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AN ULTRASONIC STUDY OF ION DIFFUSION IN THE SUPERIONIC CONDUCTORS β AND β" ALUMINA

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INTRODUCTION

Recently considerable interest has been shown in the high ionic conductivity of β-alumina and β" alumina and its possible applications as a solid electrolyte. The conductivity is caused by the diffusion of sodium ions through interconnected channels, or "conduction planes" normal to the c-axis. Adjacent conduction planes are separated by blocks of spinel-like structure. There is no significant Na^+ ion diffusion through the spinel blocks. It has been shown (Nagao and Kaneda, 1975) that the diffusion of Ag^+ ions in the solid electrolyte $RbAg_4I_5$ attenuates ultrasonic waves and that information may be thereby obtained about the diffusion process. We have now used the ultrasonic technique in a study of Na^+ ion diffusion in β-alumina and in β"-alumina.

MEASUREMENTS

Measurements have been made of the attenuation of longitudinal waves, propagating both parallel and perpendicular to the c-axis, in single crystals of β-alumina, in the temperature range ∿100 to ∿300K. Experiments were performed at frequencies from 30MHz to 90MHz using conventional pulse-echo techniques. The samples studied were "good quality" cleavage fragments of a cylindrical, single crystal boule grown by Union Carbide and supplied by the Roditi Corporation. Sample dimensions were ∿15 × 15 × 3mm, the smaller dimension being parallel to the c-axis. β-alumina cleaves readily in the basal plane and it was not possible to obtain crystals thicker than ∿3mm. This placed restrictions on the range of measurements possible, in both propagation directions. The conventional technique of bonding quartz transducers to the faces was found to be unreliable and was supplanted by the use of CdS thin film transducers. For propagation perpendicular to the c-axis, scattering from the walls of the thin samples made pulse-echoes indistinct at frequencies below ∿30MHz. For propagation parallel to the c-axis, the short acoustic paths across the thin samples caused successive pulse-echoes to interfere with each other; making single echo amplitude monitoring impossible. It was possible, however, to obtain an indication of attenuation changes by monitoring the change in amplitude of a suitable feature of the multiple echo interference pattern. Using this technique, the effective acoustic path length producing the observed attenuation changes was uncertain and for this reason the results can only be considered relative to each other in arbitrary units.

Measurements were also made of attenuation in a series of sintered polycrystalline samples containing about 70% β"-alumina and 30% β-alumina which were provided by Chloride Silent Power Ltd. These samples were 1cm right cylinders and with them both CdS and quartz transducers proved satisfactory.

Some of the measurements of attenuation change in the temperature range ∿100 to ∿300K for the two propagation directions in β-alumina are shown in Arrhenius plot format in Fig. 1 and Fig. 2.

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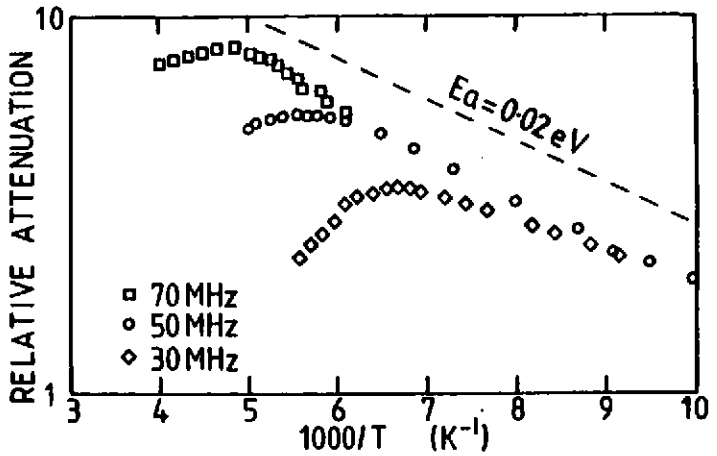

Fig. 1. Temperature dependence of the relative attenuation of longitudinal waves propagating parallel to the c-axis in β-alumina in Arrhenius plot format.

It is evident that the attenuation is anisotropic. For waves propagating parallel to the c-axis, Fig. 1, a series of frequency dependent attenuation peaks were found. These are in broad agreement with Moreira's analysis of ultrasonic attenuation in an ionic conductor. Moreira (1977) showed that attenuation, α, is related to the angular frequency of the sound wave ω and the mean time, τ, ions spend on available sites, by:

$$\alpha \propto \frac{\omega^2\tau}{1+\omega^2\tau^2}$$

Hence in Fig. 1 we assume ωτ passes through 1 at the attenuation peaks.

For waves propagating in the conduction plane, Fig. 2, the attenuation is far less frequency dependent. The observed behaviour is attributed to two separate relaxation processes associated with ionic hopping. One of these produces the rapidly increasing attenuation found at high temperatures. This data is assumed to be on the $\omega\tau > 1$ side of an attenuation peak where $\alpha \propto \tau^{-1}$ and is approximately independent of frequency. The lowest frequency measurements, 37MHz, were extended to higher temperatures and appear to peak at ∿350K. It was not possible to reach much higher temperatures than this in the apparatus used in this work and lower frequency measurements were not possible because of the sample wall scattering problem mentioned earlier. The other relaxation process contributes the slower changing attenuation which is evident at the lowest temperatures. Associated with this is a quite distinct peak in the 55 MHz data and a rather broad maximum, at a lower temperature, in the 37 MHz data. We assume that a peak in the 90 MHz data would appear at ∿230K if it were not for the rapid rise of the other attenuation contribution at this temperature.

The attenuation observed in the polycrystalline predominantly β"-alumina samples is shown in Fig. 3. Distinct thermally activated attenuation peaks were found

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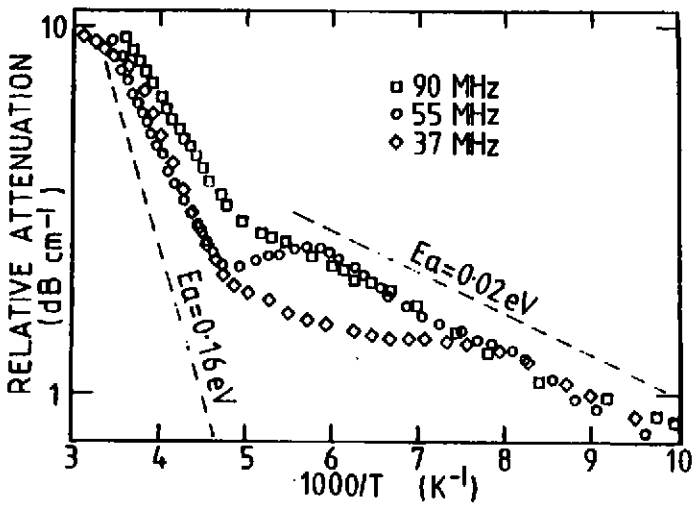

Fig. 2. Temperature dependence of the relative attenuation of longitudinal waves propagating perpendicular to the c-axis in β-alumina, in Arrhenius plot format.

in a range of temperature near 150K. These peaks clearly indicate an interaction between the sound waves and ions whose diffusion process is controlled by a 0.14 ± 0.002eV activation energy.

ANALYSIS

The analysis of the attenuation data for β-alumina has been discussed in detail by Almond & West (1978). The main conclusions drawn from this are that the ion diffusion is a two step process controlled by activation energies of 0.16 and 0.02eV with attempt frequencies of $\lesssim 0.6 \times 10^{11}$Hz and $\sim 2 \times 10^{9}$Hz respectively. The 0.16eV activation energy is in agreement with the accepted value for β-alumina but the attempt frequencies are more than an order of magnitude lower than expected.

The results presented here for β"-alumina indicate diffusion by a simple one step process controlled by an activation energy of 0.14eV. The attempt frequency for the process is clearly much higher than for β-alumina and is not inconsistent with the value of $\sim 10^{12}$Hz obtained from Raman scattering by Bates et al (1979).

The difference in attempt frequencies for the two phases casts doubt on the validity of using simple rate theory to explain the ion diffusion in β-alumina. For this phase a rather complex collective mechanism between pairs of Na^+ ions is necessary to explain the low activation energy, Wang et al (1975). By contrast for β"-alumina a high vacancy concentration in the conduction plane and a simple thermally activated diffusion process appears to occur and our results are in agreement with this.

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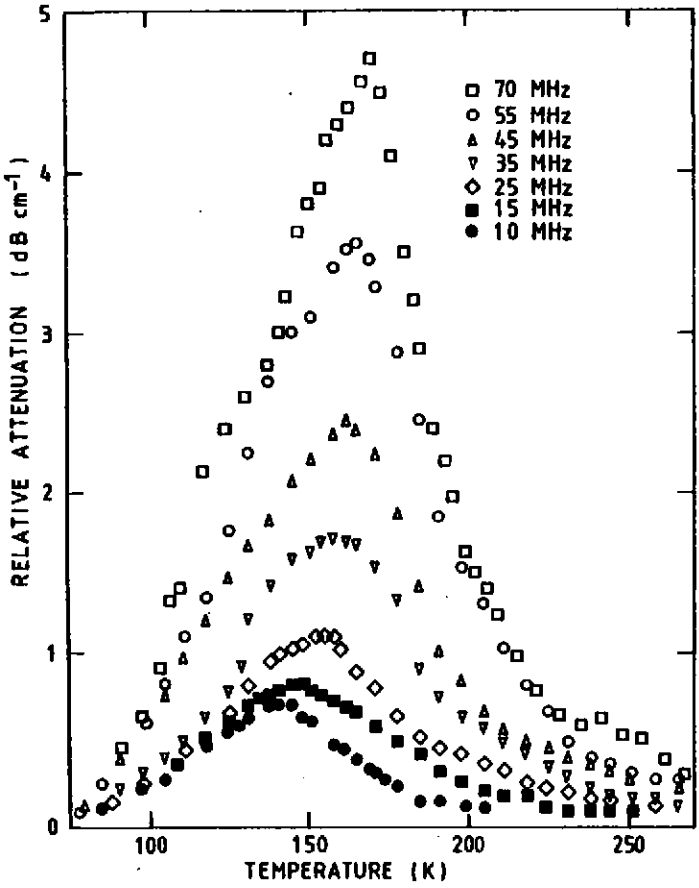

Fig. 3. Temperature dependence of the relative attenuation of longitudinal waves in polycrystalline, 70% β"-alumina.

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