

Search for new red phosphors under NUV/blue excitation – the stimulating future for solid state lighting

Sivakumar Vaidyanathan and Duk Young Jeon*

Display Materials Lab, Department of Materials Science and Engineering,
Korea Advanced Institute of Science and Technology, Deajeon 305-701,
Republic of Korea. *dyj@kaist.ac.kr

Keywords : Tungstates/molybdates, red phosphor, white LEDs and Photoluminescence

Abstract

Research on down conversion phosphor materials is the key for the development of solid state lighting (SSL). Especially finding alternative red phosphor for white LEDs based on blue or NUV LEDs are important research task. Under this view, we have synthesized a series of Eu^{3+} substituted $\text{La}_2\text{W}_{2-x}\text{Mo}_x\text{O}_9$ ($x = 0 \sim 2$, in steps of 0.1) red phosphor and characterized by X-ray diffraction (XRD) and photoluminescence. XRD results reveal a phase transition from triclinic to cubic structure for $x \geq 0$. All the compositions show broad charge transfer band due to charge transfer from oxygen to tungsten/molybdenum and red emission due to Eu^{3+} ions. Select compositions show high red emission intensity compared to the commercial red phosphor under NUV/blue ray excitation. Hence, this candidate can be possible red emitting phosphors for white LEDs.

1. Introduction

Phosphor materials are essential due to their emerging role in solid state lighting (SSL). SSL is the recent revolution in the lighting technology, wherein the low power light emitting diodes (LEDs) are used for lighting applications. Research on down conversion phosphor materials is the key for the development of SSL. The first white LEDs have been commercialized by Nichia Co., and it consists of InGaN blue LED and a yellow YAG: Ce^{3+} phosphor [1]. Blue LED with green, red emitting phosphors or blue, green, and red (RGB) emitting phosphors with near UV

(NUV) LED are the alternative way to mimic efficient white light with good color rendering index (CRI) [2]. Sulfide based commercial red phosphors are chemically unstable and the lifetime of the materials is inadequate under extended UV irradiation [3]. Hence, there is a growing interest in the development of novel families of red emitting phosphor materials with high absorption in the NUV to blue region.

In the present study, we focused on Eu^{3+} substituted tungstates, molybdates and its solid solutions $\text{La}_{1.95}\text{Eu}_{0.05}\text{W}_{2-x}\text{Mo}_x\text{O}_9$ ($x = 0 \sim 2$, in steps of 0.1). These host lattices, having broad charge transfer band (due to charge transfer from oxygen to Mo/W) and the same can be used to harvest the energy from LED emission to Eu^{3+} levels. Efficient red phosphor under NUV region has been developed and their emission intensities were compared with those of the commercial red phosphor ($\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$, Nichia).

2. Experimental

A series of $\text{La}_{1.95}\text{Eu}_{0.05}\text{W}_{2-x}\text{Mo}_x\text{O}_9$ ($x = 0 \sim 2$, in steps of 0.1) phosphor was prepared from the appropriated mixtures of La_2O_3 , Eu_2O_3 , MoO_3 , and WO_3 by high temperature solid state reaction. La_2O_3 was heated at 1200°C for 12 h prior to use for decarbonation. The oxides were mixed with agate mortar and heated air at 500°C for 6 h to decompose the carbonates. The powder samples were ground again and heated in air at 1100°C for 6 h. The compositions were checked for phase formation by X-ray powder diffraction (XRD) using $\text{Cu-K}\alpha_1$ radiation (Rigaku, D/max-IIIc (3kW) at 40 kV and 45mA). The emission

spectra were recorded using a standard spectrofluorometer setup from DARSA PRO PL System (Professional Scientific Instrument Co., Korea), which utilizes a Xe lamp as the excitation source.

3. Results and discussion

Phase formation:

$\text{La}_2\text{W}_2\text{O}_9$ exhibits two different structures, the one $\beta\text{-La}_2\text{W}_2\text{O}_9$ is the high temperature polymorph and it crystallizes in cubic structure. $\alpha\text{-La}_2\text{W}_2\text{O}_9$ is the low temperature polymorph and it crystallizes in triclinic structure [4]. Similarly $\text{La}_2\text{Mo}_2\text{O}_9$ also exhibits two different structures, the high temperature polymorph $\beta\text{-La}_2\text{Mo}_2\text{O}_9$ crystallize in cubic structure, whereas the low temperature polymorph $\alpha\text{-La}_2\text{W}_2\text{O}_9$ crystallize in monoclinic structure (exhibit a $2 \times 3 \times 4$ superstructure of the cubic form). The powder X-ray diffraction patterns of $\text{La}_{1.95}\text{Eu}_{0.05}\text{W}_{2-x}\text{Mo}_x\text{O}_9$ ($x = 0, 1.6, 1, 0.6$ and 2) with parent compounds are shown in Fig. 1. In the $\text{La}_{1.95}\text{Eu}_{0.05}\text{W}_{2-x}\text{Mo}_x\text{O}_9$ ($x = 0, 1.6, 1, 0.6$ and 2) compositions $x = 0$ crystallize in triclinic structure and on further increase of x , the system undergoes a compositionally induced phase transition from triclinic to pseudo cubic structure ($x \geq 0.1$). No impurity peak was found in the XRD patterns clearly indicating that the compounds formed are of single phase and Eu^{3+} incorporation has been achieved.

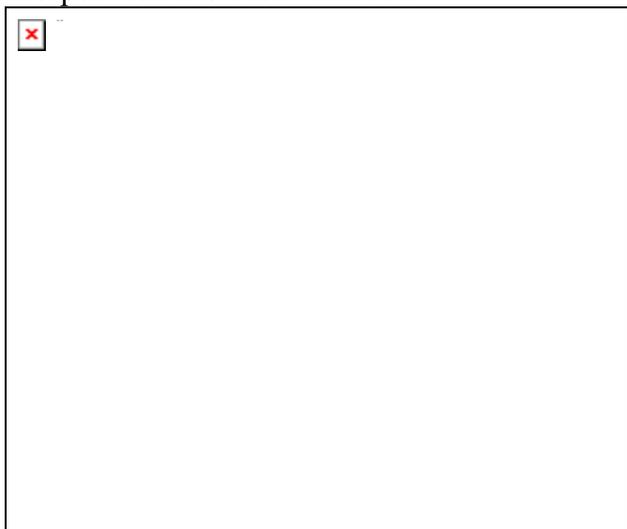


Fig. 1. The powder XRD patterns of $\text{La}_{1.95}\text{Eu}_{0.05}\text{W}_{2-x}\text{Mo}_x\text{O}_9$ ($x = 0, 1.6, 1, 0.6$ and 2) with parent compounds

Luminescence of $\text{LaEu}_{0.05}\text{W}_{2-x}\text{Mo}_x\text{O}_9$ ($x = 0 \sim 1.9$, in steps of 0.2)

The photoluminescence excitation spectrum of select compositions $\text{LaEu}_{0.05}\text{W}_{2-x}\text{Mo}_x\text{O}_9$ ($x = 0 \sim 1.9$, in steps of 0.2) is shown in Fig.2. The spectrum contains broad absorption band with peak maximum at about $250 \sim 400$ nm and this band is due to oxygen to tungsten/molybdenum charge transfer (CT) transition. In addition, the characteristic Eu^{3+} excitation lines (${}^7\text{F}_0 - {}^5\text{L}_6$, ${}^7\text{F}_0 - {}^5\text{D}_2$ and ${}^7\text{F}_1 - {}^5\text{D}_1$) are also observed in the spectrum.

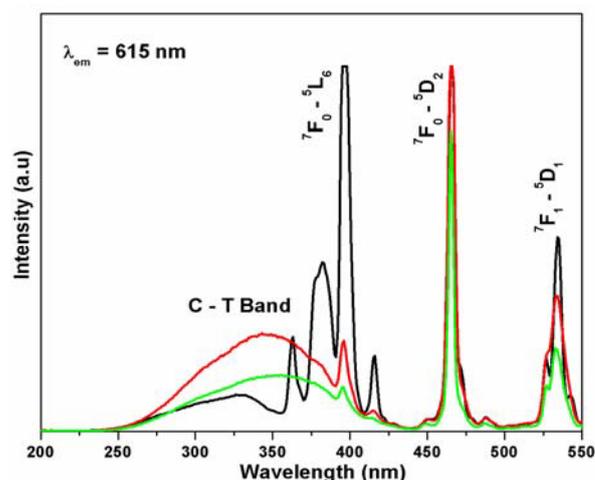


Fig. 2. The photoluminescence excitation spectrum of select compositions $\text{LaEu}_{0.05}\text{W}_{2-x}\text{Mo}_x\text{O}_9$

The photoluminescence emission spectrum of select compositions $\text{LaEu}_{0.05}\text{W}_{2-x}\text{Mo}_x\text{O}_9$ ($x = 0 \sim 1.9$, in steps of 0.2) is shown in Fig. 3. The spectrum contains sharp peaks at 615 nm and 596 nm which are due to electric dipole (ED) and magnetic dipole (MD) transitions of Eu^{3+} ion. Generally the Eu^{3+} emission peaks are hypersensitive, i.e., they are highly sensitive to the crystal chemical environment [5]. Electric dipole transition is dominant when Eu^{3+} occupies non-centrosymmetric site in the lattice [6]. In the present study, the relative intensity of ED transition is found to be high. It is clearly

indicates that the Eu^{3+} ion occupies non-centrosymmetric site in the presently studied compositions. The intensity of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ emission peak of all compositions is compared with that of the $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ commercial red emitting phosphor (Nichia) and the relative emission intensity of $\text{La}_{1.95}\text{Eu}_{0.05}\text{W}_{1.6}\text{Mo}_{0.4}\text{O}_9$ composition is found to be ~ 4.7 times higher than that of commercial one under 465 nm excitation.



Fig. 3. The photoluminescence emission spectrum of select compositions $\text{LaEu}_{0.05}\text{W}_{2-x}\text{Mo}_x\text{O}_9$

4. Summary

A series of novel red emitting phosphor $\text{La}_{1.95}\text{Eu}_{0.05}\text{W}_{2-x}\text{Mo}_x\text{O}_9$ ($x = 0 \sim 1.9$, in steps of 0.2) have been synthesized by high temperature solid state reaction. In the $\text{La}_{1.95}\text{Eu}_{0.05}\text{W}_{2-x}\text{Mo}_x\text{O}_9$ ($x = 0, 1.6, 1, 0.6$ and 2) compositions $x = 0$ crystallize in triclinic structure and on further increase of x , the system undergoes a compositionally induced phase transition from triclinic to pseudo cubic structure ($x \geq 0.1$). All the compositions show red emission under NUV or blue ray excitation. However the relative emission intensity is found to be maximum for $x = 0.4$ and the same is compared with commercial red phosphor (emission intensity ~ 4.7 times higher than that of commercial one). Therefore, the newly developed red phosphors are potential candidate for solid state lighting.

5. References

Reference:

1. S. Nakamura, T. Mukai, and M. Senoh, *J. Appl. Phys.* **76**, 8189 (1994)
2. V. Sivakumar and U. V. Varadaraju, *J. Electrochem. Soc.* **152**, H168 (2005).
3. V. Sivakumar and U. V. Varadaraju, *J. Electrochem. Soc.*, **153**, H54 (2006).
4. J. A. Collado, M. A. G. Aranda, A. Cabeza, P. Olivera-Pastor, and S. Bruque, *J. Solid State. Chem.* **167**, 80 (2002)
5. L. I. Katzin, *Inorg. Chem.* **8**, 1649 (1969).
6. G. Blasse and B.C. Grabmaier *Luminescent Materials*, Springer-Verlag, Berlin, 1994