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Photoluminescence of Eu^{3+} ion in SnO_2 obtained by sol–gel

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Abstract Photoluminescence data of Eu-doped SnO_2 xerogels are presented, yielding information on the symmetry of Eu^{3+} luminescent centers, which can be related to their location in the matrix: at lattice sites, substituting to Sn^{4+}, or segregated at particles surface. Influence of doping concentration and/or particle size on the photoluminescence spectra obtained by energy transfer from the matrix to Eu^{3+} sites is investigated. Results show that a better efficiency in the energy transfer processes is obtained for high symmetry Eu^{3+} sites and low doping levels. Emission intensity from $^5D_0 \rightarrow {}^7F_1$ transition increases as the temperature is raised from 10 to 240 K, under excitation at 266 nm laser line, because in this transition the multiphonon emission becomes significant only above 240 K. As an extension of this result, we predict high effectiveness for room temperature operation of Eu-based optical communication devices. X-ray diffraction data show that the impurity excess inhibits particle growth, which may influence the asymmetry ratio of luminescence spectra.

Introduction

The interest in rare-earth doped semiconductors has increased recently due to several applications in optoelectronic, such as displays and optical communication devices [1]. Combination of rare-earth ions with wide bandgap semiconductors brings great benefit, since thermal quenching effects are reduced [2], which allows luminescent emission from the rare-earth ion, with high quantum efficiency. SnO_2 is a wide bandgap semiconductor (bandgap energy about 3.6–4.0 eV [3]) and presents high reflectivity in the infrared and high transparency in the visible range, above 90% [3, 4]. These properties along with a high electrical conductivity leads to great potential to the production of transparent electrodes, besides gas sensors and other applications [3, 5]. The doping of the semiconductor SnO_2 with rare-earth ions combines all these properties of the matrix with luminescence of rare-earth ions, and it is very attractive to applications on new technologies.

It is known that the particle size influences the optical properties of materials. Rare-earth based luminescent nanocomposites are widely investigated for the production of high definition images, where the image resolution of cathodic ray tube is determined by the particle size [6]. The relation between particle size and quantum efficiency is an issue of constant discussion [6].

This work shows the influence of doping level, temperature and nanoscopic dimensions of particles on the luminescent properties of Eu-doped SnO_2 xerogels. These results are a good contribution for optical communication devices, which may operate at ordinary conditions, since the maximum emission efficiency is obtained close to room temperature. Besides, emission characteristics based on

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particle size and Eu^{3+} ion location are also presented, which allows controlling the luminescence fine spectra.

Experimental

Colloidal suspension of SnO$_2$:Eu was prepared by sol-gel process through dissolution of Eu$_2$O$_3$ in HCl. The desired amount of this suspension was added to an aqueous solution of SnCl$_4 \cdot 5H_2O$ (0.5 M), under stirring in a beaker with a magnetic bar, until the solution pH reaches 11. The resulting precipitated was submitted to dialysis against distilled water by about 10 days in order to eliminate Cl$^-$ and NH$_4^+$ ions. This procedure leads to a stable suspension (sol) of SnO$_2$:Eu. Xerogels are obtained by just drying this suspension at room pressure and room temperature, followed by annealing at 1,000 °C by 6 h.

In order to carry out temperature dependent photoluminescence (PL) measurements, it was used a Janis He closed cycle cryostat. Sample excitation was done by using the fourth harmonic of a Nd:YAG laser, 266 nm, as well as a Ar$^+$ laser with the 488 nm laser line. The signal was detected by a CCD detector coupled with a Jobin Yvon monochromator, model T64000.

X-ray diffraction data were obtained with a RIGAKU diffractometer, coupled with a Cu source of 40 kV and 20 mA of current, with 1°/min of scanning rate in the range de 20–80°.

Results-Discussion

The laser irradiation that was used in this work provides two different kinds of excitation of Eu^{+3} centers in the SnO$_2$ matrix: direct and indirect, by using the 488 and the 266 nm laser lines respectively. Excitation with the fourth harmonic of a Nd:YAG laser (266 nm) supplies photons with energy (4.65 eV) a little above the SnO$_2$ bandgap energy, yielding band-to-band excitation, followed by energy transfer to Eu^{3+} excited level. Moreover, it is well known that the excitation at 266 nm may photoionize Eu–O bonds in the SnO$_2$ matrix [7]. By the other hand, excitation with 488 nm (2.53 eV) is resonant with the transition $^7F_2 \rightarrow {}^5D_2$ of Eu^{3+}. After excitation to level $^5D_2$, electrons decay non-radiatively to $^5D_0$ level and then emit photons according to transition $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$.

Figure 1 shows PL spectra of 0.5%Eu doped SnO$_2$ xerogel, under excitation with 266 nm (1a) and 488 nm (1b). It is important to point out the nature of the transitions $^5D_0 \rightarrow {}^7F_1$ (590 nm) and $^5D_0 \rightarrow {}^7F_2$ (611 nm), labeled in Fig. 1. The first one is a magnetic dipole transition and its intensity is not affected by structural changes of the nearest neighborhood, whereas the transition $^5D_0 \rightarrow {}^7F_2$ is ruled by electric dipoles, being hypersensitive to the local crystalline field [8]. The ratio between the areas of these emission lines, i.e., $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ is called asymmetric ratio, and tends to zero when the excited ion is located at a symmetry site, for example Eu^{3+} substitutional to Sn^{4+} in the SnO$_2$ lattice. Excitation with 266 nm leads to a very well defined PL spectra, with peaks centered at 587.6, 592.5 and 598.4 nm, corresponding to the three components of ^{5}Do $\rightarrow {}^7F_1$, as clearly observed in Fig. 1a. In this case, the $^5D_0 \rightarrow {}^7F_2$ emission presents low intensity, which can be verified by the components at 609 and 611 nm. Then the asymmetric ratio is very close to zero, indicating that Eu^{3+} is actually located at lattice sites, substitutional to Sn^{4+} in the SnO$_2$ matrix [9], which is in good agreement with previous reports [10, 11]. By the other hand, directly excitation of Eu^{3+} ion with 488 nm (Fig. 1b) leads to an increase of the asymmetric ratio and, besides, the shape of PL spectra is broadened. Ions excited by this energy may be located at particles surface, which are asymmetric sites. Doping concentration in this sample, 0.5 at.% is superior to the solubility limit of Eu in SnO$_2$, which is about 0.05–0.06 at.% [12]. The excess of Eu segregates to particle surface as inferred by Matsuoka et al. [12, 13] using refined X-ray powder diffraction analysis, giving rise to a non-homogeneous impurity distribution. The observed broadening in the PL emission due to Eu^{3+}

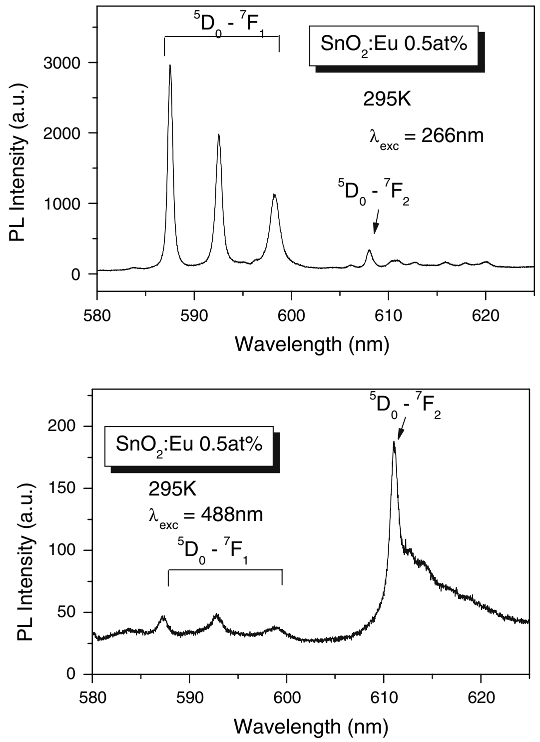

Fig. 1 Photoluminescence spectra for SnO$_2$:0.5 at.% xerogel at 295 K (**a**) under excitation with the fourth harmonic of a Nd:YAG laser (266 nm) and (**b**) under excitation with 488 nm line of Ar$^+$ laser

ions segregated at particle surface is related with the random distribution of first neighbors. It is important to mention that the SnO_2:0.1 at.% xerogel did not present any sort of emission signal under irradiation with 488 nm laser line. It is probably related to the small amount of Eu^{+3} at particles surface, because this doping level is close to the solubility limit. Then, we may conclude that the emission of Eu^{3+} substitutional in the SnO_2 lattice is more evident under excitation at 266 nm, suggesting a high-energy transfer from the matrix due to band-to-band excitation. It is also possible to verify that the emission from Eu^{3+} ions located at asymmetric sites, for instance close to particles surface, is more clearly observed by direct excitation of $^7F_2 \rightarrow {}^5D_2$ transition with the 488 nm laser line.

Figure 2 shows PL spectra obtained under excitation with 266 nm laser line for Eu-doped SnO_2 xerogels with several concentrations. For 0.1 and 0.5 at.% Eu samples the PL line shape is similar to those shown in Fig. 1, which suggests that the asymmetric ratio is very close to zero, indicating that Eu^{3+} is actually located at lattice sites, substitutional to Sn^{4+}, according to the preceding discussion. The xerogel SnO_2:1 at.%Eu, shown in the inset of Fig. 2, presents PL spectra with the electric dipole $^5D_0 \rightarrow {}^7F_2$ transition as dominant, which means that the Eu^{+3} ion, preferentially excited, has low symmetry. Considering that the excitation process is by energy transfer from lattice band-to-band transition, the most probable location of Eu^{3+} ion is close to the particle surface, occupying a lattice site but with low symmetry. An increase of asymmetry ratio from 0.01 to 5.2 is evaluated for samples with 0.1 to 1 at.% Eu, respectively. The excess of doping must cause the energy transfer to the Eu^{3+} sites belonging to the SnO_2 lattice far from the particle surface to be less effective, when compared to luminescence from other centers with lesser symmetry. These results are in good agreement with previous similar reports [8, 14].

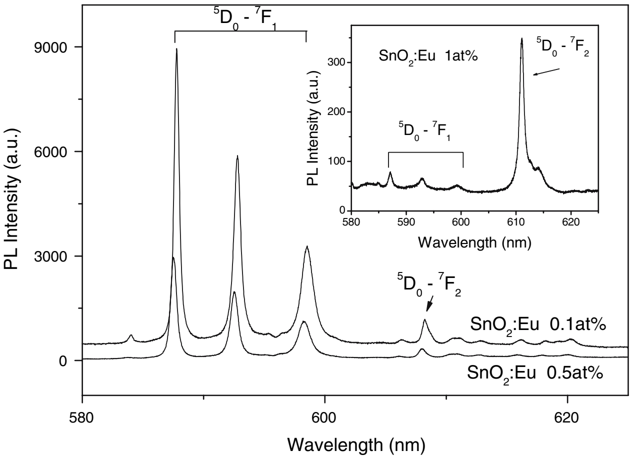

Fig. 2 PL of Eu-doped SnO_2 xerogels at 295 K under excitation with 266 nm laser line for doping concentrations of 0.1 e 0.5 at.%. Inset: PL at the same conditions for 1 at.%Eu

This behavior may be also related with decrease of particle size with increasing of Eu concentration. Figure 3 shows diffraction spectra for undoped and Eu-doped xerogels. Data show that all the samples, treated by 6 h at room atmosphere and 1,000 °C, present cassiterite structure [15]. Using Scherrer equation, the average particle size in the most defined directions was estimated, as shown in Table 1. This estimation clearly evidences that doping decreases the particle size. In other words, there is a decrease of the particle size as the Eu concentration increases, inhibiting the particle growth. Nevertheless, doping with 1 at.% of Eu largely exceeds the solubility limit, forming several centers of Eu segregated at surface [13]. Nogami et al. [16] investigating the effect of particle size on Eu emission, predicted an increase of energy transfer for Eu^{+3} of high symmetry sites with decreasing of particle size, due to quantum confinement effects. Although this result is apparently contradictory with ours, it is important to note that the particle size in our case is higher than the critical

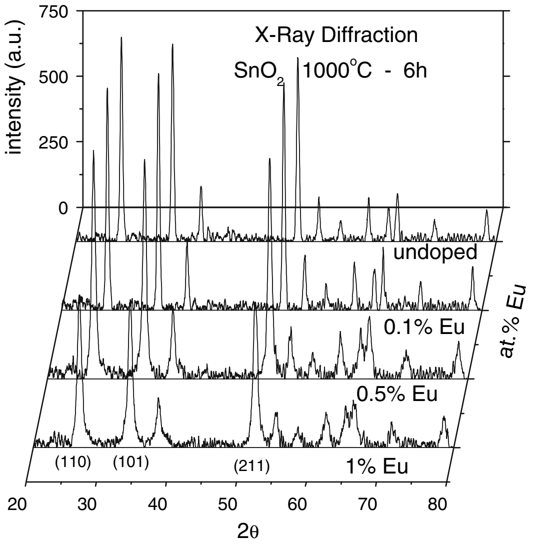

Fig. 3 X-ray diffraction data for undoped and Eu-doped SnO_2 xerogels, with the most evident directions labeled

Table 1 Particle size estimation from X-ray diffraction data for undoped and Eu-doped SnO_2 xerogel

Eu concentration (at.%)	Average particle size (nm)		
	(110)	(101)	(211)
0.0	19.5	19.8	21.1
0.1	18.7	19.8	21.0
0.5	13.2	13.9	14.3
1.0	10.7	11.6	11.6

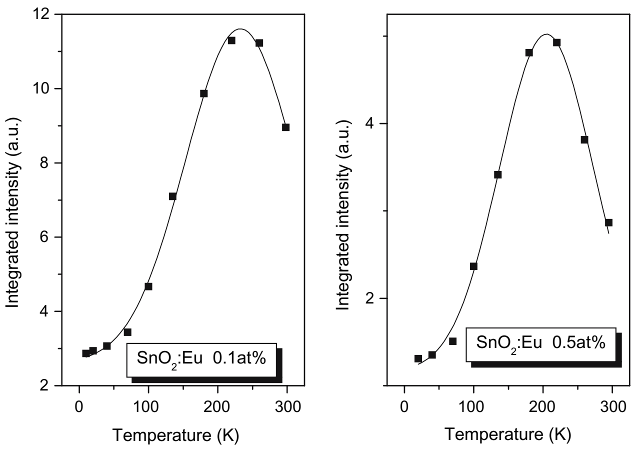

Fig. 4 Influence of temperature on the PL integrated intensity for $^5D_0$–$^7F_1$ emission of Eu^{3+} ions in theSnO$_2$ matrix, under excitation with 266 nm laser line (**a**) 0.1 at.% e (**b**) 0.5 at.%. (The solid line is only a guide to the eyes.)

size for quantum confinement, of about 10 nm [16]. In this way, it is possible that quantum confinement does not play a key role in our samples, and the main aspect of decreasing luminescence from Eu^{3+} ions at lattice sites is the location of Eu^{3+} ion, which is mainly segregated at particles surface when the solubility limit is overcome, as already discussed.

The temperature dependence of Eu emission intensity, under excitation at 266 nm, is shown in Fig. 4. The evaluated area under the emission band (integrated intensity), corresponds to 586–591 nm range, including the three component of the transition. Integrated emission associated to the transition $^5D_0 \rightarrow {}^7F_1$ is presented for concentrations of 0.1 and 0.5 at.% Eu. An increase in the integrated intensity is observed between 10 and 240 K. For higher temperatures there is a luminescence quenching, when the integrated luminescence decreases. We claim that from 10 to 240 K, temperature is not enough to promote phonon emission comparable to the radiative transition, and then, the luminescence quenching is avoided. This may be taking place due to wide gap between $^5D_0$ and ^7F_j levels, which minimizes the effect of non-radiative transition caused by phonon emission, which would ruin the luminescence. According to Weber [17], phonon assisted transition from ^5D_o level are negligible due to the wide gap (833 nm = 1.48 eV) between $^5D_0$ and the next inferior level $^7F_6$. It is observed that the lifetime of $^5D_0 \rightarrow {}^7F_6$ transition does not change with temperature [17].

A similar behavior to the one shown in Fig. 4 was observed by Peng et al. [6], with excitation at 488 nm They attribute the temperature dependence on the PL emission to the closeness between levels ^7F_j of Eu^{3+} ion, which makes possible transition originated from thermal vibration. In our case, Eu-doped samples with concentrations of 0.1 and 0.5 at.% are investigated, where energy transfer is efficient to Eu^{3+} substitutional to Sn^{4+} in the lattice. It must be taken into account that excitation energy (4.65 eV—266 nm) is a littler higher than SnO$_2$ bandgap. In a previous work, generation of electron-hole pairs was verified [18] upon irradiation at 4.65 eV, by promoting band-to-band excitation of SnO$_2$. Then, we believe that this is the dominant excitation channel of Eu-doped SnO$_2$ samples, as explored in this paper. However, we may not neglect the photoionization of Eu–O bonds and then, besides generation of electron-hole pairs, charge carrier density may be increased by electrons coming from broken Eu–O bonds, which may increase the population of $^5D_0$ level, after non-radiative decays have taken place. Although this mechanism has been observed before [7, 19], the actual influence of this broken bond to the energy transfer has not been carefully investigated. Based on our previous examination [18], we strongly believe that the excitation with 266 nm laser line promotes preferentially electron-hole pairs generation, giving rise to the energy transfer process, as already discussed.

Conclusion

Luminescent properties of Eu-doped SnO$_2$ xerogels have been investigated under different lasers excitation. We have used the 266 and 488 nm laser lines, from the fourth harmonic of a Nd:YAG laser and from an Ar$^+$ laser, respectively. This procedure allows to distinguish two Eu^{3+} families in SnO$_2$: in the first one the PL measurements show that Eu^{3+} ions are located in symmetric centers, substitutional to Sn^{4+} in the lattice, and another one, where the PL measurements allow to identify that rare-earth impurity gets preferentially at asymmetric sites, probably at particles surface, due to segregation caused by excess of doping. Excitation with 266 nm is energetically higher than the SnO$_2$ bandgap, promoting matrix band-to-band excitation and an efficient energy transfer to Eu^{3+} substitutional to Sn^{4+}. This happens for samples with doping level until 0.5 at.%. Above this doping level, energy transfer to ions located close to the particles surface, with lower symmetry, becomes operative. This behavior may be also related to the particles size, which decreases with Eu concentration, as deduced from X-ray diffraction data. The location of Eu^{3+} ion at surface lattice sites would explain the preferential excitation of low symmetry sites with 266 nm (band-to-band excitation). Concerning these results, our general conclusion is that the present work yields important knowledge for controlling the emission properties of optical communication devices based on Eu-doped SnO$_2$.

By analysis of $^5D_0 \rightarrow {}^7F_1$ emission under 266 nm laser line excitation, as function of temperature, it was clearly observed a photoluminescence quenching above 240 K. This high temperature is related to the modest phonon participation in this transition. Then Eu^{3+} doped SnO_2 presents considerable luminescence even at room temperature, which makes Eu-doped SnO_2 a very attractive material for technological applications, for instance as electroluminescence devices operating at room temperature.

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