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# TEMPERATURE DEPENDENCE OF DIELECTRIC CONSTANT OF DIVALENT DOPED MgO SINGLE CRYSTALS AT 1 KHz

M.D. Hossain and J.S. Thorp*

*Department of Applied Physics and Electronics, University of Rajshahi, Rajshahi, Bangladesh*

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The dielectric constants ($\epsilon'$) of MgO single crystals doped with $Ni^{2+}$, $Mn^{2+}$ or $Co^{2+}$ respectively have been measured at 1 KHz in the temperature range 300 K to 450 K. The values of the temperature dependence, $\left[\frac{1}{(\epsilon'-1)(\epsilon'+2)}\right]\cdot\left(\frac{\delta\epsilon'}{\delta T}\right)_p$, ranged between about $1.2 \times 10^{-5}$ $K^{-1}$ for $Ni^{2+}$/MgO (1400 ppm Ni to $1.5 \times 10^{-5}$ $K^{-1}$ for $Co^{2+}$/Mgo (8200 ppm Co). The data confirms Bosman and Havinga's postulate that, for materials in which $\epsilon' < 20$ the temperature dependence should be positive.

## INTRODUCTION

It is known that a study of the dielectric properties of solids is very useful for understanding the nature of conduction. Breckenridge [1] was among the earliest to use this type of examination to analyse the imperfections and defects in ionic crystals and subsequently a considerable amount of work has been undertaken in this area on many solids by various authors [2, 3]. In recent investigations of dopant magnesium oxide, the low frequency (500 Hz to 50 kHz) dielectric behvaiour of $Co^{2+}$/MgO [4], $Mn^{2+}$/MgO and $Ni^{2+}$/MgO [5] single crystals at room teperature have been reported. In this frequency range, the real parts of the respective dielectric constants were independent of frequency and the dielectric loss data, which agreed well with the Universal Law of dielectric response [6, 7, 8] suggested that the conductivity was due to hopping. It was noticeable that there was no evidence for any significant increase in a.c. conductivity due to addition of divalent cobalt, manganese or nickel in contrast to the increases observed with trivalent dopants in MgO, [9].

In the present work an attempt has been made to measure the temperature dependence of the dielectric constant ($\epsilon'$) in the temperature range from 300°K to 450°K. It has been shown by Havinga [10] that in cubic materials (in which $\epsilon$- is isotropic) three effects contribute to the temperature dependence of the dielectric constant. According to him the temperature dependence of the dielectric constant ($\delta\epsilon'/\delta\tau$) at constant pressure can be expressed in terms of the algebraic sum of three contributory components by the following expression:

$$\left[\frac{1}{(\epsilon'-1)(\epsilon'+2)}\right]\cdot\left(\frac{\delta\epsilon'}{\delta T}\right)_p = A+B+C$$

The physical meanings of the symbols A, B and C have been discussed in the literature [11]. The parameter A arises from volume expansion; expansion reduces the number of polarisable particles per unit volume, since the number of particles is constant, so $\epsilon$- decreases with increasing temperature. The quantity B relates to the increase of polarizability of the particles when expansion occurs and the parameter C arises from the dependence, in a constant volume, of the polarizability of the particles on temperature. Bosman and Havinga [11] have dicovered an interesting experimental relationship between the dielectric constant and its temperature dependence which holds for a surprising large and diversified number of materials. It appears that the temperature dependence of a dielectric constant, i.e. the quantity

$$\left[\frac{1}{(\epsilon'-1)(\epsilon'+2)}\right]\cdot\left(\frac{\delta\epsilon'}{\delta T}\right)_p$$

is positive for $\epsilon'$ smaller than about 20 and negative for larger values of $\epsilon'$. In this work the temperature dependence of some divalent doped MgO single crystals were made from 300°K to 450°K; to the author's knowledge no previous measurements of temperature dependence of dielectric constant of divalent (ion doped MgO single crystals ($Co^{2+}$/MgO, $Mn^{2+}$/MgO and $Ni^{2+}$/MgO) in this range of temperature have been published.

*Department of Applied Physics and Elecronics, University of Durham, Durham, U.K.

## EXPERIMENTAL

The specimens on which measurements were made were high quality single crystals of $Co^{2+}$/MgO, $Mn^{2+}$/MgO and $Ni^{2+}$/MgO. They were grown by electrofusion and were supplied (together with optical spectrographic determinations of the concentrations of the dopants to an accuracy of about 2 %) by W and C Spicer Ltd. (Cheltenham, U.K.). To ascertain the valence state of cobalt, maganese or nickel in the doped MgO single crystals, electron spin resonance measurements were made on as grown crystals [5]. These showed that the only signals observable were attributable to $Co^{2+}$ or $Mn^{2+}$ or $Ni^{2+}$ occupying mangnesium sites; consequently, no additional vancancies would be expected to arise from the doping. For measurements, specimens were made in the form of thin square plates with dimensions 10mm x 10mm x 0.3mm and the large parallel faces were polished with diamond paste to a 0.25 micron finish. Circular silver electrodes were evaporated on the opposite polished surfaces of each specimen to ensure good electrical contact over a well-defined area between the crystal and the elctrodes.

The measurements above the room temperature were obtained using a special jig, based on a design previously employed at room temperature [12], which was placed inside an ultra-thermostat (Type No.–NBER) as shown in Figure 1. The thermostat itself, being metallic, provided the electrical shielding necessary to minimise pick-up. The temperature was allowed to come to equilibrium before the measurements were made and was measured with a copper-constantan thermocouple; temperatures could be stablised and measured to ± 2 K. Measurements were made by observing the change in capacitance of the sample as its temperature was varied in steps over the range of 300°K to 450°K. The measurements were made in air at constant pressure. Since it was known that the dielectric constant $\epsilon'$ of all the specimens were relatively insensitive to frequency in the low frequency range [4, 5], the measurements were made at the single frequency of 1 kHz, which was the internal frequency of the impedance bridge used (General Radio, Type No. – 650 A).

## RESULTS

With all three types of doped single crystal the real part of the dielectric constant, ($\epsilon'$), was found to increase steadily with temperature. Over the temperature range examined the variations were nearly linear. An example is illustrated in Figure 2 which shows the results for a $Ni^{2+}$/MgO single crystal containing 1400 ppm nickel; here the actual increase in $\epsilon'$, from 9.52 at 300 K to about 9.65 at 450 K, can be readily measured and leads to a value of $\left[\frac{1}{(\epsilon'-1)(\epsilon'+2)}\right] \cdot \left(\frac{\delta\epsilon'}{\delta T}\right)_p$ of $1.2 \times 10^{-5}$ $K^{-1}$. Similarly variations were found for each of the other two doped systems examined, $Mn^{2+}$/MgO, and $Co^{2+}$/MgO, all the slopes being positive. The data for all the specimens examined in collected in Table 1 and compared with published values for the temperature of both pure MgO and doped MgO taken from the literature. As regards the present work it is noticeable that the $Co^{2+}$/MgO system gives the largest values of temperature dependence and that here there is a significant indication that the temperature dependence increases as the dopant level increases, an effect also apparent (though to a lesser degree) in the $Mn^{2+}$/MgO data. When comparing the data with the quoted values for pure MgO it should be noted that complete analytical data is not given in all the earlier references. Taking Bosman and Havinga's more recent value of $1.05 \times 10^{-5}$ for pure

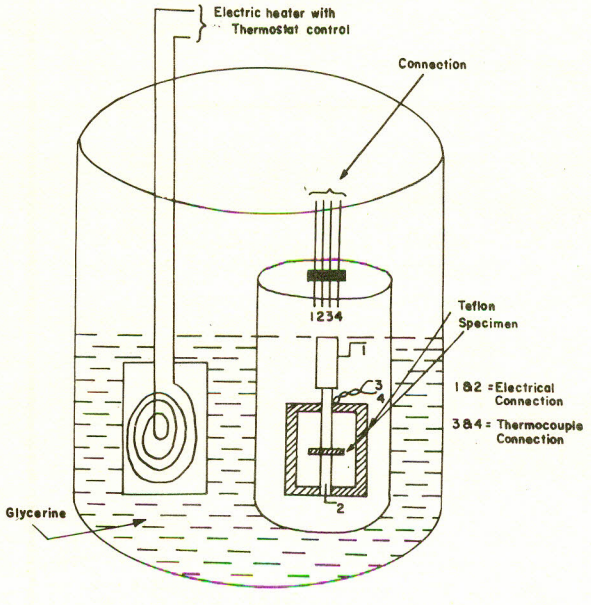


Fig. 1. Sample arrangement with thermostat control.

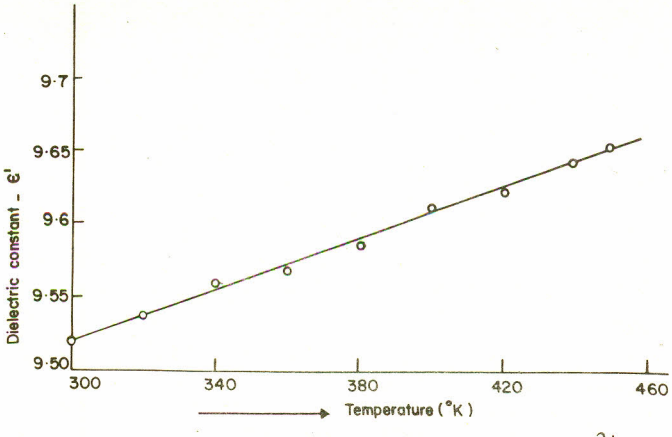


Fig. 2. Temperature dependence of dielectric constant of $Ni^{2+}$/MgO (1400 ppm), 1 kHz.

Table 1. Temperature dependence of dielectric constant; $Ni^{2+}$/MgO, $Mn^{2+}$/MgO and $Co^{2+}$/MgO at 1 kHz.

| Samples | Concentration (ppm) | Dielectric constant at 300°K | Frequency (kHz) | Temperature range°K | | Refs |
|---|---|---|---|---|---|---|
| $Ni^{2+}$/MgO | 1400 | 9.52 | 1 | 300–450 | $1.2 \times 10^{-5}$ | |
| $Mn^{2+}$/MgO | 1400 | 9.80 | 1 | 300–450 | $1.19 \times 10^{-5}$ | present work |
| $Mn^{2+}$/MgO | 2900 | 9.82 | 1 | 300–450 | $1.25 \times 10^{-5}$ | |
| $Co^{2+}$/MgO | 4800 | 9.72 | 1 | 300–450 | $1.40 \times 10^{-5}$ | |
| $Co^{2+}$/MgO | 8200 | 9.74 | 1 | 300–450 | $1.50 \times 10^{-5}$ | |
| MgO | pure | 9.8 | static | uncertain probably 293 | $1.19 \times 10^{-5}$ | (13) |
| MgO | pure | 9.8 | static | " | $1.76 \times 10^{-5}$ | (14) |
| MgO | pure | 9.8 | 250 | 293–423 | $1.05 \times 10^{-5}$ | (11) |
| MgO | pure | 9.96 | 1 & 10 | 50–293 | $0.998 \times 10^{-5}$ | (15) |
| $Ni^{2+}$/MgO | 1400 | 9.52 | 1.592 | 100–293 | $1.26 \times 10^{-5}$ | ( 5) |
| $Co^{2+}$/MgO | 4800 | 9.72 | 1.592 | 100–293 | $1.69 \times 10^{-5}$ | ( 5) |
| $Co^{2+}$/MgO | 3300 | 9.10 | $9.31 \times 10^{6}$ | 300–450 | $1.10 \times 10^{-5}$ | (16) |
| $Mn^{2+}$/MgO | 2900 | 9.00 | $9.31 \times 10^{6}$ | 300–450 | $1.15 \times 10^{-5}$ | (16) |

magnesia however, comparison suggests that it is generally true that doping increases the temperature dependence.

## DISCUSSION

The positive value of temperature dependence for all the specimen at 300°K (Table 1) in the temperature range from 300°K to 450°K confirms the Bosman and Havinga rule [11] for $\epsilon' < 20$. This positive value of temperature dependence of dielectric constant indicates the decrease of electrostatic binding between ions; therefore, less energy will be required to move charge carriers at high temperature. An examination of Table 1 shows that in the temperature range now examined, the temperature dependences of dielectric constant of the present materials are less than their temperature dependences in the temperature range from 100°K to 293°K at 1.592 kHz [5] and higher than in the teamperature range from 300°K to 450°K at 9.31 GHz [16]. This higher value of the temperature dependence at low frequency (1 kHz) than in the microwave region over the same temperature range may be due to the presence of space charge. The influence of space charge is known to be noticeable in the low frequency region [17]. The measurements summarised in Table 1 also show that the temperature dependence for $Co^{2+}$/MgO crystals is greater than for either $Ni^{2+}$/MgO or $Mn^{+}$/MgO crystals; this indicates the greater temperature dependence of polarizability in $Co^{2+}$/MgO single crystals, attributable to the presence of the $Co^{2+}$ dopant rather than either of the other divalent ions.

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