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Europium(III)-containing zinc oxide from Pechini method

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Abstract

ZnO:Eu^{3+} (0.1 and 3 at%) with average particle size of 500 nm were prepared by the Pechini method. Photoluminescence spectroscopy evidences that there is no energy transfer between ZnO and Eu^{3+} ion. The emission spectrum at 77 K shows that Eu^{3+} ions occupy at least three different sites in ZnO:Eu 3 at% sample. The experimental intensity parameter Ω_2 indicates that Eu^{3+} ions in the sample doped with 3 at% occupy sites where 4f-configurational levels can better mix with opposite-parity states than those in the sample doped with 0.1 at%.

Keywords: ZnO:Eu(III); Luminescence; Experimental intensity parameter

1. Introduction

The advantage of new technology demands more sophisticated and smaller displays for visual communication. That is why the flat panel display (FPD) market share has steadily grown, which is still dominated by the standard cathode ray tube (CRT) [1]. Among the FPD device, we can find liquid crystal displays (LCD), plasma displays (PD), field emission displays (FED), and electroluminescent displays (EL). One of the most studied phosphors to be employed for FED applications is ZnO because it has high efficiency at low-voltage operation [2].

Pure zinc oxide presents green emission when excited with wavelengths in the range from 250 to 380 nm. This emission could be attributed to oxygen vacancies or to interstitial zinc excess [7,11,12], which means electronic defects are present in the forbidden band of ZnO [8]. The luminescent properties of ZnO will be strongly influenced by experimental conditions for preparing the samples. The energy gap of ZnO (3.2 eV) would offer a large spectral area where the rare earth could emit, and give polychromatic displays [3].

The luminescent properties of trivalent rare earth (RE^{3+}) depend on their host. Different matrices doped with different RE^{3+} would exhibit a sharp emission in several wavelengths located in the visible range which implies a variety of applications to this kind of materials. RE^{3+} doped semiconductors have taken special attention since they are an important material for optoelectronic devices. ZnS and ZnSe doped with rare earths are of special interest as thin films in electroluminescent devices [3]; however, few works have reported the insertion of RE^{3+} into ZnO [3–6].

Solid state reaction was used to obtain ZnO:RE^{3+} in [3–6]. Unfortunately, it was reported that only green emission from ZnO was observed under wavelength corresponding to zinc oxide valence band (VB)–conduction band (CB) transition. The authors also reported an energy transfer from ZnO to RE^{3+}, which can merely be observed if a small amount of a coactivator or a compensator such as Li^{+} ions was added to the material. In this case, the RE^{3+} ions are located at the surface of the ZnO grains and just a few of them diffuse inside the ZnO grains, where they undergo the impact of the hot electrons generated at the grain boundaries, and then such material shows luminescence.

The aim of this study is to obtain ZnO:Eu^{3+} by using a method which allows a mixing of the components at the molecular level in solution and a stoichiometric control, the Pechini method [9].

2. Experimental

The zinc citrate solution was prepared by addition of citric acid into a zinc acetate solution in ratio of 1.2:1 mol of citric acid:zinc acetate. The europium citrate was prepared by direct reaction of solid Eu_2O_3 with citric acid

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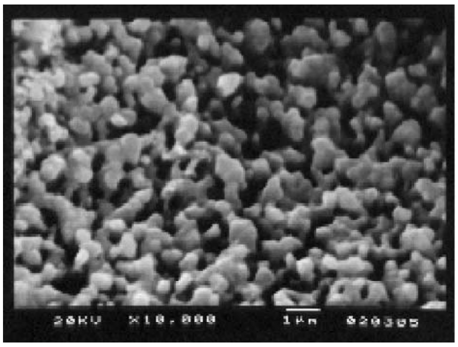

Fig. 1. SEM image of ZnO sample obtained from Pechini method.

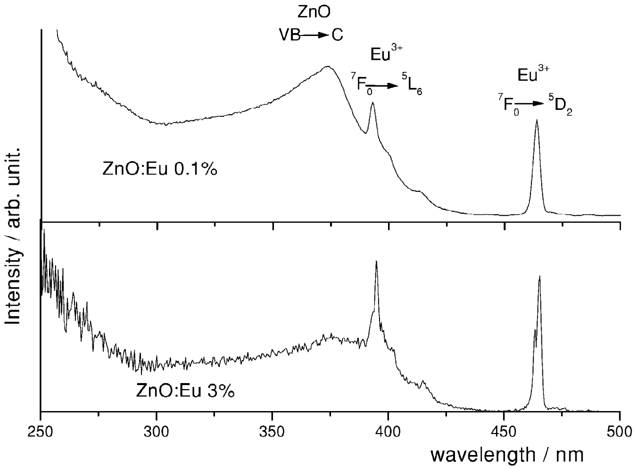

Fig. 3. Excitation spectra of ZnO:Eu 0.1 and 3 at% monitored at 612 and 616 nm, respectively, at room temperature.

in aqueous media, under heating. After the zinc and europium(III) citrate solutions were mixed, ethylene glycol was added and the mixture heated at 130 °C to obtain the polymeric resin that was fired at 900 °C in air leading to the powders.

Crystalline powder structure was checked by X-ray powder diffraction (XRD) using a Siemens D5000 diffractometer. The X-ray diffractograms were scanned over the angular range from 4 to 70° in 2θ, with Cu $K\alpha_1$ radiation. The samples were also characterized by scanning electron microscopy (SEM) (Jeol JSM T330A). The excitation and emission spectra were obtained using a Fluorolog SPEX 212L with a 450-W xenon continuous lamp. The signal was detected using a water-cooled Hammamatsu R928 photomultiplier.

3. Results and discussion

The SEM image in Fig. 1 shows that spherically shaped particles of europium-doped zinc oxide are obtained from Pechini method and subsequent thermal treatment. The samples obtained by thermal decomposition at 900 °C are crystalline and their X-ray diffractograms in Fig. 2 are characteristic of zincite. There is no evidence of Eu_2O_3 formation.

The excitation spectra of 0.1 and 3 at% doped zinc oxide in Fig. 3 present one band at 376 nm attributed to transition from valence band to conduction band (VB→CB) characteristic of ZnO semiconductor and two peaks at 395 and 464 nm attributed to $^7F_0 \rightarrow {}^5L_6$ and $^7F_0 \rightarrow {}^5D_2$ transitions of the europium(III) ion, respectively. The room temperature emission spectra of ZnO:Eu 3 at% in Fig. 4 and ZnO:Eu 0.1 at% (data not shown) were obtained with the excitation monitored on VB→CB ZnO transition and on both $^7F_0 \rightarrow {}^5L_6$ and $^7F_0 \rightarrow {}^5D_2$ transitions from the Eu^{3+} ion. For the excitation at 376 nm on VB→CB transition, the emission spectrum shows a wide band centered at 525 nm and a lower intensity band in the red region. This emission band is attributed to decay from electronic defects, which are present in the forbidden band, to the valence band or between different levels into forbidden band. The specific assignment of this band is yet

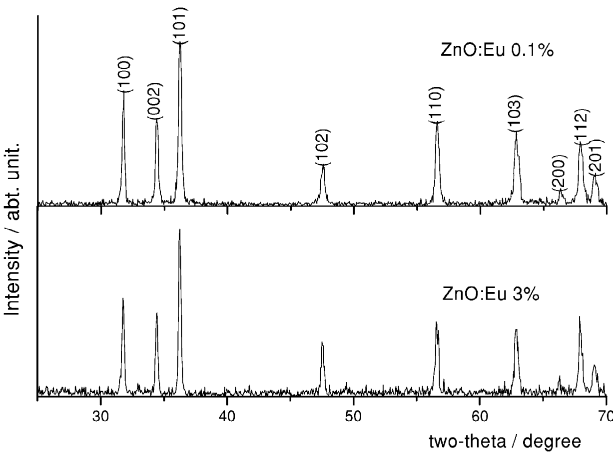

Fig. 2. XRD scans of ZnO:Eu 3 at% and ZnO:Eu 0.1 at% samples.

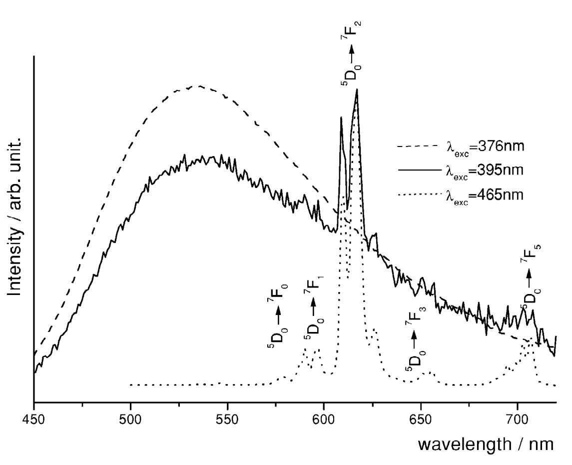

Fig. 4. Photoluminescence spectra of ZnO:Eu 3 at% obtained at different excitation wavelengths at room temperature.

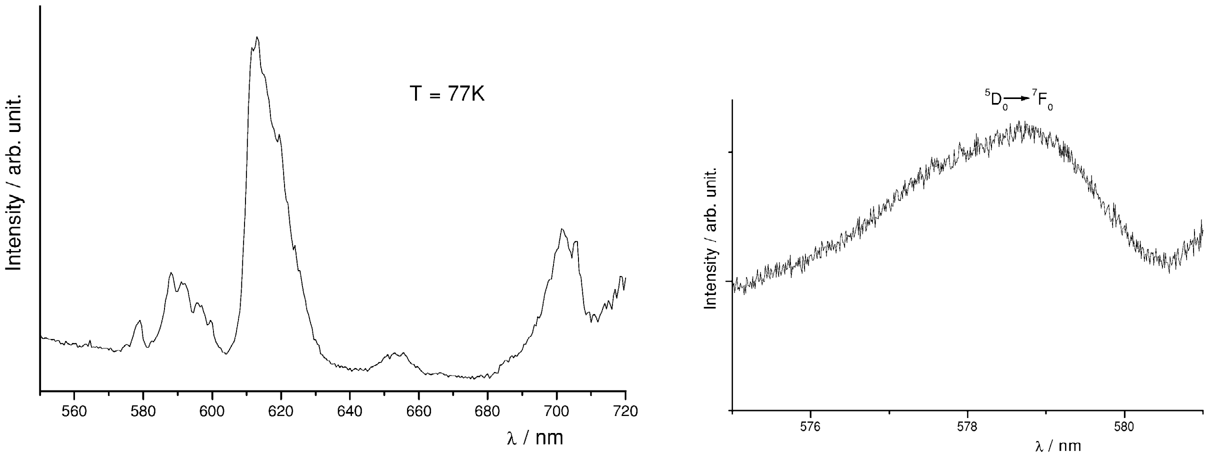

Fig. 5. Photoluminescence spectra of ZnO:Eu 0.1 at% obtained at 464 nm excitation at 77 K. The high-resolution spectrum showing the $^5D_0 \rightarrow {}^7F_0$ transition is on the right.

misleading in the literature. According to the ZnO energy levels diagram [8] the wide band centered at the yellow–green region can be attributed [7,11,12] to $Zn_i^+ \rightarrow V_{Zn}^-$ transition and the tail at red region includes the following transitions: $BC \rightarrow V_O^+$ at 1.75 eV (708 nm) and/or $V_O^+ \rightarrow BV$ at 1.75 eV too, and/or $V_{Zn}^{2-} \rightarrow V_{Zn}^-$ at 2.1 eV (590 nm). Probably all transitions occur when the sample is excited and the wide band is a result of the sum of these components. On the other hand, when this system is excited at 465 nm, that is a pure transition of Eu(III) ion, the emission spectrum in Fig. 4 presents the $^5D_0 \rightarrow {}^7F_J$ ($J=0$–4) intraconfigurational transitions. The feature and the high intensity of the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$ indicate that Eu^{3+} occupies a low symmetry site. In addition, exciting this system at 393 nm on $^7F_0 \rightarrow {}^5L_6$ transition of Eu(III) ion, that also has contributions of zinc oxide transitions, a combined emission spectrum of ZnO and Eu(III) ion has been observed. It is important to state some differences observed on emission spectra of the systems. The emission spectra of the ZnO:Eu 0.1 and 3 at% obtained at liquid nitrogen temperature are in Figs. 5 and 6, respectively. The fine structures of the 4f–4f transitions of Eu(III) ion, Fig. 6, substantially differ from the emission spectrum of Eu(III) ion in pure Eu_2O_3 (data not shown). This indicates that there are europium ions in the obtained ZnO lattice. The high relative emission intensity of europium ion in this case when compared to other work [13] that used lithium as a co-doping suggest that the charge neutrality on the present case is balanced by the presence of Zn(I) ion produced by thermal treatment. On the other hand, the emission spectrum of doped ZnO:Eu 0.1 at%, Fig. 5, present a broad band assigned to $^5D_0 \rightarrow {}^7F_2$ transition that is very sensitive to the chemical environment suggesting that europium ions are in a variety of different sites with similar symmetry. As Eu^{3+} has higher charge than Zn^{2+}, the presence of Eu^{3+} must be associated to Zn^+, these associations may occur in a similar way but not equal for each Eu^{3+} ion and this

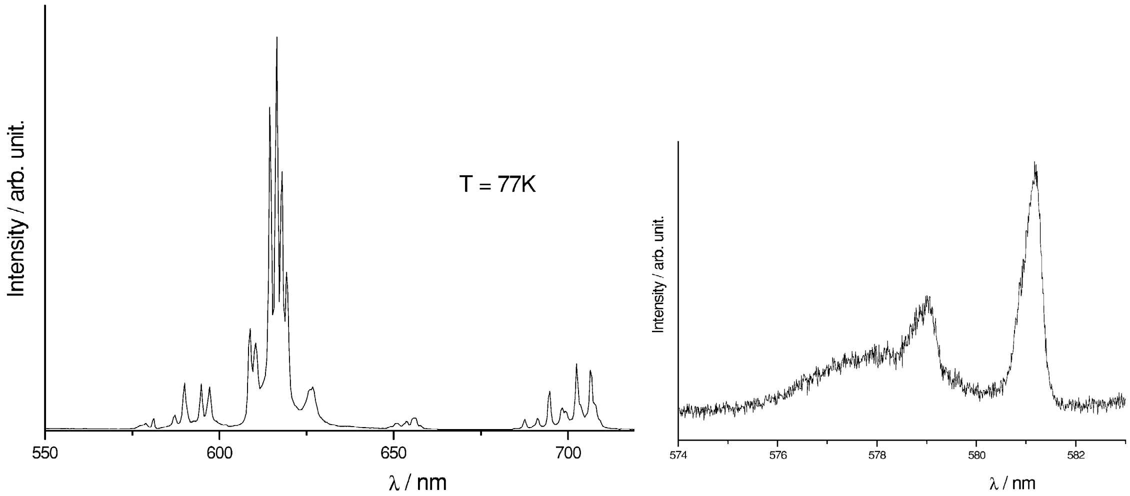

Fig. 6. Photoluminescence spectra of ZnO:Eu 3 at% obtained at 464.5 nm excitation at 77 K. The high-resolution spectrum showing the $^5D_0 \rightarrow {}^7F_0$ transition is on the right.

causes the broad line transitions observed in the spectrum. In addition, the wide $^5D_0 \rightarrow {}^7F_0$ transition band of ZnO:Eu 0.1 at% observed at liquid nitrogen temperature, Fig. 5, indicates europium ions are in a close chemical environment as observed in glasses which present an inhomogeneous broadening. Under the same measurement conditions, the ZnO:Eu 3 at% presents this transition band splitted indicating that Eu^{3+} ions occupy at least two defined symmetry sites, Fig. 6.

The experimental intensity parameters Ω_2 and Ω_4 were determined from the emission spectra obtained at room temperature by using the $^5D_0 \rightarrow {}^7F_2$ e $^5D_0 \rightarrow {}^7F_4$ transition, respectively, and by expressing the emission intensity I [10] in terms of the integrated area under the emission curves. In Eq. (1) $\hbar\omega$ is the transition energy, N is the population of the emitting level ($^5D_0$). The coefficient of spontaneous emission, A, is given by the expression (2).

$$I = \hbar\omega A_{\mathrm{rad}} N \tag{1}$$

$$A_{\mathrm{rad}} = \frac{4e^2\omega^3}{3\hbar c^3}\chi \sum_{\lambda} \Omega_\lambda \left\langle {}^7F_j \| U^{(\lambda)} \| {}^5D_0 \right\rangle^2 \tag{2}$$

where $\chi = n_0(n_0^2 + 2)^2/9$ is a Lorentz local field correction, n_o being the index of refraction of the medium considered (1.5). The magnetic dipole allowed $^5D_0 \rightarrow {}^7F_1$ transition was taken as reference. The values of reduced matrix elements are $\left\langle {}^7F_2 \| U^{(2)} \| {}^5D_0 \right\rangle^2 = 0.0032$ and $\left\langle {}^7F_4 \| U^{(4)} \| {}^5D_0 \right\rangle^2 = 0.0023$. The values of experimental intensity parameters in Table 1 can be related to changes in the chemical environment around the rare earth ion. The high Ω_2 value obtained for zinc oxide doped with 3 at% of europium is comparable to the value of crystalline Gd_2O_3:Eu 3 at% obtained by Pires et al. [14]. This high value might be interpreted as a consequence of the hypersensitive behavior of the $^5D_0 \rightarrow {}^7F_2$ transition [10], which is more intense when there is no inversion symmetry and there is a mix of opposite-parity wavefunctions into the 4f wavefunctions [15]. The Ω_2 value obtained for zinc oxide doped with 0.1 at% of europium is equivalent to europium ions present in ZnO containing glasses [16] that suggest a similar environment. The R_{02} parameter is the ratio between the intensities of the $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_2$ transitions. The ZnO:Eu 0.1 at% has a high R_{02} value indicating large J-mixing effect. In this case suggesting the presence of strong ligand field characteristic of symmetry sites.

Table 1
Values of experimental intensity parameters measured from emission spectra obtained at room temperature

Sample	R_{02}	$\Omega_{2\ \mathrm{exp}}$ (10^{-20} cm^2)	$\Omega_{4\ \mathrm{exp}}$ (10^{-20} cm^2)
ZnO:Eu 0.1 at%	0.0230	10.93	5.54
ZnO:Eu 3 at%	0.0120	15.88	5.03
Eu_2O_3	0.0120	18.14	5.03
Gd_2O_3:Eu 3 at% [14]	0.0006	20.33	6.92
Eu^{3+}-doped $4ZnO \cdot 3B_2O_3$ [16]	–	7.40	2.30

4. Conclusions

Emission spectra characteristic of europium is observed on the green–yellow band luminescence attributed to ZnO. The diffusion of europium ion into the zinc oxide lattice depends on several parameters, e.g., preparation method, thermal treatment, doping ion content. In this work the Pechini method of preparing doped zinc oxide has fundamental importance because it allows a homogeneous distribution on zinc oxide precursor. A high intense emission of europium ion on zinc oxide was observed, in particular, due to the presence of Zn^+ into zinc oxide lattice produced by thermal treatment. The Eu^{3+} in the structure allows the stabilization of Zn^+ by a charge compensation mechanism. The energy transfer from ZnO to europium ion is not observed probably due to the difference of energy levels.

Acknowledgements

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