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Cathodoluminescence and green-thermoluminescence response of $CaSO_4$:Dy,P films

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ABSTRACT

We herein report on the cathodoluminescence (CL) and green-thermoluminescence (TL) emission of $CaSO_4$:Dy,P films deposited by the spray pyrolysis method at different temperatures. The samples have been previously structurally and chemically characterized by means of Raman spectroscopy and energy dispersive spectroscopy (EDS). The CL spectra show (i) a broad emission band centered at 374 nm that corresponds to the intrinsic emission of $(SO_4)^{2-}$ and (ii) emission bands centered on 486, 574, 668, 758 nm assigned to the electronic transitions of the Dy^{3+} ions. The TL glow curves of the films showed three groups of components peaked at around of 98, 152 and 300 °C that exhibit a gradual and progressively linear shifting of the T_{max} as function of T_{stop}. This TL behavior is related to a continuum in the trap distribution associated with general or multi-order kinetics and involving continuous processes of trapping–detrapping. The activation energy in the range of 0.97–1.53 eV has been estimated using the initial rise method.

1. Introduction

At present, synthetic $CaSO_4$:Dy appears as one of the most useful detectors of ionizing radiation basically due to (i) easy preparation, good chemical stability and low cost [1] and (ii) high sensitivity to radiation, high thermoluminescence intensity and high stability of the TL signal during the storage of the material (i.e. low fading). Recent studies carried out by Garcia-Guinea et al. [2] proposed the existence of natural $CaSO_4$:Dy on plaster collected from the courtyard walls of Djehuty's tomb (Luxor, Egypt) that exhibit a good TL response of this material and suggest the presence of Na^+ ions as charge compensator for increasing the concentration of impurities of Dy^{3+}. The incorporation of the charge compensator Na^+ in the lattice of $CaSO_4$:Dy increases the formation and stabilization of the SO_4 center. In this sense, preliminary results performed by Atone et al. [3] and Bhatt et al. [4] describe the use of P^{5+} impurities of as charge compensator for increment the incorporation of Dy^{3+} ions without concentration quenching and the enhancement of the TL sensitivity (by more than 60%) in the $CaSO_4$:Dy crystals. The P^{5+} charge compensator has been incorporated in the lattice of $CaSO_4$:Dy substitutionally on the S^{6+} sites. On the other hand, important factors to be considered when using beta radiation are the thickness and the energy dependence of the TL dosimeters. Pradhan and Bhatt [5] studied the beta energy dependence as a function of the graphite concentration in thin $CaSO_4$:Dy discs mixed with graphite. They found that the beta energy dependence decreases with increasing the concentration of graphite in these samples. Additionally, they could observe a drastic reduction in the contribution of non-radiation TL signals due to the presence of graphite that is a good thermal conductor. According to Daros et al. [6] $CaSO_4$:Dy mixed with graphite exhibit less TL sensitivity than the same samples without graphite.

In this work, we study the structural, chemical and luminescent characteristics of $CaSO_4$:Dy,P films with quartz substrate using Raman spectroscopy, energy dispersive spectroscopy (EDS), cathodoluminescence (CL) and green-thermoluminescence (TL).

2. Materials and methods

The $CaSO_4$ films doped with impurities of dysprosium (Dy^{3+}, 3%) and phosphorous (P^{5+}, 6%) were deposited on quartz substrates by spray pyrolysis using the methodology described by Roman et al. [7]. The P^{5+} impurities were incorporated in the $CaSO_4$ matrix from of a precursor solution of phosphoric acid and ammonium sulfate. The precursor solutions were atomized by a nebulizer ultrasonic and sprayed at substrates temperatures in the range from 450 to 600 °C. Dry air was used as carrier gas with a flow rate of 7.5 l/min approximately. The films of $CaSO_4$:Dy,P

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were deposited by a time of 5 min. The distance between the nozzle tip and the quartz substrate was approximately 10 mm. The films were subjected to a heat treatment of 1000 °C for one hour in air environment and a heating rate of 10 °C/min. The chemical analysis of the films was carried out in a microscope ESEM XLS30 of the FEI Company using energy dispersive spectroscopy (EDS). The structural characterization by Raman spectroscopy was performed at room temperature with a Thermo Fisher DRX Raman microscope with point-and-shoot Raman capability of 1 μm spatial resolution. The Raman measurements were carried out using the 20× objective of the confocal microscope and a laser source at 532 nm of 6 MW in mode laser power at 100%. The Raman spectra were collected from 70 up to 2000 cm^{-1} and a spectral resolution of 1.92 cm^{-1}. The luminescence emission of the $CaSO_4$:Dy,P films were characterized by means of Cathodoluminescence (CL) and Thermoluminescence (TL). The CL spectra were measured using a Gatan MonoCL3 detector with a PA-3 photomultiplier tube attached to the ESEM model XLS30. The detector covers a spectral range of 250–850 nm and is the most sensitive in the blue parts of the spectrum. The samples were placed on polished slabs, at low-vacuum mode without coating to keep open way out to the CL emission. The emission of the films was collected and amplified using a retractable parabolic diamond mirror and a photomultiplier tube. The distance between the sample and the bottom of the CL mirror assembly was 15 mm. The excitation for CL measurements was provided at 25 kV electron beam. The automated Risø TL system model TL DA-12 equipped with an EMI 9635 QA photomultiplier was used to collected the glow curves of the $CaSO_4$:Dy,P films [8]. A green filter (a FIB008 of the Melles-Griot Company) with wavelength peaked at 550–575 nm was used to detect the TL emissions. The filter has a FWHM of 80 ± 16 nm and a peak transmittance of 70%. The irradiated $CaSO_4$:Dy,P films were measured from room temperature (RT) up to 400 °C with a linear heating rate of 5 °C/s in an N_2 atmosphere. The incandescent background was subtracted from the glow curves. The films were irradiated from 0.015 up to 4.5 Gy with a calibrated $^{90}Sr/^{90}Y$ beta source at a dose rate of 15 mGy/s [9]. Previously to the irradiation and TL measurements the $CaSO_4$:Dy,P films were subjected to thermal treatment for 400 °C by one hour. The distribution of traps in the films of $CaSO_4$:Dy,P was studied from the application of preheating treatments at temperatures from 40 to 320 °C. Aliquots of 5.0 ± 0.1 mg powdered samples were used for each measurement.

3. Results and discussion

3.1. Sample characterization

The chemical composition has been performed on the $CaSO_4$:Dy,P films with substrate temperature of 600 °C by means of EDS–ESEM (Fig. 1). Such analysis display contents of Ca (from 34% to 40%), O (39%–42%), S (6%–10%), P (2%–5%), Dy (~1%) and silicon, due to the quartz substrate employed as deposit films, in the range of 7%–15%. Similar results have been obtained for the films with substrate temperatures at 450, 500 and 550 °C. Additionally, the samples were characterized by means of Raman spectroscopy since is a useful technique for identification and analysis of molecular species. As illustrated in Fig. 2, it can be appreciated how the $CaSO_4$:Dy,P films with quartz substrate exhibit typical strong intensity at 1016 cm^{-1} that corresponds to ν_1SO_4 vibrational mode [10,11], the bands at 415 and 497 cm^{-1} are attributed to ν_2SO_4 vibrational mode. The ν_3SO_4 vibrational mode is related to the bands at 1110, 1128 and 1159 cm^{-1} [12]. The spectrum also displays three weak bands at 608, 626 and 675 cm^{-1} linked to the ν_4SO_4 vibrational mode. The vibrational

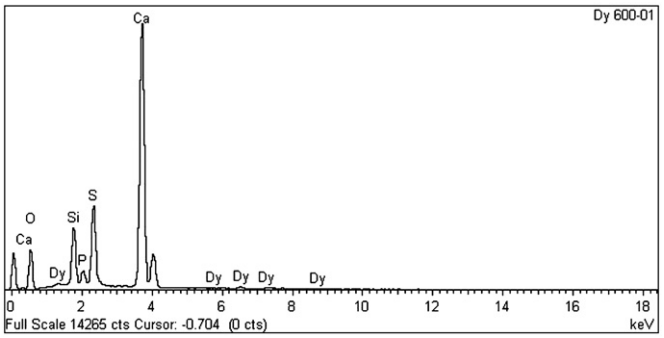

Fig. 1. Chemical composition of $CaSO_4$:Dy,P films with substrate temperature of 600 °C performed by the EDS–ESEM analysis.

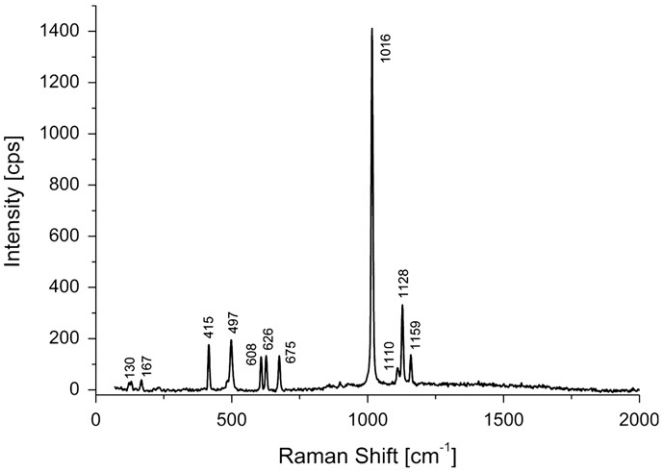

Fig. 2. Raman spectrum of $CaSO_4$:Dy,P films.

modes at 130 and 167 cm^{-1} could be assigned to types of rotational (R') and translational (T') external modes associated with $R'_y(SO_4)$, $T'_z(Ca)$ and $R'_x(SO_4)$, $T'_y(Ca,SO_4)$ respectively [13].

3.2. CL and TL characterization

The luminescence characterization of $CaSO_4$:Dy,P films was carried out by means of CL and TL techniques. The CL spectrum (Fig. 3) of all $CaSO_4$:Dy,P films displays similar behavior regardless of the thermal treatment, showing the typical emission bands of Dy^{3+} impurities, but the film with a substrate temperature of 450 °C exhibits the higher intensities than films with a substrates prepared at higher temperatures (500, 550 and 600 °C). As is observed in Fig. 3, the CL spectrum shows the stronger emission band at a wavelength of about 574 nm that corresponds the transition $^4F_{9/2} \rightarrow {}^6H_{15/2}$, the lower emission band intensity at 486 nm linked to the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition can be also appreciated. The transitions $^4F_{9/2} \rightarrow {}^6H_{11/2}$ and $^4F_{9/2} \rightarrow {}^6H_{9/2}$ giving rise to weaker emission bands at 668 and 758 nm are also associated with the presence of Dy^{3+} impurities [12,13]. The broad emission band centered at 374 nm should correspond to the intrinsic emission of $(SO_4)^{2-}$ which is the most important in the $CaSO_4$ undoped [13,14].

On the other hand, the green emission of $CaSO_4$:Dy,P films has also been studied from room temperature up to 400 °C by means of TL. As observed in Fig. 4, the TL response for these materials exhibits a reasonable intensity when it is 1.5 Gy irradiated. The TL curves measured in all of these materials show; at least, three groups of components centered at about 98, 152 and 300 °C. The ratio among the intensity of the maxima are similar in all of them