

Thermoluminescence studies of CaS phosphors activated by Ce³⁺, Na⁺ and Ag⁺

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Abstract : Thermoluminescence (TL) of Ce³⁺, Na⁺ and Ag⁺ activated CaS phosphors has been studied. The TL intensity decreases by the addition of monovalent activator (Na⁺) in CaS:Ce³⁺ phosphor. This may be due to the formation of Ce⁴⁺ ions during γ -irradiation, which do not participate in the TL process. Only one type of defect is formed in CaS due to its exposure to γ -radiation. Doping with Ce³⁺ or Ag⁺ ions in the CaS forms new defects, which are responsible for the additional TL peaks observed in these samples.

Keywords : Thermoluminescence, trapping parameter, CaS

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Alkaline earth sulphide phosphors have aroused much interest after the discovery of infrared stimulation and sensitized luminescence [1,2]. The knowledge of defect structure and its connection with distribution of energy levels in the band gap of solids is an important prerequisite for thorough understanding of luminescence phenomenon. Thermoluminescence (TL) and decay characteristics of phosphors have been widely used as a means of investigating the mechanism of luminescence. The decay characteristics offer significant information about the kinetics involved in the luminescence process and the energy distribution of trapping centers. Blokinsev [3] and De Groot [4] were the first among the early workers, who derived theoretical time-dependence of the decay of phosphorescence from consideration of electron transitions between various energy levels.

CaS phosphors were obtained using solid state reaction with control bearing between activators and CaSO₄ as starting material and fire at higher temperature (800°C) for 2 hours. The reducing agent was AR grade carbon powder used in the synthesis. This phosphor has been denoted as CaS:Ce³⁺. CaS phosphors were prepared by solid state diffusion method at higher temperature (800°C) for 2 hours using Na₂SO₄ as a flux

with starting material CaSO₄; the prepared phosphor denoted as CaS:Ce³⁺(Na⁺). The concentration of Ce and Ag were changed to optimize the lumen output and is denoted as CaS:Ce³⁺(Na⁺)Ag⁺ phosphor. After heat treatment, the resultant powder pulverized in a dry atmosphere and stored, keeping in view the extreme purity as the main consideration in preparation. Phosphor was confirmed taking into consideration of XRD patterns.

Thermoluminescence glow curves were recorded with the usual set-up consisting of a small metal plate heated directly using a temperature programmer, a photomultiplier tube (PMT), a DC amplifier and a millivolt recorder. 5 mg of phosphor was heated each time at the rate of 5°C per second. Exposure to γ -rays was performed using a ⁶⁰Co source.

Thermoluminescence has been used by a number of workers for obtaining the trapping parameters. Randall and Wilkins [5] were the first to analyse the phenomenon. They proposed the following equation for the TL process.

$$I = c \frac{dn}{dt},$$
$$I = csn \exp\left(\frac{-E}{kT}\right) \quad (1)$$

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In this equation, E is the trap depth, s the frequency factor, c an arbitrary constant and n the number of populated traps. It is assumed that the thermally released electron recombines at the luminescence center and there is no retrapping. Garlick and Gibson [6] modified the equation by considering the retrapping and proposed the following equation for second order :

$$I = c \frac{dn}{dt},$$

$$I = -cs \frac{n^2}{N} \exp\left(\frac{-E}{kT}\right). \quad (2)$$

Here, N is the total number of traps. According to Garlick and Gibson, the second order approximation applied when retrapping and recombination probabilities are equal. It was recognized that the order of kinetics need not be 1 or 2, but can be assumed to be of any intermediate value. A general order equation was proposed by May and Partridge [7].

$$I = -c \frac{dn}{dt},$$

$$I = cs' n^b \exp\left(\frac{-E}{kT}\right). \quad (3)$$

s' , the pre-exponential factor, is a constant having dimensions of $\text{cm}^3 \cdot \text{s}^{-1}$ which is not considered as a frequency factor and defined as $s' = sn_0^{-(b-1)}$. n is the concentration of trap electron in cm^{-3} and b is the order of kinetics. It can be shown that in general, order kinetics $s'n_0^{-(b-1)}$ is similar to frequency factor for Randall and Wilkins; where n_0 is the initial number of populated traps. A number of methods have been suggested to obtain trapping parameters with the help of these equations [8]. Chen [8] has connected the order of kinetics with an experimentally obtainable quantity, the form factor μ_g . All these formulations assume the order of kinetics, which represents the trapping probability to be constant.

In eq. (3), b is between 1 and 2 and gives the fraction of electrons going to recombination centers. Solving eq. (3) and applying the condition of maximum, we obtain a reasonable approximation for most of the cases.

$$\frac{\beta E}{kT_m^2} = S \exp\left(\frac{-E}{kT_m}\right) \left[1 + (b-1) \frac{2kT_m}{E}\right], \quad (4)$$

where $S = s' n^{b-1}$, $\beta =$ heating rate (K/sec). Using eq. (4), frequency factor S can be calculated for $b = 1$.

$$s = \frac{\beta E}{kT_m^2} \exp\left(\frac{+E}{kT_m}\right). \quad (5)$$

Chen [8] has related eq. 3 with experimentally obtainable

quantity, from factor denoted by μ_g . Chen [8] also empirically improved some of the expressions for trap depth and coordinated the methods, which used different parts of the glow curves for obtaining the trapping parameters.

A reasonable method which does not require prior knowledge of b is based on the accurate measurements of the temperature of TL peak maximum (T_m), low temperature half width (τ) and high temperature half width (δ). Methods using δ , τ along with T_m were developed by Luschnik [9] and Halperin and Braner [10]. Chen [8] later summed up these three methods in the form of following equations:

$$E = Ca \left[\frac{kT_m}{a} \right]^2 - Ba(2kT_m), \quad (6)$$

where a , Ca , Ba are constants, E is the activation energy. Depending on whether τ , δ or ω is used. This equation takes the forms :

$$E_\tau = [1.51 + 3(\mu_g - 0.42)] \frac{kT_m^2}{\tau} - [1.58 + 4.2(\mu_g - 0.42)] 2kT_m. \quad (7)$$

$$E_\delta = [0.976 + 7.3(\mu_g - 0.42)] \frac{kT_m^2}{\delta}, \quad (8)$$

$$E_\omega = [2.52 + 10.2(\mu_g - 0.42)] \frac{kT_m^2}{\omega} - 2kT_m. \quad (9)$$

where T_m is the temperature at which maximum intensity is observed, T_1 and T_2 are the temperatures on low and high temperature sides, respectively at which the intensity falls to half of the maximum value.

$$\delta = T_2 - T_m, \quad \omega = T_2 - T_1, \quad \tau = T_m - T_1$$

$$\text{and } \mu_g = \frac{\delta}{\omega}.$$

Except for extreme values of μ_g (< 0.42 , > 0.52), the trap depths obtained using eq. (7-9) are consistent.

Typical TL glow curves are shown in Figure 1 (exposed to γ -ray = 1.16 C/kg). TL in pure CaS is very weak (Figure 1, curve-a), only one peak is seen at 362 K. The CaS: Ce phosphor shows two peaks around 362 K and 426 K (Figure 1, curve-b). The most prominent TL peak appears around 426 K and 362 K. The 426 K TL peak intensity increases with increasing Ce^{3+} shows that concentration in CaS. TL in CaS: Ce^{3+} (Na^+) (Figure 1, curve-c), the 426 K peak intensity decreases due to Na^+ ions in CaS: Ce^{3+} phosphor. During γ -ray irradiation, holes are trapped at Ce^{3+} as well as at other site. Formation of Ce^{4+} is a wellknown mechanism of Ce^{3+} ions during γ - or X-ray irradiation [11]. On heating, thermally released holes from Ce^{4+} site recombine with the electrons at unspecified sites. γ -ray induced oxidation of Ce^{3+}

ions, viz., $Ce^{3+} \rightarrow Ce^{4+} + e^-$ shows the hole trap production. Among the RE³⁺ ions, Ce exhibits 3+ as well as 4+ valence states. The higher TL peak temperature of CaS: Ce indicates that the thermal activation energy of holes from Ce⁴⁺ sites is higher than that of the host lattice-related sulfide radicals. On the contrary, 2+ valence state can also be stable in the Ca²⁺ sub-lattice. Townsend and White [12] have recently commented that the RE³⁺ \rightarrow RE²⁺ redox model in CaSO₄: RE has a conceptual problem since the hole is not only captured by RE²⁺ ion but also stimulates RE³⁺ luminescence.

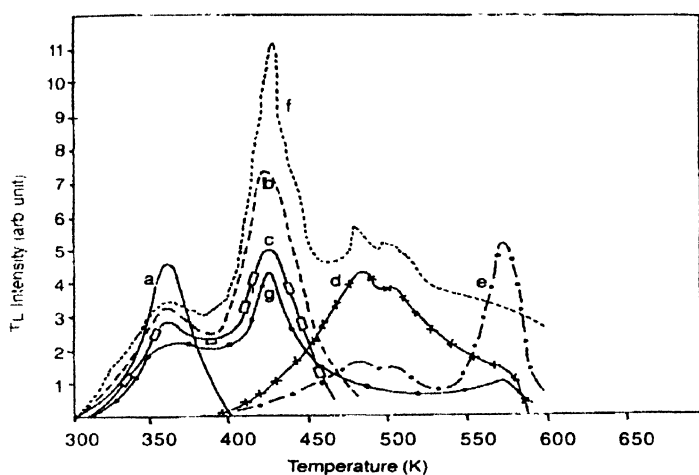


Figure 1. Typical TL glow curve of various phosphors exposed to γ -ray (1.16 C/kg) (a) CaS pure, (b) CaS: Ce³⁺, (c) CaS: Ce³⁺ (Na⁺), (d) CaS: Ag⁺ (lower concentration) (0.1 mol%), (e) CaS: Ag⁺ (higher concentration) (1.0 mol%), (f) CaS: Ce³⁺, Ag⁺, (g) CaS: Ce³⁺ (Na⁺) Ag⁺

Ag⁺ ion activated in CaS host shows two peaks at 487K, 503K and shoulder observed at higher temperature at 573K for low concentration of Ag⁺ ions (0.1 mole%) (Figure 1, curve-d). With increasing the concentration of Ag⁺ ions, the higher temperature shoulder is manifested as a prominent glow peak (Figure 1, curve-e). TL peaks of CaS: Ce³⁺, Ag⁺ (Figure 1 curve-f) was observed at 426 K, 487 K, 503 K and shoulder at 583K; the TL intensity of 426 K peak increased by 1.6 times as compared to that in CaS:Ce. This may be either due to some competitive process or energy transfer from Ag⁺ to Ce³⁺. However, this is only a speculation as we do not have any experimental evidence for this. CaS:Ce³⁺ (Na⁺) Ag⁺ phosphor shows the prominent peak at 429K and two shoulders at 362K and 573K (Figure 1, curve-g). The prominent peak observed around 426 to 429K for CaS: Ce³⁺, CaS: Ce³⁺ (Na⁺) and CaS: Ce³⁺ (Na⁺) Ag⁺ phosphors may be due to Ce³⁺ ions in CaS host lattice. In addition, shoulders are seen at 573K due to Ag⁺ ions in CaS host. TL intensity as per the results mentioned above, decreases due to presence of Na⁺ ion.

The decrease in TL intensity in CaS:Ce, Na and CaS:Ce, Ag, Na may be due to destruction of high temperature TL traps due to addition of Na in these phosphors.

For isolating the TL peak, various cleaning procedures were attempted and the shape of the cleaned peak was examined. The procedure which gave pure peak was selected. This consists heating of the phosphor at less than 10 K temperature of TL peak for 3 min and then cooling to room temperature. Heating beyond this temperature, did not change the shape of the peak but decreased TL intensity. The isolated peak was used for calculating trapping parameters.

The value of E was obtained from the shape of the isolated peak. The highest temperature peak can be most easily isolated thermally. A peak around 362 K was observed (Figure 2, curve-a) in pure CaS and E value is calculated using the Chen formulae [8] and presented in Table 1. A TL peak around 426K was isolated for CaS: Ce³⁺ phosphor, shown in Figure 2 (curve-b). To test the single nature of the trap depth, the sample was heated till the peak temperature was achieved, quickly cooled to room temperature and then again heated. It was found that the peak temperature remains the same, so in the present sample, no spread of E is indicated. The E values are shown in Table 1. Similarly, isolated peaks are shown in Figure 2 of CaS: Ce³⁺ (Na⁺) (curve-c) and CaS: Ag⁺ (curve-d). The 429 K isolated peak cannot be obtained in CaS: Ce³⁺, Ag⁺ and CaS: Ce³⁺ (Na⁺) Ag⁺ phosphors due to presence of high temperature (573K) peak in the TL glow curve. Therefore, trap depth calculation of CaS: Ce³⁺, Ag⁺ and CaS: Ce³⁺ (Na⁺) Ag⁺ phosphor is not possible by Chen [8] formula.

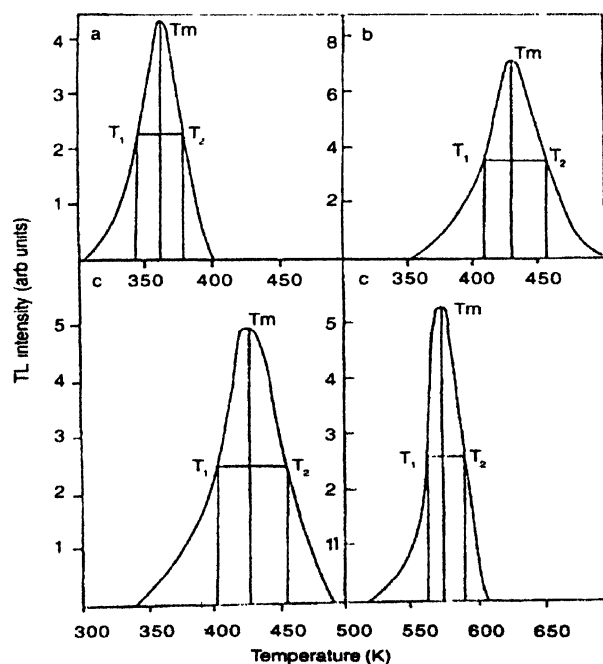


Figure 2. Thermally cleaned glow peak for use in trapping parameter calculations: (a) CaS pure, (b) CaS: Ce³⁺, (c) CaS: Ce³⁺ (Na⁺), (d) CaS: Ag⁺ (higher concentration) (1.0 mol%).

Table 1. Trapping parameters.

Phosphors	Peak Temp (K)	T ₁ (K)	T _m (K)	T ₂ (K)	μ _s	Order of kinetics	E _r (eV)	E _s (eV)	E ₀ (eV)
CaS pure	362	339	362	379	0.42	1	0.647	0.671	0.662
CaS Ce ³⁺	426	403	426	451	0.52	2	1.083	1.069	1.080
CaS Ce ³⁺ (Na ⁺)	426	401	426	453	0.52	2	0.982	0.983	0.987

Thermoluminescence glow curve shows the increase in TL intensity with introduction of Ce in CaS lattice. In CaS:Ce³⁺ phosphor, TL intensity increased by Ag⁺ ion as a co-activator probably due to either some competitive process(s) or to energy transfer from Ag⁺ to Ce³⁺ ions. Only one type of defect is formed in CaS due to its exposure to γ-ray radiation. Ce³⁺ and Ag³⁺ ions in CaS lattice result in increased formation of new defects, which are responsible for the additional TL peak observed in CaS:Ag and CaS:Ce³⁺, Ag³⁺ phosphors.

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References

- [1] R Pandey, A B Kunz and J M Vanl *J. Mater. Res.* **3** 1362 (1988)
- [2] Y Kaneko and T Koda *J. Cryst. Growth* **86** 72 (1988)
- [3] D Blokhinsev *J. Expt. Thor. Phys.* **7** 1242 (1937)
- [4] W DeGroot *Physica* **6** 275 (1939)
- [5] J J Randall and M H F Wilkins *Proc. Roy. Soc.* **A148** 366 (1945)
- [6] G F J Garlick and A F Gibson *Proc. Roy. Soc.* **60** 574 (1948)
- [7] C E May and J Patridge *J. Chem. Phys.* **40** 401 (1964)
- [8] R Chen *J. Appl. Phys.* **40** 570 (1969)
- [9] Ch D Luschik *Acad. Nauk. (USSR)* **101** 651 (1955)
- [10] A Halperin and A Braner *Phys. Rev.* **117** 408 (1960)
- [11] P Rodnyi, E Melchakov, N Zakhurov, I Munro and A Hopkirk *Lum.* **65** 85 (1995)
- [12] P D Townsend and D R White *Radiat. Prot. Dosim.* **65** 281 (1996)