Journal of Alloys and Compounds 480 (2009) 867–869

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Preparation and optical properties of Eu^{3+}/Eu^{2+} in phosphors based on exchanging Eu^{3+}-zeolite 13X

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ARTICLE INFO

Article history:
Received 30 September 2008
Received in revised form 15 February 2009
Accepted 19 February 2009
Available online 26 February 2009

Keywords:
Photoluminescence
Zeolite
Ion-exchange

ABSTRACT

The phosphors containing the structure of Eu^{3+}/Eu^{2+} were prepared via ion-exchange between europium ions and zeolite 13X. The products were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS) inductively coupled plasma optical emission spectrometry (ICP) and photoluminescence (PL), respectively. The XRD and TEM results indicate that amorphous silicate structure has been formed when the as-prepared products were sintered at 800 °C. A broad blue emission band (430–500 nm) and a sharp red emission band (600–630 nm) excited by 397 nm which are attributed to the characteristic peaks of the Eu^{2+} and Eu^{3+} ions, respectively. The blue emission intensity weakens while red emission intensity increases as increasing sintering temperature.

1. Introduction

Lanthanide ions are energetically preferred as the trivalent state according to their electronic configurations, but some lanthanide ions can also exist as divalent states such as Eu^{2+}, Sm^{2+}, and Yb^{2+} [1–4]. The Ln^{3+}-activated luminescent materials (Ln = Eu, Tb, or Ce, and so on) have been acquired and applied successfully by many methods [5–10]. However, excited bands of most these luminescence materials are at about 254 nm and the single emission of Eu^{3+}-activated luminescent materials originated from 4f–4f transitions show sharp emission peaks because of the sensitivity of lanthanide ions for their chemical environments [11]. That raises difficulties in device integration and the control of energy transfer to multicolored luminescence. Zeolites are one of the promising host materials for photonic applications in blue, green, red or white phosphors for ultraviolet light-emitting diodes (LEDs) [12,13]. Through exchanging lanthanide and zeolite 13X, lanthanide ions can be protected and multicolored luminescence can be observed because of their well-ordered arrangement of cages and channels [10].

The major objectives covered by this research were the following: (1) to prepare a novel luminescent material by a simple ion-exchanging method; (2) to investigate the optical properties of this material. Two luminescent regions of blue and red emission centered at 448 and 615 nm have been found for the as-prepared luminescent material excited by 397 nm. The blue emission intensity weakens while red emission intensity increases as increasing sintering temperature. Thus, we can obtain pure red, blue or white phosphors by controlling the reaction temperature. Moreover, the long-wavelength UV light excitation property of this material may have potential for the application in UV-LEDs.

2. Experimental details

In the typical reactions, 1.0 g of dried zeolite 13X ($Na_2O{\cdot}Al_2O_3$ $(2.8 \pm 0.2)SiO_2$ $(6–7)H_2O$, Shanghai Chemical) was immersed in 8.0 ml europium chloride solution (0.03 mol/l) for 24 h in 80 °C water bath. After cooling to room temperature, the obtained products were collected by the centrifugation and then washed with distilled water. Then the products were sintered under different temperature for 3 h.

The structure of as-prepared products were obtained using the powder X-ray diffraction (XRD) (Rigaku DMAX 2000 diffractometer equipped with Cu/Kα radiation, $\lambda = 0.15405$ nm) (40 kV, 40 mA) and transmission electron microscope (TEM, JEOL JEM-2100). X-ray photoelectron spectroscopy (XPS) measurements were performed on a PerkinElmer PHI 5000C ESCA system. All the binding energies were calibrated by using the contaminant carbon (C1s = 284.6 eV) as a reference. The content of Eu in the samples was estimated by inductively coupled plasma optical emission spectrometry (ICP). The photoluminescence (PL) spectrum was measured at room temperature by VARIAN Cary-Eclipse 500 spectrofluorometer equipped with a 60 W Xenon lamp as the excitation source.

3. Results and discussion

Fig. 1 shows two TEM images of Eu^{3+}-exchanged zeolite 13X which was respectively sintered at 600 °C (in Fig. 1(a)) and 800 °C (in Fig. 1(b)). As shown in Fig. 1(a), the complete and regular lattice stripe structure with straight parallel channels was formed and the diameter of the channels was approximately 0.949 nm. The samples sintered below 600 °C are similar to the one shown in Fig. 1(a). However, it can be seen that the distribution of the nanoparticles is uniform in the zeolite cavities and the structure of zeolite

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doi:10.1016/j.jallcom.2009.02.050

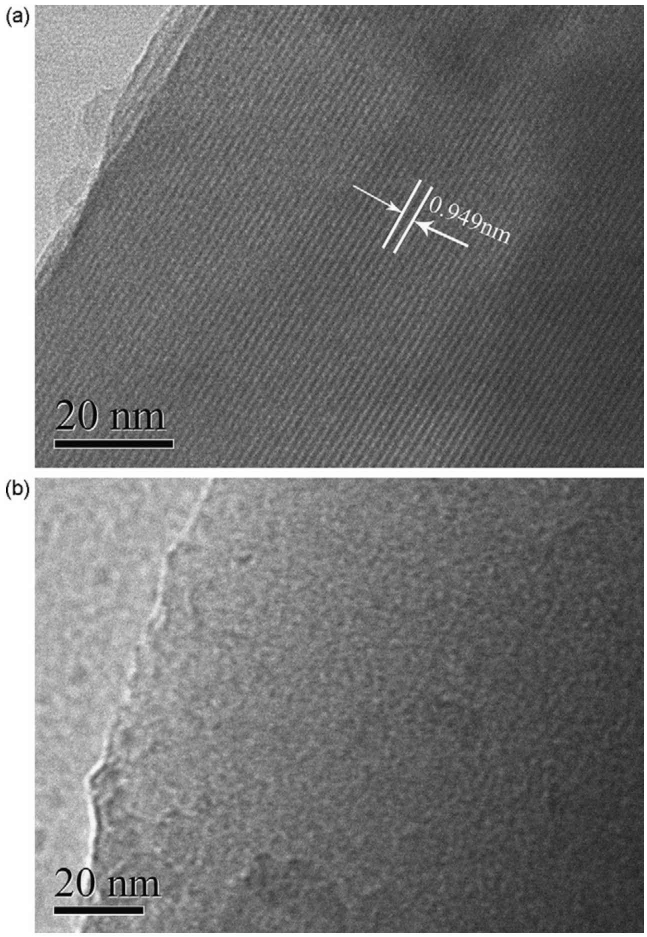

Fig. 1. TEM images (a) calcined under 600 °C (b) calcined under 800 °C of Eu^{3+}-exchanged zeolite 13X.

has been transformed to amorphous structure above 800 °C, which suggested that the zeolite framework has changed.

The Eu^{3+}-exchanged zeolite products were structurally characterized by X-ray diffraction (XRD). A typical XRD patterns have been presented in Fig. 2. It can be observed that all of these peaks of sintered temperature below 600 °C are in good agreement with zeolite (JCPDS Card, No. 04-0118). However, the diffraction peaks have been significant changed when the sample was sintered above 800 °C. Only a broad peak about 25° appears which is attributed to the collapse of zeolite 13X configuration and the formation of amorphous silicate structure. In addition, the small nanoparticles observed from Fig. 1(b) are undetected by XRD because of the low-loading nanoparticles wrapped in the zeolite cavities and the weak crystallinity for the nanoparticles.

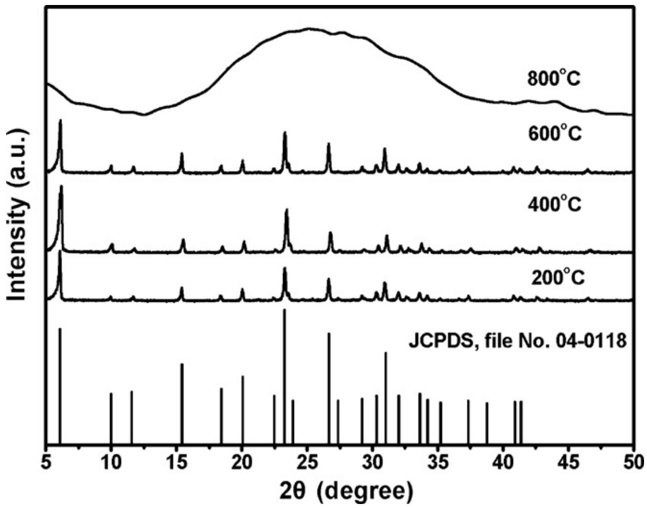

Fig. 2. XRD patterns of as-prepared products.

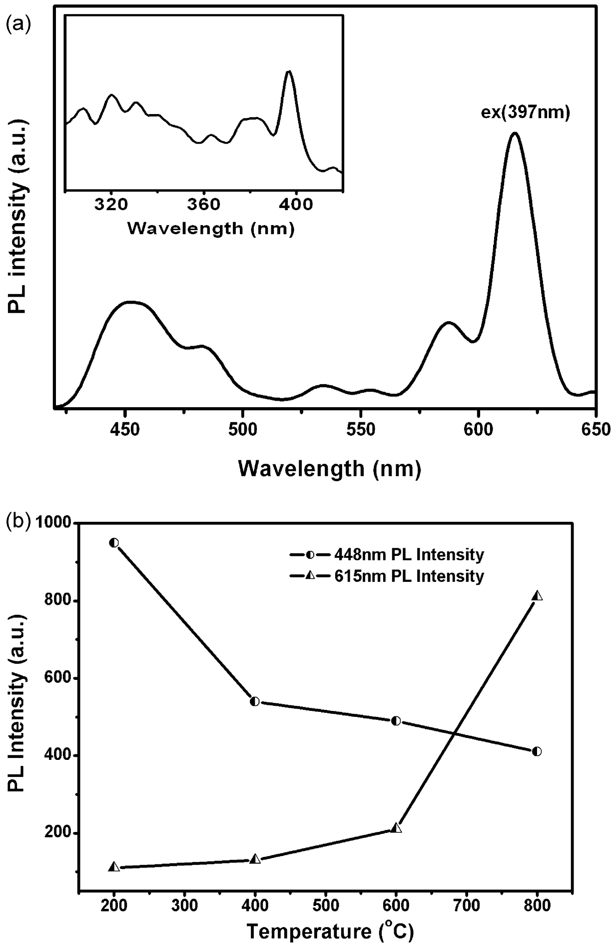

Fig. 3. (a) Emission spectrum at 397 nm excitation for samples sintered at 800 °C. The inset is the corresponding excitation spectrum. (b) The PL intensity of samples under different sintering temperature.

Room temperature photoluminescence (PL) spectrum of as-prepared sample at sintering 800 °C is shown in Fig. 3(a). The content of Eu is 8.2% in the sample measured by ICP. The photoluminescence excitation (PLE) spectra, monitored at 615 nm, show a wide excitation region (300–420 nm) with the dominant peak at 397 nm in the inset of Fig. 3(a). From the PL spectrum, a broad blue emission band (430–500 nm) mainly centered at 448 nm and a sharp red emission band (600–630 nm) centered at 615 nm can be observed under the excitation of band of 397 nm. The phosphor shows two blue broad emission bands with peaks at 448 nm and 480 nm, which are ascribed to the characteristic emission bands of Eu^{2+} ions [14]. Two emission peaks centered at 530 nm, 595 nm are assigned to the transitions of Eu^{3+} $^5D_1 \rightarrow {}^7F_1$ and $^5D_0$ to lower levels $^7F_1$ transitions [15], respectively. The strongest emission band at 615 nm is attributed to $^5D_0 \rightarrow {}^7F_2$ transition. From Fig. 3(b), the PL intensity of blue emission weakens and that of red emission enhances along the increase of sintering temperature.

The possible reasons were established: The Eu^{3+} ions exchange with the Na^+ ions in the zeolite matrix which is not an equal value substitute process and forms charge compensating lattice defects

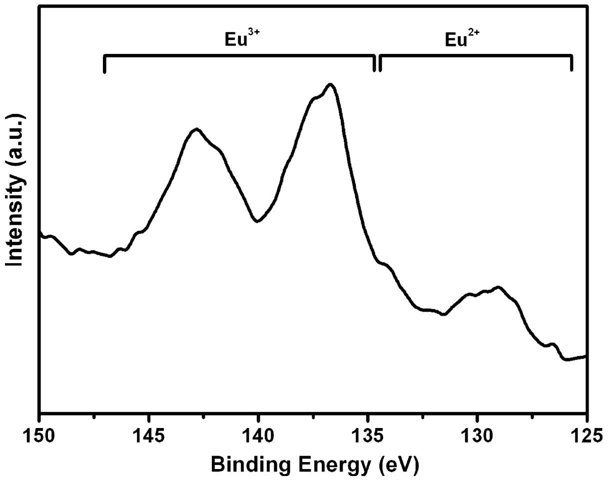

Fig. 4. XPS spectra of Eu in the as-prepared sample annealed at 800 °C.

which maintain a balance of the negative charge of the aluminosilicate framework in the zeolite cavities [16–18]. At the same time, Eu^{2+} ions are main present in zeolite matrix because of above. The bonds between Eu^{2+} ions and zeolite are unstable under the lower temperature [19]. Furthermore, there are a few Eu^{3+} ions were adsorbed in the zeolite cavities. Therefore the PL intensity of blue emission is very strong while that of red emission is quite weak when the samples were sintered under lower temperature. With the increase of sintering temperature, Eu^{2+} ions are transformed into Eu^{3+} ions gradually and incorporated in the zeolite cavities, resulting in the PL intensity of red emission enhancing. Particularly, the PL intensity of red emission enhanced significantly when the sintering temperature reached 800 °C compared with those of the above sintering samples, and increased more than 4 times. This result suggests that the zeolite cavities provide advantageous surroundings for the Eu^{n+} ($n = 2, 3$) ions emission centers, which can be UV excited and vis-iradiated. The collapse of zeolite 13X configuration plays a role in protecting the emission centers of Eu^{3+} which promote effective energy transfer between zeolite matrix and Eu^{3+} ions: on the one hand, it avoids the excessive aggregate among activators so that the concentration quenching effect that is mainly caused by the energy transfer between two activator ions is greatly reduced; on the other hand, it also plays a role in stabilizing emission centers.

To confirm the presence revealed by the structural analysis of both Eu^{2+} and Eu^{3+} species, preliminary XPS studies on the as-prepared sample annealed at 800 °C have been undertaken. This oxidation effect (presence of oxygen in the measuring apparatus) was more visible for the Eu3d XPS process than for the Eu4d one because of the smaller attenuation length of the 3d electrons. Consequently, we have focused our attention on the Eu 4d lines. The binding energy of Eu4d in the sample was shown in Fig. 4. For the sample, Eu atoms were found in two different oxidation states, namely 2+ and 3+.

4. Conclusions

A luminescent material containing Eu^{3+}/Eu^{2+} structure has been prepared successfully which can emit blue and red light in the same time by Eu^{3+} ions-exchanged zeolite 13X and sintered in different temperatures. Relatively pure red, blue or white phosphors can be acquired by controlling appropriate temperature. The red PL intensity of Eu^{3+}-exchanged zeolite enhanced greatly when the sintering temperature reached 800 °C. The collapse of zeolite 13X configuration plays a role in protecting the Eu^{3+} ions emission centers which promotes the effective energy transfer between zeolite matrix and Eu^{3+} ions. The long-wavelength excitation property of this material may have potential application for LEDs.

Acknowledgements

The authors would like to thank Science and Technology Development Fund (Shanghai, No. 0652nm023, 0752nm008), Shanghai Leading Academic Discipline Project (JY601), the special fund for improving young excellent researchers and teachers in Shanghai University (RE644) and the doctor fund of Shanghai Normal University (PL621) for supporting the research.

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