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Ion Transport in Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+} Beta″ Aluminas

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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 3×10^{-2} (ohm-cm)$^{-1}$ at 300°C. Surprisingly, Pb^{2+} beta″ alumina is much more conductive, 1.5×10^{-1} (ohm-cm)$^{-1}$ at 300°C and 4.6×10^{-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 2 mm^2 is replaced by K^+ in several minutes when the crystals are immersed in molten KNO_3 at 400–500°C.

Recently, we found that sodium beta″ alumina crystals undergo similarly rapid ion exchange reactions with a number of divalent cations, including Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, and Pb^{2+} (*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 Ba^{2+}, Sr^{2+}, and Cd^{2+} 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

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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 reexamination of Ba^{2+} and Sr^{2+} beta″ aluminas as well as new results for the Ca^{2+} and Pb^{2+} forms. In addition, we describe an approximate measurement of the diffusion coefficient of 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 Sr^{2+} beta″ alumina, we have shown that 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, Pb^{2+} beta″ alumina, is unexpectedly high, even at room temperature. We must note that much of the data presented in this paper has appeared in a prior review of the subject by two of the authors (*5*). This paper is referred to as Ref. (*3*) in that review.

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 3 × 2 × 0.2 mm) and immersed in appropriate molten salts for ion exchange. Complete exchange for crystals of this size generally occurs within 1 hr.

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}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}Na content was generally reduced to the background level, which corresponded to less than 0.1% residual Na^+ in the samples.

Both radiotracer and gravimetric techniques were employed in preparing the Ba^{2+}, Sr^{2+}, and Ca^{2+} beta″ alumina samples. Two Ba^{2+} beta″ alumina crystals were prepared by immersing tagged Na^+ beta″ alumina crystals in a melt of 67 wt% $Ba(NO_3)_2$/33 wt% $BaCl_2$ for 44 hours at 550°C. After its conductivity had been determined, one of these samples was reexchanged back to the sodium form in molten $NaNO_3$. Its conductivity was then remeasured. Sr^{2+} beta″ alumina samples were prepared in 50 wt% $Sr(NO_3)_2$/50 wt% $SrCl_2$ at 600°C. Two crystals were exchanged for 12 hr and one for 5 hr. Three samples of Ca^{2+} beta″ alumina were prepared by two different routes. One was immersed in $CaCl_2$ at 770°C for 1 hr and two others were exchanged for 3 hr at 500°C in $Ca(NO_3)_2$ to which a small amount of $CaCl_2$ had been added to decrease the melting point.

Gravimetric measurements were used in preparing Pb^{2+} beta″ alumina conductivity samples and in attempting to prepare Mg^{2+} beta″ alumina. The Pb^{2+}-containing samples were synthesized in molten $PbCl_2$ at 550°C. Eight samples were prepared using exchange times of 16–24 hr. The samples studied in this work were exchanged in an atmosphere of dry nitrogen. Subsequent 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. Mg^{2+} exchange was attempted in $MgCl_2$ at 725°C for 1–4 hr 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 hr 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 10 min 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 Sr^{2+} salt mixture. Four crystals were immersed for 15-sec 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-sec exchange period. This procedure was repeated for a total immersion time of 2 min.

Results and Discussion

Sample Preparation

The ion exchange treatments for producing Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+} beta″ alumina samples resulted in at least 99.8% replacement of 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 $M_{0.85}Mg_{0.7}Al_{10.3}O_{17}$ (M = Ba, Sr, Ca, Pb). X-ray diffraction studies of these materials are in progress (*7*). Attempts to produce 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 Mg^{2+} ion is substantially smaller than the other ions studied (0.66 Å radius vs 0.99 Å for Ca^{2+}, 1.12 Å for Sr^{2+}, 1.34 Å for Ba^{2+}, and 1.20 Å for Pb^{2+}). Thus, Mg^{2+} exchange might be expected to induce local tensile stresses which ultimately lead to fracture. Microcracks have also been observed when Li^+ ions (0.66 Å) were exchanged for Na^+ in beta″ alumina (*8*).

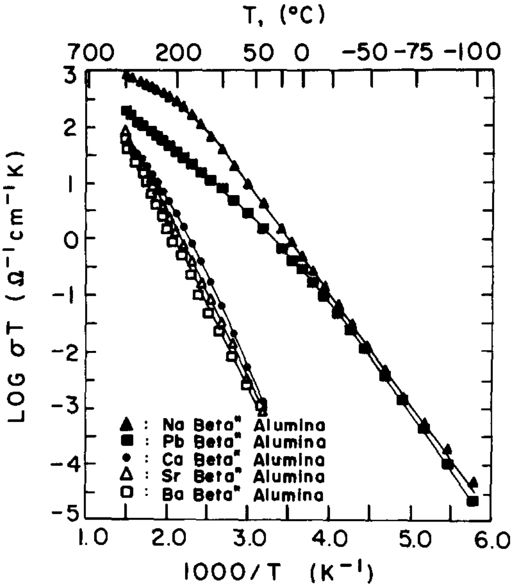

FIG. 1. The conductivities of various divalent beta″ aluminas between −100 and 400°C compared with Na^+ beta″ alumina.

Conductivity Measurements

Conductivity data for Ba^{2+}, Sr^{2+}, Ca^{2+}, and Pb^{2+} beta″ aluminas are presented in Fig. 1 along with data for Na^+ beta″ alumina. With the exception of the Na^+ com-

TABLE 1

CONDUCTIVITY CHARACTERISTICS OF VARIOUS DIVALENT BETA″ ALUMINAS

Crystal	σ at 40°C (Ω^{-1} cm^{-1})	σ at 300°C (Ω^{-1} cm^{-1})	E_a (eV)
Na^+ β''	1.3×10^{-2}	9.1×10^{-1}	—
Pb^{2+} β''	4.6×10^{-3}	1.5×10^{-1}	—
Ca^{2+} β''	3.9×10^{-6}	3.6×10^{-2}	—
Sr^{2+} β''	2.4×10^{-6}	2.4×10^{-2}	0.57
Ba^{2+} β''	2.8×10^{-6}	1.9×10^{-2}	0.57

pound, each curve represents an average of several different crystals, two for Ba^{2+} and three each for Sr^{2+}, Ca^{2+}, and 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 I 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 *et al.* (*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, $Ca_{0.927}Mg_{0.854}Al_{10.15}O_{17}$, 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 nonlinear (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 may 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 I). 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^{2+} ions have been reported to diffuse at small but measurable rates in $PbCl_2$ and PbI_2, in which Cl^- and I^- 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^{2+} ion as well as the many electron shells which shield the Pb^{2+} nucleus and diminish the strength of long-range coulomb interactions between Pb^{2+} ions and the surrounding anion sublattices may help explain the high mobilities of Pb^{2+} ions in its halides and in beta″ alumina. In addition, as has been already mentioned, the non-Arrhenius behavior of Pb^{2+} beta″ alumina conductivity as well as other monovalent and divalent beta″ aluminas suggests that order–disorder interactions among the mobile ions and vacancies in the beta″ 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″ aluminas may be unusually interesting and do much to illuminate the processes of ion transport in these compounds.

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, a radio-tracer technique with ^{22}Na was used to estimate the diffusion coefficient of one of the divalent species, Sr^{2+}, in beta″ alumina. Through the Nernst–Einstein equation, the measured diffusion coefficient could be used to calculate a value of conductivity.

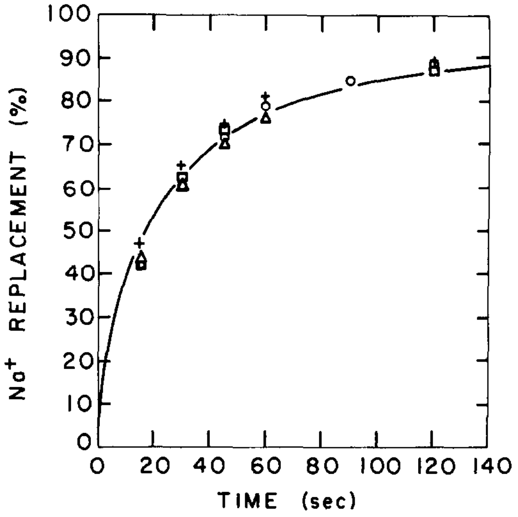

FIG. 2. Plot of percent Sr^{2+} replacement of Na^+ versus time at 600°C for four similar crystals of beta″ alumina. The dimensions were O–0.170 × 10.261 × 0.037 cm^3, +–0.166 × 0.261 × 0.028 cm^3, Δ–0.170 × 0.261 × 0.037 cm^3, □–0.160 × 0.317 × 0.038 cm^3. The short dimension is in the direction of the *c* axis.

The results in Fig. 2 plot the decrease in ^{22}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-dimensional 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 apparent diffusion coefficient by Eq. (1):

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

in which C_0 is in 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 Eq. (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, 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.

Prior interdiffusion measurements on mixed Na^+–K^+, Ag^+–Na^+, and Ag^+–Rb^+ beta aluminas have show that the interdiffusion coefficient is lower than the self-diffusion coefficient of the slowest diffusing ion (*1*). In light of these uncertainties, we suggest that the present measurements are useful only in estimating the self-diffusion coefficient of Sr^{2+} in beta" alumina and in demonstrating that the motion of Sr^{2+} is sufficiently rapid to account for the ionic conductivity observed in pure Sr^{2+} beta" alumina.

The diffusion coefficient calculated from Eq. (1) is 3.4×10^{-5} cm²/sec at 600°C. It varies only slightly for Sr^{2+} concentrations greater than 60%, which suggests that it may be 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 (2):

$$\sigma T = \frac{nq^2D}{k} \tag{2}$$

in which n was taken to be the number density of Sr^{2+} ions and q is their charge. The density of Na^+ beta" alumina single crystals of the composition used in this work is 3.25 g/cm³. 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 4.8×10^{21} cm^{-3}. After complete Sr^{2+} exchange, the density is 2.4×10^{21} cm^{-3}. With these values of n and D, Eq. (2) yields a value of σT of 660 (ohm-cm)$^{-1}$ K at 600°C, which should be considered merely an estimate of the Sr^{2+} conductivity of beta" alumina. It compares quite favorably with that of 768 (ohm-cm)$^{-1}$ obtained by extrapolation of the conductivity curve for Sr^{2+} beta" alumina. The good agreement between the conductivity and diffusion measurements clearly demonstrates that Sr^{2+} motion is

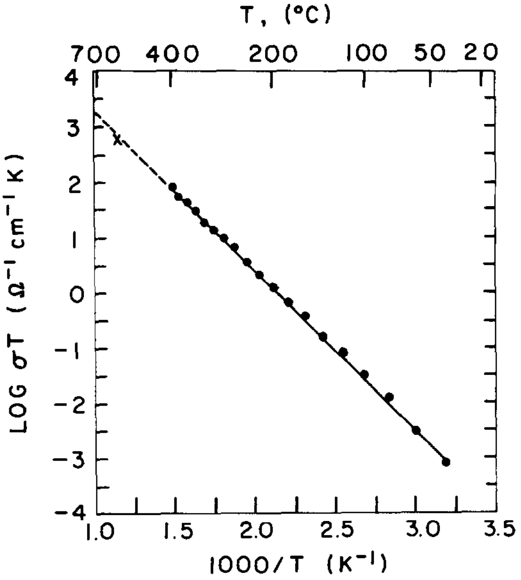

FIG. 3. Sr^{2+} beta" alumina conductivity estimated from diffusion data (×) compared to that obtained from an extrapolation of conductivity measurements (——).

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 Be^{2+} and Mg^{2+}, which are very small, highly polarizing, and may 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. The divalent beta″ aluminas may also make possible a number of new devices, such as novel specific ion sensors. Since these compounds are stable to rather high temperatures, sensors based on the divalent beta″ aluminas might be used to explore the thermodynamics of various chemical processes in high temperature ranges which are inaccessible with conventional electrochemical sensors.

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