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High temperature ionic conductivity in the trivalent ceramic electrolytes: $\text{LaAl}_{11}\text{O}_{18}$ and $\text{LaAl}_{12}\text{O}_{18}\text{N}$

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Abstract

$\text{LaAl}_{11}\text{O}_{18}$ and $\text{LaAl}_{12}\text{O}_{18}\text{N}$ which adopt the magnetoplumbite type structure were prepared by high temperature sintering techniques from La_2O_3 , $\alpha\text{-Al}_2\text{O}_3$ and AlN powders. Phase purity was confirmed by powder XRD and IR spectroscopy. Impedance data for ceramic samples with Pt electrodes revealed an intra-granular ionic (La^{3+}) conductivity with activation energies $E_a(\text{LaAl}_{11}\text{O}_{18}) = 2.5$ eV and $E_a(\text{LaAl}_{12}\text{O}_{18}\text{N}) = 1.6$ eV. At ~ 1540 K their conductivity is comparable to that for Sr–Li– β -alumina with $\sigma \sim 3 \times 10^{-5} \text{ S cm}^{-1}$.

Keywords: Aluminium lanthanum nitride oxide; Ionic conductivity; Magnetoplumbite

1. Introduction

Since the discovery of Na^+ ionic conduction in sodium β -alumina [1], various divalent and trivalent cation containing related materials have been prepared with either the β/β'' -alumina or magnetoplumbite type structures. For example, Schäfer and Weppner [2] prepared ceramic divalent Ca^{2+} , Sr^{2+} , Cd^{2+} , Pb^{2+} β - and β'' -aluminas by ion exchange in molten salts and measured their ionic conductivity. Dunn and Farrington [3] prepared single crystals of trivalent Nd^{3+} , Gd^{3+} and Eu^{3+} β'' -aluminas by ion exchange techniques, demonstrating ipso facto the mobility of the trivalent species at high temperature. Conductivity data was given for a single crystal of Gd– β'' -alumina, with $\sigma(673 \text{ K}) \sim 8 \times 10^{-5} \text{ S cm}^{-1}$. Tietz and Umland [4] prepared a single crystal of 98% ion-exchanged $\text{Na}^+/\text{Ho}^{3+}$ β'' -alumina and found it

to ionically conduct with an activation energy $E_a = 0.48$ eV.

None of the above studies present results of any electrical measurements on trivalent cation containing polycrystalline ceramic materials. In view of the structurally encouraging features of the lanthanide magnetoplumbite compounds with respect to a possible Ln^{3+} ion mobility, the high temperature electrical conductivity of $\text{LaAl}_{11}\text{O}_{18}$ and $\text{LaAl}_{12}\text{O}_{18}\text{N}$ were investigated and are reported in this present work.

2. Experimental

2.1. Synthesis

Ceramic discs of $\text{LaAl}_{11}\text{O}_{18}$ and $\text{LaAl}_{12}\text{O}_{18}\text{N}$ were prepared by high temperature sintering techniques from La_2O_3 (99.999%, Aldrich), $\alpha\text{-Al}_2\text{O}_3$ (Alcoa SG1000 corundum) and AlN (99.5% + ,

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Goodfellow) powders in a similar fashion to that described by Wang et al. [5]. In the case of $\text{LaAl}_{12}\text{O}_{18}\text{N}$, an isostatically pressed pellet comprising an intimate mixture of the powders in the appropriate stoichiometric ratio, was sintered under a static argon atmosphere, at 2023 K, for 2 h in a graphite lined furnace. The product was analysed by powder XRD using a Siemens D500 diffractometer and infra-red spectroscopy using a Bio-Rad FTS-7PC Fourier transform instrument. The powder pattern corresponded to that for the magnetoplumbite structure with the lattice constant ratio $c/a = 3.95$. The IR spectrum of $\text{LaAl}_{12}\text{O}_{18}\text{N}$ (see Fig. 1) revealed a sharp absorption band at 950 cm^{-1} which corresponds to that obtained similarly by Wang et al. [6] and is assigned to the stretching vibration of the Al–N(III) bond, hence confirming the successful insertion of nitrogen into this structure. This absorption band was not observed in the IR spectrum of $\text{LaAl}_{11}\text{O}_{18}$.

2.2. Electrical measurements

Impedance spectroscopy was performed with a Schlumberger SI1260 impedance analyzer on ceramic electrolyte discs with Pt foil electrodes, held within a high purity alumina rig which was placed upon boron nitride spacers in a graphite tube and held within the working tube of a Lenton 1600 tube furnace with a flowing argon atmosphere. The

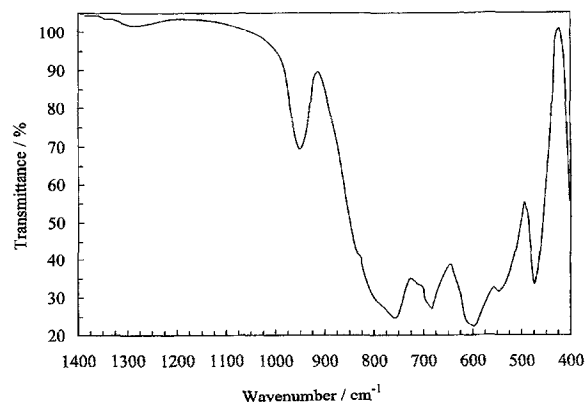


Fig. 1. Infra-red spectrum of ceramic $\text{LaAl}_{12}\text{O}_{18}\text{N}$ revealing a sharp absorption band at 950 cm^{-1} assigned to the stretching vibration of the Al–N(III) bond.

graphite tube was earthed to shield inductive noise whilst providing a low in-situ oxygen ppm (via the carbon/carbon monoxide couple) which is necessary for the stability of $\text{LaAl}_{12}\text{O}_{18}\text{N}$.

3. Results and discussion

The high frequency semi-circles (intercepting the origin) in the impedance spectra for $\text{LaAl}_{11}\text{O}_{18}$ and $\text{LaAl}_{12}\text{O}_{18}\text{N}$ ceramics are interpreted as being associated with intra-granular electrical properties. Evidence for a predominant cation (La^{3+}) conduction with a negligible electron or anion (O^{2-}) conduction is given from EMF measurements for a series of electrochemical cells in which these materials are used as solid electrolytes, cf. Warner et al. [7]. The measured capacitance for ceramic $\text{LaAl}_{12}\text{O}_{18}\text{N}$ was independent of temperature over the range 1275–1541 K with a corresponding dielectric constant $\epsilon = 56$. Arrhenius plots of the conductivity data are shown in Fig. 2.

A direct comparison of the conductivity data with that published for single crystal trivalent β/β' -aluminas is considered dubious since the ion-exchange during their preparation is often reported to be incomplete [4]. For ceramic materials the enhanced activation energies for $E_a(\text{LaAl}_{11}\text{O}_{18}) = 2.5\text{ eV}$ and $E_a(\text{LaAl}_{12}\text{O}_{18}\text{N}) = 1.6\text{ eV}$ when compared with $E_a(\text{Sr–Li–}\beta\text{-alumina}) = 0.86\text{ eV}$ [2] and $E_a(\text{Sr–Mg–}\beta''\text{-alumina}) = 0.9\text{ eV}$ [2] are consistent with an increase in the electrostatic charge associated with the mobile La^{3+} ion vis à vis Sr^{2+} . At approximately

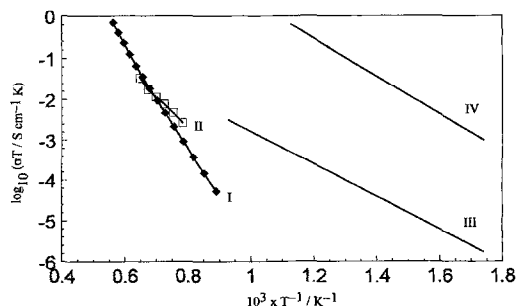


Fig. 2. Arrhenius plots for the ceramics (I) $\text{LaAl}_{11}\text{O}_{18}$, (II) $\text{LaAl}_{12}\text{O}_{18}\text{N}$, with (III) Sr–Li– β -alumina [2] and (IV) Sr–Mg– β'' -alumina [2] shown for comparison.

1540 K the conductivity of $\text{LaAl}_{11}\text{O}_{18}$ and $\text{LaAl}_{12}\text{O}_{18}\text{N}$ are comparable to the value extrapolated from lower temperature data ($\sigma \sim 3 \times 10^{-5} \text{ S cm}^{-1}$) for Sr–Li– β -alumina [2], suggesting their practical use as ceramic electrolytes at high temperature.

4. Conclusions

Ceramic discs of $\text{LaAl}_{11}\text{O}_{18}$ and $\text{LaAl}_{12}\text{O}_{18}\text{N}$ have been shown to exhibit ionic (La^{3+}) conductivity at high temperature. The activation energies are consistent with that expected for a trivalent cation in the magnetoplumbite type structure. Above 1540 K their ionic conductivity is comparable with, or even greater than that for analogous polycrystalline divalent material such as Sr–Li– β -alumina.

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