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The CaSO₄:Eu–Ag composite material: Thermo-photoluminescence study



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HIGHLIGHTS

- The Ag(NP) system enhances the number of defects and then the TL signal.
- The remaining TL signal is at 240 °C, adequate for dosimetry.
- The Ag(NP) system suppresses the PL signal of both Eu²⁺,³⁺ species.
- The Ag(NP) system has negligible influence on the emitting level lifetimes.
- One let the hypothesis that the Ag(NP) system only *hides* the luminescent ions.

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ABSTRACT

The CaSO₄:Eu powder composites with and without silver nanoparticles (NP) with selected grain size were analysed by thermoluminescence (TL), photoluminescence (PL) and time-resolved spectroscopy. Both Eu²⁺ and Eu³⁺ species are present. The former was identified by the emission around 380 nm and the latter by its typical ⁵D₀–⁷F_J transitions and two sites were identified. The addition of silver as nanoparticles enhances the TL signal (240 °C), which is adequate for dosimetry, and has quenching effect on the PL properties, because the most intense luminescence comes from the sample without silver and the lifetimes of the ionic species are not sensitive to the presence of Ag(NP).

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1. Introduction

It is well known that the presence of silver/gold ions or nanoparticles (NP) leads to changes in the PL behaviour of lanthanide (Ln) doped materials. Local field enhancement due to surface plasmon oscillations (SPO), Ag–Ln energy transfer (ET) and plasmon scattering (PS) have been the mechanisms invoked to describe the PL behaviour of the Ln containing silver composites (Abe et al., 1980; Malta et al., 1985; Couto et al., 1992; Strohhofer and Polman, 2002; Li et al., 2012; Reisfeld et al., 2012; Eckardt, 1999). The metal nanoparticle absorption and emission band positions are deeply dependent on the particle size and shape (Wiley et al., 2007; Nambi et al., 1974), and this fact means that plenty fundamentals and

applications are still to be born. In ref. 8 the interested reader will find a very important collection of pertinent knowledge.

The CaSO₄ doped with lanthanide (Ln) ions or with d-metals has been widely studied as thermoluminescent (TL) and photoluminescent (PL) materials (Folkerts et al., 1995; Zhang et al., 2002; Shinsho et al., 2006; Ingle et al., 2008; Chagas et al., 2010; Jose and Lakshmanan, 2004; Furetta, 2010; Aypar, 1978). From the application point of view, calcium sulphate doped with Dy³⁺ ions is an example of a dosimetric material. Due to its TL signal temperature (220 °C), the ⁴F_{9/2} → ⁶H_{15/2} radiative transition at 484 nm, easy preparation and low fading, this phosphor is commercially applied as an environmental or personnel dosimeter (Chagas et al., 2010; Aypar, 1978; Zeng et al., 1996; Tanner et al., 2010).

From the fundamentals point of view, CaSO₄:Eu is a suitable sample because the europium is a spectroscopic probe (Bapat, 1977) as its two ionic states, 2+ and 3+, are directly associated to its TL activity (Deng and Goldys, 2012), and the effect of the silver on the luminescence of the Eu³⁺ ions has been a matter of current

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publications, including photonics and biotechnological applications (Sampaio et al., 2010; Junot et al., 2011).

Recently, it has been reported that the composite $\text{CaSO}_4:\text{Eu}$ containing $\text{Ag}(\text{NP})$ shows TL and thermal stimulated exoelectronic emission (TSEE) signals enhanced by around 10 times (Dhabekar et al., 2006). Dhabekar et al. have studied the $\text{CaSO}_4:\text{Ag}$ system. However, the authors reported that no changes in the TL behaviour were observed due to the silver addition (Kim et al., 2006). In ref. (Dhabekar et al., 2006) the authors also reported that the addition of silver during the preparation of the $\text{CaSO}_4:\text{Eu}$ does not lead to sensitive difference in any thermally stimulated measurements. Thus, this paper aims at analysing the spectroscopic behaviour of the CaSO_4 containing Eu or $\text{Ag}(\text{NP})$ using TL, excitation, emission and time resolved spectroscopy, in order to investigate more precisely the role of the $\text{Ag}(\text{NP})$ in such system.

2. Experimental setup

2.1. Sample preparation

The samples were prepared as pointed out elsewhere (Jose and Lakshmanan, 2004). The samples were produced in powder by means of the following steps: i) mixing 1 g of CaCO_3 and 0.02 g of Eu_2O_3 in a saturated solution of H_2SO_4 , drying at 375°C in vacuum for the $\text{CaSO}_4:\text{Eu}$ powder system; ii) mixing the product of the reaction of the AgNO_3 in ethylene glycol (polyol) with the $\text{CaSO}_4:\text{Eu}$ crystal during the crystallization process. By this method silver is incorporated as NP (de Azevedo et al., 1988). The grain sizes are $<38\ \mu\text{m}$ and $>75\ \mu\text{m}$ in the $\text{CaSO}_4:\text{Eu}$ and $\text{CaSO}_4:\text{EuAg}(\text{NP})$, respectively.

2.2. TL measurements

TL measurements were made with a Harshaw 3500 TL reader using a heating rate of $10^\circ\text{C}/\text{s}$. The uncertainties superior limit has been 6.5% (Jose and Lakshmanan, 2004).

2.3. Spectroscopic measurements

Excitation, emission and time resolved spectra were obtained in the visible region using an excitation source of either a He–Cd laser (Kimmon IK5652R-G) or an Ar laser (Spectra Physics 166). The visible signals were dispersed by a monochromator (0.3 m, Thermo Jarrell Ash 82497), detected either with a photomultiplier tube (PMT) (Hamamatsu R928) or an InGaAs detector, and amplified using a lock-in amplifier (Junot et al., 2011).

3. Results and discussion

The TL spectra bring the first important information (Fig. 1). The comparison between the pure and the doped samples shows TL activity around 130°C , 160°C and in the $220\text{--}240^\circ\text{C}$ range. The structure of the maxima is similar to each other. However, the presence of silver enhances by a factor of 1.62 the peak at 130°C and slightly displaces all TL peaks. In this study the samples are in powder. The difference in the number of TL peaks, when compared to that reported elsewhere (Sampaio et al., 2010; Junot et al., 2011; Dhabekar et al., 2006), shows that the study in powder can lead to a quite different TL response profile.

The $\text{Ag}(\text{NP})$ is assumed to be spherical in average, which is not far from the truth (Eckardt, 1999). The enhancement observed is a strong indication that the $\text{Ag}(\text{NP})\text{--}\text{CaSO}_4$ interface increases the number of operative defects, and then increases the number of traps with nearly the same energy. On the other hand, the Eu containing samples, without or with $\text{Ag}(\text{NP})$, presented the

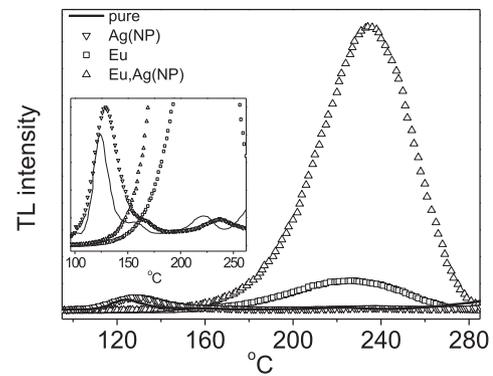


Fig. 1. TL measurements. The Eu containing samples is operative in the $220\text{--}240^\circ\text{C}$ range. In the inset one identifies that the TL activity of the pure and $\text{CaSO}_4:\text{Ag}(\text{NP})$ samples is mainly around 130°C .

suppression of the peak at 130°C . An expressive enhancement in the TL activity in the $220\text{--}240^\circ\text{C}$ range was observed: (16 and 127 times when compared the $\text{CaSO}_4:\text{Eu}$ and $\text{CaSO}_4:\text{EuAg}(\text{NP})$ samples to the pure sample, respectively). The maxima were around 220°C and 240°C in the $\text{CaSO}_4:\text{Eu}$ and $\text{CaSO}_4:\text{EuAg}(\text{NP})$ samples, respectively. In a preceding paper (Junot et al., 2011), such deeper peaks were not observed. Thus, the addition of $\text{Ag}(\text{NP})$ in powder samples enhances and displaces only the more intense TL signals. It is then worthy to reinforce that the presence of the europium ion eliminates the non-desired peak around 130°C .

The $\text{Ag}(\text{NP})$ (europium ion) inclusion affects, in a more pronounced way, shallower (deeper) traps. Thus, one has a strong indication that the $\text{Ag}(\text{NP})$ enhances the number of defects. As the same $\text{Ag}(\text{NP})$ system has been incorporated in both free and europium containing samples, it corroborates the indication that this is a nanostructured surface $\text{Ag}(\text{NP})\text{--}\text{CaSO}_4$ effect: the interface enhances the number of defects, then the intensity of the TL peaks.

The emission spectra with excitation at $265\ \text{nm}$ are shown in Fig. 2. Both Eu^{2+} ($380\ \text{nm}$) and Eu^{3+} (595 (${}^5\text{D}_0\text{--}{}^7\text{F}_1$), 616 (${}^5\text{D}_0\text{--}{}^7\text{F}_2$) and 697 (${}^5\text{D}_0\text{--}{}^7\text{F}_4$) nm) species are readily identified. In the case of the Eu^{2+} ion the peak at $380\ \text{nm}$ is an f-d electric dipole allowed transition, which explains its very strong intensity. The presence of the $\text{Ag}(\text{NP})$ reduces both the Eu^{2+} and Eu^{3+} emission intensities in all observed range. This deserves a comment: the mechanisms (SPO, ET, PS) invoked to describe the PL behaviour of $\text{Ln}\text{--}\text{Ag}(\text{NP})$ containing composites are operative if the emitting ions couple to the metal nanoparticles in some extent (Li et al., 2012). As the $\text{Ag}(\text{NP})$ system is prepared separately and added afterwards to the luminescent Eu containing powder, the metallic nanoparticles

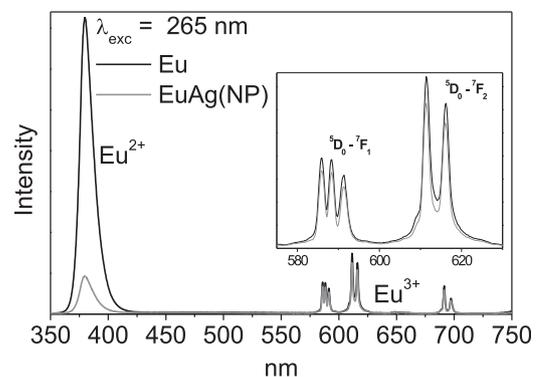


Fig. 2. Emission spectra with excitation at $265\ \text{nm}$. Both Eu^{2+} and Eu^{3+} ionic species can be readily identified. The intense peak at $380\ \text{nm}$ is from the Eu^{2+} ion (Tanner et al., 2010). The inset amplifies the visible region to show the set of Eu^{3+} ion characteristics ${}^5\text{D}_0\text{--}{}^7\text{F}_j$ ($j = 0, 1, 2, 3, 4$) transitions.

seem to *hide* the emitting ions. Thus some amount of the incident light is absorbed or scattered by the Ag(NP) before reaching some amount of Eu ions. This quenching then seems to be directly related to the way of sample preparation. Further, the Eu^{3+} ionic state is more stable than the Eu^{2+} one. Thus, the amount Eu^{2+} species is necessarily smaller than the Eu^{3+} one. The quenching response seems to be stronger to the side of the Eu^{2+} ion, because this is a transition governed by the Laport's rule. In the case of the Eu^{3+} ion the 4f–4f transitions are allowed by violating such rule. Thus, one cannot compare directly intensities described by completely different mechanisms.

The emission spectra suggest excitation measurements in order to follow the luminescence of both $\text{Eu}^{2+,3+}$ species separately (Fig. 3). One can note again that the Ag(NP) leads to lower excitation intensities of the Eu^{2+} and Eu^{3+} species in all the observed range, and thus that the nanoparticles seem to hide the emitting ions. At the charge transfer band (CTB, 265 nm) both ionic species have excitation activity. Out of the CTB, at 320 nm, one can see excitation of the Eu^{2+} ion and minor excitation of the Eu^{3+} ion. Fig. 4 shows the emission with excitation at 320 nm. Several points must be highlighted: another band centred at 480 nm is revealed (inset of Fig. 4), whose intensity can be compared to that of the Eu^{3+} ions; the structure of peaks in the region of the Eu^{3+} ion emission is different, including the presence of the ${}^5\text{D}_0\text{--}{}^7\text{F}_0$ (0–0) transition, when compared to Fig. 2. The presence of the 0–0 transition in the $\text{CaSO}_4\text{:Eu}$ sample, a very weak 0–0 transition in the Ag(NP) containing sample and the structure of lines of the ${}^5\text{D}_0\text{--}{}^7\text{F}_1$ transition is a clear indication of change in the Eu^{3+} ion local symmetry. The excitation at 320 nm then reveals that the Eu^{3+} ions occupy at least two different sites (with or without Ag(NP)), because the such profile of the Eu^{3+} ion emission is different when compared to that from excitation at 265 nm. Further, the emission band around 480 nm is assigned to Ag atoms (Li et al., 2012; de Azevêdo et al.,

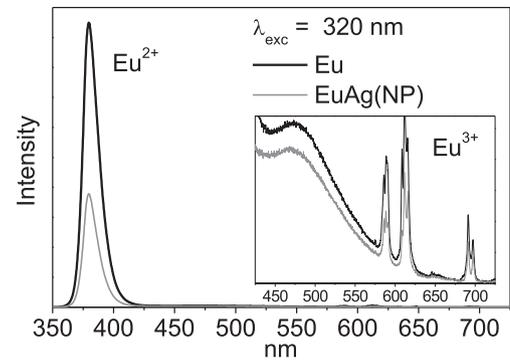


Fig. 4. Emission spectra with excitation at 320 nm; the inset shows an emission band at 480 nm assigned to emission of Ag atoms or subnanoparticles (Li et al., 2012). At least, two different sites of the Eu^{3+} ion can be readily identified.

1988). In the present case, as the Ag(NP) system is prepared before incorporation, one can interpret such weak emission as originated from remaining very small clusters of silver (*subnanoparticle*), because bigger particles (diameter > 3 nm) exhibit the plasmon absorption band. Thus, no emission can be observed, because of the electron-phonon coupling (Arbouet et al., 2003). This gives rise to the possibility of producing a white emitter by associating a suitable concentration of, one can say, Tb^{3+} or Tm^{3+} ions (emission at 490 nm).

Fig. 5a shows lifetime measurements of the ${}^5\text{D}_0$ level of the Eu^{3+} ion monitored at 616 nm and excitation at 255 nm. All samples have a similar lifetime in such conditions. Fig. 5b shows lifetime measurements of the Eu^{2+} ion (band at 390 nm). The magnitude is around seven times smaller than that of the Eu^{3+} ion lifetimes. This is expected because the 5d–4f transition is not forbidden by electric dipole selection rules. The presence of the Ag(NP) leads to a non-detectable effect on the lifetime. This corroborates the

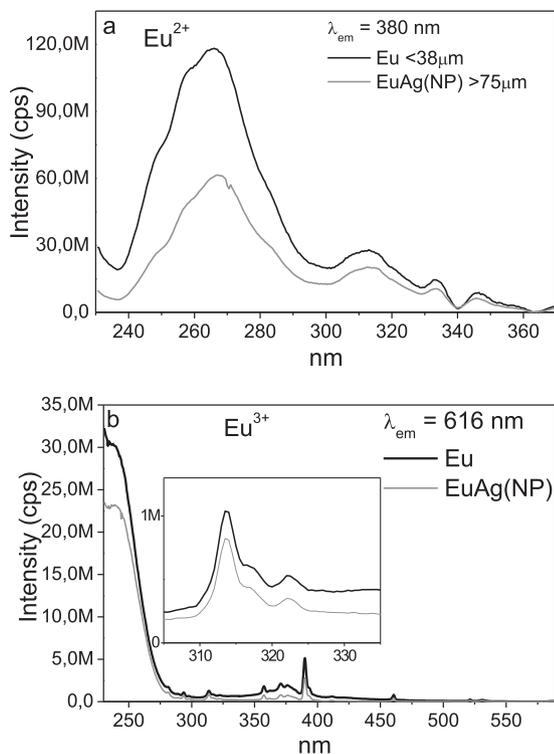


Fig. 3. Excitation spectra of the (a) Eu^{2+} ion (emission at 380 nm), and of the (b) Eu^{3+} ion (emission at 616 nm), the known are exhibited. In both cases the most intense peak is around 265 nm. The inset shows that around 320 nm the bivalent specie has a stronger excitation activity.

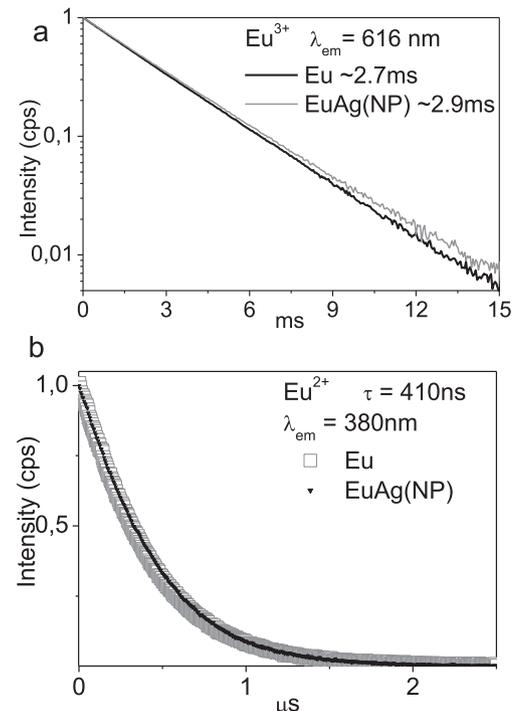


Fig. 5. a) ${}^5\text{D}_0$ level lifetime of the Eu^{3+} ion monitored at 616 nm with excitation at 255 nm (Nd:YAG) and (b) lifetime of the transition at 380 nm of the Eu^{2+} ion with excitation at 255 nm (Nd:YAG). The Ag(NP) does not have a sensitive role.

hypothesis that the presence of the Ag(NP) leads only to nanostructured defects.

4. Conclusions

The CaSO₄, CaSO₄:Eu, CaSO₄:EuAg(NP) set of samples were studied in order to investigate their thermoluminescence and photoluminescence behaviour. The presence of silver as nanoparticles seems to displace only slightly to higher temperature and enhances the more intense TL signal in both Eu free and Eu containing CaSO₄ crystal. The Ag(NP)–CaSO₄ interface seems to increase the number of defects (then the number of traps), in a slightly lower energy position. Therefore, the TL signal is enhanced around a slightly higher temperature. By doping with Eu and Ag(NP) only the TL signal around 240 °C is enhanced, which is adequate to environmental or personal dosimetric application. As the TL activity is attached to the Eu²⁺ to Eu³⁺ ionic change, one has to investigate the TL curves of the sample containing silver measured at different elapsed times. The luminescence quenching observed after the addition of silver nanoparticles is interpreted as a pure *hiding effect* directly related to the way of sample preparation. PL measurements at two different excitation wavelengths revealed at least two different sites for the Eu³⁺ ions. The emission band at 480 nm is assigned to emission of Ag atoms or subnanoparticles and suggests application of such systems as white emitters with adequate Ln co-doping species. The similarity between the lifetimes of the two ionic species is a strong indication that the nanoparticles do not interact with the Eu ions from the quantum mechanics point of view (SPO, ET, PS) directly.

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