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Dielectric properties of ionic conductors: Yttria stabilized zirconia and forsterite

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1. Introduction. — The interpretation of electrical conductivity measurements of ionic conductors is often uneasy, due to polarisation or barrier phenomena at the electrode-material interfaces [1], grain boundaries or microstructure effects [2]. The complex impedance technique [3] makes apparent these different contributions to the electrical conductivity and permits at the same time the study of the dielectric properties of the material itself. Thus two ionic conductors yttria stabilized zirconia (0.85 ZrO$_2$-0.15 Y$_2$O$_3$) and non-stoichiometric forsterite (0.99 Mg$_2$SiO$_4$-0.01 SiO$_2$) have been studied this way. The nature of the mobile species, oxygen vacancies in yttria stabilized zirconia and magnesium vacancies in forsterite, their concentrations (0.15 and 0.02 respectively) and the structure of the compounds (cubic and orthorhombic) are quite different but their dielectric properties appear to be very similar and makes the comparison interesting.

2. Experimental. — The yttria stabilized zirconia specimens used, were Czochralski grown single crystals. The forsterite ones are polycrystalline and synthesized from very pure oxide powders (Johnson-Matthey), by solid state reactions. They are disk-shaped and coated with platinum paste. A variable frequency alternating field (0.5 Hz-100 kHz) is applied and both real and imaginary parts of the sample impedance are measured with a double lock-in amplifier. The temperature ranges investigated here are 373 K-573 K for yttria stabilized zirconia and 673 K-1173 K in the case of forsterite.

3. Impedance results. — In figure 1, the experimental results obtained for yttria stabilized zirconia are displayed in the complex impedance plane. The points are distributed along circles, the centers of which are depressed below the real axis by an angle $\alpha$, independent of temperature. In the case of forsterite, the same features may be observed but the angle is slightly smaller, of the order of $9^\circ$ instead of $14^\circ$. This angle $\alpha$ cannot be explained on the basis of the...
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simple theory of Debye with one relaxation time [4]. A very broad distribution of relaxation time may be involved [5, 6] but then we do not know what physical processes are involved. In the next paragraph a new model proposed by Jonscher [7] will be considered.

The intersection of the circles with the real axis gives the bulk resistance of the material. In the temperature ranges considered, the electrical conductivity follows for both materials an Arrhenius law:

\[ \sigma = \sigma_0 \exp(-\Delta E/kT) \]

In each case the value of the pre-exponential term \( \sigma_0 \) and the activation energy \( \Delta E \) are in good agreement with previous literature data [8, 9].

4. Dielectric properties. — Considering the bulk properties of the materials, the complex permittivity \( \varepsilon^*(\omega) \) may be deduced from the admittance \( Y^*(\omega) \) measurements [7]:

\[ Y^*(\omega) = \frac{1}{Z^*(\omega)} = \frac{1}{R_0} + jC_0\omega\varepsilon^*(\omega) \]

where \( R_0 \) is the bulk resistivity of the sample, \( C_0 \) its vacuum geometrical capacity and \( \omega \) the frequency. The figure 2 presents the variations of the real \( \varepsilon' \) and imaginary \( \varepsilon'' \) parts of the complex permittivity as a function of frequency at different temperatures for both materials. They show indeed very similar behaviour. On the plot of the imaginary part \( \varepsilon'' \), two distinct frequency regions may be clearly distinguished below and above a critical frequency \( \omega_c \). In each region the data are well fitted by the relation:

\[ \varepsilon'' = B\omega^{n-1} \quad 0 < n < 1 \]

(2)

where \( B \) and \( n \) are constants. Furthermore it may be noticed that \( n \) is almost the same for both compounds and higher below \( \omega_c \) (\( n \sim 0.86 \)) than above (\( n \sim 0.63 \)); this corresponds to an increase of the energy loss [7].

As first noted by Jonscher [10] the Kramers-Krönig relations imply that the real part \( \varepsilon' \) obey to the same frequency law than \( \varepsilon'' \). Finally the dielectric function can be written as [7]:

\[ \varepsilon^*(\omega) = \varepsilon_\infty + A\left(1 - j\cotg \frac{n\pi}{2}\right)\omega^{n-1} \]

(3)

where \( \varepsilon_\infty \) is the constant value of \( \varepsilon' \) approached at high frequency and \( A \) a constant.

At low frequency, below \( \omega_c \), it may be shown that \( \varepsilon_\infty \) can be neglected and indeed the real and imaginary parts of \( \varepsilon^*(\omega) \) in logarithmic coordinates are well represented by two parallel straight lines. In this case, as predicted by Jonscher [7], the value of \( n \) may be correlated very easily to the angle \( \alpha \) previously defined:

\[ \alpha = (n - 1)90^\circ \]

(4)

The high frequency region and the critical frequency are not apparent on the complex impedance plot (Fig. 1) eventhough \( \varepsilon_\infty \) is not negligible in this part but the corresponding curve does not depart very much of a circle. Thus the complex impedance representation, although often used, does not seem the most suitable.

5. Interpretation of \( \omega_c \). — On figure 2 it may be observed that the critical frequency \( \omega_c \) is a temperature dependent parameter. An Arrhenius plot of \( \log \omega_c \) versus \( 1/T \) shows that \( \omega_c \) is thermally activated with the same activation energy as the electrical conductivity (Fig. 3) and this is verified for both compounds. So we may assume that \( \omega_c \) corresponds to the jump frequency of the mobile species, that is magnesium vacancies in forsterite, oxygen vacancies...
in the case of yttria stabilized zirconia. From simple random walk theory \[1\], the electrical conductivity is given by the relation:

\[
\sigma = \frac{Nq^2 \langle l^2 \rangle}{4\pi k_B T} \omega_c
\]

(6)

where \(N\) denotes the defect concentration, \(q\) the charge of the mobile species, \(\langle l^2 \rangle\) the mean square displacement, \(k_B\) the Boltzman constant. In figure 4 the electrical conductivity calculated this way is compared to experimental values deduced from complex impedance measurements. The very good agreement in the case of yttria stabilized zirconia allows us to conclude that \(\omega_c\) is effectively the jump frequency of charge carriers. The same conclusion can be drawn in the case of forsterite although it is not cubic and that two slightly different mean square displacements must be considered.

6. Conclusion. — The complex impedance technique permitted us the simultaneous study of the electrical conductivity at low temperature and of the dielectric properties of two ionic conductors. Above and below the jump frequency of the mobile species, the dielectric properties are different and two relaxation processes must be involved. Above \(\omega_c\), the electric field is alternating too fast and the charge carriers remain probably localized in the vicinity of a dope ion. On the opposite below \(\omega_c\) charge transport is possible on a large scale. Furthermore, we note that although very different, the two ionic conductors have in common a high concentration of defects and many body interactions may be important. Then the Debye theory is no longer applicable. In the case of the two studied compounds the model of Jonscher \[12\] fits very well the data in the frequency region investigated here.

DISCUSSION

Comment. — N. Bonanos.

You successfully used the complex impedance technique to extract conductivity data. Why not use the corresponding complex permittivity plot for studying the frequency dependance of your dielectric data?

References