Influence of Bi³⁺ content on photoluminescence of InNbO₄:Eu³⁺,Bi³⁺ for white light-emitting diodes

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A series of red-emitting phosphors InNbO₄:Eu³⁺,Bi³⁺ was prepared by a high temperature solid-state reaction. The structure, size distribution and luminescence properties of the phosphors were respectively characterized by X-ray diffraction (XRD), laser particle size and molecular fluorescence spectrometer. The XRD results indicate that the phase-pure samples have been obtained and the crystal structure of the host has not changed under the Eu³⁺ and Bi³⁺ co-doping. The test of size distribution shows that the phosphor has a normal size distribution. The excitation spectra illustrate that the dominant sharp peaks are located at 394 nm ($^7F_0 \rightarrow ^5L_6$) and 466 nm ($^7F_0 \rightarrow ^5D_2$). Meanwhile, the emission spectra reveal that the phosphors excited by the wavelength of 394 nm or 466 nm have an intense red-emission line at 612 nm owing to the $^5D_0 \rightarrow ^7F_2$ transition of Eu³⁺. Bi³⁺ doping has not changed the peak positions except the photoluminescence intensity. The emission intensity is related to Bi³⁺ concentration, and it is up to the maximum when the Bi³⁺-doping concentration is 4 mol%. Due to good photoluminescence properties of the phosphor, the InNbO₄:0.04Eu³⁺, 0.04Bi³⁺ may be used as a red component for white light-emitting diodes.

Keywords: red-emitting phosphor; photoluminescence properties; white LEDs; InNbO₄; solid-state reaction

1. Introduction

As a kind of a novel solid cold-light source, white light-emitting diodes (LEDs) have certainly been well-received thanks to a series of advantages such as large brightness, low energy consumption and good response characteristic [1-6]. Thus, it can be suggested that the white LEDs will become a new generation lighting source [7-10]. However, there are some flaws in commercial white LEDs. For example, the white LEDs have too small color rending index (CRI) and high color temperature [11-14]. In order to avoid the above mentioned shortcomings, the white LEDs that are made from red, green and blue (RGB) phosphors are coming out [15-18]. Now, investigations on the green and blue phosphors are quite advanced, while the progress on red phosphors used as white LEDs is made slowly. So, searching for the red phosphors for white LEDs is an interesting issue.

Recently, many researchers have been interested in red phosphors doped with rare-earth ions which have plentiful emitting spectra and excellent luminescence properties due to their electron structure with partially filled 4f shells [19–23]. Among these ions, Eu³⁺ ions have attracted a wide research interest because of their special luminescence characteristics. The outer electron configuration of Eu^{3+} is $4f^75d^06s^2$ and it can emit an orange or red color when it is doped into some hosts [24-26]. In order to improve the Eu^{3+} emission intensity, many works have been done through codoping with other ions in different hosts [27]. For example, the energy transfer from Bi^{3+} to Eu^{3+} in Eu³⁺ and Bi³⁺-codoped phosphors may happen under certain circumstances [28, 29]. In the current investigation, the effect of Bi^{3+} content on the luminescence properties of the InNbO₄:Eu³⁺,Bi³⁺ phosphor was studied.

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2. Experimental

2.1. Samples synthesis

In this work, samples were prepared by a conventional high temperature solid-state reaction. The analytic reagents of niobium pentaoxide (Nb_2O_5) and bismuth oxide (Bi_2O_3) , super-purity indium oxide (In₂O₃, 99.99 %) and europium oxide (Eu₂O₃, 99.99 %) were used as starting raw materials obtained from Tianjin Guangfu Fine Chemical Research Institute. The stoichiometric amounts of corresponding materials were thoroughly mixed by grinding in an agate mortar, then, the mixed powders were put into alumina crucibles with covers, preheated at 600 °C for 4 h in an electric stove under an air atmosphere, followed by sintering at 1255 °C for another 6 h. The products were obtained when the powders were cooled down to room temperature in the working stove. Theoretically, the above-mentioned solid-state reaction in this study can mainly take place as:

$$In_2O_3 + Nb_2O_5 + 0.02Eu_2O_3 + xBi_2O_3$$

$$\rightarrow 2In_{0.98-x}Eu_{0.02}Bi_xNbO_4$$

(x = 0, 0.02, 0.04, 0.06, 0.08) (1)

2.2. Measurements

The products were identified by powder X-ray diffraction (XRD) on a Shimadzu diffractometer in a scanning 2θ range from 10° to 70° using CuK α radiation, at 40 kV and 150 mA. The particle distribution was characterized on a Rise-2002 laser particle size analyzer with the dispersant in distilled water. Photoluminescence excitation and emission spectra of the products were recorded on an RF-5301 molecular fluorescence spectrometer employing a Xe lamp as an excitation source and both the excitation and emission slit widths were chosen as 3 nm. All the measurements were carried out at room temperature in air.

3. Results and discussion

3.1. Analyses of XRD and size distribution

For the purpose of identifying the structure of as-synthesized products, XRD examinations

were employed. Fig. 1 shows the XRD patterns of InNbO₄:0.04Eu³⁺ and InNbO₄:0.04Eu³⁺, 0.04Bi³⁺ phosphors. All the XRD peaks match well with the Joint Committee on Powder Diffraction Standards (JCPDS Card No. 33-0619). It can be seen that the host structure of the doped sample in the examined concentration range has not changed and impurity phases almost do not exist in both of them. Especially this demonstrates that the phosphor InNbO₄:0.04Eu³⁺ doped with Bi³⁺ ions is still a single phase with the monoclinic crystal structure and Bi³⁺, which occupies the same sites as Eu³⁺ in the host, has little effect on the structure of InNbO₄:Eu³⁺.



Fig. 1. XRD patterns of the phosphors InNbO₄:Eu³⁺ and InNbO₄:Eu³⁺,Bi³⁺.

The particle size distribution in the sample InNbO₄:0.04Eu³⁺,0.04Bi³⁺ is shown in Fig. 2. The particles have a narrow size distribution and the median diameter is about 2.3 μ m, which elucidates why the phosphors are meeting the production requirements of solid lighting facilities [30].

3.2. Excitation and emission comparison between $InNbO_4$: Eu^{3+} and $InNbO_4$: Eu^{3+} , Bi^{3+}

Fig. 3 shows the excitation spectra of the $InNbO_4:0.04Eu^{3+}$ and $InNbO_4:0.04Eu^{3+}, 0.04Bi^{3+}$ monitored at 612 nm. Both the excitation spectra can be divided into two parts. One is the broad absorption band before 362 nm which is attributed to the charge transfer



Fig. 2. Particle size distribution of the sample $InNbO_4$:0.04Eu³⁺,0.04Bi³⁺.

(CT) [31], the other is a narrow peak region above 362 nm which is assigned to the 4f⁷ configuration transitions of Eu³⁺ from the ground state to the excited state in the host lattice [32]. Among these peaks, the dominant sharp peaks occur at 394 nm (${}^{7}F_{0} \rightarrow {}^{5}L_{6}$) and 466 nm (${}^{7}F_{0} \rightarrow {}^{5}D_{2}$). Thus, the phosphors can be well excited by ultraviolet (UV) or blue light, which is compatible with the present LED chips. Moreover, the spectra of the InNbO₄:0.04Eu³⁺ and InNbO₄:0.04Eu³⁺, 0.04Bi³⁺ are very similar except the excitation intensity. The latter phosphor tends to absorb more energy, so its intensity can become strong.



Fig. 3. Excitation spectra of $InNbO_4:0.04Eu^{3+}$ and $InNbO_4:0.04Eu^{3+}, 0.04Bi^{3+}$.

Fig. shows emission spec-4 the $InNbO_4{:}0.04Eu^{3+}$ of phosphors and tra InNbO₄: $0.04Eu^{3+}$, $0.04Bi^{3+}$. Upon the excitation of blue light at 466 nm, the spectra reveal some sharp peaks corresponding to the transitions of Eu^{3+} 4f⁶ configuration from the excited ⁵D₀ level to the ${}^{7}F_{J}$ (J = 0, 1, 2, etc.) levels [33]. In the transitions, the ${}^5D_0 \rightarrow {}^7F_2$ transition of Eu³⁺ at 612 nm is dominating and other transitions are very weak, which shows that Eu^{3+} ions locate at a site without inversion symmetry [34, 35]. This phenomenon can be used for preparing a good phosphor with ideal CIE chromaticity coordinates. Furthermore, the emission intensity of the phosphor InNbO₄:0.04Eu³⁺,0.04Bi³⁺ is stronger than that of the $InNbO_4:0.04Eu^{3+}$, so the phosphor InNbO₄:0.04Eu³⁺,0.04Bi³⁺ may become a good red phosphor for white LEDs.



Fig. 4. Emission spectra of $InNbO_4{:}0.04Eu^{3+}$ and $InNbO_4{:}0.04Eu^{3+}, 0.04Bi^{3+}.$

3.3. Effect of Bi³⁺ concentration on luminescence properties of InNbO₄:Eu³⁺,Bi³⁺

Photoluminescence emission spectra and relative intensity of $InNbO_4:Eu^{3+},Bi^{3+}$ for different Bi^{3+} concentrations are presented in Fig. 5. It can be seen that the doping of Bi^{3+} does not change the peak position in the phosphor $InNbO_4:Eu^{3+},Bi^{3+}$. However, the emission intensity varies with the content of Bi^{3+} . At the beginning, the luminescence intensity of the phosphors increases with the addition of Bi^{3+} and it grows weaker later on. Only when the doped- Bi^{3+} concentration reaches 4 mol%, the intensity of the peak located at 612 nm is stronger than that of other phosphors. The experimental results make it clear that the effect of the sensitizer Bi^{3+} on the emission of Eu^{3+} is dependent on Bi^{3+} concentration. The more Bi^{3+} ions the phosphor contains, the greater Bi^{3+} aggregates the phosphor will have. These aggregates can weaken the absorbed energy, which leads to the reduction of emission intensity. As a result, the optimum mole concentration of Bi^{3+} in the phosphors $InNbO_4:0.04Eu^{3+}, xBi^{3+}$ investigated in the present work is 4 mol%.



Fig. 5. The influence of Bi^{3+} content on luminescence of InNbO₄:0.04Eu³⁺,xBi³⁺ (x = 0, 0.02, 0.04, 0.06, 0.08). The inset is the emission intensity at 612 nm at different Bi^{3+} concentrations.

4. Conclusions

Briefly, InNbO₄:0.04Eu³⁺,xBi³⁺ red-emitting phosphors were fabricated by a conventional solidstate reaction in air. The phosphors manifested a pure phase and normal size distribution. The excitation and emission spectra of the phosphor InNbO₄:0.04Eu³⁺,xBi³⁺ revealed that it can be effectively excited by UV (394 nm) or blue light (466 nm) to emit red light at 612 nm. Bi³⁺ doping has not changed the peak position in the spectra but increased the intensity of Eu³⁺ transition. The photoluminescence intensity of the asprepared phosphor increased with increasing Bi³⁺ concentration at the beginning, but then decreased. For Bi^{3+} doping concentration of 4 mol%, the maximal value of photoluminescence intensity has been obtained. On the basis of the above results, InNbO₄:0.04Eu³⁺,0.04Bi³⁺ may be a promising red-emitting phosphor for white LEDs.

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