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ABSTRACT

Measurements of Ag diffusivity (D) and ionic conductivity (σ) have been made on the same single crystals of silver beta- alumina with composition 1.23 $Ag_2$0.11 Al_2O_3. The D values were obtained from the cation exchange rate of radiotracer Ag^{110} in molten $AgNO_3$ over 210°C ∿ 400°C. The σ measurements were made using an impedance bridge with sputtered silver electrodes at a frequency of 3×10^5 Hz over R.T ∿ 450°C. Both D and σ can be expressed in a simple Arrhenius form as: $D = 1.47 \times 10^{-4}(cm^2/sec)$ exp [-4.05(Kcal/mol)/RT]; $\sigma T = 1.58 \times 10^3(ohm^{-1}cm^{-1}K)$ exp [-3.77(Kcal/mol)/RT]. The Haven ratio varies from 0.51 at 200°C to 0.56 at 400°C. The magnitude of these values is very close to the theoretical value of 0.6 for interstitialcy mechanism. The temperature dependence is strikingly similar to the case of sodium beta-alumina.

In a recent investigation[1] on sodium beta alumina of composition $1.23Na_2O_3 \cdot 11Al_2O_3$, the Haven ratio, H_R, (i.e. the ratio between tracer diffusivity(D_T) and the diffusivity(D_J) derived from conductivity(σ) via Nernst-Einstein relations) was found to be temperature dependent, ranging from 0.45 at 600°C to 0.30 at 0°C. The magnitude of these values is appreciably smaller than the theoretical value of 0.6 for interstitialcy mechanism in a two-dimensional honeycomb structure, which appears to be supported by neutron diffraction studies[2] and potential energy calculations[3]. Accordingly, Wolf[4] introduced the concept of ion blocking and binding among mobile ions and/or charge compensating defects in order to explain such a discrepancy as well as the temperature dependence of H_R.

Silver beta-alumina is an isomorph of sodium beta-alumina with similar lattice constants[5] (a = 5.594A, c = 22.530A for Na beta-alumina, a = 5.594A and c = 22.498A for Ag beta-alumina) although its cationic radius is considerably larger (0.97A for Na^+ versus 1.26A for Ag^+). The larger size of Ag^+ leads to a decreased mobility compared to Na^+ as evidenced both in the D_T[5] and σ[6] data. Whittingham and Huggins[6] derived from these transport measurements a roughly temperature-independent Haven ratio of 0.6. However, these D_T and σ measurements were not made on the same crystals, which may induce errors due to differences in the concentration of mobile ions, impurities, etc. As pointed out previously[1], while experimental determinations of the Haven ratio can provide an effective means for determining the atomic transport mechanisms, one must keep in mind that for this purpose, precise measurements of both D_T and σ are required. Accordingly, we present herein the results of D_T and σ measurements made on the same crystals of silver beta-alumina.

Silver beta-alumina samples were obtained from sodium beta-alumina samples (used previously[1] for D_T profiling and/or σ measurements) by cation exchange in molten $AgNO_3$. Samples for D_T measurements by cation exchange had dimensions of a x b x c = 0.6 x 0.6 x 0.2 cm^3. Carrier-free Ag^{110} in the form of aqueous $AgNO_3$ solution was placed on one of the narrow sides and diffused into the sample by heating in air at 300° C for 24 hours. Then all the narrow sides were ground lightly in order to remove any remnant activity and also to expose fresh surfaces for subsequent exchange experiments. Experimental procedure for tracer exchange in the molten salt baths has been described previously[1]. (In order to extend the exchange measurements to temperatures lower than the freezing point (212°C) of $AgNO_3$, an attempt was made to use baths of $AgNO_3$-AgI eutectic (eutectic temperature 80°C). The measurements were unsuccessful due to generally poor and irregular exchange rates.) The σ measurements

were made using sputtered silver electrodes from room temperature to 450°C at 5 X 10^5 Hz, where the σ had been found to be frequency independent. The details of sample preparation and σ measurements have been described previously also[7].

The values of D_T obtained from the out-diffusion of Ag^{110} in $AgNO_3$ are given in Table 1 and plotted in Fig. 1. A least-square fit of the data in Table 1 to an Arrhenius relation of the type $D = D_0 \exp(-Q/RT)$ results in $D_0 = 1.49 \times 10^{-4}$ cm^2/sec, $Q = 4.07$ Kcal/mol. The observed activation energy is in good agreement with Yao and Kummer's value of 4.05 Kcal/mol although our preexponential factor and diffusivities are about 10% lower, probably due to the different composition of the beta-alumina samples used.

Table 1 Diffusivity of Ag^{110} in Ag beta-alumina determined from ion exchange in molten salts.

Temperature (°C)	D_T (cm^2/sec) ($\times 10^{-6}$)	H_R
209.3	2.11	0.510
228.5	2.47	0.514
257.7	3.15	0.532
282.7	3.82	0.549
295.8	3.83	0.509
303.6	4.48	0.569
331.2	5.15	0.563
364.1	5.98	0.556
399.9	6.87	0.545

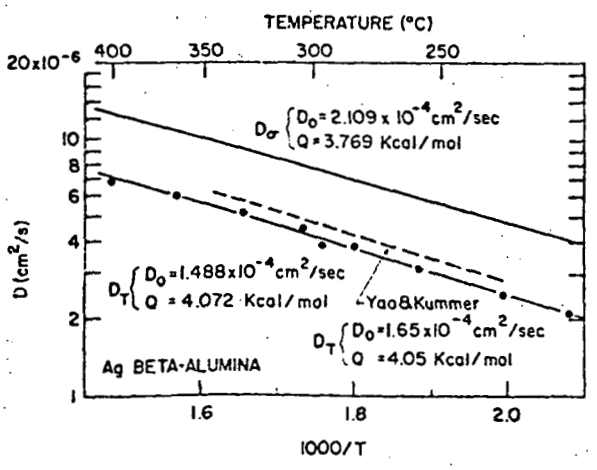

Fig. 1 Silver tracer diffusion in single-crystal silver beta-alumina. Values of D calculated from the measured conductivity are included for comparison.

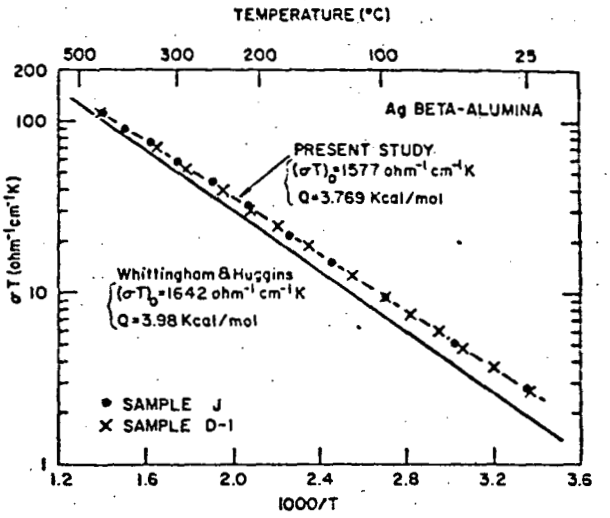

Fig. 2 Ionic conductivity of single-crystal silver beta-alumina.

The values of σT versus 1/T are plotted in Fig. 2. A least-square fit of the σ data to the relation $\sigma T = (\sigma T)_0 \exp(-Q/RT)$ results in $(\sigma T)_0 = 1577$ ohm^{-1}cm^{-1}K, $Q = 3.769$ Kcal/mol. The activation energy for conduction is smaller than that for diffusion. Our σ values are consistently higher - with lower activation energy and higher preexponential factor - than those of Whittingham and Huggins, as shown in Fig. 2. Our measured values of both D_T and σ are considerably different from those of other investigators, where different crystals were used for the two measurements. This clearly demonstrates the necessity of performing D_T and σ measurements on the same crystal in order to derive a reliable Haven ratio from the comparison of the two.

Haven ratio values were calculated based on the actual Ag concentration (not the stoichiometric concentration used by Whittingham and Huggins). The values of H_R are shown in the last column of Table 1. Fig. 3 shows the plot of H_R versus temperature for silver beta-alumina. For comparison purposes, the data for sodium beta-alumina - from which the silver beta-alumina was made by cation exchange - is also shown. The solid line represents the ratio of the least-square fits to the data of D_T and D_J. The most interesting feature of our results is the temperature dependence of the Haven ratio, ranging from 0.51 at 200 C to 0.56 at 400 C. This temperature dependence is very similar to that for Na beta-alumina but the magnitude for Ag beta-alumina is about 0.15 higher.

The decrease of H_R values with temperature in Ag beta-alumina is likely to have the same physical origin as Na beta-alumina. Wolf[4] has ascribed such a temperature dependence to changes of tracer correlation factors caused by the temperature dependence of the size of associated defects. This appears to be supported by X-ray diffuse scattering studies[8] , where the formulation of a superlattice is observed at low temperatures with increasing disorder at higher temperatures. The difference in the magnitude of H_R, however, is more difficult to explain on the basis of Wolf's theory. Since the magnitude of H_R decreases with increasing associated-defect size, so Wolf's theory would predict for the Ag beta-alumina smaller associated-defects. However, the X-ray diffuse scattering data[8] indicates the opposite situation, namely that Ag beta-alumina has larger "ordered domains" than Na beta-alumina. Also the difference between the experimental value of H_R for Ag beta-alumina and the ideal value of 0.6 for interstitialcy mechanism in a two-dimensional honeycomb structure is only 0.05, which can be accounted for by the site-blocking effect of oxygen interstitials[4]. This indicates that Wolf's theory overestimates the correlation effects for tracer diffusion in Ag beta-alumina. It is worth noting that the correlation effects for electrical conduction - as suggested by Sato and Kikuchi[9] - is not taken into account in Wolf's theory, which, if included, would have predicted larger Haven ratio values.

It is probable that the ideality of Ag beta-alumina originates from the simpler structure of mobile ions. There is evidence[10] that in Ag beta-alumina excess Ag ions occupy aBR sites as simple interstitials rather than forming mO-mO pairs as in Na beta-alumina. From a purely geometric point of view, a simple interstitialcy mechanism results in the same H_R as does the "modified" interstitialcy mechanism involving mO-mO pairs. Thus a theoretical study is needed to clarify how different basic defect structure lead to different values of H_R as observed for Ag and Na beta-aluminas.

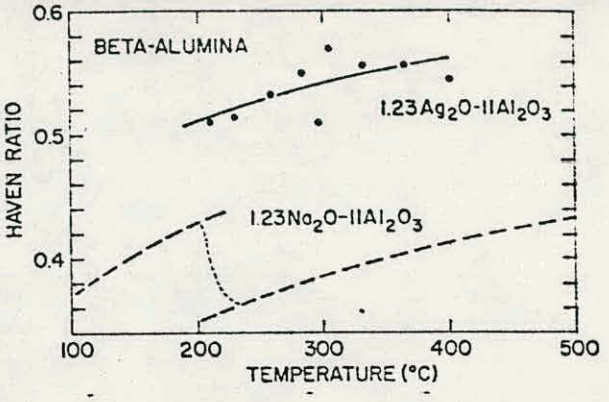

Fig. 3 The Haven ratio as a function of temperature.

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