Luminescent properties of a new red-emitting phosphor based on LaInO$_3$ for LED

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Red-emitting phosphor LaInO$_3$:Eu^{3+} for LED was synthesized by solid-state reaction at 1250 ^{o}C. X-ray diffraction, particle size analyzer and spectrometer were used to characterize the phosphor. The prepared LaInO$_3$:Eu^{3+} phosphor has an orthorhombic crystal structure with pure phase and the average diameter of LaInO$_3$:Eu^{3+}, Bi^{3+} particles is about 2.15 μm. The phosphor LaInO$_3$:Eu^{3+} can be efficiently excited by near ultraviolet and blue light to emit intense red light at 612 nm due to the Eu^{3+} transition of $^5D_0 \rightarrow ^7F_2$. The emission intensity is the strongest when the Eu^{3+} content reaches 0.20 mole fraction. The optimal Bi^{3+} concentration in the LaInO$_3$:0.20Eu^{3+} is 0.03 mole fraction. The luminescence intensity of the LaInO$_3$:0.20Eu^{3+}, 0.03Bi^{3+} is higher than that of without Bi^{3+} phosphor. The results indicate that LaInO$_3$:Eu^{3+},Bi^{3+} phosphor is a prospective potoluminescent material for white LED.

1. Introduction

The field of application for white LED has brought about a broad attention since the white LED came out [1]. However there are two main defects in the white LED [2,3]. One is higher color temperature and the other is lower color rendering index because of lacking the red spectrum ingredient [4-6]. There are two basic ways to solve those problems. Firstly, the blue LED chip is coated by red and green emitting phosphors to obtain a white source [7]. Secondly, the UV LED chip combines with three primary colors (red, green and blue) to get a promising white light fabrication [8]. Regardless of the both ways, it is necessary to develop red-emitting phosphors. At present the commercial Y$_2$O$_2$S:Eu^{3+} red phosphors for white LED have some deficiencies such as chemical unsteadiness, low luminescent efficiency and intensity [9,10]. Therefore getting high-quality red phosphors has received much concern.

Indates doped with rare-earth ions are considered as photoluminescent and cathodoluminescent phosphors. Alkali earth indate phosphors show excellent photoluminescent properties. Kao et al. doped Pr^{3+} in the SrIn$_2$O$_4$ phosphor and found that the hue of SrIn$_2$O$_4$:Pr^{3+} was obviously more orange-red than that of Y$_2$O$_2$S:Eu^{3+} [11]. Yang et al. prepared the phosphor SrIn$_2$O$_4$:Eu^{3+} by combustion and concluded that the phosphor could emit intense red light under UV and blue light excitation [12]. Rare-earth indates belongs to the materials that are stable. Generally they don't absorb moisture and they are practically insoluble in acid.

But there are no reports on the rare-earth indate phosphors. In this work, we synthesized LaInO$_3$:Eu^{3+} red-emitting phosphors and investigated the luminescent properties of them. At the same time, Bi^{3+}-doped LaInO$_3$:Eu^{3+} phosphors were also researched.

2. Experimental

The phosphors of LaInO$_3$:Eu^{3+}, Bi^{3+} were prepared by the high temperature solid-state reaction method. La$_2$O$_3$(99.99%), In$_2$O$_3$(99.99%), Eu$_2$O$_3$(99.99%) and Bi$_2$O$_3$(analytical grade) were used as the starting materials. They were weighed in right stoichiometric ratio. After the corresponding materials were entirely mixed and pulverized in an agate mortar, the mixture was put into an alumina crucible. It was preheated at 600 ^{o}C for 4h and next heated at 1250 ^{o}C for 6h at air atmosphere in an electric furnace. Then it was cooled in air with the furnace.

The phase composition of the phosphor was checked by X-ray diffraction (XRD) analysis with Cu Kα radiation under 40 kV and 150 mA. The particles size distribution was observed by the Shimadzu SA-CP3. The excitation and emission spectra were examined by RF-5301 molecular fluorescence spectrometer whose sensitivity parameter was low. Every sample was tested three times and the slit width of the excitation and emission was 3 nm. The above experiments were carried out at room temperature.

3. Results and discussion

3.1 XRD analysis and size distribution characterization

Fig. 1 shows the XRD patterns of the $LaInO_3:Eu^{3+}$ and $LaInO_3:Eu^{3+}$, Bi^{3+} samples prepared at 1250 °C. The XRD peaks of the samples were observed to be completely in accord with the Joint Committee on Powder Diffraction Standards (JCPDS No. 09-0034). According to the JCPDS, pure $LaInO_3$ has an orthorhombic crystal structure with the lattice parameters of a=1.140 nm, b=0.8198 nm and c=1.180 nm. The XRD result shows that the host structure of matrix $LaInO_3$ is not changed by doping a small amount of Eu^{3+} and Bi^{3+}. However the peak intensity of the Bi^{3+}-doped sample is stronger than that of no doping-Bi^{3+} sample owing to the crystallinity increasing. Because the ionic radii of Eu^{3+} (0.107 nm) and Bi^{3+} (0.117 nm) are similar to La^{3+} (0.116 nm) [13], it can be suggested that both Eu^{3+} and Bi^{3+} occupy La^{3+} in the matrix $LaInO_3$.
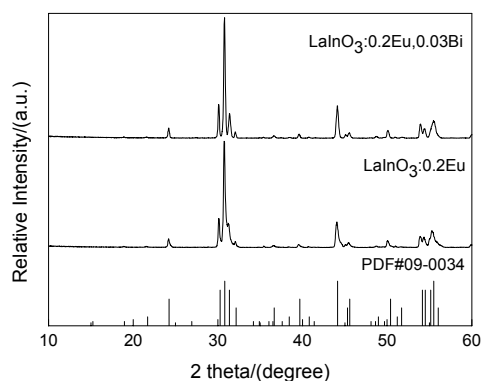

Fig. 1. XRD patterns of $LaInO_3:Eu^{3+}$ and $LaInO_3:Eu^{3+},Bi^{3+}$ samples prepared at 1250 °C.

The particle size distribution of the $LaInO_3:Eu^{3+}$, Bi^{3+} phosphor calcined at 1250 °C is shown in Fig. 2. The particles illustrate a narrow size distribution and the average diameter of the particles is about 2.15 μm, which indicates that the particles are fit to fabricate the solid-light devices [14].
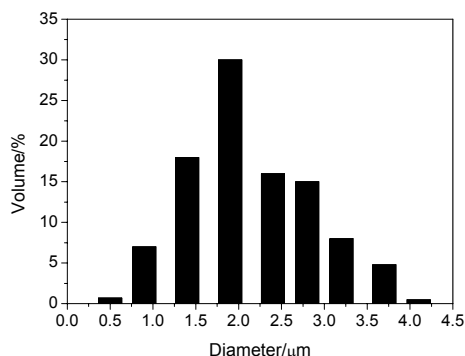

Fig. 2. Particle size distribution of $LaInO_3:Eu^{3+}$, Bi^{3+} phosphor.

3.2 Luminescence properties of $LaInO_3:Eu^{3+}$ phosphors

The excitation spectrum of phosphor $La_{0.80}InO_3:0.20Eu^{3+}$ is shown in Fig. 3. The figure can be divided into two parts. The one pertains to the broad band below 361 nm and the other belongs to the narrow band above 361 nm. The broad excitation bands correspond to the charge transfer process of Eu^{3+}-O^{2-} and the band gap transition of the $LaInO_3$ host lattice [11,15]. The narrow strong peaks are ascribed to f-f transitions of Eu^{3+}, which respectively belongs to 394 nm ($^7F_0 \rightarrow {}^5L_6$), 464 nm ($^7F_0 \rightarrow {}^5D_2$) and 533 nm ($^7F_0 \rightarrow {}^5D_1$) [16]. In these peaks, there exit two intense peaks at 394 and 464 nm, which can match well with the wavelength emitted by ultraviolet and blue LED chips. That is to say, $LaInO_3:Eu^{3+}$ phosphors can be probably used to fabricate LED as photoluminescence materials.

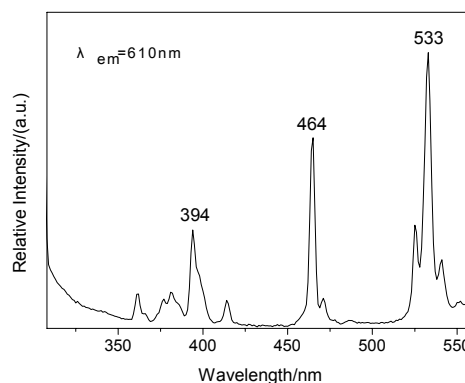*Fig. 3. The excitation spectrum of $La_{0.80}InO_3:0.20Eu^{3+}$.*

Fig. 4 shows the emission spectra of phosphor $La_{0.80}InO_3:0.20Eu^{3+}$ excited by 394 nm and 464 nm wavelength. Both of the curves have the similar shape except for the difference of the relative intensities. The strongest peak at about 612 nm is due to $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} and the peak at around 588 nm is attributed to $^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+}. The fact indicates that Eu^{3+} occupies the center site of asymmetry [17]. Moreover, among all of the emitting peaks, the peak at 612 nm has an apparently strongest intensity. It is also suggested that the phosphor $LaInO_3:Eu^{3+}$ can become a good red-emitting phosphor.

The inset of Fig. 4 describes the variation of the luminescence relative intensity with different doping-Eu^{3+} content. For the phosphor $LaInO_3:Eu^{3+}$, the emission intensity reaches the maximum when x value is 0.20. Once x value is beyond 0.20, the intensity will decrease quickly, which is considered to be the common behavior of concentration quenching. The quenching is due to the association with different effects such as the interactions among Eu^{3+}, energy migration through the lattice [18,19].
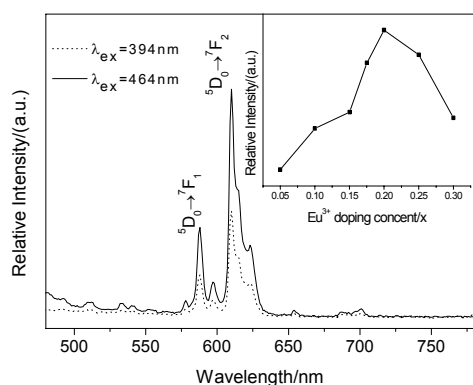
Fig. 4. The emission spectra of La$_{0.80}$InO$_3$:0.20Eu^{3+} and the inset is the variation of the luminescence intensity with the different content of Eu^{3+} in the LaInO$_3$:Eu^{3+} phosphors.
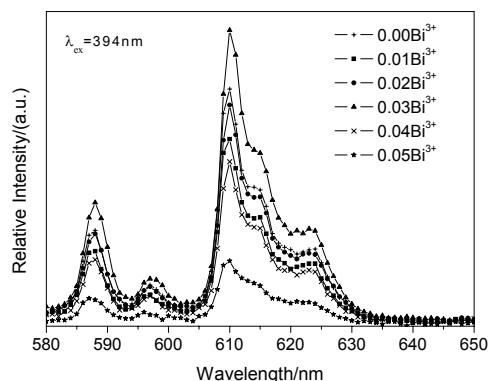

Fig. 5. Emission spectra of the LaInO$_3$:Eu^{3+},Bi^{3+} phosphors excited at 394 nm.

3.3 The influence of Bi^{3+} on LaInO$_3$:Eu^{3+} phosphors

Fig. 5 exhibits the emission spectra of the LaInO$_3$:0.2Eu^{3+} phosphors with the addition of Bi^{3+}. Compared with no Bi^{3+} phosphor, the peak position and shape in the emission spectra of the doping-Bi^{3+} phosphor remain unchanged except the luminescence intensity. It shows that the introduction of Bi^{3+} does not alter the sublattice structure near the luminescent centers of Eu^{3+} ions [20]. It is well consistent with the result of XRD characterization. The luminescent intensity of the phosphor at 612 nm is stronger than that of without Bi^{3+} phosphor when the Bi^{3+} content is 0.03 mole fraction. For the phosphor LaInO$_3$:Eu^{3+} doped with Bi^{3+}, the luminescence intensity increases with the increasing of Bi^{3+} content at first. The intensity achieves the maximum when the Bi^{3+} mole fraction is 0.03 and finally decreases with the Bi^{3+} concentration increasing. The above results show that the effect of sensitization Bi^{3+} on the activator Eu^{3+} depends on the Bi^{3+} concentration. Smaller Bi^{3+} contents are not propitious for the improvement of luminescence intensity, while higher Bi^{3+} concentration has a greater tendency to transfer more energy to Eu^{3+}. This kind of energy transfer from Bi^{3+} to Eu^{3+} improves the photoluminescence intensity. However excessive Bi^{3+} ions in the phosphor will give rise to concentration quenching due to the aggregates of Bi^{3+} [21]. The aggregates play a positive role in the trapping centers and cause the migration of excitation energy. The energy migration dissipates the absorbed energy, which results in non-radiative transition and impacts on the descent of the luminescence intensity. It is suggested that the optimal concentration of Bi^{3+} is 0.03 mole fraction and the phosphor has the strongest luminescence intensity for LaInO$_3$:0.20Eu^{3+}, Bi^{3+} phosphor. The CIE chromaticity coordinates of the phosphors are respectively calculated to be x=0.61, y=0.32 for LaInO$_3$:0.20Eu^{3+} and x=0.64, y=0.31 for LaInO$_3$:0.20Eu^{3+}, 0.03Bi^{3+}. Both of the ordinates are close to the standard of NTSC (x=0.67, y=0.33).

4. Conclusions

A new red-emitting phosphor LaInO$_3$:Eu^{3+} was synthesized by the high temperature solid-state reaction and its luminescent properties were also studied. The results show that the phosphor LaInO$_3$:Eu^{3+} can emit strong red light at 612 nm by the excitation of near ultraviolet light (394 nm) and blue light (464 nm). The concentration quenching of the phosphor LaInO$_3$:Eu^{3+} will happen when the Eu^{3+} content is beyond 0.20 mole fraction. For the Bi^{3+}-doped phosphor, the luminescence intensity increases with the increasing of Bi^{3+} content and decreases when the Bi^{3+} mole fraction is beyond 0.03. Compared with the phosphor without Bi^{3+}, the phosphor LaInO$_3$:0.20Eu^{3+}, 0.03Bi^{3+} has the strongest luminescence intensity. If it is possible, this phosphor would be used as a promising photoluminescent material for white LED.

References

[1] S. Neeraj, N. Kijima, A. K. Cheetham, Solid State Commun. **131,** 65 (2004).
[2] A. R. Zanatta, H. H. Richardson, M. E. Kordesch, Phys. Status Solidi-R. **1,** 153 (2007).
[3] Y. Arai, T. Takahashi, S. Adachi, Opt. Mater. **32,** 1095 (2010).
[4] S. Ekambaram. M. Maaza, J. Alloy Compd. **395,** 132 (2005).
[5] Z. P. Ci, Y. H. Wang, J. C. Zhang, Y. K. Sun, Physica B. **403,** 670 (2008).
[6] C. Y. Shen, Y. Yang, S. Z. Jin, J. Z. Ming, H. J. Feng, Z. H. Xu, Physica B. **404,** 1481 (2009).
[7] L. H. Yi, L.Y. Zhou, Z. L. Wang, J. H. Sun, F. Z. Gong, W. P. Wan, W. Wang, Curr. Appl. Phys. **10,** 208

(2010).

[8] M. M. Haque, D. Kim, Mater. Lett. **63,** 793 (2009).

[9] S. Neeraj, N. Kijima, A. K. Cheetham, Chem. Phys. Lett. **387,** 2 (2004).

[10] F. Xiao, Y. N. Xue, Q. Y. Zhang, Spectrochim. Acta A. **74,** 758 (2009).

[11] F. S. Kao, T. M. Chen, J. Solid State Chem. **156,** 84 (2001).

[12] Z. P. Yang, J. Tian, S. L. Wang, G. W. Yang, X. Li, P. L. Li, Mater. Lett. **62,** 1369 (2008).

[13] J. L. Huang, L. Y. Zhou, Z. P. Liang, F. Z. Gong, J. P. Han, R. F. Wang, J. Rare Earth. **28,** 356 (2010).

[14] R. P. Rao, J. Electrochem. Soc. **143,** 189 (1996).

[15] J. Liu, H. Z. Lian, C. S. Shi, Opt. Mater. **29,** 1591 (2007).

[16] Y. Guo, M. Sun, W. M. Guo, F. Q. Ren, D. H. Chen, Opt. Laser Technol. **42,** 1328 (2010).

[17] L. H. Yi, X. P. He, L. Y. Zhou, F. Z. Gong, R. F. Wang, J. H. Sun, J. Lumin. **130,** 1113 (2010).

[18] Z. F. Qiu, Y. Y. Zhou, M. K. Lu, A. Y. Zhang, Q. Ma, Mater. Chem. Phys. **109,** 556 (2008).

[19] Y. Guo, M. Sun, W. M. Guo, F. Q. Ren, D. H. Chen, Opt. Laser Technol. **42,** 1328 (2010).

[20] Z. L. Wang, H. B. Liang, Q. Wang, M. H. Chen, M. L. Gong, Q. Su, Phys. Status Solidi A. **206,** 1589 (2009).

[21] Z. L. Wang, H. B. Liang, M. L. Gong, Q. Su, Opt. Mater. **29,** 896 (2007).

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