Thermoluminescence characteristic of CaSO$_4$:Dy on $\beta$ and $\gamma$ radiation

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Abstract. The research on the developments of thermoluminescence (TL) material in nano- and microstructure are increasing in recent years. There are many new techniques developed for preparing TL material that aim to improve and investigate the structure, morphology, and TL characteristics. In this study, the TL characteristics of CaSO$_4$ doped with Dysprosium (Dy) were being observed. CaSO$_4$:Dy was performed by co-precipitation method with 0.1 mol% Dy concentration. The obtained sample was irradiated with Cs-137 for gamma source and Sr-90 for beta source with doses of 5, 10, 15, 20 and 25 mGy. After irradiation, the structure, morphology, and TL response were observed by using XRD, SEM, and TLD Reader Harshaw 3500. XRD results showed that the average crystallite size for CaSO$_4$:Dy were 58 nm. But, the presence of dysprosium could not be clearly observed from XRD results. The characterization results from SEM for CaSO$_4$:Dy had shape resembling needle-like crystal. The TL response from CaSO$_4$:Dy was compared from beta and gamma radiation source. TL responses for Cs-137 source were 26.56, 34.09, 51.85, 75.97, and 86.29 nC for 5, 10, 15, 20, and 25 mGy, respectively. Sr-90 source with the same dose obtained TL responses as follows: 35.67, 68.60, 100.87, 121.69, and 179.85 nC. The shapes of the glow curves were almost identical, but these curves had different intensities. The TL response from $\beta$-ray source obtained a higher intensity than from $\gamma$-ray source because the beta source is a particle with mass so that it will have more interaction than gamma source in TLD material.

1. Introduction

The development of ionizing radiation in the medical field has led to the developments in the field of radiation detection. Radiation measurement becomes important because radiation cannot be detected directly but can inflict injury to the human body. One of the radiation measurement devices is dose measuring instrument. The well-known instrument for dose measurement is thermoluminescence dosimeter (TLD). The thermoluminescence material that was first proposed by Daniels et al. is still undergoing development until now [1-3]. As the number of radiation user increases, the necessity of radiation dosimeter is also become greater. One of the commercially available thermoluminescence material for radiation dosimeter is CaSO$_4$. It is one of the most actively investigated materials to be applied as radiation dosimeter [4]. It produces a high sensitivity thermoluminescence response for low level doses, while maintaining low cost and inertness to radiation damage [2-8].

The research on the development of thermoluminescence material in nano- and microstructure are increasing in the recent years. Many new techniques for preparing thermoluminescence material have been developed to improve and investigate the luminescence characteristics [2-5]. The preparation
method is very important because it can control the final properties of material. The common methods that have been used to fabricate TLD are precipitation, evaporation, precipitation from solution or molten phase (flow method), chemical vapor deposition (CVD), spray-pyrolysis, and sol-gel. In this research, we used precipitation method, due to its simplicity, low cost and environmentally friendly.

Several researches on the production of TLD by using precipitation method has been reported. Salah et al. [7], which showed CaSO$_4$ nanocrystalline with grain size of 30 - 40 nm. From another reported results of Shinso et al. [8], CaSO$_4$:Dy has been synthesized with nano- and microcrystal sizes with the shape resembling needle-like crystal. The synthesis of polycrystalline constituted by microcrystalline CaSO$_4$:Dy particles with irregular form was reported by Rivera et al. [9].

Dysprosium (Dy) is one of the rare earths (RE) metals that commonly used as a dopant in thermoluminescence materials [10-13]. Dysprosium are known to have high sensitivity, slow fading, good thermoluminescence efficiency, wide dose range, good thermal and physical stability [2,15]. Furthermore, in this study, we investigated the thermoluminescence properties from CaSO$_4$:Dy with different radiation source (beta and gamma source).

2. Materials and Method

2.1. Experimental Method

Some CaSO$_4$:Dy was prepared by a co-precipitation method [7] with a reaction as shown in Eq. 1.

\[
\text{CH}_3\text{COO})_2\text{Ca} + (\text{NH}_4)_2\text{SO}_4 + \text{Dy}_2(\text{SO}_4)_3 \rightarrow \text{CaSO}_4:\text{Dy} + 2\text{CH}_3\text{COONH}_4 
\]

19.765 g of calcium acetate (MERCK) were dissolved in 80 ml double-distilled water. The solution stirred at 300 rpm for 10 minutes. Dysprosium (Dy) was used as a dopant with a concentration of 0.1 mol%. 16.517 g of ammonium sulphate (MERCK) were then dissolved in 80 mL of double-distilled water followed by the mixing of 10 mL of ethanol with dysprosium. Both solutions were mixed together to form a white precipitate. The precipitate was then washed and filtered using a vacuum pump. After that, it was dried in the oven at 100 °C for 2 hours and continued in a furnace at 650 °C for 1 hour. The obtained sample was irradiated with Cs-137 for gamma source and Sr-90 for beta source with doses of 5, 10, 15, 20 and 25 mGy. After irradiation, the thermoluminescence was observed using TLD Reader Harshaw 3500 and the reading results were compared. The obtained sample was also characterized by using XRD and SEM-EDS.

2.2. Characterization

The obtained samples of CaSO$_4$:Dy were characterized by the following instrumental methods. The structure characterization of the sample was performed by X-Ray Diffraction (XRD) Philip Analytical PW 1710 BASED. The morphology of the sample was characterized by using Scanning Electron Microscope (SEM) JEOL JCM-6000 Benchtop Neoscope. The thermoluminescence intensity was measured by TL Reader Harshaw 3500 with the maximum heating temperature of 260 °C. Before the measurements, the samples were irradiated with γ-ray from Strontium-90 (Sr-90) and β-ray from Caesium-137 (Cs-137) with the same dose set.

3. Results and Discussion

The development of ionizing radiation in the medical field has led to developments in the field of radiation detection. CaSO$_4$:Tm and CaSO$_4$:Dy were also synthesized using co-precipitation method and produced as a white precipitant. The precipitant was washed and dried at a temperature of 90 °C for four hours, and then annealing procedure was applied using a furnace at a temperature of 650 °C for one hour.

3.1. Structure
To verify the sample, an XRD procedure was performed. The diffraction pattern on Figure 1 for CaSO₄:Dy show similarities with the JCPDS 37-1496 diffraction pattern at the angles of 25.5°, 31.4°, 38.7°, 40.1°, 48.8°, 52.4°, and 55.8°. However, the presence of dysprosium could not be clearly observed from XRD result. By using Scherrer equation, the average crystallite size is 58 nm. The crystal structure of CaSO₄:Dy was orthorhombic.

![XRD pattern](image1.png)

**Figure 1.** The XRD diffraction pattern of CaSO₄:Dy and JCPDS 37-1496 references data

3.2. **Morphology**

Aside the structure of the sample, the surface morphology, size, and composition of the elements contained in the synthesized material were observed. When electrons from SEM hit the sample, two types of collisions will happen: elastic and non-elastic collision. From the non-elastic collision, secondary electron signal and X-ray characteristics could be obtained. Meanwhile the elastic collision can be used to obtain backscattered electron signal. The secondary electron interactions can be used to describe the topography of the analyzed object; the higher surface will appear brighter than the low surface. On the other hand, backscattered electrons give molecular weight differences from the atoms that make up the surface.

The high molecular weight will be brighter than the low molecular weight atoms in the SEM images. The characterization obtained from SEM for CaSO₄:Dy was shown in Figure 2. This figure illustrates a more slender and elongated crystal with average sizes of 5-15 µm. Each particle consists of many crystals because based on the calculation result using Scherer’s formula the crystallite size has the order nm. The sample has shape resembling needle-like crystal observed by Shinso [15].

![SEM images](image2.png)

**Figure 2.** Morphology of CaSO₄:Dy with magnification (a) 3000x and (b) 10000x
3.3. Thermoluminescence

Glow curve is an important parameter in determining the characteristics of a TLD. Glow curve is a graph that describes the relationship between the intensity of thermoluminescence with temperature. Glow curve can be obtained from TLD reading using a TLD reader. Glow curve can consist of one or more peaks based on the number of traps with different depths inside the crystal. The area under the glow curve shows the total luminescence emitted from the TLD and proportional to the dose received on it. The peak height shows the highest frequency of luminescence.

The red line on the graph shows the temperature gradient. At the time of reading using a TLD reader, there was a gradual warming aimed at removing electrons that were trapped inside the trap. Temperature increase occurred gradually and eventually becomes constant at 260 °C. Based on the literature, the glow curve for CaSO₄:Dy will appear at a temperature between 100 – 200 °C [19]. The channel represent with time counts where each channel shows how much luminescence has been counted.

To evaluate the performance of CaSO₄ as a radiation dosimeter, these materials were irradiated using Sr-90 and Cs-137 source. The response of CaSO₄:Dy are shown in Figure 3. The glow curve shape and peak is not significantly different, only the intensity was different.

![Figure 3. Display of TLD reader](image)

![Figure 4. Thermoluminescences of CaSO₄:Dy against gamma and beta sources](image)
TLD irradiation using various doses as shown in Figure 4 for TLD CaSO$_4$: Dy produced a glow curve which shapes and positions were almost identical. The only difference was the intensity of the glow curve. The increase in dose made the intensity of the glow curve also increasing. The peak position shift can occur. This is possible because of the difference in the rate at which electrons are released from within the trap to return to the ground state. The wider peak of the glow curve indicates the slower discharge process of the electron.

In this study, TLD CaSO$_4$:Dy was irradiated using Sr-90 and Cs-137 radiation sources. The TLD cannot distinguish the radiation energy which it receives (α, β, γ), however each TLD has different characteristics for different radiation sources. Therefore, TLD responses were tested against Sr-90 sources which are the transmitters of β and Cs-137 which are γ source. The thermoluminescence response from β source produced a higher intensity than γ-ray source because of the beta source is a particle with certain weight so that it has more interaction than gamma source in TLD material (Fig. 5).

![Figure 5. Comparison of TLD response to gamma and beta sources at 25 mGy dose](image)

The TL response of CaSO$_4$:Dy was compared with the commercial TLD (TLD-900 Harshaw and TLD BARC) in our previous study [16]. The results obtained indicate that the TLD gives a less favorable response compared to other TLDs (Table 1). Therefore, PTFE addition and increasing of annealing temperature are applied to improve its performance.

| No. | TLDs                              | Response (nC/gr) |
|-----|-----------------------------------|-----------------|
| 1   | CaSO$_4$:Dy synthesis            | 2.83            |
| 2   | TLD-900 Harshaw                  | 5.83            |
| 3   | CaSO$_4$:Dy+PTFE 700°C           | 15.21           |
| 4   | TLD BARC                         | 4.38            |

4. Conclusions
CaSO$_4$ doped with dysprosium (Dy) has been successfully synthesized by co-precipitation method. From XRD results, we obtained the average crystallite size for CaSO$_4$:Dy were 58 nm. The thermoluminescence response of this sample was investigated by irradiating the sample using beta and gamma radiation source. The results show that beta radiation source produced higher dose than gamma radiation source.

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Acknowledgements

This research was partially supported by Medical Dosimetry Laboratory. We thank our colleagues from Biophysics and Medical Physics Laboratory and Energy and Environmental Material (E2M) Laboratory who provided insight and expertise that greatly assisted the research.