Journal of Alloys and Compounds 509 (2011) L341–L343

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Letter

Multiwavelength excited novel red-emitting phosphor Eu^{3+}-activated $Li_2Zn_2(MoO_4)_3$

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ARTICLE INFO

Article history:
Received 18 April 2011
Received in revised form 17 June 2011
Accepted 17 June 2011
Available online 24 June 2011

Keywords:
Phosphors
Solid state reactions
X-ray diffraction
Luminescence

ABSTRACT

Eu^{3+}-activated $Li_2Zn_2(MoO_4)_3$ multiwavelength excited red-emitting phosphors were synthesized via a solid state reaction. The structure and photoluminescence characteristics were investigated by X-ray powder diffraction and fluorescent spectrophotometry, respectively. The excitation spectrum included a strong broadband ranging from 250 to 350 nm and some sharp peaks at 363, 384, 395, 465, and 533 nm, which matchs the radiations of near-UV or blue light-emitting diodes chip well. Upon excitation either of near-UV or blue even green light, the intense red emission with 615 nm peak can be observed, which is ascribed to the $^5D_0$–$^7F_2$ transition of Eu^{3+} ions. The chromaticity coordinates ($x = 0.65$, $y = 0.34$) of the as-obtained phosphor is very close to the National Television Standard Committee standard values ($x = 0.67$, $y = 0.33$). All these characteristics suggest that Eu^{3+}-doped $Li_2Zn_2(MoO_4)_3$ wavelength-conversion material to be suitable candidate red component for phosphor-converted white light-emitting diodes.

1. Introduction

In recent years, phosphor-converted white light-emitting diodes (pc-white-LEDs) are the subject of increasing interest due to their long lifetime, high energy-efficiency, reliability, durability and environmentally friendly characteristics [1–4]. The pc-white-LEDs are usually fabricated by a near-UV or blue emitting semiconductor chip coated with wavelength-conversion luminescent materials layer. The eventual performance of pc-white-LEDs devices strongly depends on the luminescence properties of the phosphors used. Therefore, the state-of-the-art pc-white-LEDs devices would be notably advanced by the discovery of phosphor materials that are optimized for pc-white-LEDs. The most frequently used red-emitting phosphor for near-UV LEDs is Y_2O_2S:Eu^{3+}. However, Y_2O_2S:Eu^{3+} phosphor has poor absorption in near-UV region where LED chips emission occurs. A good strategy to overcome this problem is to search for a host lattice that can absorb energy efficiently in the near-UV region and transfer the energy to the activator, resulting in emission in the red region (host sensitized emission) [5,6]. Hence, there has been a widespread and growing interest in the discovery or development of novel families of red-emitting phosphors with strong absorption in the near-UV to blue spectral region [5–11].

Double molybdates own excellent thermal and hydrolytic stability and are suitable as host for optical materials [12–14]. Eu^{3+} is an excellent red-emitting activator in many classic phosphors such as Y_2O_2S:Eu^{3+}, YVO_4:Eu^{3+}. Therefore, Eu^{3+}-doped double molybdates phosphors have attracted a great deal of attention because they exhibit intense charge-transfer absorption bands in near-UV and effective 4f–4f transitions of Eu^{3+} [10–14]. Following the excitation in the near-UV, the energy absorbed by the host can be transferred to Eu^{3+} ions via a non-radiative mechanism, which leads to pure red emission. As a member of this family, $Li_2Zn_2(MoO_4)_3$ was recently found to be a kind of tunable refractive index materials in the middle- and near-ultraviolet region [15]. Solodovnikov et al. explored the scintillating characteristics of $Li_2Zn_2(MoO_4)_3$ crystal [16,17]. This compound is expected to be used as a host lattice, because Li^+ and Zn^{2+} are randomly distributed over the same cationic sublattice, resulting in a local lattice disorder around the activator ions [15,16,18,19]. However, less information is available concerning the luminescence of $Li_2Zn_2(MoO_4)_3$ based materials. Herein, we synthesized Eu^{3+}-activated $Li_2Zn_2(MoO_4)_3$ red-emitting phosphors and investigated their composition-dependent photoluminescence properties.

2. Experimental procedures

Eu^{3+}-doped $Li_2Zn_2(MoO_4)_3$ phosphors with nominal composition of $Li_{2-2t}Zn_{1.90+t}(MoO_4)_3$:$0.05Eu^{3+}$,$0.05Li^+$ (abbreviated as LZMO:Eu^{3+} hereafter, $-0.10 \le t \le 0.30$) were prepared through a typical solid state reaction in air. The starting materials, Li_2CO_3 (98.0%), ZnO (99.95%), MoO_3 (99.5%) and Eu_2O_3 (99.99%) were thoroughly mixed in the stoichiometric ratio by grinding for 0.5 h in an agate mortar and pressed into pellets with diameter of 12 mm and thickness of 2–3 mm. A small amount of acetone was added during the grindings in order to obtain homogenous mixtures. The pellets were sintered at 600 °C in air for 2 h in a muffle

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doi:10.1016/j.jallcom.2011.06.083

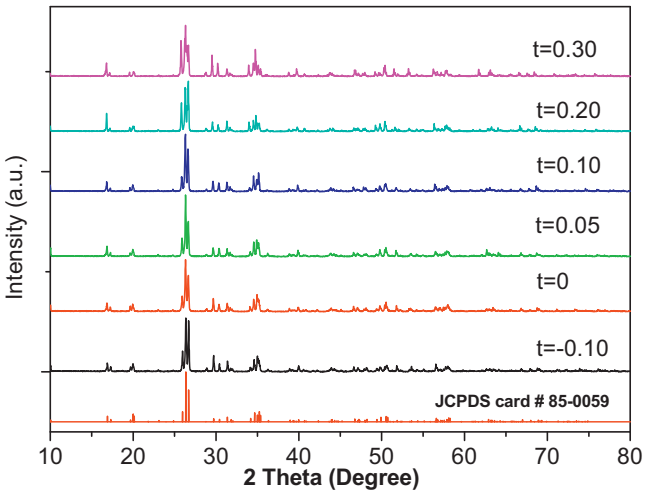

Fig. 1. XRD patterns of $Li_{2-2t}Zn_{1.90+t}(MoO_4)_3$:0.05$Eu^{3+}$,0.05$Li^+$ ($-0.10 \le t \le 0.30$) phosphors and JCPDS card no. 85-0059 as a reference.

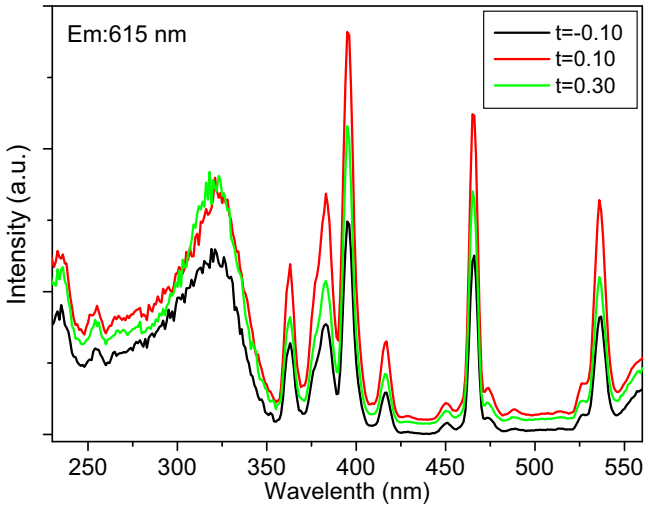

Fig. 2. Excitation spectra of $Li_{2-2t}Zn_{1.90+t}(MoO_4)_3$:0.05$Eu^{3+}$,0.05$Li^+$ phosphors with various t values (monitoring wavelength λ_{em} = 615 nm).

furnace, followed by calcination at 800 °C for another 4 h. Finally, the samples are ground into powder for characterizations.

The powder samples were characterized by X-ray powder diffraction (XRD), and fluorescent spectrophotometry. The XRD was carried out with a Japan Rigaku D/max-rA rotation anode X-ray diffractometer, using Ni-filtered Cu K_α radiation. A scan rate of 0.02°/s was applied to record the patterns in the 2θ range 10–90°. Excitation and emission spectra of powders were recorded using fluorescence spectrofluorometer (Varain Cary-Eclipse). All the measurements were performed at room temperature.

3. Results and discussion

The body colors of as-obtained phosphor powders are white. XRD patterns of LZMO:Eu^{3+} with various t values are shown in Fig. 1. All the peaks can be indexed to isostructural $Li_2Co_2(MoO_4)_3$ phase (JCPDS no. 85-0059) with orthorhombic system and space group *Pnma* [18]. The incorporation of Eu^{3+} ions with low content (5.0 mol%) does not clearly alter the lattice structure of host. As the t value varies, XRD patterns were found to be similar without showing discernable shifting. No impurity phases related to the starting materials and intermediates were found, indicating that the as-synthesized compounds are of single phase. In LZMO host lattice, Li atoms could be partially substituted by Zn atoms, resulting in the forming of solid solution in LZMO ($-0.10 \le t \le 0.30$) compound [18,19]. Thus, the framework structure of LZMO:Eu^{3+} retains stable with t ranging from −0.10 to 0.3, which is in good agreement with previous reports [15,16].

Fig. 2 displays the excitation spectra of LZMO:Eu^{3+} phosphors with various t values. When the t value changed from −0.10 to 0.30, the excitation spectra were similar except that the intensity of excitation peaks. Under monitoring at 615 nm corresponding to $^5D_0 \rightarrow {}^5F_2$ emission of Eu^{3+} ions, the phosphors exhibit one broad and strong band as well as some sharp peaks. The broad band between 230 and 350 nm can be attributed to the combinations of charge-transfer (CT) transitions from Mo^{6+}–O^{2-} and Eu^{3+}–O^{2-} [20]. The sharp peaks beyond 350 nm are ascribed to the typical Eu^{3+} intra-$4f^6$ transitions, including the peaks with maximum at 363 nm ($^7F_0 \rightarrow {}^5D_4$), 384 nm ($^7F_0 \rightarrow {}^5G_{2-4}$), 395 nm ($^7F_0 \rightarrow {}^5L_6$), 418 nm ($^7F_0 \rightarrow {}^5D_3$), 465 nm ($^7F_0 \rightarrow {}^5D_2$), and 535 nm ($^7F_1 \rightarrow {}^5D_1$), respectively. The narrowband 4f–4f transitions of Eu^{3+} are more intense than the CT broad band. Of these excitation lines, the intensities of the 395, 383 and 465 nm excitation peaks are much stronger than the others, which indicates that near-UV and blue LEDs are efficient pumping sources in obtaining Eu^{3+} emissions.

Emission spectra of LZMO:Eu^{3+} phosphors with different t values are depicted in Fig. 3. Upon excitation of 395 nm near-UV or 465 nm blue light, the samples show identical spectral emission except for the difference in intensity, which is composed of several narrow spectral lines in the range 500–750 nm. The emission peaks are observed at 592, 615, 654, 702 nm, corresponding to the $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, $^5D_0 \rightarrow {}^7F_4$ transitions of Eu^{3+}, respectively. Of these peaks, the red emission peak at 615 nm is stronger than the other peaks, which is advantageous to obtain good chromaticity coordinates near the National Television Standard Committee (NTSC) standard values [21]. The ratio of the integrated intensities of $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ (i.e. the asymmetric ratio) can be used as an index to measure the site symmetry of Eu^{3+} ions [22]. Generally, the larger the asymmetric ratio, the lower the local symmetry [23]. The asymmetric ratios of LZMO:Eu^{3+} phosphors with t value −0.10, 0.10 and 0.30 were calculated to be 7.16, 5.65, and 5.64, respectively. The larger asymmetric ratios imply that Eu^{3+} ions occupy a non centro-symmetric site in LZMO host. Zn^{2+} is coordinated with six oxygen atoms to form an distorted octahedron with different Zn–O bond lengths in LZMO lattice [18]. The radius of Eu^{3+} ion (95 pm, sixfold coordination) is relatively closer to that of Zn^{2+} ion (74 pm, sixfold coordination). Thus, Eu^{3+} ions were supposed to occupy the Zn^{2+} crystallographic sites rather than

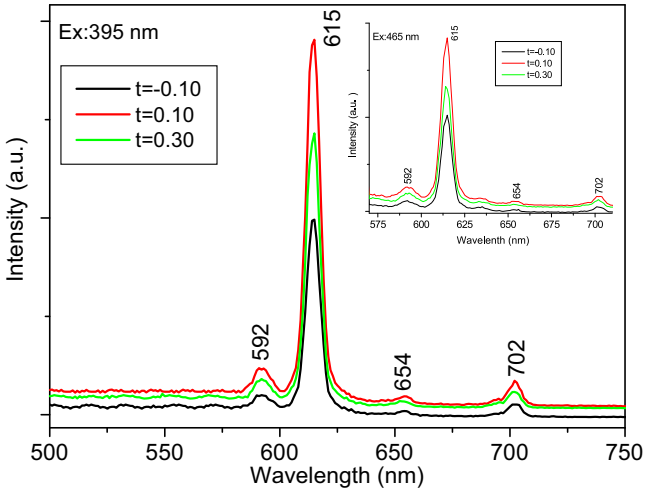

Fig. 3. Emission spectra of $Li_{2-2t}Zn_{1.90+t}(MoO_4)_3$:0.05$Eu^{3+}$,0.05$Li^+$ phosphors with different t values under various excitation wavelength λ_{ex} = 395 nm and λ_{ex} = 465 nm (the inset).

Li^+ or Mo^{6+} sites of LZMO:Eu^{3+}. Therefore, the emission spectra of LZMO:Eu^{3+} were dominated by pure red peak at 615 nm.

As shown in Fig. 3, with increasing of t value, the red-emitting intensity of LZMO:Eu^{3+} phosphors first increases, reaching a maximum value when t is 0.10, and then decreases accompanying a further increasing of t value. This can be explained as follows. As t value increases, the molar ratio of Li/Zn decreases, which will result in the forming of vacancies in cation sites to balance the excess positive charge [15]. The presence of vacancies can promote the energy transfer from excited carriers in LZMO host lattice to Eu^{3+} activator, and then enhance the luminescence.

The commission International de l'Eclairage (CIE) chromaticity coordinates of LZMO:Eu^{3+} are calculated to be $x = 0.65$, $y = 0.34$, which is closer to the standard of the NTSC ($x = 0.67$, $y = 0.33$) than that of commercial red-emitting phosphor of Y_2O_2S:Eu^{3+} (0.63, 0.35).

4. Conclusions

Multiwavelength excited narrow line red-emitting phosphors $Li_{2-2t}Zn_{1.90+t}(MoO_4)_3$:$0.05Eu^{3+}$,$0.05Li^+$ were successfully prepared via the conventional solid-state reaction. This double molybdate based phosphor presents the broad absorption from 230 to 350 nm, along with multiple excitation peaks at 363, 384, 395, 465, and 533 nm. Upon excitation with UV, near-UV rays or blue even green light, the phosphors exhibit strong red luminescence with CIE chromaticity coordinates ($x = 0.65$, $y = 0.34$). All these suggest Eu^{3+}-activated $Li_2Zn_2(MoO_4)_3$ to be promising phosphor for pc-white-LEDs application.

Acknowledgments

The authors thank Dr. Jinping Huang of Shanghai Normal University for assistance with the XRD measurements. This work was financially supported by the Natural Science Research Project of the Jiangsu Higher Education Institutions (08KJD150014), the QingLan Project of the Jiangsu Province (2008), and the Students' Sci-tech Innovation Foundation of Jiangsu Teachers University of Technology (KYX10008).

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