Pramāṇa, Vol. 10, No. 2, February 1978, pp. 173-177, © Printed in India.

Thermoelectric power and ac conductivity of A–type Nd_2O_3

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MS received 18 August 1977; revised 1 December 1977

Abstract. Measurement of thermoelectric power Θ of pressed pellets of A-type Nd_2O_3 from 550 to 1180K and electrical conductivity (σ) at dc, 50 Hz, 1·542 kHz and 3 kHz at different temperatures is reported. It is concluded that electrical conduction at high temperature (T>600K) in this solid is due to positive large polarons in O^{2-} : $2p$ (valence) band and negative intermediate polarons in Nd^{3+} : 5d (conduction band). The energy band gap of the solid has been found to be 2·44 eV. At low temperatures, conduction by hopping of charge carriers from one impurity centre to another has been predicted.

Keywords. Thermoelectric power; electrical conductivity; polarons; neodymium sesquioxide.

1. Introduction

Thermoelectric power gives useful information regarding the nature, the number and the effective mass of the charge carriers in solids (Adler 1968, Austin and Mott 1969, Adler and Feinleiv 1970, Bosman and Van Daal 1970, Sumi 1972). Together with electrical conductivity data, it can yield information regarding the drift mobility of charge carriers and on the mechanism of electrical conduction in solids (Bosman and Van Daal 1970). Recently, Dar and Lal (1976) reported the study of electrical conductivity and dielectric constant of A-type Nd_2O_3 and concluded that extrinsic and impurity conduction dominates in this material even up to a temperature of 1180K. This paper reports the data on the thermoelectric power Θ and ac electrical conductivity (σ) of the same compounds.

2. Materials and experimental procedure

The materials used in these measurements are the same as used by Dar and Lal (1976). For the measurement of thermoelectric power, powder samples were pressed into pellets with typical dimension of 0·6 $cm^2 \times 0{\cdot}50$ cm at pressures ranging from 3×10^6 to 10×10^6 gm cm^{-2}. The pellet was annealed for a few hours at 1000K, cleaned, dried and gently silver painted on two faces before being put into the sample holder for measurements. The sample holder was specially designed for the purpose. A thermal gradient ($\Delta T \sim 20$K) is produced across the sample with the help of a small heater put just below one of the hard electrodes. The thermo emf (ΔE) developed across the pellet was measured by a Keithley digital multimeter type 171 with an internal impedance of $10^{10}\Omega$. The temperature (ΔT) was measured using chromel alumel thermocouple. The ratio ($\Delta E/\Delta T$) gives the value Θ. The overall accuracy in the measurement of Θ was about 10%. Electrical conductivity (dc) was measured using a Keithley digital multimeter type 171. AC conductivity at 1·542 kHz was measured using Wein Kerr bridge and at 50 Hz and 3 kHz by Toshniwal conductivity bridge type CLO1/02A.

3. Results and discussion

Measurement of Θ of different pellets with different dimensions indicates that it is practically independent of the dimensions. It is also independent of the temperature gradient across the pellet. However, it does depend slightly on the pelletizing pressure and thermal history of the pellets. Repeatable and consistent values of Θ independent of cooling and heating cycles, are obtained for pellets made at pelletizing pressure greater than 6×10^6 gm cm^{-2} and annealed for several hours round 1000°C. At a particular temperature a slightly larger value of ΔE is obtained just after the application of thermal gradient across the pellet which, however, decreases with time and becomes constant after about 30 min. This constant value of ΔE was recorded for calculating the value of Θ at a particular temperature.

Figure 1 shows the variation of Θ with $1/T$. It is found that for $T>600$K Θ is positive indicating the dominance of the positive charge carriers in the conduction mechanism of the solid. The electrical conduction in solids is usually explained using band theory. According to this theory the variation of thermoelectric power Θ and electrical conductivity (σ) in intrinsic semiconducting solids are given by the expressions (Adler 1968).

$$\Theta = \left[\frac{E_g}{2e}\left(\frac{1}{T}\right) + \frac{3}{4}\frac{k}{e}\log\left(\frac{m_h}{m_e}\right) + a\right] \tag{1}$$

$$\sigma = 2\left[\frac{2\pi kT}{h^2}\right]^{3/2} (m_e m_h)^{3/4}\, e(\mu_h+\mu_e) \exp\left(-\frac{E_g}{2kT}\right)$$

$$\simeq \sigma_0(T)\exp(-e_g/2kT) \tag{2}$$

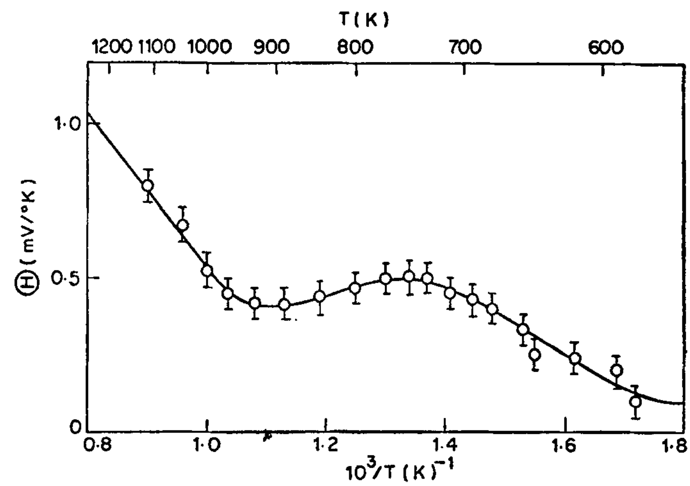

Figure 1. Plot of thermoelectric power (Θ mV/K) vs inverse of temperature ($(1/T(\mathrm{K})^{-1})$) for pressed pellet of Nd_2O_3.

where E_g is the energy band gap of the solid, e is the electronic charge, m_h and m_e are the effective masses and μ_h and μ_e are the mobilities of the charge carriers in valence and conduction band respectively, k and h are the Boltzman and Planck constants respectively. $\sigma_0(T)$ is a constant which has a slight dependence on temperature. Dar and Lal (1976) have concluded that O^{2-} : $2p$ and Nd^{3+}: $5d$ band are the valence and conduction band of this solid. Due to a large band width of O^{2-} : $2p$ band in comparison to cation $5d$ band (Adler 1968, Methfessel and Mattis 1968) $\mu_h > \mu_e$. In intrinsic conduction, holes and electrons have the same number and therefore in view of the fact that $\mu_h > \mu_e$, the former should dominate in the conduction process. Θ has positive value for $T > 600$ K, indicating the dominance of positive charge carriers in conduction and strengthens the above conclusion. The σ data of Dar and Lal (1976) also seem to confirm this conclusion. The plot of log σ vs $1/T$ in their measurement is a good straight line above 600 K as one expects from theory for such a conduction (Kittel 1971). However, the energy value (1·22 eV) evaluated by Dar and Lal (1976) from the slope of the log σ vs $1/T$ straight line is wrong, which makes their conclusion for the conduction mechanism incorrect. It should be 2·44 eV. Since charge transfer excitation from valence O^{2-}:$2p$ band to cation $5d$ band is expected to be $\sim$ 3 eV, the energy (2·44 eV) can be interpreted as the energy band gap of the solid. Thus conduction mechanism in this solid above 600K is due to the band conduction of intrinsic charge carriers and not due to impurities as suggested by Dar and Lal (1976). Band conduction of charge carrier is usually frequency independent (Adler 1968) and thus the frequency independent nature of σ observed by us at higher temperature (figure 2) seem to confirm the above conclusion.

From eq. (1), it is clear that if m_h and m_e do not change with temperature, then a

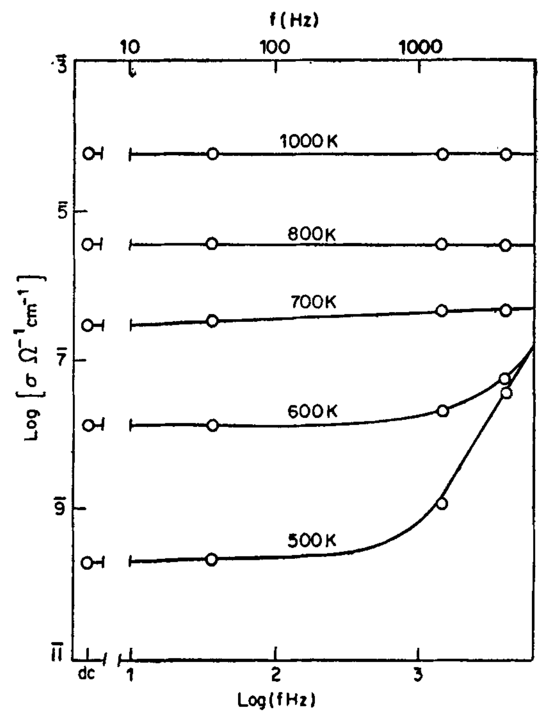

Figure 2. Plot of Logarithm of electrical conductivity (σ ohm^{-1} cm^{-1}) vs log of frequency for pressed pellet of Nd_2O_3 at different temperature.

plot of Θ vs I/T curve should be straight line. But it is seen from figure 1 that Θ vs $1/T$ curve has a typical nature far from a straight line. Θ initially increases linearly with increase in temperature, shows a maximum around 750K and then decreases with increase in temperature. However, for $T > 1000$K, Θ again starts increasing with increase in temperature. In terms of m_h and m_e, this curve suggests that at lower temperatures ($T < 750$K) $m_h < m_e$, with increase of temperature m_e decreases at a much faster rate than m_h. Analysing it in terms of mobility, it means that at a temperature just above 600K, the mobility of holes is very much larger than the electrons. This hole mainly contributes to σ as well as to Θ. As the temperature increases, the mobility of electrons in the conduction band also increases and they start contributing to Θ. This movement of electrons in turn reduces the value of Θ because both charge carriers (electrons and holes), moving towards lower temperature end of the sample to have lower energy, will neutralize the net thermoelectric voltage. Thus an increase in the mobility of electrons with temperature will lead to a peak in Θ vs $1/T$ curve.

In normal band conduction, the mobility of a charge carrier is expected to decrease or almost remain constant with temperature (Methfessel and Mattis 1968). Then how does the mobility of electrons in $5d$ band increase with temperature? The answer may lie in the formation of polarons which is to be expected in view of the ionic nature of the compound (Appel 1968). Since the relevant bands are not very narrow, one can expect the formation of large polarons, which conduct via band mechanism. In fact they are the quasiparticles with enhanced effective mass compared to electrons or holes. Large polarons are of two types and this division depends upon the value of dimensionless coupling constant (α). If $\alpha < 1$ the polarons are called large and if $1 < \alpha < 5$ it is called intermediate polarons. The value of α indirectly depends upon the band width (or rigid band effective mass of the charge carrier). Larger the band width lesser is the value of α (Appel 1968, Austin and Mott 1969). Now since O^{2-} : $2p$ band is wide ($\sim$4 eV), we expect in it formation of large polarons with $\alpha < 1$. Large polarons with $\alpha < 1$ conduct just like electrons (or holes) with increased effective mass and as such their mobility is expected to go down with temperature (Mathfessel and Mattis 1968). In Nd^{3+}: $5d$ band, electrons will form intermediate polarons ($1 < \alpha < 5$) in view of their small band width. The mobility of intermediate polarons increases with T by the following relation (Bosman and Van Daal 1970)

$$\mu_e = \mu_0 \exp\left[-\frac{\hbar\,\omega_0}{kT}\right] \tag{3}$$

where ω_0 is the longitudinal optical mode frequency of the lattice. ω_0 for A-type Nd_2O_3 is $4{\cdot}64 \times 10^{14}$ Hz (Denning and Ross 1972) giving $\hbar\,\omega_0 \sim 0{\cdot}1$ eV. Since at all temperatures Θ is positive, it means that $\mu_h \gg \mu_e$ at all temperatures and even at a temperature of 1000K. The increase of Θ above 1000K may be due to the onset of ionic conduction (probably the movement of oxygen ion vacancies).

Figure 2 shows the variation of electrical conductivity (σ) with ac frequencies. At lower temperature σ depends upon frequency. This frequency dependence of σ indicates that band conduction becomes insignificant at lower temperatures and conduction mechanism becomes hopping type. In view of the higher band gap of the solid ($Eg \sim 2{\cdot}44$ eV) dominance of impurity conduction is expected at a lower temperature. The quoted impurities in this solid are Pr_6O_{11} and Sm_2O_3. Thus one can anticipate impurity centres like Pr^{4+} : e (Pr^{4+} ion attached with an electron), some O^{2-} ion in interstial positions and Sm^{3+} ion. From figure 1, one observes that at lower temperature Θ becomes small and its tendency is to become negative. This suggests that an electron attached to Pr^{4+} ion may conduct by hopping from one Pr^{4+} ion to other or from one Pr^{4+} ion to Sm^{3+} ion.

Acknowledgement

Authors are grateful to Dr H B Lal for providing the material and many useful discussions.

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