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K. NARAYANDAS,
M. RADHAKRISHNAN,
C. BALASUBRAMANIAN
Department of Physics,
Madras University,
Autonomous Post-Graduate Centre,
Coimbatore-641 041,
India

Electrical conductivity of α-sialon ceramics

A sialon with the α-Si_3N_4 structure, α-sialon, has recently been developed [1–3]. α-sialon ceramics were fabricated by hot pressing or reaction sintering (pressureless sintering). The bending strength and thermal shock resistance were found to be better than those of β-sialons ($Si_{6-z}Al_zO_zN_{8-z}$) [3].

The general formula for α-sialons may be represented by $M_n(\text{Si, Al})_{12}(\text{O, N})_{16}$ where M is Li, Mg, Ca, Y or a rare earth metal except La or Ce, and $0 < n \leqslant 2$. The formula shows that M dissolves in an interstitial site in the α-Si_3N_4 structure [1]. The metal to non-metal ratio in α-sialon, Si + Al/O + N, is always 3/4 as in Si_3N_4 and β-sialon. This means that Al and O atoms dissolve in Si_3N_4 without the formation of vacancies. The maximum number of interstitial sites for metal dissolution in a unit cell of α-sialon is 2. When some of the interstitial sites were occupied, i.e. $0 < n < 2$, the rest of the sites could be regarded as vacant sites, through which the diffusion of small ions might be allowed.

The electrical conductivity of β-sialon was very low [4–6]; the application of β-sialons in electric materials was restricted to insulating uses. The structure of α-sialon suggests that sialon ceramics with high electrical conductivity could be prepared.

The present report shows the results of electrical conductivity measurements of α-sialons and compares them with those obtained for β-sialon.

The sialon ceramics were prepared by hot pressing appropriate powder mixtures [1, 3] to form, (a) $Y_{0.41}(Si_{10.2}Al_{1.8})(O_{0.6}N_{15.4})$ (α-1), (b) $Li_2(Si_9Al_3)(ON_{15})$ (α-2), (c) $Li_{0.53}Y_{0.20}(Si_{10.3}Al_{1.7})(O_{0.6}N_{15.4})$ (α-3), and (d) $Si_4Al_2O_2N_6$ (β-1). The starting powders were Si_3N_4 (Advanced Material Engineering, England, high purity grade), AlN (Toshiba Ceramics, Japan), Y_2O_3 (Shin-etsu Chemical, Japan, 99.9% pure), Al_2O_3 (Sumitomo Chemical, Japan, AKP-20) and Li_2CO_3 (Junsei Chemical, Japan). The hot pressing was performed at 1700 to 1750° C for 1 h under a pressure of $20\,\text{MN m}^{-2}$. The porosity of sintered materials was less than 3 per cent. The materials were cut into discs, about 5 mm square and 3 mm thick and then polished. Silver paste electrodes and platinum wires were used as terminals and lead wires, respectively. Platinum paste was also used as the terminal for (α-2) and (α-3) to confirm the agreement in conductivity with that by silver paste at high temperature. The d.c. bridge method was employed in the present work. The measurements were carried out in air in the range room temperature to 980° C.

The electrical conductivities of α- and β-sialons are shown in Fig. 1. The value of (α-1) is about the same as that of (β-1). The values of (α-2) and (α-3), on the other hand, are higher than those of (α-1) and (β-1). The higher conductivities might be

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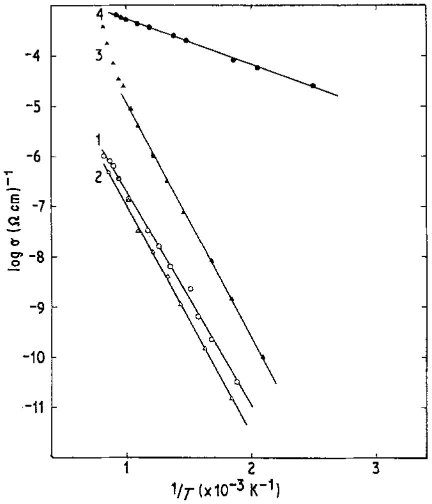

Figure 1 Electrical conductivity plotted against temperature for: (1) β-1; (2) α-1; (3) α-2; (4) α-3.

related to the presence of Li ions. The difference in slope between (α-2) and (α-3) suggests that the two materials have different conducting mechanisms.

The electrical conductivity is expressed by

$$\sigma = \sigma_0 \exp(-E/kT),$$

where E is the apparent activation energy, T is the temperature and k is a constant. The electrical conductivities at 700° C and apparent activation energies obtained in the present work are listed in Table I and they compare with those published for β-sialons [4–6]. The conductivity of (β-1) is about the same as that measured by Thorp and Sharif [4]. The a.c. conductivities of β-sialons were largely dependent on frequency and temperature, so that they could not be compared with the d.c. values. The present work showed that conductivities of (α-1) and (β-1) were about the same with those of other β-sialons. The values of (α-2) and (α-3) which contained Li were higher than those of β-sialons. The value of (α-3) was close to that produced by Li conduction in sintered Li_3N [7] which is known as an ionic conductor.

Thorp and Sharif [4] measured a.c. and d.c. electric conductivities of hot-pressed Si_3N_4 and β-sialons. They showed by thermo-electric power measurements that the materials were all p-type below 900° C and n-type above 900° C. The apparent activation energies for β-sialons were 1.05 to 1.22 and 1.55 to 1.64 eV for p- and n-type carriers, respectively.

Ukyo *et al.* [6] obtained electrical conductivities of β-sialon, X-phase, and mixtures of them at 850 to 1400° C. The charge carriers were identified by electrolysis. They showed that pure β-sialons gave ionic conduction with Si^{4+} migration. The conduction in pure X-phase was ionic by Si^{4+} above 1000° C and electronic by impurities below 1000° C. The apparent activation energies for ionic and electronic conduction were 1.95 and 0.87 eV, respectively. The electric conduction of materials containing β-sialon and X-phase was intermediate between values for β-sialon and X-phase.

The apparent activation energies for (β-1), (α-1) and (α-2) were nearly the same for electric conduction except for (α-2) at high temperature. The value for (α-3) was very low compared with those for ionic and electronic conduction. The value was similar to that for solid electrolyte, e.g. β-alumina [8].

Present work showed the possibility of preparing sialon ceramics with high electric conductivity. The determination of the carrier and the path is left for further work.

TABLE I Electrical conductivity and apparent activation energy for sialon

Sialon	Composition	Conductivity at 700° C $(\Omega cm)^{-1}$	E(eV)	Method	Temperature range (° C)	Reference
β-sialon	$z = 3.2$	2×10^{-7}	1.55	d.c.	700–1000	[4]
			1.05	d.c.	400–500	[4]
	$z = 1.5$	$2–9 \times 10^{-9}$	1.80	a.c.	500–1000	[5]
	$z = 2$	2×10^{-8}*	1.95	a.c.	850–1400	[6]
	$z = 2$	1.5×10^{-7}	0.96	d.c.	200–980	present work
α-sialon	(α-1)	1.0×10^{-7}	1.07	d.c.	200–980	present work
	(α-2)	9.0×10^{-6}	0.93	d.c.	200–980	present work
	(α-3)	4.9×10^{-4}	0.15	d.c.	25–980	present work

*Extrapolated.

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MAMORU MITOMO
YOICHIRO UEMURA
National Institute for Researches
in Inorganic Materials,
Namiki,
Sakura-mura,
Niihari-gun,
Ibaraki, 305,
Japan

A systematic study of the electrical properties of Fe-doped InP single crystals

The doping of indium phosphide (InP) single crystals with iron (Fe) to induce semi-insulating properties is a well established procedure [1–4] but no detailed systematic investigation of changes in electrical resistance, carrier concentration and Hall mobility induced by changes in Fe concentration and which occur due to normal segregation effects, has been reported. In view of the importance of minimizing Fe concentration because of the possibility of out-diffusion into epitaxial layers grown onto semi-insulating Fe-doped substrates, this paper reports the electrical properties determined along InP single crystals grown using melts containing between 0.005 and 0.15 wt% Fe, in order to cover the complete range of electrical properties from n-conducting to semi-insulating.

All crystals used in this investigation were grown on the ⟨1 1 1⟩ axis by the liquid-encapsulation Czochralski (LEC) technique [5] incorporating the crucible weighing method of automatic diameter control [6, 7]. The melts were contained in silica crucibles surrounded by a carbon susceptor and radio-frequency heating (450 kHz) was employed. Nitrogen gas at a pressure of 30 atm was used throughout and all the crystals were grown at pulling and rotation rates of 15 mm h^{-1} and 10 rpm, respectively. The boric oxide used as the encapsulant was supplied by BDH Limited and the polycrystalline InP starting material was provided by MCP Limited. In control experiments, where no Fe was added to the melt, the polycrystalline InP was converted into single crystals which had a residual free-electron concentration, $(N_D - N_A)$, consistently within the range 2 to 4×10^{15} cm^{-3} and a Hall mobility within the limits 25 000 to 35 000 $cm^2 V^{-1} sec^{-1}$, both these properties being measured at 77 K. A detailed chemical analysis of these materials is published elsewhere [8].

Five different concentrations of Fe were studied; the concentrations as added to the starting charge prior to melting in the form of metallic Fe were: 0.005 wt% (L781, L857), 0.01 wt% (L776, L808), 0.02 wt% (L772, L775), 0.04 wt% (L749, L750) and 0.15 wt% (L677, L729), the numbers in brackets denoting the crystal reference code. For the conducting samples, resistivity, Hall mobility and the free-electron concentration were determined at both 77 K and 298 K using the Van der Pauw technique. Resistivities for all samples were determined by measuring the resistance of a bar sample, typically 1.2 cm long. The amount of Fe present was determined in some of these samples by spark-source mass spectrometry (SSMS).

Resistivity is plotted as a function of mass fraction of melt converted into single crystal (g) for the five pairs of crystals in Fig. 1; for clarity, at the highest Fe levels, not all the results available have been plotted but all substantiate the trends shown. The Van der Pauw resistivities for the lightly-doped crystals, L781 and L857, have been included for completeness but the bar resistivities are