

## Crystal growth and electrical properties of CaSO<sub>4</sub>:Dy single crystals

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**Abstract.** Single crystals of CaSO<sub>4</sub>:Dy, with and without charge compensator were grown by the solution growth technique. Electrical conductivity was studied at room temperature for diverse concentrations of Dysprosium and showed that it increases upto 0.2 wt % of Dy, beyond which saturation sets in. Electrical conductivity was studied in the region 400 to 700°K and the migration energies estimated for various dopant concentrations. The variation of electrical conductivity and migration energy with diverse dopant concentration is explained on the basis of the theory of defects. The thermoelectric power measurements reveal that the crystals grown are of *P* type.

**Keywords.** Crystal growth; resistivity; magnetoresistance; thermoelectric power; CaSO<sub>4</sub>:Dy single crystals

### 1. Introduction

It is well-known that CaSO<sub>4</sub> is one of the luminescent materials and shows characteristic luminescence when the impurity ions are added (Nambi *et al* 1974; Sabnis 1980; Mulla 1980). Application of rare earth-doped (particularly Dy, Sm and Tm) CaSO<sub>4</sub> phosphors in radiation dosimetry is of recent origin. Most of these investigations are confined to their TL behaviour and spectral studies. Very little attention has however been paid to their electrical properties such as electrical resistivity, thermoelectric power and magnetoresistance, presumably due to the difficulty in growing the CaSO<sub>4</sub> crystals doped with an activator.

An attempt has therefore been made to grow single crystals doped with diverse concentrations of Dysprosium along with flux (Na<sub>2</sub>SO<sub>4</sub>) to study their electrical properties such as electrical resistivity, thermoelectric power and magnetoresistance and to understand the nature of the defects which play a predominant role in the process of luminescence.

### 2. Experimental

Single crystals of CaSO<sub>4</sub> activated with Dysprosium as an impurity were prepared from Indian Mineral gypsum. The purification of gypsum is reported by Mulla and Pawar (1977). Purified gypsum powder (120 g) was taken in a corning glass beaker and a hot concentrated solution of sulphuric acid (AR grade) was added to

dissolve the powder. The solubility of gypsum in sulphuric acid was 56.46 mol%. The saturated solution of gypsum in sulphuric acid was equally distributed among 12 corning glass beakers (250 cc). Solutions of  $\text{Dy}_2\text{O}_3$  and sodium sulphate were prepared in various mol% in double-distilled water. Measured drops of activator ( $\text{Dy}_2\text{O}_3$ ) and flux ( $\text{Na}_2\text{SO}_4$ ) solutions were then added to the beakers.

The beakers containing the solution were kept in the oven. The oven temperature was maintained at  $200^\circ\text{C}$  for the first 4 days and the fumes of  $\text{H}_2\text{SO}_4$  were exhausted from an oven outlet. The temperature of the oven was then reduced to  $175^\circ\text{C}$  and kept constant for another 2 days when crystal nuclei were formed. The temperature of the oven was then reduced at the rate of  $25^\circ\text{C}/\text{day}$  for the subsequent 4 days until the solution completely evaporated and only transparent crystals remained. The size of the single crystals grown was of the order of  $3 \times 3 \times 1$  mm.

### 2.1 Resistivity measurements

The specimen crystals with silver paint contact were employed to measure electrical conductivity. The samples were mounted between circular brass electrodes inside a cylindrical furnace. AC current controlled by a dimmerstat was used for heating the furnace and the constant temperature was measured by a chromel-alumel thermocouple. To measure the conductivity a potential difference of 20 V was applied across the crystal which was measured by a Simpson VTVM model-321 and the current measured using an Aplab FET nanoammeter.

### 2.2 Magnetoresistance measurements

Single crystals coated with silver paint on their surfaces were employed. The crystal was mounted between two circular brass electrodes of a crystal holder. One of the electrodes was guided by a small spring to hold the crystal under mild pressure. The crystal holder was mounted between the pole pieces of an electromagnet which is capable of providing a transverse magnetic field up to 6700 gauss.

A PD of 20 V from a well-stabilised DC supply was applied across the sample which was measured by a Simpson VTVM Model-321. The current flowing through the specimen at various fields was measured by an Aplab FET nanoammeter Model TFM-13.

### 2.3 Thermoelectric power measurements

The apparatus for thermoelectric power measurement consists of two brass electrodes. The lower electrode was heated by passing the current through the heating coil wound round it. The temperature of the lower electrode varied the current through the heating coil. The temperature was measured using a chromel-alumel thermocouple.

The upper electrode is kept at constant temperature *i.e.* at room temperature which was measured using a chromel-alumel thermocouple.

The single crystals coated with silver paint was employed for thermoelectric power measurements. The thermo EMF generated between the two brass electrodes was measured using an Aplab microvoltmeter.

### 3. Results and discussion

#### 3.1 Electrical conductivity

The variation of current with voltage was studied at room temperature. The nature of the current *vs* voltage curves for almost all the crystals studied (pure CaSO<sub>4</sub>, doped with various conc. of Dy and doped with various concentrations of Dy along with flux) is similar. To avoid repetition, a typical *I vs V* plot is shown in figure 1. This consists of a low voltage (region I) and a high voltage region (region II). At low voltage region *I vs V* plot is not a straight line, which means that the current flowing through the crystal is not proportional to the applied voltage. However the plot of  $\log I$  *vs*  $\log V$  is a straight line (figure 2) with a slope 2 in the low voltage region (region 1) and obeys the relation given by Mott and Gurney (1940)

$$j = g\mu V^2/32\pi L^3$$

where  $V$  = voltage drop across the crystal;  $\mu$  = mobility of the electron;  $L$  = length of the crystal;  $j$  = current flowing through the crystal.

At higher voltages above 20 V, *I vs V* plot is a straight line *i.e.* current flowing through the crystal is proportional to the applied voltage (region II) and obeys the relation given by Mott and Gurney (1940).

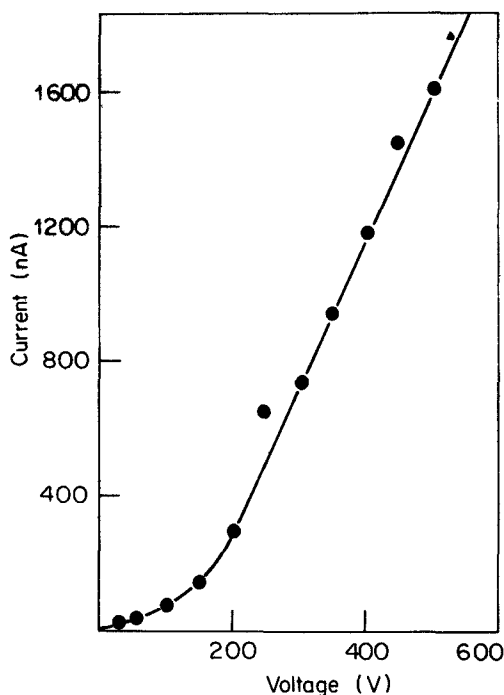
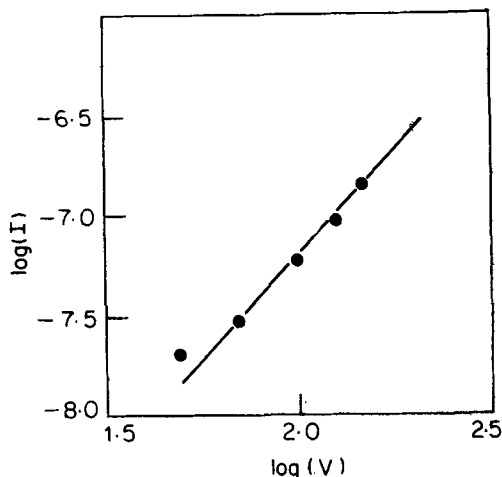


Figure 1. Plot of current ( $I$ ) *vs* voltage ( $V$ ) for a typical CaSO<sub>4</sub>:Dy single crystal.

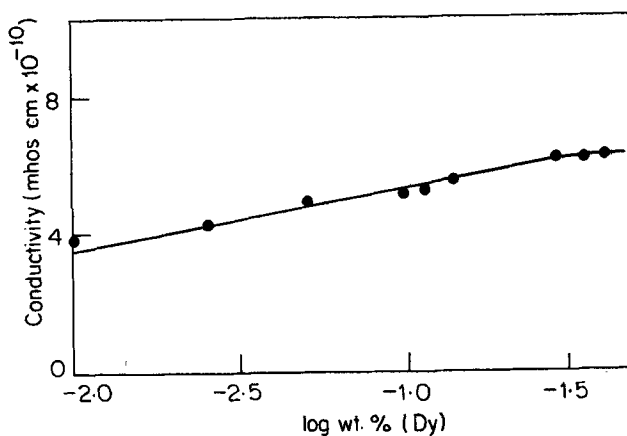
$$j = e\mu N_0 V/L$$

where  $e$  = charge on electron;  $\mu$  = mobility of the electron;  $N_0$  = density of the electrons in the insulator immediately at the metal boundary.

The variation of conductivity of  $\text{CaSO}_4$  single crystals with diverse concentration of Dy at room temperature is shown in figure 3. It is found that conductivity increases up to 0.2 wt % of Dy beyond which saturation sets in. This increase in conductivity by adding Dy can be explained on the basis of the theory of defects.



**Figure 2.** Log  $I$  vs log  $V$  for  $\text{CaSO}_4$ : Dy single crystal.



**Figure 3.** Conductivity vs log wt. % of Dy in  $\text{CaSO}_4$  single crystals.

The concentration of defects can be altered in ionic crystals at low temperature by adding suitable impurities because of the electrical neutrality condition. A positive ion vacancy appears to carry a negative charge and vice versa. Since the CaSO<sub>4</sub> crystals are prepared in an atmosphere of H<sub>2</sub>SO<sub>4</sub>, it is assumed that initially cation vacancies (Ca<sup>2+</sup>) with atomic radius 0.99 Å are present in the matrix. If ions like Dy<sup>3+</sup> having atomic radius 0.92 Å are introduced into the CaSO<sub>4</sub> crystal, the positive ion concentration increases for charge compensation. Two Dy<sup>3+</sup> ions replace three Ca<sup>2+</sup> ions for charge neutrality and one more cation vacancy is created, in addition to the cation vacancies present at thermal equilibrium. Increase in conductivity of CaSO<sub>4</sub> single crystals with the addition of Dy<sup>3+</sup> ions suggests that the mechanism of conductivity in CaSO<sub>4</sub>:Dy single crystals is due to vacancy jumps. On the other hand if the conduction is by the motion of interstitials the conductivity reduces. A similar behaviour has been observed in silver halides doped with Cd (Ebert and Teltow 1955) and in sodium nitrate doped with barium (Ramasastry and Murti 1968). From figure 3 it is found that above 0.2 wt % of Dy conductivity does not increase but saturation sets in. This may be due to the fact that creation of cation vacancy requires greater energy and therefore the entry of more Dy<sup>3+</sup> ions is restricted and the number of cation vacancies remains constant.

The effect of addition of monovalent impurity (Na<sup>+</sup>) along with a trivalent impurity (Dy<sup>3+</sup>) is studied in the divalent matrix of CaSO<sub>4</sub>. Figure 4 shows the variation of conductivity due to doping of diverse concentrations of Na<sub>2</sub>SO<sub>4</sub> single crystals. It shows two distinct regions, regions I and II where conductivity decreases and increases respectively with increase in concentration of Na<sub>2</sub>SO<sub>4</sub>. Decrease in conductivity with increase in concentration of Na<sub>2</sub>SO<sub>4</sub> (region I) can be explained as follows.

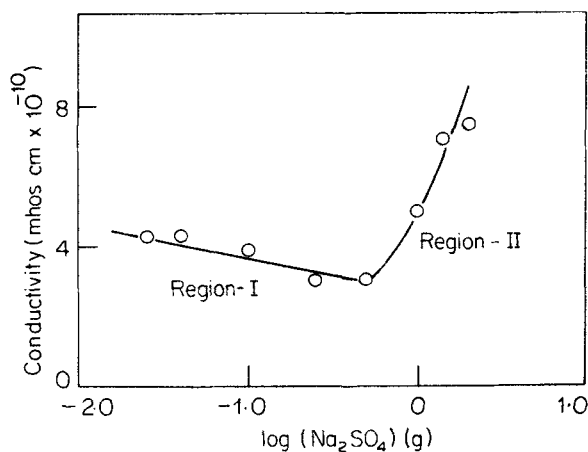


Figure 4. Conductivity vs log (gm of Na<sub>2</sub>SO<sub>4</sub>) in CaSO<sub>4</sub> single crystals.

Addition of two  $\text{Dy}^{3+}$  ions to  $\text{CaSO}_4$  matrix at the place of  $\text{Ca}^{2+}$  ions, creates a cation vacancy to preserve the charge neutrality *i.e.*  $2 \text{Dy}^{3+} \rightarrow 3 \text{Ca}^{2+}$ . Addition of  $\text{Dy}^{3+}$  ions increases the number of cation vacancies which in turn increases conductivity. However a trivalent impurity ion ( $\text{Dy}^{3+}$ ) doped with a monovalent impurity ion ( $\text{Na}^+$ ) does not create any vacancy to have charge neutrality *i.e.*  $\text{Dy}^{3+} + \text{Na}^+ \rightarrow 2 \text{Ca}^{2+}$

This suggests that as the concentration of  $\text{Na}_2\text{SO}_4$  increases the number of vacancies created decreases, which results in decreasing conductivity. Conductivity observed by adding 0.75 g of  $\text{Na}_2\text{SO}_4$  to  $\text{CaSO}_4$  single crystals is minimum and nearly equal to the conductivity of pure  $\text{CaSO}_4$  single crystal.

If the dopant concentration ( $\text{Na}_2\text{SO}_4$ ) is greater, region II is observed where conductivity increases with increase in concentration of  $\text{Na}_2\text{SO}_4$ . This can be explained as follows.

The excessive  $\text{Na}^+$  ions may be placed at interstitial sites moving *via* vacancy and contribute to increase in conductivity or these ions may be precipitated in a separate phase so that the vacancy mechanism becomes prominent. Such an increase in conductivity due to the addition of excessive impurity ions has been observed by Lidiard (1957), Frederick (1967) and Ebert and Teltow (1955).

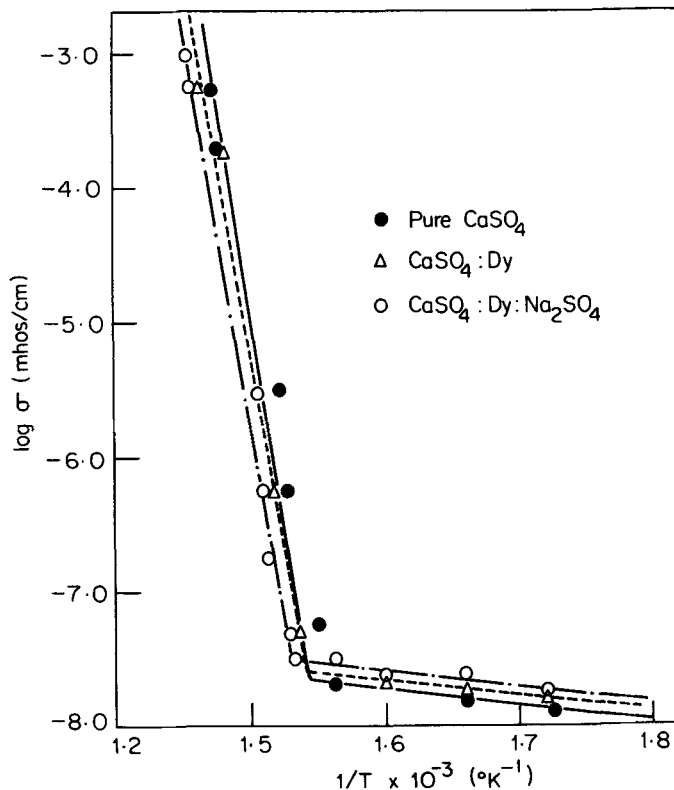


Figure 5. Plot of log conductivity ( $\sigma$ ) vs  $1/T$  for typical crystals.

Steady-state conductivity for single crystals of CaSO<sub>4</sub>, CaSO<sub>4</sub>:Dy, and CaSO<sub>4</sub>:Dy along with flux is studied in the temperature range 400 to 700°K and some typical plots of  $\log \sigma$  vs  $1/T$  are shown in figure 5. These curves for all the crystals studied consist of two straight line portions. Hence there are two activation energies for the two different temperature ranges. The temperature of break varies with the purity of the crystals. The observed variation of  $\sigma$  with temperature follows the expression

$$\sigma = A \exp [-(E_m + \phi/kT)]$$

where  $A$  = constants;  $E_m$  = activation energy for migration;  $\phi$  = formation energy of the vacancy pair;  $k$  = Boltzman's constant;  $T$  = Temperature in °K.

In the formation energy, migration energy and temperature of break for some typical crystals (CaSO<sub>4</sub>, CaSO<sub>4</sub>:Dy and CaSO<sub>4</sub>:Dy along with flux) are given in table 1. The energy for migration observed for CaSO<sub>4</sub>:Dy single crystals is smaller than that for CaSO<sub>4</sub> single crystals. This may be due to the fact that at lower temperature the number of vacancies becomes temperature-independent and the thermal energy is only large enough to allow the migration of atoms into vacancies already present in the crystal. The migration energy for CaSO<sub>4</sub>:Dy single crystals is (in the low temperature region) lower than that for CaSO<sub>4</sub> single crystals because the number of vacancies present in CaSO<sub>4</sub>:Dy single crystal is more due to the doping of Dy<sup>3+</sup> ions. Similarly the higher value of migration energy for CaSO<sub>4</sub>:Dy with flux than for CaSO<sub>4</sub>:Dy single crystals may be explained.

Table 1 also shows that activation energies (migration and formation) calculated in the high temperature region do not differ considerably presumably because at higher temperatures the number of thermally produced vacancies would predominate over the number due to impurity atoms. At the high temperature region, the thermal energy is sufficiently large to toss up the ions or atoms from their lattice sites to produce the so-called intrinsic defects, namely Schottky or Frenkel pairs and concentrations of defects increase exponentially besides the increase in jump probability. The activation energy in this region represents  $E_m + \phi/2$ .

We have considered only the ionic conduction because the electron-hole conduction is generally negligible in pure ionic crystals due to large band gap though the temperature is high.

**Table 1.** Variation of activation energy and temperature of knee with addition of Dy and Na<sub>2</sub>SO<sub>4</sub>.

	Migration energy (low temp. region) (eV)	Migration + formation energy (high temp. region) (eV)	Temp. of knee (°K)
CaSO <sub>4</sub>	0.3021	4.984	658.9
CaSO <sub>4</sub> :Dy	0.2263	4.971	650.2
CaSO <sub>4</sub> :Dy with Na <sub>2</sub> SO <sub>4</sub>	0.2831	4.982	655.3

## 3.2 Thermoelectric power

In ionic crystals (solid) the thermoelectric power is due to diffusion of vacancies or interstitials and is given by the expression (Robert *et al* 1961)

$$\alpha = -\frac{k}{q} \left[ (2\varepsilon - 1) \frac{\Delta H}{kT} - I_n \left( \frac{\nu}{\nu'} \right)^{3z} + I_n \frac{\varepsilon}{1 - \varepsilon} - \int_0^T C_p(m) \frac{dT}{kT} \right],$$

where  $\alpha$  is the thermoelectric power;  $\nu'$  is the frequency of the neighbouring ions on a vacancy;  $z$  is the number of nearest neighbours;  $\Delta H$  is the activation energy for jump process;  $\varepsilon \approx 1$  for vacancy diffusion and  $1/2$  for interstitials diffusion.

Figure 6 shows the variation of thermoelectric power ( $\alpha$ ) with mean temperature. It is observed that thermoelectric power for  $\text{CaSO}_4:\text{Dy}$  single crystals is greater than that for  $\text{CaSO}_4:\text{Dy}$  with  $\text{Na}_2\text{SO}_4$  single crystals. This maximum thermoelectric power for  $\text{CaSO}_4:\text{Dy}$  can be attributed to the presence of more cation vacancies.

Further in the measurements of the thermoelectric power of all the single crystals it is found that the polarity of the thermo EMF developed across the sample is positive at the cold end which might be due to the presence of  $\text{Ca}^{2+}$  vacancies. This reveals that the crystals grown in the present investigation are *P* type.

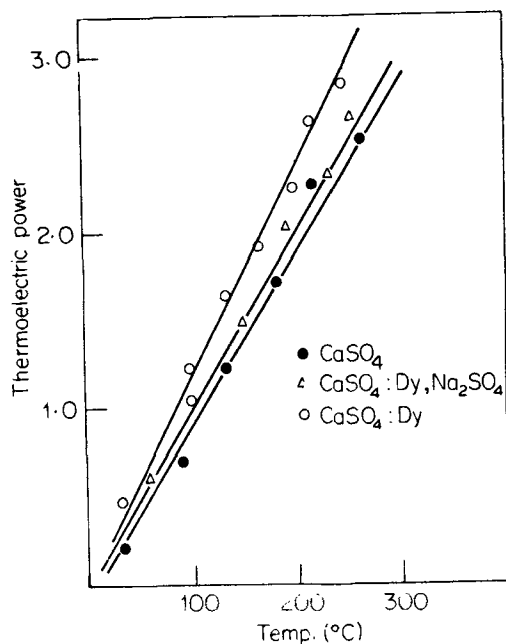
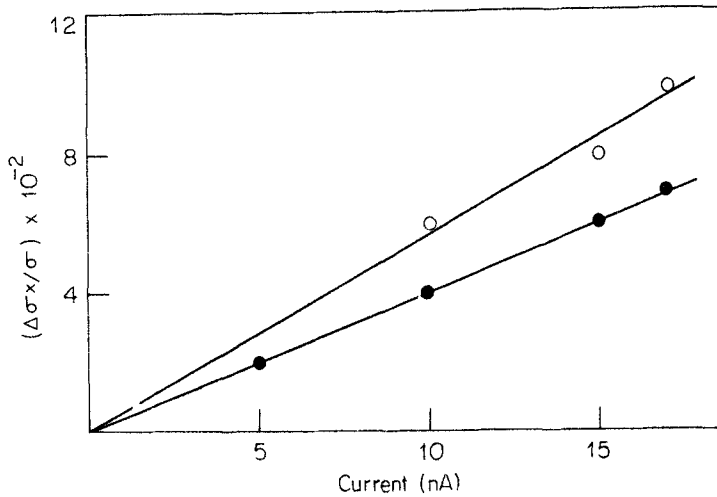


Figure 6. Plot of thermoelectric power vs temperature for  $\text{CaSO}_4$ ,  $\text{CaSO}_4:\text{Dy}$  and  $\text{CaSO}_4:\text{Dy}$  with  $\text{Na}_2\text{SO}_4$  single crystals.





**Figure 7.** Plot of  $\Delta\sigma/\sigma$  vs field strength for CaSO<sub>4</sub>, CaSO<sub>4</sub>: Dy and CaSO<sub>4</sub>: Dy with Na<sub>2</sub>SO<sub>4</sub> single crystals.

### 3.3 Magnetoresistance

Figure 7 shows the variation of magnetoresistance with the applied field for CaSO<sub>4</sub>, CaSO<sub>4</sub>:Dy and CaSO<sub>4</sub>:Dy along with Na<sub>2</sub>SO<sub>4</sub>, single crystals. In ionic crystals conduction due to electron-hole pair is negligible because of the large band gap (Lidiard 1957). Band gap energy of CaSO<sub>4</sub> reported is found to be 10 eV (Gray 1972). In the present investigation conductivity is due to the migration of cation vacancies which may contribute to magnetoresistance. Further the magnetoresistance for CaSO<sub>4</sub>:Dy single crystals is greater, which is attributed to the presence of increased number of vacancies due to doping of Dy<sup>3+</sup>, as compared to CaSO<sub>4</sub> and CaSO<sub>4</sub>:Dy with Na<sub>2</sub>SO<sub>4</sub>.

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