

Thermoluminescence of x-irradiated $\text{CaSO}_4:\text{Dy}$ phosphors and role of Na_2SO_4 as a charge compensator

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Abstract. The thermoluminescence of x-irradiated $\text{CaSO}_4:\text{Dy}$ phosphors has been studied for diverse activator concentrations. The concentration-dependence of these phosphors on the increase of glow peak intensities has been found to be remarkable. For higher concentration of dysprosium the concentration quenching effect has been observed. This has been attributed to the resonant transfer of energy from one activator atom to another, bringing the possible migration of energy in a solid, which is likely to get dissipated without luminescence, at the quenching site itself. The effect of irradiation time on the glow peak intensities reveals the initial linearity and a subsequent decrease indicating the possible radiation damage. The role of Na_2SO_4 as a charge compensator has been studied in detail. An attempt has been made to unravel the type of kinetics involved in the process, by calculating the activation energies by different methods. It has been concluded that the type of kinetics involved in the process is bimolecular.

Keywords. Phosphors; thermoluminescence; charge compensation; dosimetry.

1. Introduction

Since the pioneering work of Wiedemann and Schmidt (1895) a large number of papers have appeared on the thermoluminescence (TL) properties of alkaline earth sulphate phosphors. Recently, there has been a revival of interest in these phosphors, because of their wide application in the field of TL dosimetry (Pradhan *et al* 1975a, b; Vishwanathan *et al* 1975, Murthy *et al* 1975) and easy laboratory preparation techniques. Dysprosium-doped calcium sulphate phosphor is becoming increasingly popular in thermoluminescence because of its efficiency and sensitivity (Yamashita *et al* 1968; Nambi 1973; Lakshmanan and Ayyangar 1975; Nambi *et al* 1974). The TL response of $\text{CaSO}_4:\text{Dy}$ to ultraviolet, α -rays, γ -rays, thermal neutrons and fast neutrons is well-known (Bhuwan *et al* 1975, Lakshmanan and Ayyangar 1975; Ayyangar *et al* 1974; Sunta *et al* 1972). Relatively little effort has gone into the study of TL response of $\text{CaSO}_4:\text{Dy}$ phosphor to x-rays, despite the fact that such studies are important in the measurements of diagnostic x-ray doses in medicine (Vishwanathan *et al* 1975).

Moreover, very little studies appear to have been made on the role of charge compensator on the enhancement of glow peak intensity of $\text{CaSO}_4:\text{Dy}$ phosphors. An attempt has therefore been made to study different aspects of the TL phenomenon in x-irradiated $\text{CaSO}_4:\text{Dy}$ phosphors. Na_2SO_4 has been used as charge compensator for preparing some phosphors. The effect of charge compensator on

glow peak intensity has also been studied. The type of kinetics has been decided analysing different methods and the basic mechanism involved in the process has been investigated.

2. Experimental

2.1. Phosphor preparation

Calcium sulphate phosphors activated with dysprosium, with diverse activator concentration were prepared from Indian mineral gypsum in the atmosphere of H_2SO_4 fumes using methods reported earlier (Mulla and Pawar, 1977). Pure gypsum powder was dissolved in concentrated H_2SO_4 and a predetermined quantity of Dy_2O_3 solution was added. The charge was kept at 300°C for evaporation. The residue, washed with distilled water to remove impure soluble sulphate, was dried and heated to 600°C for 2 hr and quenched. The sample was finally crushed, sieved out and collected in a sealed tube. The concentration of dysprosium weight percentage was varied from 0.005 to 0.5. Some phosphors were prepared by adding Na_2SO_4 as a charge compensator.

2.2. X-ray irradiation

The phosphors were irradiated using a Phillips x-ray machine, operated at 32 kV and 11 mA, for 1 hr at room temperature. The target used in the x-ray tube was molybdenum.

2.3. Thermoluminescence glow curve recorder

The glow curves were recorded above room temperature to about 600°K at a linear heating rate of $50^\circ\text{C min}^{-1}$. The glow curve recorder mainly consisted of IP21 photo-multiplier tube the amplified output of which was fed to 'Omniscribe' strip chart recorder. A specified quantity of irradiated phosphor was uniformly spread over a tiny brass strip. The chromel-alumel thermocouple was spot-welded for simultaneous measurement of phosphor temperature. The brass strip was linearly heated.

3. Results

3.1. Glow curves for CaSO_4 :Dy Phosphors and their concentration-dependence

The glow curves for CaSO_4 :Dy phosphors, in the temperature range 300°K to 600°K , are shown in figure 1. The activator concentration has been increased from 0 to 0.5 wt % of Dy. The glow peaks are found to be concentration-dependent. Similar results have been reported by Merz (1966) for CaF_2 :RE phosphors above room temperature. The glow curve for undoped heat treated CaSO_4 was found to be weak and diffused exhibiting only two peaks at about 390°K and 500°K . However, the glow curves for the dysprosium doped CaSO_4 phosphor exhibit four peaks although these are not distinctly resolved in every phosphor due to overlapping. The peak temperatures occur at approximately 387°K (peak I), 407°K (peak II), 480°K (peak III),

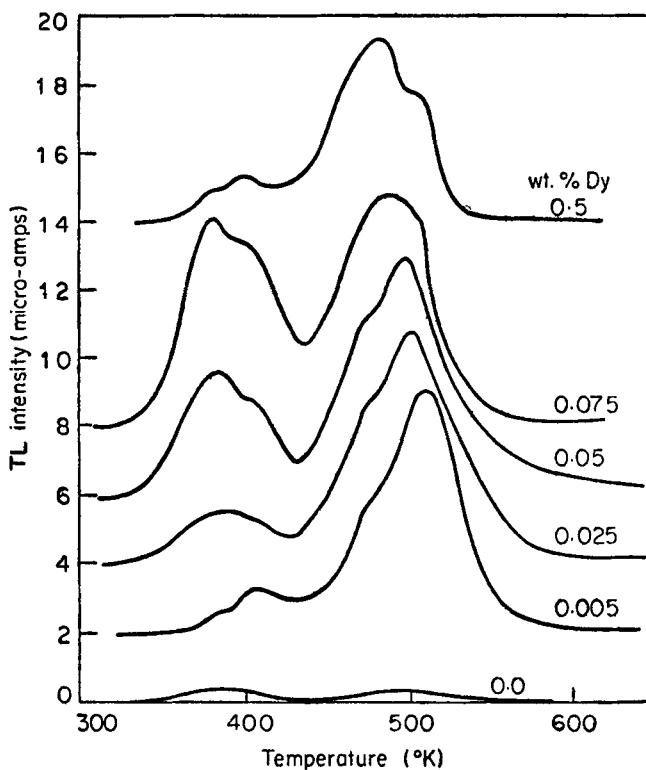


Figure 1. Influence of activator concentration on thermoluminescence glow curves of $\text{CaCO}_3 : \text{Dy}$ phosphors.

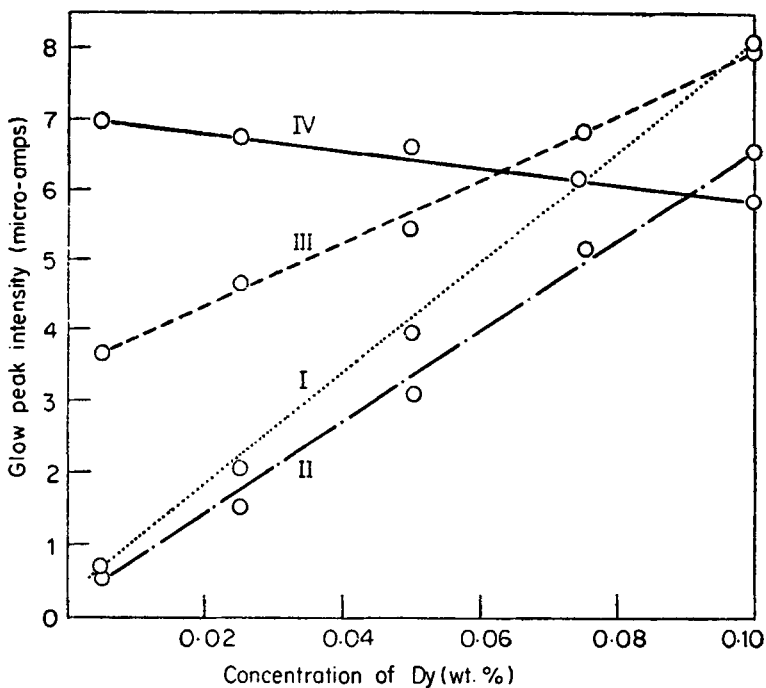


Figure 2. Plot for glow peak intensities with respect to the activator concentration for different peaks observed in figure 1.

510°K (peak IV). The overall glow peak intensities enhance as the concentration of dysprosium increases. However, at the highest concentration (0.5 wt %) there is an overall decrease in all the four glow peak intensities. This phenomenon is popularly known as 'concentration quenching'. Peak II and peak IV are prominent for lower concentration (0.005 wt %) of dysprosium. However, these peaks become less prominent at a higher concentration, while peaks I and III, which are less prominent at lower concentrations, become quite prominent at higher concentrations. However, this is not true for concentration quenched phosphor.

Certain peaks are found to be more sensitive to concentration variation (figure 2). It is seen that peak I enhances most rapidly with concentration while peak IV falls off. Peaks II and III are found to grow with concentration, but their rates of growth are slower as compared to peak I.

The normalised TL intensity versus concentration has been plotted both theoretically and experimentally (figure 3). The theoretical curve shows a very close fit to the experimental one, showing the effect of concentration quenching for higher activator concentrations. It is seen that 0.1 wt % Dy is the optimum concentration. Table 1 gives a list of the activation energies for CaSO_4 : Dy phosphors without

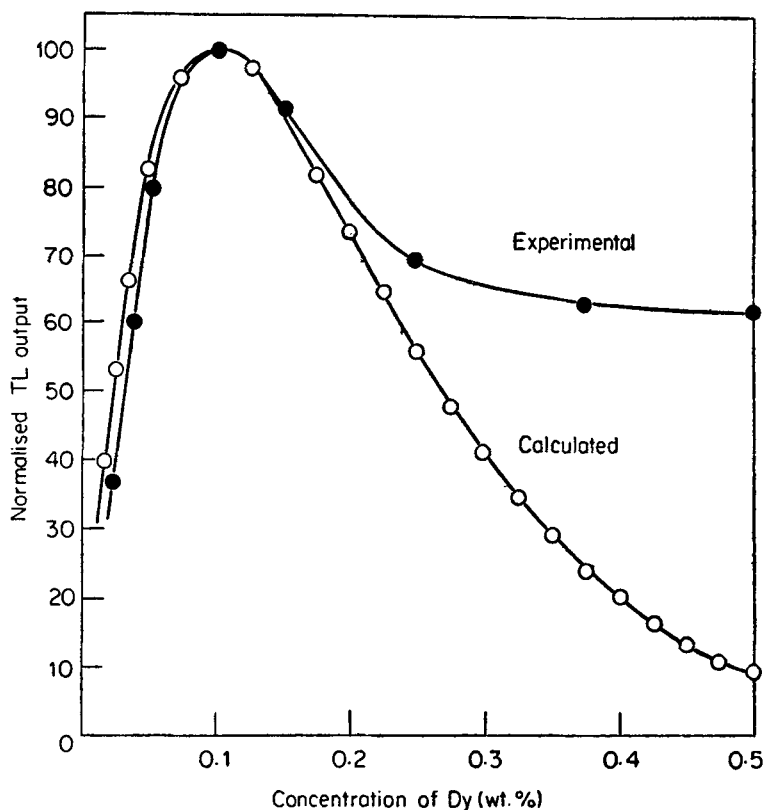


Figure 3. Theoretical fit for concentration quenching observed in Dy doped CaSO_4 phosphor.

Na_2SO_4 . Figure 1 and table 1 reveal that the glow peak temperatures decrease slightly with increase of concentration in most of the cases.

3.2. X-ray dosage dependence of TL

Dosage dependence of thermoluminescence was studied to investigate the optimum condition of irradiation. The irradiations were made at 32 kV, 11 mA x-rays, from

Table 1. Activation energies and glow peak temperatures for different concentrations of dysprosium in CaSO_4 phosphors.

Concentration of Dy. wt. %	Glow peak temperatures and activation energies (eV)							
	I		II		III		IV	
	T_g	E	T_g	E	T_g	E	T_g	E
0	390	0.99	—	—	—	—	500	1.33
0.005	387	0.98	407	1.04	479	1.26	510	1.36
0.025	384	0.97	404	1.03	476	1.25	502	1.34
0.05	382	0.96	402	1.02	474	1.25	500	1.33
0.075	380	0.96	406	1.04	484	1.28	504	1.34
0.5	378	0.95	402	1.02	478	1.26	500	1.33
Mean	383.5	0.97	404.2	1.03	478.2	1.26	502.66	1.34
Mean Deviation	3.5	0.01	1.84	0.01	2.64	0.01	2.89	0.01

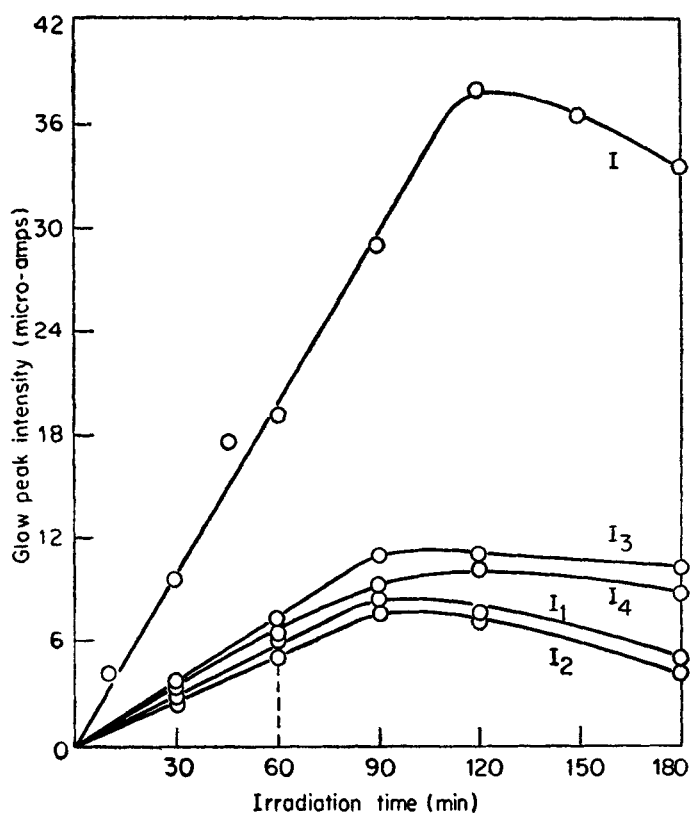


Figure 4. X-ray dosage dependence of glow peaks.

10 min to 3 hr. The curves for different peaks show initial linear growth upto 90 min for most peaks, followed by decrease (figure 4) for $\text{CaSO}_4:0.075 \text{ wt } \% \text{ Dy}$. In the case of peak I_4 linearity has been observed upto 60 min. Peak I_3 is more susceptible to exposure time compared to other peaks, while peak I_2 is relatively less affected. The Na_2SO_4 added $\text{CaSO}_4:0.075 \text{ wt } \% \text{ Dy}$ shows maximum response to the x-ray dosage (curve I). The integrated TL intensity when plotted against exposure time (figure 5) for $\text{CaSO}_4:0.075 \text{ wt } \% \text{ Dy}$ without and with Na_2SO_4 curves I and II respectively) also give similar results. The promising enhancement of integrated glow peak intensity for Na_2SO_4 added phosphor is apparent from figure 5.

3.3. Effect of Na_2SO_4 on TL of $\text{CaSO}_4: \text{Dy}$ phosphors

The charge compensator Na_2SO_4 has a marked effect on the TL of $\text{CaSO}_4:\text{Dy}$ phosphor. The typical glow curves for $\text{CaSO}_4:0.075 \text{ wt } \% \text{ Dy}$ (curve I) and with Na_2SO_4 (curve II) are presented in figure 6. Glow curve I exhibits four peaks at the temperature mentioned earlier. However, glow curve II exhibits a single peak, coinciding with the first peak of curve I. This clearly shows that the addition of Na_2SO_4 has subsided three peaks (II, III, and IV), while peak I has been enhanced almost thrice that of peak I of curve I.

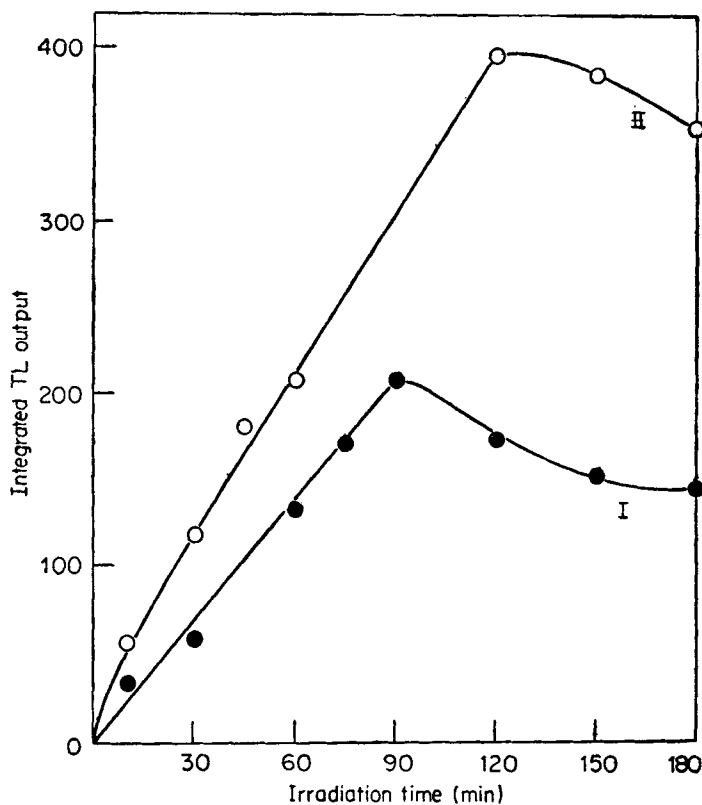


Figure 5. Plot for integrated glow peak intensity versus time exposure for $\text{CaSO}_4:0.075 \text{ wt } \% \text{ Dy}$ with Na_2SO_4 (curve II) and without Na_2SO_4 (curve I).

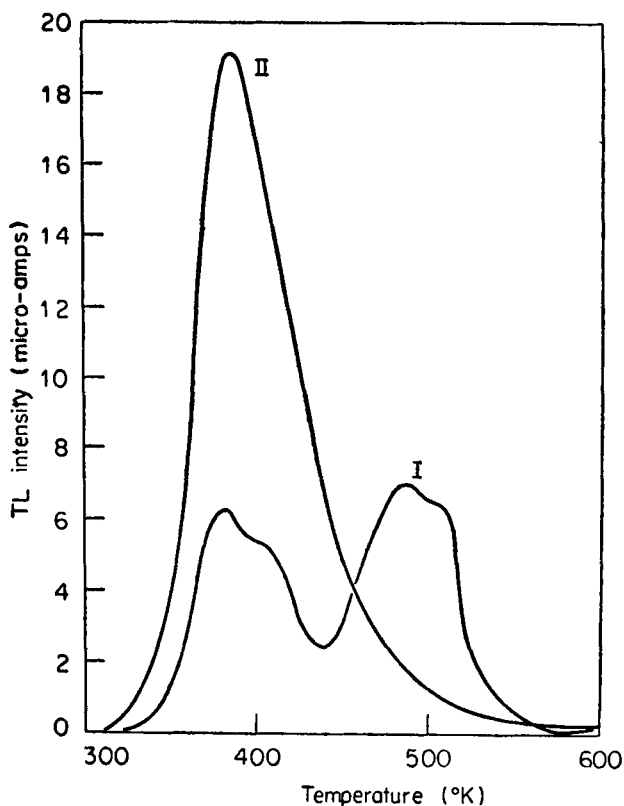


Figure 6. Thermoluminescence glow curves for CaSO₄: 0.075 wt. % Dy with Na₂SO₄ (curve II) and without Na₂SO₄ (curve I).

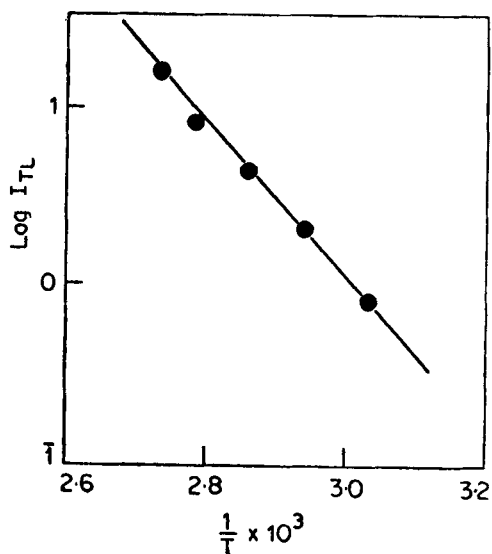


Figure 7. Plot for $\log I_{TL}$ versus $1/T$ in the initial part of glow curve for Na₂SO₄ added CaSO₄: 0.075 wt. % Dy phosphor.

Table 2. Activation energies and order of kinetics for Na₂SO₄ added CaSO₄:0.075 wt % Dy phosphor.

Methods used for calculation of activation energy E	Activation energies (eV) (E_g)			Order of kinetics
	E	E_1	E_2	
Initial rise method	0.88	—	—	—
Nambi's empirical relation	0.96	—	—	—
Halperin and Braner Method	—	0.78	0.87	II
Chen's Method	—	0.77	0.90	II

The activation energy corresponding to a typical Na₂SO₄ added CaSO₄:0.075 wt % Dy phosphor estimated by 'initial rise method' (figure 7) comes out to be 0.88 eV. Various other methods have been employed to study the type of kinetics involved in the process. The values of the activation energies so obtained are tabulated in table 2.

4. Discussion

4.1. Analysis of glow curves and order of kinetics

TL of calcium sulphate phosphors activated with various rare earth impurities have been investigated by Nambi (1973), and the kinetics revealed is of the second order. A similar observation has been obtained for x-irradiation induced TL, in CaSO₄:Dy phosphors but is not discussed at length here. The activation energy E has been evaluated from the glow peak temperatures T_g using nomograph, which obeys the relation (Nambi *et al* 1974).

$$E = (3.12 \times 10^{-3} \times T_g - 0.23) \text{ eV.} \quad (1)$$

The values of activation energies and glow peak temperatures are shown in table 1.

As data regarding thermoluminescence and the type of kinetics involved in CaSO₄:Dy phosphors, prepared with Na₂SO₄ are not available in literature, our results are discussed in detail. The single, sharp and intense glow peak observed in Na₂SO₄ added CaSO₄:Dy phosphors, has simplified our analysis. Figure 6 shows a typical glow curve (curve II) for Na₂SO₄ added phosphor. The initial part of glow curve can be described by a relation (Randall and Wilkins 1945; Garlick and Gibson 1948)

$$I_{TL} = F \exp(-E_i/kT) \quad (2)$$

The above equation is the basis of the 'initial rise method,' in which activation energy E_i can be obtained by plotting $\log I_{TL}$ versus $1/T$ (figure 7). The slope of the plot directly gives the value of E_i for the phosphor and is listed in table 2.

The submodel (b) in the method of Halperin and Braner (1960), in which the recombination is via the conduction band, has been employed to analyse the glow curves,

as these phosphors show TSC. The activation energies for first and second order kinetics are respectively,

$$E_1 = [1.72 k T_g^2 (1 - 2.58 \Delta)]/\tau, \quad (3)$$

and
$$E_2 = [2 k T_g^2 (1 - 3 \Delta)]/\tau \quad (4)$$

where k is Boltzmann's constant and $\tau = w - \delta$, w being the half intensity width of the peak

$$\Delta = \frac{2 k T_g}{E} \ll 1.$$

E_1 and E_2 values obtained from (3) and (4) are listed in table 2 for Na_2SO_4 added $\text{CaSO}_4 \cdot 0.075$ wt % Dy phosphor.

Chen (1969) has modified the above equations and has given the equations for first and second order kinetics

$$E_3 = (1.52 k T_g^2)/\tau - (3.16 k T_g), \quad (5)$$

and
$$E_4 = (1.813 k T_g^2)/\tau - (4 k T_g). \quad (6)$$

A close study of the activation energy values listed in table 2 for the typical phosphor reveals that the kinetics involved in the process is of the second order.

Halperin and Braner (1959) have suggested a simple approach for the order of kinetics from the shape of the glow curve. It has been shown that

$$\delta/w \leq 1/e \text{ for first order kinetics}$$

while $\delta/w \geq 1/e$ for second order kinetics.

The observed value of δ/w (figure 6, curve II) comes out to be 0.68 which is greater than $1/e$. This confirms the second order kinetics as suggested above. For second order kinetics, which originates due to the dominant role of retrapping, the Garlick and Gibson (1948) theory gives the expression for activation energy E_g

$$E_g = kT_g \log \left(\frac{ST_g}{\beta} \right) [1 + f(S, \beta, E_g)] \quad (7)$$

where
$$f(S, \beta, E_g) = \frac{\log \left\{ \frac{2n_0}{N} \frac{kT_g}{E_g} \left[1 + \frac{n_0}{N} \int_0^{T_g} \frac{S}{\beta} \exp \left(-\frac{E_g}{kT} \right) \right]^{-1} \right\}}{\log \left(\frac{ST_g}{\beta} \right)} \quad (8)$$

where T_g = glow peak temperature, S = frequency factor, β = linear heating rate, n_0 = number of holes trapped at irradiation temperature which equals the number of

active luminescent centres, and N = total concentration of hole traps. For first order kinetics, where there is no retrapping, one gets the same equation (7) for E_g , except the value of

$$f(S, \beta, E_g) = \frac{\log(kT_g/E_g)}{\log(ST_g/\beta)} \quad (9)$$

The value of (8) in second order kinetics is dependent on n_0/N , which is not the case in the first order kinetics (9). The value of n_0/N can be altered either by increasing the concentration of dopant in the phosphor or by increasing the irradiation dosage. The increase in the value of n_0/N will increase $f(S, \beta, E_g)$ and decrease T_g . The insinuating evidence of the variation of T_g with increase in concentration (figure 1) can be noted in support of second order kinetics.

4.2. Role of Na_2SO_4 on TL of $\text{CaSO}_4:\text{Dy}$ phosphors

Incorporation of charge compensator Na_2SO_4 in the phosphor has a promising effect in the enhancement of first peak (figure 6), while the remaining peaks subside. The possible explanation for this peculiar behaviour of Na_2SO_4 added phosphor can be given as follows.

The $\text{CaSO}_4:\text{Dy}$ phosphor without Na_2SO_4 exhibits four peaks (figure 6) which correspond to four defect levels at the electron trap site of the phosphor. It is believed that out of four, the first defect level is activator-induced, and the remaining three are due to host lattice defects formed during the preparation of phosphor. In the preparation of phosphor, two ions of Dy^{3+} replace three Ca^{2+} ions, creating Ca^{2+} ion vacancies. The dysprosium ion can easily enter the lattice, in place of Ca^{2+} ion, as the ionic radius of Dy^{3+} is close to ionic radius of Ca^{2+} ion. (The ionic radius of Ca^{2+} is 1.06 A.U., while the ionic radius of Dy^{3+} is 1.07 A.U.). The addition of Na_2SO_4 in $\text{CaSO}_4:\text{Dy}$ removes Ca^{2+} vacancies created during the preparation of phosphor. This may be explained by the fact that Na^+ being the charge compensator ion, which along with Dy^{3+} ion, removes two ions of Ca^{2+} . This enables introduction of more number of Dy^{3+} ions in the host lattice, on account of charge balancing



This is in accordance with the famous charge compensation theory given by Kroger and Hellingmann (1949). The increased number of Dy^{3+} ions in the host lattice, increases the number of active luminescent centres (n_0). At the same time the presence of charge compensator (Na^+) removes all Ca^{2+} vacancies and hence all the three defect levels formed in the preparation of phosphors are wiped out leaving behind only one activator-induced defect level corresponding to first peak. This explains why only one peak is observed in Na_2SO_4 added phosphor. This peak is naturally remarkably enhanced as there is increase of n_0 , the active luminescent centres, with the addition of Na_2SO_4 . The increase of n_0 has a direct bearing on TL intensity (I_{TL}), since

$$I_{TL} = \frac{n_0^2 S \exp\left(-\frac{E_g}{kT}\right)}{N \left[1 + \frac{n_0}{N} \int_0^S \frac{S}{\beta} \exp\left(-\frac{E_g}{kT}\right) dT\right]^2} \quad (10)$$

The above explanation is further strengthened by the fact that the undoped heat-treated CaSO_4 shows weak thermoluminescence, while Na_2SO_4 added undoped heat-treated CaSO_4 does not show TL at all. In this case the charge compensator wipes out all the host crystalline defect levels, which are the only levels present in undoped CaSO_4 ; the activator-induced level being absent.

4.3. TL and its activator concentration dependence

The basic mechanism involved in the TL of $\text{CaSO}_4:\text{Dy}$ has already been reported by Nambi *et al* (1974). They have attributed the origin of TL to the reduction of Dy^{3+} to Dy^{2+} by the capture of electron in irradiation process and its reconversion back to Dy^{3+} in heating process of TL. The reconversion has been attributed to the recombination of hole with electron at Dy^{2+} , which acts as luminescent centre, giving rise to emission of photon:



This mechanism has also been supported by Bapat (1977).

It is observed from figure 1 that the increase of activator concentration enhances the TL indicating that the TL of $\text{CaSO}_4:\text{Dy}$ is concentration-dependent. In the present phosphors, as the kinetics involved is of the second order, the concentration-dependence can be explained on the basis of equation (10) given by Garlick and Gibson (1945), for second order kinetics. The total number of hole traps N cannot be expected to vary strongly with concentration (Merz 1966). As the concentration of activator increases, more dysprosium ions are reduced to the divalent state; so more hole traps must be filled. Therefore n_0 is expected to increase with concentration. As a result, the glow intensity increases with concentration as seen from equation (10). However, the glow intensity cannot be expected to increase indefinitely with concentration, since the rate of formation of active luminescent centres by capturing the holes during the irradiation, might be fading rapidly and concentration quenching is affected.

The concentration quenching can also be considered in terms of the resonant transfer of energy from one activator atom to the other, thus bringing in the possible migration of energy from one activator atom to the other, which has greater probability of getting dissipated without luminescence at quenching site (Nambi 1973). This has been treated theoretically by Johnson and Williams (1950), and later modified by Ewles and Lee (1953). Nambi has shown that the equation of Ewles and Lee give somewhat nearest fit to experimental points in case of irradiated $\text{CaSO}_4:\text{Dy}$ phosphor. The luminescence efficiency, η is given by the relation,

$$\eta = \frac{k}{1 + \alpha c^{-1} \exp(nc)}, \quad (11)$$

where $k(=101.6)$, is the normalising constant, $\alpha(=0.037)$ is the constant involving the absorption coefficients of activator and structure centres, and $n(=100)$ is the

number of lattice ions associated with radiative centres. Similar results have been obtained in the case of x-irradiated Na_2SO_4 added CaSO_4 : Dy phosphors (figure 3).

4.4. X-ray dosage dependence of TL

The study of x-ray irradiation dose, which ensures no crystal damage, is essential before undertaking systematic studies of thermoluminescence. Only those doses are chosen that produce minimum amount of crystal damage. However, one should bear in mind that lower doses hamper the glow peak intensity of TL. Considering these two factors, 1 hr has been chosen as irradiation time throughout the experiment, since after 1 hr nonlinearity begins in certain peaks (figure 4). The initial linear growth with respect to time as depicted in figure 4 is attributed to linear increase of n_0 with irradiation time and subsequent emission of TL due to reoxidation of Dy^{2+} into Dy^{3+} during heating. Thus the intensity increases linearly in initial stage. The dosage saturation of TL can be explained on the assumption that only limited number of trivalent dysprosium ions are available for charge reduction. In the case of Na_2SO_4 added phosphor since the availability of n_0 is large, the initial linear growth has been quite rapid, showing that the dosage dependence of TL intensity of Na_2SO_4 added phosphor is more compared to that without Na_2SO_4 added phosphor (curve I).

5. Conclusions

(i) The TL of CaSO_4 :Dy phosphors have been found susceptible to the variations of activator concentration and time exposure to x-rays. (ii) The charge compensator plays an important role in the enhancement of first glow peak intensity. (iii) The kinetics involved in the process is of the second order for both with and without Na_2SO_4 added phosphors. (iv) There are four defect levels corresponding to four glow peak temperatures in the case of phosphors without Na_2SO_4 . The first defect level is activator-induced, while the remaining three arise during the preparation of phosphors.

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