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Social Science Journal

Analysis of Thermoluminescence Glow Curves of X-ray irradiated $CaSO_4$:Dy phosphor

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Abstract:

This research article presents a detailed analysis of the thermoluminescence (TL) glow curves exhibited by calcium sulphate doped with dysprosium ($CaSO_4$:Dy) crystals following X-ray irradiation. TL is a phenomenon where certain materials emit light when heated after being exposed to ionizing radiation. $CaSO_4$:Dy is known for its thermoluminescent properties, making it a valuable material in dosimetry and radiation monitoring applications. The investigation of the glow curve characteristics of $CaSO_4$:Dy crystals by CGCD deconvolution at different heating rates reveals both consistent trends and noteworthy differences. The activation energy (E) consistently varies from 0.8 to 1.5 eV, and the value of frequency factor (s) ranges from 2.38E+08 to 7.76E+11. The order of kinetics (b) exhibits variation between 1 and 2, suggesting a complex interplay of thermoluminescent mechanisms influenced by the heating rate.

Keywords: Thermoluminescence, Glow curve, $CaSO_4$:Dy, X-ray, Dosimetry, Radiation detection.

1. Introduction

The use of thermoluminescent materials for radiation dosimetry has gained significant attention due to their ability to store and release energy in the form of light upon thermal stimulation. $CaSO_4$:Dy is particularly interesting because dysprosium doping enhances its thermoluminescent properties, making it suitable for various applications in radiation detection and dosimetry. Calcium sulphate doped with dysprosium, stands out as a highly promising phosphor material within the realm of luminescent materials because of its high sensitivity to X-ray and γ-radiation (H. N. Singh et.al 2023).

The incorporation of dysprosium into the calcium sulphate crystal lattice imparts unique optical characteristics to the material. Dysprosium acts as a dopant, introducing energy levels and electron traps that enhance the material's ability to absorb and re-emit light. This phenomenon is particularly advantageous for applications in luminescence, where the efficient conversion of absorbed energy into visible light is crucial. Moreover, the wide band gap of $CaSO_4$:Dy further contributes to its suitability for luminescent applications. A wide band gap signifies a greater energy difference between the valence and conduction bands, allowing for a broader range of excitation energies. This characteristic not only expands the spectrum of incident light that can be absorbed but also enhances the material's stability and resistance to environmental factors, making it an excellent candidate for radiation dosimetry applications (Yamashita T et.al 1968, Yamashita, T et al 1971, Lakshmanan, A.R et al. 1986, Gerome V et al. 1996, Azorin J and Salvi A 1980.

The dysprosium ions (Dy) in the crystal lattice of Calcium sulphate ($CaSO_4$) represent a deliberate modification aimed at augmenting the thermoluminescent characteristics of the material. This process involves the substitution of calcium ions with dysprosium ions within the lattice structure, resulting in a modified material denoted as $CaSO_4$:Dy. Dysprosium, as a dopant, brings about a crucial alteration in the energy landscape of the crystal lattice. The incorporation of dysprosium introduces additional energy levels within the band structure of $CaSO_4$. These additional energy levels act as electron traps, influencing the material's response to ionizing radiation. When the doped material is exposed to radiation, electrons are excited to higher energy levels and become trapped in these dysprosium-induced states.

In this paper, the TL glow curves of X-ray irradiated $CaSO_4$:Dy were analysed by general order kinetic order (May and Partridge 1964) and the lifetime of the trap in general order kinetics was calculated using the lifetime equation formulated by Lovedy and Gartia (2011).

2. Experimental details

The $CaSO_4$:Dy crystals used in this study were synthesized using the co-precipitation method (Salah et.al 2003). First, 10.8gm of Calcium Sulphate dehydrate ($CaSO_4$:$2H_2O$ at 99% purity) in the form of power was dissolved in concentrated sulphuric acid (H_2SO_4) of 200 millilitres by heating the solution at 200°C for 2 hours under a reflux condenser. Then 0.216 gm of Dysprosium oxide (Dy_2O_3, 99% pure) was dissolved in 20 ml of concentrated sulphuric acid by heating at 200°C for 2hr under a reflux condenser. The two solutions were mixed after cooling then the mixture was heated at 300°C for 2 hours through a magnetic stirrer to ensure a perfect homogeneous mixture. After colling the mixture about 200 ml of deionised water was added drop by drop, and then crystals of $CaSO_4$:Dy appeared due to its poor solubility. The process of removing water from the mixture and adding deionised water was repeated at least five or six times to remove sulphuric acid from the mixture completely. Finally, the crystal was removed from the solution by filtration and the crystal was heated to about 300°C for 4 hours in a furnace.

The resulting power was then ground manually in an agate mortar and sprinkled a few drops of 2-5% of Polyvinyl Alcohol (PVA) solution on it. Then the powder was ground with the help of a pestle till fine powder was obtained. Again, add a few drops of PVA and repeat the process until the powder is ready for palletisation. The pallet samples were again reader annealed to about 300°C for 2 hours in a furnace.

The pallets were then irradiated with X-rays using a calibrated X-ray source. The irradiated crystals were subsequently subjected to thermoluminescence measurements using a PC-controlled TL Reader (1009I), Nucleonix System, Hyderabad, at the Department of Physics, Oriental College, Takyel, Imphal. The TL glow curves were recorded at different constant heating rates. A second read-out was also carried out to record the background emission, including the black body radiation from the kanthal heating strip. All the glow curves presented in this paper are subtracted from their background radiation.

3. Result and Discussion

The normalised TL glow curves of $CaSO_4$:Dy following X-ray irradiation (1 Gy) recorded at different heating rates are presented in Fig. 1. The glow curves exhibit distinct peaks and features. Each peak corresponds to the release of stored energy at specific temperature ranges. The analysis of these peaks provides valuable information about the trapping and retrapping processes within the crystal lattice.

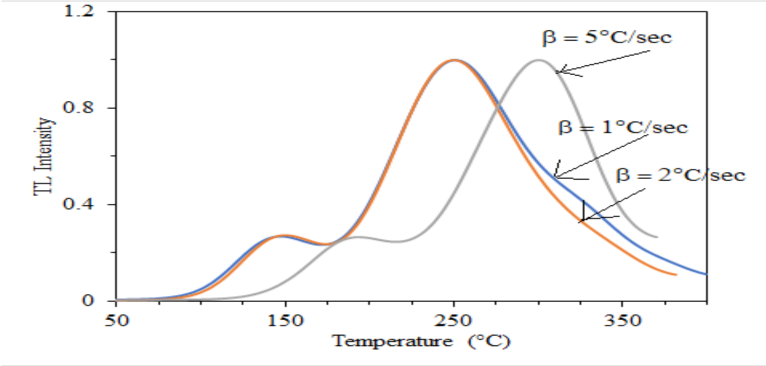

Figure 1: TL glow curves of CaSO4: Dy phosphor for different heating rates, irradiated with X-ray of 1Gy.

From Fig. 1, it is seen that for heating rates 1 & 2°C/sec, the peak temperatures are almost equal, but with the increase of heating rate (5°C/sec) the glow curve is shifted to the higher temperature side due to thermal lag. The main peaks of heating rate 1 & 2°C/sec are found at 250°C and for heating rate 5°C/sec is found to be at 300°C. The glow curves appear to consist of two constituents' peaks one at a lower temperature and the other at a higher temperature. However, the glow curves when subjected to computerized glow curve deconvolution (CGCD) in the kinetic formalism are found to consist of 4 constituent peaks. The deconvolution of the glow curves of heating rates 1°C/sec and 5°C/sec are presented in Fig. 2a and Fig. 2b respectively.

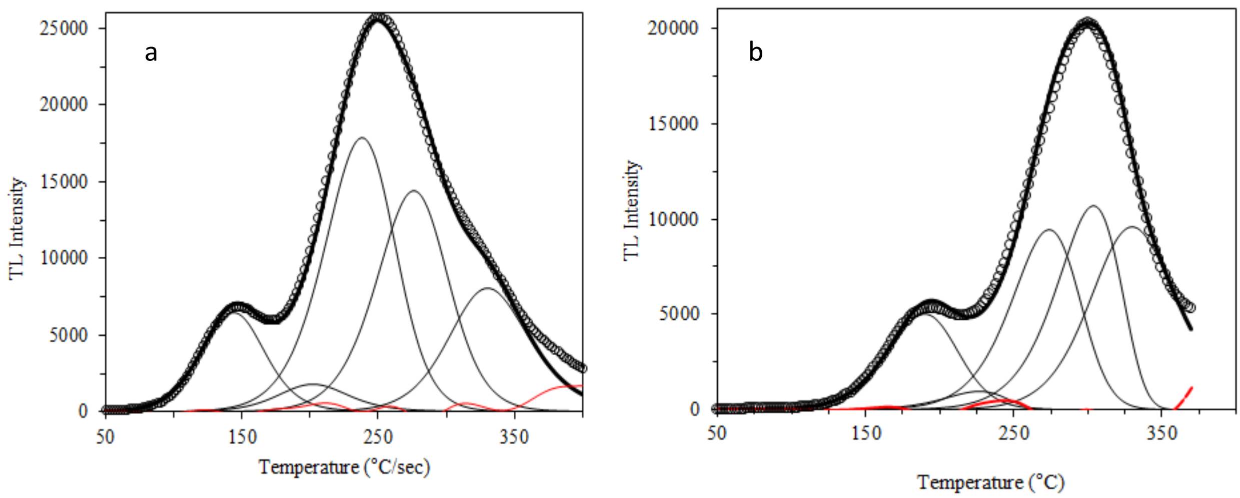

Figure 2: Computerized Glow curve deconvolution of X-ray irradiated $CaSO_4$:Dy in the framework of kinetic formalism (a) Heating rate 1°C/sec and b) heating rate 5°C/sec

oooooo Experimental Glow Curve
——— Numerically generated best fit curve
——— Numerically generated total best fit curve
——— Error

The trapping parameters obtained by the deconvolution of the glow curves with different heating rates are presented in Table 1:

Table 1: Trapping parameters obtained by CGCE of X-irradiated CaSO4:Dy for different heating rates

Heating rate (°C/sec)	Peak Temperature (°C)	Activation Energy E (eV)	Frequency factor s (s^{-1})	Order of Kinetic b	FOM
1	144	0.80	2.38E+08	1.60	1.85%
	202	1.00	1.98E+09	1.80	
	238	1.00	3.15E+08	1.38	
	276	1.20	4.63E+09	1.50	
	330	1.50	1.55E+11	2.00	
2	144	0.80	4.86E+08	1.33	1.57%
	178	1.00	1.62E+10	1.80	
	238	1.00	6.19E+08	1.60	
	276	1.20	9.08E+09	1.80	
	332	1.50	2.85E+11	1.70	
5	190	0.90	1.48E+09	1.40	2.44%
	227	1.00	2.79E+09	1.00	
	274	1.20	2.61E+10	1.20	
	304	1.30	5.13E+10	1.00	
	330	1.50	7.76E+11	2.00	

The positions, shapes, and intensities of the peaks in the glow curve are indicative of the type and concentration of traps within the material. By carefully analysing these characteristics, we can gain insights into the radiation-induced defects and the efficiency of energy trapping and release mechanisms in $CaSO_4$:Dy. The presented table provides a comprehensive overview of the thermoluminescent properties of a material under different heating rates. Three distinct heating rates—1°C/sec, 2°C/sec, and 5°C/sec—are investigated, with corresponding data on temperature (T in C), activation energy (E in eV), pre-exponential factor (s in s^{-1}), the order of kinetics (b) and figure of merit (FOM).

At a heating rate of 1°C/sec, the material exhibits a range of activation energies from 0.8 to 1.5 eV. The pre-exponential factor (s) display a substantial variation, spanning from 2.38E+08 to 1.55E+11. This suggests a notable diversity in the efficiency of thermoluminescent processes within the material at this heating rate. The order of kinetics (b) also varies, indicating a nuanced dependence on the heating rate.

For the 2°C/sec heating rate, the activation energy range mirrors that of the 1°C/sec rate, while the pre-exponential factor shows a broader spectrum, ranging from 4.86E+08 to 2.85E+11. The order of kinetics remains variable, emphasizing the sensitivity of thermoluminescent characteristics to changes in the heating rate.

At the highest heating rate of 5°C/sec, the activation energy varies between 0.9 and 1.5 eV, demonstrating a consistent trend with the other heating rates. The pre-exponential factor ranges from 1.48E+09 to 7.76E+11, indicating a considerable diversity in the efficiency of thermoluminescent processes. The order of kinetics continues to exhibit variability.

Overall, the table highlights the intricate relationship between the heating rate and the thermoluminescent behaviour of the material. The observed variations in activation energy, pre-exponential factor, and order of kinetics provide valuable insights into the complex dynamics of charge release and recombination processes during thermal stimulation. Further exploration and analysis of these findings could contribute to optimizing the material for applications in dosimetry and radiation detection.

The lifetime of the dosimetry peaks was calculated by using the formula recently developed by Lovedy and Gartia 2011 which is given by eqn (1).

$$\tau = \frac{e^{E/kT}}{(2-b)s} \quad \text{for } 1 \leq b \leq 2 \quad \ldots\ldots (1)$$

The average lifetime of the dosimetry peak ~ 276°C and ~ 330°C are obtained as 2.27 kyr and 4230 kyr respectively. The average lifetime of a dosimetry peak is a measure of the duration over which the material remains thermoluminescent and capable of recording radiation exposure. The peaks at ~ 276°C and ~ 330°C demonstrate considerable stability, with average lifetimes spanning thousands of years. This extended temporal range makes them viable candidates for dosimetry applications, indicating that the material retains its thermoluminescent properties for a prolonged period. The dosimetry peaks, characterized by their specific temperatures and now supported by their substantial average lifetimes, can serve as reliable indicators for measuring radiation exposure. The extended lifetimes of the dosimetry peaks contribute to the robustness and reliability of the material in applications such as environmental monitoring, medical dosimetry, and radiation protection.

Conclusion

The analysis of thermoluminescence glow curves of $CaSO_4$:Dy following X-ray irradiation provides valuable information about the material's dosimetric properties. Understanding the characteristics of TL peaks aids in optimizing the use of $CaSO_4$:Dy in various radiation detection applications. Further research may focus on fine-tuning the material's properties and exploring its potential in personalized dosimetry and radiation therapy monitoring. The lifetime of the dosimetry peaks ~ 276°C and ~ 330°C are 2.27 kyr and 4230kyr demonstrate considerable stability indicating the material can retain its thermoluminescent properties for a prolonged period indicating that the material is a good candidate for dosimetry.

Acknowledgement

The authors are thankful to Dr. M. Nara Singh, Dr. Baruah Cancer Hospital, Guwahati, Assam for providing us the irradiation of the sample by X-ray.

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