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C H A P T E R VI

THERMALLY STIMULATED ELECTRICAL

CONDUCTIVITY AND PHOSPHOR

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\_C\_H\_A\_P\_T\_E\_R\_:VI\_THERMALLY STIMULATED ELECTRICAL CONDUCTIVITY OF PHOSPHORS6.1 INTRODUCTION :

All the materials are divided into three categories according to their resistivity at room temperature. The materials having resistivity between  $10^{-6} \Omega \text{ m}$  to  $10^{-3} \Omega \text{ m}$  are referred as good conductors of electricity. The materials having resistivity between  $10^{-2} \Omega \text{ m}$  to  $10^{-2} \Omega \text{ m}$  are referred as semiconductor and the material having higher resistivity are called band conductor or insulator of electricity.

As temperature of metal increases its resistivity increases, but for the case of semiconductor and insulator resistivity decreases. Ca is alkaline earth metal and CaS having cubic structure, it may behave as an insulator at room temperature. As host material is doped by activator and second activator, probably the behavior of phosphor may be as semiconductor. An attempt is made in this chapter to understand electrical behavior of phosphor.

6.2 RESISTIVITY MEASUREMENTS ON A LARGE SAMPLE :

In present case  $\text{Ca}^{++}$  may be replaced by  $\text{RE}^{+++}$  by method of substitution, so vacancies may be created in the micro-crystalline powder and it behaves as semiconductor. Band gap energy of doped insulator (semi-conductor) is less than band gap energy of insulator (CaS Undoped) (1,2,3). The behavior of doped phosphors can be studied with the help of four probe set-up.

To estimate resistivity and band gap of solid state semiconductor experimental set-up of 'Scientific equipment and services' Roorkee, is used. The same apparatus is used

to estimate resistivity ( $\rho$ ) ( Conductivity  $\frac{1}{\rho}$ ) and an attempt is made to estimate band gap energy for phosphor.

$$\rho_0 = \frac{V}{I} \cdot 2\pi \cdot s \quad \dots\dots\dots(6.1)$$

Where  $\rho_0$  is resistivity of the material, I is current between pair of probe 1 and 4, V is potential difference between pair of probe ( 3 & 4 ) and s is equal spacing between probes equal to .2 cm. for the case of non conducting bottom surface equation (1) is modified by the manufactures.

$$\rho = \frac{\rho_0}{G_7 \left( \frac{W}{S} \right)} \quad \dots\dots\dots(6.2)$$

where  $G_7 \left( \frac{W}{S} \right)$  is function of thickness of crystal and distance between probe, for the samples ( KD 19 and KD 30 ) value of  $G_7 \left( \frac{W}{S} \right)$  is obtained from the table given by the manufacturer equal to 1.

Band gap energy  $E_g$  is given by

$$E_g = 2k \frac{\log_e \rho}{\left( \frac{1}{T} \right)} \quad \dots\dots\dots(6.3)$$

Value of  $\frac{\log_e \rho}{\frac{1}{T}}$  is obtained from slope of the graph.

values of resistivity ( $\rho$ ) and conductivity ( $\sigma$ ) for different temperature is shown table ( 6.1 and 6.2 )

### 6.3 RESULT AND DISCUSSION :

#### a) Conductivity of phosphor :

With the help of four probe set up conductivity (  $1/\rho$  resistivity ) - determined <sup>at</sup> different temperatures for phosphor , CaS : Sm :Nd sample no KD 19 and CaS:Dy:Tb sample no. KD 30. Table no. (6.1 - 6.2 ) and fig. ( 6.1 - 6.2 ) are

shown respectively, From graph fig ( 6.1 - 6.2 ). It is obvious that nature of the shape of curve is same for KD19 and KD 30.

At room temperature phosphors are behaving as insulator. However as temperature of the phosphor is increased, at higher temperature around  $165^{\circ}\text{C}$  conduction takes place in the phosphor. As shown in fig ( 6.1 - 6.2 ) in the region a-b conductivity decreases while in the region bc conductivity increases. This will be a clue that phosphors are behaving as semiconductor at higher temperature. The temperature at point 'b', fig. ( 6.1 - 6.2 ) is called inversion temperature. Such an inverse temperature may be observed for ( Germanium<sup>and</sup>/silicon doped material ) for doped semiconductor. For Such sample temperature < inversion temperature ( ab curve ) conduction is mainly due to impurity carrier ( Extrinsic region ) and Temperature of sample > inversion temperature conduction is due to electrons transferred to the conduction band or corresponding holes created in the valence band ( intrinsic region ).

For the phosphor  $\text{CaS}:\text{Sm}:\text{Nd}$  inverse temperature  $171^{\circ}\text{C}$  ( Sample no. 19 ) and  $\text{CaS}:\text{Dy}:\text{Tb}$  inverse temperature  $161^{\circ}\text{C}$  ( sample no.30 ). However it is difficult to draw the remarkable conclusion from few readings It<sup>is</sup> required to take a set of reading for different concentration. Low conduction in phosphors below inversion temperature may suggest that there are very few amount of impurities aded<sup>d</sup> in the phosphors

b) Band gap energy :

In case of CaS phosphor reported value of band gap energy is expected around 4.5 eV (1,2,3)

Band gap energy estimated by four probe method do not match with the reported value of band gap energy for CaS. However it is tried to explain briefly.

Calculation of band gap may be done using formula (6.3) for sample KD 19,  $E_g = 1.68$  eV and for sample KD 30  $E_g = 1.95$  eV, both of these values do not satisfy reported value of  $E_g$  for CaS. Following may be probable factors which divert calculated band gap energy of CaS phosphor.

This formula is applicable for semiconducting material (at room temperature). The factor  $G_{(7)}$  included in the formula is developed by the manufacturer of the instrument, so as to meet the band gap value estimated by other methods. It is therefore felt that modified factor suitable for materials which become semiconductor at high temperature is required to be used instead of  $G_{(7)}$ . In present work such efforts are not made. Other possible reason for low value of band gap apparently seems to be as follows :

It is argued (3) (Patil M.G.) that incorporation of Ag; Dy probably gives rise to perturbed valance and conduction band there by effectively modifying band gap structure and value. The low value of band gap estimated in present work CaS: Sm: Nd and CaS :Dy :Tb phosphors may be due to similar perturbed valance band and conduction band. The possibility of

such a energy band model how ever requires study of optical absorption edge and study of emission spectra to support such a possibility.

The resistivity of the phosphors <sup>is</sup> determined in the limited range of temperature. Probably this low conductivity may be due to the electrons which are trapped in the forbidden gap. <sup>As</sup> temperature increases these electrons may come in conduction band ( .5, 6,7 ). However it requires ~~fu~~ further study.

#### 6.4 SUMMARY :

i) Low conduction takes place in phosphor material at higher <sup>e</sup>temperature. ( Phosphor behaves semiconductor at hiher <sup>e</sup>temperature ).

ii) Detection of presence of impu<sup>y</sup>ity may be possible using four probe method.

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TABLE - 6.1 :- SAMPLE No. KD 19

Conductivity at different temperatures.

Temp. $^{\circ}\text{K}$	$\frac{1}{T} \times 10^{-3} \text{ } ^{\circ}\text{K}^{-1}$	Resistivity $10^7 \times \Omega \text{ cm}$	Conductivity $= \frac{1}{\rho} \times 10^{-8} (\Omega \text{ cm})^{-1}$	$\log \frac{\rho}{10}$
443	2.2573	2.7850	3.590	7.4448
448	2.2321	4.2046	2.378	7.6237
453	2.2075	4.0439	2.472	7.6068
458	2.1834	3.4336	2.912	7.5257
463	2.1598	2.9499	3.389	7.4698
468	2.1367	2.3837	4.195	7.3772
473	2.1141	1.9938	5.015	7.2996
478	2.0920	1.7014	5.877	7.2308
483	2.0703	1.3598	7.354	7.1335
488	2.0491	1.2041	8.304	7.0806
493	2.0283	.9811	10.192	6.9917
498	2.0080	.8260	12.105	6.9176
503	1.9880	.7049	14.186	6.8481
508	1.9685	.5859	17.067	6.7678
511	1.9569	.5294	18.889	6.7238

TABLE- 6.2 : SAMPLE No. KD 30

Conductivity at different temperatures.

Temp. (T) O <sub>K</sub>	$\frac{1}{T} \times 10^{-3} \text{O}_K^{-1}$	Resistivity $\rho \text{ cm} \cdot 10^7 \Omega \text{m}$	Conductivity $= \frac{1}{\rho} \times 10^{-8} (\Omega \text{m})^{-1}$	Log $\rho$ 10
428	2.3364	8.3775	1.193	7.9231
433	2.3094	12.5663	.7957	8.0992
438	2.2831	12.0427	.8307	8.0807
443	2.2573	10.9670	.918	8.0400
448	2.2321	9.5331	1.048	7.9792
453	2.2075	7.9049	1.265	7.8979
458	2.1834	6.3798	1.567	7.8048
463	2.1598	5.3358	1.874	7.7272
468	2.1367	4.4339	2.255	7.6464
473	2.1141	3.6795	2.718	7.5657
478	2.0920	3.1078	3.217	7.4924
483	2.0703	2.7198	3.676	7.4345
488	2.0491	2.3379	4.277	7.3688
493	2.0283	1.9547	5.115	7.2910
498	2.0080	1.6961	5.896	7.2294
503	1.9880	1.5067	6.637	7.1780
508	1.9685	1.3194	7.579	7.1203
513	1.9493	1.1868	8.426	7.0743
518	1.9305	1.0502	9.521	7.0212
523	1.9120	1.0372	9.64	7.0158



