Applied Radiation and Isotopes 68 (2010) 623–625

Contents lists available at ScienceDirect

Applied Radiation and Isotopes

journal homepage: www.elsevier.com/locate/apradiso

Preparation of $CaSO_4$:Dy by precipitation method to gamma radiation dosimetry

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ARTICLE INFO

Keywords:
Thermoluminescence
Dy^{3+}
Gamma radiation
$CaSO_4$
Chemical co-precipitation
Dosimetry

ABSTRACT

This paper presents the results of the preparation and characterization of dysprosium-doped calcium sulfate ($CaSO_4$:Dy) phosphor, which was obtained by homogeneous precipitation from calcium acetate $Ca(CH_3COO^-)_2$. Structural and morphological characteristics were studied using a scanning electronic microscope (SEM). The structure of all compounds was determined by X-ray diffraction method too. Thermoluminescence (TL) emission properties of $CaSO_4$:Dy under gamma radiation effects were studied. This phosphor powder presented a TL glow curve with two peaks (Tmax) centered at around of 180 and 300 °C, respectively. The TL response of $CaSO_4$:Dy as a function of gamma absorbed dose was linear in a wide range. Both emission and excitation spectra were also obtained. Results showed that this new preparation method of $CaSO_4$:Dy TL phosphor is less expensive, cleaner and safer than the conventional preparation method.

1. Introduction

Thermoluminescence (TL) is a phenomenon which is exhibited by a number of materials and consists in the emission of luminous radiation when the material, which has been previously irradiated, is heated at a sufficiently high temperature below its incandescence temperature. Light emission is due in particular to excitation of atomic electrons which are induced to undergo a transition and brought into traps in metaestable states existing in the forbidden gap. When the material is heated, these electrons return to ground state emitting luminous radiation.

A large number of different materials have already been employed as ionizing radiation dosimeters. In particular, lithium fluoride (LiF) and calcium sulfate ($CaSO_4$) doped with small proportions of impurities such as magnesium or dysprosium have been employed due to their high sensitivity (Azorín et al., 1980; Azorín and Gutiérrez, 1989). However, the materials which have been employed as dosimeters up to the present time are not appropriate for measuring high radiation doses. The traditional $CaSO_4$ phosphors exhibit some disadvantages for high dose gamma radiation measurements. Then it is not feasible to employ these materials as constituents of such dosimeters which must be provided in a large number within areas which are liable to be exposed to high doses of ionizing radiation in the event of an accident, and which are intended to be read only in such event. To overcome these disadvantages, we propose a new method for preparing $CaSO_4$:Dy TL phosphor based on the homogenous precipitation from $Ca(CH_3COO^-)_2$.

$CaSO_4$:Dy phosphor prepared by conventional evaporation method has shown to have useful properties for applications in thermoluminescence dosimetry of low doses of ionizing radiation, as reported by Azorín et al. (1980, 1983, 1993), Azorín and Furetta (1989), Yamashita et al. (1968) and Yamashita et al. (1971). These authors reported $CaSO_4$:Dy phosphor having high TL sensitivity. Owing to its high sensitivity and ease of preparation in large batches $CaSO_4$:Dy phosphor, it is used for radiation measurements to different applications.

The aim of this work is to study both optical and thermoluminescent (TL) properties of gamma irradiated $CaSO_4$:Dy powder prepared by the new method based on the homogenous precipitation from $Ca(CH_3COO^-)_2$. The TL dosimetric material thus obtained fulfils practical requirements more effectively than any comparable material proposed before (especially in the field of accident dosimetry). The fulfillment of this objective entails the need for a material which has suitable properties for the detection of high doses, which is extremely inexpensive to produce it.

2. Experimental

2.1. Material preparation

Co-precipitation method was used for preparing $CaSO_4$:Dy phosphor from organic starting reactants. The method consists in the following: about 5 g of calcium acetate are dissolved in a minimum quantity of double distilled water to which 80 ml ethanol

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doi:10.1016/j.apradiso.2009.09.033

are added. About 1 mol solution of thiourea in water is added to calcium acetate solution. $Dy(SO_4)_3$ in appropriate amount is also added to the solution so as to give a ratio Ca:Dy of 1000:1. About 3 g of $(NH_4)_2SO_4$ are also dissolved in a minimum amount of distilled water to which 80 ml ethanol are added. $(NH_4)_2SO_4$ solution is then added to calcium acetate solution drop wise under vigorous stirring. White precipitate powder is formed which is then centrifuged and washed several times to remove the residual salts. The precipitate is dried at 80 °C for 2 h in an oven. Finally, the dried sample is submitted to a thermal treatment at 900 °C during 2 h in air.

2.2. Structural characterization

The $CaSO_4$:Dy powders obtained from the above processing route were characterized using EDS analysis and X-ray diffractograms which were obtained with a Siemens D-5000 diffractometer, using CuKα radiation (α=0.1548 nm) at 40 kV and 30 mA). Scanning electronic microscopy (SEM) was done with JEOL, model LV6300 with a X-ray detector Oxford model INCA Energy +.

2.3. Luminescent characterization

The photoluminescence for all the samples were recorded using a Perkin Elmer LS 5 fluorescence spectrophotometer. A ^{60}Co radiation source giving a dose rate of 6 Gy/min was used for exposing the samples to gamma radiation at room temperature. A set of irradiations were performed changing the exposure time and hence the dose. To determine the TL response as a function of absorbed dose, the samples were exposed to ^{60}Co gamma radiation by varying the absorbed dose. TL measurements were made in a Harshaw TL analyzer, model 4000, connected to a PC to record and process the experimental data. The TL signal was integrated from room temperature up to 350 °C using a heating rate of 10 °C/s. All TL measurements were made in a nitrogen atmosphere in order to reduce the spurious signals resulting from the heating planchet in the TL reader.

3. Results and discussions

3.1. Structural and morphological characteristics

Fig. 1 shows SEM photograph of $CaSO_4$:Dy powder after annealing at 900 °C during 2 h in air. In this figure it can be observed the surface morphology of the powders. It is possible to observe a material with crystalline properties. In some regions appear samples with rectangular regular forms. It is shown that the morphology of the powders is basically polycrystalline constituted by microcrystalline $CaSO_4$:Dy particles. The grain powder size observed by SEM is in good agreement with those results obtained by X-ray diffractograms whose spectrum is shown in Fig. 2. The peaks located at 2θ=25.51°, 31.45°, 36.35°, 38.69°, 40.89°, 48.74°, 52.31° and 57.77° correspond to the (0 2 0), (0 1 2), (2 2 0), (2 0 2), (2 1 2), (0 3 2), (4 0 0) and (3 3 1) reflections, respectively. These reflections correspond to the $CaSO_4$ Orthorhombic phase, according to the JCPDS 37–1496 diffraction card (with a lattice parameters of a=6.993, b=7001, and c=6.241). In order to know the composition of the TL material, samples were analyzed under EDS method. This composition is verified and plotted in Fig. 3. In this figure it can be observed that 61.53% of weight is constituted by O_2, 17.54% corresponds to S ion and the rest is constituted by Ca ions.

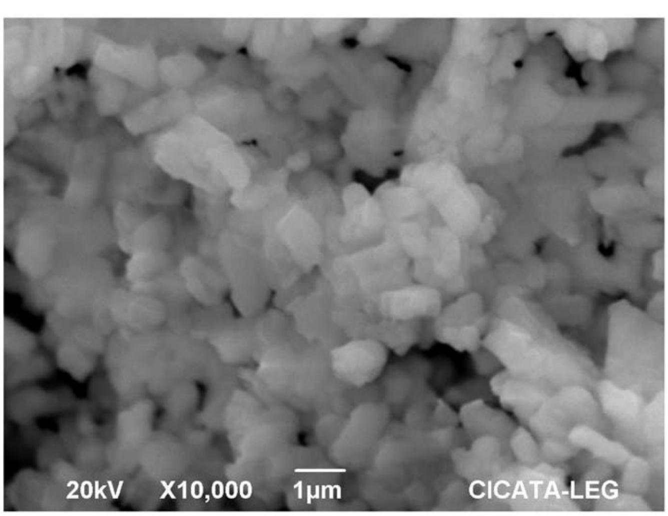

Fig. 1. SEM photograph of $CaSO_4$:Dy after annealing at 900 °C during 2 h in air.

3.2. Luminescent properties

The optical properties of a material are important, as they provide information on the electronic band structures, localized states and types of optical transitions. Fig. 4 shows a typical plot of the excitation spectra for two different concentrations of the dopant. In this figure, both emission spectra consist of an intrinsic

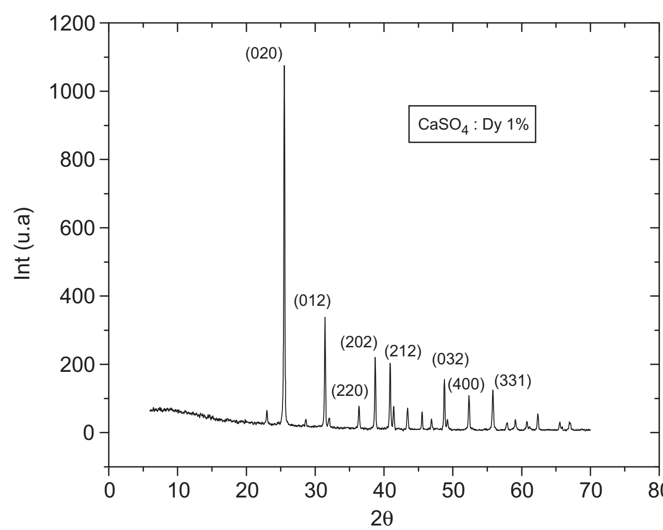

Fig. 2. X-ray diffractograms of $CaSO_4$:Dy.

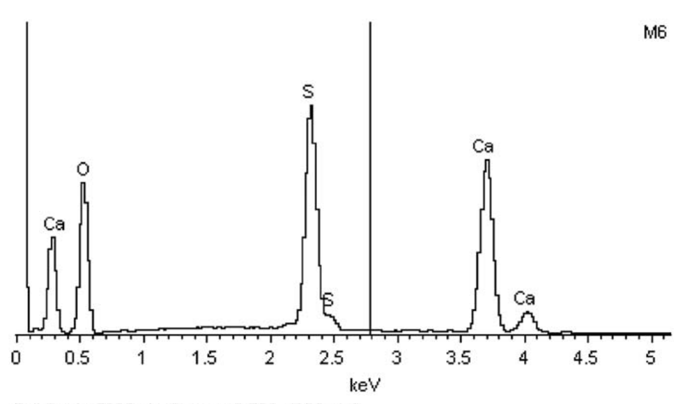

Fig. 3. Composition's Plot of $CaSO_4$:Dy determined by EDS method.

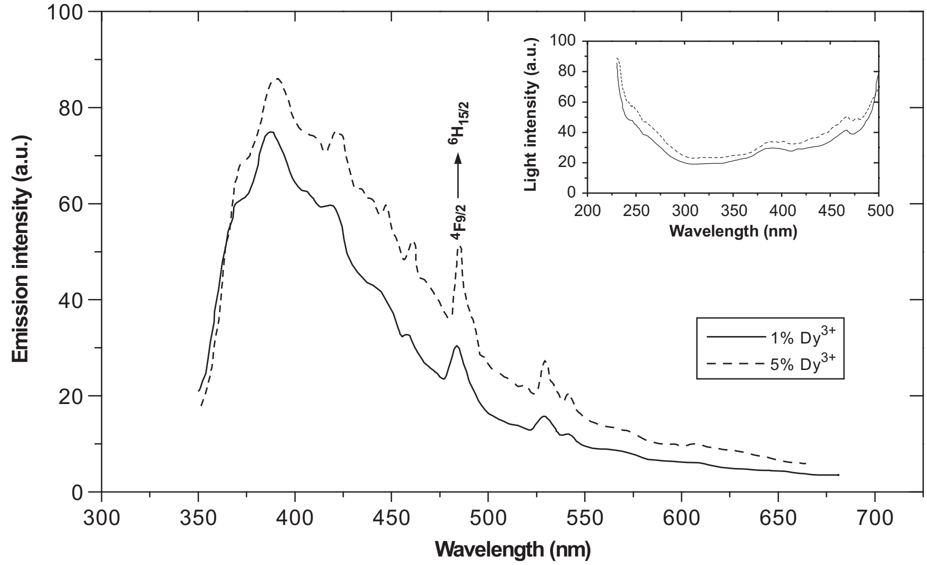

Fig. 4. Photoluminescence spectra of $CaSO_4$:Dy.

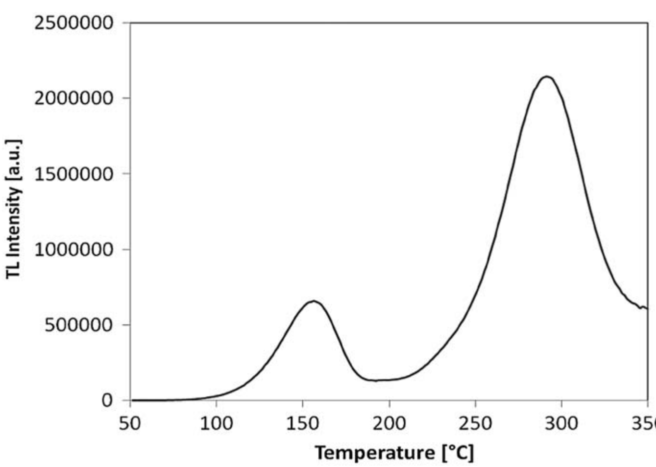

Fig. 5. Typical TL glow curve of gamma irradiated $CaSO_4$:Dy.

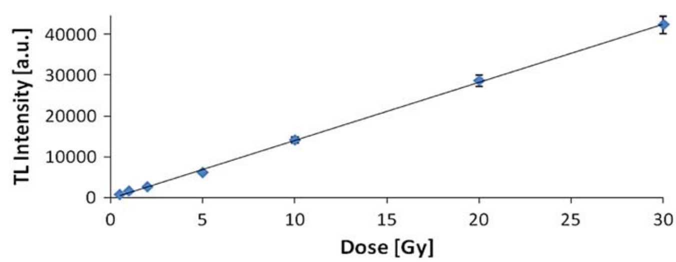

Fig. 6. TL response of $CaSO_4$:Dy as a function of gamma absorbed dose.

broad band corresponding to a $CaSO_4$ matrix and two fluorescence emission peaks taking place at 483 and 576 nm, respectively, corresponding to $^4F_{9/2}$–$^6H_{15/2}$ and $^4F_{9/2}$–$^6H_{13/2}$ transitions of the Dy^{3+} ion. The scanning range of the excitation spectra was from 230 to 500 nm when the detection wavelength was located at 530 nm. More experimental work will carried out to understand the optical properties of this material. Fig. 5 shows the glow curve of $CaSO_4$:Dy powder exposed to an absorbed dose of 10 Gy of ^{60}Co gamma radiation. This TL glow curve exhibits two main peaks centered at 180 and 300 °C, respectively. The variation of the TL intensity of the $CaSO_4$:Dy as a function of gamma absorbed dose is showed in Fig. 6. As can be seen, the TL response is linear in the range from 1 to 30 Gy. The shape of the glow curve remains almost the same for exposures between 1 to 300 Gy but the relative heights of the two peaks change as a function of gamma radiation. The TL intensity of the peaks increases as the gamma dose increases without change in the glow curve shape.

4. Conclusions

The possibility of using $CaSO_4$:Dy as a dosimeter for high doses of gamma radiation was explored. $CaSO_4$:Dy phosphor powders were developed using the co-precipitation method. The evolution of the TL glow curve shape under gamma radiation effects is shown in Fig. 5. Both TL and optical properties of $CaSO_4$:Dy powders were observed up to a certain dose level. Structural characteristics allow to open the possibility for considering $CaSO_4$:Dy phosphor, prepared by this new method, as an effective material for gamma radiation dose measurement, mainly in high absorbed dose range.

Acknowledgments

This work is supported by CONACYT Grant no. 67733 and IPN Research Project 20080106.

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