Electrical conductivity and dielectric constant of A-type Nd₂O₃

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Abstract. The measurements of electrical conductivity (σ) from 300 to 1200 K and dielectric constant (ϵ') from 4·2 to 1200 K of A-type Nd₂O₃ pellets are reported here. Electrical conductivity (σ) data can be explained in terms of impurity. The dielectric constant (ϵ') increases slowly up to 500 K as is expected for ionic solids. The increase of ϵ' becomes much faster above 500 K, which is attributed to space charge polarization of thermally generated charge carriers.

Keywords. Electrical conductivity; dielectric constant; niodymium oxide.

1. Introduction

This paper is a part of our study programme of electrical transport and magnetic properties of rare-earth sesquioxides and tungstates (Lal *et al* 1974, 1975, Lal and Dar 1975, 1976) and reports our results regarding the electrical conductivity (σ) and dielectric constant (ϵ') of hexagonal (A-type) Nd₂O₃ pellets. Because of the very high melting point ($\sim$2500° C) of the material we were unable to prepare single crystals due to experimental limitations.

A fine grained powder of Nd₂O₃ in hexagonal form has light bluish colour. The lattice parameter of the unit cell (Wyckoff 1964) are $a = 3\cdot831$ Å and $c = 5\cdot991$ Å and each cell contains one molecule. The electrical conductivity (σ) of cubic (*c*-type) Nd₂O₃ (pinkish colour) has been measured by many earlier workers (Noddach and Walch 1959, Zyrin *et al* 1969, Subba Rao *et al* 1970, Naito *et al* 1974, etc.). But such studies have not been reported for Nd₂O₃ which has hexagonal structure at room temperature.

2. Sample and experimental techniques

A-type Nd₂O₃ with stated purity of 99·9% in powdered form was procured from Rare-Earth Products Ltd., England. The impurity contents quoted by them are Pr₆O₁₁ + Sm₂O₃ with small quantity of other sesquioxides. We have used the material as such in our study. For the measurements of σ and ϵ' powdered specimens have been pelletized at different pressures (2×10^6 to 10×10^6 g cm⁻²) using hand operated hydraulic press and suitable die. These pellets were cleaned, dried and electrodes were fixed on its two faces. Two electrode method was employed using proper sample holder, in which quartz rod is used for insulation. Capacitance (C) and conductance (G) of these pellets were measured employing Weine-Kerr bridge. The arrangement of the bridge in principle is similar to Schering bridge

with holder introducing additional load in one of its arms. The balance is obtained by changing C and G in opposite arm of the bridge. There are seven ranges in the bridge for measuring conductance from 10^{-1} to 10^{-12} ohm^{-1} cm^{-1} and capacitance from $0 \cdot 1$ pF to 500 μF. The bridge is self-balancing, and after choosing the proper range, unknown capacity and conductance can be read directly on Keithley digital multimeter filled with the bridge. The bridge operates at an internal frequency of $1 \cdot 542$ kHz. For high impedance sample (low conductance and low capacitance < 10 pF) the accuracy of the capacitance measurement is $0 \cdot 0001$ pF. DC conductivities of the pellets were computed by recording the current through them using a Keithley digital multimeter. The experimental details are described elsewhere (Dar 1976).

3. Results and discussion

The density of the pellets approaches a constant value for $p > 6 \times 10^6$ $g\,cm^{-2}$. The parameters σ and ϵ' are very much dependent on the thermal history of the samples. However, consistent and repeatable results are obtained for pellets annealed around 1200 K for about two days. Both σ and ϵ' for annealed pellets approach and constant value for $p > 6 \times 10^6$ $g\,cm^{-2}$. None of these parameters depend upon the electrode materials within the accuracy of our apparatus. A little inconsistency is observed using silver electrodes at higher temperatures (T $>$ 900 K). This may be due to oxidation of electrodes because we did our measurement in air. No such discrepancy was noticed within the experimental limit using platinum foil electrodes. We preferred the platinum foil electrodes for this reason and have used it for the measurement of σ and ϵ'. Since σ is not found frequency dependent at high temperature, we conclude that any grain boundary effect is insignificant. The independence of the density, dielectric constant and electrical conductivity with pressure ($p > 6 \times 10^6$ $g\,cm^{-2}$) led us to believe that our measured parameters are probable approach to the crystalline value. We have measured the σ of a pellet made at a pressure of $(P) = 10 \times 10^6$ $g\,cm^{-2}$ in the temperature range 300 to 1200 K at dc and $1 \cdot 542$ kHz. The results are plotted in figure 1. This figure shows the variation of log σ vs $10^3/T$ $(K)^{-1}$ in the temperature range 300 to 1200 K. From the nature of the curve the conductivity results can be divided into two parts (i) Temperature region of 600 to 1200 K, (ii) 300 to 600 K.

The rare-earth sesquioxides are known to be electronic conductors (Bogroditskii *et al* 1965, Zyrin *et al* 1969, Subba Rao *et al* 1970). *p*-type conductivity at high temperature in hexagonal phase of Nd_2O_3 has been detected by Naito *et al* (1974). Thus usual band theory can be employed in explaining the result of electrical conductivity. The relevant bands for conduction in this solid are empty Nd^{3+} : 5d band, the filled O^{2-} : 2p band and the narrow Nd^{3+} : $4f^3$ band that is correlation split from the Nd^{2+} : $4f^4$ by nearly 20 eV. The only known oxides of neodymium is Nd_2O_3, where Nd ions are presumed to exist in trivalent state. The fact that neither Nd^{2+} nor Nd^{4+} ions are found in oxides places the filled Nd^{3+} : $4f^3$ band below the top of the O^{2-} : 2p band and the empty Nd^{2+} : $4f^4$ band above the bottom of the conduction band. The existence of paramagnetic susceptibility (Lal and Pratap 1976) compatible with free ion Nd^{3+} : $4f^3$ cores is consistent with this model, which eliminate the Nd : 4f electrons from consideration in any discussion
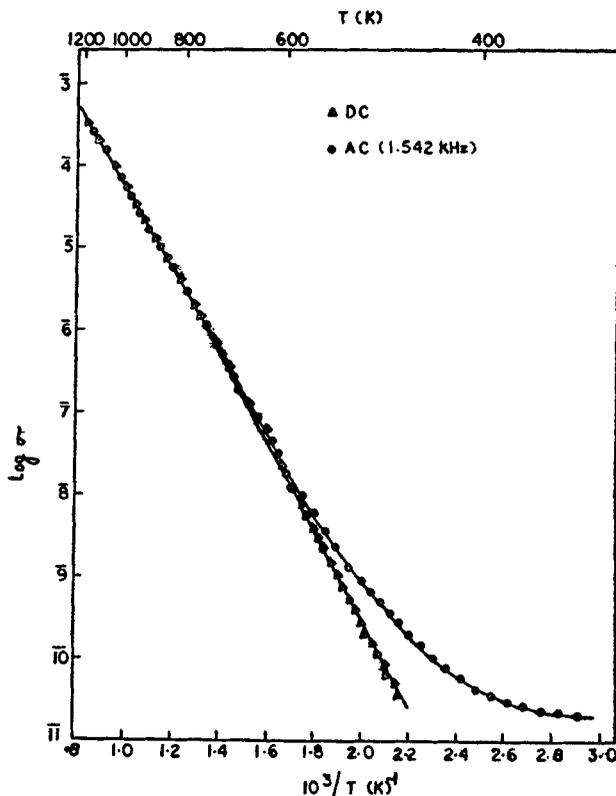
Figure 1. Variation of $\log \sigma$ *vs* $10^3/T$ $(K)^{-1}$ for A-type Nd_2O_3 pellet from 300 to 1200 K.

of the transport properties. The O^{2-}: $2p$ band is probable valence band and Nd^{3+}: $5d$ empty band is the conduction band of the solid. The charge transfer excitation of an electron from the valence O^{2-}: $2p$ band to the cation $5d$ band is expected to be of the order of 3 eV. This is the reason why a stoichiometric pure Nd_2O_3 is a good insulator at room temperature.

The conductivity (σ) data in the temperature range 300 to 1200 K can be expressed as the sum of two contributions σ_1 and σ_2 such that

$$\sigma = \sigma_1 + \sigma_2$$

$$\sigma = C_1 \exp\ (-W_1/2kT) + C_2 \exp\ (-W_2/2kT) \tag{1}$$

$$\sigma = 2\cdot3 \times 10^{-10} \exp\ (-0\cdot12/2kT) + 6\cdot2 \times 10^{-2} \exp\ (1\cdot22/2kT)$$

where σ_1 dominates in the temperature range 300 to 600 K and σ_2 in the temperature range 600 to 1200 K, respectively. Both the activation energies are low enough to be interpreted as energy band gap of the solid. Hence they have to be assigned to impurities.

The quoted impurities in the solid are Pr_6O_{11} and Sm_2O_3. On the basis of these impurities one can anticipate impurity ions like Pr^{4+}, Pr^{3+}, Sm^{3+} and oxygen vacancies (O_e^{2-}). Oxygen vacancies are well known (Lal 1970) to act as a donor center capable of giving electrons when singly or doubly ionized. Picturing them as a solid state analogue of helium atom and taking into consideration the high value of the static dielectric constant of the solid, it can be seen that first activation

P=3 (a)

energy will be of the order of 1/10 of an electron volt. Besides these Pr^{4+} can act as acceptor centers with energy level involved lying close to valence band giving value (0·1 eV) of activation energy. Also the Nd_2O_3 may contain excess metal ions which can act as acceptor centers of relatively lower activation energy. Perhaps these types of extrinsic conduction are responsible for lower activation energy. The higher activation energy observed at $T > 600$ K are associated with some deep traps. Such deep traps below the conduction band may associate with Pr^{3+}: $4f^2$ and Sm^{3+}: $4f^3$ ions. Besides this second ionization of oxygen vacancies may give the activation energy of the same order.

Figures 2 and 3 show the variation of dielectric constant (ϵ') *vs* temperature from 4·2 to 1200 K, measured at 1·542 kHz. It is seen from figure 2 that ϵ'
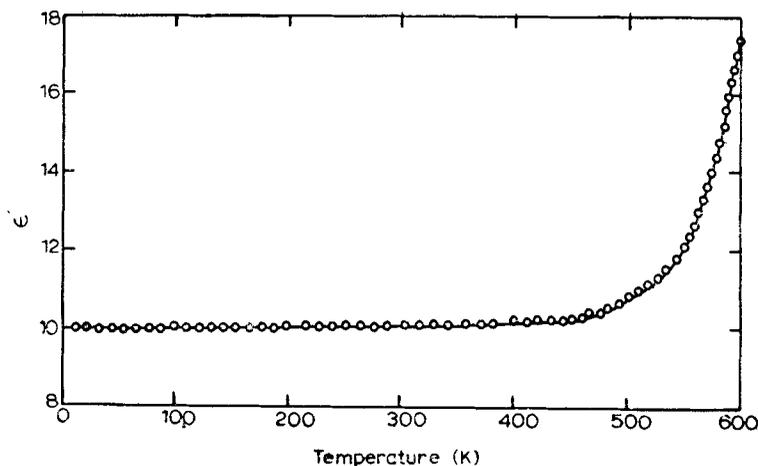

Figure 2. Variation of dielectric constant (ϵ') *vs* temperature (K) for A-type Nd_2O_3 pellet from 4·2 to 600 K.

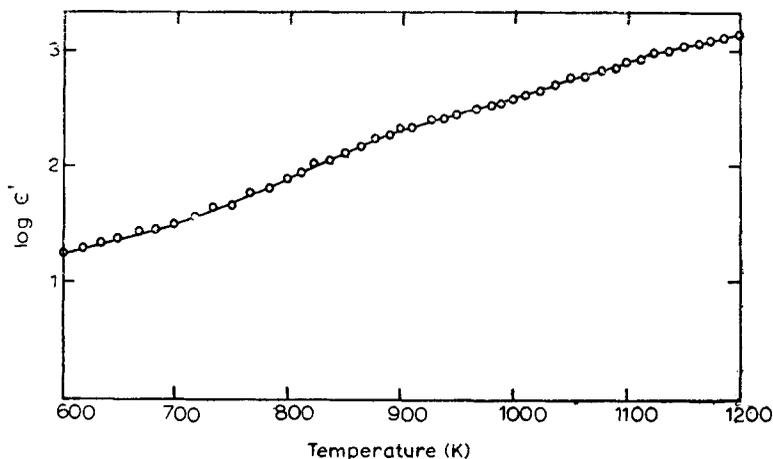**Figure 3.** Variation of log ϵ' *vs* temperature (K) for A-type Nd_2O_3 pellet from 600 to 1200 K.

slowly increases with temperature up to 500 K as is usual for ionic solids (Smyth 1955). This happens because lattice expands and polarizability of the constituent ions are affected by the change in temperature and available volume. Besides this the atomic polarizabilities also increase considerably due to loosening of bands at high temperature effecting an increase in the ϵ' value. Figure 3 shows the plot of log ϵ' *vs T*. The logarithmic plot has been taken just to accommodate the data. It is seen from this figure that ϵ' increases at much faster rate above 600 K (the rate of increase of ϵ' between 500 and 600 K is 0·065/K, whereas it becomes 1·41/K in the temperature range 800 to 1000 K). This increase is due to the increase of thermally generated charge carriers.

It happens in most of the semiconducting solids, that thermally generated charge carriers are not able to move free with electric field and give their charge at the electrodes to produce conduction current. If these charges are impeded by any source (by trapping in material or interfaces or not discharge at the electrodes, etc.) a space-charge builds up and macroscopic field distortion results (Von Hippel 1954). Thus, they result in the increase of ϵ'. This type of polarization as is well known (Von Hippel 1954) is called space-charge or interfacial polarization. When temperature is increased the number of charge carriers generated increase exponentially. All these charges contribute in producing space charge polarization and hence dielectric constant increases at much faster rate.

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