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D.C. electrical properties of hot-pressed nitrogen ceramics

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The d.c. electrical properties of some hot-pressed polycrystalline nitrogen ceramics have been measured between 18 and 500° C in applied electric fields up to 1.1×10^4 V cm^{-1}. The materials examined were Si_3N_4, 5 wt%, MgO/Si_3N_4 and two sialons having $z = 3.2$ and $z = 4.0$. The conduction in all the materials showed similar general features. The time dependent charging (I_C) and discharging currents (I_D) were observed which followed a $I(t) \alpha t^{-n}$ law at room temperature with $n = 0.7$ to 0.8. The exponent n for I_C decreased with increasing temperature. The current density–field (J_s–E) characteristics were ohmic in applied fields of less than 3×10^3 V cm^{-1}; conductivity increased with electric field above that range. Above about 280° C, σ was independent of E, its temperature dependence following $\log \sigma \propto T^{-1}$. Below about 230° C conductivity fitted a $\sigma \propto \exp(-B/T^{1/4})$ law in both low and high fields. There is a good correlation between the temperature and field variations of time dependent current and the steady current. The conductivities were in the range of 10^{-15} to 10^{-16} Ω^{-1} cm^{-1} at 18° C and rose to 4×10^{-10} to 2×10^{-12} Ω^{-1} cm^{-1} at 500° C. The activation energies were in the range of 1.45 to 1.80 eV and 0.05 to 0.15 eV at above 300° C and near room temperature respectively. Various models to explain the data are considered.

1. Introduction

The d.c. and low frequency a.c. electrical conductivity behaviour of some hot-pressed polycrystalline nitrogen ceramics at temperatures between 400 and 1000° C has been reported [1] by the authors. At low temperatures the a.c. conductivity σ_{ac} was weakly dependent on temperature but strongly dependent on frequency following the relation $\sigma_{ac} \propto \omega^n$; where $0.7 < n < 1$ while at high temperatures σ_{ac} became frequency independent and both σ_{dc} and σ_{ac} followed a $\log \sigma \propto T^{-1}$ variation suggesting that the conduction mechanism is 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}). The temperature dependent conduction and the precise nature of the mechanism were not established from these measurements. Further the dielectric properties of the materials over the frequency range 200 Hz to 9.3 GHz at room temperature and at high temperatures up to 500° C have been reported recently [2] by the authors. The conductivity followed $\sigma(\omega) \propto \omega^n$ and approximately satisfied the Kramers–Kronig relation

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

where $0.5 < n < 0.95$ decreased with increasing temperature. This behaviour suggested that the conduction was due to either non-Debye dipolar or hopping processes. However, without detailed study of the d.c. electrical properties at elevated temperatures it is difficult to establish the precise nature of conduction and the nature of the charge carrier [3]. The purpose of the present work was to investigate the d.c. electrical properties especially in the range from room temperature to 500° C omitted in the previous measurements. Information about the nature of hopping conduction processes can be obtained from electric field and temperature dependence of the d.c. conductivity e.g. Jonscher and Hill [3] and Mott and Davis [4]. Further information can be obtained from time dependence of the charging and discharging currents at different

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temperatures which generally follow the Universal law of dielectric response, i.e. $I(t) \propto t^{-n}$ with $0.5 < n < 0.8$, (n decreases with increasing temperatures). These effects have been analysed by Johscher [5]. High fields effects give confirmation of the mode of conduction inferred from low field measurements [13]. Here the time variations of the charging and discharging currents were studied, together with their field and temperature dependencies.

2. Experimental

The specimens used in the present investigation were Si_3N_4, 5 wt% MgO/Si_3N_4 and two sialons having $z = 3.2$ and $z = 4.0$ of the same composition as mentioned in the previous work [1, 2]. Thin plate specimens with circular gold electrodes were used as before [2]. This type of specimen and electrode arrangement made the surface path greater than the thickness so that the surface contribution in the total conduction was reduced considerably [6]. The d.c. electrical properties of the specimens in applied fields up to about $1.1 \times 10^4 \text{ V cm}^{-1}$ were measured using two probe pressure contact methods over the temperature range between 18 and 500° C in an ambient of air, the upper temperature limit being determined by the need to avoid gold diffusion into the specimen. The apparatus and the special jig arrangement for measurement at the above mentioned temperature range are shown in Fig. 1. Special precautions were taken to minimize possible errors in the results, as described by Tallan [6]. Signals due to thermal noise and the atmosphere around the specimens, as well as the circuit arrangement, were minimized by using a brass tube as the inner wall of the furnace and shielded earthing connections. The perspex insulator used to separate the electrodes was outside of the furnace, where it could be kept cold. The apparatus was first tested by measuring the resistance of a standard high value resistor of $10^{13}\ \Omega$. Small currents of about 5×10^{-14} A were able to be measured with the d.c. amplifier (Elliott Process Inst. Ltd). With the voltages applied (<350 V) across the electrodes the total leakage current (without specimen) between them was less than 1×10^{-13} A. Under all circumstances the experimental error did not exceed about ±10%.

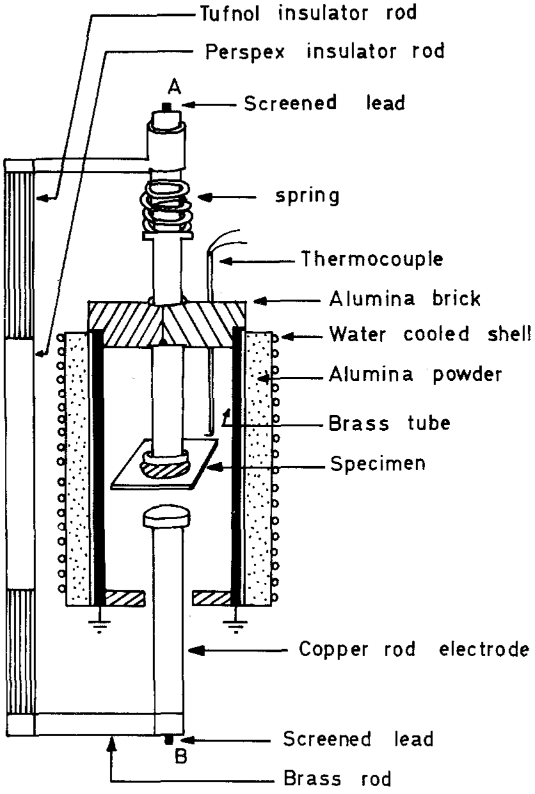

Figure 1 Apparatus for measuring d.c. electrical properties at high temperatures.

The decaying, steady and discharging currents were measured under different applied fields up to about $1.1 \times 10^4 \text{ V cm}^{-1}$ between 18 and 500° C. Two series of measurements were performed on each specimen. In the first, a voltage was applied and the current allowed to reach a steady value I_s. The applied voltage was then removed and the specimen was short-circuited via the current measuring unit until the observed reverse current had decayed. The next higher voltage was then applied and the process repeated at each increment. The whole series of measurements took more than 6 days per specimen. In the second method once the steady current was reached, next voltage was applied without discharging. The times taken to reach subsequent steady current values were much shorter. The steady currents obtained by the two methods at room temperature were the same within the limits of experimental error. The second method was used to measure the steady currents at room temperature and the high temperature measurements were made using the first method. The temperature variation of the steady current was found by first allowing equilibrium to be reached at room temperature and then raising the temperature successively. This data was used to derive the temperature variation of conductivity. Specimens which had previously been heated often

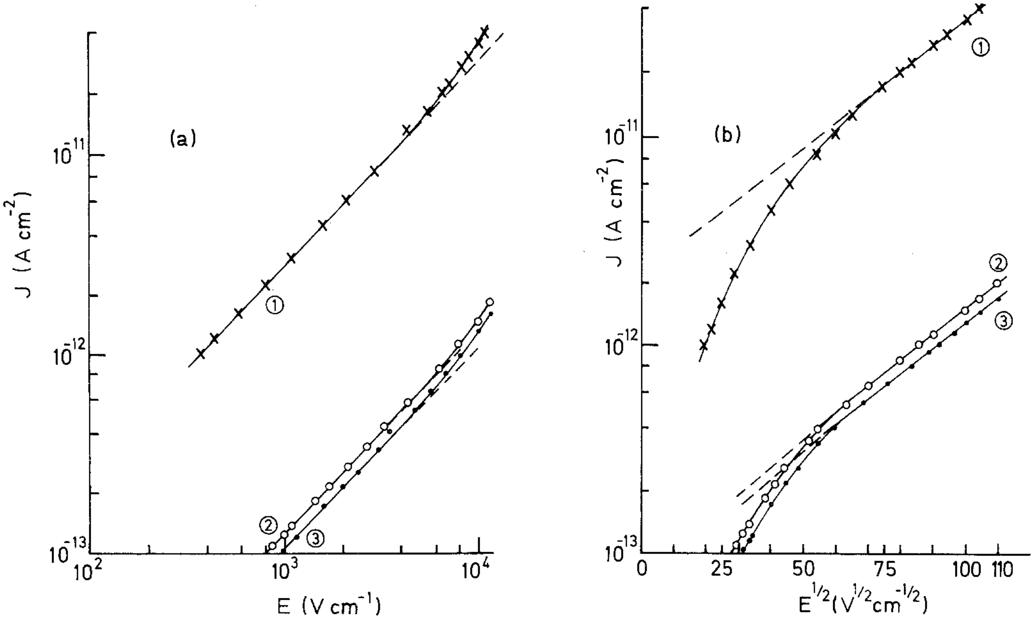

Figure 2 (a) Log J versus log E and (b) Log J versus $E^{1/2}$ for (1) Si_3N_4 (x); (2) 5 wt% MgO/Si_3N_4 (o) and (3) $z = 4.0$ sialon (•) at room temperature.

showed space-charge effects at temperatures below about 130° C. This behaviour was reduced by giving the specimen a heat treatment in air (65° C for 20 h) while short-circuited between successive sets of measurements at different fields. Similar treatments were applied to measure the temperature and field variations of the decaying and discharging currents in order to discharge the specimen completely between successive stages of measurement.

3. Results

3.1. Steady current behaviour

Particular interest attaches to the variations of the steady current with field and temperature. The electrical properties were very similar in all the materials examined. The variation of steady current with applied field at room temperature is shown in Fig. 2, in which the current density J was obtained from I_s by division by the known electrode area. In Fig. 2a the plot of log J versus log E is a linear at low electric fields ($<3\,kV\,cm^{-1}$) but is not at high electric fields. The same data are replotted in Fig. 2b, which shows that log J versus $E^{1/2}$ is a straight line in the high electric field region. The conductivity is almost independent of E in the low applied fields but in the high field region varies as $\log \sigma \propto E$ (Fig. 3). The temperature variations of conductivity for the three specimens at a low applied field are shown in Fig. 4 in which log σ is plotted as a function of inverse temperature. The relationship between log σ and T^{-1} is linear between 773 and 550 K and becomes non-linear at lower temperatures; consequently the activation energy in the higher temperature region is constant, but below 550 K it decreases slowly with decreasing temperature. Values for activation energies (E_A) were calculated from the relation

$$\sigma = \sigma_0 \exp(-E_A/kT) \qquad (1)$$

in the linear high temperature region and from the slopes of the curves at lower temperatures; these are listed in Table I. The pre-exponential factor

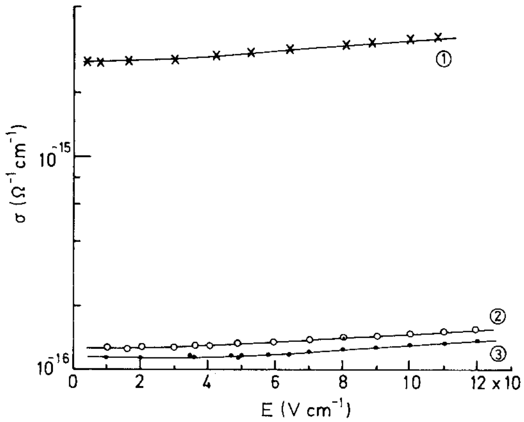

Figure 3 Log σ versus E for (1) Si_3N_4 (x); (2) 5 wt% MgO/Si_3N_4 (o) and (3) $z = 4.0$ sialon (•) at room temperature.

TABLE I D.C. electrical parameters of nitrogen ceramics used in the present investigation.

Sample reference	Nominal composition (hot-pressed)	D.C. conductivity (Ω^{-1} cm^{-1})		High temperature region		Low temperature region		Characteristic hopping length '*a*' (Å)	μ_D (cm^2 V^{-1} sec^{-1})	Exponent *n* at 18° C	
		500° C	18° C	E_A (eV)	σ_0 (Ω^{-1} cm^{-1})	E_A (eV)	B (Ω^{-1} cm^{-1} K$^{1/4}$)			I_c	I_d
1	Si_3N_4	3×10^{-10}	1.8×10^{-15}	1.46	1.0	0.08	75	72	1.7×10^{-8}	0.80	0.80
2	5 wt% MgO/Si_3N_4	2×10^{-12}	1.2×10^{-16}	1.8	1.0	0.15	83	58	5.4×10^{-9}	0.85	0.80
3	$Si_{6-z}Al_zO_zN_{8-z}$ with $z = 3.2$	1.5×10^{-11}	7×10^{-17}	1.45	0.05	0.05	53	–	7.35×10^{-8}	0.70	0.80
4	$Si_{6-z}Al_zO_zN_{8-z}$ with $z = 4.0$	–	1×10^{-16}	–	–	–	–	62	6.15×10^{-8}	0.70	0.80

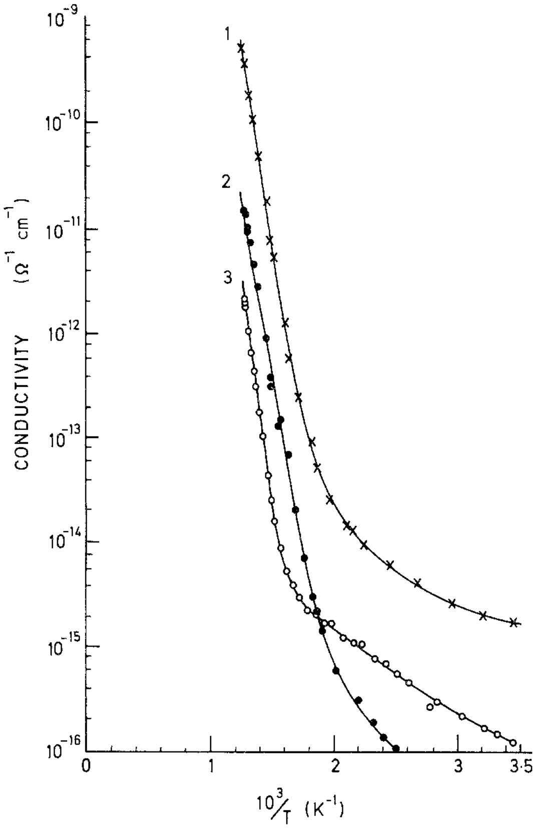

Figure 4 Temperature variation of d.c. conductivity for (1) Si_3N_4 (x); (2) 5 wt% MgO/Si_3N_4 (○) and (3) $z = 3.2$ sialon (●).

was calculated from the linear high temperature region and gives $\sigma_0 \sim 1\,\Omega^{-1}\,cm^{-1}$. In Fig. 5 the effect of different applied fields on the temperature variations are shown for $z = 3.2$ sialon. The conductivity is independent of applied fields at temperature above about 550 K; below that, the conductivity increases with applied field and is weakly dependent on temperature. The slopes of the log σ versus E plots decrease slowly with increasing temperatures. It is noticeable that the conductivity of sialon is less than that of MgO/Si_3N_4 below 525 K and the former is higher above that temperature. The conductivity of Si_3N_4 is more than one order of magnitude higher than both sialons and MgO/Si_3N_4 throughout the temperature range.

3.2. Time dependent behaviour

The charging and discharging currents of 5 wt% MgO/Si_3N_4 and $z = 3.2$ sialon at different temperatures under a low constant field are shown in Fig. 6a and Fig. 7 respectively. The time for the current to decay to the steady value (I_s) varied from 2 to 15 h, depending on the temperatures; the shortest times were for high temperatures. Initially the charging current followed $I \propto t^{-n}$ but during the subsequent slower decrease the characteristic showed a fluctuation, for all materials, before levelling off to a steady value. The time of occurrence of the fluctuation region is almost independent of temperature. The exponent n lies between 0.70 and 0.80 at room temperature and decrease with increasing temperature to about 0.4 at 400° C.

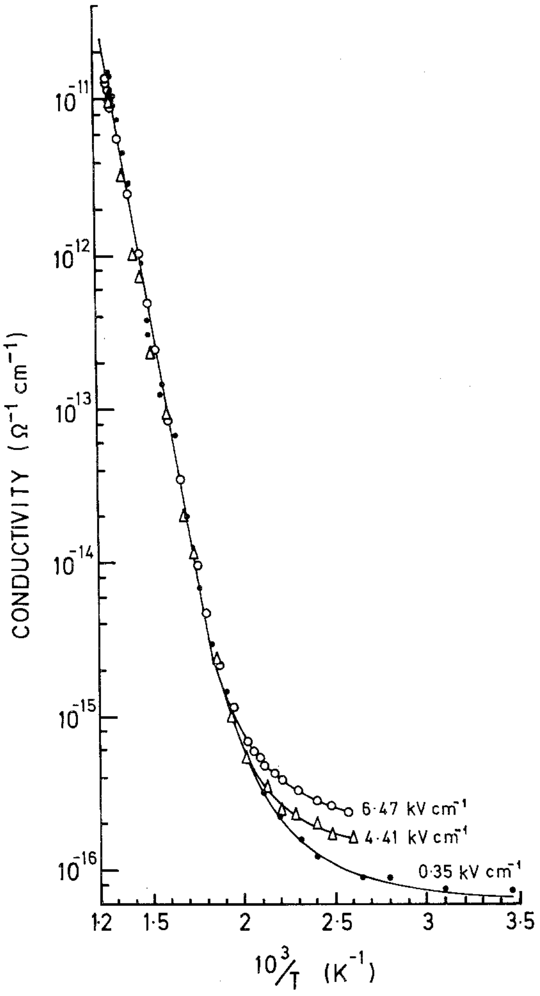

Figure 5 Temperature dependence of conductivity for $z = 3.2$ sialon at different applied fields.

The discharging currents were always of opposite polarity to the charging current following the same t^{-n} law with $n = 0.8$, almost independent of temperature. The temperature variation of I_c and I_d for 5 wt% MgO/Si_3N_4 after $t = 0$, i.e. 90 and 120 sec (Fig. 6a) is replotted in log I versus T^{-1} (Fig. 8a). Two distinct temperature dependences of

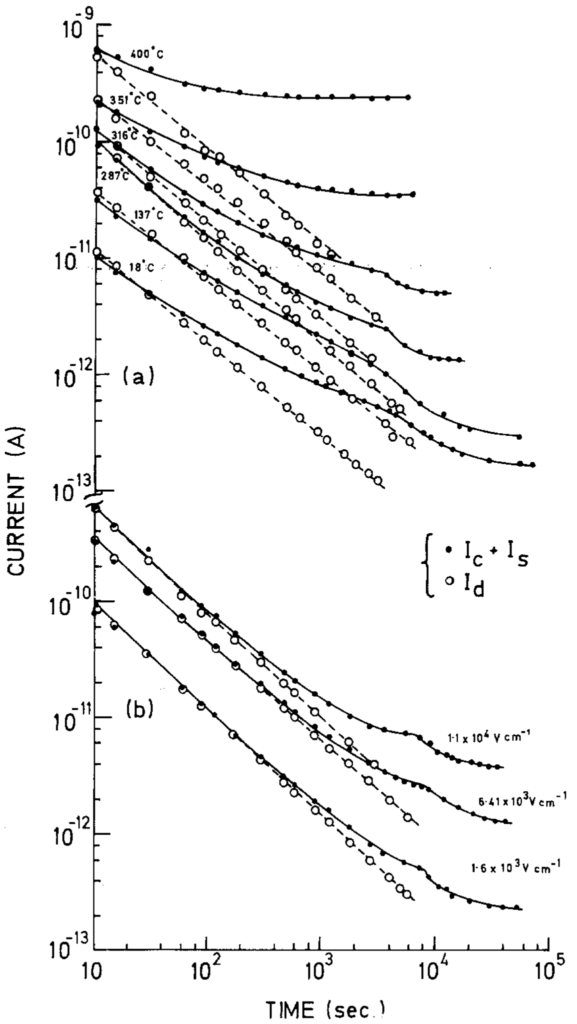

Figure 6 (a) Typical charging and discharging currents for 5 wt % MgO/Si_3N_4 at different temperatures under an electric field 1.6 kV cm^{-1}, (b) Field dependence of charging and discharging currents for the same specimen at 232° C.

both I_c and I_d are observed the transition occurring at 555 K. Although the log I_d versus T^{-1} plots are linear in both the high and low temperature parts the slopes differ; the log I_c versus T^{-1} plots show a similar transition but are not quite so linear. The temperature variation of I_c is very similar to that of I_s (Fig. 4) and the activation energies derived from the temperature variation of I_c agreed well with those derived from I_s.

The charging and discharging currents for the same specimen in different applied fields at a constant temperature are given in Fig. 6b. This shows that n is almost independent of applied field and that the time taken to reach a steady value of the charging current decreases slightly with increasing field. At high fields I_c following the t^{-n} law is observed for a longer time. Similar fluctuations are observed at high fields but the times at which they

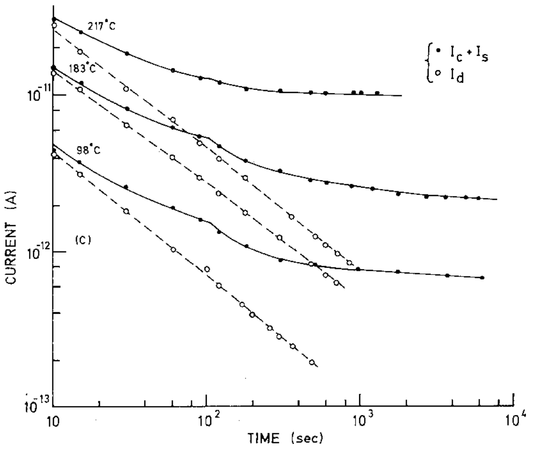

Figure 7 Typical charging and discharging currents for $z = 3.2$ sialon at different temperatures under a constant applied field (1.7 kV cm^{-1}).

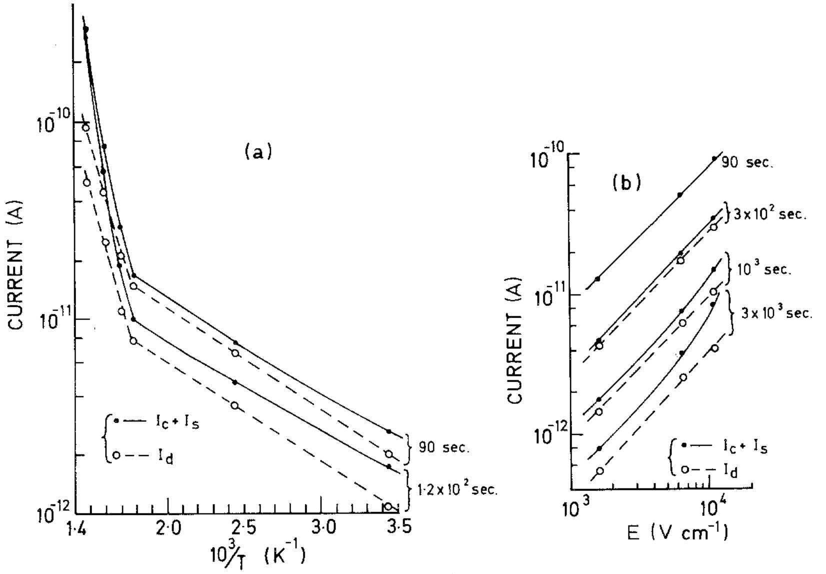

Figure 8 (a) Temperature dependence of charging and discharging currents, (b) Field dependence of charging and discharging currents. Data replotted from Figs. 6a and b respectively.

occur become shorter with increasing field. This behaviour is significant and its effect will be discussed in Section 4. In general I_c is higher than I_d at high temperatures and at high fields. Some typical values of I_c and I_d after 90 sec, 3 × 10^2 sec, 10^3 sec and 3 × 10^3 sec taken from Fig. 6b are replotted as $\log I$ versus $\log E$ in Fig. 8b. The $\log I_c - \log E$ plot is initially linear at both low and high fields and gradually becomes non-linear with increasing time in the high field region. The variation of $\log I_d$ is linear throughout which implies that I_d obeys Ohm's law to much higher fields than does I_c. The slopes of I_c and I_d and their variations with E are exactly the same as those of I_s (Fig. 2a). Similar effects were noted in other specimens, though the times involved varied somewhat.

4. Discussion

4.1. Steady current behaviour

4.1.1. Low fields

The low fields steady-current behaviour clearly shows that the $\log J$ versus $\log E$ characteristic is linear (Fig. 2) and the slope (1.01) shows that Ohm's law is obeyed. The temperature dependence of conductivity in this region shows that the activation energy, E_A is constant at temperatures above about 555 K; below that temperature E_A decreases slowly with decreasing temperature and reaches finite values near room temperature in the range of 0.06 to 0.09 eV for different materials. One would expect $\sigma \propto \exp(-B/T^{-1/4})$ law to be followed at low temperatures [3, 4, 8], where B is constant. Within experimental error the conductivity data below about 525 K agrees well with $\ln \sigma \propto T^{-1/4}$. The value of B calculated from the slope of $\ln \sigma$ versus $T^{-1/4}$ was in the range of 50 to 80 for the four materials. This behaviour is characteristic of variable range hopping conduction by carriers with energies near the Fermi level [3, 4, 7]. Similar values of E_A and B have been observed in many amorphous semiconductors. According to theory, the $T^{-1/4}$ law occurs at low temperatures and requires $E_a < 10\,kT$, therefore this condition is met in the present results where $10\,kT \approx 0.3$ eV below 400 K and E_A was less than 0.09 eV. In the previous work [1] however, although the data fits to a $T^{-1/4}$ law an interpretation on the same basis does not seem to be valid in the range 600 to 900 K because $E_A \sim 1.0$ eV. At high temperatures, the value of E_A (approximately 1.5 eV) and the pre-exponential factor $\sigma_0 \sim 1\,\Omega^{-1}\,\text{cm}^{-1}$ favour interpretation as hopping by carriers excited into the localized states near the edge of the conduction or valence bands [4].

4.1.2. High fields

The departure from a $\log J \propto \log E$ variation in the J–E characteristic may be due to several effects as noted by Jonscher and Hill [3], Hill [8], and Pollak and Reiss [9]. In the case of percolation theory and variable range hopping conduction near the Fermi level, the field dependence of conductivity can be expressed as

$$\sigma \propto \exp(eFa/kT) \qquad (2)$$

where a is the characteristic hopping length and F

is a linear function of applied field. The $\log \sigma$ versus E plots are linear at room temperature (Fig. 3), fitting well with Equation 2. This relation also applies at temperatures up to 550 K but the slope $\log \sigma$ versus E decreases with increasing temperature (Fig. 5). The values of "a" calculated from the slopes at room temperature were in the range of 60 to 72 Å; these are listed in Table I. The data from Fig. 5 shows that "a" decreases with increasing temperature. It corresponds to the extension of the low field $T^{-1/4}$ law beyond the ohmic region. The effect of the field should be greater as the average hopping distance increases; i.e. for lower temperatures and for low densities of states.

An alternative explanation would suppose that there may be a field-assisted contribution to the bulk dominated current due to the Poole–Frenkel effect [3] given by

$$\log J_{\mathrm{PF}} = \text{constant} + \frac{e\beta E^{1/2}}{kT} \qquad (3)$$

where $\beta = \{e/\pi\epsilon'\epsilon_0\}^{1/2}$ is the Poole–Frenkel constant and ϵ' is the high frequency dielectric constant of the material. This shows that a graph of $\log J$ versus $E^{1/2}$ ought to give a straight line with a slope $e\beta/kT$. A fit to $\log J$ versus $E^{1/2}$ for nitrogen ceramics is observed at room temperature (Fig. 2b), but the value of $\epsilon' = 1.2$ derived from the relation [3] is smaller than experimentally measured microwave value $\epsilon' = 4.5$ [2]. Although the value of ϵ' at optical frequencies may be somewhat less than the microwave value quoted, the fit to Equation 3 does not seem good. Moreover, at temperatures above 550 K, σ is independent of E (Fig. 5) which implies that there is no field-assisted contribution.

4.2. Decaying and discharging currents behaviour

At any given temperature the time dependence of the charging and discharging current follows the Universal Law of dielectric response suggested by Jonscher [5].

$$I(t) \propto t^{-n} \qquad (4)$$

with $n < 1$. The present measurements give values of n derived from I_c and I_d between 0.7 and 0.8 at room temperature, from the I_c data it was found that n decreases to 0.45 at 673 K. The exponent n is almost independent of applied field up to $10^4\,\mathrm{V\,cm^{-1}}$ (Fig. 6b). This behaviour has been observed in many amorphous materials and insulators. Jonscher [5] and Lewis [10] have suggested that Equation 4 provides an alternative treatment equivalent to the frequency domain approach which results in the Universal dielectric loss law $\epsilon''(\omega) \propto \omega^{n-1}$ or $\sigma'(\omega) \propto \omega^n$ with $n < 1$. This type of loss behaviour has been observed previously [2] in these materials. Comparison of the n values obtained by both methods shows very close agreement, both in respect of the room temperature magnitudes and the temperature variations. Further analysis shows that the temperature dependences of I_c and I_d (Fig. 8a) are very similar of I_s (Fig. 4). Two distinct temperature dependent regions of I_c and I_d, above and below about 550 K, are observed and the activation energies from I_c are 1.4 eV and 0.06 eV respectively. It is relevant to mention that similar temperature dependences of $\sigma'(\omega)$ and $\epsilon'(\omega)$ of the same materials have been reported [2] and the values of E_A derived from $\log \sigma'(\omega)$ versus T^{-1} above and below $T_t = 550$ K were very similar; only at low temperatures were the activation energies found to decrease slowly with increasing frequency. Comparison of Figs. 2 and 8b shows that the slopes of $\log I_c$ versus $\log E$ and also of $\log I_d$ versus $\log E$ are very similar to the steady current variation below the transition temperature 550 K. At short times the relation of I_c is linear over the whole field range but at longer times there is a tendency for non-linearity at high fields.

The behaviour discussed in this section may be due to the following mechanism. Most available carriers in the system respond initially to the applied field; later they are impeded by having to make difficult hops over longer distances; this may lead to "piling up" of other carriers behind those so held up, ultimately giving a steady value after a long time. The tendency for non-linearity at high fields may be due to nearest neighbour correlation between successive hops and increased critical links in the percolation paths [9]. This evidence indicates further that the origin of the low and high field conduction mechanisms is probably the same as discussed before. It seems that the d.c. conduction is likely to be determined by the most difficult hops where bottlenecks occur, while in a.c. conductivity the carriers hop back and forth over a limited number of "easy hops". On the basis of this the value of σ_{dc} is expected to be lower by some orders of magnitude than that of $\sigma'(\omega)$; this difference is observed in these materials. The above analysis suggests that the dominant d.c.

conduction mechanism is hopping. Further, the correlation between the temperature variations of d.c. and a.c. parameters and especially the similarity between the respective activation energies show a strong evidence for the conduction being due to hopping charge carriers rather than dipoles. If the mechanism were dipolar, the d.c. and a.c. responses would not be expected to correlate at all [5].

Some comments may be made about space charge effects. Jonscher has proved that if these are present the I_c and I_d curves will intersect (under conditions of high field and high temperature) so that, at sufficiently short times $I_d > I_c$; in the absence of space charge there is no intersection and $I_c > I_d$ at all times. In almost all the experimental data, $I_c > I_d$ and no intersections at high field and high-temperature were observed. This confirmed that the heat treatment given to the specimens (Section 2) was effective in minimizing space charge and thus it can be assumed that the behaviour is due to dielectric response of a bulk-dominated time-domain current.

As mentioned earlier slight fluctuations in the decays of I_c are observed (Figs. 6 and 7). The effect has been reported for other materials and several explanations of this behaviour have been given. The most recent explanation is a transit time effect for injected carriers [11]. On this assumption the results shown in Figs. 6a, and b, and Fig. 7, have been used to calculate drift mobilities from the relation

$$\mu_D = d/t_t E \tag{5}$$

where d, t_t and E are the thickness of the specimen in cm; the transit time in seconds and the electric field in $\mathrm{V\,cm^{-1}}$ respectively; these are listed in Table I. The fluctuation time is almost independent of temperature which implies that μ_D is independent of temperature. Similar effects were noted for other specimens. This very low value of mobility coupled, with its temperature independence, further supports the concept of conduction in the localized states.

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