Ionic conductivity of Na, K and Ag β''-alumina–ZrO$_2$ composites

S. M. PARK*, E. E. HELLSTROM
Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, WI 53706, USA

Composite samples of Na β''-alumina with 15 vol % ZrO$_2$ stabilized with 4.5 wt % Y$_2$O$_3$ were fabricated using two sintering schedules. K and Ag β''-alumina composites were prepared from the Na β''-alumina composite by ion exchange. The ionic conductivities of the Na, K, and Ag composites at 300 °C were 1.3×10^{-1}, 5.9×10^{-2} and 6.8×10^{-3} S cm^{-1}, respectively. K_{1c} for the K composite was as high as 3.7 MPa m$^{1/2}$.

1. Introduction

Na β''-alumina, which has high Na ion conductivity, can be toughened by incorporating ZrO$_2$ particles into the microstructure [1–4]. This toughening is due to two mechanisms, namely transformation and dispersion [4, 5]. The ZrO$_2$ additions do not significantly affect the electrical properties, as ZrO$_2$ additions up to 15–20 vol % only increase the resistivity by about a factor of two at 300 °C compared to commercially available pure Na β''-alumina [4, 5]. Toughening is beneficial in two ways: it improves the mechanical properties of the ceramic, making it more robust so it does not break as easily, and it increases the maximum current the ceramic can carry without cracking, as described below.

A serious problem with the two-dimensional, mica-like β''-alumina structure is that abnormal grain growth occurs during sintering, forming a duplex microstructure with large plate-like grains amongst the smaller grains. These large grains, which can cleave easily, serve as crack initiation sites that can limit the strength of the ceramic. Sintering schedules have been developed that minimize this abnormal grain growth [6]. It has been shown that adding ZrO$_2$ refines the β''-alumina microstructure in the β''-alumina–ZrO$_2$ composite, with additions of > 7.5 vol % ZrO$_2$ preventing abnormal grain growth, leading to a fine-grained, equiaxed microstructure [7]. The refined composite microstructure is not only tougher than pure β''-alumina, it is also stronger since there are no large grains to initiate cracking [7]. From a practical point of view this allows thinner pieces of composite than pure β''-alumina ceramic to be used in electrochemical devices, which decreases the electrolyte resistance.

One failure mechanism for β''-alumina in battery applications is cracking due to pressure from the Na current that flows through the ceramic. The critical ionic current above which cracking occurs is proportional to the critical stress intensity factor (K_{1c}) to the fourth power [8]. Thus, increasing the toughness of the ceramic by a small amount can significantly increase the current-carrying capacity of the ceramic. Together, the increased strength, toughness and higher critical current density of toughened β''-alumina offer promise for improving electrolyte performance in electrochemical devices, such as batteries.

In β''-alumina the mobile Na ions have been replaced by a wide variety of mono-, di-, and trivalent cations using ion exchange techniques [9, 10]. Many of the monovalent cations have been shown to have high conductivity in polycrystalline β''-alumina [11]. This paper reports a two-step sintering process to make Na β''-alumina–ZrO$_2$ composites and reports the ionic conductivity of Na, K and Ag β''-alumina composites.

2. Experimental procedure

We prepared Na β''-alumina of overall composition Na$_{1.67}$Mg$_{0.67}$Al$_{10.33}$O$_{17}$ following the general procedures of Sheng et al. [4]. Powdered Na$_2$CO$_3$, MgO and α-Al$_2$O$_3$ (A-1000 S.G., Alcoa Chemicals) were mixed and ball-milled for 24 h with ethanol in a polyethylene jar with ZrO$_2$ balls. The powder was dried, lightly hand-ground, pressed into pellets and fired at 1000 °C for 12 h. The pellets were then ground, mixed with 15 vol % ZrO$_2$–4.5 wt % Y$_2$O$_3$ (Zircar Products) and the mixture ball-milled as before. The resultant powder was dried, lightly hand-ground, and cold-pressed into pellets that were isostatically pressed at 50 000 psi (345 MPa), then placed in a high-purity alumina crucible and covered with powder of the same composition. The pellets were fired in air using two heating schedules. In the one-step process, the samples were heated to 1620 °C in ~ 1 h, held at 1620 °C for 30–180 min, furnace-cooled to ~ 200 °C in ~ 3 h, then removed from the furnace. In the two-step process the samples were heated to 1620 °C in ~ 1 h, held at 1620 °C for 20 min, furnace-cooled to 1475 °C in

* Department of Materials Engineering, Hankuk Aviation University, Kyonggi-Do 411-791, Korea.

~ 12 min, held for 30–240 min, furnace-cooled to ~ 200 °C in ~ 3 h, then removed from the furnace. The composites were X-rayed to determine the relative amounts of Na β- and Na β″-alumina present.

K β″-alumina–ZrO_2 samples were prepared from pellets of Na β″-alumina–ZrO_2 by high-temperature vapour-phase exchange in KCl vapour [12]. The maximum exchange temperature was 1150 °C for 24 h. After vapour-phase exchange, the pellets were immersed in molten KNO_3 at 350 °C for 48 h. The KNO_3 was changed four times during this period. Ag β″-alumina–ZrO_2 was prepared from pellets of Na composite by molten-salt exchange in $AgNO_3$ at 350 °C for 48 h. The $AgNO_3$ was changed twice during this period. The Na composite we used to make the Ag composite had been back-exchanged from K composite pellets (K → Na) using similar procedures to those used to make the K composite (1150 °C for 48 h in NaCl vapour, then immersed in $NaNO_3$ at 330 °C for 24 h).

TABLE I Data for Na samples

Material	σ at 300 °C (S cm⁻¹)	ΔH at 300 °C (kJ mol⁻¹)	f(β)
Single crystal[a]	1.1	14	–
Ceramic[b]	0.16	23	–
Composite[c]	0.11	31	–
Composite with one-step sintering (1620 °C)			
Time at 1620 °C (min)			
30	0.22	20	–
60	0.097	25	–
120	0.24	20	–
180	0.15	21	–
Composite with two-step sintering (1620/1475 °C)			
Time at 1475 °C (min)			
30	0.12	22	0.04
60	0.13	22	0.03
120	0.13	22	0.05
180	0.14	22	0.04
240	0.13	20	0.03

[a] Data from Park and Hellstrom [16].
[b] Na β″-alumina from Ceramatec Inc. (Salt Lake City, Utah).
[c] Data from Sheng et al. [4].

The electrical conductivity was measured between 25 and 600 °C over a frequency range of 5 Hz to 10 MHz using an HP 4192a impedance analyser. Pt electrodes were sputtered on the samples for the electrical conductivity measurements. The conductivity data were analysed in terms of an equivalent circuit using a non-linear least-squares error-fitting program [13] from which the ionic conductivity of the samples was extracted.

The samples were prepared for mechanical testing and microscopy by polishing through 0.05 µm Al_2O_3. The fracture toughness of the K composite was determined using the indentation technique [14]. A 5 kg load was applied for 10 s and the lengths of the indent diagonals and cracks emanating from the corners of the indent were measured immediately after making the indent. Young's modulus was determined from the transverse and longitudinal sound velocities in the samples. The density of the composite, needed to calculate Young's modulus, was measured using the Archimedes method in ethanol. The samples for microscopy were thermally etched at 1500 °C for 10 min in air. SEM back-scattered electron images were used to distinguish the ZrO_2 and β″-alumina grains. The grain size was determined by the linear intercept method from SEM secondary-electron micrographs.

3. Results and discussion

The X-ray diffraction pattern showed strong β″-alumina peaks, weak β-alumina peaks, no peaks from $NaAlO_2$, and tetragonal and monoclinic ZrO_2 peaks. Since no measurable intensity was observed for the $NaAlO_2$ peaks, we determined the weight fraction of Na β-alumina, f(β), using the two-phase analysis method of Shen et al. [15] given by

$$f(\beta) = \frac{1.11 I_{\beta(0\ 1\ 7)}}{1.11 I_{\beta(0\ 1\ 7)} + I_{\beta''(0\ 2\ 10)}}$$

where $I_{i(h\ k\ l)}$ is the integrated intensity of the respective X-ray peak. The f(β) values determined from this analysis (Table I) show that the samples contained mainly Na β″-alumina.

TABLE II Data for K samples

Material	σ at 300 °C (S cm⁻¹)	ΔH at 300 °C (kJ mol⁻¹)	K_{1c} (MPa m¹ᐟ²)	H (GPa)	E (GPa)	Grain size (µm) β″-Al_2O_3	ZrO_2
Single crystal[a]	0.77	10	–	–	–	–	–
Ceramic[b]	0.037	27	–	–	–	–	–
Composite with two-step sintering (1620/1475 °C)							
Time at 1475 °C (min)							
30	0.064	22	2.8	9.6	193	0.76	0.61
60	0.053	25	2.4	9.2	193	–	–
120	0.057	24	3.7	9.4	194	–	–
180	0.059	23	3.7	9.5	192	–	–
240	0.055	24	–[c]	–	–	0.82	0.67

[a] Data from Engstrom et al. [18].
[b] Sample prepared using Na β″-alumina from Ceramatec Inc. (Salt Lake City, Utah).
[c] These samples indented poorly.

The one-step sintering schedule was similar to that used by Sheng et al. [4] and others [1, 2, 7]. The two-step sintering schedule used here is similar to that used to make Na β''-alumina ceramic [6]. The reasons for incorporating a lower-temperature sintering step when preparing pure Na β''-alumina are to reduce Na_2O loss and to minimize abnormal grain growth.

Sheng and Nicholson [17] measured grain growth in the Na composite at 1620 °C and found that the grain size of β''-alumina and ZrO_2 increased as $t^{1/3}$ and no abnormal grain growth occurred. We measured the grain size in composites made by the two-step process after the K ion exchange. Since this exchange was carried out at a maximum temperature of 1150 °C, we believe no significant grain growth occurred during exchange. Table II lists the β''-alumina and ZrO_2 grain sizes for the two-step composites sintered for 30 and 240 min at 1475 °C. In each sample, both phases had equiaxed, submicrometre grains that were about the same size as reported earlier by Sheng et al. [17] for samples sintered 20 min at 1620 °C. With continued sintering at 1620 °C, for 120 min, they reported that the β''-alumina grains had grown to about 2.1 μm in size. We observed submicrometre-sized grains in samples that were sintered for 20 min at 1620 °C followed by 240 min at 1475 °C. This shows that grain growth is slow at 1475 °C, and that the grain size was essentially determined by the time at 1620 °C. These results show that processing schedules developed for pure Na β''-alumina can be used for the composite.

In a 15 vol % ZrO_2 composite, the ZrO_2 grains are isolated from one another and since no liquid is present at 1475 °C [19], growth of the ZrO_2 grains most likely occurs by Zr and Y diffusion along grain boundaries. We did not observe intragranular ZrO_2 as reported by Sheng et al. [4].

Table II also lists K_{1c}, hardness and Young's modulus for K β''-alumina composites. K_{1c} was calculated from the following formula [14]:

$$K_{1c} = 0.016 \left(\frac{E}{H}\right)^{1/2} \left(\frac{P}{c^{3/2}}\right)$$

where E is the Young's modulus, H the Vickers hardness of the sample, P the applied load and c the crack length. K_{1c} values between 2.4 and 3.7 MPa m$^{1/2}$ were measured for the K composite. For pure Na β''-alumina ceramic, reported K_{1c} values range from 2.3 to 3.0 MPa m$^{1/2}$ [2, 4, 7] and for Na β''-alumina–15 vol % ZrO_2 composites, values up to 4.5 MPa m$^{1/2}$ have been reported [1, 2, 4, 5]. Young's modulus for our K composites (192–194 GPa) is comparable to that reported for Na β''-alumina with 15 vol % ZrO_2 (199 GPa) [4].

When pure, polycrystalline Na β''-alumina bodies are directly exchanged in molten KNO_3 they crack because the larger K ions that replace Na ions expand the structure in the c direction. A high-temperature vapour-phase exchange is needed to prevent this cracking [12]. We tested whether the ZrO_2 additions toughened and strengthened the composite enough to undergo molten-salt exchange from Na to K without breaking. A pellet of Na composite was immersed in molten KNO_3 at 350 °C. After several hours the pellet

disintegrated into powder, showing that even with the toughened composite, high-temperature vapour-phase exchange is needed to prevent cracking. In addition, we carried out molten-salt exchange of Ag for K in the composite using molten $AgNO_3$ at 350 °C. Here microcracks formed in the pellet as the smaller Ag ions replaced the larger K ions. We back-exchanged Na for K at high temperature and then carried out the molten salt exchange (Na → Ag) to prevent cracking.

Fig. 1 shows impedance plots for the K composite at 90 °C. The response for all samples measured in this study was similar to that in Fig. 1. Equivalent circuits were fitted to the experimental impedance data (see Fig. 1) and the elements in the equivalent circuit were identified with physical processes in the sample. The calculated response from the equivalent circuit shown in Fig. 1 is in good agreement with the experimental data. In these samples, the high-frequency response was due to a combination of lattice (also called bulk or grain) and grain-boundary elements, and the low-frequency response was due to the electrodes. In all of our samples, the lattice and grain-boundary responses overlapped to such an extent that we could not separate them, even using equivalent-circuit fitting. From the fitting we extracted the series combination of lattice and grain-boundary resistivities, commonly referred to as the total resistivity.

Figs 2–5 plot the total conductivity for Na, K and Ag samples, respectively. Included in these plots are conductivity data for the composites, single crystals
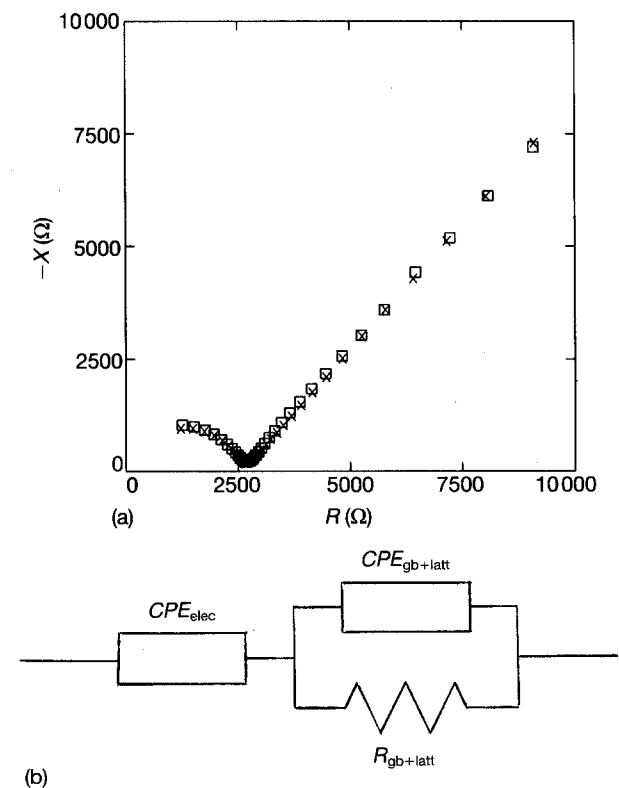

Figure 1 (a) Impedance plot for K β''-alumina at 90 °C showing the experimental and fitted data between 19 Hz and 2.7 MHz: (□) experimental data, (X) fitted data. (b) The equivalent circuit used to fit the data is shown. CPE designates a constant phase element, whose admittance response is given by Y_0 (jω)^n [20]. gb = grain boundary, elec = electrode, latt = lattice.

and polycrystalline samples made from commercially available Na β''-alumina ceramic (see Table I). The conductivity of the single crystals is higher than that of the polycrystalline samples, and at 300 °C the magnitudes of the conductivities are $\sigma_{Na} > \sigma_K > \sigma_{Ag}$ for each type of sample. Tables I–III list the total conductivity and activation enthalpy for conduction at 300 °C for the samples.

Figs 2 and 3 show the total conductivity for the Na composites fabricated with the one- and two-step sintering schedules, respectively. These data show that both sintering schedules yield composites whose total conductivity is essentially equal to that of commercially available Na β''-alumina ceramic. Samples prepared by the one-step process exhibited more scatter in conductivity than those made in the two-step process. If we assume that the grain size increases proportionally to $t^{1/3}$ at 1620 °C [4], the data in Fig. 2 show that there is no systematic relation between grain size and conductivity.

The curvature in the conductivity plot for single-crystal Na β''-alumina is attributed to gradual disordering of vacancies in the conduction plane with increasing temperature [21]. Engstrom *et al.* [18] found that the curvature of the conductivity was not constant but varied with the temperature at which the crystal was grown, the type and concentration of stabilizing ion in the crystal, and even the electrode material used for the conductivity measurement. This same disordering phenomenon is expected to occur in the pure polycrystalline and composite samples, leading to curvature in the conductivity plots.

The total and lattice conductivities for an Na composite from Sheng *et al.* [4] are plotted in Figs 2 and 3. They measured the conductivity between − 124 and 300 °C, and fitted their data to straight lines. Their temperature range was not high enough to observe the curvature in the conductivity. As seen in Figs 2 and 3, their total conductivity agrees well with our measurements.

Fig. 4 shows the conductivity of K samples. The conductivity plot of the single crystals has a slight curvature that is smaller than that for the Na single crystals. The conductivity of the composite was slightly higher than for polycrystalline K β''-alumina prepared from commercially available Na β''-alumina. The curvatures for the composite and pure K β''-alumina are very similar above 225 °C.
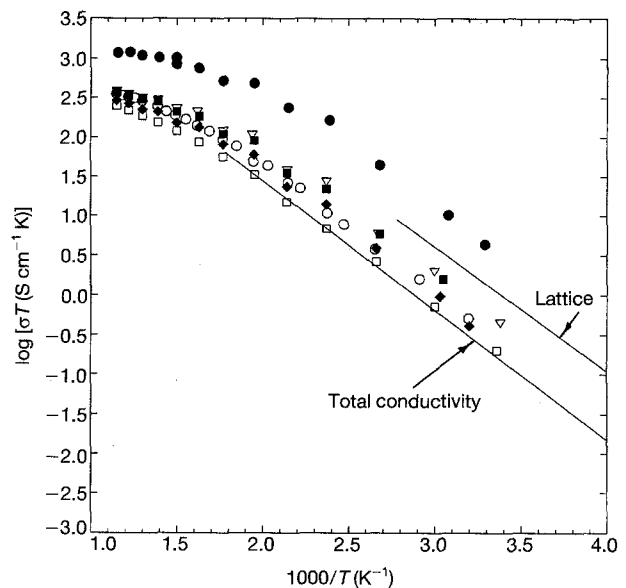

Figure 2 Conductivity plots for Na β''-alumina composites prepared by the one-step sintering process. (●) Single crystal; (○) commercial ceramic; samples sintered at 1620 °C for (■) 30 min, (□) 60 min, (▽) 120 min, (◆) 180 min. The lines labelled "lattice" and "total conductivity" are literature data for composites [4].
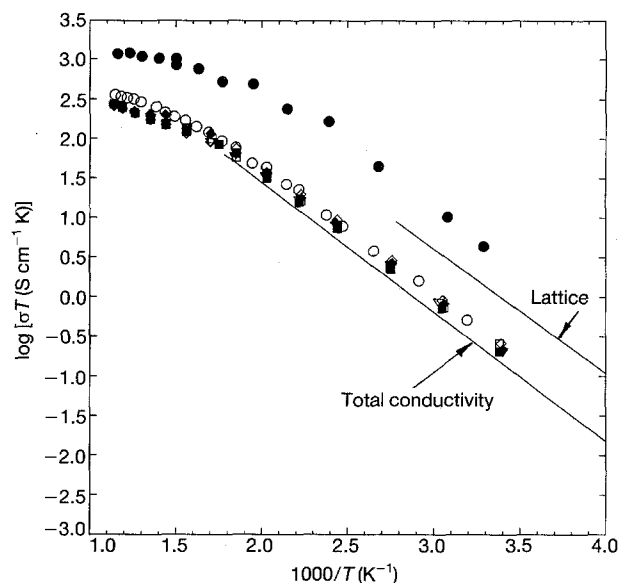

Figure 3 Conductivity plots for Na β''-alumina composite prepared by the two-step sintering process. (●) Single crystal; (○) commercial ceramic; samples sintered at 1475 °C for (■) 30 min, (□) 60 min, (▽) 120 min, (◆) 180 min, (◇) 240 min. The lines labelled "lattice" and "total conductivity" are literature data for composites [4].

Fig. 5 shows the conductivity of Ag β''-alumina. In the temperature range we used, the single-crystal data do not show the curvature observed for Na and K single crystals, and were fitted to a straight line. The total conductivity of the Ag composite was slightly lower than that of polycrystalline Ag β''-alumina prepared from commercially available Na β''-alumina. The conductivity data for the Ag composite were fitted to two straight lines. The activation enthalpy for the high-temperature region, 22–24 kJ mol^{-1}, is in reasonable agreement with that for the single crystal

TABLE III Data for Ag samples

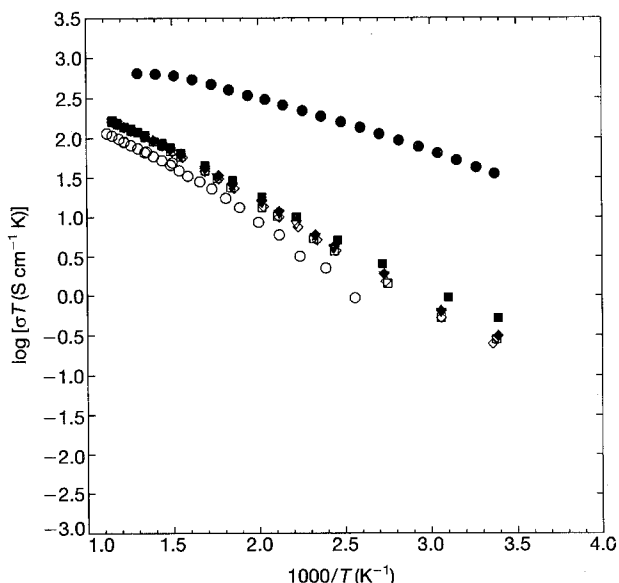| Material	ρ at 300 °C (Ω cm)	ΔH at 300 °C (kJ mol^{-1})	ΔH (kJ mol^{-1})	
			Low-T region	High-T region
Single crystal[a]	6.1×10^{-2}	17	–	–
Ceramic[a]	9.6×10^{-3}	24	–	–
Composite with two-step sintering (1620/1475 °C)				
Time at 1475 °C (min)				
30	6.0×10^{-3}	29	33	24
240	7.8×10^{-3}	26	32	22

[a] Data from Park and Hellstrom [16].

Figure 4 Conductivity plots for K β″-alumina composite made from Na β″-alumina fabricated by the two-step sintering process. (●) Single crystal; (○) commercial ceramic; samples sintered at 1475 °C for (■) 30 min, (□) 60 min, (▽) 120 min, (◆) 180 min, (◇) 240 min.
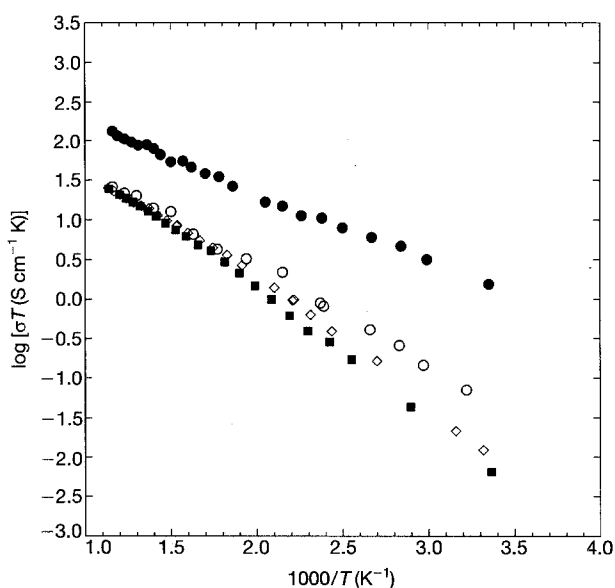

Figure 5 Conductivity plots for Ag β″-alumina composite made from Na β″-alumina fabricated by the two-step sintering process. (●) Single crystal; (○) commercial ceramic; samples sintered at 1475 °C for (■) 30 min, (◇) 240 min.

(17 kJ mol^{-1}), suggesting that in the high-temperature region the total conductivity corresponds to the lattice conductivity. In the low-temperature region we assume that the total conductivity corresponds to the grain-boundary conductivity, and the activation enthalpy for grain-boundary conductivity in the composite is about 32 kJ mol^{-1}.

In general we expect that at high temperatures the lattice conduction dominates, and at low temperature the grain-boundary conductivity dominates, as shown for the Ag composites. However, because of the curvature of the conductivity plots in single-crystal Na and

K β″-alumina, and the variation in curvature with stabilizer concentration and stabilizer ion [18, 21] (Mg for the single crystals and Li for the composites), we cannot unambiguously determine the temperature ranges where the lattice and grain-boundary conductivities dominate. However, since the low-temperature conductivity of the Na and K composites is similar to that for commercially available Na β″-alumina and the K β″-alumina made from it, we conclude that the grain-boundary conductivities of the composites are not much different from those of the pure ceramics.

4. Summary

The conductivity of Na β″-alumina–ZrO$_2$ composite made by a two-step sintering process showed less variation than that made with a one-step sintering process. At 300 °C, the conductivity of Na composite made by the two-step sintering process was about 0.13 S cm^{-1}. This conductivity is due to a series response of lattice and grain-boundary resistivities. In the temperature range studied, these responses could not be separated. K and Ag composites were made by ion exchange from the Na composite. Their conductivities were comparable to those for K and Ag β″-alumina prepared from commercially available Na β″-alumina ceramic. The grain-boundary conductivity in all the composites appears to be quite similar to that in the corresponding sample prepared from commercially available Na β″-alumina ceramic.

References

1. F. F. LANGE, B. I. DAVIS and D. O. RALEIGH, *Commun. Amer. Ceram. Soc.* **66** (1983) C-50.
2. L. VISWANATHAN, Y. IKUMA and A. V. VIRKAR, *J. Mater. Sci.* **18** (1983) 109.
3. J. G. P. BINNER, R. STEVENS and S. R. TAN, in "Advances in Ceramics", Vol 12, edited by N. Claussen, M. Ruhle and A. H. Heuer (American Ceramic Society, Columbus, Ohio, 1984) p. 428.
4. Y. SHENG, P. SARKAR and P. S. NICHOLSON, *J. Mater. Sci.* **23** (1988) 958.
5. D. J. GREEN, *ibid.* **20** (1985) 2639.
6. G. E. YOUNGBLOOD, A. V. VIRKAR, W. R. CANNON and R. S. GORDON, *Amer. Ceram. Soc. Bull.* **56** (1977) 206.
7. D. J. GREEN and M. G. METCALF, *ibid.* **63** (1984) 803.
8. A. J. VIRKAR, *J. Mater. Sci.* **16** (1981) 1142.
9. G. C. FARRINGTON and B. DUNN, *Solid State Ionics* **7** (1982) 267.
10. G. C. FARRINGTON, B. DUNN and J. O. THOMAS, *Appl. Phys. A* **32** (1983) 159.
11. J. B. BATES, *Mater. Sci. Forum* **1** (1984) 135.
12. G. M. CROSBIE and G. J. TENNENHOUSE, *J. Amer. Ceram. Soc.* **65** (1982) 187.

13. B. A. BOUKAMP, Equivalent circuit fitting program equivert (Technical University Twente, Twente, The Netherlands).
14. G. R. ANSTIS, P. CHANTIKUL, B. R. LAWN and D. B. MARSHALL, *J. Amer. Ceram. Soc.* **64** (1981) 533.
15. J. L. SHEN, S. A. HOWARD, J. LIU and P. D. OWNBY, *ibid.* **75** (1992) 52.
16. S. M. PARK and E. E. HELLSTROM, *Solid State Ionics* **44** (1990) 55.
17. Y. SHENG and P. S. NICHOLSON, *J. Mater. Sci.* **23** (1988) 982.
18. H. ENGSTROM, J. B. BATES, W. E. BRUNDAGE and J. C. WANG, *Solid State Ionics* **2** (1981) 265.
19. J. D. HODGE, *J. Amer. Ceram. Soc.* **67** (1984) 183.
20. J. R. MACDONALD, "Impedance Spectroscopy: Emphasizing Solid Materials and Systems" (Wiley, New York, 1987).
21. J. C. WANG, *Phys. Rev. B* **26** (1982) 5911.