Conductivity dispersion in single-crystal β-alumina electrolyte

We report data which demonstrate the existence of a conductivity dispersion in single-crystal β-alumina and, we believe, for the first time, a distribution of conductivity relaxation times in any single-crystal ionic conductor. A cylindrical boule of high quality Na β-alumina grown at Union Carbide was supplied to us by Roditi International Corporation. Figure 1 shows the frequency-dependent conductivity of this crystal in the range 10^2 to 10^5 Hz, measured at various subambient temperatures (for details of the apparatus see refs 1 and 2). At normal temperatures, electrode effects produce an apparent dispersion in conductivity. At these lower temperatures, however, the dispersion seems to be an intrinsic property of the bulk material since it starts at frequencies which are related to the level of the d.c. conductivity \( \sigma \propto \omega^{-1.3} \) as indicated by arrows in (Fig. 1). This behaviour closely resembles the dielectric behaviour which has been studied in silicate and other glasses.\(^2\)

The dispersions in conductivity cannot be accounted for in terms of the conventional (Debye) theories of dielectric loss; indeed, the departures from Debye behaviour are probably more marked in single-crystal β-alumina than in many vitreous electrolytes.

This result can be interpreted in terms of a broad distribution of conductivity relaxation times, which could plausibly be related to the random distribution of sodium ions over distinct crystallographic sites within the conduction planes (as revealed for example by recent X-ray and neutron diffraction studies).\(^4\)

These studies have shown that at \( T \approx 90 \) K, sodium ions are localised at three distinct sites, but with increasing temperature there is increasing cation mobility, and at 620 K the disorder resembles that of a two-dimensional fluid. The details of this picture have been confirmed by NMR spectroscopy,\(^5\) but of special relevance to this discussion, it should be noted that the existence of a 'wide distribution in ion jump frequencies' was postulated, to account for certain aspects of the data. The conductance dispersion which we have observed would then follow directly from a model involving sequential hopping of ions over the different crystallographic sites.

It is also possible, however, to place a different interpretation on these data. In Fig. 1, it is apparent that at low temperatures, the high-frequency or a.c. conductivities fit a 'universal law' which has been described by Jonscher.\(^3\) In the region of conductance dispersion, the a.c. conductance \( \sigma(\omega) \) is given by:

\[
\sigma(\omega) = A \omega^n
\]

where \( n \approx 0.78 \) at 87 K, and is somewhat insensitive to changes in temperature. This 'law' is obeyed by a wide range of materials, and an interpretation has been given by Jonscher in terms of a 'screened charge model' where the ratio of energy stored to energy lost per cycle is independent of frequency. On the basis of this theory the conductivity dispersion in β-alumina need not be related to a microscopic distribution of ionic jump...
frequencies, but could be understood in terms of an interionic 'drag effect' which gradually relaxes with increase in frequency. (It is tempting to relate this approach to a previous treatment of dielectric loss in vitreous materials which invoked the Debye-Falkenhagen effect.)

It is difficult to say that either of these explanations is 'right' and the other 'wrong'. Thus, according to the Jonscher model, highly 'lossy' electrolytes, such as β-alumina, need a high concentration of mobile ions to give effective charge-screening, but these are precisely the electrolytes which have a strong tendency to cation disorder and hence are likely to exhibit a wide spread in ionic jump frequencies. The main point which emerges from the above discussion is a need for further detailed comparisons of structural, spectroscopic and electrical data, and hence the need for work with crystalline rather than vitreous systems. β-alumina is in many ways a model system, since measurements can be made over a wide range of d.c. conductivities, and extensive cation substitution is possible.

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