensation mechanism due to Na^+ ions in spinel block change to Frenkel-type defects in NH_4^+-β''-gallate.

(2) *Conduction Plane and Spinel Block*

K^+ ions locate at the K(1) (6(*c*)) and the off-centered K(2) (18(*h*)) sites in K^+-β''-gallate (Table III). The ions at the K(2) site were explained by relaxation toward the neighboring vacant K(1) site (*8–10*). The occupancies refined for these sites do not agree with the microdomain model proposed by Roth *et al.* (*6*). It is possible that H_3O^+ ions introduced in the conduction plane affect the ion distribution, but the thermal motion of K^+ ions makes it difficult to discuss in detail the occupancy at these sites.

Thomas and co-workers (*22, 23*) reported that both NH_4^+ and H_3O^+ ions existed in the conduction plane of NH_4^+-β''-alumina. NH_4^+-β''-gallate used in the present study also contains these protonic ions and the results of refinement indicate that these protonic ions locate only at the 6(*c*) position, not at the off-centered 18(*h*) position. This is consistent with those in the literature (*22, 23*). The microdomain model of Roth *et al.*, therefore, may not apply to protonic β''-alumina-type compounds because protonic ions may form hydrogen bonds with surrounding oxygen atoms.

Some changes in coordinating polyhedra caused by ion exchange for NH_4^+ ions are summarized as follows: The Ga(2)–O bonding distances decreased after ion exchange because Na^+ ions at the Ga(2) site are expelled. The Ga(3)–O(5) bonding distances are increased, showing large NH_4^+ ions are incorporated into the conduction plane. These changes cause the deformation of other coordinating polyhedra in the spinel block; i.e., the Ga(4) octahedron is flattened, while the Ga(1) octahedron is elongated along the *c*-axis. The features of these deformities are markedly different from the case of β-gallate (*28*), which may be associated with the difference in the stacking array of oxygen layers between the β- and β''-alumina structure.

Conclusions

The crystal structures of K^+-β''-gallate prepared from Na^+-β''-gallate and NH_4^+-β''-gallate were refined using a single-crystal X-ray diffraction method. The main conclusions obtained were that (1) the positive charges of excess K^+ ions over the stoichiometric β-alumina composition were compensated by substituting Na^+ ions for Ga^{3+} ions at the Ga(2) site in K^+-β''-gallate, (2) Na^+ ions in the spinel block were expelled from the crystals by ion exchange with NH_4^+ ions, and (3) the excess positive charges in NH_4^+-β''-gallate were neutralized by O^{2-} ions at the *mO* site associating with Frenkel-type defects—Ga atoms migrated from the Ga(1) and Ga(3) sites to interstitial tetrahedral and octahedral sites close to the conduction plane. Ion exchange for protonic species changes the charge-compensation mechanism of β- and β''-alumina-type compounds. Further understanding of the compensation mechanism is desirable because it significantly affects the conductivities of these materials.

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