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ION TRANSPORT IN Ca\(^{2+}\), Sr\(^{2+}\), Ba\(^{2+}\),
AND Pb\(^{2+}\) BETA\(^\prime\prime\) ALUMINAS

by

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ION TRANSPORT IN Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, AND Pb$^{2+}$ BETA" ALUMINAS

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Abstract

Single crystals of Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, and Pb$^{2+}$ beta" alumina were prepared from sodium beta" alumina by ion exchange. The ionic conductivities of Ca$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$ beta" alumina are comparable, about $2-4 \times 10^{-2}$ (ohm-cm)$^{-1}$ at 300°C. Surprisingly, Pb$^{2+}$ beta" alumina is much more conductive, $1.5 \times 10^{-1}$ (ohm-cm)$^{-1}$ at 300°C and $4.6 \times 10^{-3}$ (ohm-cm)$^{-1}$ at 40°C. Its conductivity approaches that of sodium beta" alumina at temperatures below 25°C. The diffusion coefficient for Sr$^{2+}$ in beta" alumina at 600°C was estimated from radiotracer experiments. It is consistent with that expected from conductivity measurements.
Introduction

It is well known that the entire sodium ion content of the solid electrolytes, beta and beta" alumina, can be replaced by a variety of monovalent cations [1,2]. Ion exchange generally takes place when crystals of sodium beta or beta" alumina are immersed in a fused salt containing a monovalent cation other than Na⁺. The time required for complete exchange varies with crystal size, temperature, and the diffusion rates of the ions involved. For example, Na⁺ in beta alumina crystals which are about 2mm square is replaced by K⁺ in several minutes when the crystals are immersed in molten KNO₃ at 400-500°C.

Recently, we were surprised to find that sodium beta" alumina crystals undergo similarly rapid ion exchange reactions with a number of divalent cations, including Ca²⁺, Sr²⁺, Ba²⁺, Cd²⁺, and Pb²⁺ [3,4]. The resulting divalent beta" aluminas are stable, retain the beta" alumina structure, and can be reversibly exchanged back to the sodium composition. In contrast, the diffusion rates of these ions in the beta alumina structure are lower by many orders of magnitude, even at 500-600°C.

The divalent beta" aluminas are the first family of high conductivity solid electrolytes for divalent cations. Initial measurements [3] on the Ba²⁺, Sr²⁺, and Cd²⁺ forms indicated that their conductivities are in the range of 10⁻⁷ (ohm-cm)⁻¹ at 40°C and 10⁻² (ohm-cm)⁻¹ at 300°C. The existence of the divalent beta" aluminas demonstrates that the phenomenon of fast ionic transport in solids is not restricted to a few monovalent cations, such as Na⁺, Ag⁺, and Li⁺, but is far more general and is observed with alkaline earth and transition metal ions as well.
This paper presents a thorough conductivity study which includes a re-examination of \( \text{Ba}^{2+} \) and \( \text{Sr}^{2+} \) beta-aluminas as well as new results for the \( \text{Ca}^{2+} \) and \( \text{Pb}^{2+} \) forms. In addition, we describe a measurement of the diffusion coefficient of \( \text{Sr}^{2+} \) in beta-alumina. Our results confirm that the divalent beta-aluminas are high conductivity solid electrolytes for divalent cations. By comparing conductivity and diffusion data for \( \text{Sr}^{2+} \) beta-alumina, we have shown that \( \text{Sr}^{2+} \) ions are sufficiently mobile in the structure to account for the high conductivities which are observed. In addition, we have found that the conductivity of one divalent composition, \( \text{Pb}^{2+} \) beta-alumina, is unexpectedly high, even at room temperature.

**Experimental**

The sodium beta-alumina crystals used in this work were grown by the flux evaporation method described previously [2,6]. Crystals were cut to a suitable size (generally 3mm x 2mm x 0.2mm) and immersed in appropriate molten salts for ion exchange. Complete exchange for crystals of this size generally occurs within one hour.

The extent of ion exchange was determined both gravimetrically and radiochemically. The former method is based on measuring the weight change associated with the exchange reaction. The latter involves initially tagging the sodium beta-alumina crystals with radioactive \( ^{22}\text{Na} \). Thereafter, the extent of exchange can be determined by measuring the change in the activity level of a sample. The correlation between the gravimetric and radiochemical
methods was excellent. The $^{22}\text{Na}$ content was generally reduced to the background level, which corresponded to less than 0.1% residual $\text{Na}^+$ in the samples.

Both radiotracer and gravimetric techniques were employed in preparing the $\text{Ba}^{2+}$, $\text{Sr}^{2+}$, and $\text{Ca}^{2+}$ beta" alumina samples. Two $\text{Ba}^{2+}$ beta" alumina crystals were prepared by immersing tagged $\text{Na}^+$ beta" alumina crystals in a melt of 67 w/o $\text{Ba(NO}_3\text{)}_2$/33 w/o $\text{BaCl}_2$ for 44 hours at 550°C. After its conductivity had been determined, one of these samples was re-exchanged back to the sodium form in molten $\text{NaNO}_3$. Its conductivity was then re-measured. $\text{Sr}^{2+}$ beta" alumina samples were prepared in 50 w/o $\text{Sr(NO}_3\text{)}_2$/50 w/o $\text{SrCl}_2$. Two crystals were exchanged for 12 hours and one for 5 hours. Three samples of $\text{Ca}^{2+}$ beta" alumina were prepared by two different routes. One was immersed in $\text{CaCl}_2$ at 770°C for one hour, and two others were exchanged for three hours at 500°C in $\text{Ca(NO}_3\text{)}_2$ to which a small amount of $\text{CaCl}_2$ had been added to decrease the melting point.

Gravimetric measurements were used in preparing $\text{Pb}^{2+}$ beta" alumina conductivity samples and in attempting to prepare $\text{Mg}^{2+}$ beta" alumina. The $\text{Pb}^{2+}$-containing samples were synthesized in molten $\text{PbCl}_2$ at 550°C. Eight samples were prepared using exchange times of 16-24 hours. The samples studied in this work were exchanged in an atmosphere of dry nitrogen. Subsequent $\text{Pb}^{2+}$ exchanges which were monitored radiochemically were consistent with the gravimetric data which indicated greater than 99.8% exchange was achieved under these conditions. $\text{Mg}^{2+}$ exchange was attempted in $\text{MgCl}_2$ at 725°C for 1-4 hours in dry nitrogen. It did not yield
samples suitable for conductivity measurements. Conductivity measurements were made using an automated system for complex impedance analysis over the frequency range of 0.1 to 1.0 MHz (Solartron 1174 Frequency Response Analyzer controlled by a Hewlett-Packard 9845 computer). Each crystal was contacted with two sputtered gold electrodes over which silver paste was applied to ensure satisfactory electrical contact. The samples were held between platinum electrodes under slight spring tension in an aluminum conductivity cell. All measurements were carried out in a stream of dry nitrogen or argon.

Samples were initially baked at 450°C for 4 hours to remove residual moisture. Conductivity data were then obtained at 20°C intervals as the temperature was decreased from 400 to 40°C. Samples were equilibrated for at least ten minutes at each temperature before data were collected. For measurements below 25°C, the cell was cooled by chilled nitrogen gas. Temperatures as low as -100°C were easily achieved.

The diffusion coefficient of Sr\(^{2+}\) in beta" alumina was estimated by measuring the change in \(^{22}\)Na activity in tagged crystals of sodium beta" alumina upon exposure to a molten the Sr\(^{2+}\) salt mixture. Four crystals were immersed for 15 second intervals in Sr(NO\(_3\))\(_2\)/SrCl\(_2\) at 600°C. After each exchange period, the samples were cooled rapidly to room temperature, rinsed with water, and the \(^{22}\)Na activities counted. The samples were then returned to the melt for an additional 15 second exchange period. This procedure was repeated for a total immersion time of 2 minutes.
**Results and Discussion**

**Sample Preparation**

The ion exchange treatments for producing $\text{Ca}^{2+}$, $\text{Sr}^{2+}$, $\text{Ba}^{2+}$, and $\text{Pb}^{2+}$ beta" alumina samples resulted in at least 99.8% replacement of $\text{Na}^+$ as determined by either gravimetric or radiochemical measurements. Exchanged crystals were clear, free of cracks, and retained the beta" alumina structure. The composition of these single crystals corresponded to $\text{M}_{0.85}\text{Mg}_{0.7}\text{Al}_{10.30\text{.17}}$ ($\text{M} = \text{Ba, Sr, Ca, Pb}$). X-ray diffraction studies of these materials are in progress [7]. Attempts to produce $\text{Mg}^{2+}$ beta" alumina were unsuccessful. The crystals shattered into fragments containing numerous fissures, and preliminary results indicated that only partial substitution occurred. It is worthwhile noting that the $\text{Mg}^{2+}$ ion is substantially smaller than the other ions studied (0.66 Å radius vs. 0.99 Å for $\text{Ca}^{2+}$, 1.12 Å for $\text{Sr}^{2+}$, 1.34 Å for $\text{Ba}^{2+}$, and 1.20 Å for $\text{Pb}^{2+}$). Thus, $\text{Mg}^{2+}$ exchange might be expected to induce local tensile stresses which ultimately lead to fracture. Microcracks have also been observed when $\text{Li}^+$ ions (0.66 Å) were exchanged for $\text{Na}^+$ in beta" alumina [8].

**Conductivity Measurements**

Conductivity data for $\text{Ba}^{2+}$, $\text{Sr}^{2+}$, $\text{Ca}^{2+}$, and $\text{Pb}^{2+}$ beta" aluminas are presented in Fig. 1 along with data for $\text{Na}^+$ beta" alumina. With the exception of the $\text{Na}^+$ compound, each curve represents an average of several different crystals, two for $\text{Ba}^{2+}$ and three each for $\text{Sr}^{2+}$, $\text{Ca}^{2+}$, and $\text{Pb}^{2+}$. Measurements of additional samples of
each composition over more restricted temperature ranges were completely consistent with the data presented here. For example, eight different samples of Pb$^{2+}$ beta" alumina were analyzed in order to confirm its high conductivity. All of the data were highly reproducible.

The curve shown in Fig. 1 for Na$^+$ beta" alumina was actually measured on a sample which had been exchanged back to the sodium isomorph from Ba$^{2+}$ beta" alumina. The conductivity values for this crystal are in excellent agreement with as-grown material [2], which confirms the reversibility of the ion exchange process. Table 1 summarizes critical data for each of the curves shown in Fig. 1.

In earlier papers [3,4], we have reported preliminary ionic conductivity measurements for Ba$^{2+}$ and Sr$^{2+}$ beta" aluminas. The present work offers a far more careful and comprehensive investigation of these materials in addition to new results for Ca$^{2+}$ and Pb$^{2+}$ beta" aluminas. The new data for the Ba$^{2+}$ beta" alumina compositions are comparable to the previous results. The new data for Sr$^{2+}$ beta" alumina, however, differ from the previous work. The activation energy for conductivity in Sr$^{2+}$ beta" alumina is lower than was first reported, and the conductivity is correspondingly higher. The new data have been obtained with crystals of much high quality than were previously available, and we believe them to be more accurate.

The data shown in Fig. 1 for Ca$^{2+}$ beta" alumina are somewhat different from data reported for Ca$^{2+}$ beta" alumina single crystals by Ni, Tsai, and Whitmore [10]. They observed conductivities that
are lower by about one order of magnitude at 300°C and also found Arrhenius behavior over the temperature range of 250-450°C. The composition of their samples, Ca$_{0.927}$Mg$_{0.854}$Al$_{10.150}$, is different from ours, and contains considerably more Ca$^{2+}$. These results strongly suggest that small changes in the stoichiometry of the divalent beta" aluminas significantly influence their conductivities.

We find that the Arrhenius-type plot for Ca$^{2+}$ beta" alumina is non-linear (Fig. 1), as are the plots for Pb$^{2+}$ and Na$^+$. Even though the curve in the Ca$^{2+}$ beta" alumina plot is slight, it is quite reproducible. The curvature is pronounced for the Pb$^{2+}$ and Na$^+$ forms. These curves suggest that order-disorder transitions among the mobile ions and vacancies in the conduction plane of beta" alumina critically influence the process of ion motion in the structure, as has been suggested by other recent investigations [9]. Structural studies which should help in understanding these interactions in the divalent beta" aluminas are underway [7].

The most surprising result of the present work is the high conductivity of Pb$^{2+}$ beta" alumina. At 40°C its conductivity is about 10$^3$ times greater than that of any other divalent beta" alumina and only slightly less than that of Na$^+$ beta" alumina (see Table 1). Furthermore, the conductivity of Pb$^{2+}$ ions in beta" alumina is comparable to that of Na$^+$ ions from 0 to -90°C. This high conductivity was shown by every sample of Pb$^{2+}$ beta" alumina measured, eight in all.

The exceptionally high conductivity of Pb$^{2+}$ ions in beta" alumina has some precedent among classical halide salts. While we found no previous reports of divalent cation diffusion in salts
such as the alkaline earth halides, Pb\textsuperscript{2+} ions have been reported to diffuse at small but measurable rates in PbCl\textsubscript{2} and PbI\textsubscript{2}, in which Cl\textsuperscript{-} and I\textsuperscript{-} ions also are mobile. It appears that these compounds are the only materials previously known to be solid state conductors of divalent cations.

The high electronic polarizability of the Pb\textsuperscript{2+} ion as well as the many electron shells which shield the Pb\textsuperscript{2+} nucleus and diminish the strength of long-range coulomb interactions between Pb\textsuperscript{2+} ions and the surrounding anion sublattices may help explain the high mobilities of Pb\textsuperscript{2+} ions in its halides and in beta\textsuperscript{"} alumina. In addition, as has been already mentioned, the non-Arrhenius behavior of Pb\textsuperscript{2+} beta\textsuperscript{"} alumina conductivity as well as other monovalent and divalent beta\textsuperscript{"} aluminas suggests that order-disorder interactions among the mobile ions and vacancies in the beta\textsuperscript{"} alumina structure are important influences upon the rates of ion/vacancy diffusion in the structure. A study of local ion/vacancy order and domain formation in the divalent beta\textsuperscript{"} aluminas may be unusually interesting and do much to illuminate the processes of ion transport in these compounds and in solid electrolytes in general.

**Diffusion Studies**

Our conductivity results were highly reproducible, and there is little reason to doubt that ion transport in these electrolytes is the result of divalent cation motion. Nevertheless, conductivity measurements are not ion-specific. So, we decided to use a radiotracer technique with \textsuperscript{22}Na to measure the diffusion coefficient for one of the divalent species, Sr\textsuperscript{2+}, in beta\textsuperscript{"} alumina. Through the
Nernst-Einstein equation, the measured diffusion coefficient could be used to calculate a value of conductivity.

The results in Fig. 2 plot the decrease in $^{22}\text{Na}$ activity vs time for four tagged Na$^+$ beta" alumina single crystals immersed in a Sr(NO$_3$)$_2$-SrCl$_2$ melt at 600°C. The data for the different crystals agree closely, and from them, a diffusion coefficient can be calculated.

Sutter has shown [14] that for the case of two-dimension diffusion in a crystal of width, w (in the x-direction), and length, L (in the y-direction), the time required to achieve a particular extent of exchange (reduction in radioactivity) can be related to the diffusion coefficient by Equation 1

$$\frac{C(x,y,t)}{C_0} = \left(\frac{4}{\pi^2}\right)^2 \sum_{n_x=1 \text{ odd}}^{\infty} \sum_{n_y=1 \text{ odd}}^{\infty} \frac{1}{n_x} \sin\left(\frac{n_x x}{w}\right) \frac{1}{n_y} \sin\left(\frac{n_y y}{L}\right) \exp\left[-\frac{w^2}{D} \frac{t}{2} \left(\frac{n_x^2}{w^2} + \frac{n_y^2}{L^2}\right)\right]$$  \hspace{1cm} (1)

in which $C_0$ is the initial uniform tracer concentration in the crystal, $C$ is the tracer concentration at time $t$, and $D$ is the diffusion coefficient. The solution uses a Fourier sum with integers $n_x$ and $n_y$ in order to match the initial condition of uniform tracer concentration. The Fourier coefficients are taken as $1/n_x$ (or $1/n_y$) for odd $n_x$ (or $n_y$) and zero for even $n_x$ (or $n_y$) as in a Fourier square wave.

The form of Eqn. 1 is virtually identical to that used by Yao and Kummer [1] for determining diffusion coefficients of monovalent ions in beta alumina. Yao and Kummer, however, used a slightly
different approach for measuring diffusion coefficients from that used in this work. They immersed beta alumina crystals with tagged mobile ions in molten salts containing the same but untagged ions. In the present work, however, crystals labeled with $^{22}$Na were immersed in a melt containing only Sr$^{2+}$ cations. The resulting ion exchange process involves the interdiffusion of Sr$^{2+}$ and Na$^+$ ions in a mixed Na$^+$-Sr$^{2+}$ crystal. Interpreting such interdiffusion data in terms of self-diffusion coefficients can be misleading. However, prior work on the beta aluminas has clearly indicated that, in crystals containing a high concentration of the slower-moving species, i.e. above about 80% Sr$^2+$, the calculated diffusion coefficient is quite close to the self-diffusion coefficient of the slower-moving ion [1]. Based on this approach, we were able to determine an approximate diffusion coefficient for Sr$^{2+}$ in beta" alumina and thus estimate the Sr$^{2+}$ conductivity at the same temperature using the Nernst-Einstein equation (Eqn. 2).

The diffusion coefficient for Sr$^{2+}$, calculated from Eqn. 1, is $3.4 \times 10^{-5}$ cm$^2$/sec at 600°C. It varies only slightly for Sr$^{2+}$ concentrations greater than 60%, which suggests that it is quite close to the actual self-diffusion coefficient for Sr$^{2+}$ at this temperature. This value of $D$ was inserted into the Nernst-Einstein equation (Eqn. 2)

$$\sigma \tau = \frac{\eta q^2 D}{k}$$

2.
in which \( n \) is the number density of \( \text{Sr}^{2+} \) ions and \( q \) is their charge. The density of \( \text{Na}^+ \) beta" alumina single crystals of the composition used in this work is 3.25 g/cm\(^3\). Structural data for crystals of this composition show that the sodium ions occupy five of every six Beevers-Ross type sites \([15]\), which yields a carrier density of 4.8 \(\times\) \(10^{21}\) cm\(^{-3}\). After complete \(\text{Sr}^{2+}\) exchange, the density is 2.4 \(\times\) \(10^{21}\) cm\(^{-3}\). With these values of \( n \) and \( D \), Eqn. 2 yields a value of \(\sigma T\) of 660 (ohm-cm)\(^{-1}\) K at 600°C. It compares quite favorably with that of 768 (ohm-cm)\(^{-1}\) obtained by extrapolation of the conductivity curve for \(\text{Sr}^{2+}\) beta" alumina. The good agreement between the conductivity and diffusion measurements clearly demonstrates that \(\text{Sr}^{2+}\) motion is sufficiently rapid to account for the conductivity observed for these materials.

Conclusions

We believe that the experimental results reported in this paper clearly demonstrate that divalent cations diffuse rapidly in beta" alumina and that the divalent beta" aluminas are the first general family of solid electrolytes for divalent cations. Many questions concerning the properties and applications of these compounds are unexplored. First, we do not yet know the full extent of the divalent beta" aluminas. We suspect that it will be possible to replace sodium in the structure with most divalent cations, with the possible exception of a few, such as \(\text{Be}^{2+}\) and \(\text{Mg}^{2+}\), which are very small, highly polarizing, and lead to the breakup of the structure.
In addition, little is known about why divalent cations diffuse so rapidly in the beta" alumina structure. This question is even more interesting considering that divalent cations diffuse in the closely-related beta alumina structure at rates that are slower by many orders of magnitude. A comparison and contrast between the divalent beta" and beta aluminas should help in understanding how relatively small changes in structure can dramatically alter the processes of ion diffusion in a solid electrolyte.

The fact that divalent cations diffuse rapidly in beta" alumina also demonstrates that the phenomenon of fast ionic transport in solid is not limited to a few monovalent cations, such as Na⁺, Ag⁺, and Li⁺, and that other compounds may exist which also are good conductors of multivalent cations. It also provides a tantalizing opportunity for new technological devices. It may take some time before applications of the divalent beta" aluminas emerge. One intriguing possibility is that of novel sensors. The divalent beta" aluminas make it possible to develop specific ion sensors for a range of ions for which no solid electrolytes have previously existed. In addition, since these compounds are stable to rather high temperatures, sensors based on the divalent beta" aluminas may make it possible to explore the thermodynamics of various chemical processes in high temperature ranges which are inaccessible with conventional electrochemical sensors.
Acknowledgements

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References

8. J. L. Briant, private communication.
Table 1. Conductivity Characteristics of Various Divalent Beta" Aluminas

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$\sigma$ at 40°C($\Omega^{-1}\text{cm}^{-1}$)</th>
<th>$\sigma$ at 300°C($\Omega^{-1}\text{cm}^{-1}$)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$ β&quot;</td>
<td>1.3 x 10$^{-2}$</td>
<td>9.1 x 10$^{-1}$</td>
<td>-</td>
</tr>
<tr>
<td>Pb$^{2+}$ β&quot;</td>
<td>4.6 x 10$^{-3}$</td>
<td>1.5 x 10$^{-1}$</td>
<td>-</td>
</tr>
<tr>
<td>Ca$^{2+}$ β&quot;</td>
<td>3.9 x 10$^{-6}$</td>
<td>3.6 x 10$^{-2}$</td>
<td>-</td>
</tr>
<tr>
<td>Sr$^{2+}$ β&quot;</td>
<td>2.4 x 10$^{-6}$</td>
<td>2.4 x 10$^{-2}$</td>
<td>0.57</td>
</tr>
<tr>
<td>Ba$^{2+}$ β&quot;</td>
<td>2.8 x 10$^{-6}$</td>
<td>1.9 x 10$^{-2}$</td>
<td>0.57</td>
</tr>
</tbody>
</table>
Figure Captions

Figure 1. The conductivities of various divalent beta" aluminas between -100°C and 400°C compared with Na⁺ beta" alumina.

Figure 2. Plot of per cent Sr²⁺ replacement of Na⁺ versus time at 600°C for four similar crystals of beta" alumina. The dimensions were:

0 - 0.170 x 10.261 x 0.037 cm³,
+ - 0.166 x 0.261 x 0.028 cm³,
- 0.170 x 0.261 x 0.037 cm³,
- 0.160 x 0.317 x 0.038 cm³.
The short dimension is in the direction of the c-axis.

Figure 3. Sr²⁺ beta" alumina conductivity estimated from diffusion data (X) compared to that obtained from an extrapolation of conductivity measurements (---).
FIGURE 1

\[ \log \sigma T \left( \Omega^{-1} \text{cm}^{-1} \text{K} \right) \]

\[ 1000 / T \left( \text{K}^{-1} \right) \]

- \( \Delta : \text{Na Beta'' Alumina} \)
- \( \text{■ : Pb Beta'' Alumina} \)
- \( \bullet : \text{Ca Beta'' Alumina} \)
- \( \text{△ : Sr Beta'' Alumina} \)
- \( \text{□ : Ba Beta'' Alumina} \)
Figure 2

$\text{Na}^+$ REPLACEMENT (%) vs. TIME (sec)
FIGURE 3