



THERMOLUMINESCENCE CHARACTERISTICS OF Ce³⁺ IN HALOSULPHATE PHOSPHOR SYNTHESIZED BY SOLID STATE DIFFUSION REACTION

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ABSTRACT

The halosulphate phosphor K₂Ca₃(SO₄)₃F:Ce³⁺ synthesized by solid state diffusion are reported in this paper. The prepared sample is characterized for its thermoluminescence properties. The TL glow curve of prepared sample K₂Ca₃(SO₄)₃F:Ce³⁺ shows a single broad peak at 2060C. The trapping parameters are also evaluated by Chen's method. The values of trap depth (E) and frequency factor (s) were found to be 0.78 eV and 3.73 x 10⁷ s⁻¹ respectively.

Keywords: Thermoluminescence, halosulphate phosphor, kinetic parameters.

I. INTRODUCTION

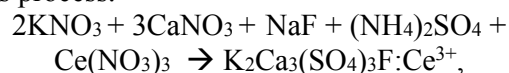
Sulfates are known to be good photoluminescence and thermoluminescence materials. CaSO₄:Dy is an efficient phosphor that is used in thermoluminescence dosimetry for ionizing radiation [1]. Alkaline earth sulfate activated rare earth ions are known as phosphors for thermoluminescence dosimetry, imaging plates and thin film electroluminescence displays [2, 3]. Alkaline earth sulfates activated with Eu³⁺ and Sm³⁺ ions are promising candidates for optical information storage [4]. Gong et. al. [5, 6] showed the influence of gamma ray irradiation on crystal structure and photoluminescence of alkaline earth sulfates activated with Eu³⁺ and Sm³⁺ ions. They stated that PL quenching in alkaline earth sulfates nano-crystalline materials is due to dipole-quadrupole interaction [7].

Many rare earth activated alkaline earth sulfates and their related compounds are of interest due to their unusual stability and useful luminescence properties. They are used in different applications such as lamps, color T.V. screens, long lasting devices, laser host, scintillation and pigments. The spectroscopic properties of Ce³⁺ ions are very well investigated in various phosphors, crystals, solutions and glasses.

In order to investigate the luminescence properties of in halosulphate phosphor, rare earth activator Ce has been incorporated in K₂Ca₃(SO₄)₃F, characterized it for their thermoluminescence studies and reported in this paper.

II. METHODS AND MATERIALS

K₂Ca₃(SO₄)₃F:Ce³⁺ phosphor was synthesized by conventional solid state diffusion method. For the preparation of K₂Ca₃(SO₄)₃F:Ce³⁺, stoichiometric amounts starting raw materials NaNO₃, CaNO₃, NaF, (NH₄)₂SO₄, and Ce(NO₃)₃ (AR Grade, Merk) were thoroughly mixed and grounded in an agate mortar for 1-2 hrs. The mixture was kept in preheated furnace at 800 °C for 24 hours using porcelain crucibles in air atmosphere. After the heat treatment of 24 hour, followed by subsequent air-cooling with furnace again all the samples were crushed in an agate mortar to obtain the white powder of the sample. The following chemical reaction is undergone in this process.



The prepared host lattice was taken in powdered form, each weighing 2gm for its TL characterization. The thermoluminescence glow curves were studied using Thermoluminescence Reader. The Co^{60} radioisotope gamma dose employed for irradiation is 5 Gy. In order to reduce error TL- glow curve measurements are done just after irradiation. The TL response was then measured up to 400 °C using TL reader with temperature rate of 5 °C/s.

III. RESULT AND DISCUSSION

a. TL study of $\text{K}_2\text{Ca}_3(\text{SO}_4)_3\text{F}:\text{Ce}^{3+}$

The TL glow curve of $\text{K}_2\text{Ca}_3(\text{SO}_4)_3\text{F}:\text{Ce}^{3+}$ for different concentrations from 0.1 mol% to 2 mol% is shown in **figure 1**. Before taking the TL, the sample is initially annealed at a temperature of 300 °C and then irradiated it for gamma ray dose of 5 Gy. To avoid possibility of any error, the TL measurements are done soon after irradiation of the sample. The TL is observed upto 400 °C with the heating rate of 5 °C/s. The glow curve reveals well defined single isolated peak at 190 - 206 °C. The increase in concentration of dopant Ce^{3+} in sulphate host have considerable influence on the position of peak and also highly affects TL intensity. As the concentration of the dopant Ce is increased the peak position is slightly shifted to higher temperature side from 190°C to 206°C. The pure host does not show any thermoluminescence characteristics but the TL intensity increases as we increase the concentration of dopant from 0.1 mol% to 2 mol% as is shown in **figure 1**. The TL intensity of this sample is small as compared with the standard TLD material, hence it don't have any direct application in dosimetry. Therefore, in order to study the energy level structure, the defect centers its kinetic parameters are evaluated.

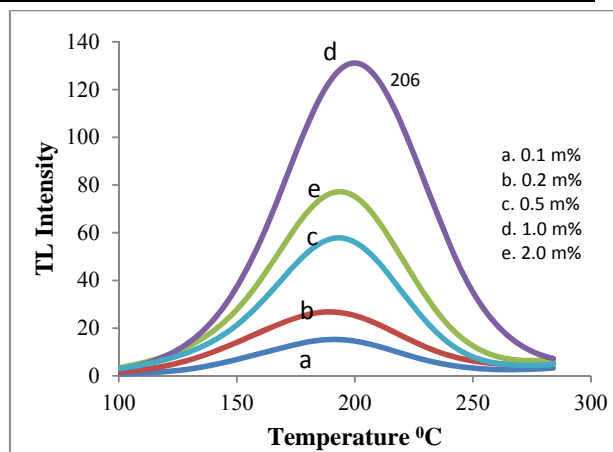


Fig.1. The TL Glow curve of as prepared $\text{K}_2\text{Ca}_3(\text{SO}_4)_3\text{F}:\text{Ce}^{3+}$ phosphor when irradiated by a gamma ray dose of 5 Gy.

b. Study of kinetic parameters

The study of kinetic parameters such as activation energy E and frequency factor s provides information about the defect centers responsible for TL in the material [8, 9]. Therefore, we have calculated here kinetic parameters of the prepared TL sample. The peak shape method of Chen (general order kinetics) was used to calculate the kinetic parameters viz. geometrical factor μ_g , activation energy E and the frequency factor s .

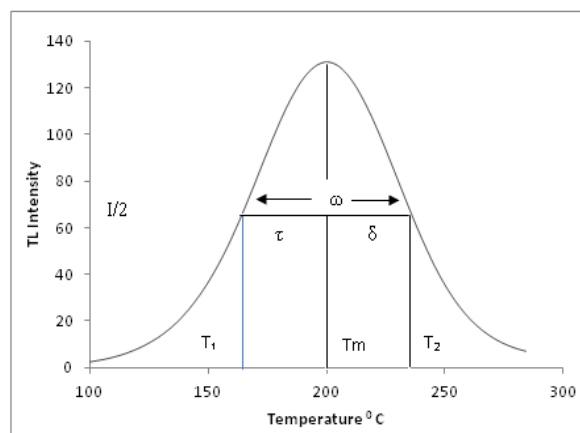


Fig.2. Peak shape parameters for calculation of trapping parameters

The peak shape parameters for a given TL glow curve are obtained as shown in the **Figure 2**. The peak shape method is generally used to calculate the order of kinetics and is obtained from geometric factor (peak shape parameter). The peak shape parameters τ , δ and ω were initially determined for temperatures T_1 , T_m and T_2 . These values are used to calculate the geometrical factor μ_g , which determines the order

of kinetics. The values activation energy E and the frequency factor s were then calculated and values obtained are tabulated in Table 1. It is also concluded that by studying the effect of different annealing temperatures on the trap depth and frequency factor may further reveal some more important aspects of TL.

Table.1. Experimental peak shape parameters and Values of trap depth E (eV) and frequency factor s (s^{-1}) for the peak of 1 mol% concentration of dopant Ce.

<i>Peak Temperature T_m ($^{\circ}C$)</i>	<i>Half Width (τ)</i>	<i>Half Width h (δ)</i>	<i>Full Width h (ω)</i>	<i>Geometric factor (μ_g)</i>
200.7	36.34	37.28	73.72	0.51
<i>Order of Kinetics (b)</i>	<i>Trap Depth E (eV)</i>	<i>Frequency Factor s (S^{-1})</i>		
2	0.81	8.86 x 10 ⁷		

IV. CONCLUSIONS

The halosulphate phosphors $K_2Ca_3(SO_4)_3F:Ce^{3+}$ was synthesized by solid state diffusion. The prepared samples are also characterized for its thermoluminescence properties. The TL glow curve of prepared sample $K_2Ca_3(SO_4)_3F:Ce^{3+}$ shows a single broad peak at 206 $^{\circ}C$. The values of trap depth (E) and frequency factor (s) were found to be 0.78 eV and 3.73 x 10⁷ s⁻¹ respectively.

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