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Garnet-based red emitting phosphors $Li_6MLa_2Nb_2O_{12}$: Eu^{3+} (M=Ca, Sr, Ba): Photoluminescence improvement by changing crystal lattice

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Abstract

A series of novel red emitting phosphors $Li_6M(La_{1-x}Eu_x)_2Nb_2O_{12}$ (M=Ca, Sr, Ba; $0 \le x \le 0.3$) were synthesized by solid state reaction, and their structures and photoluminescence properties were investigated in detail. The excitation spectrum of $Li_6M(La_{1-x}Eu_x)_2Nb_2O_{12}$ revealed two mainly excitation bands at 393 nm and 464 nm, which match well with the two popular emissions from near-UV and blue LED chips. Upon the 464 nm light excitation, $Li_6MLa_2Nb_2O_{12}$:Eu^{3+} phosphors exhibit a red emission centered at 608 nm, originated from the $^5D_0$–$^7F_2$ transition of Eu^{3+} ions. The Eu^{3+} surrounding crystal lattice environment in the garnet-based host was changed by altering the *c* sites element with different radii alkaline earth Ba, Sr, and Ca. The evident photoluminescence enhancement was observed in $Li_6M(La_{1-x}Eu_x)_2Nb_2O_{12}$ phosphors with the decreasing of the *c* sites ionic radius. The emission intensity of the optimized $Li_6Ca(La_{0.8}Eu_{0.2})_2Nb_2O_{12}$ (λ_{exc}=464 nm) phosphor is about two times higher than that of Y_2O_3:Eu^{3+} (λ_{exc}=467 nm) under blue light excitation. In addition, the quenching mechanism and the relationship between the structure and photoluminescence property were also discussed.

Keywords: Red phosphor; Garnet structure; W-LEDs; Photoluminescence

1. Introduction

White light emitting diodes (W-LEDs) are considered as the next-generation lighting source for general illumination due to their superior features such as high brightness, high efficiency, long lifetimes, low power consumption and environment friendliness [1–3]. Currently, the commercial W-LEDs are mostly fabricated by combining a blue-emitting LED chip with yellow-emitting phosphor (YAG:Ce^{3+}). However, this type of white light suffers from low color rending index and unsatisfactory high color temperature because of the lack of red spectral component in the emission spectra of the YAG:Ce^{3+} phosphor [4,5]. One alternative solution to this problem is to excite red/green/blue tricolor phosphors by using near-UV LED, such as by the pumping of red, green and blue phosphors with a UV LED or by using a blue LED in conjunction with green and red phosphors [6]. However, the current red phosphors are not stable like sulfides and oxysulfides (SrY_2S_4:Eu^{2+} [7], Y_2O_2S:Eu^{3+} [8]), or have rigorous synthesis conditions like nitrides and oxynitrides ($Ba_2Si_5N_8$:Eu^{2+} [9], $CaAlSiN_3$:Eu^{2+} [10], β-SiAlON:Pr^{3+} [11]). Therefore, the red phosphors still require more attention.

Garnet-type materials own stable lattice and large heat conductivity, and are suitable as host for optical materials [12,13]. For example, YAG, a represent of garnet type compound, was widely researched as scintillation counter and laser host material [14,15]. YAG:Ce^{3+} was also widely used as yellow emitting phosphor and commercially available [16]. Therefore, the development of phosphors based on garnet-type materials is of great interest. Garnet-like structured metal oxides with the general formula $Li_6MLa_2Nb_2O_{12}$

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(abbreviated as LMG) are isostructural with the parent compound $Li_5La_3Nb_2O_{12}$ [17,18]. The mechanism of Li-ion transport has been widely investigated in the LMG [17–20]. However, to the best of our knowledge, there is no report on the research of Eu^{3+}-doped LMG phosphors. Thus, in this paper we reported the preparation and investigation on luminescence properties of a series of novel red-emitting LMG:Eu^{3+} phosphors. XRD, UV-abs spectra and Photoluminescence (PL) were used to characterize the properties of the as-prepared phosphors. Furthermore, the relationship between the structure and photoluminescence properties was also investigated in detail. Our research of this work also provides an inspiration to explore novel phosphors used in W-LEDs.

2. Experimental

2.1. Sample preparation

Samples of $Li_6M(La_{1-x}Eu_x)_2Nb_2O_{12}$ $(0 \le x \le 0.3)$ were prepared by solid state reaction, using stoichiometric amounts of Li_2CO_3, MCO_3 (M=Ca, Sr, Ba; Adamas-beta; all A.R.) and Nb_2O_5, La_2O_3,Eu_2O_3 (Adamas-beta, 99.99%). Powders were thoroughly mixed in an agate. The mixtures were then transferred to the corundum crucibles, and heated at 1000 °C for 24 h in air to produce the final samples. In addition, the available commercial red phosphor Y_2O_3:Eu^{3+} was bought from company (Xinchangji Luminate material Co., Ltd.), which has been widely used in the LEDs production.

2.2. Characterization

The phase purity of the samples were characterized using powder X-ray diffraction (XRD) analysis on a Bruker D8 Focus diffractometer with Cu K_a radiation operated at 40 kV and 40 mA. UV–visible spectra were obtained by a diffuse reflection method with a Spectrophotometer (Hitachi U-3010) by $BaSO_4$ as a reflectance standard. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were analyzed using a FluoroMax-4 fluorescence spectrometer with a 450 W Xenon lamp as light source at room temperature.

3. Results and discussions

3.1. X-ray diffraction analysis

XRD patterns of LMG:Eu^{3+} phosphors are shown in Fig. 1. The diffraction peaks of the LMG samples are similar and in excellent agreement with the results reported by V. Thangadurai, et al. [17,18]. The garnet structure belongs to the space group *Ia3d* with cations 16(*a*), 24(*c*) and 24(*d*) positions [21], and M is located at *c* sites in $Li_6MLa_2Nb_2O_{12}$. Fig. 1a shows the XRD patterns of the $Li_6Ba(La_{1-x}Eu_x)_2Nb_2O_{12}$($x$=0, 0.02, 0.05; abbreviated as LBG:$x$$Eu^{3+}$) and $Li_6Sr(La_{0.98}Eu_{0.02})_2Nb_2O_{12}$ (abbreviated as LSG:0.02Eu^{3+}). When Eu^{3+} content was more than 2 mol%, impurity phase ($Ba_2EuNb_2O_6$, JCPDS No. 49-1530) was detected in the LBG:Eu^{3+} samples, and impurity phase of $Sr_5Nb_4O_{15}$ (JCPDS No. 83-0132) was also detected in LSG:0.02Eu^{3+}. Fig. 1b shows the XRD patterns of the $Li_6Ca(La_{1-x}Eu_x)_2Nb_2O_{12}$($0 \le x \le 0.30$; abbreviated as LCG:$x$$Eu^{3+}$). No impurities were detected in the samples with the doped Eu^{3+} ions concentration below 20 mol%. However, some impurities ($EuNb_8O_{14}$ JCPDS No.83-0870, $Ca_3Nb_2O_8$ JCPDS NO.15-0553, Li_3NbO_4 JCPDS NO.82-1198) were observed when Eu^{3+} content reached 30 mol%, due to an occurrence of solubility saturation. The ionic radius of Eu^{3+} (1.066 Å, coordination number (CN)=8) is close to La^{3+} (1.16 Å, CN=8). In view of the similar ion radius and valence, the Eu^{3+} ions are expected to substitute of the La^{3+} ions sites in LMG host structure. The eight-fold coordination ionic radius of Ca^{2+} (1.12 Å, CN=8) is smaller than those of Sr^{2+} (1.25 Å, CN=8) and Ba^{2+} (1.42 Å, CN=8). Therefore, the changing of *c* sites ions may lead to changes of the Eu^{3+} surrounding environment in the lattice, and cause Eu^{3+} ions exhibit different PL performances in different hosts. These will be discussed in the latter section.

3.2. Absorption spectra

UV–vis absorbance spectra of the selected samples are shown in Fig. 2. The absorption spectra of Eu^{3+}-doped LMG exhibit a strong absorption band below 400 nm, attributing to the charge transfer absorption (CTA) between the valance band and the empty conduction in the host crystal

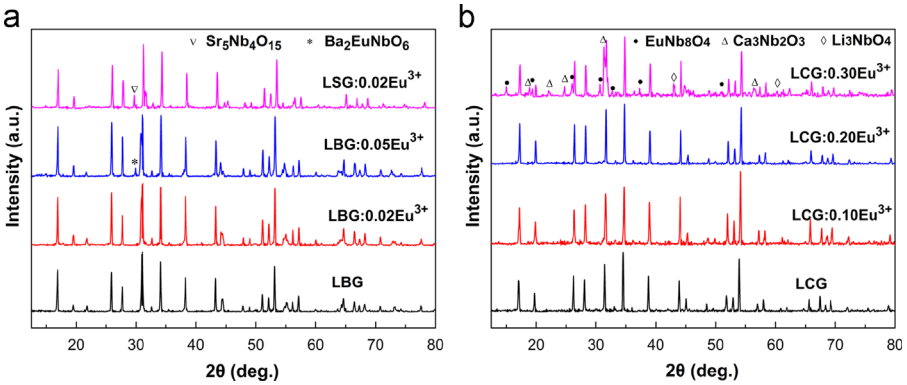

Fig. 1. XRD patterns of (a) LBG:$x$$Eu^{3+}$ (x=0, 0.02, 0.05) and LSG:0.02Eu^{3+}, (b) LCG:$x$$Eu^{3+}$ ($0 \le x \le 0.30$) phosphors. All peaks of impurities are labeled.

[22]. The peaks located at 393 nm and 464 nm in LCG:0.2Eu^{3+} sample are associated with typical intra–4f forbidden transitions of the Eu^{3+} ions. They exhibit weak intensities in other samples due to the low doping concentration of Eu^{3+}.

3.3. Photoluminescence properties of Eu^{3+}-doped $Li_6MLa_2Nb_2O_{12}$ phosphors

Fig. 3a illustrates the excitation spectra of LMG:0.02Eu^{3+}. The broad excitation band (260–340 nm) is originated from the charge transfer transitions between metal cations and oxygen anions in the host crystal, and the sharp lines at wavelengths 361, 378, 383, 393, 415 and 464 nm are assigned to the intra-configurational 4f–4f forbidden transitions of Eu^{3+} $^7F_0$–$^5D_4$, $^7F_0$–^5G_J, $^7F_0$–$^5L_7$, $^7F_0$–$^5L_6$, $^7F_0$–$^5D_3$ and $^7F_0$–$^5D_2$, respectively [6]. It can be seen clearly that the excitation peaks mainly exist at 393 nm and 464 nm, which indicate that the LMG:Eu^{3+} phosphors may be suitably excited by near-UV and blue LED chips. The emission spectrum of LMG:Eu^{3+} and Y_2O_3:Eu^{3+} are shown in Fig. 3b. For LMG:Eu^{3+} samples, peaks at 578 nm, 588 nm, 608 nm, 627 nm and 654 nm in emission spectra can be ascribed to $^5D_0$–^7F_J (J=0–4) transitions of Eu^{3+} ions [23]. Among these peaks, the peak at 608 nm is dominant, which is from the Eu^{3+} electric dipole transitions of $^5D_0$–$^7F_2$, indicating Eu^{3+} occupies a non-symmetry site in the host lattice [24,25].

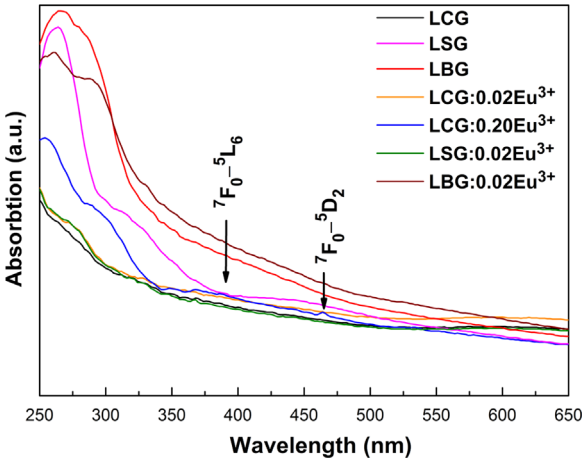

Fig. 2. The absorption spectra of LMG:Eu^{3+} (M=Ca, Sr, Ba).

Fig. 3c shows emission intensity of LCG:$x$$Eu^{3+}$ as a function of Eu^{3+} content. The optimal concentration for LCG:$x$$Eu^{3+}$ to obtain the strongest PL intensity is 20 mol%. For samples with higher Eu^{3+} concentration, PL intensity decreased, due to the concentration quenching effect. Concentration quenching is caused by the energy transfer between luminescent centers, and these energy-transfer chains trigger energy migration to the energy sink such as crystalline defects or trace ions [26]. The critical distance (R_c) was used to characterize the distance of active centers (Eu^{3+} ions) corresponding to the critical concentration (x_c). This critical distance can be estimated using the Blasse's relation [27]: $R_c \approx 2(3V/4\pi x_c N)^{1/3}$. Where V represents a

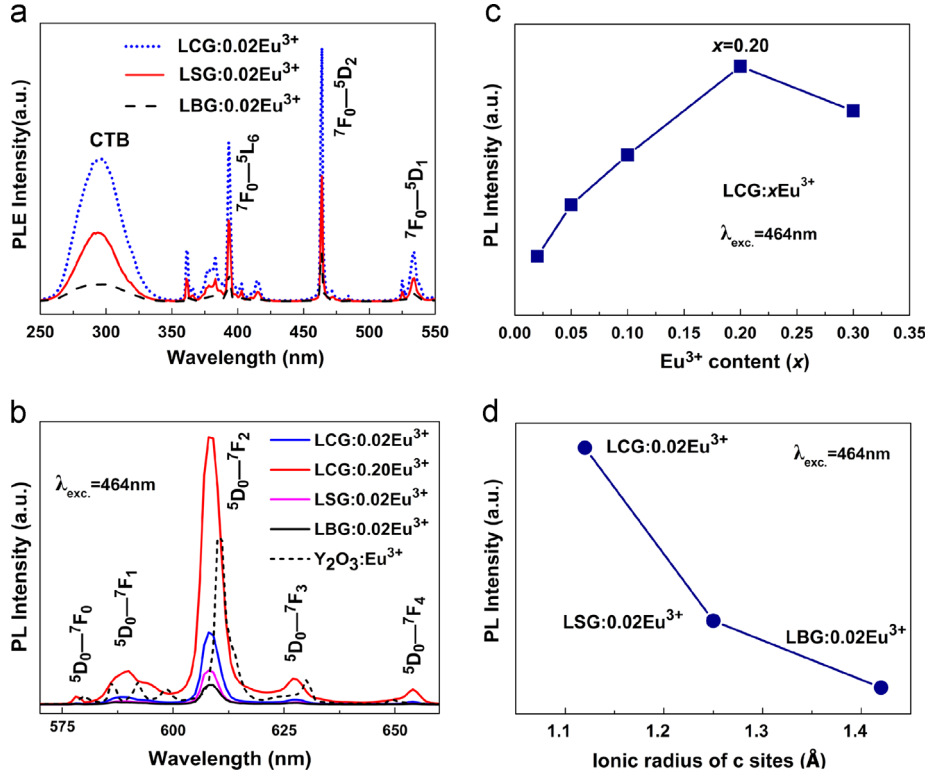

Fig. 3. (a) PLE spectra ($\lambda_{em.}$=608 nm) of LMG:0.02Eu^{3+} (M=Ca, Sr, Ba), (b) PL spectra of LMG:Eu^{3+} (M=Ca, Sr, Ba) ($\lambda_{exc.}$=464 nm) and $(Y_{0.95}Eu_{0.05})_2O_3$ ($\lambda_{exc.}$=467 nm), (c) PL intensity of LCG:$x$$Eu^{3+}$ (x=0.02, 0.05, 0.10, 0.20, 0.30) as a function of Eu^{3+} content, and (d) the plot of the intensity from $^5D_0$ to $^7F_2$ versus ionic radius of c sites for LMG:0.02Eu^{3+} (M=Ca, Sr, Ba).

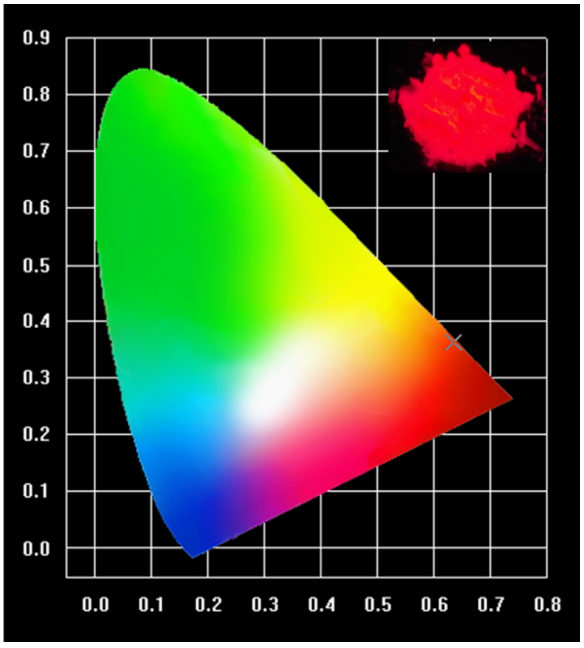

Fig. 4. The 1931 CIE chromaticity diagram with points indicating coordinates for the LCG:0.2Eu^{3+} phosphor excited by 464 nm blue light. Inset: photographs of the lighting $Li_6Ca(La_{0.8}Eu_{0.2})_2Nb_2O_{12}$ powder.

volume of the unit cell, x_c means the critical concentration, and N is the number of total Eu^{3+} sites in the unit cell, respectively. For LCG:Eu^{3+}, $N=8$, $V=2046.93$ Å^3, and $x_c=0.20$, the obtained R_c value is 13.47 Å, which is larger than 5 Å. The average distance between the Eu^{3+} ions is large enough, so that the migration is hampered and the killers are not reached, which make the high concentration quenching possible in the LCG:Eu^{3+}. However, as the concentration of Eu^{3+} ions continue to increase, the distance between the Eu^{3+} ions declines sharply, favoring the nonradiative pathway energy transfer among Eu^{3+} ions. On the other side, disturbance from the impurity phases can also lead to a fluctuation of the PL intensity.

The plot of the intensity from $^5D_0$–$^7F_2$ versus c sites ionic radius is shown in Fig. 3d. It can be see clearly that PL intensity increased with the decreasing of the c sites ionic radius. It's well known that the $^5D_0$–$^7F_2$ transition of Eu^{3+} is normally hypersensitive to the crystal environment [28]. The altering of c sites ions lead to changes of the Eu^{3+} surrounding crystal lattice environment. Eu^{3+} ions exhibit different PL performances in these three hosts (as shown in Fig. 3d). The PL intensity of $^5D_0$–$^7F_2$ was improved gradually from LBG:Eu^{3+} to LSG:Eu^{3+} and eventually to LCG:Eu^{3+}. The red emission intensity of the composition-optimized LCG:0.2Eu^{3+} even reached two times higher than that of Y_2O_3:Eu^{3+} under blue excitation.

3.4. CIE chromaticity coordinates of LCG:Eu^{3+} phosphor

The color coordinates of LCG:Eu^{3+} phosphor are shown in Fig. 4. The inset diagram shows the $Li_6Ca(La_{0.8}Eu_{0.2})_2Nb_2O_{12}$ powder photographed under the 365 nm UV on a quartz slide in the dark room. The CIE chromaticity coordinates of the composition-optimized LCG:0.20Eu^{3+} phosphor are ($x=0.635$ and $y=0.363$), which are close to the standard of NTSC ($x=0.670$ and $y=0.330$). Thus, it can be used to compensate the red color deficiency of YAG:Ce^{3+} based white LEDs or create white light by combining with a blue chip and a green phosphors. So LCG:Eu^{3+} red phosphors may have a potential application for white LEDs.

4. Conclusions

In summary, we have successfully prepared Eu^{3+}-activated $Li_6MLa_2Nb_2O_{12}$ (M=Ca, Sr, Ba) red phosphors by solid state reaction method. Under 464 nm light excitation, the phosphors show strong red emission at 608 nm, corresponding to the $^5D_0$–$^7F_2$ transition of Eu^{3+} ion. The photoluminescence properties were gradually improved by changing the c sites element and component optimization. The red emission intensity of the composition-optimized LCG:0.2Eu^{3+} was about two times higher than that of phosphor Y_2O_3:Eu^{3+} under blue light excitation. The CIE chromaticity coordinates of LCG:0.2Eu^{3+} were ($x=0.635$, $y=0.363$), Which are close to the standard of NTSC ($x=0.670$ and $y=0.330$). All the results show that the series of $Li_6M(La_{1-x}Eu_x)_2Nb_2O_{12}$ phosphors are a promising red emitting phosphor for W-LEDs application. This work also provides an inspiration to explore novel phosphor used in W-LEDs.

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