



Luminescent characteristics of CaSO₄:Dy films obtained by spray pyrolysis method

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ABSTRACT

The present paper reports the experimental results of dysprosium doped calcium sulphate (CaSO₄:Dy) films deposited by spray pyrolysis method. CaSO₄:Dy films were deposited on three different surfaces: glass, aluminum and quartz substrates at temperatures in the range from 450 to 600 °C. Structural and morphological characteristics of CaSO₄:Dy films were observed. Thermoluminescent characteristics of films were determined by irradiating ultraviolet energy region. Thermoluminescent glow curve of CaSO₄:Dy films with glass and aluminum substrates showed a peak under environmental irradiation. Both TL response glow shape and intensity of CaSO₄:Dy films UV irradiated as a function of substrates were studied.

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1. Introduction

Calcium sulphate doped with dysprosium (CaSO₄:Dy) is a solid state material and in the past two decades has been taken in the investigation for detecting and measuring radiation. Solid state materials (principally CaSO₄:Dy) used as thermoluminescent dosimeters are synthesized mainly in the form of crystalline powder by the precipitation and crystallization method (Ingle et al., 2008), other authors have used CaSO₄:Dy in pellet form mixed with Teflon (PTFE) (Lakshmanan and Madhusoodanan, 1998). Thermoluminescent response in CaSO₄:Dy is essentially affected by the synthesis preparation method, heat thermal treatment history, particle size (Salah Numan et al., 2006) in the crystal structure, the type of precursors used, as well as the dopant concentration.

Other authors have centered their works on the thermoluminescent (TL) response in materials such as calcium sulphate doped with rare earths (CaSO₄:RE, eg. Dy, Eu, Tm) during the last forty years. These authors focused their purpose on the thermoluminescent properties to be considered as radiation detectors, including: fading of the TL response as a function of storage time, high sensitivity and stability in CaSO₄:Dy. (Aypar, 1978; Ingle et al., 2008).

Other investigations are focused on dosimetric characteristics of CaSO₄:Dy for measuring different kinds of radiation e.g: X-rays, beta rays, high energy electrons (Chatterjee et al., 2009) and high doses of ⁶⁰Co (Mathur et al., 1999). Nunes and Campos (Nunes

and Campos, 2008) observed CaSO₄:Dy sensitivity compared with LiF:Mg,Ti and they proposed they are good for use in the radiation therapy area using high energy electrons beams.

The aim of the present work is the preparation, morphological characterization and luminescent characterization of CaSO₄:Dy films UV exposed.

2. Experimental details

Films of CaSO₄:Dy were deposited by spray pyrolysis method using stoichiometric spray solutions of calcium acetate [Ca(CH₃COO⁻)₂] with dysprosium sulphate [Dy₂SO₄] (3%) and ammonium sulphate [(NH₄)₂SO₄] in ethanol-water environmental. The films were deposited on three different substrates of glass, aluminum and quartz at different temperatures from 450 up to 600 °C. The spray solutions were sprinkling on the substrates at the spray rate of 7.5 L/min for each deposit temperature. The deposit time on the substrates was of 5 min. After this processes, for CaSO₄:Dy films deposited on quartz substrate where submitted a thermal treatment at 1000 °C for one hour. The morphology and chemical composition of the films deposited on glass, aluminum and quartz substrates were analyzed by scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) from JEOL model LV6300. All CaSO₄:Dy films were exposed with ultraviolet light (200 to 300 nm). The irradiations of the samples were carried out using a monochromator. The experimental conditions of irradiation were at room temperature and using dark light. Thermoluminescent glow curves (GC) of the films were obtained immediately after the irradiation.

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3. Results and discussion

3.1. Characterization techniques studies

In the SEM photographs of $\text{CaSO}_4:\text{Dy}$ films with glass substrate (Fig. 1) the formation a homogeneous film for a temperature of 450 °C (Fig. 1a) are observed. The homogeneity in the films is modified when the deposit temperature is increased up to 600 °C (Fig. 1b, c, d). In these photographs $\text{CaSO}_4:\text{Dy}$ films show less uniformity, sites where the absence of film is significant and the formation of clusters on the films. The $\text{CaSO}_4:\text{Dy}$ film deposited on quartz substrate and the $\text{CaSO}_4:\text{Dy}$ film deposited on aluminum substrate at 500 °C are shown in Fig. 2a and b respectively. In Fig. 2a the formation of crystalline stones of $\text{CaSO}_4:\text{Dy}$ is observed. In the same Fig. 2b also observed a uniform film similar to that film deposited on glass substrate.

The chemical composition in the films of $\text{CaSO}_4:\text{Dy}$ were reported in Fig. 3. This figure shows the basic elements that form of films of $\text{CaSO}_4:\text{Dy}$. The atomic percentage of contribution for each material was 76.78 for O, 7.92 for S, 15.25 for Ca and 0.15 for Dy^{3+} .

3.2. Luminescent characterization

TL Response of $\text{CaSO}_4:\text{Dy}$ films deposited at 550 °C using three different substrates were compared (Fig. 4). The $\text{CaSO}_4:\text{Dy}$ films were irradiated with ultraviolet light (200 nm) during 5min. TL glow curve of $\text{CaSO}_4:\text{Dy}$ films on aluminum substrate showed two peaks at around 138.75 °C and 285 °C. Meanwhile, the films deposited on glass substrates also exhibited two peaks at around 146.25 °C and 296.25 °C. Also, the films deposited on quartz substrates (without thermal treatment) showed one peak at 120.5 °C (Fig. 4a). TL intensity of $\text{CaSO}_4:\text{Dy}$ films deposited on glass substrate showed the highest at one.

$\text{CaSO}_4:\text{Dy}$ films deposited on quartz substrate (Fig. 4b) exhibited a TL glow curve with a very prominent peak in intensity at a temperature of 81.5 °C and a little perceptible peak at 231.5 °C. TL intensity of $\text{CaSO}_4:\text{Dy}$ films deposited on quartz substrates is greatest than the TL intensity obtained by the $\text{CaSO}_4:\text{Dy}$ films deposited on aluminum, glass and quartz substrates without thermal treatment applied. TL intensity increasing obtained in $\text{CaSO}_4:\text{Dy}$ films deposited on quartz substrate is due to thermal treatment at 1000 °C during one hour.

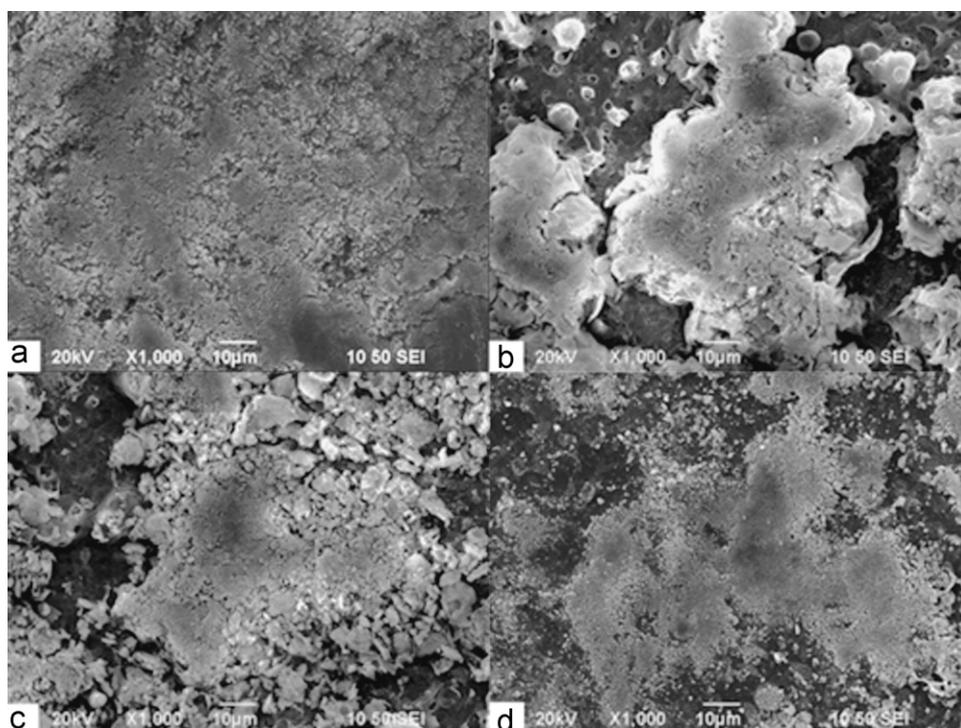


Fig. 1. SEM photographs of $\text{CaSO}_4:\text{Dy}$ films deposited on glass substrates at different temperatures: (a) 450 °C, (b) 500 °C, (c) 550 °C and (d) 600 °C.

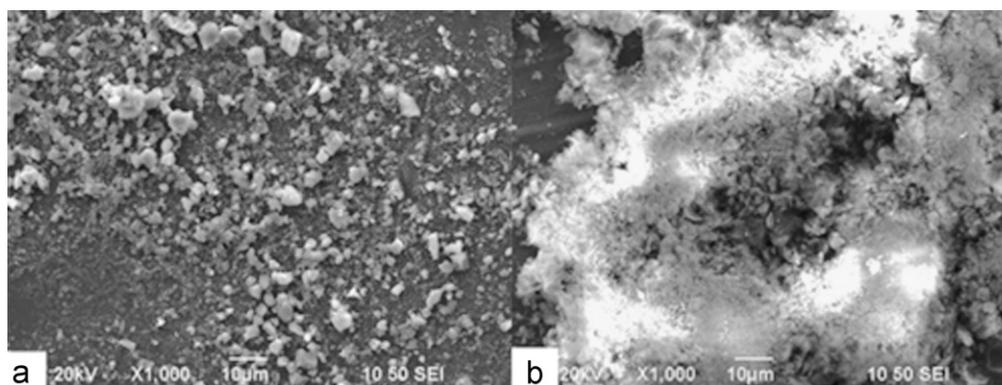


Fig. 2. SEM photographs of $\text{CaSO}_4:\text{Dy}$ films deposited on quartz substrates (a) and deposited on aluminum substrates (b) at 500 °C of temperature of deposit.

TL response of $\text{CaSO}_4:\text{Dy}$ as a function of UV wavelength is observed in Fig. 5. TL response is decrease as wavelength is increased. The insert in the Fig. 5 shows the formation of TL curve when the $\text{CaSO}_4:\text{Dy}$ films on quartz substrate are irradiated at wavelengths of 280 and 300 nm.

Finally, $\text{CaSO}_4:\text{Dy}$ films deposited on aluminum and glass substrates showed a TL response when these films were kept in normal conditions and at room temperature for 8 day. The TL response presented a peak around 287.5 °C for the aluminum substrates and 300 °C for the glass substrates (Fig. 6). This response in the $\text{CaSO}_4:\text{Dy}$ films with glass and aluminum substrates could be induced by the environmental radiation.

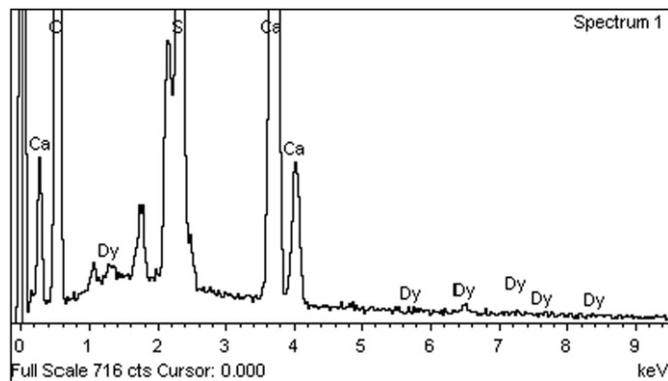


Fig. 3. Spectrum of basic elements in $\text{CaSO}_4:\text{Dy}$ films deposited on glass substrate.

4. Conclusions

The intensity and the shape of the TL curve glow of $\text{CaSO}_4:\text{Dy}$ films were analyzed as a function of the substrate. TL response of $\text{CaSO}_4:\text{Dy}$ films deposited on quartz substrate were the most sensitive. Also, thermal treatment (1000 °C for one hour) applied

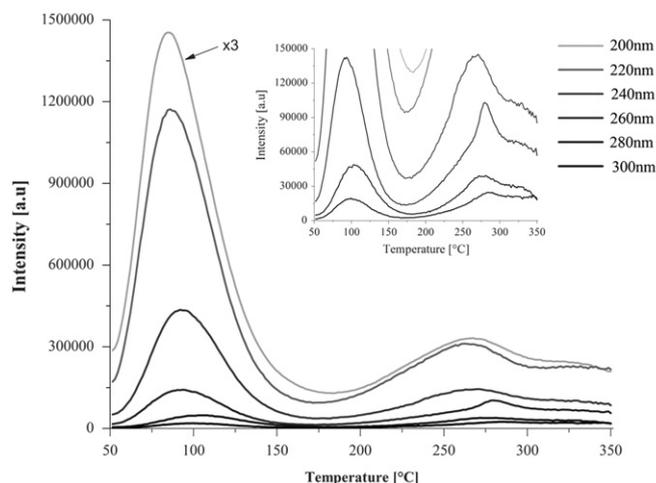


Fig. 5. TL response of $\text{CaSO}_4:\text{Dy}$ films deposited on quartz substrates irradiated from 200 to 300 nm.

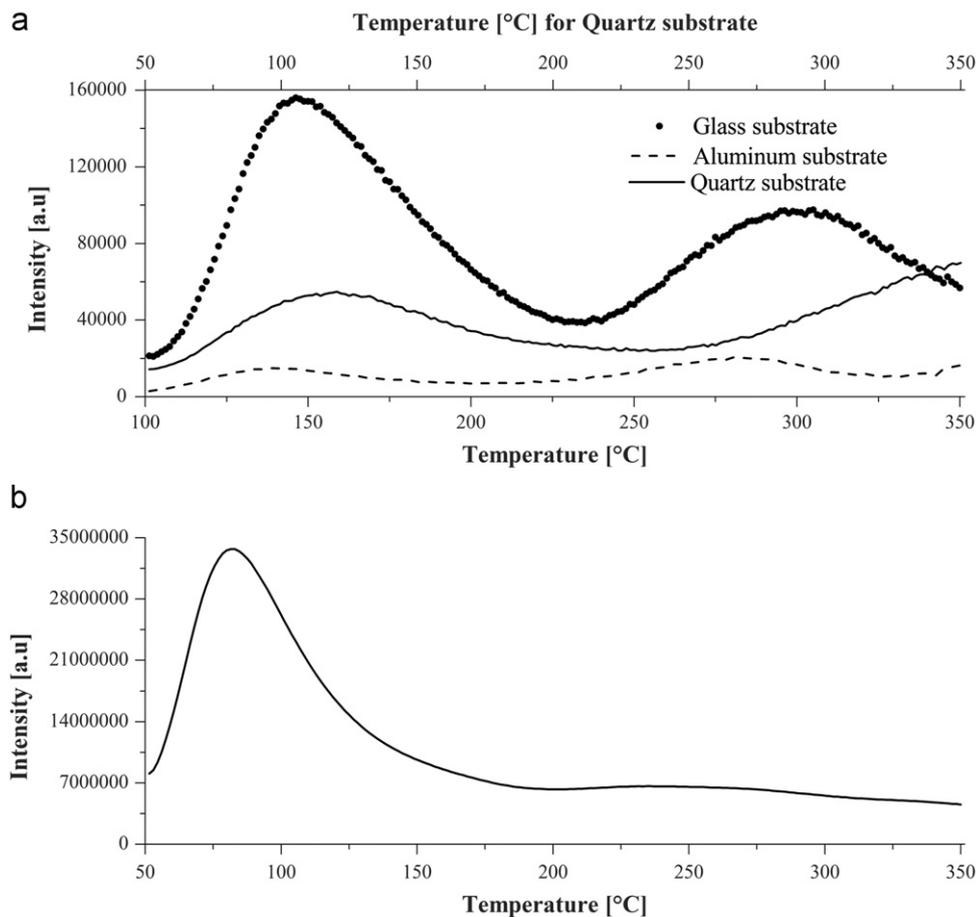


Fig. 4. TL response of $\text{CaSO}_4:\text{Dy}$ films: (a) on quartz (without thermal treatment), glass and aluminum substrates, (b) on quartz substrates with thermal treatment at 1000 °C.

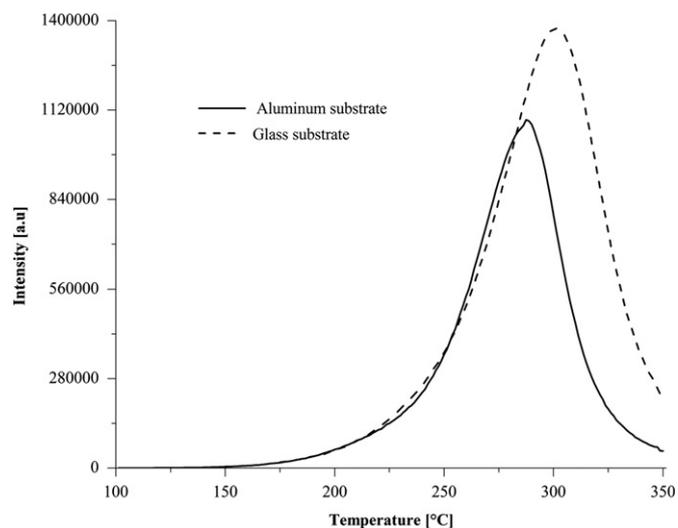


Fig. 6. TL response of $\text{CaSO}_4:\text{Dy}$ films deposited on glass and aluminum substrates without exposure to radiation.

to the $\text{CaSO}_4:\text{Dy}$ films deposited on quartz substrate induce an increasing in sensitivity in the samples. The shapes of the glow curve in all films were similar in the number of peaks.

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References

- Aypar, A., 1978. Studies on thermoluminescent $\text{CaSO}_4:\text{Dy}$ for dosimetry. *Int. J. Appl. Radiat. Isot.* 29, 369–372.
- Chatterjee, S., Bakshi, A.K., Kinshikar, R.A., Chourasiya, G., Kher, R.K., 2009. Response of $\text{CaSO}_4:\text{Dy}$ phosphor based TLD badge system to high energy electron beams from medical linear accelerator and estimation of whole body dose and skin dose. *Radiat. Meas.* 44, 257–262.
- Ingle, N.B., Omanwar, S.K., Muthal, P.L., Dhopte, S.M., Kondawar, V.K., Gundurao, T.K., Moharil, S.V., 2008. Synthesis of $\text{CaSO}_4:\text{Dy}$, $\text{CaSO}_4:\text{Eu}^{3+}$ and $\text{CaSO}_4:\text{Eu}^{2+}$ phosphors. *Radiat. Meas.* 43, 1191–1197.
- Lakshmanan, A.R., Madhusoodanan, U., 1998. Behaviour of $\text{CaSO}_4:\text{Dy}$ embedded Teflon discs at high annealing temperatures. *Radiat. Meas.* 29 (5), 527–530.
- Mathur, V.K., Lewandowski, A.C., Guardala, N.A., Price, J.L., 1999. High dose measurements using thermoluminescence of $\text{CaSO}_4:\text{Dy}$. *Radiat. Meas.* 30, 735–738.
- Nunes, M.G., Campos, L.L., 2008. Study of $\text{CaSO}_4:\text{Dy}$ and $\text{LiF}:\text{Mg,Ti}$ detectors TL response to electron radiation using a SW Solid Water phantom. *Radiat. Meas.* 43, 459–462.
- Numan, Salah, Share, P.D., Lochab, S.P., Kumar, Pratik, 2006. TL and PL studies on $\text{CaSO}_4:\text{Dy}$ nanoparticles. *Radiat. Meas.* 41, 40–47.