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Effect of Thermal Treatments on the Glow Curve and Stability of $CaSO_4$:Dy for Radiation Dosimetry Applications

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Abstract

A comprehensive investigation was carried out into the optimisation of Dysprosium-doped Calcium Sulphate ($CaSO_4$:Dy) for high-precision thermoluminescence (TL) dosimetry through controlled post-synthesis thermal annealing. By comparing samples annealed at 600°C and 900°C, we demonstrate that high-temperature treatment is a critical step in the material's physical and dosimetric properties. Structural analysis via X-ray diffraction confirmed the phase purity of the orthorhombic anhydrite structure in both samples. However, scanning electron microscopy revealed that the 900°C anneal induces significant microstructural evolution, promoting substantial grain growth and refining the phosphor's morphology, while energy-dispersive X-ray analysis verified a consistently uniform Dy^{3+} distribution. The 600°C sample exhibits a complex, multi-component glow curve with a prominent, low-temperature peak (~160°C) and a main dosimetric peak (~250°C). In contrast, the 900°C annealing process effectively eliminates the shallow trap corresponding to the 160°C peak, yielding a clean, single, and highly stable dosimetric peak. This suppression of the unstable, low-temperature signal is paramount for minimising thermal fading and ensuring long-term dosimetric accuracy. To elucidate the underlying trap kinetics, a Computerized Glow Curve Deconvolution (CGCD) was performed using a probability-based general-order model. The analysis revealed that annealing at 900°C fundamentally reconfigures the material's defect structure, favouring the formation of deeper, more thermally stable traps and significantly reducing the probability of charge carrier retrapping.

Key Parameters: Thermoluminescence, Phosphor, TLD, Morphology, Crystal structure.

1. Introduction:

Calcium sulphate doped with dysprosium ($CaSO_4$:Dy) is one of the most extensively studied and widely used thermoluminescent (TL) phosphors for radiation dosimetry. Its adoption in both personal and environmental dosimetry stems from its high sensitivity, wide dose linearity, excellent reproducibility, and relatively simple preparation methods [1–6]. When compared with the widely used LiF-based TLD-100, $CaSO_4$:Dy shows significantly higher sensitivity—approximately 15 times greater at 662 keV and over 100 times at lower gamma-ray energies like 33 keV [3]. For X-ray detection, it is reported to be about 82% more sensitive than TLD-100 [7].

The thermoluminescence glow curve of $CaSO_4$:Dy typically features a prominent dosimetric peak around 230–240°C, which is thermally stable and less prone to fading compared to lower-temperature peaks [1–5,8–10]. This characteristic makes it especially suitable for applications where delayed readout is necessary. However, TL performance is significantly affected by factors such as dopant concentration [1,6,11–13], particle morphology [14], and post-synthesis treatments, particularly annealing [9-10,14].

Annealing plays a crucial role in determining the TL sensitivity, glow curve shape, and reusability of the phosphor. While moderate annealing temperatures around 400°C have historically been employed [9], recent studies have shown that this treatment can lead to up to 30% sensitivity loss due to partial dehydration of dysprosium sulfate within the host lattice, which disturbs the crystal structure and reduces the number of active luminescent centres [14]. Furthermore, such

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temperatures alter the relative intensities of glow curve peaks, compromising reproducibility. In contrast, higher annealing temperatures in the 600–650°C range have been shown to restore and stabilise TL sensitivity while maintaining favourable glow curve features [10,14]. However, excessive heating beyond 900°C may induce irreversible structural transitions, peak shifts, and a decline in photoluminescence (PL) intensity [2,14].

Another area requiring attention is the kinetic analysis of TL glow curves. Although CGCD is widely used to extract trap parameters, most studies rely on general order kinetics as proposed by May and Partridge [15], which includes empirically derived parameters like the order of kinetics (*b*) that lack clear physical meaning.

In this context, the present work investigates the influence of annealing temperature on the TL characteristics of $CaSO_4$:Dy, with a focus on glow curve evolution, fading behaviour, and kinetic parameters derived through CGCD. The findings aim to support optimised reuse and improved stability of $CaSO_4$:Dy for practical dosimetry applications.

2. Experiment

Thermoluminescent (TL) phosphors of calcium sulphate doped with dysprosium ($CaSO_4$:Dy) were synthesised using the Yamashita method [16], a well-established solid-state technique for phosphor preparation. The prepared phosphor was first dried at 200°C for 4 hours in a muffle furnace, followed by drying at 100°C for 24 hours in a hot-air oven to ensure complete removal of residual moisture. After drying, the phosphor was allowed to cool rapidly in open air to inhibit the formation of undesired crystalline phases and to stabilise the host matrix.

The synthesised samples were characterised by X-ray diffraction (XRD) measured at the Department of Physics, Manipur University, Canchipur, and the crystalline structure. Elemental composition and surface morphology were examined through Energy-Dispersive X-ray Analysis (EDAX) and Scanning Electron Microscopy (SEM), also performed at the same department.

For dosimetric evaluation, the phosphor samples were irradiated with a ^{60}Co gamma source at various doses at the Department of Radiology, Regional Institute of Medical Sciences (RIMS), Imphal, Manipur. The thermoluminescence glow curves were recorded using a TL Research Reader (Model TL-1009I, Nucleonix Systems Pvt. Ltd., Hyderabad) at the Department of Physics, Oriental College (Autonomous), Takyel, Imphal, Manipur. A second readout was performed for background correction.

3. Result and Discussion

The X-ray diffraction (XRD) patterns of $CaSO_4$:Dy (0.1, 0.2 and 0.3 mol%) phosphors annealed at 600°C and 900°C are presented in Figure 1a and 1b. Both diffraction profiles exhibit characteristic peaks corresponding to pure anhydrous calcium sulphate (anhydrite**)** with orthorhombic symmetry, in good agreement with the JCPDS card No. 37-1496 [17]. The absence of additional diffraction peaks related to hydrated phases such as $CaSO_4\cdot 2H_2O$ (gypsum) or $CaSO_4\cdot \frac{1}{2}H_2O$ (bassanite**)** confirms that complete dehydration was achieved during the high-temperature annealing process.

The most intense reflection, observed at 2θ ≈ 25.7°, corresponds to the (200) plane, which is characteristic of the orthorhombic anhydrite structure with space group C222 or Cmcm [17]. This result confirms the successful formation and structural stability of the anhydrite phase in the synthesised phosphors.

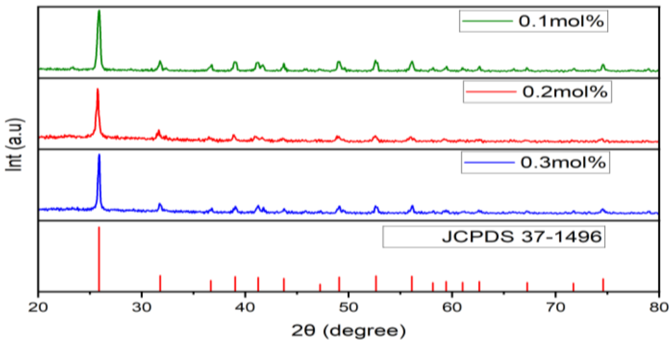

Figure 1a: The X-ray diffraction (XRD) patterns of $CaSO_4$:Dy (0.1, 0.2 and 0.3 mol%) phosphors annealed at 600°C along with JCPDS data.

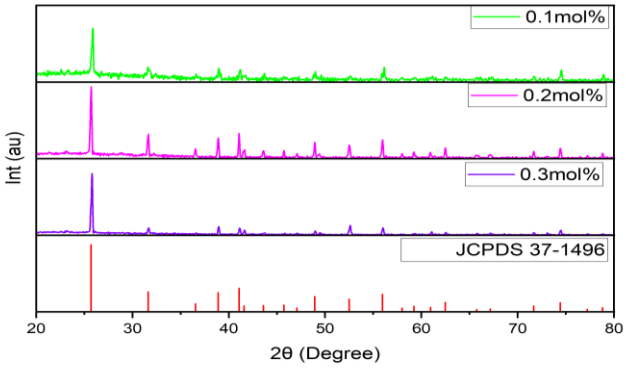

Figure 1b: The X-ray diffraction (XRD) patterns of $CaSO_4$:Dy (0.1, 0.2 and 0.3 mol%) phosphors annealed at 900°C along with JCPDS data.

The SEM micrographs of $CaSO_4$:Dy (0.1 mol%) samples annealed at 600°C and 900°C are presented in Figure 2**.** The surface morphology reveals distinct temperature-dependent microstructural evolution. At 600°C, the sample exhibits fine, irregularly shaped or needle-like particles, typically forming small agglomerates. The crystallites at this stage are relatively small—ranging from tens to a few hundred nanometers—indicating an incomplete crystallisation process and a polycrystalline microstructure**.**

Upon annealing at 900°C, the phosphor shows significant grain growth, characterised by larger, faceted grains formed through sintering and recrystallisation. This morphological transformation suggests the attainment of a more ordered crystalline structure, consistent with the orthorhombic anhydrite phase of $CaSO_4$ [18–19]. The enhanced grain size and improved crystal definition indicate that the material has approached thermodynamic equilibrium at this temperature.

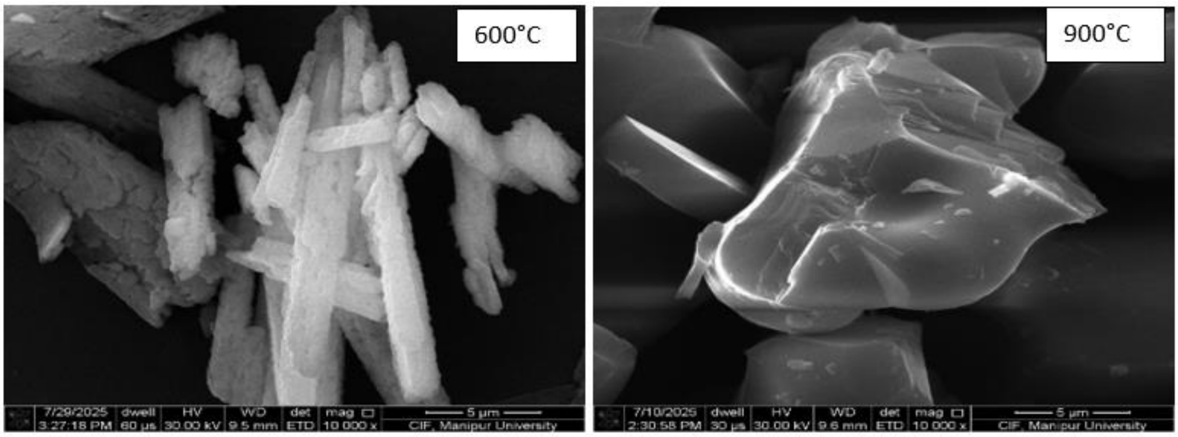

Figure 2: The SEM micrographs of $CaSO_4$:Dy (0.1 mol%) samples annealed at 600°C and 900°C.

The EDAX spectra of $CaSO_4$:Dy (0.1 mol%) samples annealed at 600°C and 900°C are presented in Figure 3**.** Both spectra confirm the expected elemental composition of the doped calcium sulphate phosphor, showing prominent peaks corresponding to calcium (Ca Kα ≈ 3.7 keV)**,** sulfur (S Kα ≈ 2.3 keV)**,** and oxygen (O Kα ≈ 0.5 keV)**,** which collectively verify the presence of the $CaSO_4$ matrix [18].

A weak but distinct Dy Lα peak (~6.5 keV) is observed in both samples, indicating the successful incorporation of dysprosium ions (Dy^{3+}) at the intended doping level (~0.2 mol%). The detection of Dy, despite its low concentration, confirms the effectiveness of the doping process. Importantly, no extraneous elements or impurity peaks were detected, demonstrating the high chemical purity of the synthesised phosphors.

A comparison between the 600°C and 900°C annealed samples shows no qualitative change in composition, indicating that higher-temperature annealing does not alter the elemental distribution or dopant homogeneity. Thus, the EDAX analysis corroborates the successful synthesis, compositional integrity, and uniform Dy incorporation in $CaSO_4$:Dy phosphors across both annealing conditions.

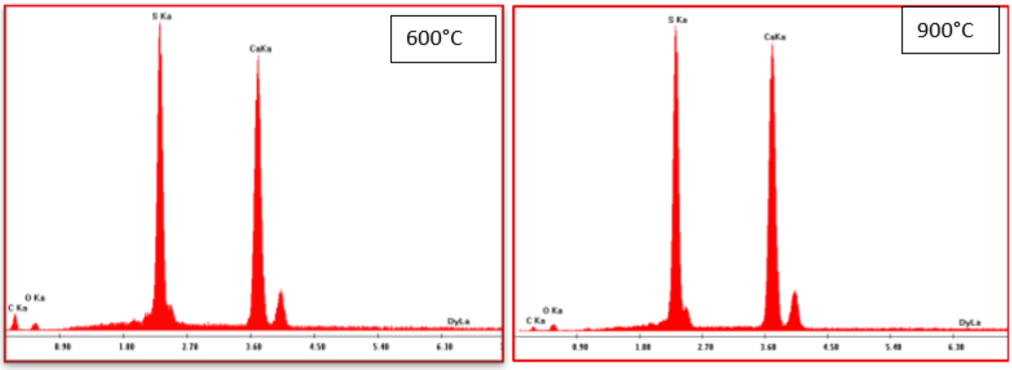

Figure 3: The EDAX spectra of $CaSO_4$:Dy (0.1 mol%) samples annealed at 600°C and 900°C.

The thermoluminescence (TL) behaviour of phosphor samples annealed at 600°C and 900°C was examined following gamma irradiation at doses of 0.5 Gy, 2.5 Gy, and 5 Gy, using a constant heating rate of 5°C/s. The sample annealed at 600°C exhibited a near-linear dose–response relationship across the investigated dose range. This behaviour was primarily due to the combined contributions of two distinct TL glow peaks at approximately 160°C and 250°C. The presence of both shallow and deeper trapping centres led to enhanced sensitivity, especially at lower doses, where the shallow traps (160°C peak) contributed significantly to the total TL signal.

Conversely, the sample annealed at 900°C demonstrated a different TL response. The glow curve was dominated by the 250°C peak, with the 160°C peak substantially suppressed. Although the dose–response curve (DRC) retained approximate linearity, its slope was notably reduced, indicating a decline in sensitivity. This behaviour is attributed to high-temperature annealing effects, which likely induce defect annealing and lattice reconfiguration, resulting in the depletion of shallow traps responsible for low-temperature emission.

To investigate the trap mechanisms in the phosphor, the TL glow curve from a 0.5 Gy gamma-irradiated sample was analysed using the general-order kinetic equation proposed by Lovedy [20]. The peak location was determined through a second-order derivative plot [21-22]. CGCD analysis, utilising a hybrid genetic algorithm [23], is shown in Figure 4, with trapping parameters summarised in Table 1.

For the 600°C-annealed $CaSO_4$:Dy sample, the trapping depth varied between 0.50–1.28 eV, indicating the presence of both shallow traps (~0.5–0.6 eV, responsible for the 160°C peak) and deeper traps (≥1.2 eV, linked to the 250°C and higher temperature peaks). In contrast, the 900°C-annealed sample exhibited a shift to higher trap energies, with E values ranging from ~0.50 to 1.84 eV. This increase in average trap depth reflects the elimination of weaker traps during high-temperature annealing, leaving behind predominantly deeper, thermally stable traps.

The frequency factors range from 10^8–10^{13} s^{-1}, typical of TL materials. These changes in the frequency factor suggest modifications in the trap environment due to the annealing process.

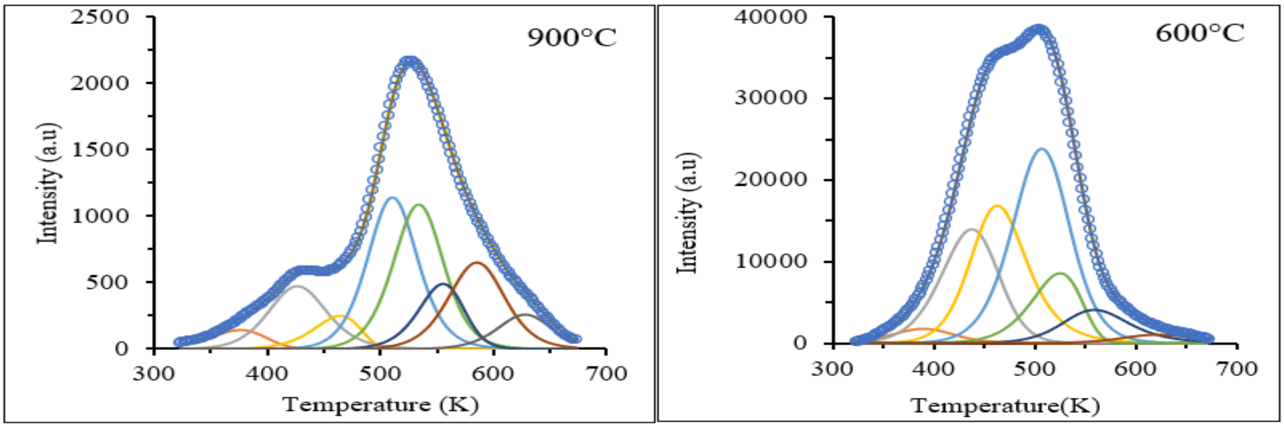

Figure 4: CGCD of $CaSO_4$:Dy(0.2mol%) annealed at 900°C & 600°C, heating rate at 5°C/s irradiated at 0.5 Gy.

Table 1: Peak parameters of CGCD analysis of $CaSO_4$:Dy, irradiated at 0.5Gy

Annealing Temperature	Peak position	T_m (K)	E (eV)	s (s^{-1})	α	γ	Im
600°C	1	388.40	0.500	3.29×10^{8}	0.496	1.00	1849.64
	2	436.70	0.641	2.51×10^{8}	0.317	1.00	14029.64
	3	462.27	0.913	8.13×10^{9}	1.000	1.00	16907.55
	4	506.40	0.945	2.39×10^{13}	0.542	1.00	2.3842.80
	5	524.74	0.945	5.14×10^{12}	0.014	1.00	8627.01
	6	558.64	1.136	7.13×10^{12}	1.000	1.00	4185.39
	7	620.47	1.289	7.01×10^{12}	1.000	1.00	1037.88
	Peak position	T_m (K)	E (eV)	s (s^{-1})	α	γ	I_m
900°C	1	375.46	0.500	1.13×10^{8}	0.117	1.00	143.68
	2	425.97	0.790	4.21×10^{8}	0.743	1.00	473.69
	3	464.20	0.882	6.23×10^{9}	0.000	1.00	250.73
	4	510.27	1.353	1.33×10^{13}	0.790	1.00	1136.38
	5	533.49	1.429	7.11×10^{12}	0.685	1.00	1081.40
	6	555.10	1.538	6.43×10^{13}	0.356	1.00	487.89
	7	584.99	1.549	9.11×10^{12}	0.701	1.00	646.92
	8	627.62	1.836	6.40×10^{12}	0.678	1.00	257.81

The Comprehensive General-Order Computerised Glow Curve Deconvolution (CGCD) analysis conclusively shows that annealing $CaSO_4$:Dy (0.2 mol%) at 900°C produces a thermoluminescent dosimeter with far superior characteristics for practical radiation dosimetry compared to annealing at 600°C. The higher temperature treatment effectively engineers the material's trap structure to yield a clean, single-peak glow curve centred around 250°C. This process simultaneously suppresses the shallow traps responsible for the 160°C peak, thereby eliminating the significant signal fading (~15% per week) that compromises the long-term stability of the 600°C sample.

While the 900°C anneal results in a modest reduction in overall TL output, this trade-off is highly favourable for dosimetric applications. The resulting material provides a stable, highly reproducible signal with a linear dose-response, ensuring that dosimetric readouts are both reliable and straightforward to interpret. In contrast, the 600°C sample, though initially more sensitive, suffers from a composite glow curve and significant fading, which can compromise accuracy.

The underlying physical changes revealed by the CGCD analysis explain these improvements. High-temperature annealing shifts the trap distribution toward higher activation energies (mean $E \approx 1.35$ eV), creating deeper, more stable traps. Furthermore, it strongly suppresses the probability of retrapping (most $\alpha < 0.1$), causing the material to behave closely to an ideal first-order TL dosimeter. This is a marked improvement over the 600°C sample, which exhibits significant second-order kinetics ($\alpha \approx 1$) and peak overlap, complicating accurate dose assessment.

Conclusion:

The combined structural and thermoluminescent analyses conclusively reveal that annealing $CaSO_4$:Dy (0.2 mol%) at 900°C results in enhanced dosimetric performance compared to the sample annealed at 600°C. Although both annealing conditions maintain the orthorhombic anhydrite phase and ensure a uniform distribution of Dy^{3+} ions within the host lattice, the higher annealing temperature at 900°C induces pronounced grain growth and improved crystallinity. These structural refinements contribute to the superior thermoluminescent sensitivity and stability observed in the 900°C annealed phosphor, confirming its suitability for dosimetric applications.

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