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Electrical conductivity in hot-pressed nitrogen ceramics

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The a.c. and d.c. electrical conductivities of some hot-pressed polycrystalline nitrogen ceramics have been measured between 400 and 1000° C. The materials examined were Si_3N_4, 5.0% MgO/Si_3N_4 and two sialons, $Si_{(6-z)} \cdot Al_z \cdot O_z \cdot N_{(8-z)}$ having $z \approx 3.2$ and $z \approx 4.0$ respectively. The electrical behaviour of all the materials showed similar general features. The d.c. conductivities were about $10^{-10}\ \Omega^{-1}\ cm^{-1}$ at 400° C and rose to between 10^{-6} and $10^{-5}\ \Omega^{-1}\ cm^{-1}$ at 1000° C. The a.c. data, taken over the frequency range 15 Hz to 5 kHz showed that below about 500° C the a.c. conductivity ($\sigma_{a.c.}$) varied with frequency as $\sigma_{a.c.} \propto \omega^s$ where $0.7 < s < 1$ indicative of a hopping process; in this temperature range the d.c. conductivity ($\sigma_{d.c.}$) agreed well with the relation $\sigma_{d.c.} = A \exp(-B/T^{1/4})$. Above 700° C both the a.c. and d.c. conductivities followed $\log \sigma \propto T^{-1}$. Hall effect and thermoelectric power measurements enabled the Hall mobility to be estimated as less than $10^{-4}\ cm^2\ V^{-1}\ sec^{-1}$ at 400° C and showed that the materials were all p-type below 900° C and n-type above 900° C. The electrical properties of all four materials are consistent with the presence of a glassy phase.

1. Introduction

Silicon nitride, β-Si_3N_4 has been established for some years as a refractory ceramic. It has a wide range of applications; as a bulk polycrystalline material many of these utilize primarily the advantageous heat resistant and mechanical properties, as in heat exchangers and turbine blades, while in its thin film form silicon nitride has been used as an insulator in electronic semiconductor devices. Recently a new range of nitrogen ceramics, the sialons, have been developed [1–3] as alternative high strength refractory materials. These were first thought to have the general formula $Si_{(6-0.75x)}Al_{0.67x}O_xN_{(8-x)}$ where x, the number of nitrogen atoms in the unit cell replaced by oxygen, varied from 0 to 5. It is now established (see Jack [23]) that the homogeneity range is given by $Si_{6-z}Al_zO_zN_{8-z}$ where z reaches a maximum of about 4.2. Additional metal atoms, such as magnesium or lithium, together with aluminium may replace silicon if the metal:non-metal atom ratio is maintained at 3:4 together with appropriate charge compensation. X-ray studies have shown that the crystal structures of this range of solid solutions are hexagonal and similar to that of β-Si_3N_4 but with increased lattice parameters. A potential advantage of the sialons is that they may offer flexibility for altering the composition so as to optimize particular physical parameters.

Many of the physical properties of silicon nitride, such as high temperature creep and tensile strength [4, 5] thermal shock and high temperature oxidation [6], have been fairly extensively studied. There is also some information on the electrical properties e.g. [7, 8] of thin film silicon nitride but there appears to be only one report of the electrical conductivity of bulk silicon nitride [9] and, equally, only one [10] describing electrical resistivity measurements on materials of the MgO–Si_3N_4 system. To the authors' knowledge there have been no previous reports of the electrical properties of sialon ceramics, and the purpose of the work described here was primarily to investigate electrical conductivity in hot-pressed silicon nitride, 5% MgO/Si_3N_4, and two compositions of sialon ceramic.

2. Experimental

All the specimens were obtained from the Crystallography Laboratory, Department of Metallurgy, University of Newcastle-on-Tyne [1, 11]. Some X-ray data and knowledge of the phases present in the specimens was provided by Jack [12]. The approximate specimen compositions are given in Table I in which β'-sialon indicates the Si–Al–O–N solid solution with an expanded β–Si_3N_4 structure. The component designated as "X-phase" is a monoclinic crystalline phase (see Jack [23]) with a composition slightly more alumina-rich than $SiAlO_2N$. Specimen 1 was hot-pressed from silicon nitride pre-washed with NaOH in an attempt to remove the surface silica always present on the powder particles [24]. Most of the materials were supplied as discs and specimens were cut with a diamond wheel into rectangular blocks with plane surfaces; typical specimen dimensions were 1.6 cm x 0.4 cm x 0.2 cm which gave a conveniently defined shape for conductivity measurements and were near the optimum length-to-thickness ratio for Hall effect studies.

TABLE I Composition of specimens (phases identified by X-ray diffraction and electron microscopy)

Sample no.	Nominal composition	Phases identified
1	Si_3N_4 (washed with NaOH) hot-pressed at 1700° C for 1 h	β-Si_3N_4 with glass impurity
2	Si_3N_4–5 wt% MgO hot-pressed at 1700° C for 1 h	β-Si_3N_4 with Mg-Si-oxynitride glass impurity
3	$z \approx 3.2$ sialon hot-pressed at 1700° C for 1 h	β'sialon with trace amounts of X-phase and a glass
4	$z \approx 4.0$ sialon hot-pressed at 1700° C for 1 h	β'-sialon with glass impurity

For both a.c. and d.c. conductivity measurements a two-probe method was employed using platinum/platinum paste electrodes as contacts. A compact furnace surrounded the specimen and all measurements were made in air as it was known that there was no risk of oxidation up to 1000° C. For d.c. measurements the current (I) was measured directly on to galvanometer (sensitivity 0.009 μA per mm deflection) and for the a.c. measurements from the voltage developed across a standard resistance. With a constant voltage (V) applied the conductivity was derived from

$$\sigma = \frac{d}{A} \cdot \frac{I}{V} \tag{1}$$

where d and A, the length and cross-sectional area respectively, were obtained accurately from the measured dimensions of the rectangular specimen. The impedance of all the specimens was very high at room temperature ($\sigma < 10^{-12}\ \Omega^{-1}\ \text{cm}^{-1}$), consequently measurements were made over the temperature range 400 to 1000° C, the lower limit being determined by the onset of measurable conductivity and the upper by the furnace. A.c. measurements were made over the frequency range 15 Hz to 5 kHz. Platinum/platimum–13% rhodium thermocouples were used for temperature measurements.

The d.c. Hall effect was also investigated, using a conventional five probe method, over the same temperature range. Platinum/platinum paste contacts were again used. The furnace was mounted between the poles of a Newport Type D electromagnet with which magnetic fields of up to 1 T could be obtained. By using a Keithley Type 149 nanovolt null detector for increasing the sensitivity of a Pye precision decade potentiometer, into which the output of a high input impedance ($10^{12}\ \Omega$) d.c. amplifier was fed, fairly high sensitivity was obtained and Hall voltages of as little as 0.01 μV could be detected.

Some thermoelectric effects were also investigated, over the same temperature range, by mounting a subsidiary heater at one end of the specimen; with this temperature differences of a few degrees could be established across the specimen. Platinum/platinum–rhodium thermocouples were used for temperature determination and the platinum wires also served as electrodes for measurement of the thermoelectric voltages. The sign of the carriers was determined by observing the polarity of the lower temperature end of the specimen.

3. Results

3.1. D.c. and a.c. conductivities

Application of a d.c. voltage to all of the specimens resulted in current flow which was initially large and then decayed, over a period of some minutes, to a steady value. To avoid these polarization effects all the d.c. conductivity measurements were made only after equilibrium conditions had

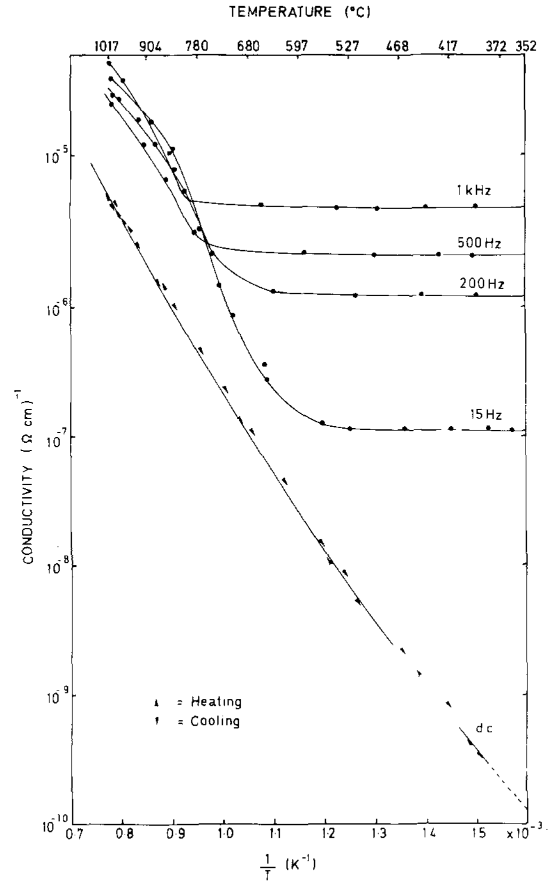

Figure 1 Variation of d.c. and a.c. conductivity with reciprocal temperature for hot-pressed Si_3N_4.

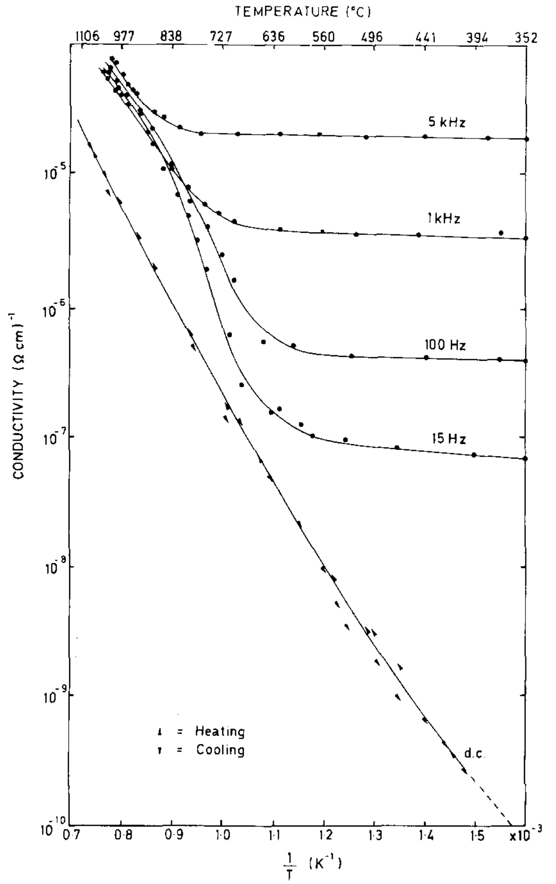

Figure 2 Variation of d.c. and a.c. conductivity with reciprocal temperature for hot-pressed 5 wt % MgO/Si_3N_4.

been attained. No polarization effects were observed when using a.c. voltages. Some conductivity data are given in Figs. 1 to 3 in which the logarithms of the conductivities are plotted as functions of inverse temperature.

As regards the d.c. conductivity ($\sigma_{\text{d.c.}}$) curves readings were taken both on heating and cooling. The curves show that the behaviour was reversible, indicating that there were no significant changes in either the specimens or the contacts during temperature cycling. There is a striking similarity between the form of the results for the four different materials. The relationship between log $\sigma_{\text{d.c.}}$ and $1/T$ is linear between 1000 and about 700° C and becomes non-linear at lower temperatures; consequently the activation energy in the higher temperature region (i.e. 1000 to 700° C) is constant, but below 700° C it decreases slowly with decreasing temperature. Values for activation energy (E_A) were calculated from the d.c. conductivity results using the relation

$$\sigma_{\text{d.c.}} = \sigma_0 \exp \frac{-E_A}{kT} \qquad (2)$$

in the linear high temperature region and from the slopes of the curves at lower temperatures (Table II).

The a.c. behaviour shows several features which are common in the results from each of the specimens. In the lower temperature region, (below about 600° C), $\sigma_{\text{a.c.}}$ is strongly dependent on frequency but is almost independent of temperature. At higher temperatures $\sigma_{\text{a.c.}}$ for a given specimen was found to be the same at all frequencies but it became temperature dependent giving a log $\sigma_{\text{a.c.}}$ – $(1/T)$ variation very similar to that found for $\sigma_{\text{d.c.}}$ at high temperatures. The activation energies derived from these high temperatures a.c. results agreed closely with the estimates based on the d.c. data. It is noticeable that in the high temperature

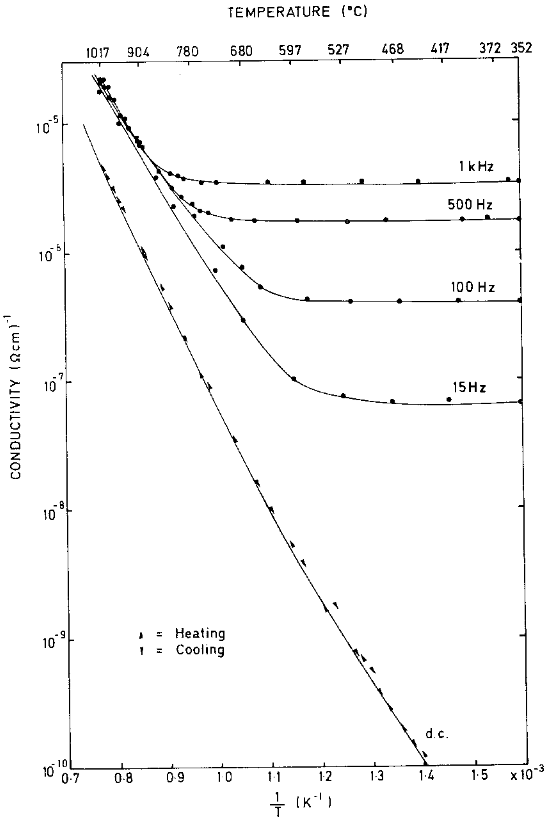

Figure 3 Variation of d.c. and a.c. conductivity with reciprocal temperature for hot-pressed $z \approx 4.0$ sialon.

region the a.c. conductivity can also be fitted to a relation of the form of Equation 2 and the activation energies so derived are also given in Table II.

3.2. Hall effect and thermo-electric power

No Hall voltage was observed in any of the specimens between 400 and 1000° C and below 400° C the high impedance of the specimens precluded measurement by the apparatus available. As the equipment would have detected a Hall voltage of greater than 0.01 μV, this observation implied that the Hall mobility in the specimens was very low, probably less than 10^{-4} cm^2 V^{-1} sec^{-1} over the temperature range explored. Because of the difficulties inherent in the d.c. method, including the risk of polarization in the specimen, other methods of measurement are being investigated.

Some difficulties were encountered in attempts to measure thermoelectric powers. In the first place the voltage, ΔV, developed across the specimen was measured as a function of the temperature gradient, ΔT, at various fixed temperatures between 400 and 1000° C; in evaluating the data, ΔV was taken to be positive if the hotter electrode was positive. Preliminary measurements showed that even at $\Delta T = 0$ a finite voltage difference (ΔV_0) was observed. As the presence of this prevented actual thermoelectric power determinations an attempt to remove ΔV_0 was made by annealing in air at 1000° C for 48 h. Treatments of this kind have proved successful in overcoming similar effects in potassium chloride [13] and some other materials [14]. With the nitrogen ceramics, however, annealing reduced the value of ΔV_0 considerably, but did not remove it completely, and thus it was possible only to deduce the sign of the carriers from the sign of ΔV. Some results for

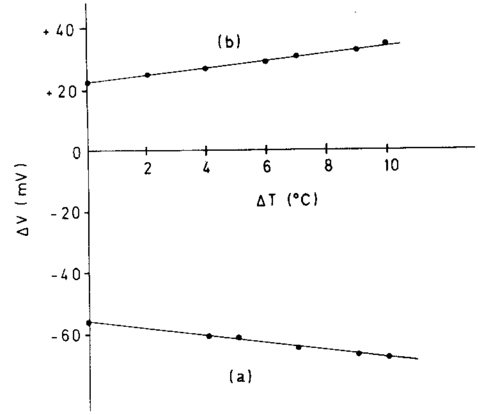

Figure 4 Variation of ΔV with temperature gradient ΔT at (a) 690° C and (b) 932° C for hot-pressed Si_3N_4.

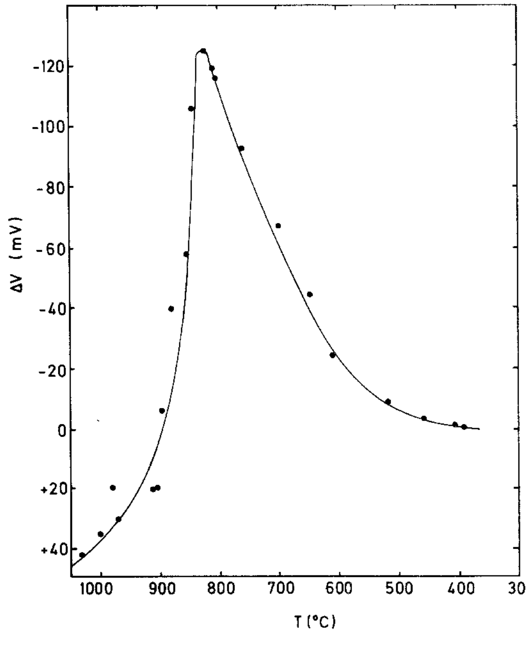

Figure 5 Temperature dependence of ΔV_0 for hot-pressed Si_3N_4.

Si_3N_4 are given in Fig. 4; below 900° C the material is p-type and above 900° C it is n-type. Similar behaviour was observed in all the other ceramics examined. The change in the sign of the carriers is revealed also by the temperature dependence of ΔV_0, the voltage developed with zero temperature gradient. This variation is shown for Si_3N_4 in Fig. 5 which shows that ΔV_0 changes sign near 900° C. Again, similar effects were found in the other materials.

4. Discussion

The measurements of a.c. conductivity as a function of frequency at low temperatures suggest immediately that hopping processes may be involved. Data was taken from Figs. 1 to 3 at 468° C, below which temperature $\sigma_{\text{a.c.}}$ was independent of temperature, and this was used to plot log $\sigma_{\text{a.c.}}$ versus ω. As Fig. 6 shows, linear variations were obtained for all the materials. In the low temperature range the a.c. conductivity increases with angular frequency ω following a relation of the form

$$\sigma_{\text{a.c.}} = A \cdot \omega^s \tag{3}$$

The values of s and A derived from Fig. 6 are listed in Table II and it is found that $s \simeq 0.9$. This type of frequency dependence was first observed by Pollak and Geballe [15] for impurity conduction in silicon; for this material their analysis, based on the assumption that hopping occurred exclusively between pairs of majority impurities, yielded an $\omega^{0.8}$ dependence over several decades of frequency. Similar behaviour has also been observed in many glasses containing transition metal ions [16]. Austin and Mott suggest that in these glasses the conductivity is due to the presence of ions of more than one valency; an electron can then pass from one ion to another and the mechanism gives a frequency dependence similar to that for impurity conduction. It may be noted also that in both chalcogenide glasses [17] and other amorphous semiconductors [16, 18] values of s in the range $0.7 < s < 1.0$ have been reported.

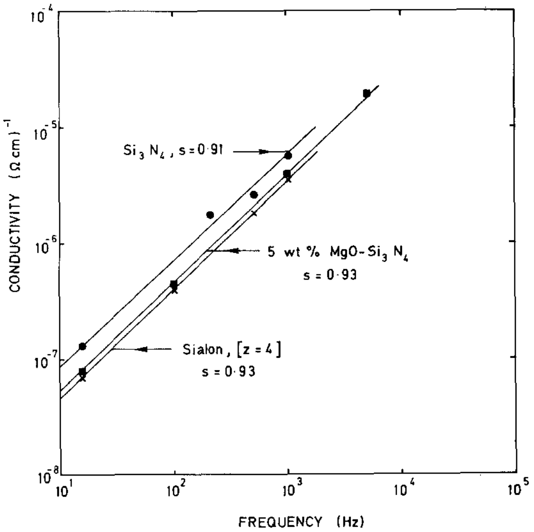

Figure 6 Frequency dependence of a.c. conductivity for hot-pressed Si_3N_4, 5 wt % MgO/Si_3N_4 and sialon $z \approx 4.0$.

As regards the d.c. conductivity data we find that, for all the specimens, the log σ versus $1/T$ plots are not linear below about 700° C. The data were plotted in the form of graphs of log $\sigma_{\text{d.c.}}$ versus $T^{-1/4}$, (Fig. 7); these were straight lines indicating that the variation in $\sigma_{\text{d.c.}}$ followed the relation

$$\sigma_{\text{d.c.}} = A \exp^{-B/T^{1/4}}. \tag{4}$$

This type of variation has been shown to hold in several substances in which hopping mechanisms occur, e.g. in nickel oxide [16] and in As_2Se_3 [18], and supports the view that hopping dominates in the nitrogen ceramics in the lower temperature range. In the higher temperature region $\sigma_{\text{d.c.}}$ and $\sigma_{\text{a.c.}}$ both follow a T^{-1} variation which shows that hopping is no longer the dominant mechanism. The behaviour is similar to that of intrinsic

TABLE II Numerical values of conductivities, activation energies and the parameters s and A.

Specimen no.	d.c. results				a.c. results		
	Conductivity $(\Omega\ \text{cm})^{-1}$		Activation energy (eV)		Activation energy (eV)	s 468° C	A 468° C
	1000°C	400°C	1000–700° C	500–400° C	1000°–800° C		
1	6.5×10^{-6}	4.6×10^{-10}	1.28	0.94	1.23	0.91	1.1×10^{-8}
2	8.2×10^{-6}	2.65×10^{-10}	1.38	1.01	1.15	0.93	6.81×10^{-9}
3	4.3×10^{-6}	9.25×10^{-11}	1.55	1.05	–		
4	4×10^{-6}	3.8×10^{-11}	1.64	1.22	1.32	0.93	5.66×10^{-9}

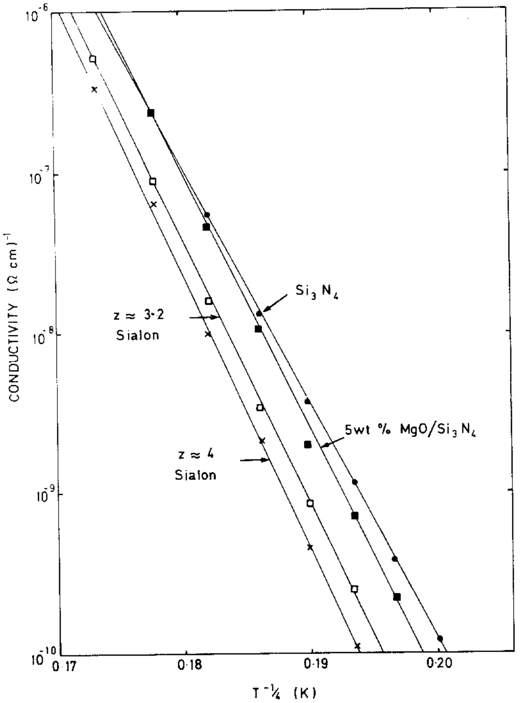

Figure 7 Variation of $\sigma_{d.c.}$ with $T^{-1/4}$ in the low temperature range.

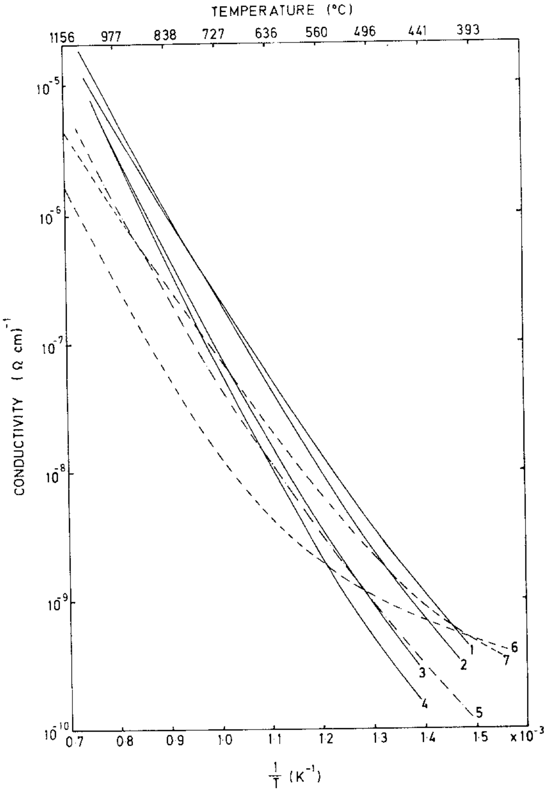

Figure 8 Comparison of d.c. conductivity data for hot-pressed and reaction-bonded ceramics. Key: hot-pressed materials (1) Si_3N_4, alkali washed (2) 5 wt % MgO/Si_3N_4, (3) $z \approx 3.2$ sialon, (4) $z \approx 4$ sialon; reaction-bonded materials (5) Si_3N_4, (6) 6.72 wt % MgO/Si_3N_4 and (7) 16.1 wt % MgO/Si_3N_4.

materials and the mechanism for both a.c. and d.c. conductivity appears to be the same. We may note also that here the carriers are n-type as distinct from p-type at lower temperatures. It is known that in semiconducting glasses [19, 20] and other amorphous materials the sign of the thermoelectric power is positive in the hopping region.

The effects of changes in the composition of the materials examined are indicated by Fig. 8 which includes for comparison the available data on reaction-bonded ceramics of similar composition. In Si_3N_4, the hot-pressed material has, at all temperatures, a greater conductivity than that of reaction-bonded material. The addition of magnesia to silicon nitride (5% MgO/Si_3N_4) produced a small decrease in conductivity relative to Si_3N_4 hot-pressed without MgO additive but pre-washed with alkali; it seems probable that traces of alkali are not completely removed. With the hot-pressed 5% MgO/Si_3N_4 the conductivity was an order of magnitude higher than that reported [10] for 6.7% MgO/Si_3N_4 made by reaction-bonding. As regards the sialons both gave lower conductivities than either the hot-pressed Si_3N_4 or 5% MgO/Si_3N_4 and the $z \approx 4.0$ sialon had a lower conductivity than the $z \approx 3.2$ sialon. In the preparation of nitrogen ceramics by hot-pressing techniques there is a likelihood of the formation of a glassy phase; the presence of such phases has been directly demonstrated by X-ray and electron microscope studies [1–4, 21–24] which have also shown that the materials are not homogeneous. The occurrence of a thermoelectric electromotive force at zero temperature gradient, (which has also been reported elsewhere [13]), supports the view that the materials contain uneven distributions of impurities. It is likely that the reaction-bonded ceramics would contain a smaller amount of glassy phase than the hot-pressed materials. If the glassy phase had a relatively high conductivity, as might be expected, this could account for the higher observed conductivities of the hot-pressed materials. All the electrical properties reported here appear to be consistent with the presence of a glassy phase, and it seems probable that this determines the conductivity behaviour.

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