

Electrical conductivity, thermoelectric power and dielectric constant of a $\text{Gd}_2\text{Ti}_2\text{O}_7$ single crystal

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Electrical conductivity, thermoelectric power and dielectric constant of a $\text{Gd}_2\text{Ti}_2\text{O}_7$ single crystal have been studied in the temperature range 300–1000 K. $\text{Gd}_2\text{Ti}_2\text{O}_7$ is found to be a *n*-type semiconductor with energy band gap 1.5 eV. It exhibits an extrinsic nature up to 675 K and an intrinsic nature above 675 K. The thermoelectric power increases with temperature in the region 300–675 K whereas it decreases with temperature in the region 675–1000 K. The dielectric constant increases slowly in the temperature range 300–675 K but this increase becomes fast in the temperature range 675–1000 K.

1. Introduction

Single crystals of $\text{Gd}_2\text{Ti}_2\text{O}_7$ have pyrochlorine-type structure (Fd3m). It possesses cubic symmetry; and the parameter of the elementary cell is $a = 1.0762$ nm [1]. Only the crystallographic properties of a $\text{Gd}_2\text{Ti}_2\text{O}_7$ single crystal have been studied till now. This paper reports on the electrical conductivity, thermoelectric power and dielectric constant of $\text{Gd}_2\text{Ti}_2\text{O}_7$ single crystals in the temperature range 300–1000 K.

2. Experimental procedure

Single crystals of $\text{Gd}_2\text{Ti}_2\text{O}_7$ were grown by the flux method at the Clarendon Laboratory Oxford, UK. Details about the crystal growth and identification techniques are given elsewhere [2]. The crystal on which the measurements were carried out, has a dimension $3.07 \times 3.01 \times 1.45$ mm. The d.c. electrical conductivity and thermoelectric power have been measured with the help of a digital multimeter (PM 2522/90, Philips, India) with an accuracy better than $\pm 0.25\%$ and $\pm 0.20\%$ for resistance and e.m.f. measurements, respectively. The a.c. electrical conductivity and dielectric constant have been determined using an autocomputing digital LCR-Q meter (4910, Applied Electronics Ltd. Thane, India) at an internal frequency of 1 kHz. For the dielectric measurement, the crystal was used as a dielectric medium. For all the measurements perpendicular to the *c*-axis, the two-probe method was employed. Platinum foils and silver paint were used as electrode materials. Temperatures were recorded with the help of a chromel–alumel thermocouple attached to the platinum electrodes. The details regarding the sample holder assembly and measuring techniques are given elsewhere [3].

3. Results and discussion

The electrical conductivity (σ) of a $\text{Gd}_2\text{Ti}_2\text{O}_7$ single crystal has been measured in the temperature range 300–1000 K, perpendicular to the *c*-axis. Due to the small size of the crystal, it was not possible to measure the electrical conductivity parallel to the *c*-axis. Variation of the $\log \sigma$ with the reciprocal of absolute temperature ($10^3 T^{-1}$) is shown in Fig. 1. The curve follows the well known exponential relation [4]

$$\sigma = \sigma_0 \exp(-W/kT) \quad (1)$$

where σ_0 is a constant, W is the activation energy and k is the Boltzmann constant, and has two different slopes below and above 675 K. The data can be expressed by two straight lines, one below 675 K and the other above 675 K as follows:

$$\sigma_I = 1.348 \times 10^{-7} \exp\left(-\frac{0.07 \text{ eV}}{kT}\right) \Omega^{-1} \text{ cm}^{-1} \quad (2)$$

$300 \text{ K} \leq T \leq 675 \text{ K}$

$$\sigma_{II} = 1.6527 \exp\left(-\frac{0.75 \text{ eV}}{kT}\right) \Omega^{-1} \text{ cm}^{-1} \quad (3)$$

$675 \text{ K} \leq T \leq 1000 \text{ K}$

where eV is the activation energy.

The values of $\sigma_0(T)$, energy gap and activation energy in different temperature ranges are presented in Table I.

The activation energy of 0.07 eV below 675 K is very small and it cannot be assigned as the activation energy of the intrinsic conduction. Such a value of the activation energy is a characteristic of extrinsic conduction due to impurities, point defects or interstitials, which are often present in the forbidden energy gap of the crystal. Such types of impurities

TABLE I Activation energy, $\sigma_0(T)$ and energy gap for a $\text{Gd}_2\text{Ti}_2\text{O}_7$ single crystal

Temperature range (K)	Activation energy (eV)	$\sigma_0(T)$ ($\Omega^{-1} \text{cm}^{-1}$)	Energy gap (eV)
300–675	0.07	1.348×10^{-7}	0.14
675–1000	0.75	1.6527	1.50

present in mixed oxides, cannot be removed easily [5]. The contributions of defects or impurities to conduction in a solid can be explained in terms of donors and acceptors, and is represented by the expression [6]

$$\sigma_d = A \exp(-E_i/kT) \quad (4)$$

where E_i is the ionization energy of donors or acceptors and is usually $E_i \approx 0.1 \text{ eV}$ for semiconducting materials. The activation energy found below 675 K is approximately comparable to the ionization energy E_i . Therefore the conclusion that electrical conduction is certainly due to impurities, point defects or interstitials, seems to be reasonable. The higher value of activation energy above 675 K indicates that conduction is of an intrinsic type. So the change in the nature of the $\log \sigma$ versus $10^3 T^{-1}$ curve at $T \approx 675 \text{ K}$ is due to a change in the conduction mechanism i.e. the transition from extrinsic to intrinsic conduction. However, this change may be also due to the change in the crystal structure of the specimen.

The relevant bands for conduction in this solid are $\text{O}^{2-}:2p$ filled, $\text{Gd}^{3+}:4f$ partially filled, and $\text{Ti}^{6+}:4d$ and $\text{Gd}^{3+}:5d$ empty bands. The only partially filled band expected in this solid is the 4f band but it has

been shown that 4f electrons have almost atomic character even in rare-earth solids and form only very narrow and highly correlated bands [7, 8]. The value usually quoted for band width is 0.05 eV. Hence the participation of 4f electrons in conduction is almost not possible [9, 10]. The 5d band in rare-earth solids is regarded as the conduction band [8]. Thus it seems likely that electrons in 5d bands, caused by the thermal excitation of electrons from 4f or 5p bands and holes left, are responsible for electrical conduction above $T \approx 675 \text{ K}$. So the only appropriate bands for high mobility electrical conduction are the $\text{Gd}^{3+}:5d$ empty band and the $\text{O}^{2-}:2p$ filled band. The 2p band is expected to be an ordinary band (about 4 eV wide) and the large polaron theory of conduction should be applied in this band. The 5d band is in comparison a narrow band, the mobility of charge carriers in this band is thus expected to be low in comparison to mobility of charge carriers in $\text{O}^{2-}:2p$ band. Thus intrinsic conductivity should be dominated by large polarons. The electron or hole current domination will depend on the effective mass of the charge carriers in the empty band $\text{Gd}^{3+}:5d$ and the filled band $\text{O}^{2-}:2p$ [11, 12]. However, both these holes and electrons are expected to interact with the lattice and this may lead to the formation of large polarons as discussed by several authors [13–15]. The electrical conduction of a large polaron is of the band-type and the expression for the conductivity is

$$\sigma = \sigma_0 \exp(-E_g/2kT) \quad (5)$$

where E_g is the energy gap of the solid. In the temperature range 675–1000 K, the $\log \sigma$ versus $10^3 T^{-1}$ curve is a straight line and conduction is probably the

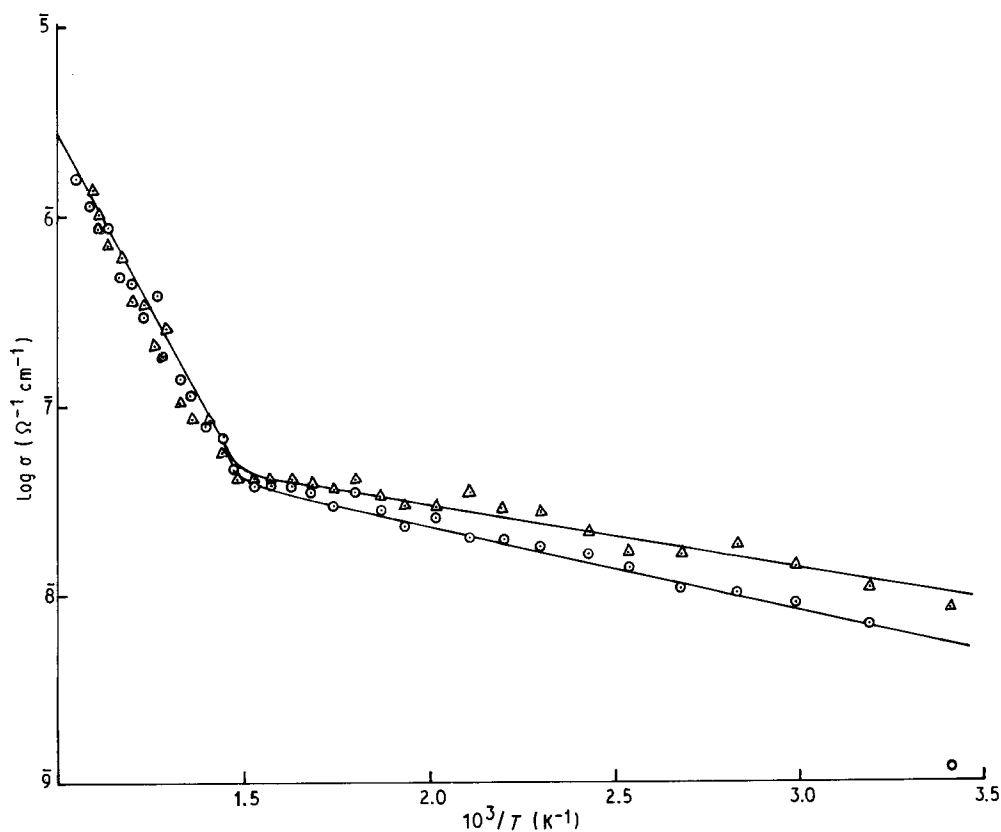


Figure 1 Variation of $\log \sigma$ with the reciprocal of absolute temperature ($10^3 T^{-1}$) \odot : d.c. conductivity \triangle : a.c. conductivity.

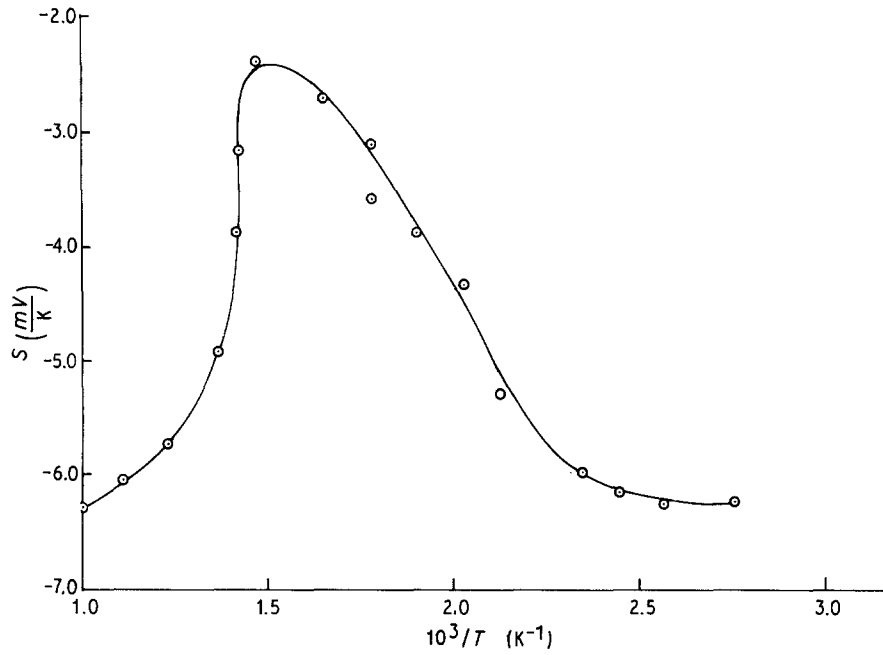


Figure 2 Variation of the thermoelectric power (S) with the reciprocal of absolute temperature ($10^3 T^{-1}$).

band-type due to the large polarons. From this part of the curve, the energy band gap is calculated as $E_g = 1.5$ eV and $\sigma_0 = 1.6527 \Omega^{-1} \text{cm}^{-1}$.

It is observed from Fig. 1 that a.c. conductivity is slightly higher than d.c. conductivity in the temperature range 300–675 K, which predicts that the conductivity in this temperature region is ionic as well as electronic. The higher value of the a.c. conductivity also suggests that some sort of impurities are present in the crystal resulting in dielectric loss. Coincidence of the a.c. and d.c. conductivities at higher temperatures shows that the material is predominantly an electronic semiconductor.

The thermoelectric powers (S) were estimated using the relation

$$S = \lim_{\Delta T \rightarrow 0} \frac{\Delta E}{\Delta T} \quad (6)$$

where ΔE is the potential difference across the crystal due to temperature difference $\Delta T \approx 20^\circ \text{C}$. The variation of the thermoelectric power (S) as a function of $10^3 T^{-1}$ is shown in Fig. 2. The negative polarity of the thermo e.m.f. shows that $\text{Gd}_2\text{Ti}_2\text{O}_7$ is a n -type semiconductor and the majority charge carriers are electrons. We have calculated the charge carrier mobility in the two temperature ranges 300–675 and 675–1000 K from the electrical conductivity and thermoelectric power data, using the relations [4]

$$\sigma_0(T) = 2e \left[\frac{2\pi kT}{h^2} \right]^{3/2} (m_e m_h)^{3/4} (\mu_e + \mu_h) \quad (7)$$

and [21]

$$S = -\frac{E_g}{2e} \left(\frac{c-1}{c+1} \right) \frac{1}{T} - \frac{2k}{e} \left(\frac{c-1}{c+1} \right) - \frac{3k}{4e} \log_e(a) \quad (8)$$

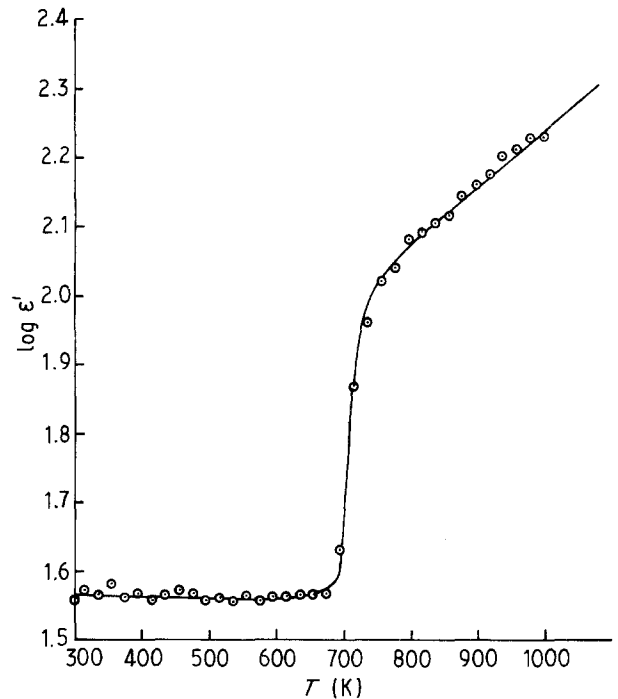


Figure 3 Variation of the dielectric constant (ϵ') with absolute temperature (T).

or

$$S = \frac{\eta}{T} + K \quad (9)$$

where

$$\eta = -\frac{E_g}{2e} \left(\frac{c-1}{c+1} \right) \quad (10)$$

$$K = -\left[\frac{2k}{e} \left(\frac{c-1}{c+1} \right) + \frac{3k}{4e} \log_e(a) \right] \quad (11)$$

$$c = \frac{\mu_e}{\mu_h}, \quad a = \frac{m_e}{m_h}$$

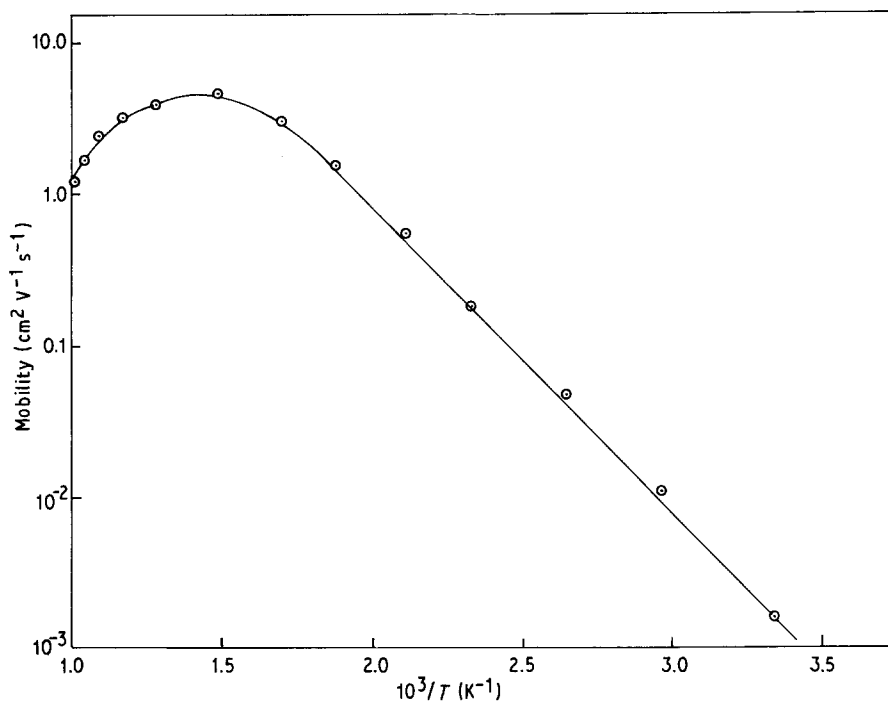


Figure 4 Variation of the carrier mobility (μ) with the reciprocal of absolute temperature ($10^3 T^{-1}$).

and m_e , μ_e , m_h and μ_h are effective mass and mobility of the electron and hole, respectively, and k and h are Boltzmann and Planck's constants, respectively. Variation of carrier mobility μ and the reciprocal of the absolute temperature ($10^3 T^{-1}$) is shown in Fig. 4. From Fig. 4, it is clear that the temperature dependence of carrier mobility in the expression $\sigma = nq\mu_e + pq\mu_h$ is small enough to make Equation 1 etc. a reasonable approximation.

Thermoelectric power increases with temperature up to $T \approx 675$ K. The increase in thermoelectric power with temperature shows that the electrical conduction in this solid is due to a small polaron-hopping mechanism in which mobility of the charge carrier increases with increase in temperature. The conduction in this compound is the extrinsic type below 675 K, governed by impurities, defects, vacancies etc., therefore the number of impurity charge carriers will become constant after a certain temperature [16]. In the high temperature region i.e. $T > 675$ K, the decrease in thermoelectric power with temperature is in accordance with our conclusion of a large polaron band conduction in which the number of charge carriers increases exponentially with the temperature and, the mobility of charge carriers decreases with temperature. Thus it is clear that due to these factors, the thermoelectric power decreases with temperature in the region 675–1000 K.

The static dielectric constant (ϵ') of a single crystal of $Gd_2Ti_2O_7$ has been measured perpendicular to the c -axis in the temperature range 300–1000 K. The dielectric constant at various temperatures has been calculated using the relation [17]

$$\epsilon' = C \frac{11.3t}{A} \quad (12)$$

where C is the capacitance in picoFarads, t is the

thickness of the crystal in cm and A is the area of the electrode in cm^2 . The variation of the dielectric constant (ϵ') with absolute temperature is shown in Fig. 3. The trend of increasing ϵ' with temperature is similar to the trend of increasing conductivity. The increase of ϵ' with temperature is very slow up to 675 K and above this it increases rapidly with temperature rise. The slow increase in ϵ' with temperature is the usual trend in ionic solids [18–20]. Due to the increase in temperature, the lattice of the crystal expands with a consequent increase in polarizability of ions and thus the dielectric constant of the material increases. Above 675 K formation of the large polarons which increases the polarizability of the ions of the crystal to a greater extent, takes place. Due to the high increase in polarizability of the ions, the dielectric constant of the material increases very rapidly in the temperature range 675–1000 K.

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