JOURNAL OF MATERIALS SCIENCE 10 (1975) 918–922

The dielectric constants of $CaWO_4$, Nd/$CaWO_4$ and Gd/$CaWO_4$

J. S. THORP, E. A. E. AMMAR
Department of Applied Physics and Electronics, University of Durham, Durham, UK

The dielectric constants and loss for pure single crystals of calcium tungstate and for neodymium- and gadolinium-doped crystals have been measured from 1 to 40 MHz. At 20°C the values for pure calcium tungstate are $\epsilon_a' = 11.3 \pm 0.4$, $\epsilon_c' = 9.1 \pm 0.4$, at 1 MHz. These agree closely with Brower and Fang's data and increase very slightly with frequency. Doping at levels of less than 1.0 at.% produced no measurable change in ϵ_a' or ϵ_c'. The dielectric loss, tan δ, which was isotropic, was about 5×10^{-3} for all specimens at 1 MHz; at higher frequencies, tan δ increased and, in the neodymium-doped crystals, the high frequency loss was found to be concentration dependent.

1. Introduction

Although two measurements of the dielectric constants of pure calcium tungstate have been reported [1, 2], the values quoted show a considerable divergence. In the earlier paper [1], Komandin *et al.* who used an immersion method, stated that the dielectric constant was $\epsilon' = 21.4$ at 25°C and 1.72 MHz for solid material, apparently in powder form. Calcium tungstate, however, crystallizes in the scheelite structure; it belongs to the tetragonal space group $C_{4h}{}^6 - I4_{1/a}$ having $a = b = 5.243$ Å and $c = 11.376$ Å [3] and, consequently, two components are necessary to describe the dielectric tensor. In the later paper, Brower and Fang [2] gave results for measurements on oriented pure single crystal slices. They found that the dielectric constant was anisotropic, that the dielectric constants parallel to the *a*-axis and *c*-axis were 11.7 and 9.5, respectively, at 24.5°C, and that these values were the same for frequencies at 1.59 KHz and 1 MHz. The measurements reported here were made primarily to clarify the situation in pure calcium tungstate and also to obtain data on some neodymium- and gadolinium-doped calcium tungstate single crystals in order to assist optimization of the matching conditions during electron spin resonance studies of linewidth [4] and relaxation [5] in them; to the authors' knowledge no previous measurements on doped calcium tungstate have been published.

2. Experimental

The single crystals used, (obtained from I.R.D. Co Ltd, Newcastle), were grown by the Czochralski method. In the pure and gadolinium-doped crystals, charge compensation was achieved by vacancy incorporation, and in the neodymium-doped crystals by sodium addition. The single crystal boules, whose dimensions were typically 6 cm long and 1.5 cm diameter, were first oriented by Läue back-reflection X-ray methods which gave orientation accuracies of ± 15′ of arc. Specimens of known orientation were then prepared by making appropriate slices with a diamond wheel cutting machine and precision polishing their faces with diamond paste to a 0.25 µm finish. The larger faces of the specimens were limited by the boule dimensions to about 1 cm × 1 cm in area and were cut in the plane of either the *a*- or *c*-axis (Fig. 1), the specimen thickness, usually 0.3 mm, represented the minimum which could readily be achieved without fracturing the slice during fabrication. Circular gold electrodes were deposited by evaporation on the larger polished faces to ensure good electrical contact over a defined area between the crystal and the electrodes of the dielectric testing jig.

The measurements were made in air at room temperature over the frequency range 1 to 40 MHz using a standard *Q*-meter, (Marconi TF 1245), the dielectric testing jig, (Marconi TJ 155C/1) was modified to allow the use of 10 or 6

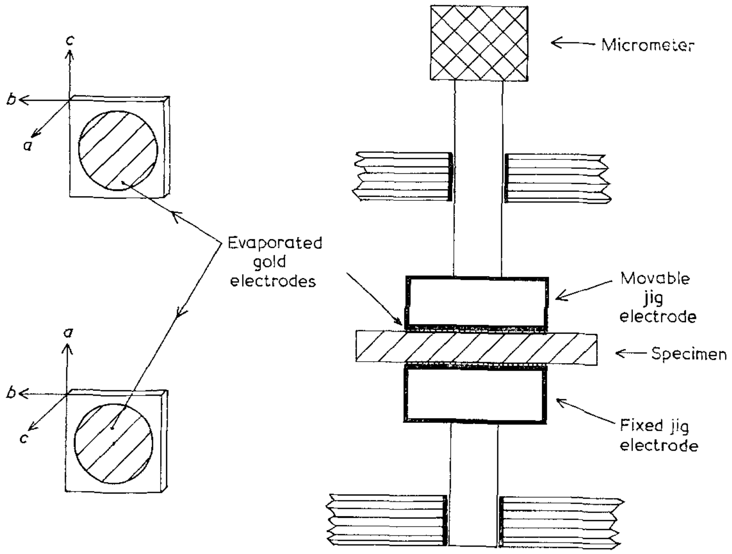

Figure 1 General form of specimens and dielectric testing jig.

mm diameter circular jig electrodes as specimen dimensions were limited by the size of the single crystals available. In this technique, measurements were made firstly with the specimen mounted in the jig and secondly, at the same jig electrode spacing, without the specimen. The difference in capacity enabled the real part of the dielectric constant, ϵ', to be derived; in a similar manner the difference in Q-value with and without the specimen allowed the dielectric loss, $\tan\delta$, to be evaluated.

3. Derivation of ϵ' and $\tan\delta$

In the Q-meter method outlined above, the numerical values of the dielectric constant, ϵ', and loss, $\tan\delta$, can be obtained, neglecting edge effects, from the expressions [6]

$$\left.\begin{aligned}\epsilon' &= \frac{C_1 - C_2}{C_0} + 1\,,\\ C_0 &= \epsilon_0 \cdot \frac{A}{d}\end{aligned}\right\} \qquad (1)$$

and

$$\tan\delta = \frac{Q_1 - Q_2}{Q_1 \cdot Q_2} \cdot \frac{C_1}{C_1 - C_2} \qquad (2)$$

in which C_1 and C_2 are the capacitances at resonance with the specimen out and in respectively, A the electrode area, d the specimen thickness and Q_1 and Q_2 the Q-values at resonance without and with the specimen.

In the present experiments, however, the specimens were, for convenience, cut in the form of squares and so some crystal protruded beyond the circular jig electrodes. Consequently, a correction for edge effects was necessary. Various formulae have been given previously [7] and, following similar methods, Equation 1 can be modified to

$$\epsilon' = \frac{C_1 - C_2}{C_0 - C_e} + 1 \qquad (3)$$

where

$$C_e = \frac{1.113D}{8\pi}\left[\ln\frac{8\pi D}{d} - 3\right] \qquad (4)$$

for the experimental conditions used in which, for any electrode diameter D employed, the thickness of each evaporated gold electrode was very small compared with the specimen thickness. These equations were used in deriving the numerical data presented; it was found that the correction term amounted to about 8%. The edge effect correction for $\tan\delta$ was negligible.

4. Results

The dielectric constant data obtained at 1 MHz are summarized in Table I in which the values given under "present work" represent averages for several measurements on each individual specimen. For the pure material at 1 MHz we find that parallel to the a-axis, $\epsilon_a' = 11.3 \pm 0.4$

TABLE I Dielectric constants for $CaWO_4$, $Nd/CaWO_4$ and $Gd/CaWO_4$ at 1 MHz (doping levels given in at. %)

Reference	Pure $CaWO_4$			$Nd/CaWO_4$			$Gd/CaWO_4$		
	ϵ'	ϵ_a'	ϵ_c'	Doping level	ϵ_a'	ϵ_c'	Doping level (nominal)	ϵ_a'	ϵ_c'
Kamandin *et al.*	21.4								
Brower and Fang		11.7 ±0.1	9.5 ±0.2						
Present work		11.3 ±0.4	9.1 ±0.4	1%	11.5 ±0.4	9.5 ±0.4	0.05%	11.8 ±0.4	9.1 ±0.4
				0.1%	11.1 ±0.4	9.3 ±0.4	0.01%	11.1 ±0.4	8.9 ±0.4
				0.05%	11.5 ±0.4	9.4 ±0.4			

and that parallel to the c-axis, $\epsilon_c' = 9.1 \pm 0.4$. In the doped crystals, the values of ϵ_a' and ϵ_c' at 1 MHz were the same, within experimental error, as those for pure calcium tungstate.

The variation of the dielectric constants at frequencies above 1 MHz is shown in Fig. 2. A very slight increase in both ϵ_a' and ϵ_c' was observed above about 20 MHz but the anisotropy of the dielectric constant, as measured by the ratio ϵ_a'/ϵ_c' remained unaltered. There was no significant difference between the behaviour of the pure calcium tungstate crystals and the neodymium- or gadolinium-doped specimens.

With regard to dielectric loss, tan δ for pure calcium tungstate increased slowly from 0.005 at 1 MHz to about 0.01 at 40 MHz. In contrast to the anisotrophy of the dielectric constant, the losses measured parallel to the a- and c-axes were the same. With both neodymium- and gadolinium-doped crystals, similar increases in loss at the higher frequencies were observed (Figs. 3 and 4). The measurements on the doped crystals also showed that, above about 20 MHz, the dielectric loss was larger the higher the dopant concentration. With neodymium doping the effect was quite marked; the true neodymium concentrations in these specimens were determined by optical spectrographic analysis (The Chemical Inspectorate) and, as Fig. 3 shows, the loss at 40 MHz increased from 4.5×10^{-3} to 7.2×10^{-3} as the concentration rose from 0.05% Nd to 0.1% Nd. In the gadolinium-doped specimens, the effect was not so marked, probably because the true gadolinium concentrations were all very low, ~ 50 ppm or less, and the differences between the specimens were not so pronounced. (The analyses were made by emission spectrochemistry by the Analytical Services Laboratory, Imperial College.) It was also found, as with the pure material, that in all the doped specimens examined, the dielectric loss parallel to the a-axis was the same as that measured parallel to the c-axis.

5. Discussion

Considering first the pure calcium tungstate single crystals, the measured values of ϵ_a' and ϵ_c' at 1 MHz (11.3 ± 0.4 and 9.1 ± 0.4 res-

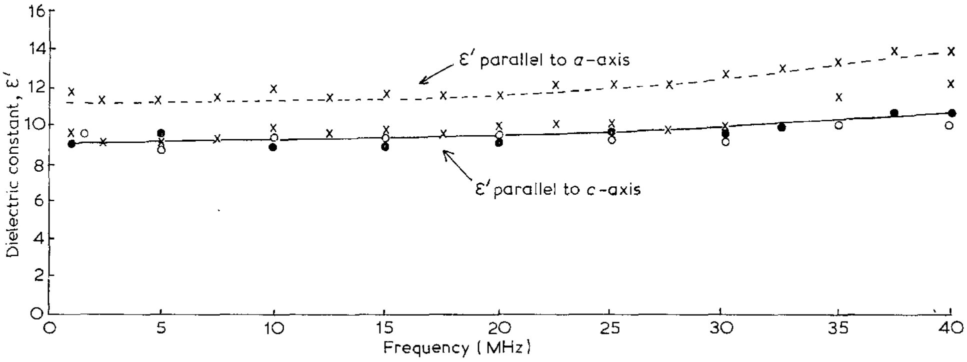

Figure 2 Variation of dielectric constant ϵ' with frequency. ×, 0.05% Nd, ○, 0.05% Gd, ●, pure $CaWO_4$.

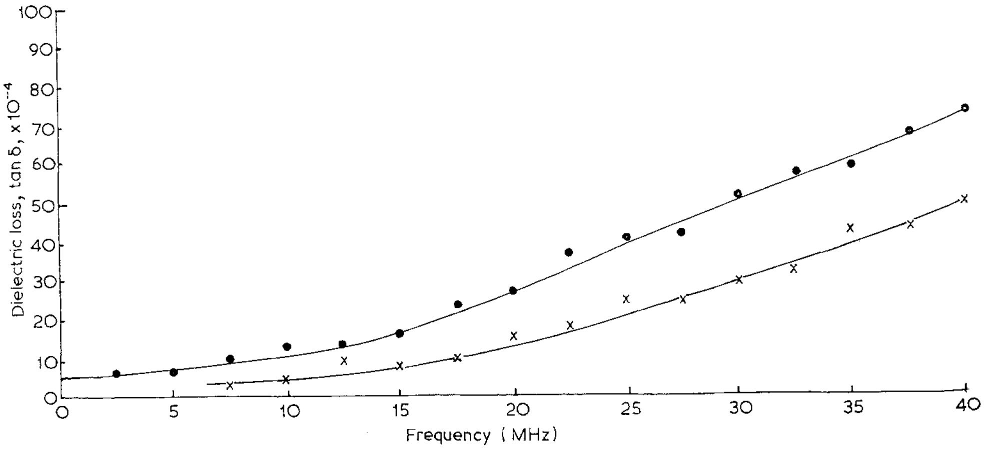

Figure 3 Variation of dielectric loss tan δ with frequency for neodymium-doped calcium tungstate. ×, 0.05% Nd, ●, 0.1% Nd.

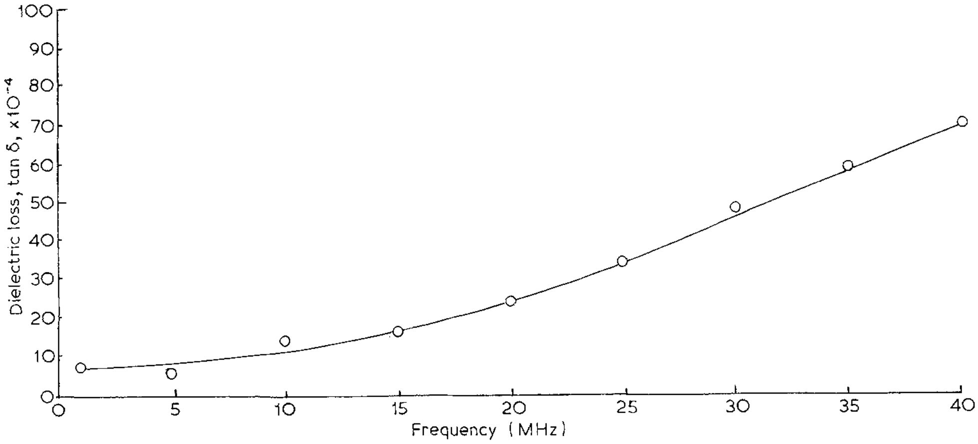

Figure 4 Variation of dielectric loss, tan δ, with frequency for gadolinium-doped calcium tungstate.

pectively) agree very closely with those given by Brower and Fang both as regards the numerical values and in that $\epsilon_a' > \epsilon_c'$. The measurements reported here were made on vacancy compensated crystals, whereas those of Brower and Fang were made on sodium compensated crystals, so it appears that the dielectric constants are not very sensitive to differences in growth method. The present work shows further that there is little increase in either ϵ_a' or ϵ_c' over the frequency range 1 to 40 MHz.

With regards to the dielectric constants of the doped single crystals, the results showed that doping with neodymium or gadolinium did not produce a measurable change in either ϵ_a' or ϵ_c'; this conclusion was not unexpected as both the neodymium and gadolinium concentrations were low and electron spin resonance data [4] had previously confirmed that the rare earth ions entered the tungstate lattice subsitutionally and occupied calcium sites.

The dielectric loss data, on the other hand, established that in the neodymium calcium tungstate, the high frequency value of tan δ was concentration dependent. This effect may be associated with Debye relaxation of the neodymium ion, although this has not yet been proved. Experimentally, the loss measurement is a more sensitive detector of small composition changes than the dielectric constant measurement; this might be useful in an analytical context where the application of conventional methods, particularly for gadolinium, is difficult.

Acknowledgement

We wish to thank Mr T. Harcourt for his assistance in preparing the crystal slices. One of us (E.A.E.A.) also wishes to thank the University of Alexandria, Egypt, for the award of a research scholarship.

References

1. A. V. KOMANDIN, R. D. SHAPOVALOVA and N. P. MIKHAILOVA, *Russian J. Phys. Chem.* **34** (1960) 979.
2. W. S. BROWER and P. H. FANG, *J. Appl. Phys.* **40** (1969) 4988; *ibid* **38** (1967) 2391.
3. A. ZALKIN and D. H. TEMPLETON, *J. Chem. Phys.* **40** (1964) 501.
4. G. BROWN, C. J. KIRKBY and J. S. THORP, *J. Mater. Sci.* **9** (1974) 65.
5. J. S. THORP, H. P. BUCKLEY and G. BROWN, *ibid* **9** (1974) 864.
6. Marconi Instruments Ltd., Handbook No. OM 1245, (1960).
7. A. H. SCOTT and H. L. CURTIS, *J. Res. Nat. Bur. Stand.* **22** (1939) 747.

Received 13 November and accepted 25 November 1974.