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The dielectric constants of current-blackened single crystral yttria-stabilized zirconia

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The dielectric constants of 8 mol % single crystal yttria-stabilized zirconia have been measured, using both radio-frequency and microwave methods, before and after blackening by high temperature electrolysis. For as-grown material $\epsilon' = 38 \pm 4$ and $\tan \delta = 0.004$. After electrolysis both the dielectric constant and loss tangent of the current-blackened material increased; this experimental data has been compared with theoretical predictions for composite dielectrics. The dielectric behaviour in the current-blackened material was consistent with the formation of metallic particles; these initially appeared to be spherical but elongated as electrolysis proceeded.

1. Introduction

Yttria-stabilized zirconia is a refractory oxide which conducts at high temperatures [1] owing to oxygen ion transport in a lattice where anion vacancies have been created by the substitution of yttrium for some of the zirconium. A reduction process occurs, however, during current passage in reducing atmospheres; this leads, in both single crystal and polycrystalline material to blackening and ultimately to disintegration. Some of the structural and optical consequences of blackening have recently been studied by electron spin resonance [2] and optical [3] methods. After electrolysis, the optical transmission fell although the band edge position remained the same. In lightly discoloured regions the transmission showed a broad minimum centred at 480 nm; in the blacker regions it was reduced drastically over the whole visible range. The low transmisison was shown to be due to absorbing centres. The resonance studies showed no marked changes in the elecron spin resonance spectrum as a result of blackening; although defects with unpaired spins were present in material as grown there was no detectable change in their density with blackening. Thus it was concluded that the absorbing centres were not singly charged vacancies and they were attributed to the formation of vacancy aggregates which ultimately produced colloidal metallic particles.

At room temperature, yttria-stabilized zirconia is an insulator. No dielectric data on single crystals of the present compositions, 8 and 12 mol % yttria, appear to have been reported. However, some measurements have been made previously on related materials and a value $\epsilon' = 22 \pm 3$ quoted for pure monoclinic zirconia [4]. It has also been shown in some stabilized zirconias [5] that ϵ' is not very sensitive to minor changes in the concentration of the stabilizing agent. If during the electrolysis of yttria-stabilized zirconia metallic particles were formed, as suggested by the optical evidence an inhomogeneous dielectric would be predicted. Consequently, the dielectric constants and loss tangents have been measured before and after electrolysis in an attempt to establish whether the dielectric behaviour is consistent with the metallic particle hypothesis.

2. Theory

For many years it has been accepted that certain peculiarities in the dielectric behaviour of solids are due to the presence within them of regions having higher conductivity than the general bulk of the material. At the interfaces between dielectrics of differing conductivity space charges build up because of the different voltage gradient requirements of each material for conduction of a constant current density. This results in large scale field distortions or interfacial polarization and leads to dielectric anomalies.

The simplest model of an inhomogeneous dielectric is the two layer capacitor of Maxwell [6]. This consists of two parallel sheets of materials characterized by different dielectric constants, conductivities and thicknesses. Here the total impedance is not altered by dividing each layer into a number of equal sub-layers and stacking them in any sequence and so the complex permittivity of the composite dielectric remains unchanged. This result is only true provided that the geometrical shape and orientation parameters are constant. A more realistic model, due to Wagner [7], is to assume that the conducting particles are spheres distributed sparsely through the bulk material. The most general model, proposed by Sillars [8], assumed that ellipsoidal conducting particles, whose shape could vary from that of a flattened lens to an elongated needle, were embedded in an insulator. This model has been adopted here.

Consider an inhomogeneous dielectric consisting of a medium of dielectric constant ϵ_1', assumed a perfect insulator, containing a number of very small spheroids of dielectric constant ϵ_2' and conductivity σ_2 dispersed through it. The distance between the spheroids is taken to be so much greater than their size that each may be regarded as being under the influence of a uniform alternating field E (of angular frequency ω); furthermore, the spheroids are assumed so numerous that the whole matrix can be regarded as having a mean dielectric constant $\epsilon = \epsilon' - j\epsilon''$. To simplify the treatment only spheroids having their unique axes parallel to the field E are considered. This assumption is not a very plausible representation of a real dielectric. It has been shown by Sillars, however, that the nature of the general conclusions is not affected. The effect of having the spheroids distributed with their axes in all possible directions is small compared with the elongation effect. A coefficient n is introduced ($n = 4\pi/l_a$, see [8]) to specify the eccentricity of the spheroid. The value of n varies from $n = 1$ for a very flat oblate spheroid, to $n = \infty$ for a very long prolate spheroid; in the particular case of a sphere $n = 3$. The absolute size of the particles, provided they are small, does not enter into the calculations; the important parameter is the fractional volume q occcupied by the conducting particles. In these terms the values of ϵ', ϵ'' and $\tan\delta$, following Sillars' notation are

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_1' N}{1 + \omega^2 \tau^2} \qquad (1)$$

$$\epsilon'' = \frac{\epsilon_1' N \omega \tau}{1 + \omega^2 \tau^2} \qquad (2)$$

and

$$\tan\delta = \frac{\epsilon''}{\epsilon'} = \frac{N \omega \tau}{N + (1 + \omega^2 \tau^2)(\epsilon_\infty/\epsilon_1')} \qquad (3)$$

In these equations

$$\epsilon_\infty = \epsilon_1' \left[1 + \frac{qn(\epsilon_2' - \epsilon_1')}{\epsilon_1'(n-1) + \epsilon_2'} \right] \qquad (4)$$

$$\tau = \frac{\epsilon_1'(n-1) + \epsilon_2'}{4\pi \sigma_2} \qquad (5)$$

and

$$N = \frac{qn^2 \epsilon_1'}{\epsilon_1'(n-1) + \epsilon_2'}, \qquad (6)$$

This model embraces the earlier models mentioned in that when $n = 3$, one is considering Wagner's spherical particles and when $n = 1$, the expressions reduce to those of a layered dielectric; similarly, the value $n = \infty$ represents conducting cylinders.

The effect of increasing the volume fraction q of conducting material has received much attention. The dielectric characteristics, plotted as functions of q, must correspond initially to those of the insulator and finally to those of the conductor. In the intervening range the distorted field areas round each conducting particle begin to overlap. In this region Lichtenecker [9] used a logarithmic mixing rule

$$\log \epsilon' = q \log \epsilon_2' + (1 - q) \log \epsilon_1' \qquad (7)$$

to determine the dielectric constant ϵ' of the composite dielectric in terms of ϵ_1', ϵ_2' and q. This has been shown by Büchner [10] to be followed closely for mixed dielectrics containing rutile (TiO_2), as one of the two components. However, the rule takes no account of the shape, size or distribution of the particles; an estimation of these effects can be obtained from Equations 1, 2 and 3.

In the particular case of yttria-stabilized zirconia, some simplification of the foregoing equations can be made. The previous work on the nature of high temperature electrolysis suggested that the absorbing centres produced might be attributable to particles of zirconium metal. For a metal the conductivity σ_2 is large (2.2×10^{16} esu for zirconium) and evidence from studies on colloidal F-centres [11] indicates that $\epsilon_2' \geq 10^4$. With these values Equation 1 becomes

$$\epsilon' = \epsilon_\infty + \epsilon_1' N = \epsilon_1' (1 + qn) \tag{8a}$$

for $\omega\tau \ll 1$, i.e. for $1 < \omega < 10^{10}$, and

$$\epsilon' = \epsilon_\infty = \epsilon_1' (1 + qn) \tag{8b}$$

for $\omega\tau > 1$, i.e. for $\omega > 10''$. These indicate that ϵ' should be frequency independent. Equation 8a has been used to draw a series of curves of ϵ' versus q for different values of n using the specific value for ϵ_1' determined for crystals before electrolysis. The variation predicted by the mixing rule, Equation 7, has also been calculated this depends mainly on ϵ_2' rather than on n.

3. Experimental

The single crystals, grown by electrofusion from the pure powdered oxides, were obtained from W. & C. Spicer Ltd (Cheltenham) and two compositions, containing respectively 8 and 12 mol % yttria, were examined. Because of the cubic structure of ytttria-stabilized zirconia and the consequent isotropy of the dielectric constant it was not necessary to use oriented specimens.

For measurements in the range 1 kHz to 40 MHz the capacities of thin crystal slices were found using a standard Q-meter (Marconi T.F. 1245) and dielectric loss test jig. Evaporated gold electrodes were used. The dimensions of the available crystals generally restricted the maximum electrode diameter to 6 mm and, to obtain reasonably high capacities, the slice thickness was reduced to 0.3 mm. Specimens of as-grown material were first prepared by cutting with a diamond wheel and precision grinding to yield parallel faces polished to a quarter micron diamond finish. The fragility of the slices, particularly after electrolysis, was the limiting factor determining the minimum thickness. Electrolysis was carried out at 800°C in argon using platinum paste/platinum electrodes (Fig. 1a). To ensure the removal of any conducting surface layers [2] specimens were, after electrolysis, dipped into hot phosphoric acid. It was found as described in detail in the subsequent section, that ϵ' varied over different parts of the blackened tongue [3] formed after electrolysis; the use of small diameter electrodes (3 mm) enabled measurements to be made at various positions on an electrolysed slice (Fig. 1b).

The variation of ϵ' limited the suitability of the Q-meter method for obtaining an estimate of ϵ' representative of bulk material and therefore suitable for correlation with the corresponding q value. To obtain a more realistic estimate of ϵ' for bulk material a microwave method was adopted. This was based on that of Roberts and von Hippel [12, 13] in which the specimen was used to terminate a short-circuited waveguide. Frequencies in the 33 GHz range were used because the available crystals just allowed specimens to be cut to fill the no. 22 waveguide required whose internal cross-section was 7.11 mm × 3.56 mm. The length of the specimens, which were carefully ground and polished to give an exact fit in the guide, was about 1 cm; electrolysis was performed in a similar way to that used for the thin slices. The positions of the maxima and minima of the standing wave pattern in the guide were found with and without the specimen. In this method the displacement L of the position of the minimum, produced by a thickness, d, of dielectric, enabled a parameter X to be determined such that

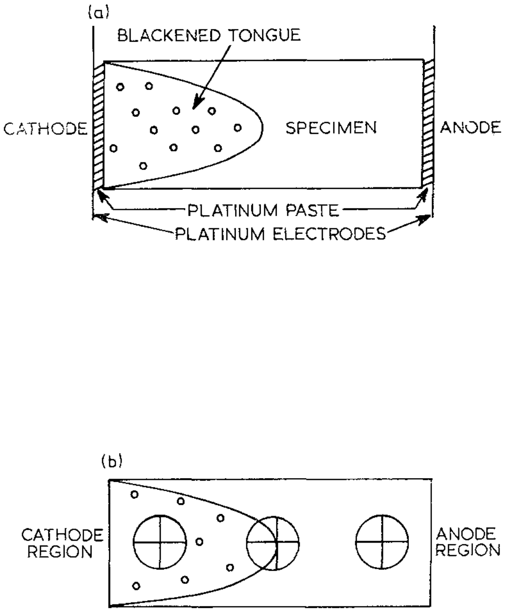

Figure 1 Details of specimen preparation; (a) specimen mounting for electrolysis, (b) gold electrode positions on thin specimens.

$$X = \frac{\lambda_g}{d} \tan \frac{2\pi (L + d)}{\lambda_g} \tag{9}$$

where λ_g was the wavelength in the air-filled guide. The number of wavelengths, V, of radiation in the dielectric was then given by

$$X = \frac{\tan 2\pi V}{V} \tag{10}$$

and ϵ' could be found from

$$\epsilon' = 1 - \left(\frac{\lambda_0}{\lambda_g}\right)^2 + \left(\frac{\lambda_0 V}{d}\right)^2 \qquad (11)$$

where λ_0 was the free space wavelength. Equation 10 shows that V is many valued for a given value of X so that, for a given frequency of measurement, a series of possible values for V and ϵ' were obtained. To resolve the ambiguity measurements were also made at a second frequency; plotting for each frequency ϵ' against a parameter representing V then gave two curves whose point of intersection yielded the unique value of ϵ'. The use of frequency rather than specimen thickness as a variable was preferred because of the difficulty of ensuring that nominally similar specimens of different lengths would in fact have the same dielectric properties; the two-frequency method allowed ϵ' to be found for each specimen separately. The attenuation of the specimens was also measured. All the dielectric constant measurements were made at room temperature.

During electrolysis a virtual cathode was formed and, as electrolysis proceeded, this moved towards the anode. The electrolysis products formed near this virtual cathode. The total quantity of metal produced was estimated for each specimen from Faraday's laws of electrolysis using the measured values of current (I), specimen volume (V_S) and duration of electrolysis (t). Where V_S was not directly measurable it was found from the measured specimen mass using a density of 6 g cm^{-3} for as-grown single crystal 8 mol % yttria-stabilized zirconia. The reaction at the electrodes was taken to proceed as

$$Zr^{4+} + 4e \rightarrow Zr \qquad (12a)$$

$$2O^{2-} - 4e \rightarrow O_2\,. \qquad (12b)$$

The total quantity of metal was used to estimate the volume fraction q in the electrolysed specimen. On this basis the value of q was given by

$$q = 3.63 \times 10^{-5}\,\frac{It}{V_S} \qquad (12c)$$

where I, t and V_S were expressed in amperes, seconds and cm^3 respectively.

This method of estimation gave no indication of the distribution of metal throughout the crystal; comparison was not prevented however because the theory only involved the total volume fraction q.

TABLE I Dielectric constants and loss for 8 mol % yttria-stabilized zirconia as-grown single crystals.

Specimen reference	Dielectric constant ϵ'	Dielectric loss tan δ	
(a) r.f. measurements			
		150 kHz	40 MHz
1	40	0.0045	0.018
2	39	0.0047	0.009
3	41	0.0047	0.011
4	35	0.0055	0.01
5	40	0.0042	0.014
6	36	0.0027	0.006
7	36	0.007	0.015
(b) Microwave measurements		Attenuation (dB mm^{-1})	
8	48	1.04	
9	21	—	
10	44	1.14	
11	44	—	
12	25	—	
13	46	0.97	
14	43	0.55	
15	31	0.81	
16	49	0.42	
17	31	0.51	
18	28	0.82	
19	39	0.58	
20	41	1.29	

4. Results

4.1. As-grown material

Some results obtained in the frequency range 150 kHz to 40 MHz are listed in Table I. For any particular specimen there was little variation of ϵ' with frequency; both ϵ'' and tan δ increased steadily with frequency and their initial and final values are given. The average value of ϵ' for 8 mol % yttria crystals was 38.0 $\pm$ 3. The results for 12 mol % yttria crystals were very similar and did not suggest a strong dependence on yttria content. The values of tan δ were all low and justified classifying the material as a fairly low loss dielectric at room temperature.

The microwave measurements, made on a separate series of as-grown specimens, are also given in Table I. There was a considerable spread, markedly greater than the experimental error of $\pm$ 10%, between specimens which, by visual examination of colour (pale yellow), appeared to be nominally identical. The mean value, $\epsilon' = 37.5 \pm 4$, agreed closely with that obtained in the lower frequency range. The attenuation (at 33 GHz), was generally less than 1 dB mm^{-1}. Combining all the measurements gave an average ϵ' of 38 ± 4. This is considerably higher than the previously published values for related materials. For pure zirconia (ZrO_2) the determinations fall into two groups with ϵ' around 11 or 25 respectively; for powdered polycrystalline monoclinic zirconia an early determination gave $\epsilon' = 12.4$ at 1 kHz [14] while more recent work gave $\epsilon' = 13.5$ between 10 and 100 kHz [5]. In the limited amount of work reported on single crystals Charlesby [15] found $\epsilon' = 20$ for bulk baddeleyite, a value fairly close to the $\epsilon' = 22 \pm 3$ at 1.59 kHz given by Harrop and Wanklyn [4] for synthetic pure monoclinic zirconia. The latter authors also reported that for calcia- and magnesia-stabilized zirconia ϵ' was 26 ± 4 and 27 ± 4 respectively and concluded that ϵ' was insensitive to changes in composition. Sanesi *et al* [5] however found some variation of ϵ' with calcia content in calcia-zirconia and explained this in terms of composition dependent density changes.

TABLE II Effect on ϵ' of heat-treatment in argon or oxygen (microwave measurements, 32 to 34 GHz).

Duration (h)	Dielectric constant ϵ'	Attenuation (dB mm^{-1})
(a) Heat-treatment in argon at 800° C (specimen 17)		
0	31	0.57
1	31	0.66
3	26	0.66
5	27	0.46
9	26	0.49
14	27	0.43
(b) Heat-treatment in oxygen at 800° C (specimen 19)		
0	39	0.58
1.5	38	0.68
3	33	0.57
4	31	0.51
5	35	0.61
6	32	0.60
7	29	0.60

4.2. Heat-treatment in argon and oxygen

The electrolysis of the yttria-stabilized zirconia crystals was carried out at 800°C in an atmosphere of de-oxidized argon. In order to assess the magnitude of any changes occasioned by the heat-treatment, reference measurements were made on as-grown crystal slices heat-treated in argon or oxygen. The results are shown in Table II. Heating in oxygen produced a gradual decrease in ϵ'; heating in argon also caused a slight reduction though at a slower rate. The results showed that in the times usually used for blackening by current pasage, which were less than 30 min. the change in ϵ' due solely to the heat-treatment would be negligible; longer times would have given a small reduction in ϵ'.

4.3. Current-blackened material.

The r.f. measurements on electrolyzed single crystals, Table III, primarily served to establish the general features of the consequences of electrolysis. On each specimen measurements were made near the anode and cathode ends of the crystal and, where appropriate, at intermediate points within the blackened tongue (see Fig. 1b). For current densities of 0.1 A cm^{-2} and below neither ϵ' nor tan δ showed any significant variation between the anode or cathode regions (specimens 21, 22). At a higher current density (specimens 23, 24, 25) a variation of ϵ' along the crystal was observed. A distinctly larger value of ϵ' was found in the blackened region near the cathode than in the unchanged yellow region near the anode; at points in the interfacial region near the tip of the blackened tongue ϵ' had an intermediate value. The extreme fragility of the current-blackened crystal slices restricted the number of measurements possible and their extension to higher current densities. There was some indication of an increase in tan δ in the blackened areas of the specimens.

In the microwave measurements ϵ' was measured as a function of the time of passage of current at a constant current density (4 A cm^{-2}). In this way the change in ϵ' could be monitored with increase in volume fraction of blackened material. This corresponds to the growth and movement towards the anode of the blackened tongue, which originated at the cathode. (For each specimen this involved fixing fresh electrodes for each successive electrolysis and, after each one, regrinding the crystal faces to eliminate any traces of platinum paste; 4 A cm^{-2} was chosen as a convenient current density to ensure blackening without an undue failure rate due to macroscopic cracking.) Electrolysis was stopped either when the whole specimen was blackened or earlier if the crystal fragmented. The results are given in Table IV. These show that there was a successive increase in the average ϵ' for the bulk crystal as electrolysis proceeded; this was accompanied by an appreciable rise in attenuation.

TABLE III Dielectric data for electrolysed crystals; r.f. measurements. (tan δ values quoted for 150 kHz, all electrolysis carried out at 800° C in argon).

Specimen	Electrolysis conditions	Anode region		Cathode region	
		ϵ'	tan δ	ϵ'	tan δ
21 8 mol %	0.1 A cm^{-2} 2.25 h	35	0.0055	37	0.006
22 12 mol %	0.1 A cm^{-2} 2.25 h	29	0.0058	30	0.0057
23 8 mol %	4.0 A cm^{-2} 8 min	40	0.0042	43	0.0055
24 8 mol %	3.3 A cm^{-2} 20 min	37	0.004	64	0.029
	(ϵ' = 44 at tip of blackened tongue)				
25 8 mol %	6.2 A cm^{-2} 12 min	36	0.0046	52 part way along blackened tongue (cathode end broken)	0.018

TABLE IV Variation of ϵ' and attenuation with duration of current passage; current density 4 A cm^{-2} (microwave measurements)

Specimen	Duration of current passage (min)	Dielectric constant, ϵ'	Attenuation (dB mm^{-1})	Volume fraction, q
8	0	48	1.04	0
	10	66	1.20	0.091
	12	87	2.0	0.113
10	0	44	1.14	0
	10	61	1.15	0.094
13	0	46	0.97	0
	10	98	2.02	0.106
	12	114	2.5	0.13
	14	98	3.55	0.15
	16	94	3.84	0.173
14	0	42	0.55	0
	2	47	0.90	0.015
	4	46	0.82	0.03

The volume fractions q of zirconium metal were derived from the current density and time as explained in Section 3.

5. Discussion

The data of Table IV was first considered in the context of the logarithmic mixing rule in order to obtain an estimate for the dielectric constant ϵ_2' of the particles assumed to have been formed by electrolysis. The application of the mixing rule to this system seemed justifiable since the optical [3], X-ray [16, 17] and ultrasonic [18] results all indicated that, after electrolysis, the yttria-stabilized zirconia unit cell remained substantially unchanged; the electrolysed crystal could, therefore, be regarded as a mixture rather than as a new single compound. The comparison is made in Fig. 2 in which the full lines show the theoretical variation of ϵ with q calculated from Equation 7 for different values of ϵ_2'. The

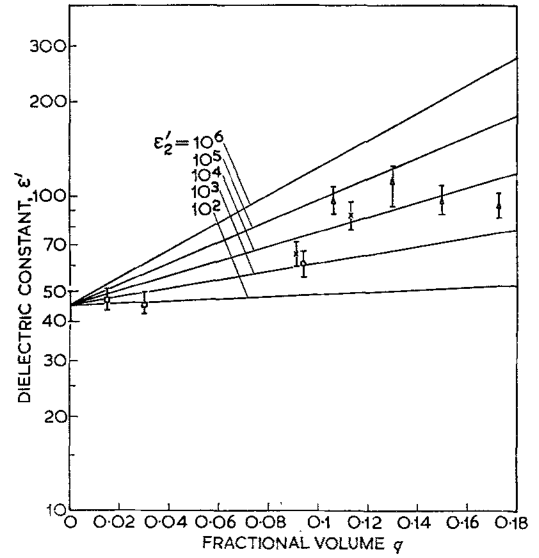

Figure 2 Comparison of data with the mixing rule (key: crosses, specimen 8; open circles, specimen 10; triangles, specimen 13; squares, specimen 14).

positions of the experimental points show that $\epsilon_2' \approx 10^4$. This value agrees closely with the estimate of $\epsilon_2' > 10^4$ for metal particles deduced by Sikorskii [11] from studies on colloidal F-centres. (It may be noted that single dispersed F-centres would not give a rise in ϵ' with q.) Thus, Fig. 2 indicated that the particles produced by electrolysis were metallic.

The possible shapes of the particles were next investigated by comparison with the Sillars' model, Fig. 3. In deriving these theoretical curves from Equation 8 it was assumed that the electrolysed crystal was a composite dielectric consisting of a matrix of yttria-stabilized zirconia with $\epsilon_1' = 45$ (the average for the specimens listed in Table IV) in which metal particles having $\epsilon_2' = 10^4$ were embedded. At fairly low values of q the observations correspond reasonably well with the theoretical curve for $n = 3$. This implies that initially the particles are nearly spherical. In the intermediate ranges the experimental points lay well above the theoretical curve for $n = 3$ and tended to give a better fit with the variation expected for $n = 10$. This would correspond to an elongation of the particles. Such a conclusion is compatible with recent observations on electrolysed polycrystalline yttria-stabilized zirconia [17]. In these experiments Casselton, Penny, and Reynolds showed, from optical micrographs and electron probe micro-analysis, that zirconia metal built up along inter-grain boundaries; they also found that a heavily blackened single crystal exhibited considerable cracking along habit planes with free zirconium within the cracks. In the high q region ϵ' is lower than would be expected if simple increases in q or n were involved. The rather scanty evidence suggests that ϵ' has reached a limiting maximum value for the particular conditions of electrolysis used. This would imply that a change in the conductivity mechanism had occurred giving rise to an overestimation of q; though the present evidence is not conclusive previous studies of electrical conductivity show that several activation energies may be involved and thus lend some support to this interpretation. Taken as a whole the observed dielectric constant behaviour appears to be consistent with the formation during electrolysis of metallic particles.

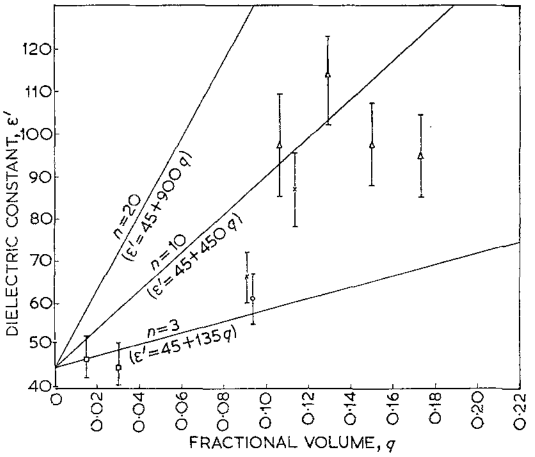

Figure 3 Comparison of data with the Sillars theory (key: crosses, specimen 8; open circles, specimen 10; triangles, specimen 13; squares, specimen 14).

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