# Electrical Conductivity of Mixed Alkali (Na+–K+)β"-Alumina

N. TSURUMI, G. SINGH, AND P. S. NICHOLSON

*Ceramic Engineering Research Group, Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario, Canada*

The electrical conductivities of single crystals of mixed alkali (Na+–K+)β"-alumina have been measured for different alkali compositions. A typical log $\sigma T$ vs $1/T$ curve of the mixed alkali $\beta$"-alumina consists of three regions exhibiting different activation energies. The electrical conductivity isotherms show that (1) no mixed alkali effect is observed above 200°C and (2) at low temperatures, the electrical conductivity does not change significantly for $[K^+]/[K^+] + [Na^+] = 0.0$ to 0.9 but thereafter increases sharply. These observations are discussed in terms of the degree of disorder and the site distribution of the alkali ions in the conduction planes at different temperatures.  © 1987 Academic Press, Inc.

The nonlinear behavior of some properties on substitution of one alkali ion for another in alkali-containing solids is known as "the mixed alkali effect." It was originally observed in some alkali glasses but its cause remains unclear (*1, 2*). Na+β- and β"-alumina exhibit high sodium ion conductivity and are widely studied solid electrolytes. A significant mixed alkali effect has been observed in β-alumina (*3–5*). However, studies of the β"-alumina system have been limited (*5–7*). In the present study, electrical conductivities have been measured for (Na+–K+)β"-alumina single crystals with different alkali ratios ($[K^+]/[K^+] + [Na^+]$).

Single crystals of Na+ β"-alumina were grown by the method reported by Briant and Farrington (*8*): 59.6 mole% Al₂O₃, 32.5 mole% Na₂CO₃, and 7.8 mole% MgO were mixed and calcined at 1100°C for 2 hr. The calcined powder was heated at 1680°C for 72 hr in a Pt crucible and the transparent crystals extracted from the solidified bulk were cut into a rectangular shape (~2.5 × 1.5 × 0.4 mm). Laue photographs were taken to identify the crystal type, and the crystals were ion exchanged in NaCl/KCl melts of different compositions at 810°C for 4 days. The chemical compositions were determined from data for β"-alumina powders reported by Tan *et al.* (*9*) (Fig. 1). The residual alkali chlorides were dissolved in distilled water and methyl alcohol after exchange. The cleaned samples were than ion exchanged in Ag NO₃ at 220°C and the residual nitrate was removed by distilled water. The sodium and potassium content of the resultant solution was analyzed by atomic emission spectroscopy. Before measurement of the electrical conductivity, the prepared crystals were dried under vacuum at 400°C for ~6 hr to avoid the effects of moisture (*10, 11*). The electrical conductivities were measured by the complex impedance method using silver paste as elec-
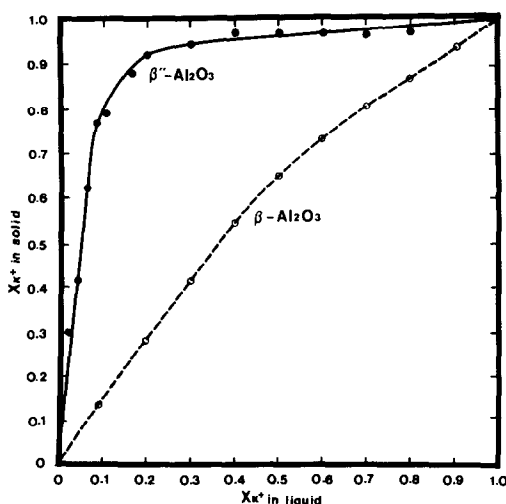
FIG. 1. Solid-melt equilibrium curve between $\beta$, $\beta''$-alumina, and NaCl/KCl melts at 810°C taken from Ref. (9).

trodes. The impedances and phase angles were measured using a computer-controlled LF impedance analyzer (HP-4192A). The electrical conductivity was measured between electrodes on opposite faces of the crystal. The connected wires emerged from an alumina tube coaxially placed inside one of silica-glass fitted with a cork. The glass tube was placed in a flat-bottomed aluminum tube and wrapped with heating coils to control the specimen temperature. The whole assembly was placed in liquid nitrogen to facilitate measurements between −70 and 210°C.

The electrical conductivities of pure $K^+$ and $Na^+\beta''$-alumina are shown in Fig. 2. The measured conductivities of these $\beta''$-aluminas are consistent with the reported values (8), indicating the reliability of the experimental procedure. The observed changes of activation energy at ~170°C for the $Na^+\beta''$-alumina and ~20°C for the $K^+\beta''$-alumina are considered the result of an order–disorder transformation at these temperatures (12, 13). A typical log $\sigma T$–$1/T$ plot for a mixed alkali $(Na^+-K^+)\beta''$-alumina

($[K^+]/[K^+] + [Na^+] = 0.63$) is also shown in Fig. 2. The curve consists of three nearly linear segments, Regions I, II, and III. Region I at high temperatures represents the disordered state wherein the alkali ions move almost freely on the conduction plane (14). Regions II and III, on the other hand, suggest an increasing degree of ordering of the structure. The activation energy values for the conduction processes in Regions II and III are 0.34 and 0.43 eV, respectively. The occurrence of the highest activation energy in Region III suggests that a particular type of ordering in the mixed alkali $\beta''$-alumina occurs at low temperatures.

The electrical conductivity isotherms as a function of potassium ratio ($[K^+]/[K^+] + [Na^+]$) in the crystal are shown in Fig. 3. No significant conductivity minimum exists in the $(Na^+-K^+)\beta''$-alumina system in contrast with the $(Na^+-K^+)\beta$-alumina system (3–5). The electrical conductivity isotherms exhibit no significant variation be-



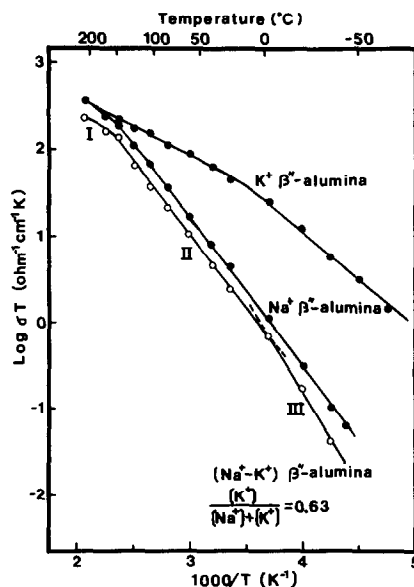FIG. 2. The electrical conductivities of single crystals of pure $K^+$, $Na^+$, and mixed alkali $(Na^+-K^+)\beta''$-alumina with a potassium ratio $[K^+]/[K^+] + [Na^+] = 0.63$.
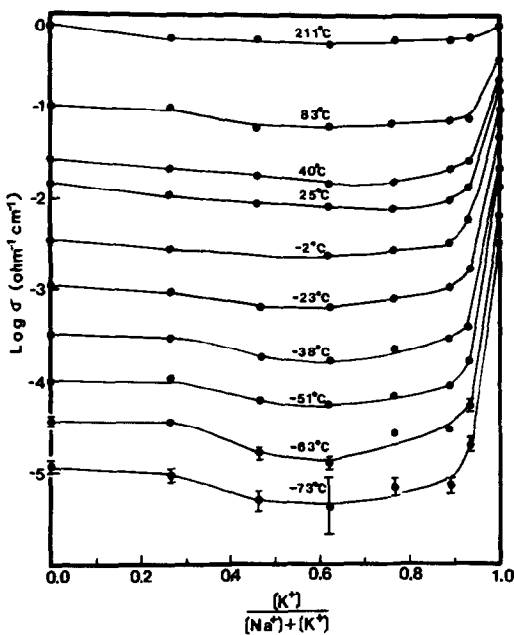
FIG. 3. The electrical conductivity isotherms of mixed alkali $(Na^+-K^+)\beta''$-alumina single crystals as a function of the potassium ratio $[K^+]/[K^+] + [Na^+]$.

tween $[K^+]/[K^+] + [Na^+] = 0.0$ and 0.9 except at low temperatures where a shallow conductivity minimum develops $[K^+]/[K^+] + [Na^+] \sim 0.6$. On the potassium-rich side $([K^+]/[K^+] + [Na^+] > 0.9)$, the electrical conductivity increases steeply to reach that of $K^+\beta''$-alumina. Ni *et al.* (6) measured the electrical conductivity of $(Na^+-Ca^{2+})\beta''$-alumina monocrystals and observed similar behavior in the conductivity isotherms, i.e., the conductivity behavior did not change significantly except for a very steep increase in the vicinity of the more highly conductive $Na^+\beta''$-alumina. Chandrashekhar and Foster (5) also reported that the electrical conductivity of $(Na^+-K^+)\beta''$-gallate crystals increased steeply in the vicinity of $Na^+\beta''$-gallate whose conductivity is higher than its potassium counterpart.

In the high temperature Region I, the conductivity does not change with the chemical composition, indicating that no

mixed alkali effect occurs in the disordered state of $\beta''$-alumina. Alkali ions on the conduction plane of the disordered $\beta''$-alumina might move freely like those in a liquid. Therefore, attractive interactions between unlike alkali ions and/or their cooperative motion will be unlikely and no change in conductivity with composition is expected. The degree of mixed alkali effect in the alkali glasses and $\beta$-alumina also decrease with temperature.

In the temperature Region II, the conductivities and activation energies for $[K^+]/[K^+] + [Na^+] = 0.0$ to 0.9 were almost the same as those for $Na^+\beta''$-alumina. This suggests that potassium ions in this composition range behave almost like sodium ions. This behavior might be explained by assuming that the alkali ions form ordered domains which move as a whole, thus maintaining the ordered structure. The mobility of such a domain would be controlled by its constituent sodium ions of low mobility. The mixed alkali effect in $\beta$-alumina is thought to be the result of attractive interactions between unlike alkali ions producing mixed $mO$ pairs and/or triplets (4, 15, 16). The source of the mixed alkali effect in $\beta''$-alumina seems entirely different from $\beta$-alumina, which is to be expected from the different nature of the conduction mechanisms in the two phases.

In the low temperatures in Region III, the main features of the conductivity isotherms are similar to those in Region II; however, a shallow minimum appears at $[K^+]/[K^+] + [Na^+] \sim 0.6$. Ideally the alkali ion site in $\beta''$-alumina is unique (BR(aBR)) but some of the alkali ions are actually displaced toward the $mO$ sites surrounding vacant Br(aBR) sites (13, 17). The arrangement of ions on off-centered Br(aBR) sites and those on BR(aBR) sites gives rise to the ordered structure. The cause of the shallow minimum of conductivity is not clear at the present time but a possible explanation is the development of a regular pattern of dis-

tribution of the sodium and potassium ions on BR(aBR) and off-centered (BR(aBR)) sites at low temperatures. If the attractive interaction between unlike ions outweighs the thermal vibrations seeking to disperse them, the triplets around the vacancies could become immobile like mixed pairs and/or triplets at the $m$O sites in $\beta$-alumina. The existence of such triplets is consistent with the high activation energy for conduction observed in this temperature range.

$\beta$- and $\beta''$-alumina have similar chemical composition, crystal structure, and high sodium ion conductivity. The mixed alkali effects observed in the two phases are, however, entirely different. Crystal structure investigations are underway to elucidate the exact cause of mixed alkali effects on the two phases and will be reported in due course.

## References

1. D. E. DAY, *J. Non-Cryst. Solids* **21**, 343 (1976).
2. M. D. INGRAM, C. T. MOYNIHAN, AND A. V. LESIKAR, *J. Non-Cryst. Solids* **38** and **39**, 371 (1980).
3. R. H. RADZILOWSKI, Y. F. YAO, AND J. T. KUMMER, *J. Appl. Phys.* **40**, 4716 (1969).

4. J. A. BRUCE AND M. D. INGRAM, *Sold State Ionics* **9** and **10**, 717 (1983).
5. G. V. CHANDRASHEKHAR AND L. M. FOSTER, *Solid State Commun.* **27**, 269 (1978).
6. J. NI, Y. T. TSAI, AND D. H. WHITMORE, *Solid State Ionics* **5**, 199 (1981).
7. M. MASIUCIONEK, J. GARBARCZYK, AND W. JAKUBOWSKI, *Solid State Ionics* **14**, 113 (1984).
8. J. L. BRIANT AND G. C. FARRINGTON, *J. Solid State Chem.* **33**, 385 (1980).
9. A. TAN, G. SINGH, T. TSURUMI, AND P. S. NICHOLSON, *Solid State Ionics,* **21**, 67–72 (1986).
10. P. L. KUHNS, L. J. RICHTER, AND M. S. CONRADI, *J. Chem. Phys.* **76**, 6 (1982).
11. D. C. AILION AND C. E. HAYES, "Fast Ion Transport in Solids," North-Holland, Amsterdam, p. 301 (1979).
12. J. B. BATES, H. ENGSTROM, J. C. WANG, B. C. LARSON, N. J. DUDNEY, AND W. E. BRUNDAGE, *Solid State Ionics* **5**, 159 (1981).
13. J. P. BOILOT, G. COLLIN, PH. COLOMBAN, AND R. COMES, *Phys. Rev. B: Condens. Matter* **22**, 5912 (1980).
14. H. ENGSTROM, J. B. BATES, W. E. BRUNDAGE, AND J. C. WANG, *Solid State Ionics* **2**, 265 (1981).
15. J. C. WANG, J. B. BATES, T. KANEDA, H. ENGSTROM, D. F. PICKETT JR. AND SANG-IL CHOI, "Fast Ion Transport in Solids," North-Holland, Amsterdam, p. 379 (1979).
16. I. M. FOSTER, M. P. ANDERSON, G. V. CHANDRASHEKHAR, G. BURNS, AND R. B. BRADFORD, *J. Chem. Phys.* **75**, 2412 (1981).
17. G. M. BROWN, D. A. SCHWINN, J. B. BATES, AND W. E. BRUNDAGE, *Solid State Ionics* **5**, 147 (1981).