



Thermoluminescent analysis of CaSO₄:Tb,Eu crystal powder for dosimetric purposes



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HIGHLIGHTS

- Thermoluminescent properties of CaSO₄ doped with Tb and Eu were evaluated.
- Crystals were grown using a new production route based in the Yamashita method.
- The CaSO₄:Tb,Eu samples presented a 170 °C suitable for TL dosimetry.
- The TL response of the CaSO₄:Tb,Eu material was linear and reproducible.
- TL signal fading of samples was around 30% after one month of irradiation.

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ABSTRACT

The motivation of this work was to produce crystals of CaSO₄ doped with an unusual combination of RE elements such as terbium (Tb) and europium (Eu) in different concentrations, and analyze its thermoluminescent (TL) properties. The crystals were produced by the slow evaporation route using calcium carbonate (CaCO₃) as precursor, and incorporating the dopants (Tb₂O₃ and Eu₂O₃) in a solution of sulfuric acid, that is evaporated and collected again, leaving just CaSO₄:Tb,Eu crystal powder. The terbium and europium ions were incorporated in concentration ratios of 1:1, 2:1 and 5:1 (weight proportions). X-ray diffraction analyses showed that samples of doped CaSO₄ exhibit only a single phase corresponding to the crystal structure of anhydrite. The radioluminescence confirmed the presence of Tb³⁺ and Eu²⁺ in the crystal matrix. The CaSO₄:Tb,Eu crystal powders showed TL emission glow curves with three peaks centered around 170 °C, 270 °C and 340 °C, after irradiation with a ⁹⁰Sr/⁹⁰Y source. Thermoluminescent (TL) characteristics such as linearity, reproducibility and fading were evaluated. Samples produced with concentration ratio of 2:1 of Tb and Eu showed the highest TL intensity. The produced CaSO₄:Tb,Eu samples present TL properties useful for dosimetric purposes.

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1. Introduction

Since the thermoluminescence started to be applied to the dosimetry of ionizing radiation, in 1940, different materials have been proposed as dosimeters, and one of the most common is CaSO₄, which has been doped with various rare earth (RE) elements in the last years (Lakshmanan, 1999; Ingle et al., 2008; Junot et al., 2014a, b). Many CaSO₄-based materials are already well known and widely used in dosimetry applications because of their high sensitivities, low minimum detectable doses, wide ranges of linearity

and high saturation levels (Lakshmanan, 1999), but it is important to continue to perform research on addition of new elements for doping the sulfate matrix, in order to improve the sensitivity and TL response of new materials. It is also important to advance research seeking new viable and inexpensive production routes.

Recent research (Kása et al., 2007; Junot et al., 2014a, b; Doull et al., 2014) have proposed the incorporation of new elements as co-dopants of well-known dosimeters, such as CaSO₄:Dy, CaSO₄:Eu and CaSO₄:Tb. Junot et al. (2011) observed that the incorporation of silver in CaSO₄:Eu enables TL and thermally stimulated electronic emissions (TSEE) more intense than in the non-silver materials. Nunes and Campos (2008) studied the cerium element as co-activator of CaSO₄:Eu and obtained an alternative dosimeter, with low cost and energy dependence as main advantages over the

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already employed $\text{CaSO}_4:\text{Dy}$ (TLD-900) and $\text{LiF}:\text{Mg,Ti}$ (TLD-100) dosimeters. Kudryavtseva et al. (2009, 2014) studied the electron–hole and excitonic processes in $\text{CaSO}_4:\text{Tb,Na}$ and $\text{CaSO}_4:\text{Tb}$ and observed that the electron transfer to a central ion of an oxyanion provides efficient energy transfer to Tb^{3+} .

The motivation of this work was to produce crystals of CaSO_4 doped with an unusual combination of RE elements such as terbium (Tb) and europium (Eu) in different concentrations (1:1, 2:1 and 5:1 wt). The Yamashita et al. (1971) method of developing CaSO_4 crystals, the well-known slow evaporation route, was sought in the present work. The new route has a controlled air atmosphere, an improved distillation system, and it is fully isolated from the external environment, such as made by Nunes and Campos (2008), but with a new adjustment to the circuit, which is the reuse of the evaporated sulfuric acid, aimed at sustainability. The thermoluminescent (TL) properties of the produced samples was analyzed. Thus, the main purpose of this study was to evaluate the feasibility of the new route employed as well as the dosimetric characteristics of samples produced, seeking new viable and inexpensive production routes and samples.

2. Materials and methods

In the new growth route, adapted from Yamashita's method (Yamashita et al., 1968, 1971), the crystals were produced from calcium carbonate (CaCO_3) (J.T. Baker 99%), by incorporating the dopants (Tb_2O_3 and Eu_2O_3) (Sigma–Aldrich 99.9%) in a solution of sulfuric acid (H_2SO_4) (Vetec 95–99%), that is evaporated leaving just $\text{CaSO}_4:\text{Tb,Eu}$ crystal powder. The Tb^{3+} and Eu^{3+} ions were incorporated in concentration ratios of 1:1, 2:1 and 5:1.

To perform the crystal growth, the mixtures of $\text{CaCO}_3+\text{H}_2\text{SO}_4$ +dopants were carried to a beaker and remained on a magnetic stirrer until the complete homogenisation. Then, the mixtures were introduced into a volumetric flask on a heating mantle at 375 °C until all the acid evaporated and remained only the doped calcium sulfate, which took around 24–48 h. Acid vapors were then condensed and recaptured again in an Erlenmeyer flask at the condenser outlet. Possible uncondensed vapors were taken for gas washing bottles containing sodium hydroxide solution and were neutralized. The whole system is sealed and a vacuum pump drag the vapors.

After the growing process, the doped crystals were rinsed three times with cold (room temperature) and hot (100 °C) distilled water, crumbled, rinsed again, and grain-selected to obtain grain sizes between 75 and 150 μm . The powder is calcined at 600 °C for 1 h. For comparison purposes, $\text{CaSO}_4:\text{Eu}$ and $\text{CaSO}_4:\text{Tb}$ samples were produced by the same route.

To analyze the samples, X-ray diffraction data were obtained in a Rigaku diffractometer of Bragg-Brentano geometry using $\text{Cu-K}\alpha$ radiation. The measurements were performed in the continuous mode with a scan range of 20–80°, scan step of 0.02 and scan speed of 2°/min.

The samples were irradiated with beta ($^{90}\text{Sr}/^{90}\text{Y}$) at a rate of 0.1 Gy/s and gamma (^{60}Co) at a rate of 0.316 Gy/s sources at a dose range from 0.1 Gy to 100 Gy.

Radioluminescence spectra were obtained by exciting the samples with X-radiation (40 kV and current 40 mA) at room temperature using a high-resolution spectrometer from Ocean Optics. The emission spectra were measured in the range of 200 nm–800 nm with excitation time of 3 s and integration time of 1000 s.

TL analyses were performed in a Harshaw 3500 TL reader and in a Risø TL/OSL reader using a heating rate of 10 °C/s.

To study the fading of the samples, TL analyses were performed in the following times after irradiation: immediately, one week,

two weeks, and one month. The percentage decay of the TL intensity during the storage period was calculated by comparison with the TL signal of the sample read immediately after irradiation. During the time interval between irradiation and reading, all of the samples were stored in opaque packaging at room temperature, approximately 25 °C, and under low light conditions.

3. Results

3.1. Crystalline structure and radioluminescence spectra

Fig. 1 shows the X-ray diffraction scans of samples of pure CaSO_4 (JT Baker 99%) and $\text{CaSO}_4:\text{Tb,Eu}$. The diffraction patterns obtained for all of the samples had diffraction peaks and relative intensities corresponding to the crystalline structure of anhydrite (JCPDS 01-072-0916). These results confirm that the samples are composed of crystals with orthorhombic symmetry and spatial group Amma. It is the same CaSO_4 crystalline structure obtained in previous investigations (Junot et al., 2014a, b) using the conventional slow evaporation synthesis method.

The radioluminescence (RL) spectra were analyzed in order to verify the presence of dopants in the samples, as well as their luminescent transitions. Fig. 2 shows RL spectra of the prepared

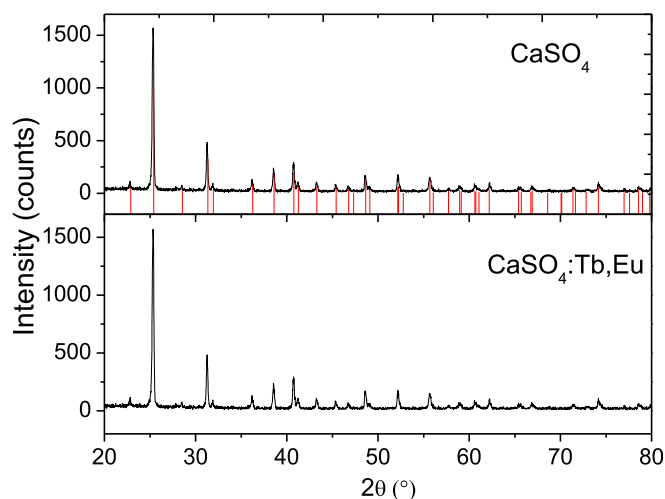


Fig. 1. X-ray diffraction of crystalline samples of CaSO_4 and $\text{CaSO}_4:\text{Tb,Eu}$.

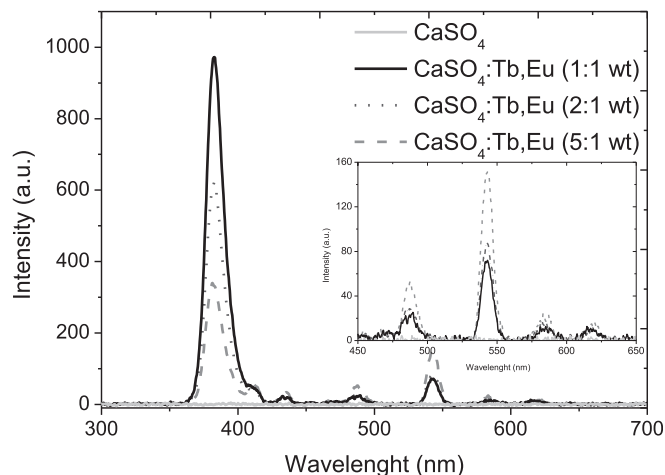


Fig. 2. Radioluminescence of crystalline samples of pure CaSO_4 and $\text{CaSO}_4:\text{Tb,Eu}$ at different dopant concentrations (zoom from 450 nm to 650 nm).

CaSO₄ and CaSO₄:Tb,Eu samples. CaSO₄ showed no luminescence, as expected. Analyzing the spectra of samples of CaSO₄:Tb,Eu, one can clearly identify the presence of Eu²⁺ ions whose main emission is around 380 nm and Tb³⁺ with primary emission at 544 nm, corresponding to the transition between the levels ⁵D₄ → ⁷F₅, and less intense emission at 412 nm (⁵D₃ → ⁷F₅), 435 nm (⁵D₃ → ⁷F₄), 488 nm (⁵D₄ → ⁷F₆), 586 nm (⁵D₄ → ⁷F₄) e 620 nm (⁵D₄ → ⁷F₃). It was not possible to observe the presence of Eu³⁺ ion, whose main emission occurs at 614 nm. In the case of the Eu²⁺ ion, the peak at 380 nm is allowed by a f-d dipole transition, which explains its high intensity. It is noteworthy that the increase of terbium concentration in the matrix of the samples increased the luminescence intensity of Tb³⁺ ions, but reduced the luminescence intensity of the Eu²⁺ ions, suggesting a competitive process between the ions in the site occupation of Ca²⁺ in the CaSO₄ matrix, due to greater compatibility of the ionic radius.

3.2. Glow curves

The best way to characterize a TL material is through its glow

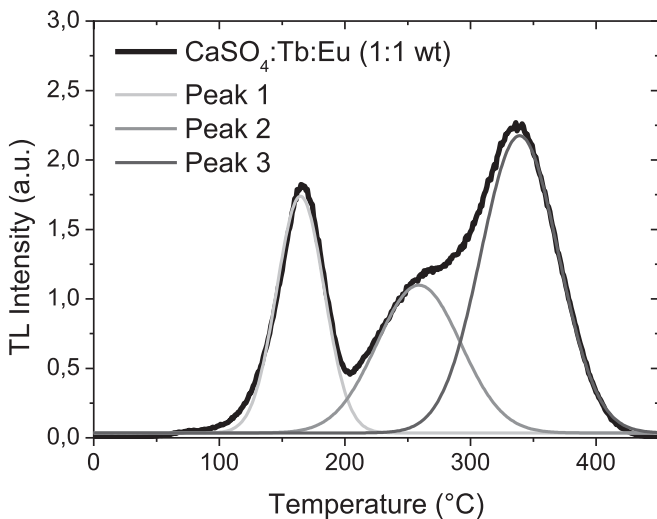


Fig. 3. Typical TL glow curves of CaSO₄:Tb,Eu (1:1) samples after exposure to beta radiation (⁹⁰Sr/⁹⁰Y).

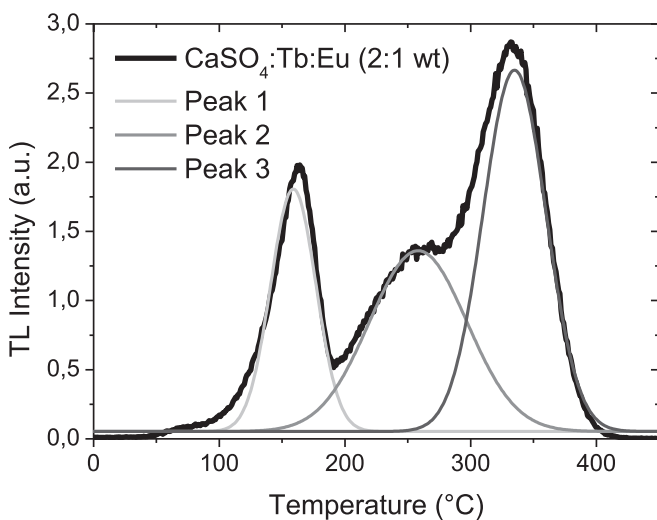


Fig. 4. Typical TL glow curves of CaSO₄:Tb,Eu (2:1) samples after exposure to beta radiation (⁹⁰Sr/⁹⁰Y).

curve. Fig. 3 shows the glow curves of CaSO₄:Tb,Eu (1:1 wt) crystals, after exposure to 1.0 Gy of beta radiation (⁹⁰Sr/⁹⁰Y). The presence of three peaks can be observed at the temperatures of 170 °C, 270 °C and 340 °C and a slight shoulder corresponding to a peak of low intensity related to shallow traps around 90 °C. The appearance of three major peaks indicates the existence of 3 populated and distinct recombination centers. The peak at 170 °C is associated with defects generated by europium, and is characteristic of Eu²⁺ ion recombination centers (Junot et al., 2014a, b). It is believed that the peaks at 270 °C and 340 °C are related to defects caused by the insertion of terbium in the CaSO₄ matrix, and its luminescent intensities are related to the Tb³⁺ ion recombination centers.

Figs. 4 and 5 show the glow curves of the CaSO₄:Tb,Eu in concentrations of 2:1 and 5:1, respectively, after exposure to 1.0 Gy of beta radiation (⁹⁰Sr/⁹⁰Y). The curves follow the same behavior found in the samples with 1:1 ratio between Tb and Eu. However,

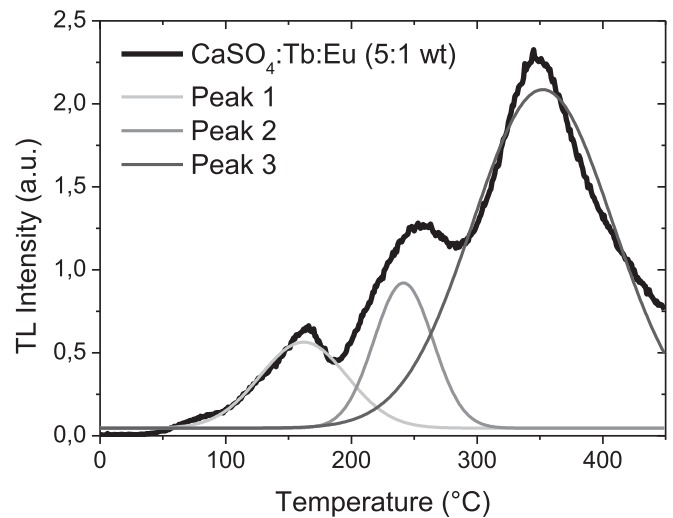


Fig. 5. Typical TL glow curves of CaSO₄:Tb,Eu (5:1) samples after exposure to beta radiation (⁹⁰Sr/⁹⁰Y).

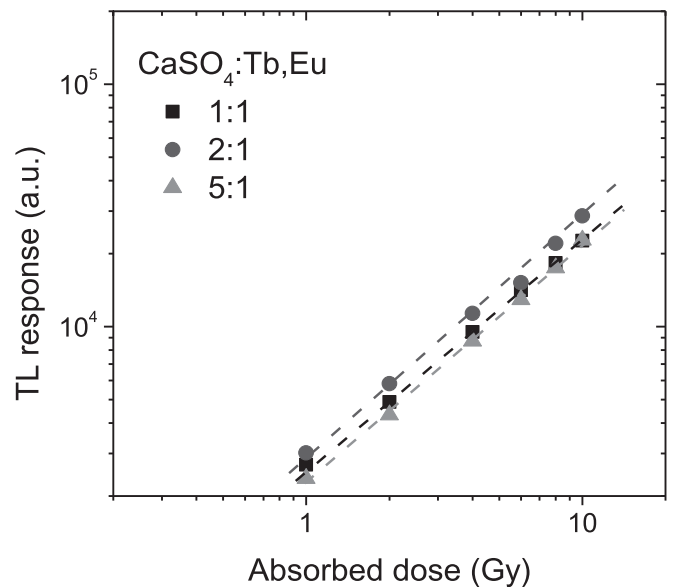


Fig. 6. TL response of CaSO₄:Tb,Eu samples as a function of the absorbed dose for ⁹⁰Sr/⁹⁰Y source.

increasing concentration of Tb, the 170 °C peak intensity, related to Eu^{2+} ions, is reduced. This was expected, because as observed in the RL spectra, the luminescence of Eu^{2+} ions is reduced with increasing concentration of Tb^{3+} ions. One can also notice small shifts in the TL peak positions. These shifts are due to the non-perfectly uniform distribution of heat between the heating plate and the powder sample, which may lead to small delays in the process of recombination between electrons and holes and thus slightly move the TL peak position. In the dosimetric point of view, both 170 °C and 270 °C peaks can be used, but the peak at 170 °C is preferable, because in addition to suffer no interference from other peaks, it is at a lower temperature, which minimizes the time spent in the reading process.

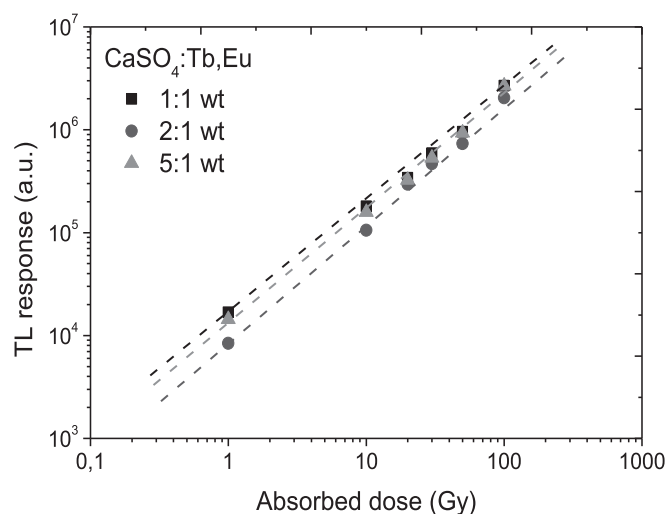


Fig. 7. TL response of $\text{CaSO}_4:\text{Tb,Eu}$ samples as a function of the absorbed dose for ^{90}Sr source.

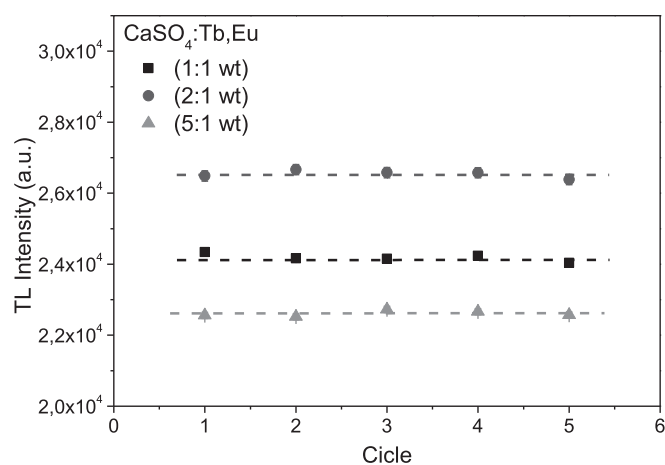


Fig. 8. TL response of $\text{CaSO}_4:\text{Tb,Eu}$ samples after each irradiation–reading–annealing cycle.

Table 1

Decay of TL response of $\text{CaSO}_4:\text{Tb,Eu}$ samples after storage time.

Material	Fading in 24 h (%)	Fading in 7 days (%)	Fading in 15 days (%)	Fading in 30 days (%)
$\text{CaSO}_4:\text{Tb,Eu}$ (1:1)	3 ± 5	9 ± 5	16 ± 5	29 ± 5
$\text{CaSO}_4:\text{Tb,Eu}$ (2:1)	8 ± 5	19 ± 5	29 ± 5	36 ± 5
$\text{CaSO}_4:\text{Tb,Eu}$ (5:1)	2 ± 5	7 ± 5	12 ± 5	16 ± 5

TL curves of pure CaSO_4 , $\text{CaSO}_4:\text{Eu}$ and $\text{CaSO}_4:\text{Tb}$ are well known in the literature (Lakshmanan, 1999). Pure CaSO_4 TL intensity is negligible at low doses, $\text{CaSO}_4:\text{Eu}$ has a non-stable 170 °C TL peak with unacceptable fading, and $\text{CaSO}_4:\text{Tb}$ has a low luminescent intensity. The complexity of TL curves, mainly the ones composed of many peaks, has been reported by several researchers (Nunes and Campos, 2008; Doull et al., 2014; Kulkarni et al., 2014) who reported that TL peaks are usually an overlapping of several peaks near a broad temperature range. Thus, it is necessary to analyze the curves of TL materials in order to check the overlapping peaks. This procedure indicates also the feasibility of the composite as temperature indicators, as proposed by Doull et al. (2014) for $\text{CaSO}_4:\text{Ce,Tb}$.

3.3. Linearity, reproducibility and fading

Analyzing the dose–response curves with log axes in the same scale, as observed in Fig. 6, it can be observed that the TL responses of composites are linear due to the curve slope equal to 45° in the dose range of 0.1–1 Gy, after exposure to beta radiation ($^{90}\text{Sr}/^{90}\text{Y}$). The samples were also exposed to gamma radiation (^{60}Co) over a large dose range from 1 to 100 Gy, in order to observe the linearity of their TL response. Fig. 7 shows the dose–response curves of the samples of $\text{CaSO}_4:\text{Tb,Eu}$ exposed to ^{60}Co . These samples presented a linear response in the dose range of 1 Gy–30 Gy, as well as $\text{CaSO}_4:\text{Dy}$, which has its linear range reported from 1 mGy to 30 Gy (Campos, 1998). From 30 Gy to 100 Gy the samples showed a supralinear response.

A key advantage of TL dosimeters is its reusability after a suitable heat treatment (annealing). To study the reproducibility of $\text{CaSO}_4:\text{Tb,Eu}$ samples, the crystal powder was compacted into pellets with a controlled mass of 40 mg. Five samples were irradiated with 1 Gy of beta radiation, read, annealed, and irradiated again; this cycle was repeated 5 times. As observed in Fig. 8, all of the TL responses were similar, with only an approximately 8% deviation.

As TL dosimeters are passive, their fading should be as low as possible. Parameters such as storage temperature and packaging to avoid exposure to visible light are crucial in maintaining the stability of the trapped charge carriers in the forbidden band gap of the crystal. Table 1 shows the decay of the TL signal of the produced $\text{CaSO}_4:\text{Tb,Eu}$ samples. Fading analysis was performed in peak 1, centered at 170 °C. The TL signal of samples fades by 29% for a 1:1 ratio of Tb to Eu, 36% for a 2:1 ratio, and 16% for a 5:1 ratio, after one month.

4. Conclusions

The production route used in the crystal growth was simple and viable. The acid evaporated in the syntheses was collected and can be reused. The x-ray diffraction analyses showed that samples of doped CaSO_4 exhibit only a single phase corresponding to the crystal structure of anhydrite. The radioluminescence results confirmed the presence of Tb^{3+} and Eu^{2+} in the crystal matrix. The $\text{CaSO}_4:\text{Tb,Eu}$ produced samples showed TL emission glow curves with three peaks centered around 170 °C, 270 °C and 340 °C. The

peak centered in 170 °C is situated in an ideal temperature for TL dosimetry. The $\text{CaSO}_4:\text{Tb},\text{Eu}$ material has also presented some TL properties appropriated for dosimetric purposes, such as linearity and reproducibility. TL signal fading of samples was reasonably satisfactory and may be corrected with an appropriate correction factor. The radiation sources and the dose range used in the irradiations of this study are quite common in industrial procedures, so the materials produced present usefulness in this type of monitoring. Furthermore, as the samples presented a TL signal with many peaks, they can also be used as temperature sensors.

Acknowledgments

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