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MODEL STUDIES OF MIXED-ION BETA-ALUMINAS*

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ABSTRACT

Conductivity anomalies observed in mixed ion beta-aluminas have been investigated by model calculations. These calculations include Coulomb, short-range repulsive, and polarization energy terms and show that: 1. When large mobile cations are introduced into beta-aluminas having smaller cations, the large cations tend to occupy positions near Beevers-Ross sites alone. 2. Small mobile cations introduced into a beta-alumina having larger mobile cations tend to form pairs either with themselves or with the larger cations. 3. For a mixed ion pair, the activation energy of the larger ion to escape from the shared potential well is much higher than that of the smaller ion.

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INTRODUCTION

Recent results of NMR [1], Raman scattering [2,3], IR [2], diffusion [4], and ionic conductivity [3,5-9] measurements on mixed-ion beta-aluminas have revealed several important phenomena in these systems. These include anomalies in conductivity and the preferential occupancy of particular kinds of sites for certain types of ions. We have tried to understand these phenomena by calculating the potential energies of various mobile cation arrangements in the conducting plane in order to find the most stable configurations and the activation energies of diffusion. The calculations take into account Coulomb, short-range repulsive, and polarization energy terms, and are similar to those reported previously [10].

Beta-aluminas have a layered structure consisting of densely packed spinel blocks of oxygen and aluminum ions separated by open conducting planes (mirror planes). The conducting planes are occupied by oxygen ions (called "column" oxygen ions) and mobile cations. There are three kinds of cation sites in the conducting plane. A Beavers-Ross (BR) site is formed by six O^{2-} ions (three above and three below) from the neighboring spinel blocks, but an anti-Beavers-Ross (aBR) site is formed only by two (one above and one below). In the conducting plane, however, both the BR and aBR sites have three neighboring column oxygen ions (Fig. 1). The mid oxygen (mO) site lies between two column oxygen ions and midway between neighboring BR and aBR sites.

In the ideal structure of beta-alumina, the number of mobile cations is equal to the number of BR sites. Each mobile cation in this case tends to occupy a BR site because of the deep potential well formed by three neighboring aBR sites and three column oxygen ions [10], as indicated by the dotted lines in Fig. 1. Beta-alumina nominally contains about 15 to 30 % excess cations compared to the ideal structure. If an excess cation is put into the ideal structure, it tends to share a potential well with another cation. The previous calculations [10] indicated that, because of the correlative motion of paired ions, the activation energy for one of the ions in a pair to move out of the potential well to form a new pair in a neighboring potential well is quite small. As a result, the conductivity of beta-aluminas is mainly determined by the excess ions.

When mixed-ion beta-aluminas are formed through ion exchange, it is important to know which ions tend to form pairs and which ions tend to occupy BR sites alone. Changes in the activation energy of breaking interstitial ion pairs in mixed ion beta-aluminas as compared to the pure materials can result in unexpected changes in the ionic conductivity.

The crystal structure parameters used for the Na and Li beta-alumina calculations were taken from Peters et al. for Na beta-alumina [11], and those for the K beta-alumina calculations were taken from the data of Dernier and Remeika [12]. All parameters such as ionic radii and polarizabilities used in this work are the same as those used in [10]. All mobile cations, except Li^+ , were restricted to move along the conducting paths connecting neighboring BR and aBR sites. Because of their small radius, single Li^+ ions tend to deviate above and below the conducting plane at the BR sites, and paired Li^+ ions tend to deviate toward column oxygen ions in the conducting plane [13]. The calculations allowed for this deviation, but the parameters of the short-range repulsive term were changed whenever the distance between a Li^+ and an O^{2-} ion became smaller than the sum of their radii in order to prevent the ions from collapsing (polarization catastrophe). This problem was handled in the same manner as described in a previous work [14].

ION CONFIGURATIONS

When a K^+ ion is introduced into the ideal structure of Na beta-alumina, it may either occupy a position near a BR site alone or share a potential well to form a pair with a Na^+ ion as shown in Fig. 2. The potential energy difference between the two situations is given by

$$V(\text{Na--K}, \text{Na}) - V(\text{Na--Na}, \text{K}) = 0.11 \text{ eV},$$

where $V(\text{X--Y}, \text{Z})$ represents the potential energy of the system when X and Y form a pair and Z occupies a neighboring BR site alone. The first term of the equation corresponds to the potential energy of the configuration shown in Fig. 2. Because $V(\text{Na--Na}, \text{K}) < V(\text{Na--K}, \text{Na})$, a K^+ ion in Na beta-alumina tends to occupy a position near a BR site alone.

On the other hand, when a Na^+ ion is introduced into the ideal structure of K beta-alumina, it tends to form a pair with a K^+ ion:

$$V(\text{K--K}, \text{Na}) - V(\text{K--Na}, \text{K}) = 0.14 \text{ eV.}$$

These and similar results calculated for other mixed crystals are summarized in Table I. It is generally true that when larger mobile cations are introduced into a beta-alumina containing a smaller mobile cations, they tend to occupy positions near BR sites alone. In contrast, smaller mobile cations introduced into a beta-alumina containing larger mobile cations tend to form pairs either among themselves or with the larger cations.

Our calculations also show that when a doubly charged cation is introduced into the ideal structure of beta-alumina, it will not form an ion pair with a singly charged cation. Rather, from charge neutrality considerations, the doubly charged cation will replace a mobile ion pair.

ACTIVATION ENERGIES

The activation energy for the escape of one type of ion out of the potential well of a mixed ion pair, as illustrated in Fig. 2, may be quite different from that of the other ion type. Because of the difference in ionic radii and polarizabilities, the two ions experience different potentials in the same potential well. As the ions attempt to escape from the region through correlative motion, the smaller ion receives more help from the larger ion than that the larger ion can receive from the smaller one. The calculated activation energies for the escape of a cation from a mixed cation pair in Li, Na, and K beta-aluminas are given in Table II. In the notation of this table, $(\text{X--Y}^*, \text{Z})$, Y^* denotes the ion escaping from the mixed X-Y pair, and Z denotes the ion with which Y forms a new pair. For example, the calculated activation energy for the escape of the K^+ ion in Fig. 2 out of the potential well which it shares with a Na^+ ion to form a new $\text{K}^+\text{-Na}^+$ pair in a neighboring potential well is

$$E(\text{Na--K}^*, \text{Na}) = 0.30 \text{ eV ,}$$

The activation energy for the Na^+ ion to escape from the shared potential well is much smaller:

$$E(\text{K--Na}^*, \text{Na}) = 0.15 \text{ eV .}$$

In general, for a mixed ion pair, the activation energy for escape of the larger ion from the shared potential well is higher than that of the smaller ion.

INTERPRETATION OF EXPERIMENTAL RESULTS

The Raman spectrum of K beta-alumina shows two pronounced bands near 69 and 80 cm^{-1} due to K^+ ions [3]. Introduction of a small amount of Na^+ [2] or Li^+ [3] ions into the crystal causes the intensity of the 69 cm^{-1} band to decrease while the intensity of the 80 cm^{-1} band remains essentially the same. These results can be explained by assigning the 80 cm^{-1} band to single K^+ ions and the 69 cm^{-1} band to K^+ - K^+ pairs. From Table I we see that smaller ions such as Li^+ introduced into K beta-alumina tend to form Li^+ - K^+ pairs first and Li^+ - Li^+ next. This reduces the number of K^+ - K^+ pairs but, at least in the early stages of ion exchange, will not significantly change the number of single K^+ ions. Introduction of small amounts of Sn^{2+} into K beta-alumina [3] also reduced the intensity of only the 69 cm^{-1} band, a result which supports the above assignments.

High field NMR spectra of mixed Na-Li beta-alumina by Highe and Vaughan [1] showed a pair of satellites due to nuclear magnetic quadrupolar interaction in samples of 50% or more substitution of Na^+ by Li^+ . The positions of the satellites depend on the lithium concentration. For a 91% substituted sample, the spectrum near the central peak shows definite structure. From our calculations we believe that for low Li concentrations, Li^+ - Na^+ and Li^+ - Li^+ pairs are formed in the conducting plane. Although points in the conducting plane have zero electric field in the c-direction (because of the reflection symmetry of the mirror plane), they have high field gradients along the c-direction. It is possible that a pair of satellites exist in this case far away from the central peak and were not observed. As more Li^+ ions are introduced into the crystal, they begin to occupy positions near BR sites alone and deviate about $\pm 0.8 \text{ \AA}$ away from the conducting plane [13,14]. Our preliminary calculations indicate that the field gradients are very small in this case, and we believe that this produces the satellite pair observed by Highe and Vaughan. Thus, the structure of the central peak is due to the occupancy of more than one kind of site by the Li^+ ions at high Li concentrations. We believe that the concentration dependence of the satellite position is due to the mutual Coulomb repulsive interaction between the Li^+ layers next to a conducting plane (about 1.6 Å apart). When

more Li^+ ions go into these two layers at higher concentrations, the field gradient along the c-direction becomes stronger, and the separation between the two satellites becomes larger.

Roth and Farrington [5] reported that in Na-Li beta-alumina (~50% Li^+ substitution), the conductivity is much higher than that of the pure Li beta-alumina but is almost completely due to Li^+ ions. To understand this phenomenon, we show in Fig. 3 a Li^+ - Na^+ pair in Na beta-alumina. Notice that the Li^+ ion can jump out of the shared potential well along two possible paths, in contrast to the situation shown in Fig. 2 for a Na^+ - K^+ pair in which there is only one path available for a sodium jump. From Table II we see that the activation energy required to move the Li^+ ion out of the shared potential well (0.24 eV) is much smaller than that needed to move the Na^+ ion (0.65 eV). It is also smaller than the activation energy for Li^+ in pure Li beta-alumina (0.38 eV). Therefore, the Li^+ ion can move quite easily from one Na^+ ion to another. The calculated activation energy (0.24 eV) is quite close to that observed from conductivity measurements of mixed Li-Na beta-aluminas [3]. Similar arguments can also qualitatively explain the reduction of diffusivity and conductivity observed after introducing K^+ ions into Na beta-alumina [4,7,8], doubly charged ions into Na and K beta-aluminas [3,4,9] and Na^+ ions into K beta-alumina [7].

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TABLE I. CALCULATED POTENTIAL ENERGIES OF VARIOUS ION CONFIGURATIONS IN Li, Na, AND K BETA-ALUMINAS.

Host Material	Ion Configuration ^(a)	Potential Energy (eV) ^(b)
Li-beta	(Li--Li, Na)	V1
	(Li--Na, Li)	V1 + 0.20
Na-beta	(Li--Li, Na)	V2
	(Li--Na, Li)	V2 + 0.29
	{Na--Li, Na}	V3
	{Na--Na, Li}	V3 + 0.65
	{Na--Na, K}	V4
	{Na--K, Na}	V4 + 0.11
K-beta	{K--Na, K}	V5
	{K--K, Na}	V5 + 0.15
	(Li--Li, K)	V6
	(Li--K, Li)	V6 + 0.39
	{K--Li, K}	V7
	{K--K, Li}	V7 + 0.84
	(Na--Na, K)	V8
	(Na--K, Na)	V8 + 0.12
{K--Na, K}	V9	
{K--K, Na}	V9 + 0.14	

(a) In the notation, (X--Y, Z), X--Y denotes the paired ions, and Z denotes the ion occupying a neighboring BR site alone.

(b) V1, V2, ..., V9 represent arbitrary reference potential energies.

TABLE II. ACTIVATION ENERGIES OF DIFFUSION IN
Li, Na, AND K BETA-ALUMINAS.

Host Material	Ion Configuration	Activation Energy (eV)	
		Calc.	Obs.
Li-beta	(Li--Li*, Li) ^(a)	0.38	0.378 ^(b)
	(Na--Li*, Li)	0.24	
	(Li--Na*, Li)	0.65	
Na-beta	(Na--Na*, Na)	0.20	0.165 ^(b)
	(Na--Li*, Na)	0.24	
	(Li--Na*, Na)	0.65	
	(Li--Li*, Na)	0.43	
	(K--Na*, Na)	0.15	
	(Na--K*, Na)	0.30	
K-beta	(Na--Na*, K)	0.24	0.233 ^(b)
	(K--K*, K)	0.27	
	(Li--Li*, K)	0.54	
	(Li--K*, K)	0.84	
	(K--Li*, K)	0.28	
	(Na--K*, K)	0.37	
(K--Na*, K)	0.16		

(a) In the notation (X--Y*, Z), Y* denotes the ion escaping from the X-Y pair, and Z denotes the ion with which Y forms a new pair in a neighboring potential well.

(b) From Reference 4.

FIGURE CAPTIONS

Fig. 1. Ideal structure of the conducting plane of beta-alumina. Solid circles are column oxygen ions; open circles are mobile cations on BR sites; unoccupied hexagon vertices are aBR sites; and sites between neighboring BR and aBR sites are mO sites. A mobile cation in the ideal structure is in a deep potential well indicated by the dotted lines.

Fig. 2. Minimum potential energy configuration of a Na^+ - K^+ pair in Na beta-alumina. The large open circle is the K^+ ion, and the smaller open circles are Na^+ ions.

Fig. 3. Minimum potential energy configuration of a Na^+ - Li^+ pair in Na beta-alumina. The small open circle is the Li^+ ion, and the larger open circles are Na^+ ions.

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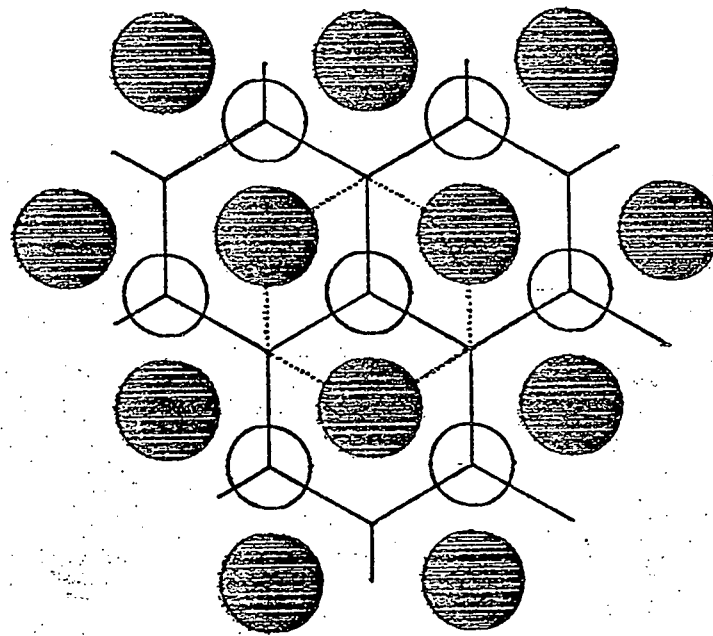


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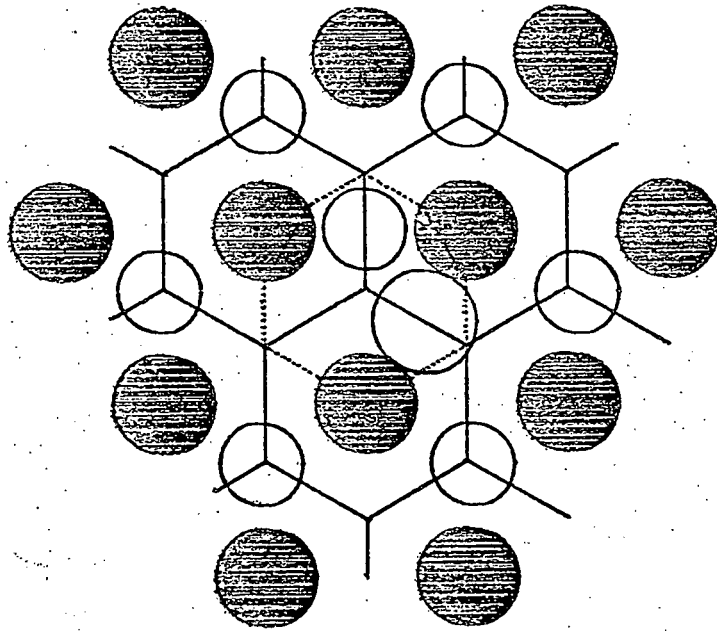


Fig. 2. Minimum potential energy configuration of a Na⁺-K⁺ pair in Na beta-alumina. The large open circle is the K⁺ ion, and the smaller open circles are Na⁺ ions.

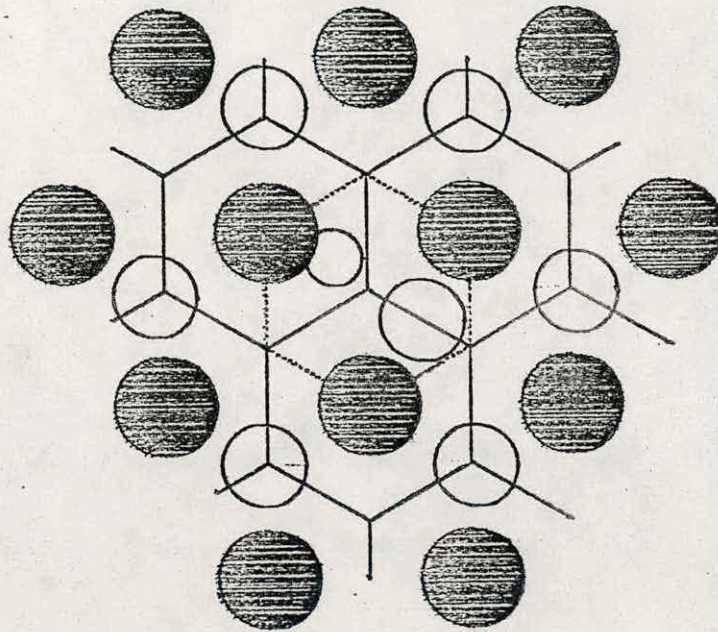


Fig. 3. Minimum potential energy configuration of a Na⁺-Li⁺ pair in Na beta-alumina. The small open circle is the Li⁺ ion, and the larger open circles are Na⁺ ions.