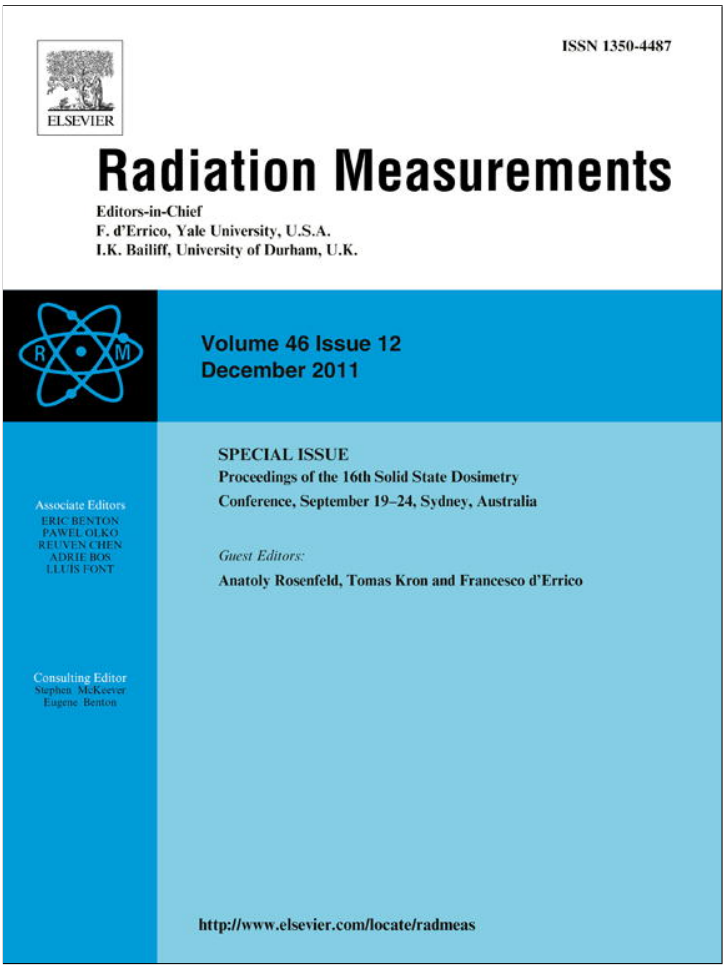

Radiation Measurements 46 (2011) 1500–1502

Contents lists available at ScienceDirect

Radiation Measurements

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

Silver addition in $CaSO_4$:Eu, TL and TSEE properties

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ARTICLE INFO

Article history:
Received 22 November 2010
Received in revised form
14 June 2011
Accepted 18 June 2011

Keywords:
TL
TSEE
Dosimetry
$CaSO_4$:Eu,Ag

ABSTRACT

$CaSO_4$:Eu with Ag incorporation was studied in order to evaluate the improvement in its response to dosimetry. Thermoluminescence and thermally stimulated exoelectronic of $CaSO_4$:Eu,Ag showed responses to absorbed doses from a beta radiation source that were significantly enhanced when silver was incorporated as a co-dopant in the form of nanoparticles (NP).

1. Introduction

Sulphates doped with rare earth (RE) elements are frequently used to exhibit good properties for thermoluminescent (TL) dosimetry purposes, such as TL glow curves with high intensity within an appropriate temperature range. The most often RE used for $CaSO_4$-based TL detectors are Dy, Tm and Eu. Several methods have been developed with the aim of producing TL detectors (McKeever et al., 1995; Ingle et al., 2008), including synthesizing samples through simple and environmental friendly methods, such as the one developed by Bernal et al. (2007). In some cases, the interest is the particle size such as the submicron range $CaSO_4$:Eu particles produced by Patil et al. (2007).

The motivation for the present study came from the observation that Ag particles have been used to improve luminescent characteristics in some materials. Strohhöfer and Polman (2002) reported that the photoluminescence of Er^{3+} in glass is strongly enhanced by the presence of silver. Madhusoodanan et al. (2009) reported the development of the new doubly doped thermoluminescent material $KMgF_3$:Eu,Ag as opposed to the singly doped $KMgF_3$:Eu.

In this work we present a way of improving the luminescence of $CaSO_4$:Eu through Ag incorporation with the aim of improvement its TL response to radiation dose. TL and thermally stimulated exoelectronic emission (TSEE) of $CaSO_4$:Eu,Ag have been studied aiming to evaluate its applicability to dosimetry. In order to characterize the samples by these techniques composites were produced using glass or Teflon.

Although TL is commonly used in radiation dosimetry, TSEE was also found to be a very useful technique to be applied in dosimetry because it is good at detecting the radiation that does not deeply penetrate into the material, like low energy X-ray and alpha and beta particles (Melo et al., 2008).

2. Materials and methods

The phosphorus $CaSO_4$:Eu and $CaSO_4$:Eu,Ag were produced by means of the following steps:

I. Mix 1 g of calcium carbonate ($CaCO_3$) and 0.02 g of europium oxide (Eu_2O_3) in a saturated solution of sulfuric acid (H_2SO_4), dry at 375 °C in vacuum, leading to $CaSO_4$:Eu samples.
II. Step I plus Ag_2O (0.02 g) incorporation, which results in $CaSO_4$:Eu,Ag samples.
III. Mix the product of the oxidation–reduction reaction of the $AgNO_3$ in ethylene glycol (polyol) and the $CaSO_4$ crystal doped with Eu, during its crystallization process. By this method silver was incorporated as nanoparticles (NP), resulting in $CaSO_4$:Eu,Ag(NP) samples.

The reduction of metallic ions in an alcoholic medium (so-called polyol route) was first described by Fièvet et al. (1989). Silver nanoparticles synthesis was performed by adding 0.1 $molL^{-1}$ of

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1350-4487/$ – see front matter © 2011 Published by Elsevier Ltd.
doi:10.1016/j.radmeas.2011.06.049

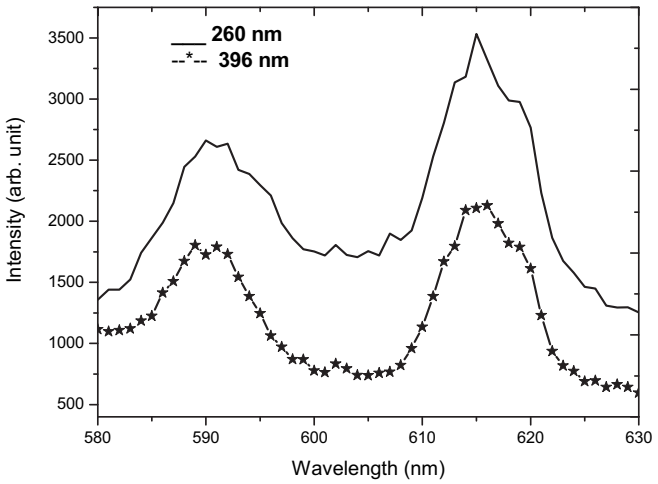

Fig. 1. $CaSO_4$:Eu,Ag(NP) emission spectra for 260 nm and 396 nm excitation.

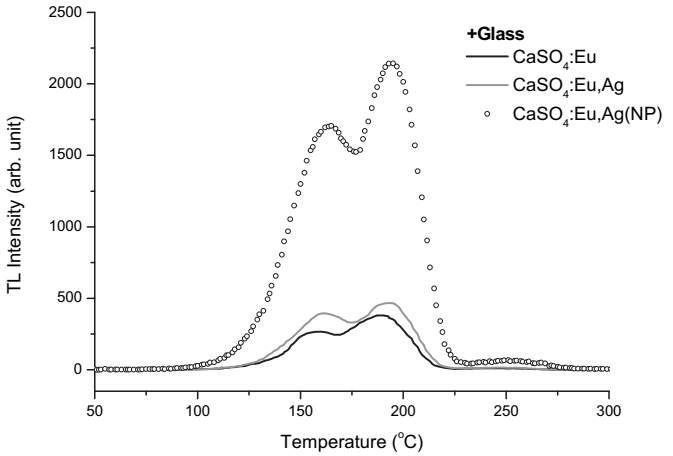

Fig. 3. Typical TL glow curves of $CaSO_4$:Eu + G, $CaSO_4$:Eu,Ag + G $CaSO_4$:Eu,Ag(NP)+G samples.

$AgNO_3$ to 40 mL of ethylene glycol. The solution was heated to 140 °C and the reducing agent ($NaBH_4$) was added. The heating was kept for 2 h, under magnetic stirring. After that, the heating was interrupted. The resulting solid product was separated from reactional medium by centrifugation, washed three times with ethanol and dried at a temperature of 80 °C.

The samples were then prepared in the form of pellets of 6 mm in diameter and 1 mm thickness. Pellets were made using a 2:1 (by weight) mixture of the phosphor and powdered commercial glass and 1:1 (by weight) mixture of the phosphor and Teflon. After uniaxial pressing, the phosphor + glass pellets were sintered at 750 °C for 1 h and the phosphor + Teflon at 300 °C. After each irradiation–readout cycle the pellets were annealed for 1 h at 300 °C. The pellets were cooled to room temperature at a free rate. For simplicity, the sintered glass pellets were called $CaSO_4$:Eu + G, $CaSO_4$:Eu,Ag + G, $CaSO_4$:Eu,Ag(NP)+G. Similarly, those prepared with the Teflon addition were indicated by + T.

UV–Vis spectrometry analysis was performed using a PerkinElmer's LAMBDA 45 UV/Vis system in a room at 25 °C. TL analysis was performed with a Harshaw 3500 in nitrogen atmosphere at a 10 °C/s heat rate. TSEE emission was obtained using a system with a 2π windowless gas-flow proportional counter (the gas mixture is 90%Ar + 10%CH_4). The samples were irradiated with a $^{90}Sr + {}^{90}Y$ source at a rate of 0.45 Gy per minute. The source used is part of a secondary standard system, with sources calibrated by the German primary laboratory Physikalisch Technische Bundesantstalt, Braunschweig.

Photoinduced fluorescence spectra were collected between 580 and 630 nm with excitation at 230 and 396 nm using as ISS PC1 spectrofluorimeter with 300 W xenon lamp at a 25 °C room temperature. A 25 cm monochromator, equipped with a photomultiplier with a resolution of 0.05 nm in the visible range was utilized. The excitation and emission slit widths were 2.0 mm and 1.0 mm, respectively. Both monochromators had 1200 grooves/mm.

3. Results

Initially, with the goal of determining the size of the silver particles obtained by the reduction reaction of the $AgNO_3$ in ethylene glycol, measurements of UV–VIS spectrophotometry were performed. The absorption spectra revealed a single maximum at about 400 nm which is characteristic of the surface plasmon resonance of particles which are roughly spherical in shape

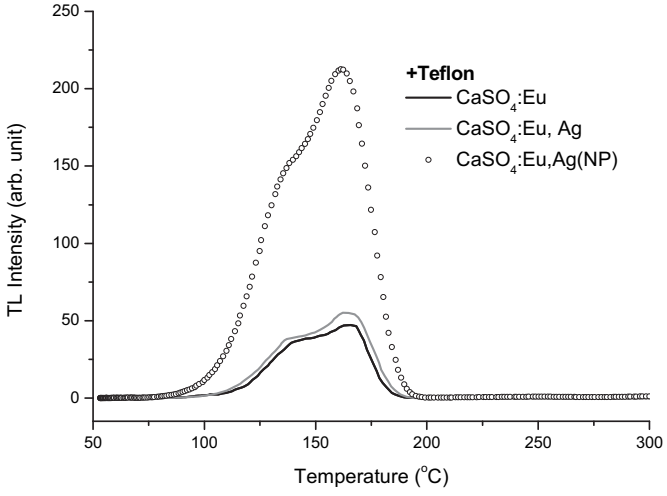

Fig. 2. Typical TL glow curves of $CaSO_4$:Eu + T, $CaSO_4$:Eu,Ag + T $CaSO_4$:Eu,Ag(NP)+T samples.

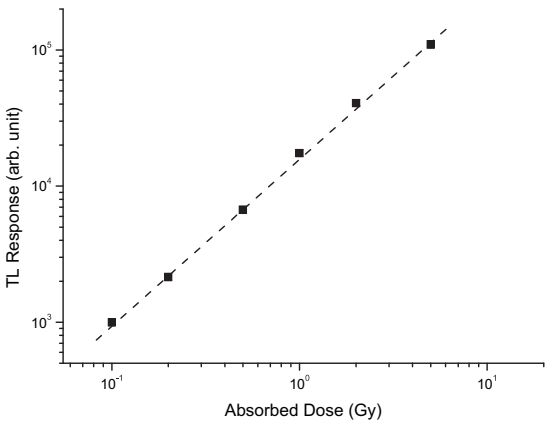

Fig. 4. TL response of $CaSO_4$:Eu,Ag(NP)+G samples as a function of absorbed dose from beta radiation.

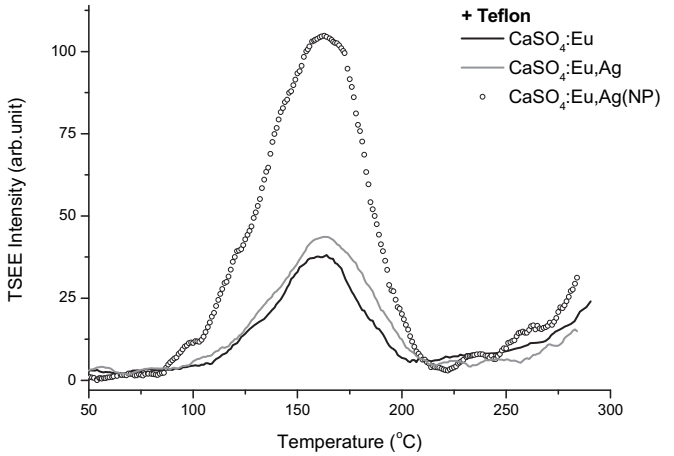

Fig. 5. Typical TSEE glow curves of $CaSO_4$:Eu + T, $CaSO_4$:Eu + Ag + T $CaSO_4$:Eu + Ag(NP)+T samples.

(Guingab et al., 2007). The produced silver particles showed a single optical absorption peak around 360 nm. Couto et al. (1992) observed that nanoparticles with diameter smaller than 3 nm have the wavelength of maximum absorption in the ultraviolet region (around 350 nm), while an increase in the average size of nanoparticles induces a red shift in the absorption spectrum. This indicates that our nanoparticles should be smaller than 3 nm.

Fig. 1 shows that $CaSO_4$:Eu,Ag photoinduced fluorescence exhibited two bands between 580 and 630 nm. This emission is comparable to the Eu^{3+} emission spectrum for 254 nm excitation (Ingle et al., 2008), which proves that this element was incorporated into $CaSO_4$.

TL analysis of $CaSO_4$:Eu + T, $CaSO_4$:Eu,Ag + T and $CaSO_4$:Eu,Ag(NP) + T pellets exhibited glow curves with a TL emission in the temperature range from 100 to 190 °C. In Fig. 2 is presented a comparison among the glow curves of these three samples after exposure to 0.2 Gy of beta radiation. $CaSO_4$:Eu,Ag(NP) + T pellets presented a more intense TL emission than the other two types of Teflon pellets.

Pellets prepared with glass addition showed TL glow curves at a higher temperature range than those prepared with Teflon. After irradiated with 0.2 Gy of beta radiation, all samples presented TL emission between 120 and 220 °C. Similarly as observed for pellets with the addition of Teflon, the $CaSO_4$:Eu,Ag(NP) + G showed a more intense TL emission, as can be seen in Fig. 3. TL response of the $CaSO_4$:Eu,Ag(NP) + G was supralinear to the absorbed dose from $^{90}Sr + ^{90}Y$ in a range from 0.1 to 5 Gy (Fig. 4).

The same behavior was observed in the TSEE measurements, by observing that $CaSO_4$:Eu,Ag(NP) + G and $CaSO_4$:Eu,Ag(NP) + T showed the more intense emissions (Figs. 5 and 6). While from the analysis of pellets with glass can be assumed that the TL signal is composed of two peaks, TSEE emission shows only one peak. The TSEE response as a function of absorbed dose is supralinear in the range evaluated (0.1–5 Gy).

Even assuming that the mass of phosphorus contained in glass pellets is twice that in Teflon pellets, one can infer that the pellets with glass exhibit a better TL response by mass, since its intensity is about 10 times higher than that showed in Teflon pallets. The variation in the temperature range is related to the larger amount of mass of pellets with glass which causes a difference in gradient heating of the sample and then changes the position of TL peaks.

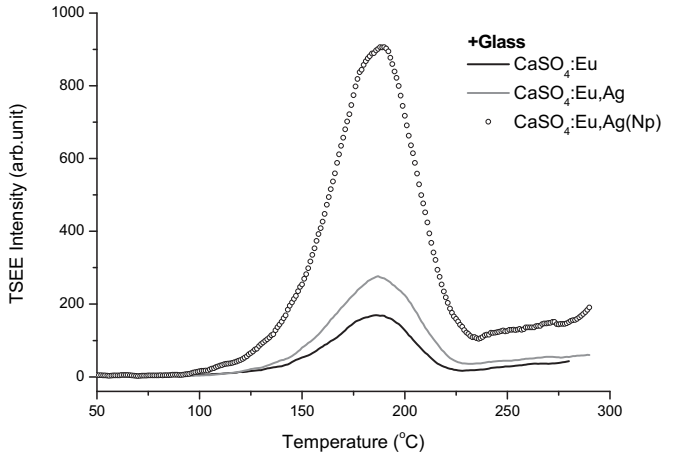

Fig. 6. Typical TSEE glow curves of $CaSO_4$:Eu + G, $CaSO_4$:Eu + Ag + G and $CaSO_4$:Eu + Ag(NP)+G samples.

4. Conclusions

Phosphors based on $CaSO_4$:Eu,Ag analyzed in this work showed TL and TSEE emissions more intense than those based on CaSO4:Eu. This increase was very significant when silver was incorporated as co-dopant in the form of nanoparticles. The increase in emissions intensity can bring major advantages for the response range of these materials to the absorbed dose of ionizing radiation. To be incorporated to phosphors produced commercial colorless glass and Teflon demonstrated appropriate for the production of dosimeters in form of pellets. However, the glass proved most appropriate for dosimetry because pellets with addition of glass have TL and TSEE responses more intense that tablets with Teflon.

Acknowledgments

The authors thank FAPITEC, CNPq, CAPES, FAPESP, MCT (project INCT for Radiation Metrology in Medicine) and INCT-INAMI for the partial financial support.

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