



Red phosphor $\text{Li}_2\text{Mg}_2(\text{WO}_4)_3: \text{Eu}^{3+}$ with lyonsite structure for near ultraviolet light-emitting diodes [☆]



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ABSTRACT

A series of Eu^{3+} -activated $\text{Li}_2\text{Mg}_2(\text{WO}_4)_3$ (LMW) materials were synthesized by high temperature solid state reactions. The phosphor can be effectively excited by 394 nm near ultraviolet light and emit intense red light with high color purity. Prepared phosphors can be indexed to LMW with particular lyonsite structure. The occupation of Eu^{3+} in LMW is selective. Most of Eu^{3+} comes into ¹A sites without inversion symmetry. The present research suggests that LMW is a suitable host for luminescence applications and Eu^{3+} -activated LMW is a promising phosphor for phosphor-converted white light-emitting diodes.

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1. Introduction

Recently, phosphor-converted white light-emitting diodes (pc-white-LEDs) have been widely used in the field of lighting and display. The eventual performance of these pc-white-LEDs strongly depends on the luminescence properties of the phosphors employed. Thus, relevant devices would be remarkably advanced by the discovery of optimized phosphor materials. The most commonly used red phosphor for near ultraviolet (UV) LEDs is $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ [1–3]. However, it has poor absorption in near UV region. Simultaneously, it is chemically unstable for its nature of sulfide and uneconomical for the usage of rare earth oxide in the host. Therefore, a red phosphor with high absorption in the near UV region, satisfying chemical stability and low cost, is urgently needed for commercial applications. In order to obtain desirable color purity, Eu^{3+} is indispensable for red phosphors. Therefore, the current pivotal task is to find a stable, cheap and easily synthesized host. Simultaneously, such a Eu^{3+} doped phosphor should be fit for near UV LEDs which have been extensively commercialized now.

Lyonsite is a mineral which can be the archetypal structure for large numbers of materials, such as perovskite, garnet, apatite, and

spinel. Oxide classes such as these can accommodate a wide variety of metal cation while retaining their unique structure. Adaptable framework structures can have different properties because of the varying elemental compositions [4]. Currently, investigations about lyonsite structure mainly focus on two properties: ionic conduction and catalysis. $\text{Li}_2\text{Mg}_2(\text{WO}_4)_3$ (LMW) is a peculiar lyonsite-type tungstate found in 1994 [5]. It is orthorhombic in Pnma (62) space group with lattice parameters: $a = 5.1129 \text{ \AA}$, $b = 10.462 \text{ \AA}$, and $c = 17.612 \text{ \AA}$ at room temperature (RT). Few studies involve the luminescent properties of rare earth ions in LMW till now. Thus we prepared a series of pure and Eu^{3+} doped LMW and investigated their luminescence properties and structure. The results indicate that Eu^{3+} activated LMW is a promising red phosphor for pc-white-LEDs and LMW is a desirable host for luminescent materials. The results found in this work can blaze a new way in finding a proper phosphor.

2. Experimental

All the phosphors were synthesized by high temperature solid state reaction (HTSSR). Raw materials Li_2CO_3 , MgO , WO_3 , and Eu_2O_3 , were weighed according to the composition of $\text{Li}_{2-x}\text{Mg}_{2-x}(\text{WO}_4)_3, \text{Eu}^{3+}_x$ ($x = 0, 0.02, 0.04, 0.06, 0.08, 0.10$). The weighed materials were put into an agate mortar and ground with an agate muller for 2 h. Then they were heated up to 700 °C in a tubular furnace. The samples were preserved at 700 °C for 30 h with twice intermediate regrinding. To be clear, these samples

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are abbreviated as LMW, LMW-2, LMW-4, LMW-6, LMW-8, and LMW-10, respectively.

Phase identification of prepared phosphors was carried out by a Beijing MSAL-XD-2 powder X-ray diffractometer (XRD). The excitation, emission spectra and decay curves of all the samples were measured with a Hitachi F-7000 fluorescence spectrophotometer. The morphology of the samples was studied with a Hitachi S3400N scanning electron microscope (SEM). The absorption spectra of the samples were recorded with a Shimadzu UV-2450 UV-Vis spectrophotometer. All the measurements were performed at room temperature. As for the details of these instruments, the reader can refer to our previous literatures [6,7].

3. Results and analysis

In order to determine the phase structure, the powder XRD analysis was carried out. The XRD patterns of several typical samples are shown in Fig. 1. JCPDS card No. 82-1804 (LMW, found in the International Center for Diffraction Data) is also listed in Fig. 1 for comparison. From Fig. 1, one can see that the XRD patterns of samples LMW-0, LMW-2, and LMW-6 are consistent with the standard card. Thus these samples can be indexed to LMW with a single phase. Impurity peaks appear from LMW-8 on and get enhanced in LMW-10. It indicates that the solid solution extreme of Eu^{3+} in LMW is 6%mol. The effective radii of involved ions in samples are as follows. $r(\text{Li}_6^+) = 0.76 \text{ nm}$, $r(\text{Mg}_6^{2+}) = 0.72 \text{ nm}$, $r(\text{W}_4^{6+}) = 0.42 \text{ nm}$, and $r(\text{Eu}_6^{3+}) = 0.947 \text{ nm}$ (Here subscript denote the coordination number of cation) [8]. Doped Eu^{3+} is bigger than any cation in the host. It is almost impossible for Eu^{3+} to replace W^{6+} sites because there is a notable difference in charge number and ionic radii between W^{6+} and Eu^{3+} . Therefore, only Li^+ and Mg^{2+} ions can be substituted by Eu^{3+} . The reason for the appearance of impurity peaks might be that substitution of one Eu^{3+} for one Li^+ and one Mg^{2+} introduces volume unbalance and change of the number of total ions. From Fig. 1, we can also see that the intensity of the main diffraction peaks is different. This indicates that samples with different composition have different crystallinity. The strongest diffraction peak at 26.40° can be the best probe. Pure LMW presents the strongest diffraction intensity for its best crystallinity. All samples can be ranked according to crystallinity from high to low as LMW, LMW-2, LMW-4, LMW-6, LMW-8, and LMW-10. The reason for the change of main diffraction peaks is also volume unbalance and change of the number of total ions.

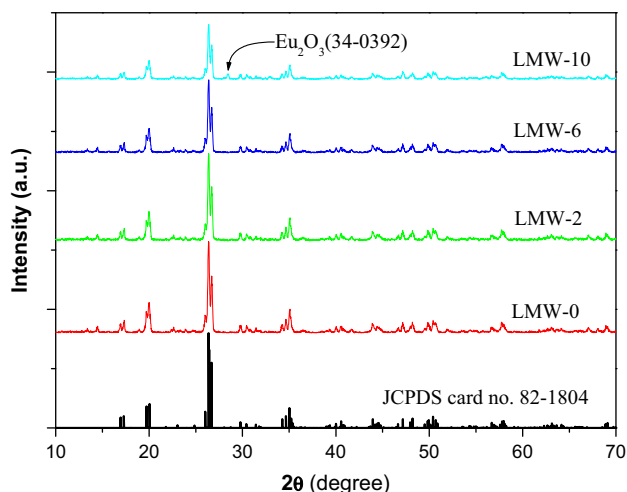


Fig. 1. Comparison of XRD patterns of several typical samples with JCPDS card no. 82-1804.

The SEM image of one typical Eu^{3+} doped sample, i.e. LMW-6, is shown in Fig. 2. From Fig. 2, it is observed that the particle size is inhomogeneous within ranges from 0.2 to 2.0 μm . It is well known that the particle size can significantly affect luminescence intensity of phosphors. The general rule is that sample with larger particle size presents higher luminescence intensity. The particle size of prepared phosphors with HTSSR method generally is in micrometer. Though the particle size of our samples is inhomogeneous, they also can present a good luminescence performance. This can be proved by the measurements of excitation, emission and absorption spectra (see later).

Fig. 3(a) shows the excitation spectrum of a typical sample LMW-6 monitoring the emission at 613 nm corresponding to $^5\text{D}_2 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} . The excitation spectrum is composed of one broad band between 240 and 310 nm and a group of excitation lines in UV and visible region. The broad band can be attributed to the combinations of charge transfer (CT) transitions from $\text{W}^{6+}\text{-O}^{2-}$ to $\text{Eu}^{3+}\text{-O}^{2-}$ [9]. The excitation lines are ascribed to the typical Eu^{3+} intra- $4f^6$ transitions, including the peaks with maximum at 362 ($^7\text{F}_0 \rightarrow ^5\text{D}_4$), 383 ($^7\text{F}_0 \rightarrow ^5\text{G}_{2-4}$), 394 ($^7\text{F}_0 \rightarrow ^5\text{L}_6$), 416 ($^7\text{F}_0 \rightarrow ^5\text{D}_3$), 466 ($^7\text{F}_0 \rightarrow ^5\text{D}_2$), and 536 ($^7\text{F}_1 \rightarrow ^5\text{D}_1$) nm, respectively [10–12]. The $^7\text{F}_0 \rightarrow ^5\text{L}_6$ transitions of Eu^{3+} at 394 nm are more intense than the CT band. Many excitation lines overlap together and form an excitation band from 370 to 410 nm. The perfect matching of this excitation band with the emission wavelength of near UV LED chips makes these phosphors used in white LEDs conveniently.

The emission spectra of all Eu^{3+} doped samples were recorded with a Hitachi F-7000 fluorescence spectrophotometer. The emission spectrum of one typical sample LMW-6 excited with 394 nm was shown in Fig. 3(b). Some emission lines are observed from 500 to 750 nm. The strongest emission line at 613 nm with a crystal field splitting component at 621 nm is attributed to the transitions from $^5\text{D}_0$ to $^7\text{F}_2$. The second strongest emission line at 592 nm can be attributed to the transitions from $^5\text{D}_0$ to $^7\text{F}_1$. The other emission lines can also be observed at 705 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_4$), 656 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_3$), but they are much weaker than the former two ones.

Fig. 4 shows the emission spectra of all Eu^{3+} doped samples. These spectra show almost the same shape, except for different intensity. The subgraph of Fig. 4 shows the relationship between the relative intensity of Eu^{3+} luminescence with the concentration of Eu^{3+} . As the concentration increases, the emission intensity increases and reaches the maximum value at $x = 0.06$, which was

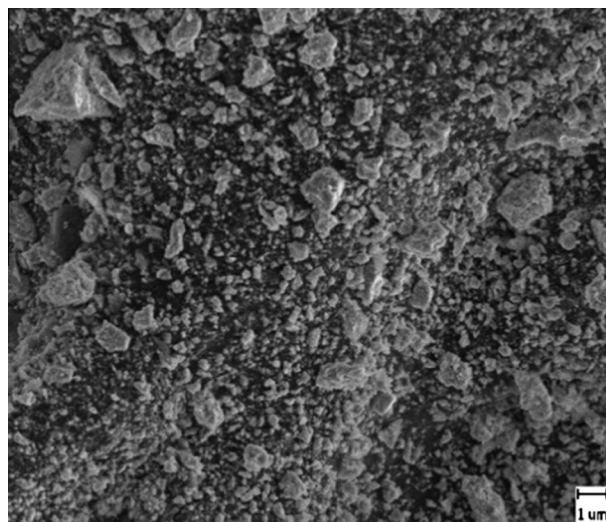


Fig. 2. SEM image of one typical sample LMW-6.

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