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Dielectric properties of some hot-pressed nitrogen ceramics

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The dielectric properties of some hot-pressed nitrogen ceramics have been measured at room temperature over the frequency range 200 Hz to 75 MHz and also at 9.3 GHz; low frequency measurements were also made at temperatures up to 500° C. The materials examined were Si_3N_4, 5.0 wt % MgO/Si_3N_4 and two sialons $Si_{(6-z)} \cdot Al_z \cdot O_z \cdot N_{(8-z)}$ having $z = 4.0$ and 3.2 respectively. At room temperature, the variation of the real part of the conductivity with frequency over the range 200 Hz to 9.3 GHz followed $\sigma'(\omega) \propto \omega^n$, with $n = 0.9$. The dielectric constant ϵ', and loss $\tan \delta$, both fell slightly over this frequency range, the average values at 10^5 Hz being about 9.5 and 5.5×10^{-3}, respectively. The data fits well with the "universal dielectric law", $\epsilon'' \propto \omega^{n-1}$ $(n < 1)$ and approximately fits the Kramers–Kronig relation $\epsilon''(\omega)/(\epsilon'(\omega) - \epsilon_\infty) = \cot(n\pi/2)$. This behaviour applies also at temperatures up to 500° C except that the value of n decreases as the temperature increases. The effects may be caused by either dipolar or hopping charge phenomena.

1. Introduction

The low frequency a.c. and d.c. electrical conductivity behaviour of some hot-pressed polycrystalline nitrogen ceramics at room temperatures between 400 and 1000° C, has been reported recently [1] by the authors. Below 700° C, the a.c. conductivity $\sigma_{a.c.}$ was weakly dependent on temperature, but strongly dependent on frequency following the relation $\sigma_{a.c.} \propto \omega^n$, where $0.7 < n < 1$, while above that temperature $\sigma_{a.c.}$ became frequency independent and both $\sigma_{a.c.}$ and $\sigma_{d.c.}$ followed a $\log \sigma \propto T^{-1}$ variation. At the lower temperatures $\sigma_{d.c.}$ agreed with the relation $\sigma_{d.c.} = A \exp(-B/T^{1/4})$, and thus the conductivity data suggested that the conduction mechanism in this temperature regime was hopping. Additional support was given by the observation that the mobility, determined from Hall effect measurements, was very low ($< 10^{-4}\,cm^2\,V^{-1}\,sec^{-1}$), and the general feature that hopping is one of the most usual transport mechanisms in low mobility materials. However, the previous series of experiments were not completely unambiguous in so far as the measurements made were of complex conductivity. Dielectric measurements, on the other hand, permit the separate determination of the real and imaginary parts of the conductivity, and so allow a more reliable comparison with theory to be made. Several theories of hopping conduction, for example those of Pollak [2] and of Mott and Davis [3], indicate that a frequency dependence of the real part of the conductivity following a $\mathrm{Re}\,\sigma(\omega) \propto \omega^n$ law should be observed where $n < 1$. More recently Jonscher [4–5] has suggested that several hopping models may lead to this behaviour, and has shown further that a wide range of materials follow "universal dielectric laws" according to which $\epsilon''(\omega) \propto \omega^{(n-1)}$, and $\epsilon' - \epsilon_\infty \alpha \omega^{(n-1)}$, where again $n < 1$. The main purpose of the present work was to establish the frequency variations of dielectric constant and loss over a wide frequency range. Although the majority of the measurements were made at room temperature, a preliminary study was also made of the temperature dependencies of the frequency variations.

TABLE I Dielectric data for nitrogen ceramics at room temperature.

Sample reference	Nominal Composition	Q-meter at 10^5 Hz		Microwave at 9.3 GHz	
		ϵ'	$\tan\delta$	ϵ'	$\tan\delta$
1	Si_3N_4 (washed with NaOH) Hot-pressed at 1700° C for 1 h.	7.98	5.9×10^{-3}	3.2	1.05×10^{-2}
2	Si_3N_4–5 wt % MgO Hot-pressed at 1700° C for 1 h.	9.58	5.0×10^{-3}	5.65	4.02×10^{-3}
3	$z \approx 4.0$ sialon hot-pressed at 1700° C for 1 h.	8.71	6.02×10^{-3}	5.07	3.69×10^{-2}
4	$z \approx 3.2$ sialon	8.2	4.0×10^{-3}	–	–
Reported data on reaction-bonded materials		ϵ'	$\tan\delta$	ϵ' (8–10 GHz)	$\tan\delta$ (8–10 GHz)
Godfrey review [9]	Si_3N_4	(a) 7.2 (b) 9.4 (c) 5.8	2×10^{-2} (average)	–	–
Walton [10]	Si_3N_4	(frequency uncertain but $< 10^6$ Hz		5.6	2×10^{-3}
T.V. Andreeva *et al* [11]	6.72 wt % MgO–Si_3N_4	8 to 7 between 5×10^4 and 3×10^7 Hz	5×10^{-3} to 1×10^{-3} between 5×10^4 and 3×10^7 Hz	–	–

2. Experimental

The specimens examined in the present investigation were of the same compositions as studied previous [1]; these are listed in Table I. Most of the specimens were supplied as discs, from which thin plates were cut with a diamond wheel cutting machine; the large area faces of the specimens were polished to a 0.25 micron finish using a precision polishing machine. Specimen dimensions were typically 15 mm × 15 mm × 0.3 mm and circular gold electrodes of 1 cm diameter were evaporated on to the opposite polished faces to ensure good electrical contact.

2.1. Room temperature measurements

The dielectric properties of the specimens were measured over the frequency range 200 Hz to 50 kHz using a Wayne–Kerr bridge (Type B224) and at higher frequencies, 100 kHz to 75 MHz, with a standard Q-meter, (Marconi Type 1245). A dielectric testing jig, made with perspex insulators, of the type described elsewhere [6], was used to hold the specimen in both the techniques.

In the bridge method the conductance G and capacitance C were determined directly as functions of frequency and the data was used to derive the real part of the conductivity Re(σ), the loss tangent $\tan\delta$, and the real part of the dielectric constant (ϵ') from the relations

$$\mathrm{Re}(\sigma) = \frac{d}{A}G, \tag{1a}$$

$$\tan\delta = \frac{G}{\omega C} = \frac{\epsilon''}{\epsilon'}, \tag{1b}$$

and

$$\epsilon' = \frac{C}{\epsilon_0}\frac{d}{A}, \tag{1c}$$

where ω is the angular frequency, d the specimen thickness and A the area of the electrode. In all the specimens both G and C decreased slightly with time (by about 1%) from their initial values at frequencies below 5 kHz, but attained equilibrium values within 10 min.

In the Q-meter method, the numerical values of the required parameters can be found [6] from the corresponding set of relations;

$$\epsilon' = \frac{C_1 - C_2}{C_0} + 1$$

$$\left(C_0 = \epsilon_0 \frac{A}{d}\right)$$

$$\tan\delta = \frac{Q_1 - Q_2}{Q_1\,Q_2} \quad \frac{C_1}{C_1 - C_2} = \frac{\epsilon''}{\epsilon'}, \tag{2}$$

and

$$\mathrm{Re}\,(\sigma) = \frac{d}{A}\frac{1}{R}$$

where

$$R = \frac{Q_1 Q_2}{Q_1 - Q_2}\frac{1}{\omega}\frac{1}{C_1}$$

in which C_1 and C_2, Q_1 and Q_2 are the capacitances, and Q-values observed, respectively, without and with the specimen. At higher frequencies, a correction was applied for circuit inductance L_R, using the relation

$$C_{\mathrm{eff}} = \frac{C^*}{1 + \omega^2 L_R C^*}, \qquad (3)$$

where C^* refers to C_1 and to C_2 in turn; this correction amounted at most to about 8%. Q-meter measurements were not possible above 75 MHz, because of the difficulty in obtaining sufficiently thin large-diameter specimens. Edge corrections were applied in both techniques using the different edge correction formulae [7]. In the bridge method, Equation (1c) was modified by

$$\epsilon' = \frac{C}{C_e + C_n}. \qquad (4)$$

The edge correction for the Q-meter technique and definitions of the parameters are described in [6]. The overall accuracy of the measurements was ± 6%.

Some measurements were also made at 9.3 GHz using a microwave perturbation method [8]. In this, a specimen could be mounted at the centre of a cubical cavity (Fig. 1) and the resonant frequency and Q of the system measured with and without the specimen present. The cavity, whose internal dimension was 2.23 cm, was made of copper and had a Q of about 2640; specimens of size 5 mm × 5 mm × 1 mm were used. The real and imaginary parts of the dielectric constant were found from the relations

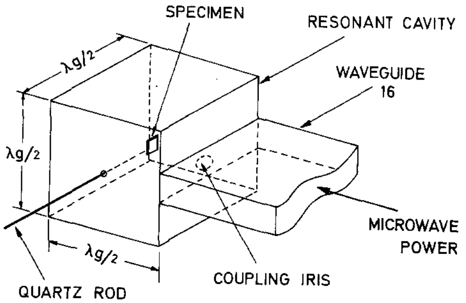

Figure 1 Cavity and specimen arrangement for measurement of dielectric properties at 9.3 GHz.

$$\epsilon' - 1 = \frac{1}{2}\frac{\Delta f}{f}\frac{V}{\Delta V} \qquad (5)$$

$$\epsilon'' = \frac{\mathrm{Re}\,(\sigma)}{\omega\epsilon_0} = \frac{1}{4}\frac{V}{\Delta V}\left(\frac{1}{Q_s} - \frac{1}{Q_0}\right)$$

and (6)

$$\tan\delta = \frac{\epsilon''}{\epsilon'}$$

in which f represents the cavity resonant frequency without the specimen but with the quartz rod in position and Δf is the frequency shift due to attaching the specimen; V and ΔV are the cavity and specimen volumes respectively, while Q_0 and Q_s are the Q-values without and with the specimen. The estimated accuracy of the microwave results, all of which were made in air at room temperature, was ± 10%.

2.2. High-temperature measurements

The high-temperature measurements were made with a specially designed jig and furnace arrangement, in which the insulator supporting the electrodes, located outside to the furnace, could be kept cool. Particular care was necessary, both in the furnace design and in shielding, to minimize pickup. The measurements were confined to frequencies below 1 MHz and the parameters G and C were found, at any particular frequency, first at room temperature and then as the specimen was heated. For temperatures below 150°C, it was found that on returning to room temperature G and C had both increased by about 5%; these effects, attributed to space charge [1], were overcome by heat-treating the specimens in air for 12 h at 65° C between successive measurements at different frequencies.

3. Results

3.1. Room temperature measurements

It was found that the frequency variations of conductivity $\mathrm{Re}\,\sigma(\omega)$, dielectric constant ϵ', and loss $\tan\delta$, were very similar in both form and magnitude for all three materials. The conductivity variation, derived directly from the experimental data assuming, as proved below, that the d.c. contribution was negligible, is shown by the continuous line of Fig. 2. Over the frequency range

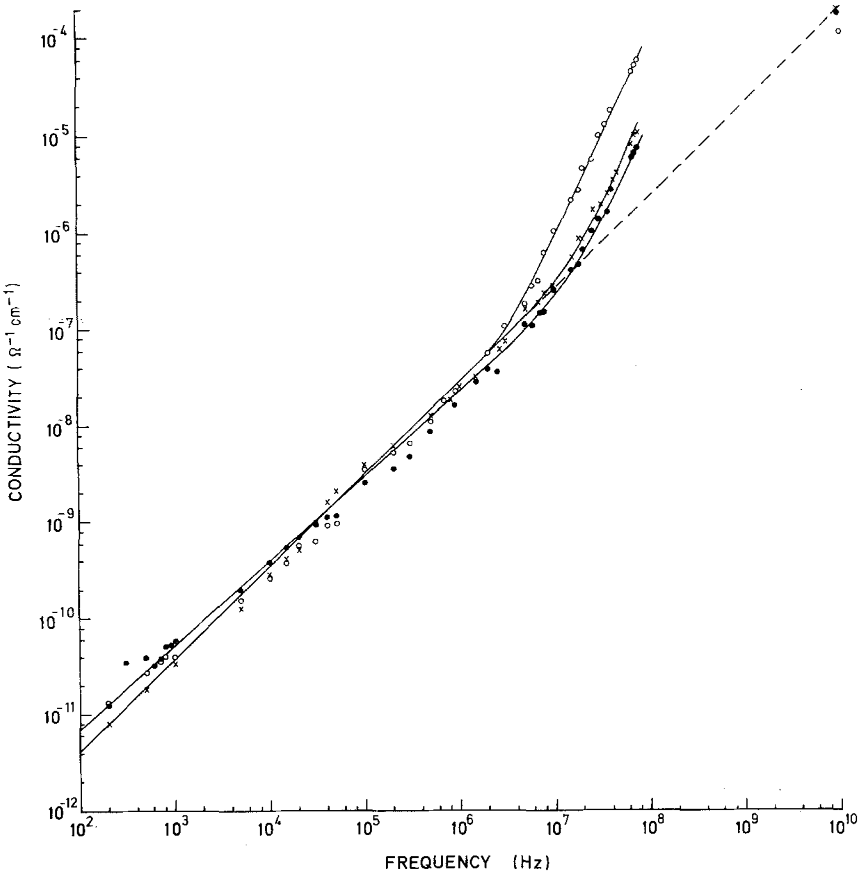

Figure 2 The frequency dependence of the real part of the conductivity Re(σ); for Si_3N_4 ●, $z = 4$ sialon X, and 5 wt % MgO/Si_3N_4 ○ at room temperature.

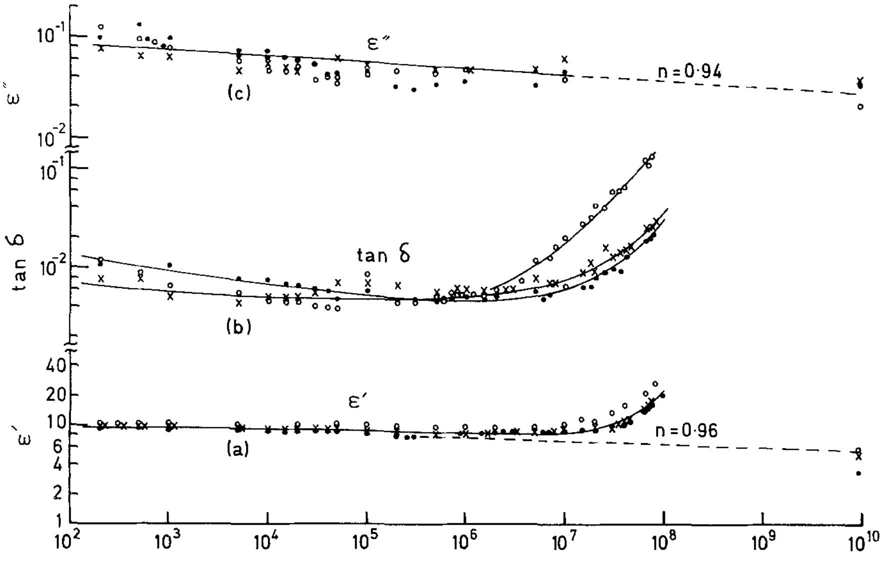

Figure 3 The frequency dependence of dielectric loss ϵ'', tan δ and dielectric constant ϵ'; for Si_3N_4 ●, 5 wt % MgO/Si_3N_4 ○, and $z = 4$ sialon X at room temperature.

200 Hz to 5 MHz, this fits well with the relation

$$\mathrm{Re}\,\sigma(\omega) \propto \omega^n, \qquad (7)$$

where n has the value 0.9. Several authors [5] have noted that high-frequency bridge and Q-meter measurements may be misleading because of the effects of small series resistances or inductances originating in the contacts and leads to the specimen. Here it is noticeable that the data obtained by the microwave cavity technique, (which is free from this shortcoming) lies close to the extrapolation of the low-frequency variation. Thus the apparent ω^2 variation above 5 MHz appears to be spurious, and we interpret the experimental data as indicating that a $\omega^{0.9}$ variation holds over the whole frequency range from 200 Hz to 9.3 GHz.

The observed variations of ϵ' and $\tan\delta$ with frequency are shown by the continuous lines of Fig. 3a and b. The experimental Q-meter data shows increases in both above 5 MHz, and these apparent rises are again thought to be spurious because the microwave data fits reasonably well on the extrapolation of the low frequency ϵ' variations. There is good agreement between the present data and that reported (Table I) on reaction-bonded materials of similar composition. The variation of ϵ'' with frequency was derived from Fig. 2 and Fig. 3a, assuming linear variation in each case; this is given in Fig. 3c.

3.2. High-temperature data

Fig. 4 illustrates the type of temperature dependence found for both $\sigma_{\mathrm{d.c.}}$ and $\mathrm{Re}\,\sigma(\omega)$; it refers specifically to the $z = 3.2$ sialon, but the other two ceramics gave similar results thought with less marked linearity at high temperatures. The general pattern confirms the observations made in the earlier conductivity studies [1] and shows that whereas a single activation energy may be used at high temperatures, this does not apply at lower temperatures; here the activation energy is finite though small and decreases with increasing frequency. The salient feature is that the d.c. contribution to the conductivity is negligible even at high temperatures.

The effects of temperature on the frequency variations of ϵ'' and ϵ' are shown in Fig. 5. Because of the occurrence of errors in the high frequency measurements noted above, measurements were restricted to frequencies below 10^5 Hz. Up to 773 K the variation of ϵ'' with ω still follows the

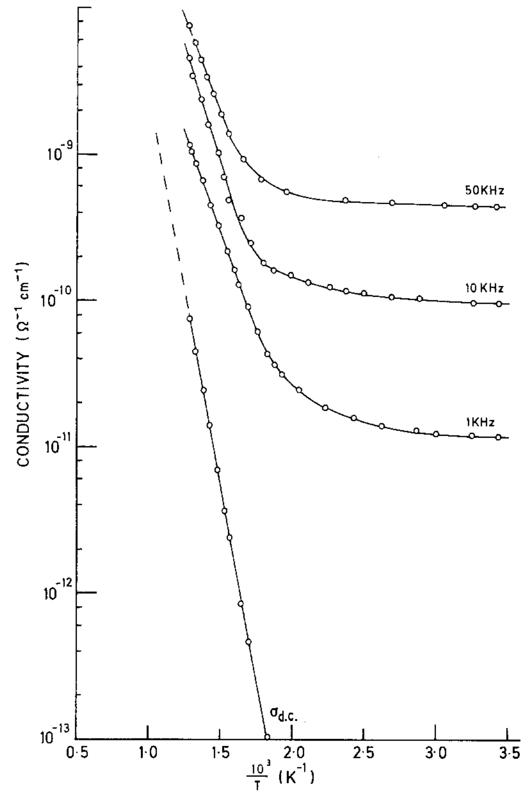

Figure 4 Temperature and frequency variation of the real part of conductivity for $z = 3.2$ sialon.

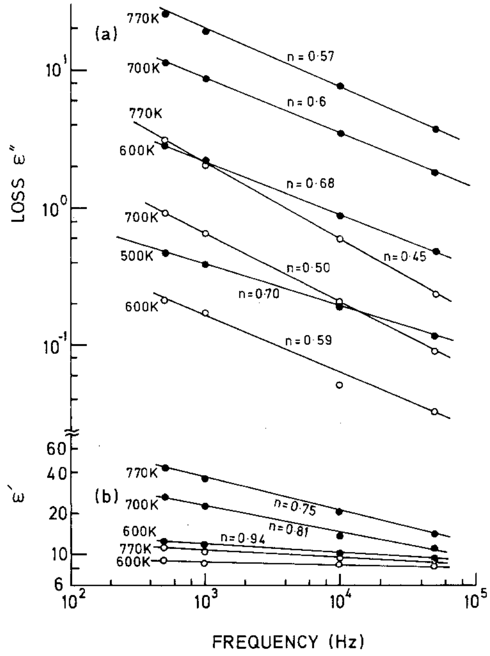

Figure 5 Typical temperature variations of the power law Characteristics of (a) $\epsilon'' \propto \omega^{n-1}$ and (b) $\epsilon' \propto \omega^{n-1}$ for 5 wt% MgO/Si$_3$N$_4$ ●, and $z = 3.2$ sialon ○.

form $\epsilon'' \propto \omega^{n-1}$, but n decreases as the temperature increases; for $z = 3.2$ sialon the change is from $n = 0.94$ at 291 K to $n = 0.44$ at 770 K, and for 5% MgO/Si_3N_4 from $n = 0.90$ at 291 K to $n = 0.57$ at 770 K. There is a smaller effect of temperature on ϵ', Fig. 5b. The dielectric constant data suggested that ϵ' followed $\log \epsilon' \propto T$ rather better than $\log \epsilon' \propto T^{-1}$.

4. Discussion

In a wide range of low-conductivity materials it is generally found that the frequency dependence of the conductivity involves two components, such that the measured conductivity $\sigma_m(\omega)$ is related to the true conductivity $\sigma'(\omega)$ by

$$\sigma_m(\omega) = \sigma'(\omega) + \sigma_{d.c.}, \qquad (8)$$

and that the frequency variation of $\sigma'(\omega)$ follows

$$\sigma'(\omega) \propto \omega^n \qquad (9)$$

where usually $0.7 < n < 1$ at low temperatures. There is general agreement that the a.c. conductivity in hopping systems will follow Equation 9, but there are several approaches, e.g. those of Mott and Davis [3], Pollak [2] and Jonscher [4–5] to the detailed mechanisms involved. With the present materials the experimental evidence indicates that $\sigma_{d.c.}$ is negligible and that $\sigma'(\omega)$ is proportional to ω^n with $n = 0.9$ at room temperature over eight frequency decades up to 9.3 GHz. The precise details of the hopping mechanisms involved are not yet clear although it appears that Mott's law [3] cannot apply, since the Mott formulae predict a continuous curvature convex upwards which is not observed.

The room temperature dielectric loss data fit well with the "universal law" suggested by Jonscher [4–5] according to which

$$\epsilon'' \propto \omega^{n-1} \text{ where } n < 1 \qquad (10)$$

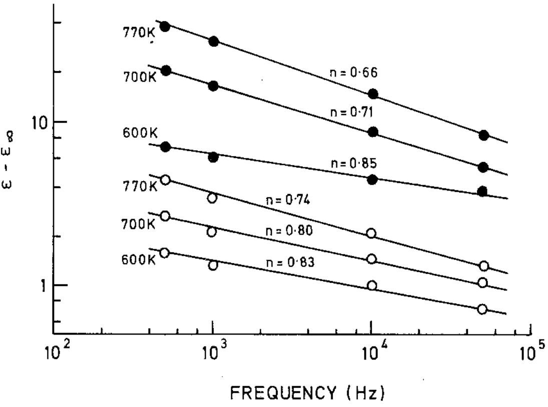

Figure 6 Temperature variations of the power law characteristics of $(\epsilon' - \epsilon_\infty) \propto \omega^{n-1}$.

and

$$\epsilon'' = \frac{\sigma'(\omega)}{\epsilon_0 \omega}. \qquad (11)$$

In many disordered materials, amorphous semiconductors and insulators, this law is obeyed, and a striking feature is that in all these materials the loss falls in a narrow band only two decades wide on the loss axis. The room temperature variation for the nitrogen ceramics covers only one decade in loss. The law is also obeyed at temperatures up to at least 770 K, although the value of n falls progressively, as shown in Fig. 5, as the temperature increases in agreement with theory [4].

A tentative analysis of the dielectric constant data has been attempted in the following way. An estimate of the limiting value ϵ_∞ was made by extrapolating the variation at each individual temperature to 9.3 GHz. The values of $(\epsilon' - \epsilon_\infty)$ so obtained are plotted in Fig. 6 as $\log(\epsilon' - \epsilon_\infty)$ versus $\log f$ at different temperatures. It is found that these follow $(\epsilon' - \epsilon_\infty) \propto \omega^{n-1}$ with values of n decreasing from 0.95 at room temperature to 0.65 at 770 K. At any temperature, the value of n

TABLE II Comparison of values of the exponent n obtained by different methods at various temperatures.

Temperature (K)	n from $\epsilon' - \epsilon_\infty$		n from ϵ''		Measured average $\epsilon''/\epsilon' - \epsilon_\infty$		Expected value of n $(2/\pi)\cot^{-1}[\epsilon''/(\epsilon' - \epsilon_\infty)]$	
	MgO/Si_3N_4	$z = 3.2$ sialon	MgO/Si_3N_4	$z = 3.2$ sialon	MgO/Si_3N_4	$z = 3.2$ sialon	MgO/Si_3N_4	$z = 3.2$ sialon
291	0.96	0.96	0.92	0.93	1.58×10^{-2}	1.26×10^{-2}	0.98	0.99
500	0.88	–	0.70	0.77	0.12	–	0.92	–
600	0.85	0.83	0.68	0.59	0.31	0.103	0.81	0.93
700	0.71	0.80	0.60	0.50	0.49	0.30	0.71	0.81
770	0.66	0.74	0.57	0.45	0.61	0.51	0.65	0.70

in the $(\epsilon' - \epsilon_\infty)$ variation is higher than the corresponding value in the $\epsilon'' \propto \omega^{n-1}$ law. The ratio of $\epsilon''(\omega)$ to $(\epsilon'(\omega) - \epsilon_\infty)$ approximately satisfies the Kramers–Kronig relation

$$\frac{\epsilon''(\omega)}{(\epsilon'(\omega) - \epsilon_\infty)} = \cot\left(n\frac{\pi}{2}\right), \qquad (12)$$

which can apply to either non-Debye dipolar or to hopping carrier systems. This is illustrated by Table II in which a comparison is made, for different temperatures, of the values of n obtained from the ϵ'' and $(\epsilon' - \epsilon_\infty)$ variations with those derived from Equation 12 by substitution of the experimental values of the ratio $\epsilon''/(\epsilon' - \epsilon_\infty)$. The effects of both frequency and temperature variations are noticeably smaller on ϵ' than on ϵ''; this implies that the carriers make a relatively small contribution to ϵ', a feature characteristic of the hopping mechanism suggested recently by Jonscher [12].

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