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Ionic Conductivity in Na^+, K^+, and Ag^+ β''-Alumina

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This paper presents measurements of the ionic conductivity in single crystals of β''-alumina (0.84 M_2O · 0.67 MgO · 5.2 Al_2O_3, M = Na, K, Ag). Single crystals of sodium β''-alumina were grown from a melt of Na_2O, MgO, and Al_2O_3 at 1660 to 1730°C. Selected crystals were converted to the other isomorphs by ion exchange. The conductivity of sodium β''-alumina varies from 0.18 to 0.01 $(\text{ohm} \cdot \text{cm})^{-1}$ at 25°C depending upon crystal growth conditions. Potassium β''-alumina has the unusually high room temperature conductivity of 0.13 $(\text{ohm} \cdot \text{cm})^{-1}$. Silver β''-alumina has a slightly lower conductivity, 4×10^{-3} $(\text{ohm} \cdot \text{cm})^{-1}$ at 25°C. The activation energies of sodium and potassium β''-alumina decrease with increasing temperature, while that of silver β''-alumina is constant from −80 to 450°C.

Introduction

Sodium β-alumina (typically 1.24 Na_2O · 11 Al_2O_3) and sodium β''-alumina (typically 0.84 Na_2O · 0.67 MgO · 5.2 Al_2O_3) have exceptionally high ionic conductivities (10^{-2} to 10^{-1} $(\text{ohm} \cdot \text{cm})^{-1}$) at 25°C. Both compounds are nonstoichiometric crystalline solids with electronic conductivities of less than 10^{-11} $(\text{ohm} \cdot \text{cm})^{-1}$ at 25°C. Other investigators have reviewed the structures of sodium β-alumina (*1*) and of sodium β''-alumina (*2*) and discussed the crystal chemical basis of rapid ion migration in them.

The entire sodium content of β-alumina can be exchanged for a variety of monovalent cations including Li^+, K^+, and Ag^+ (*3*) as well as H^+ (*4*), H_3O^+ (*5, 6*), and NH_4^+ (*3*). Similar ion exchange chemistry has been observed for sodium β''-alumina with H_3O^+ (*7*) and NH_4^+ (*8*), and in this investigation with K^+ and Ag^+. The conductivities of sodium, potassium, and silver β-alumina have been determined by tracer diffusion, dielectric loss, and direct dc measurements (*9, 10*) (see Table I). These conductivities obey simple Arrhenius relationships (Eq. (1)) with single activation energies (E_a) over wide ranges of temperature.

$$\sigma T = \sigma_0 \exp(-E_a/kT). \qquad (1)$$

In contrast, little is known about the single-crystal properties of the β''-alumina isomorphs. Single-crystal conductivity measurements have been reported only for sodium β''-alumina (*4*), which was found to have a conductivity of 5.4×10^{-2} $(\text{ohm} \cdot \text{cm})^{-1}$ at 25°C, four times larger than that of sodium β-alumina. The activation energy for conductivity was observed to decrease with increasing temperature. This paper presents the results of a new investigation into the conductivity of single crystals of sodium β''-alumina from 75 to 440°C as well

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TABLE I

CONDUCTIVITY IN β-ALUMINA

Mobile ion	σ at 25°C (ohm^{-1} cm^{-1})	E_a (eV)	σ_0 (ohm^{-1} cm^{-1} °K)	Ref.
Na^+	1.4×10^{-2}	0.16	2.2×10^3	(*11*)
K^+	6.5×10^{-5}	0.29	1.6×10^3	(*4*)
Ag^+	6.7×10^{-3}	0.17	1.4×10^3	(*12*)

as the first measurements of the conductivities of potassium and silver β''-alumina.

Experimental

Single crystals of sodium β''-alumina were grown from a eutectic melt of Na_2O (32.5 mole%), MgO (7.8 mole%), and Al_2O_3 (59.6 mole%). This composition is richer in Na_2O than β''-alumina and melts at about 1650°C. When it is held above this temperature for 1 to 5 days in an unsealed crucible, Na_2O slowly evaporates and β''-alumina crystals grow.

Weber and Venero first described this technique of growing large single crystals (100–200 mm^3) with various stabilizing agents, including Mg^{2+} (*13*). We have previously reported growing crystals by this technique in Pt or α-alumina crucibles held at 1660°C for 1 to 3 days (*7*). Researchers at Oak Ridge National Laboratory were able to grow larger crystals (200–300 mm^3) by holding the melt at a higher temperature (1700°C) for a longer time (*14*). In this paper we report on crystals grown under two sets of conditions: in α-alumina crucibles at 1660°C for 1 to 3 days and in Pt crucibles at 1690–1730°C for 2 to 6 days.

The composition of both sets of crystals is $0.84\ Na_2O \cdot 0.67\ MgO \cdot 5.2\ Al_2O_3$ ($Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$). The sodium content was determined by weight change upon silver ion exchange and the magnesium content by chemical analysis. This composition is consistent with the ideal formula of MgO-stabilized β''-alumina proposed by Bettman and Peters, $Na_{1+x}Mg_xAl_{11-x}O_{17}$, in which the charge of all the excess Na^+ is balanced by Mg^{2+} substitution in Al^{3+} sites (*2*).

Potassium and silver β''-alumina were prepared by ion exchange of sodium β''-alumina crystals in molten KNO_3 at 400°C or molten $AgNO_3$ at 250°C for several days. Weight change as a function of time was used to establish the completeness of ion exchange. To demonstrate the accuracy of the conductivity measurement technique, the conductivity of a sodium β-alumina single crystal obtained from the Union Carbide Corporation was also measured.

For conductivity measurements optically clear crystals were squared and mounted on α-alumina disks with a high-temperature inorganic cement. Separate experiments determined that the surface conductivity of the α-alumina and the conductivity of the mounting cement were insignificant. Each crystal was contacted with two thin film (10,000 Å) gold or platinum/palladium electrodes deposited by molecular beam sputtering. The sputtered films were backed with a layer of silver paste cured at 300–500°C. The samples were suspended in a quartz tube surrounded by a resistance heater or chilling bath and maintained either at 10^{-3} Torr or in flowing dry He during experiments. The temperature was determined by a thermocouple located about 5 mm from the sample within the quartz tube. Conductivity data were recorded every 10°C as temperature was scanned at about 10°C/hr. At each temperature the impedance was scanned from 10^2 to 10^7 Hz using

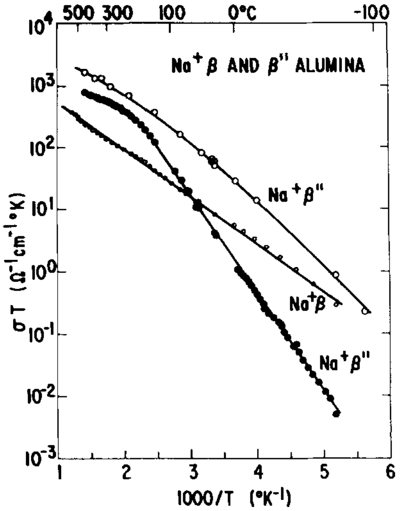

FIG. 1. The conductivities of sodium β''-alumina single crystals grown under different conditions compared with the conductivity of sodium β-alumina.

a Hewlett–Packard 9825A calculator, HP 3570A network analyzer, and HP 3330B frequency synthesizer. Data were presented as complex admittance plots which closely agreed with that expected for a model circuit describing the samples (e.g., Ref. (*15*).

Results

Figure 1 summarizes the conductivity data observed for sodium β- and β''-alumina as a function of temperature. The conductivity of the single crystals of sodium β-alumina follows a straight line in an Arrhenius plot from −75 to 450°C with an activation energy of 0.15 eV. At 25°C the conductivity is 2.5×10^{-2} (ohm · cm)$^{-1}$. These values agree well with 1.4×10^{-2} (ohm · cm)$^{-1}$ at 25°C and 0.16 eV reported for Monofrax sodium β-alumina (*11*) and 3×10^{-2} (ohm · cm)$^{-1}$ and 0.16 eV measured for Union Carbide single crystals (*16*).

The conductivity of sodium β''-alumina grown at 1660°C is plotted in the upper curve of Fig. 1. Room temperature conductivities varied from 1.0×10^{-1} to 1.8×10^{-1} ohm^{-1} cm^{-1}, partly as the result of uncertainty in geometric factors. The activation energy is nearly constant at 0.20 eV below 25°C and decreases smoothly to reach 0.12 eV at 400°C.

The lower curve on Fig. 1 represents measurements on sodium β''-alumina crystals grown at 1690–1730°C. The room temperature conductivities range from 3.3×10^{-2} to 1.4×10^{-2} ohm^{-1} cm^{-1}, values 5 to 10 times lower than those of the 1660°C crystals, but comparable to those of sodium β-alumina at 25°C. The Arrhenius plots of these samples appear to consist of two straight lines with activation energies of 0.31 eV below 150°C and 0.09 eV above 300°C. The conductivities of all sodium β''-alumina samples measured appear to approach a common value and activation energy above 225°C. (The conductivities differ by at most a factor of 2 above this temperature.) However, differences in low-temperature activation energies produce a range of an order of magnitude in room temperature conductivities and more than two orders of magnitude at −80°C. Perhaps all these crystals possess a common conductivity mechanism above 225°C while below the mechanism is extrinsic and depends on particular structures, compositions, defects, or impurities.

Radzilowski reported the earliest conductivity measurements on melt-grown sodium β''-alumina crystals (*4*). He measured a room temperature conductivity of 5.4×10^{-2} ohm^{-1} cm^{-1} and found curvature in the Arrhenius plot; the activation energy decreased smoothly from 0.22 eV at 25°C to 0.12 eV at 350°C. We have confirmed the general features of this work, the decreasing activation energy in particular, but also demonstrated that the conductivity of sodium β''-alumina varies substantially with the method of crystal growth.

Figure 2 shows conductivity data for sodium β''-alumina crystals grown at 1690–1730°C and for such crystals ion exchanged

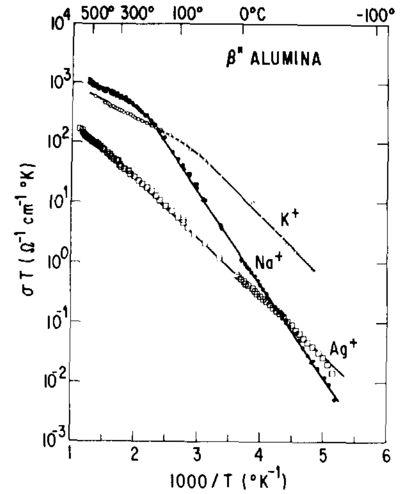

FIG. 2. Conductivity as a function of inverse temperature in single-crystal sodium, potassium, and silver β"-alumina. (All crystals were grown at 1690–1730°C.)

to the potassium and silver isomorphs. Potassium β"-alumina has an extremely high ionic conductivity, 1.3×10^{-1} ohm^{-1} cm^{-1} at 25°C. Its Arrhenius plot also appears to consist of two straight lines, but the temperature of the bend is somewhat lower than that in sodium β"-alumina. The activation energy is 0.21 eV below 25°C and 0.11 eV above 100°C. No difference in conductivity was seen between samples whose parent crystals were grown at 1660 or 1690–1730°C. This room temperature conductivity is 2000 times higher than that of potassium β-alumina, and 10 times higher than that of sodium β"-alumina grown at 1690–1730°C.

Silver β"-alumina conductivity is comparable to that of silver β-alumina (see Tables I and II). The room temperature conductivity is about 4×10^{-3} ohm^{-1} cm^{-1} and a constant activation energy of 0.19 eV was measured from −80 to 450°C. This conductivity appears to be the same whether the parent sodium β"-alumina crystals were grown at 1660 or 1690–1730°C.

We have seen evidence that molecular water can reversibly enter the β"-alumina conduction planes in a reaction similar to that observed with β-alumina (*17*). The room temperature resistivities of sodium β- and β"-alumina crystals increase with exposure to air, but decrease to constant values upon heating to 500°C. The conductivity measurements of all the β"-alumina isomorphs are closely reproducible in a dry atmosphere (vacuum or dry He).

Discussion

Our results indicate that the factors which influence ionic conductivity in β"-alumina are more complex than expected. While it is impossible to explain all our observations now, we offer here several possible interpretations of the major effects seen.

First, the conductivity of sodium β"-alumina varies with the method of crystal

TABLE II

CONDUCTIVITY IN β"-ALUMINA

Mobile ion	σ at 25°C (ohm^{-1} cm^{-1})	E_a at 25°C (eV)	σ_0 at 25°C (ohm^{-1} cm^{-1} °K)	E_a at 300°C	σ_0 at 300°C
Na^{+a}	1.0×10^{-1}	0.20	7×10^4	0.12	1.4×10^4
Na^{+b}	1.4×10^{-2}	0.31	7.1×10^5	0.09	5.0×10^3
K^+	1.3×10^{-1}	0.21	1.3×10^5	0.11	2.6×10^3
Ag^+	4×10^{-3}	0.19	2.0×10^3	0.19	2.0×10^3

[a] Crystals grown at 1660°C.

[b] Crystals grown at 1690–1730°C.

growth, although it is reproducible for each method. The two methods we used involved the same principle (isothermal Na_2O evaporation) and the same melt composition, but differed in temperature, length of time at temperature, rate of soda loss, rate of heating and cooling, and crucible material. We are currently trying to determine which of these factors are important and whether there are impurity differences between our two sets of crystals.

Second, the conductivities of the alkali β″-isomorphs cannot be characterized by single activation energies and preexponential factors. It appears, however, that the conductivities fall into two temperature regions, each described by a single activation energy and prefactor.

$$\frac{1}{\sigma T} = \frac{1}{\sigma_1} e^{E_1/kT} + \frac{1}{\sigma_2} e^{E_2/kT}. \tag{2}$$

The low-temperature activation energies and prefactors are all anomalously high. (See Tables I and II for a comparison with the β-alumina isomorphs, silver β″-alumina, and the high-temperature alkali β″-alumina values.)

One possible explanation for this behavior is that an order–disorder transition occurs at the transition temperature. The electrostatic repulsion of the mobile ions may set up an ordered configuration at low temperatures which maximizes the distances between ions. At higher temperatures, the entropy of lattice disorder may outweigh the gain in electrostatic energy and push the system to a disordered state. Such transitions have been observed in other solid electrolytes (AgI, for example). Recent experimental evidence supports the occurrence of such a transition in sodium β″-alumina. Using X-ray diffuse scattering, Collin *et al.* (*18*) have seen superstructure reflections from the conducting planes of sodium and potassium β″-alumina. Coherence length measurements on sodium β″-alumina show a constant coherence length of about 70 Å below 250°K. It decreases to reach about 20 Å above 600°K. The center of the drop is 420°K, close to the temperature of the bend in the Arrhenius plot. No superstructure reflections were observed at any temperature for silver β″-alumina, for which we observed a constant activation energy from −80 to 450°C. Therefore, our observations are consistent with those of Collin *et al.* In sodium β″-alumina, both conductivity and X-ray diffuse scattering experiments suggest an order–disorder reaction occurring about 400°K. In silver β″-alumina, no such reaction is seen by either technique.

We can only begin to explain the relative magnitudes of the conductivities of various isomorphs. One should first note that they are all very high. The lowest value at 25°C is 4×10^{-3} ohm^{-1} cm^{-1}. The unusually high potassium conductivity is striking, but consistent with the structures of β- and β″-alumina. Because of the different relative orientations of the layers of oxygen atoms which bound the conduction planes, the smallest gap through which a traveling ion must pass is 2 Å in β-alumina, but 3 Å in β″-alumina. This suggests that ions larger than sodium (1.94 Å diameter) should have lower activation energies for conduction and higher conductivities in the β″-alumina structure. The results for potassium ion (2.7 Å diameter) conductivity confirm this prediction. While sodium seems to be the ion of optimum size for conduction in β-alumina (with the lowest activation energy), potassium appears to be of optimum size for β″-alumina.

However, ion size is clearly not the only factor affecting conductivity because silver β″-alumina (2.3–2.5 Å diameter) has a lower conductivity than sodium or potassium β″-alumina or silver β-alumina. It is also the only β″-isomorph measured here to have a constant activation energy. This behavior, as well as the decrease in lattice parameter upon silver exchange of both sodium β- and β″-alumina, can probably be attributed to the ability of the silver ion to form bonds with appreciable covalent character.

These questions cannot be answered without further investigation of the structure and properties of β″-alumina. We are currently investigating the effects of various crystal growth conditions and the properties of mixed lithium–sodium β″-alumina.

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