



Feasibility study of CaSO₄:Eu, CaSO₄:Eu,Ag and CaSO₄:Eu,Ag(NP) as thermoluminescent dosimeters



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HIGHLIGHTS

- Thermoluminescent properties of CaSO₄ doped with Eu, Ag and Ag nanoparticles were evaluated.
- Crystals were grown using a production route based in the Yamashita method.
- Glass or Teflon was incorporate to the crystals in order to obtain composites.
- The TL responses of the composites are proportional to the dose absorbed.
- The CaSO₄:Eu,Ag(NP) + glass has potential to be used as a thermoluminescent dosimeter.

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ABSTRACT

This work evaluates the dosimetric properties of crystals of CaSO₄ doped with unusual elements, such as europium (Eu) and silver (Ag), including their nanoparticle forms, after the incorporation of glass or Teflon and compares them with well-known thermoluminescent dosimeters (TLD). X-ray diffraction analyses showed that samples of doped CaSO₄ exhibit only a single phase corresponding to the crystal structure of anhydrite. Optical spectroscopy confirmed the presence of Eu³⁺ in the crystal matrix and a luminescent gain due the presence of silver nanoparticles. The composites showed thermoluminescent emission glow curves, with a single peak centered at approximately 200 °C for pellets with Teflon and at 230 °C for pellets with glass. The dosimeters based on calcium sulfate doped with europium and silver nanoparticles provided the most intense thermoluminescent (TL) emission of the composites studied. In comparison with commercial TLD, such as LiF:Mg,Ti and CaSO₄:Dy, the CaSO₄:Eu,Ag(NP)+glass produced in this work presented similar low detection limits and higher sensitivity. The new methods for the preparation of dosimeters and the incorporation of glass are shown to be viable because all of the samples presented a linear, reproducible and first order kinetic TL emission.

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1. Introduction

Rare Earth (RE) elements have been widely employed as dopants for the production of CaSO₄ thermoluminescent detectors (TLD). Yamashita et al. (1971) developed a relatively simple and efficient method for using CaSO₄ doped with rare earths. This method has been widely used and modified by various researchers (Kása et al., 2007). Many authors have studied doped detectors, revealing their properties. These properties include the

thermoluminescent (TL) response to dose, kinetic emission, specific ionization density, enabled dopants and their concentrations, co-dopants, processes of energy transfer, optical absorption and measurements of paramagnetic resonance.

It was observed that in addition to RE elements, Ag particles improved the luminescent characteristics in some materials. Madhusoodanan et al. (2009) reported the development of a new doubly doped thermoluminescent material, KMgF₃:Eu,Ag, which has improved TL characteristics compared to KMgF₃:Eu. Strohhöfer and Polman (2002) reported that the photoluminescence of Er³⁺ in glass is greatly enhanced by the presence of silver. In recent years, there has been much research involving luminescent materials on a nanometric scale. Salah et al. (2006) and Zahedifar et al. (2007)

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argue that nanoparticles increase the band gap, improve the TL intensity and decrease fading compared to microcrystalline materials. Junot et al. (2011) found that the incorporation of silver in $\text{CaSO}_4:\text{Eu}$ allows more intense TL and thermally stimulated exoelectronic emissions than in materials without silver. The increase in emission intensity is more significant when silver is incorporated as a co-dopant in the form of nanoparticles ($\text{CaSO}_4:\text{Eu,Ag(NP)}$).

Thus, the motivation of this work was to evaluate the dosimetric properties of $\text{CaSO}_4:\text{Eu}$, $\text{CaSO}_4:\text{Eu,Ag}$ and $\text{CaSO}_4:\text{Eu,Ag(NP)}$ produced by the method of Junot et al. (2011) after the incorporation of glass or Teflon as resistive agents and to compare them with well-known TLDs, such as LiF:Mg,Ti (TLD-100) and $\text{CaSO}_4:\text{Dy}$ (TLD-900). The TL of the samples was studied with the goal of evaluating their applicability to dosimetry, considering characteristics such as sensitivity, dose response, linearity, reproducibility, lower detection limit, fading and kinetic order.

2. Materials and methods

Silver nanoparticle synthesis was performed by the method applied by Junot et al. (2011), which consists of the dissolution of the precursor agent AgNO_3 in ethylene glycol followed by the slow addition of a reducing agent (NaBH_4).

Crystals of $\text{CaSO}_4:\text{Eu}$, $\text{CaSO}_4:\text{Eu,Ag}$ and $\text{CaSO}_4:\text{Eu,Ag(NP)}$ were produced through a route adapted from Yamashita's method (1968, 1971). To produce $\text{CaSO}_4:\text{Eu}$, a mixture of calcium carbonate (CaCO_3) (J.T. Baker 99%) and europium oxide (Eu_2O_3) (Sigma–Aldrich 99.9%) was added to an excess of sulfuric acid (H_2SO_4) (Vetec 95–99%) and dried at 375 °C. Productions of $\text{CaSO}_4:\text{Eu,Ag}$ and $\text{CaSO}_4:\text{Eu,Ag(NP)}$ followed the same steps used to produce $\text{CaSO}_4:\text{Eu}$, with the addition of silver oxide (Ag_2O) and silver nanoparticles (Ag(NP)), respectively. The dopants were incorporated at concentration of 0.1 mol%. After the growing process, the doped crystals were rinsed three times with cold and hot distilled water, calcined at 600 °C for 1 h, crumbled, rinsed again, and grain-selected to obtain grain sizes between 75 and 180 μm .

Pellets were made using a 2:1 (weight) mixture of the phosphor and powdered glass (silicon oxide) or Teflon to improve physical resistance. This material was compacted by the application of a uniaxial pressure of 100 kgf, resulting in pellets with a 6 mm diameter, 1 mm thickness and 20 mg weight. Pellets with the addition of glass were sintered at 600 °C for 6 h, and pellets with the addition of Teflon were sintered at 400 °C for 1 h. After each irradiation-readout cycle, the pellets were annealed for 1 h at 400 °C. Fig. 1 shows the composite production method schematically.

The samples were irradiated with beta ($^{90}\text{Sr}/^{90}\text{Y}$ at a rate of 6.08 mGy/min) and gamma (^{137}Cs at a rate of 0.98 mGy/min) sources at a dose range from 0.1 Gy to 1 Gy.

TL analyses were performed in a Harshaw 3500 TL reader using a heating rate of 10 °C/s. The maximum shunting line found in the measures was $\pm 6.0\%$.

To study fading, TL analyses were carried out at the following time intervals after irradiations: immediately and after one week, two weeks, and one month. During the time interval between irradiation and reading, all of the samples were stored in opaque packaging at room temperature, approximately 23 °C, and under low light conditions.

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.

Photo-induced fluorescence spectra were collected between 570 and 630 nm with excitation at 245 nm using an ISS PC1 spectrofluorimeter with a 300 W xenon lamp.

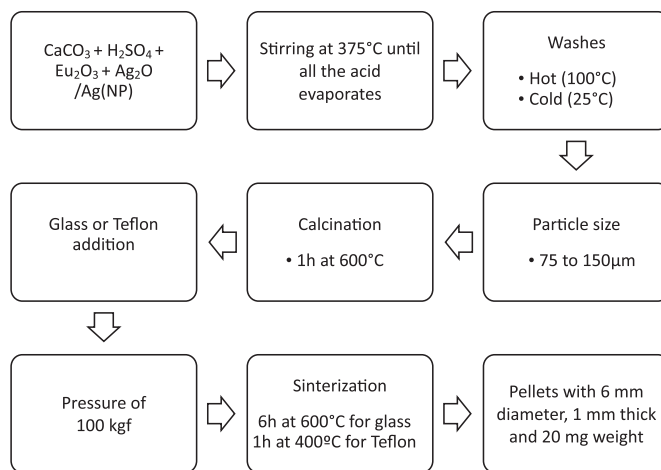


Fig. 1. Step-by-step scheme of the production process of the samples.

3. Results

3.1. Crystalline structure and fluorescence spectrum

Fig. 2 shows the X-ray diffraction scans of samples of pure CaSO_4 (JT Baker 99%), $\text{CaSO}_4:\text{Eu}$, $\text{CaSO}_4:\text{Eu,Ag}$ and $\text{CaSO}_4:\text{Eu,Ag(NP)}$. 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). It was found that the samples of pure and doped CaSO_4 had only one phase because it was not possible to observe the presence of dopants. These results confirm that the samples are composed of crystals with orthorhombic symmetry and spatial group Amma.

Fig. 3 shows the photo-induced fluorescence exhibiting two bands between 570 and 630 nm. This emission is comparable to the Eu^{3+} emission spectrum for 254 nm excitation (Ingle et al., 2008), which shows the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions at 590 nm and 614 nm, respectively. This demonstrates that the Eu^{3+} was incorporated into CaSO_4 .

3.2. Glow curves

Fig. 4 presents a comparison of the glow curves of all of the samples produced and also of the pure glass after exposure to

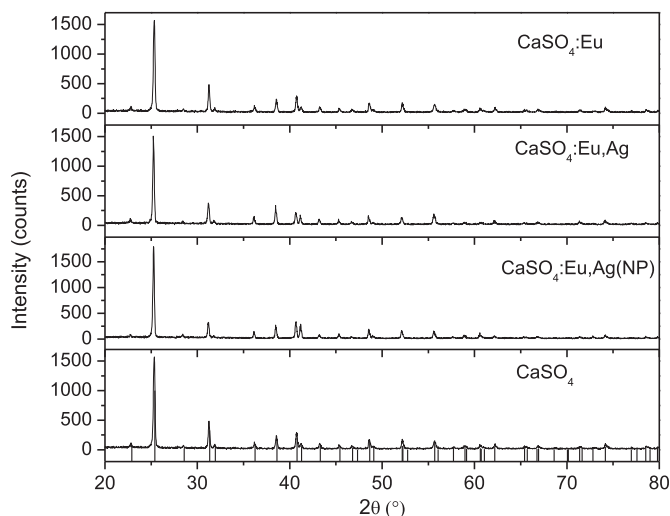


Fig. 2. X-ray diffraction of the crystalline samples of CaSO_4 ; $\text{CaSO}_4:\text{Eu}$; $\text{CaSO}_4:\text{Eu,Ag}$ and $\text{CaSO}_4:\text{Eu,Ag(NP)}$.

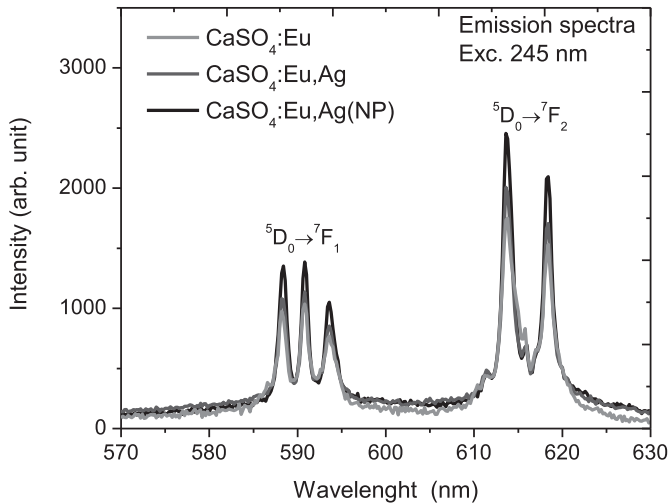


Fig. 3. Emission spectra of the crystalline samples of $\text{CaSO}_4:\text{Eu}$; $\text{CaSO}_4:\text{Eu,Ag}$ and $\text{CaSO}_4:\text{Eu,Ag(NP)}$, with excitation at 245 nm, showing characteristic transitions of Eu^{3+} .

1.0 Gy of beta radiation ($^{90}\text{Sr}/^{90}\text{Y}$), with a zoom in the glow curves of the $\text{CaSO}_4:\text{Eu}$ and $\text{CaSO}_4:\text{Eu,Ag}$ samples. TL analysis of phosphorous + glass samples exhibited glow curves with emission over the temperature range of 170–270 °C, with a single peak centered at approximately 230 °C. Phosphorous + Teflon samples showed a TL signal between 160 °C and 240 °C, with a maximum intensity of approximately 200 °C. The displacement of the TL peak in pellets containing glass must occur due the thermal resistivity of glass, which requires higher temperatures for emission. $\text{CaSO}_4:\text{Eu,Ag(NP)}$ + glass pellets presented a more intense TL emission than the other pellets. It is also important to note that pure glass has a minimal TL emission that can be neglected in comparison to phosphorous TL emission. Junot et al. (2011) observed that samples of powdered $\text{CaSO}_4:\text{Eu,Ag(NP)}$ show a considerably more intense emission (approximately 5 times greater) than the samples containing only europium or silver. This was also observed in this study in the samples with the addition of glass (see Fig. 4) and suggests that silver nanoparticles may be altering the crystal lattice of the material, creating new defects and traps for electrons. Thus, because $\text{CaSO}_4:\text{Eu,Ag(NP)}$ samples have more potential to be used as a TLD, their dosimetric characteristics have been studied.

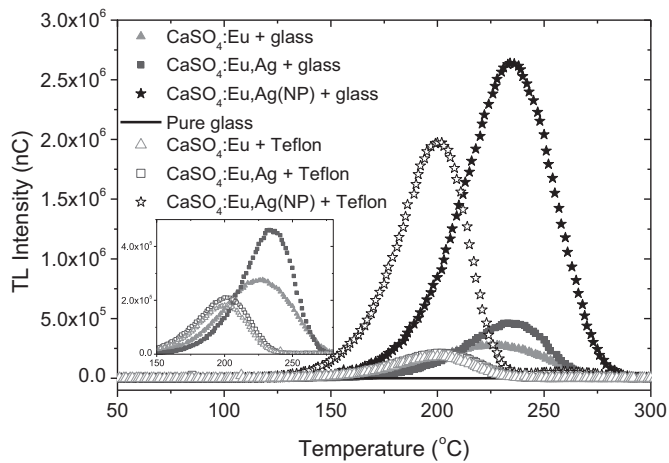


Fig. 4. Typical TL glow curves of $\text{CaSO}_4:\text{Eu}$ + Teflon; $\text{CaSO}_4:\text{Eu,Ag}$ + Teflon, $\text{CaSO}_4:\text{Eu,Ag(NP)}$ + Teflon, $\text{CaSO}_4:\text{Eu}$ + glass; $\text{CaSO}_4:\text{Eu,Ag}$ + glass, $\text{CaSO}_4:\text{Eu,Ag(NP)}$ + glass and pure glass samples irradiated with 1.0 Gy from a $^{90}\text{Sr}/^{90}\text{Y}$ source.

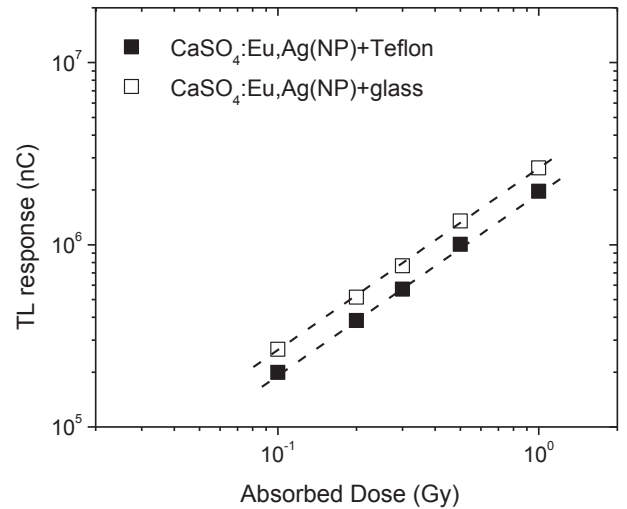


Fig. 5. TL response of $\text{CaSO}_4:\text{Eu,Ag(NP)}$ + Teflon and $\text{CaSO}_4:\text{Eu,Ag(NP)}$ + glass samples as a function of the absorbed dose from a $^{90}\text{Sr}/^{90}\text{Y}$ source for doses ranging from 0.1 to 1.0 Gy.

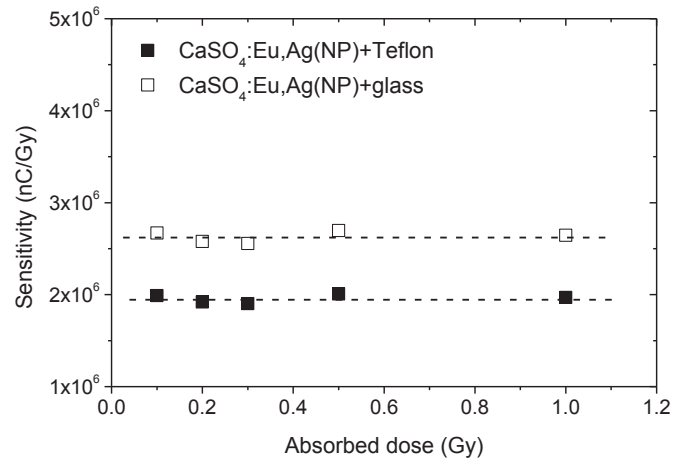


Fig. 6. Sensitivity of $\text{CaSO}_4:\text{Eu,Ag(NP)}$ + Teflon and $\text{CaSO}_4:\text{Eu,Ag(NP)}$ + glass samples after irradiation with a $^{90}\text{Sr}/^{90}\text{Y}$ source in the dose range from 0.1 to 1.0 Gy.

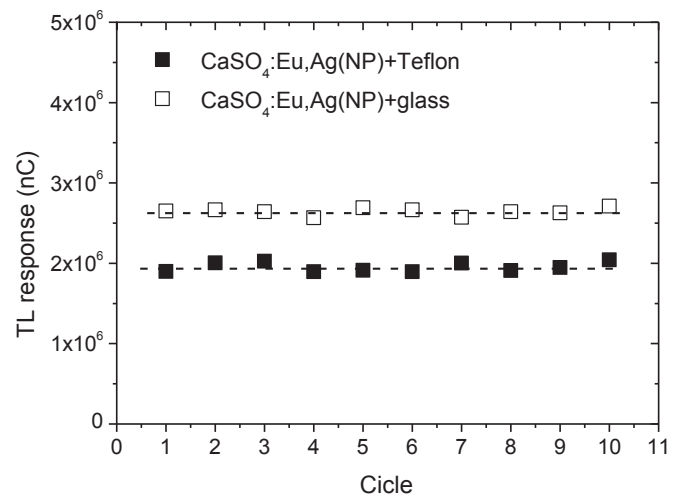


Fig. 7. TL response of $\text{CaSO}_4:\text{Eu,Ag(NP)}$ + Teflon and $\text{CaSO}_4:\text{Eu,Ag(NP)}$ + glass samples after each irradiation–reading–annealing cycle.

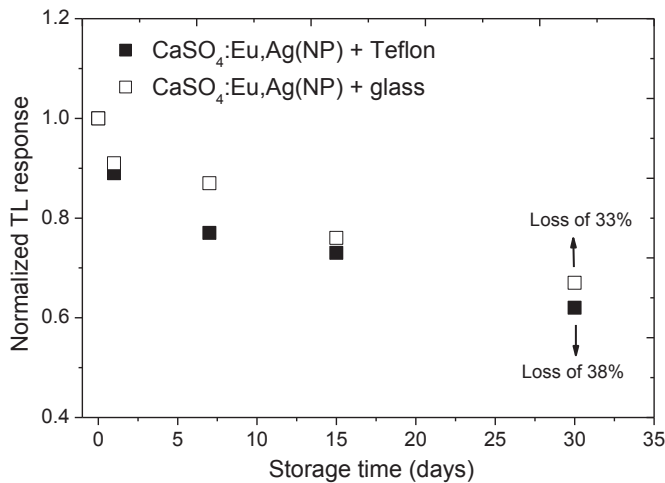


Fig. 8. Normalized TL response of CaSO₄:Eu,Ag(NP) + Teflon and CaSO₄:Eu,Ag(NP) + glass samples after storage time.

Table 1

Lower detectable dose of CaSO₄:Eu,Ag(NP) + Teflon and CaSO₄:Eu,Ag(NP) + glass composites.

Material	Lower detectable dose (mGy)	
	Irradiated with ¹³⁷ Cs	Irradiated with ⁹⁰ Sr/ ⁹⁰ Y
CaSO ₄ :Eu,Ag(NP) + Teflon	0.85 ± 0.04	0.45 ± 0.02
CaSO ₄ :Eu,Ag(NP) + glass	0.66 ± 0.03	0.33 ± 0.02

3.3. Linearity, sensitivity and reproducibility

Analyzing the calibration curves with log axes in the same scale, as observed in Fig. 5, it can be observed that the TL responses of composites are linear due to the calibration curve slope being equal to 45° in the dose range used for all radiation sources. The maximum uncertainty associated with the measurements was 8%.

To evaluate the TL sensitivity of the samples, we used the relationship between the absorbed dose and TL response because all of the samples had the same mass, as observed in Fig. 6. TL sensitivity for the CaSO₄:Eu,Ag(NP) + glass samples was higher than for the CaSO₄:Eu,Ag(NP) + Teflon samples. This suggests that the presence of silicon oxide may create more defects in the material and consequently increases its sensitivity.

To study the reproducibility of the composites, five samples were irradiated with 1 Gy of beta radiation, read, annealed, and irradiated again; this cycle was repeated 10 times. As observed in Fig. 7, all of the TL responses were similar, with only an approximately 5% deviation.

3.4. Fading, minimum detectable dose and kinetic order

Because TL dosimeters are passive, their fading should be as low as possible when these materials are stored under suitable conditions, such as room temperature and low light. This is because these

Table 2

Kinetic order of CaSO₄:Eu,Ag(NP) + Teflon and CaSO₄:Eu,Ag(NP) + glass composites.

Material	T _m	T ₁	T ₂	ω	δ	μ _G	Kinect order
CaSO ₄ :Eu,Ag(NP) + Teflon	200 ± 1	178 ± 1	217 ± 1	40 ± 1	17 ± 1	0.42 ± 0.01	1 ^a
CaSO ₄ :Eu,Ag(NP) + glass	236 ± 1	209 ± 1	257 ± 1	48 ± 1	21 ± 1	0.43 ± 0.01	1 ^a

^a McKeever, 1985.

Table 3

Comparison between the main commercial dosimeters and the CaSO₄:Eu,Ag(NP) + glass produced.

Material	LiF:Mg,Ti (TLD-100)	CaSO ₄ :Dy (TLD-900)	CaSO ₄ :Eu,Ag(NP) + glass
Emission peak (°C)	210 ^a	220 ^a	230
Effective atomic number	8.14 ^{a,b}	15.3 ^{a,b}	12.9
Relative sensibility	1.0 ^a	38 ^b	108
TL response in the dose range from 0.1 to 1 Gy	Linear ^a	Linear ^a	Linear
Lower detection limit	540 μGy ^c	65 μGy ^c	420 μGy
Fading	10% per year ^b	30% in 6 months ^b	33% in one month

^a McKeever, 1985.

^b Campos, 1998.

^c Nunes and Campos, 2008.

parameters are crucial in maintaining the stability of the trapped charge carriers in the forbidden band gap of the crystal. Fig. 8 presents the normalized TL response of CaSO₄:Eu,Ag(NP) + Teflon and CaSO₄:Eu,Ag(NP) + glass samples after storage, showing the decay of the TL intensity of the glow peaks of the composites. It can be observed that the TL signal decays of the two composites are similar; however, the CaSO₄:Eu,Ag(NP) + glass samples exhibited a more satisfactory result because their TL signal was reduced by approximately 25% over 15 days and 33% after one month, as opposed to a 38% loss in CaSO₄:Eu,Ag(NP) + Teflon.

To calculate the minimum detectable dose D_0 of the samples, we used the equation $D_0 = (\bar{B} + 3\sigma_{\bar{B}})f_c$, where \bar{B} is the average of the readings of non-irradiated dosimeters, $\sigma_{\bar{B}}$ is the standard deviation of the measures of non-irradiated dosimeters and f_c is the calibration factor (Oberhofer and Scharmann, 1981). The average \bar{B} was calculated by the TL responses of 5 non-irradiated dosimeters. The calibration factor represents the inverse of the slope of the line of TL response to absorbed dose, expressed in Gy/nC. Table 1 shows the minimum detectable doses obtained for the dosimeters irradiated with ¹³⁷Cs and ⁹⁰Sr/⁹⁰Y. CaSO₄:Eu,Ag(NP) + glass presented the best lower detection limit (0.33 mGy). Calculations were also performed by the peak shape method (McKeever, 1985) to determine the kinetic order of the samples irradiated with a dose of 1 Gy from the ⁹⁰Sr/⁹⁰Y source, as observed in Table 2. All of the TL peaks presented first order kinetics, indicating that re-trapping is negligible when the material is heated and that trapped electrons recombine soon after heating.

3.5. Comparison of the samples with commercial dosimeters

Finally, the TL sensitivities of the composites were compared with the two major commercial dosimeters. Table 3 shows the main characteristics of LiF:Mg,Ti (TLD-100) and CaSO₄:Dy (TLD-900) drawn from the literature (McKeever, 1985; Campos, 1998; Nunes and Campos, 2008) and of CaSO₄:Eu,Ag(NP) + glass analyzed experimentally. These three compounds show emission peaks at similar temperatures and have very similar effective atomic numbers. TL sensitivity is expressed as the glow curve area per unit mass of the dosimeter and per unit dose of gamma rays, and the data are given relative to the TL sensitivity of LiF:Mg,Ti (TLD-100) (Campos, 1998). We observed that CaSO₄:Eu,Ag(NP) + glass is

approximately 100 times more sensitive than TLD-100. All dosimeters exhibit a linear response in the dose range used, and the minimum detectable doses are presented in the same order of magnitude. The main negative feature of the dosimeters of the $\text{CaSO}_4:\text{Eu},\text{Ag}(\text{NP}) + \text{glass}$ produced is the fading of the TL emission. While commercial dosimeters have maximum fading of 5% per month, our composites exhibited fading six times faster.

4. Conclusions

The new route for the preparation of dosimeters has been shown to be viable. The incorporation of Teflon and colorless glass in the phosphors proved to be adequate to produce pellets, but samples with glass presented a TL signal that was more intense and that occurred at higher temperatures. The dosimeter based on calcium sulfate doped with europium and silver nanoparticles showed an intense TL emission, with high sensitivity and low detection limit, and its TL emission was linear, reproducible, and had first order kinetics. Thus, even with considerable fading, it is possible to establish the feasibility of using $\text{CaSO}_4:\text{Eu},\text{Ag}(\text{NP}) + \text{glass}$ as a thermoluminescent dosimeter. However, when compared with commercial TL dosimeters, the applicability of the composites is still limited for personal dosimetry. Therefore, it is necessary to find ways to minimize the TL fading. On the other hand, the sources of radiation and the dose range used in the irradiations are quite common in industrial procedures in which fading is not a crucial characteristic so that the dosimeters produced may come to be used in this type of monitoring.

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