Preliminary Studies of Thermoluminescence Dosimeter (TLD) 
CaSO$_4$:Dy Synthesis

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Abstract. Thermoluminescence dosimeter (TLD) CaSO$_4$:Dy was synthesised by co-precipitation. The TLD was observed after radiation exposure to Strontium-90. The thermoluminescence intensity was read using a TLD Reader Harshaw 3500. The thermoluminescent response obtained was 59.29 nC. Then re-annealing was conducted with the temperature varied at 700, 800 and 900 °C. The thermoluminescent intensity obtained at temperatures of 700 °C, 800 °C and 900 °C was 66.12 nC, 169.45 nC, and 552.37 nC respectively. The sensitivity of the TLD increase in response to the re-annealing temperature rise. In addition to observing the thermoluminescence properties, a comparison was made between the TLD obtained from this experiment with an existing TLD in the market. Finally, also the glow-curve characteristics of the TLD were observed.

1. Introduction
Radiation exists in everyday life. Radiation comes from nature but there is also artificial radiation. Artificial radiation is widely used in the health sector (diagnosis and therapy) and industry [1]. Because of the increasing number of users of radiation it is necessary to monitor radiation on people involved in the use of radiation [2]. The type of radiation dosimeter most commonly used for medical physics, personnel monitoring and environmental monitoring is the thermoluminescence dosimeter (TLD). When a thermoluminescent (TL) material is exposed to ionising radiation some of the liberated charge carriers (electrons or holes) are trapped in lattice imperfections in the crystalline solid. TL is light emission from materials when heated, following previous absorption of energy from radiation [3]. The structure of the defects can be controlled by the preparation method.

The technology of TLD fabrication was developed along with the development of material synthesis. One of the fabrication methods is co-precipitation. This method has the advantage of involving a simple and rapid preparation process, it is easy to control the particle size and composition, and it offers several possibilities to modify the particle surface state and overall homogeneity [4,5].

This study aimed to investigate the effect of re-annealing at various temperatures on the crystal structure and thermoluminescence properties of calcium sulphate doped with dysprosium (CaSO$_4$:Dy). Furthermore, the glow-curve characteristics of each type of TLD were observed. Besides that, we
compared the thermoluminescence response of CaSO$_4$:Dy obtained from this experiment to that of an existing TLD in the market.

2. Materials and method

2.1. Material Preparation (co-precipitation)
TLD CaSO$_4$:Dy was synthesized using a co-precipitation method [6] with the reaction as shown in Equation 1:

$$(\text{CH}_3\text{COOH})_2\text{Ca}^{+}(\text{NH}_4)_2\text{SO}_4^{+}\text{Dy}_2(\text{SO}_4)_3 \rightarrow \text{CaSO}_4:\text{Dy} \downarrow + 2\text{CH}_3\text{COONH}_4$$

(1)

Calcium acetate ((CH$_3$COO)$_2$Ca (AR grade, Merck) was dissolved in double distilled water, then mixed with a mixture of dysprosium sulphate and ammonium sulphate ((NH$_4$)$_2$SO$_4$ (AR grade, Merck) in the presence of ethanol. Dysprosium sulfate was used as doping with a concentration of 0.1 mol %, made from Dy$_2$O$_3$ (Sigma Aldrich) and an appropriate H$_2$SO$_4$ (AR grade Merck). The precipitate was then washed several times with distilled water and dried in an oven for 4 hours. After drying, the TLD was annealed at a temperature of 650 °C for 1 hour in a furnace.

After that, the obtained TLD CaSO$_4$:Dy was re-annealed at various temperatures (700 °C, 800 °C and 900 °C). An illustration of the TLD CaSO$_4$:Dy synthesis process is shown in Figure 1.

![Figure 1. Schematic representation of co-precipitation method for synthesizing CaSO$_4$:Dy.](image)

2.2. Characterization
The structure of the obtained result was characterized using an XR diffractometer (XRD, Philips Analytical PW 1710 BASED) before re-annealing and after re-annealing (700 °C). Then the thermoluminescence response was observed using a TLD Reader Harshaw 3500 at a maximum temperature of 260 °C after radiation exposure to Strontium-90 before re-annealing and after all re-annealing temperature variations (700°C, 800°C, 900°C).
3. Results

From the XRD we could identify that our result was exactly CaSO$_4$ according to JCPDS no. 37-1496.

![XRD spectrum](image)

**Figure 2.** XRD of pure CaSO$_4$:Dy and CaSO$_4$:Dy after re-annealing at 700 °C.

Using the Scherrer equation, the crystal size of the obtained CaSO$_4$:Dy from the experiment was 54.09 nm for the pure CaSO$_4$ while it was 50.91 nm:Dy for the CaSO$_4$:Dy re-annealed at 700 °C respectively. The crystal size decreased after the re-annealing treatment. This phenomenon shows that the pure CaSO$_4$:Dy was still more porous, so when the re-annealing treatment was applied, the crystal size of CaSO$_4$:Dy became smaller. The correlation between re-annealing temperature and thermoluminescence intensity of CaSO$_4$:Dy is shown in figure 3.

![Correlation graph](image)

**Figure 3.** Correlation between re-annealing temperature vs. TL intensity of CaSO$_4$:Dy.
Besides applying the re-annealing temperature variations, the glow-curve characteristics of each type of TLD were observed. From the glow curve, the luminescence intensity distribution can be seen and the temperature range required for producing luminescence. A comparison of the glow curves from the experiment and from an existing TLD are shown in Table 1.

**Table 1.** Comparison of Glow Curve Characteristics From TLD CaSO₄: Dy Obtained From Experiment With the Existing TLD

| Type of TLD            | Main peak (°C) | Remaining e⁻ | Glow curve     |
|------------------------|----------------|--------------|----------------|
| TLD CaSO₄: Dy experiment | 160            | No           | Full curve     |
| TLD 900                | 190            | No           | Full curve     |
| TLD BARC               | 260            | Yes          | Truncated curve|

The TLD CaSO₄: Dy from the experiment and the TLD BARC have a simple glow curve, but the TLD-900 has a complex glow curve. According to Azorin [4], a good TL material usually has a relatively simple glow curve and has its main peak at about 200 °C. The TLD CaSO₄: Dy from the experiment has a simple glow curve and all the electrons in the trap were read out. To determine the TL intensity performance of the TLD CaSO₄: Dy from the experiment, a comparison with the existing TLD was made, as shown in Figure 4.

**Figure 4.** Comparison of TL intensity of TLD CaSO₄: Dy from the experiment vs. existing TLD.

4. **Conclusion**

Re-annealing caused a decrease in grain size or crystal size of CaSO₄: Dy. On the other hand, an increase of the re-annealing temperature increased the sensitivity of the TLD (high TL intensity). The TL response of the TLD obtained in the experiment was higher than that of an existing TLD in the market. The main peak of the obtained TLD in this experiment was between 160 and 200 °C. The TLD obtained in the experiment had good glow-curve properties; all radiation stored in the TLD was read out.
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