



SYNTHESIS AND PHOTOLUMINESCENCE PROPERTIES OF THE HIGH-BRIGHTNESS Eu^{3+} DOPED $\text{Li}_{0.5}\text{Al}_{0.5}\text{Mg}_2(\text{MoO}_4)_3$ RED PHOSPHORS

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ABSTRACT

Eu^{3+} doped red phosphors $\text{Li}_{0.5}\text{Al}_{0.5}\text{Mg}_2(\text{MoO}_4)_3$ were prepared by the combustion method, and their luminescent properties were studied. Under the excitation of near-UV 395 nm, the phosphors show intense red emission with the peaks located at 615 and 595 nm. The influence of Eu^{3+} concentration on the luminescent properties of Eu^{3+} doped $\text{Li}_{0.5}\text{Al}_{0.5}\text{Mg}_2(\text{MoO}_4)_3$ was investigated and the 3% (mole fraction) was the appropriate molar concentration. By sintering $\text{Li}_{0.5}\text{Al}_{0.5}\text{Mg}_2(\text{MoO}_4)_3:\text{xEu}^{3+}$ phosphor at 750°C, PL intensity has a maximum value at 615 nm with Commission Internationale de l'Eclairage 1931 (CIE 1931) chromaticity coordinates (0.6616, 0.3336). The phosphor could be suitable for the application of white light-emitting diodes.

Keywords: Phosphors; Combustion Method; $\text{Li}_{0.5}\text{Al}_{0.5}\text{Mg}_2(\text{MoO}_4)_3:\text{xEu}^{3+}$; Luminescence

1. INTRODUCTION

In recent years, white light emitting diodes (WLEDs) had emerged as the next generation solid-state lighting because of their higher conversion efficiency of electricity to visible light over traditional light bulbs. Researchers had made great efforts in attempting different realization modes of white light as well as exploring novel luminescent materials with high luminescence efficiency [1-5]. Many kinds of inorganic compounds had been investigated, such as phosphate, silicate, aluminate,

molybdate and tungstate [6-10]. So far, the commercial market is still dominated by WLEDs realized by blue chips coating with yellow phosphors. However, WLEDs with this combination possess low colour rendering index and high correlated colour temperature due to the lack of red phosphors which can improve the lumen equivalency and colour rendering of the obtained white light [11,12]. To have warm white light, WLEDs realized by near UV chips with tricolour phosphors (blue, green and red) were proposed and expected to dominate the market due to their high performance and easily controlled luminescence properties. Considering that red phosphor plays an important role in this kind of WLEDs, it is urgently needed to find UV light excited red phosphors with superior luminescence properties. The europium is one kind of common and important activator for rare earth ions doped phosphors. As we know that the emission of Eu^{2+} ions varies in a wide range (n-UV to red region) in different hosts [13]. The strong interaction between ligands and activators will increase the energy splitting of $4f^65d^1$ excited states, resulting in a longer Stokes shift of the Eu^{2+} ions. In this case, many Oxynitride, nitride and sulfide phosphors doped with Eu^{2+} ions have been prepared [14-18]. However, these red phosphors either need rigorous synthesis conditions or suffer poor chemical stability. Taking account of the Eu^{3+} emission ($^5\text{D}_0$ - $^7\text{F}_2$ transition) in the red region, developing Eu^{3+} -activated phosphors is of great

importance due to their superior red colour purity.

In literature survey the lithium/aluminium dimagnesium tetra-kis [orthomolybdate (VI)], was prepared by a solid-state reaction route. [19] The crystal structure is built up from MgO_6 octahedra and MoO_4 tetrahedra sharing corners and edges, forming two types of chains running along [100]. These chains are linked into layers parallel to (010) and finally linked by MoO_4 tetrahedra into a three-dimensional framework structure with channels parallel to [001] in which lithium and aluminium cations equally occupy the same position within a distorted trigonal-bipyramidal coordination environment.

In this paper, trivalent Europium ion (Eu^{3+}) activated $Li_{0.5}Al_{0.5}Mg_2(MoO_4)_3$ phosphor was fabricated with combustion reaction, and its luminescent properties were investigated.

2. EXPERIMENTAL

$Li_{0.5}Al_{0.5}Mg_2(MoO_4)_3:Eu^{3+}$ phosphor was prepared by combustion synthesis. All chemicals were analytic grade and directly used without further purification. Distilled water was used throughout. The synthetic process of the products $Li_{0.5}Al_{0.5}Mg_2(MoO_4)_3:Eu^{3+}$

can be divided into two stages. Firstly, solution A was prepared by dissolving Eu_2O_3 with concentrated nitric acid, the excess HNO_3 was removed by further evaporation. Solution B was obtained by dissolving Lithium Nitrate- KNO_3 , Aluminum Nitrate - $Al(NO_3)_3 \cdot 3H_2O$, Magnesium Nitrate $Mg(NO_3)_2 \cdot 2H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 24H_2O$ in distilled water. Then the two solutions were fully mixed to get a transparent solution. A weighted amount of Urea ($NH_2-CO-NH_2$) was dissolved in the transparent solution as fuel and accelerator, respectively. The mixture gel was obtained after stirring and heating at $70^\circ C$ for 2h. The sticky gel was introduced into a preheated muffle furnace at a temperature of $750^\circ C$ and maintained for 5min. Initially, the solution boiled and underwent dehydration, followed by decomposition with the escape of large amounts of gases (oxides of carbon, nitrogen and ammonia). Then spontaneous ignition occurred and smouldering combustion ensued, with enormous swelling, producing voluminous white foamy ashes. The whole process was over within less than 5 min, after the ashes were cooled to room temperature, milled slightly and $Li_{0.5}Al_{0.5}Mg_2(MoO_4)_3:Eu^{3+}$ phosphor thus obtained.

3. RESULT & DISCUSSION

3.1 PL Characteristics of $Li_{0.5}Al_{0.5}Mg_2(MoO_4)_3:x Eu^{3+}$ Phosphor:

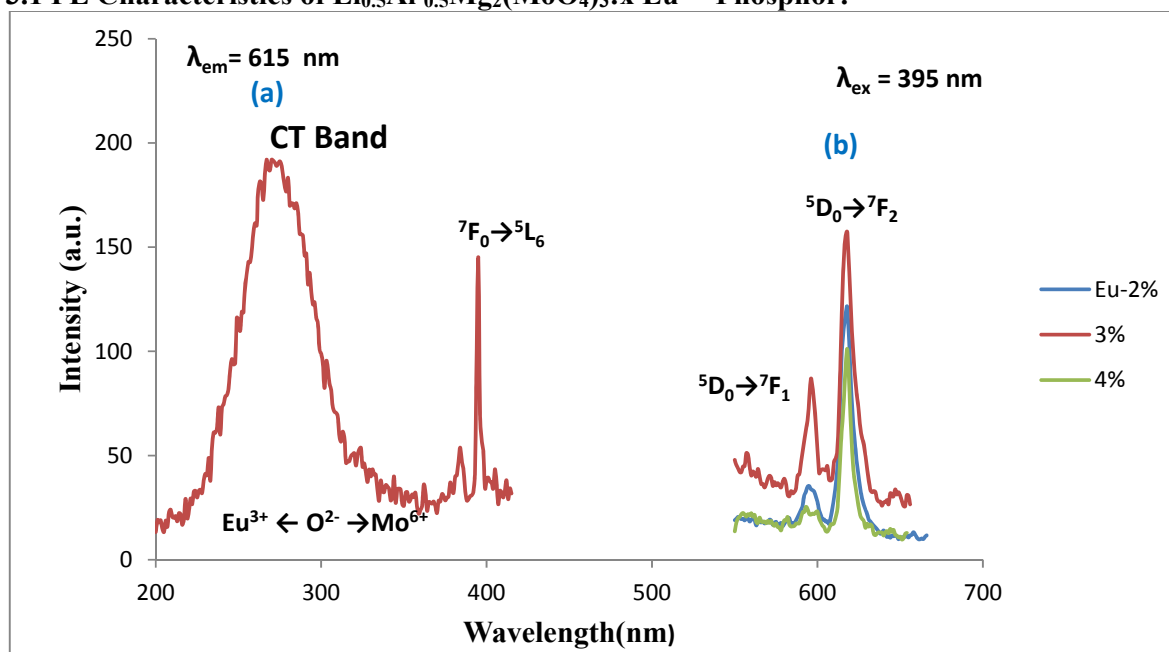


Fig.1. Excitation (left) and emission (right) spectra of $Li_{0.5}Al_{0.5}Mg_2(MoO_4)_3:x Eu^{3+}$ ($x=2, 3$ & 4%) phosphor.

Fig. 1 shows the excitation (the Red lines) and emission (the red, blue & green lines) spectra of Eu^{3+} doped $\text{Li}_{0.5}\text{Al}_{0.5}\text{Mg}_2(\text{MoO}_4)_3$ samples. As shown in **Fig.1(a)** the excitation spectra all exhibit a broad band absorption due to charge transfer transition of $\text{Mo}^{6+} - \text{O}^{2-}$ [ligand-to-metal charge-transfer (LMCT)] at 288 nm. The CT band of $\text{Eu}^{3+} - \text{O}^{2-}$, which also appears in the range of 200–300 nm in the excitation spectra, might have overlapped with the CT band of molybdate group [20,21]. As one of the most frequently used red emitting activators in rare earth ions doped materials, the Eu^{3+} ion mainly shows characteristic emissions resulting from the transitions of ${}^5\text{D}_{0,1,2} \rightarrow {}^7\text{F}_J$ ($J = 0, 1, 2, 3, 4$). [22,23] As shown in the **Fig.1(a)**, the excitation spectrum monitored with 615 nm consists of broad excitation bands from 200 to 320 nm and some narrow lines beyond 350 nm. The strong band with a maximum at 288 nm is due to the charge transfer transition between O^{2-} and Mo^{6+} , as discussed above. The narrow lines beyond 350 nm are the characteristic $f \rightarrow f$ transition of Eu^{3+} within its $4f^6$ configuration. Moreover, the two stronger excitation peaks at 395 nm and 466 nm can match well with near-UV and blue LED chip [32]. The both peaks can be attributed to the ${}^7\text{F}_0 - {}^5\text{L}_6$ and ${}^7\text{F}_0 - {}^5\text{D}_2$

transitions of Eu^{3+} , respectively. The other $f \rightarrow f$ transitions of Eu^{3+} at 363 nm (${}^7\text{F}_0 - {}^5\text{D}_4$), 382 nm (${}^7\text{F}_0 - {}^5\text{L}_7$) and 416 nm (${}^7\text{F}_0 - {}^5\text{D}_3$) are also seen but have less intensity [24]. In **Fig.1(b)** The emission spectrum of Eu^{3+} ($\lambda_{\text{ex}} = 395$ nm) is mainly composed by the sharp red emission: ${}^5\text{D}_0 - {}^7\text{F}_2$ transition of Eu^{3+} at 615 nm and a weak ${}^5\text{D}_0 - {}^7\text{F}_1$ transition at 595 nm. These peaks at 615 and 595 nm are assigned to the electric dipole transition and magnetic dipole transition, respectively. The domination of electric dipole transition in the emission spectrum confirms that Eu^{3+} ions are located at sites without inversion symmetry [25]. The other emission transitions from ${}^5\text{D}_J$ ($J = 0, 1$) excited levels to ${}^7\text{F}_J$ ($J = 0-4$) ground states are very weak. This is advantageous to obtain good chromaticity coordinates near the National Television Standard committee standard values. Moreover, no emission corresponding to molybdate group can be observed, indicating the efficient energy transfer from the host MoO_4^{2-} group to Eu^{3+} ions. This phenomenon indicates that $\text{Li}_{0.5}\text{Al}_{0.5}\text{Mg}_2(\text{MoO}_4)_3$ is a good host materials for Eu^{3+} luminescence.

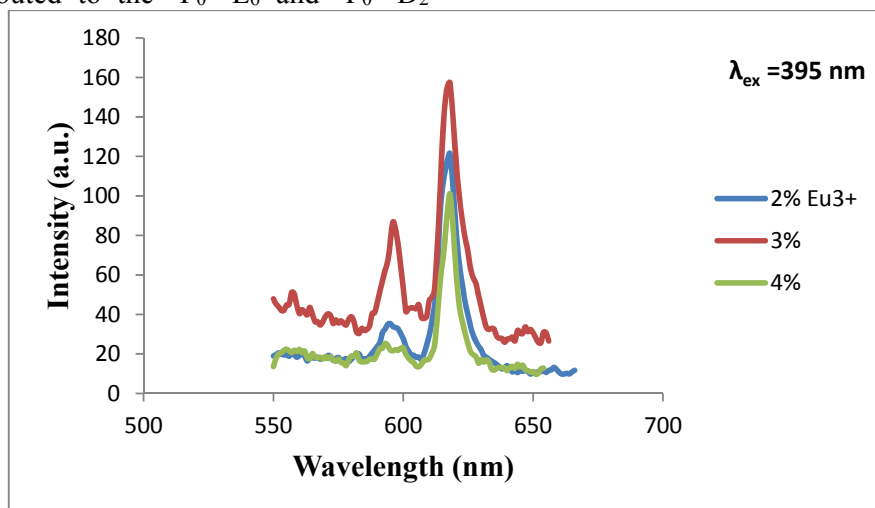


Fig. 2. Emissions spectra of $\text{Li}_{0.5}\text{Al}_{0.5}\text{Mg}_2(\text{MoO}_4)_3 : x\text{Eu}^{3+}$ ($x=2, 3$ and 4 %) phosphor

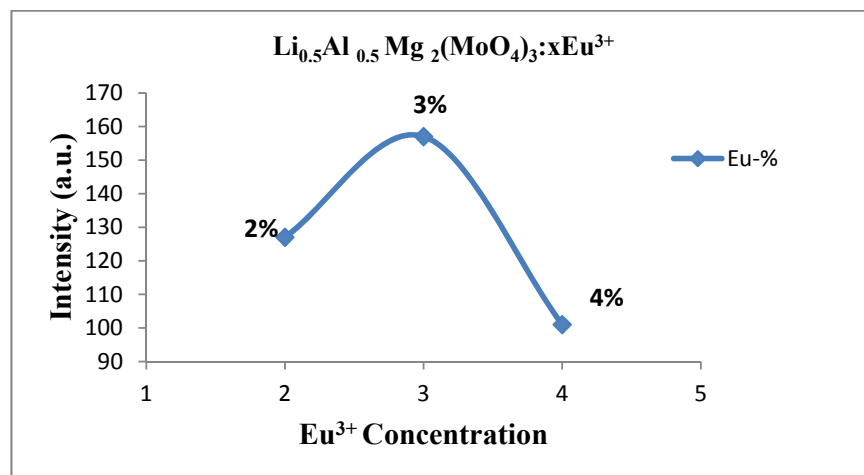


Fig.3. Luminescence intensity of $\text{Li}_{0.5}\text{Al}_{0.5}\text{Mg}_2(\text{MoO}_4)_3:\text{xEu}^{3+}$ as function of Eu^{3+} concentration.

To obtain the optimal doping concentration, the emission spectra of a series of phosphors $\text{Li}_{0.5}\text{Al}_{0.5}\text{Mg}_2(\text{MoO}_4)_3:\text{xEu}^{3+}$ with $x = 0.02, 0.03$ and 0.04 were recorded and presented in **Fig.(2)**, and the comparison of their integrated intensity in the spectral range $500 - 700$ nm was also presented in the inset. Under the excitation of 395 nm, all the samples show similar emission spectra with the sample $\text{Li}_{0.5}\text{Al}_{0.5}\text{Mg}_2(\text{MoO}_4)_3:0.03 \text{Eu}^{3+}$, but their emission intensities are obviously different. In **Fig.(3)** with the increasing doping concentration, the emission intensity gradually rises to a maximum and then decrease. The

strongest emission is obtained when the doping concentration (x -value) is 0.03 . This indicates that the optimal doping concentration is about 0.03 . The color coordinates are one of the important factors for evaluating phosphors. The color purity of the PL emission is usually characterized by the Commission Internationale de l'Eclairage (CIE) chromaticity coordinates (x, y). The calculated CIE values of $\text{Li}_{0.5}\text{Al}_{0.5}\text{Mg}_2(\text{MoO}_4)_3:\text{xEu}^{3+}$ phosphors under 395 nm excitation are $(0.6616, 0.3336)$ is shown in **Fig.(4)**, which is rather close to the standard red light $(0.670, 0.330)$.

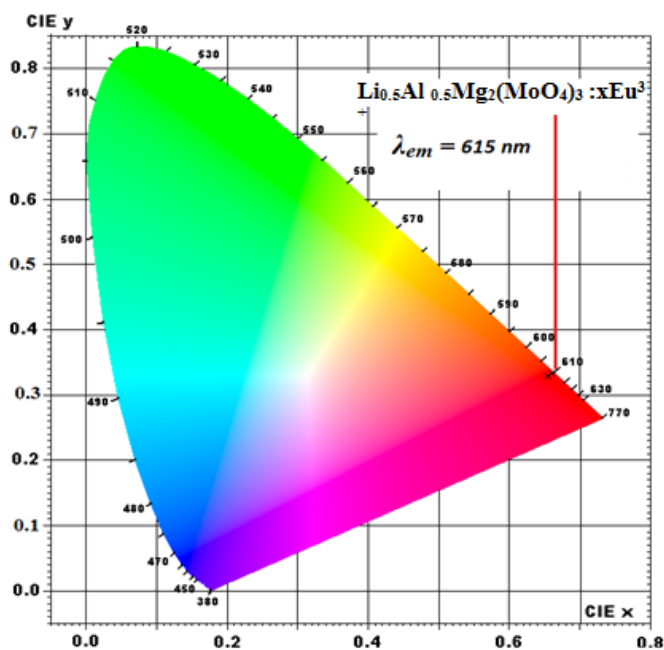


Fig. 4. CIE chromaticity coordinates (x, y) of $\text{Li}_{0.5}\text{Al}_{0.5}\text{Mg}_2(\text{MoO}_4)_3:\text{xEu}^{3+}$ ($\lambda_{\text{ex}} = 395$ nm).

4. CONCLUSIONS

The red phosphors, $\text{Li}_{0.5}\text{Al}_{0.5}\text{Mg}_2(\text{MoO}_4)_3:\text{xEu}^{3+}$ were synthesized at a 750°C by the

combustion method. The photoluminescence results show that all samples can be excited efficiently by near-UV (395 nm). In the emission spectra, the strongest emission is the electric-dipole transition red emission ${}^5D_0 \rightarrow {}^7F_2$ (615nm), while the magnetic-dipole transition orange emission ${}^5D_0 \rightarrow {}^7F_1$ (595 nm) is subordinate. Therefore, $\text{Li}_{0.5}\text{Al}_{0.5}\text{Mg}_2(\text{MoO}_4)_3:\text{xEu}^{3+}$ is a good red phosphor for white LED. When the molar concentration of Eu^{3+} was 3%, the strongest luminescent intensity was reached.

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