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The dielectric behaviour of single-crystal MgO, Fe/MgO and Cr/MgO

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The dielectric constants ϵ' and loss factors, ϵ'', for pure single-crystal MgO and for Fe- and Cr-doped crystals have been measured at frequencies, ω, from 500 Hz to 500 kHz at room temperature. For pure MgO at 1 kHz the values of ϵ' and the loss tangent, tan δ, (9.62 and 2.16×10^{-3}, respectively) agree well with the data of Von Hippel; the conductivity, σ, varies as $\sigma \propto \omega^n$ with $n = 0.98 \pm 0.02$. In Fe-doped crystals σ increases with Fe-concentration (at any given frequency); for a crystal doped with 12 800 ppm Fe, σ was about four times the value for pure MgO. At all concentrations the variation of log σ with log ω was linear and $n = 0.98 \pm 0.02$. A decrease in ϵ' with increasing Fe-concentration was also observed. A similar, although less pronounced, behaviour was found in Cr-doped crystals. The effects are discussed in terms of hopping mechanisms.

1. Introduction

Magnesium oxide is of considerable importance as an insulating material and several determinations of its electrical conductivity have been published [1–5]. In some early measurements on single-crystal MgO, Yamaka and Sawamoto [1] suggested that at room temperature the charge carriers are electrons; Mitoff [2] also confirmed that near room temperature the conductivity is electronic rather than ionic. In contrast, Schmalzried [4] has obtained experimental evidence for ionic conduction. Later work by Mitoff [3] has shown that the nature of the charge carriers depends on temperature and also on the impurity content of the crystal. Although there is conflicting evidence on the nature of the mechanisms involved it is generally held that ionic conductivity predominates in the lower temperature range but that at high temperatures (> 1300° C) the nature of conduction changes and the electronic conductivity predominates. However, the nature of the charge carriers, even in pure magnesium oxide, has not been determined although it has been suggested that they may be vacancies associated with impurities.

In the present work, a systematic study of the effect of transition group dopant ions on the electrical characteristics of MgO has been undertaken and an attempt has been made to interpret the data obtained in terms of Jonscher's "Universal Law" in which the conductivity is assumed to arise from hopping processes. This paper compares the dielectric properties (measured at room temperature over the frequency range 500 Hz to 50 kHz) of pure MgO single-crystal and MgO doped with various concentrations of iron or chomium, respectively.

2. Conductivity mechanisms

The mechanism of conductivity in magnesium oxide has been studied by many workers [1, 2]. In some early studies Mitoff [2] obtained experimental evidence for electronic conduction. He has pointed out that the number of charge carriers is controlled by the number of lattice vacancies, which, in turn, are governed mostly by impurities or by defects which are caused by the presence of these impurities; thus the conductivity is dominated by impurities. Yamaka and Swamoto [1] have also shown that the charge carriers in the conduction mechanism in MgO are electrons which originate from impurity levels.

Later work by Pollak and Geballe [6] first suggested hopping as a conductivity mechanism. They measured the complex conductivity of n-type silicon containing various kinds of impurities and attributed their results to polarization caused by hopping processes. Jonscher [7] interpreted the conductivity behaviour of over sixteen different

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TABLE I Compositions of specimens investigated in this work

Sample number	Nominal sample composition
1	MgO (pure)
2	MgO + 310 ppm Fe
3	MgO + 2300 ppm Fe
4	MgO + 4300 ppm Fe
5	MgO + 12800 ppm Fe
6	MgO + 800 ppm Cr
7	MgO + 1300 ppm Cr
8	MgO + 3600 ppm Cr

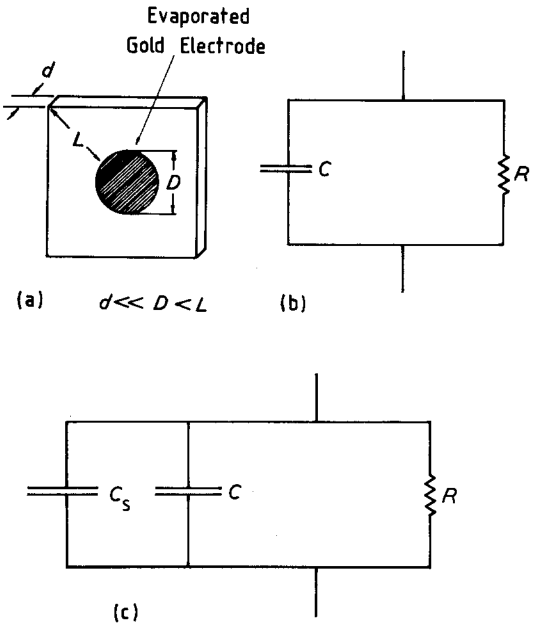

Figure 1 (a) General form of sample and (b and c) its equivalent circuits.

materials in terms of the proposed hopping mechamism. He has shown that the hopping mechanism (similar to ionic and electronic conduction) leads to a characteristic frequency dependence [8, 9]. Further, the dielectric responses of quite a wide range of materials show that the behaviour obtained departs from the Debye response and follows a "Universal Law" in which the dielectric constant, ϵ' and loss factor, ϵ'' can be written as

$$(\epsilon' - \epsilon_\infty) \propto \omega^{(n-1)} \tag{1}$$

$$\epsilon'' \propto \omega^{(n-1)}, \tag{2}$$

respectively, where ϵ_∞ is the limiting permittivity of the material. The frequency dependence of the real part of the conductivity follows a relationship

$$\sigma(\omega) \propto \omega^n, \tag{3}$$

where the exponent, n, may lie in the range $0 < n < 1$ but is usually close to unity [7, 10]. One of the characteristics of this universal relationship is that the ratio of the imaginary part to the real part of the permittivity is independent of frequency:

$$\frac{\epsilon''(\omega)}{\epsilon'(\omega) - \epsilon_\infty} = \cot \frac{n\pi}{2}. \tag{4}$$

This relationship is known as the Kramers–Krönig equation. The "Universal Law" has been extensively discussed by Jonscher [10] who pointed out that n is temperature dependent and by Austin and Mott [11].

3. Experimental procedure

The specimens which were measured in this experiment were pure MgO, Fe/MgO and Cr/MgO. They were grown by electro-fusion from powders supplied by W & C Spicer Ltd, Cheltenham. All the specimens were single crystals and their compositions are tabulated in Table I. For the measurements, the specimens were made in the form of square plates with dimensions 10 mm x 10 mm x 0.3 mm (Fig. 1a) and the large parallel faces were polished to a 0.25 μm finish. Circular gold electrodes were evaporated onto the opposite polished surfaces of each specimen to ensure good electrical contact over a well-defined area between the crystal and the electrodes. To minimize the contribution to the conductance due to surface leakage over the edge of the sample [12] the diameter of the gold electrode was chosen to allow the crystal to project as much as possible beyond the electrodes.

The measurements of dielectric constant, ϵ', and loss tangent, $\tan\delta$, (and consequently of a.c. conductivity) were made using a Wayne–Kerr bridge (Type B224), over the frequency range 500 Hz to 50 kHz.

In this technique the capacitance and conductance of the specimen were measured directly. The components of the complex dielectric constant, ϵ^*, the loss tangent, $\tan\delta$, and the conductivy, σ, were derived from the equations:

$$\epsilon' = \frac{C}{C_0}; \tag{5}$$

$$\tan\delta = \frac{\epsilon''}{\epsilon'}; \tag{6}$$

$$\sigma(\omega) = \frac{dG}{A}; \tag{7}$$

$$C_0 = \epsilon_0 \frac{A}{d};\qquad (8)$$

where C is the measured capacitance with specimen, C_0 is the capacitance at the same spacing without specimen, G is the conductance of specimen, d is the specimen thickness, A is the area of electrode.

Since the changes in dielectric behaviour to be examined were small, the maximum precision in measurement was required and two correction factors, for surface leakage and stray capacitance, were necessary.

A correction term is required because of the edge effect resulting from the extension of the crystal beyond the electrodes [13]. The correction for the edge effect, C_e, ($\times 10^{-12}$ F) (with circular electrodes of the same diameter) is given by [14]

$$C_e = \frac{1.113D}{8\pi}\left[Ln\left(\frac{8\pi D}{d}\right) - 3\right]\qquad (9)$$

where D is the diameter of each electrode, and L is the distance shown in Fig. 1a. Equation 5 then becomes

$$\epsilon' = \frac{C}{C_0 + C_e}.\qquad (10)$$

The formula assumes that the thickness of the gold electrode is negligible compared with the thickness of the specimen, d, a condition which was easily met.

A specimen can be represented by the equivalent circuit [15] shown in Fig. 1b. In the capacitance measurement any stray capacitance due to the electrodes is included in the total quantity measured and so another correction factor is required before the actual capacitance of the specimen, C can be evaluated. The stray capacitance associated with the electrodes and connecting cables, C_s, is shown in Fig. 1c. At low frequencies the inductance effect is not significant. It is assumed that the leakage admittance is eliminated by the use of the edge effect correction factor. The total capacitance, C_t, measured by the bridge when the specimen is placed between the electrodes is given by

$$C_t = C + C_s.\qquad (11)$$

When the sample is removed from between the electrodes, the capacitance due to air and stray capacitance, C_A is measured; it is given by

$$C_A = C_0 + C_s,\qquad (12)$$

where C_0 is the theoretical capacitance for air. By substitution for C_s from Equations 11 and 12 the capacitance of the sample is then given by

$$C = C_t - C_A + C_0.\qquad (13)$$

For measurements on the type of material used in this work these corrections are significant and amount to about 8% of the total capacitance measured.

4. Results

The variation of ϵ'' with frequency was first

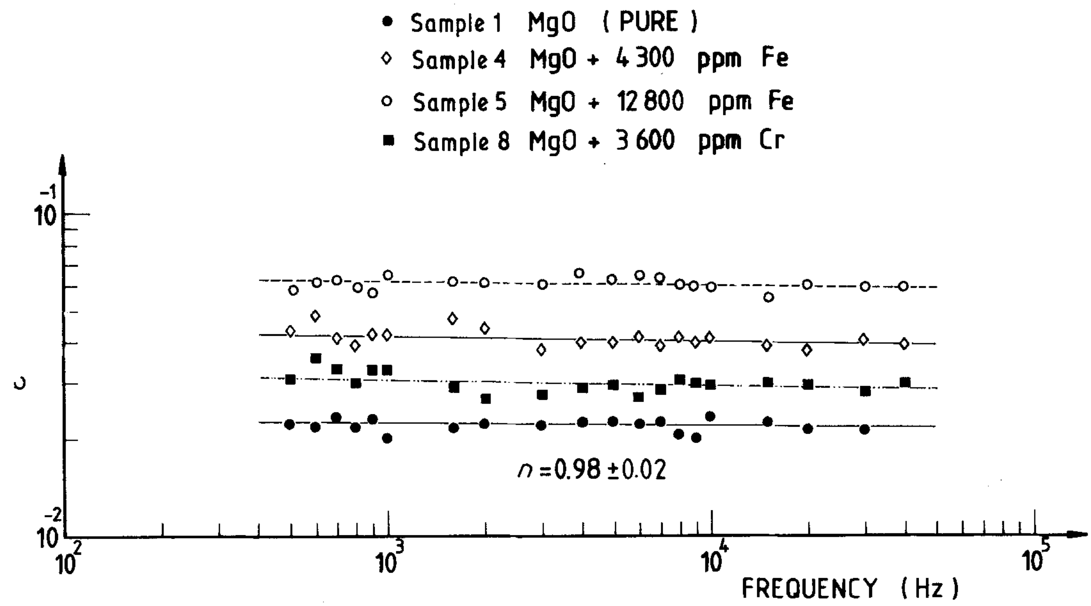

Figure 2 Variation of ϵ'' with frequency.

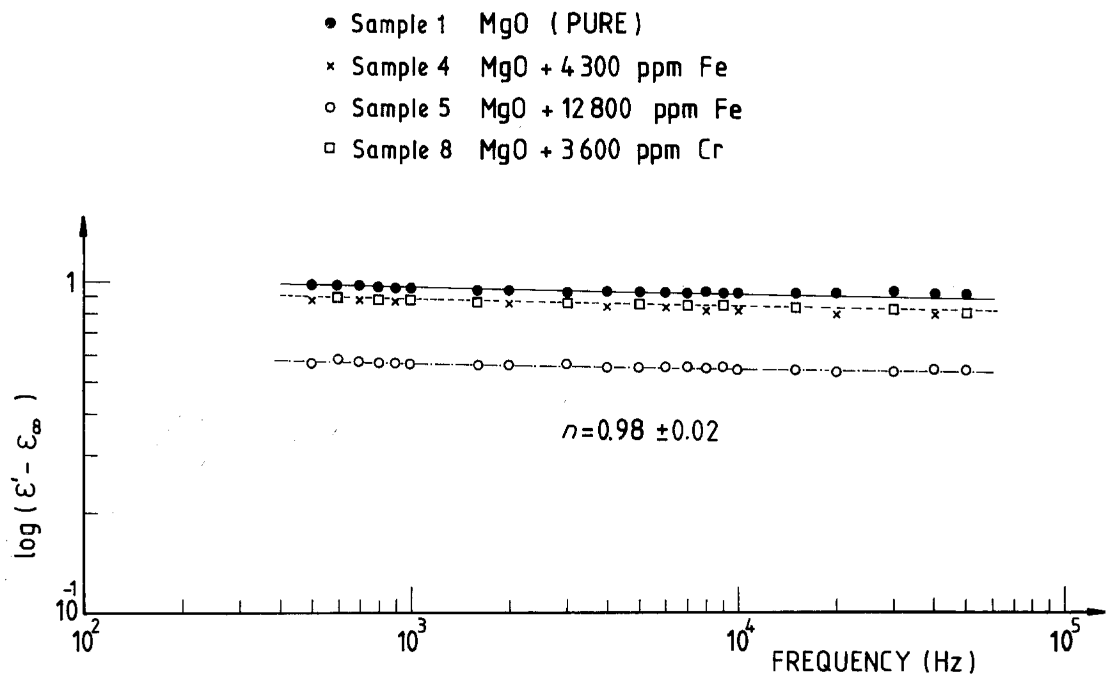

Figure 3 Variation of log ($\epsilon' - \epsilon_\infty$) with log frequency.

measured and it is shown in Fig. 2. The plots are linear, following a relationship

$$\epsilon''(\omega) \propto \omega^{(n-1)}, \qquad (14)$$

with $n = 0.98 \pm 0.02$; it should be noticed that the magnitude of n is the same for all the specimens. The loss factor, ϵ'', at a particular frequency is higher for the doped specimens than for the pure MgO, giving corresponding increases in conductivity. Adding an equivalent concentration of chromium does not increase ϵ'' by as much as does the addition of iron.

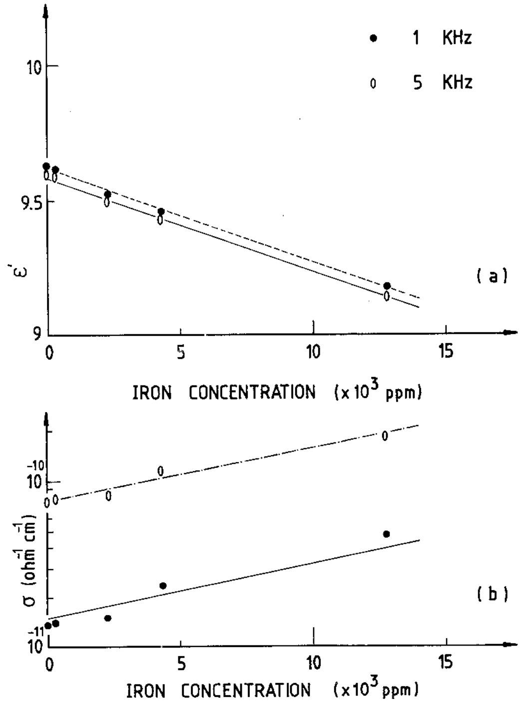

Figure 4 The dependence of (a) ϵ' and (b) σ on Fe-concentration.

The variation of log ($\epsilon' - \epsilon_\infty$) with log ω was also plotted for the same specimens (Fig. 3). In deriving this variation, ϵ_∞, the limiting value of dielectric constant at high frequencies, was taken to be the value obtained in microwave dielectric constant measurements at 9.3 GHz. Once again all the plots of this variation for the doped specimens showed the same characteristic shape; all the characteristics are linear with the same slope, and all again fit the relation

$$\epsilon'(\omega) \propto \omega^{(n-1)}, \qquad (15)$$

with $n = 0.98 \pm 0.02$.

In order to clarify the effect of impurity concentration on permittivity and conductivity, plots of ϵ' against Fe-concentration and also of σ against concentration are shown in Fig. 4a and b, respectively. It is seen that the variations of both ϵ' and σ are linear over the concentration range examined. There is inverse proportionality between ϵ' and concentration while σ is directly proportional to the concentration of Fe.

TABLE II Dielectric data for investigated samples at room temperature

Specimen number	Nominal sample composition	ϵ'	$\tan \delta$ ($\times 10^3$)	Frequency, ω (Hz)
1	MgO Pure	9.62	2.16	1×10^3
2	MgO + 310 ppm Fe	9.62	2.49	1×10^3
3	MgO + 2300 ppm Fe	9.52	2.87	1×10^3
4	MgO + 4300 ppm Fe	9.46	3.91	1×10^3
5	MgO + 12800 ppm Fe	9.40	7.47	1×10^3
6	MgO + 800 ppm Cr	9.60	2.44	1×10^3
7	MgO + 1300 ppm Cr	9.28	3.15	1×10^3
8	MgO + 3600 ppm Cr	9.43	3.15	1×10^3

5. Discussion

The conductivity of MgO is the sum of the d.c. conductivity and the pure a.c. conductivity. In this experiment calculations based on the extrapolation of Fig. 2 show that the d.c. conductivity, σ_0, is very small ($\sim 10^{-14}$ ohm^{-1} cm^{-1}) for all the specimens examined and thus can be neglected. Considering first the data for pure MgO it is found that $\sigma_{\text{a.c.}}(\omega)$ follows Equation 16 with $n = 0.98 \pm 0.02$ over three frequency decades. As regards the dielectric constant, ϵ', there is a good agreement between the present data on pure MgO (Table II) and that reported by other workers (Table III).

The major conclusions of this work concern the effect of doping. The data for all specimens fits the Jonscher laws, i.e. good agreement was obtained with the relations

$$\sigma_{\text{a.c.}}(\omega) \propto \omega^n, \tag{16}$$

$$(\epsilon' - \epsilon_\infty) \propto \omega^{(n-1)} \tag{17}$$

and

$$\epsilon''(\omega) \propto \omega^{(n-1)}. \tag{18}$$

The magnitude of the exponent, n, for all samples is $n = 0.98 \pm 0.02$. The two methods for determination of n, as shown in Figs 2 and 3 give values of the same magnitude, to within experimental error. This value of n is independent of the nature of the dopant and also independent of dopant concentrations. Since all the specimens yield identical values of n it can be concluded that the mechanism of conduction is the same in each case; only the magnitudes of $\sigma_{\text{a.c.}}(\omega)$ are different and these increase with increasing dopant concentration. This suggests that the hopping probability increases with increasing concentrations of the dopant impurity; this implies that the number of hopping centres increases but that this occurs without a change in hopping mechanism. It is known from electron spin resonance (ESR) studies [16] that both Fe and Cr enter into the magnesium oxide crystal on magnesium sites as Fe^{3+} and Cr^{3+}, respectively. Adding Fe-ions introduces further vacancies; since Fe^{3+} is occupying a Mg^{2+} site in the lattice one extra vacancy per two Fe^{3+}-ions is produced in the crystal. Similar vacancy formation will occur with Cr^{3+}-ions.

It is of interest to compare the behaviour of Fe and Cr as dopants. For two specimens doped to almost the same concentration but with different impurity ions, [i.e. Sample 4 (Fe/MgO) and Sample 8 (Cr/MgO)] the conductivities at any particular frequency were different and the conductivity of Fe-doped MgO was higher than that for Cr-doped MgO. Iron appears to be more effective in changing both ϵ'' and ϵ' than chromium. This would not be expected on the simple vacancy production model and the reasons for this effect are not yet clear.

Work is now being undertaken to extend the measurements to higher frequencies in order to establish the behaviour over a wider range.

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TABLE III Dielectric data for MgO at room temperature

Sample composition	ϵ'	$\tan \delta$ ($\times 10^4$)	Frequency, ω (Hz)	Reference number
MgO	9.8	–	0	[20]
MgO	9.65	< 3	$1 \times 10^2 - 1 \times 10^8$	[21]
MgO	9.65	< 3	$1 \times 10^2 - 1 \times 10^3$	[22]

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