Photoluminescence properties and analysis of spectral structure of $R_2(MoO_4)_3 : Eu^{3+}$ (R = La, Gd) phosphors

Zuoling Fu,[1,2] Qi Wu,[1] Wangda Gong,[1] Liang Shi,[3] Wenhao Li,[4] and Zhenwen Dai[1,2,*]

[1]*College of Physics, Jilin University, Key Lab of Coherent Light, Atomic and Molecular Spectroscopy, Ministry of Education, Changchun 130023, China*
[2]*State Key Laboratory of Superhard Materials, Jilin University, Changchun 130021, China*
[3]*Department of Physics, Pukyong National University, Busan 608-737, South Korea*
[4]*Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China*
*Corresponding author: dai@jlu.edu.cn

The site-selective excitation and emission spectroscopy and luminescence decay (lifetime) have been investigated in the $^5D_0 \rightarrow {^7F_0}$ region using a pulsed, tunable, and narrowband dye laser. We observed two crystallographic sites for Eu^{3+} in $La_2(MoO_4)_3$ and one crystallographic site for Eu^{3+} in $Gd_2(MoO_4)_3$. The stark energy levels for Eu^{3+} at different sites were assigned from site-selective emission spectra. The luminescent properties of the as-synthesized samples were also investigated, which showed strong lines at 395 nm in excitation spectra and intensive red emission, indicating that they could be used as red components for white LEDs. © 2011 Optical Society of America

OCIS codes: 250.5230, 300.6320.

1. INTRODUCTION

Rare earth (RE) ion-doped phosphors have attracted great interest during the past several decades due to their unique physical and chemical properties [1–3]. RE ions can display many significative properties in optics, electronics, and magnetics, originating from f–f electronic transitions within the 4f shell. Among these RE ions, the Eu^{3+} ion is an important activator that can emit red fluorescence centered at around 616 nm, corresponding to the $^5D_0$—$^7F_2$ transition, while located in a noncentrosymmetric site. Thus, many materials doped with Eu^{3+} can be used as red phosphors and have potential application in color television displays [4].

The RE–molybdenum (VI) oxides ($Ln_2Mo_nO_{3n+3}$, n as integer or fractional) system constitutes a very rich family within which a great variety of compounds can be synthesized that differ in stoichiometry and structure. The RE sesquimolybdates with $n = 3$ are probably the most interesting group of the family because the compounds of this series are not isostructural; they have very interesting structural, physical, and chemical properties; and they show special magnetic, optical, and superconducting properties [5–10]. They constitute a versatile host series to which the spectroscopic analysis can be applied to confirm the structure. Generally, Eu^{3+} luminescence is of special importance as a spectral probe from its application in phosphor materials. This is possible because Eu^{3+} has several structure-dependent transitions enabling one to gain insight about the site that it occupies in a given host. On this basis, we have attempted to explore the different cationic sites present in the molybdates system.

$Gd_2(MoO_4)_3$ and $La_2(MoO_4)_3$ sharing a scheelite-related structure have been studied widely, which were synthesized by varieties of methods. The compounds of this series, which belong to the family of $Ln_2Mo_3O_{12}$ type, are not isostructural and occur in at least eight structural types, depending on both

the RE atom and the conditions of synthesis. Guo *et al.* [8] gave a survey of luminescent properties of $R_2(MoO_4)_3 :$ Eu^{3+} (R = La, Y, Gd) phosphors prepared by sol–gel process, and Cho *et al.* [11] used the hydrothermal method to prepare $Gd_2(MoO_4)_3 : Eu^{3+}$ with similar purposes. More and more attention was paid to the molybdates doped with Eu^{3+} because of its broad and intense charge–transfer (C–T) absorption bands in the near-UV and effective f–f transition of Eu^{3+}. Nevertheless, most of the previous work on RE molybdate compounds are mainly concentrated on the material synthesis and luminescence; little has been done on the luminescence of the europium dependence of the molybdate crystal structure.

In this work, the site-selective excitation and emission spectra along with the decay times have been investigated under the pulsed dye–laser excitation in the $^5D_0$—$^7F_0$ region of Eu^{3+} in $R_2(MoO_4)_3$ (R = La, Gd). Luminescence excitation and emission spectra in the UV region and emission spectra under the UV excitation were also applied to investigate its luminescence properties. The obtained results reveal that Eu^{3+} normally occupies in two crystallographic sites in $La_2(MoO_4)_3$ and one crystallographic site in $Gd_2(MoO_4)_3$, which are characterized and discussed.

2. EXPERIMENT

All reagents from Beijing Chemical Company were analytical grade and used directly without further purification. The compounds $R_2(MoO_4)_3$ (R = La, Gd) doped with Eu^{3+} powders were prepared by high-temperature solid-state reaction. The starting materials were R_2O_3 (R = La, Gd; 99.99%) and Eu_2O_3 (99.99%). According to the nominal compositions of compounds $R_2(MoO_4)_3 : 4\%Eu$, the appropriate amount of starting materials were thoroughly mixed and ground, and then heated at 500 °C for 4 h. After being reground, they were calcined at 800 °C for 4 h in air. The resulting material was

analyzed by x-ray diffraction, showing no residue. After the reaction, the material was pressed in pellets (no transparency) for the luminescence measurements.

The UV-visible photoluminescence (PL) excitation (PLE) and emission spectra were recorded with a spectrophotometer (Hitachi F-7000) equipped with Xe lamp as an excitation source. The laser-selective excitation experiment and high-resolution emission spectra were achieved by means of a Rhodamin 6G tunable dye laser (Sirah Cobra-Stretch), which was pumped by a frequency-tripled 355 nm Nd:YAG laser (Spectra-Physics Quanta-Ray Pro-Series) with a 10 Hz repetition and a 10 ns pulse duration. The laser-induced fluorescence was collected by a lens ($f = 15$ cm), filtered by a 0.5 m monochromator, and finally detected by a photomultiplier tube (Hamamatsu R3896). The intensity response of the detection system to the fluorescence signals at different wavelengths was calibrated by a standard lamp. The time-resolved fluorescence decay signals from the detector were recorded by a digital oscilloscope ((LeCroy 9410) and processed with a boxcar integrator (Stanford Research Systems SR250). All the measurements were performed at room temperature.

3. RESULTS AND DISCUSSION

A. PL and PLE Spectra of $R_2(MoO_4)_3$: Eu^{3+} (R = La, Gd) Phosphors

The PL and PLE spectra of phosphors $R_2(MoO_4)_3$ (R = La, Gd) doped with Eu^{3+} were shown in Fig. 1, showing that the shapes of the PL of phosphors are similar. The excitation spectra (Fig. 1, left) were obtained by monitoring the emission of the Eu^{3+} $^5D_0-^7F_2$ transition at 616 nm. It can be observed clearly that the excitation spectra both consist of a broadband from 200 to 350 nm, which is ascribed to the $O-Mo$ C–T transition. The C–T band of $O-Eu^{3+}$, which usually appears in the range of 250–300 nm in the excitation spectrum [12], might have overlapped with the C–T band of molybdate group and, hence, was not observed clearly. In the longer wavelength region (360–500 nm), the sharp lines are intraconfigurational 4f–4f transitions of Eu^{3+} in the host lattices, and the strong excitation band at 395 and 465 nm is attributed to
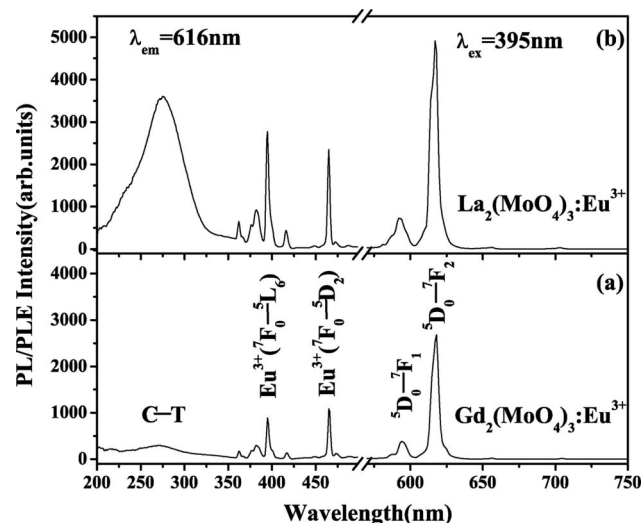
the $^7F_0-^5L_6$ and $^7F_0-^5D_2$ transitions of Eu^{3+}, respectively, which are matched well with near-UV and blue LED chip. Both spectra exhibit similar profiles except for two specific features: (1) the spectrum of the $La_2(MoO_4)_3$: Eu^{3+} phosphor shows a high-intensity broadband with a maximum at ~275 nm, indicating that 275 nm may become good excitation light to obtain strong intensity red emission as well as the 395 nm. One also reported that energy absorbed by the MoO_4^{2-} group can transferred to Eu^{3+} ions levels efficiently in the $La_2(MoO_4)_3$: Eu^{3+} phosphor. (2) For the $Gd_2(MoO_4)_3$: Eu^{3+} phosphor, its C–T band from $O-Mo$ with a maximum at ~270 nm is very weak compared with the lines at 395 nm and 465 nm, which indicates that the $Gd_2(MoO_4)_3$: Eu^{3+} phosphor is more suited for the near-UV and blue LED chip. These different features between $La_2(MoO_4)_3$: Eu^{3+} and $Gd_2(MoO_4)_3$: Eu^{3+} may be explained by the differences between the ionic radii of La^{3+} (1.02 nm), Gd^{3+} (0.94 nm), and Eu^{3+} (0.95 nm) ions. It is possible that the La^{3+} ion could be distorting the molybdate structures due to its larger ionic radius, while the Gd^{3+} ion, being smaller, could be forming almost regular tetrahedral molybdates when the Eu^{3+} is doped.

The emission spectra of Eu^{3+} (Fig. 1, right) excited under 395 nm near-UV light are mainly dominated by the hypersensitive red emission, showing a strong transition $^5D_0-^7F_2$ at 616 nm and a weak $^5D_0-^7F_1$ transition. The two peaks are assigned to the electric dipole transition and magnetic dipole transition, respectively, and the presence of electric dipole transition confirms that Eu^{3+} ions are located at sites without inversion symmetry. Other transitions from the $^5D_0$ excited level to ^7F_J ground states are very weak, which is advantageous to obtain good Commission Internationale del'Eclairage (CIE) chromaticity coordinates for phosphors. In addition, from the emission at 616 nm, it can be seen clearly that the PL intensity of phosphor $La_2(MoO_4)_3$: Eu^{3+} is about two times stronger than phosphor $Gd_2(MoO_4)_3$: Eu^{3+}. In summary, since the $R_2(MoO_4)_3$ (R = La, Gd) doped with Eu^{3+} powders prepared in our experiment show strong absorption around 400 nm, much intense red emission with good CIE chromaticity coordinates, and low Eu^{3+} (4%) consumption, they may be applied as a cheap and excellent red component for fabrication of near-UV GaN-based white (W)-LEDs.

B. High-Resolution $^7F_0 \rightarrow {}^5D_0$ Excitation and Selectively Excited Emission Spectra

The electronic spectra of ions are broadened by various mechanisms. The broadening obscures features in the spectra and can be especially problematic in trying to make quantitative measurements in mixtures of energy levels. High-resolution laser spectroscopy of ions in crystals requires the narrowband width excitation sources that are only achievable with lasers. Studies in the visible spectral region, typically, use a tunable dye laser including the laser-selective excitation experiments and high-resolution emission spectra [13]. As far as we know, the Eu^{3+} ion is sensitive to the surrounding environment, and the effect of the crystal field will cause shifts and splittings of crystal field levels. Therefore, the laser-selective excitation experiments and high-resolution emission spectra were performed on the as-synthesized samples to clarify the site occupation of Eu^{3+} doped in α-$La_2(MoO_4)_3$ and α-$Gd_2(MoO_4)_3$.

The laser-selective PL excitation spectra of $La_2(MoO_4)_3$: Eu^{3+} were measured by monitoring the $^5D_0-^7F_2$ emission

Fig. 1. Excitation (left, $\lambda_{em} = 616$ nm, from 200 to 550 nm) and emission (right, $\lambda_{ex} = 395$ nm, from 550 to 750 nm) spectra of (a) $Gd_2(MoO_4)_3$: Eu^{3+} and (b) $La_2(MoO_4)_3$: Eu^{3+} phosphors.
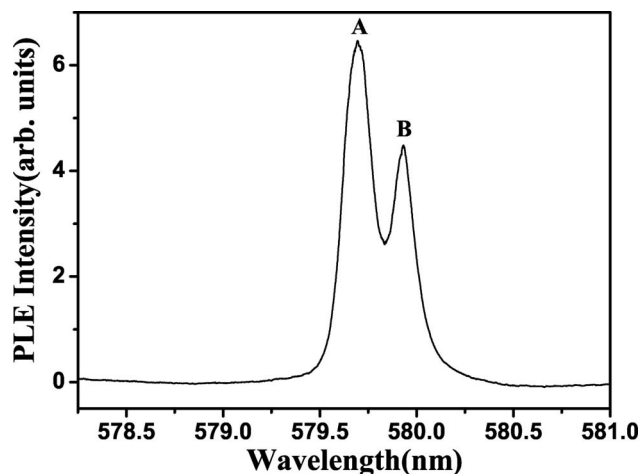
Fig. 2. Site-selective PL excitation spectra of $La_2(MoO_4)_3 : Eu^{3+}$ phosphors measured by monitoring at 616.01 nm.

Table 1. Wavelength and Energy Assignment of $^5D_0-^7F_j$ ($J = 0-2$) Transitions for $La_2(MoO_4)_3 : Eu^{3+}$ Phosphors

Transition Site	A (nm)	B (nm)
$^7F_0-^5D_0$	579.69	579.93
$^5D_0-^7F_1$	589.70 (A_1)	588.81 (B_1)
	592.30 (A_2)	591.82 (B_2)
	595.50 (A_3)	594.86 (B_3)
$^5D_0-^7F_2$	609.19 (A_4)	608.09 (B_4)
	612.77 (A_5)	611.96 (B_5)
	613.66 (A_6)	612.78 (B_6)
	616.01 (A_7)	615.49 (B_7)
	621.15 (A_8)	619.68 (B_8)

at 616.01 nm and displayed in Fig. 2. It is well-known that the initial and final energy state involved in the $^5D_0-^7F_0$ transition is nondegenerate; only a single transition is expected. However, two lines for the $^7F_0-^5D_0$ transition were recorded at 579.69 (site A) and 579.93 nm (site B), indicating that the Eu^{3+} ions occupy at least the two nonequivalent point sites
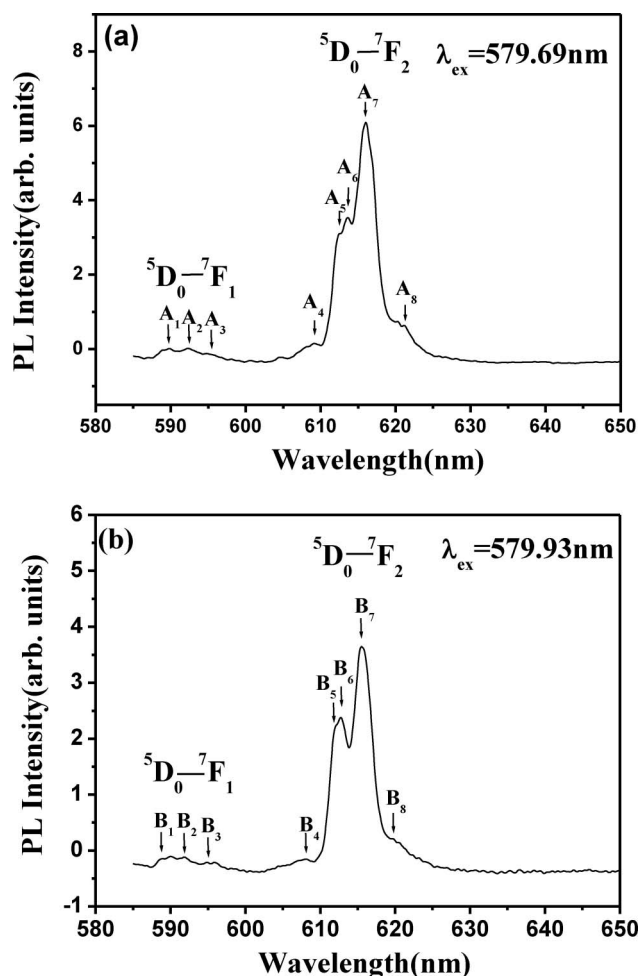
of the La^{3+} ion. To our best knowledge, the $La_2(MoO_4)_3$ structure is best described as a defect scheelite structure [14]. The formula may be rewritten as $La_{2/3}\square_{1/3}MoO_4$ where $\square$ stands for the vacant sites. It comprises nine scheelite subcells and there are 12 f.u. per unit cell. Nearest-neighbor environments of the cations resemble those of scheelite. La is in eightfold and Mo is in slightly distorted tetrahedral oxygen coordination. One third of the oxygen atoms are coordinated by one Mo and two La atoms, and other two thirds are coordinated by one Mo and one La atom. The space group of the $La_2(MoO_4)_3$ is C2/c, and the RE atoms are located at three nonequivalent general crystallographic positions 8f (C_1). In this case, it is possible that a third site exists whose $^5D_0$ level is close to the $^5D_0$ of site A or B, which is in agreement with the structure of α-$La_2(MoO_4)_3$, whose symmetries are more or less distorted from S_4. Figure 3 shows the highly resolved emission spectra of $La_2(MoO_4)_3 : Eu^{3+}$ upon excitation in the A and B bands. One can observe that there is a distinct difference in the two emission spectra. According to the relative intensity of emission, the A_1, A_2, and A_3 lines are ascribed to the $^5D_0-^7F_1$ transition of site A ($\lambda_{em} = 579.69$ nm), and the B_1, B_2, and B_3 lines are ascribed to the $^5D_0-^7F_1$ transition of site B ($\lambda_{em} = 579.93$ nm). The transitions between $^5D_0$ and ^7F_J ($J = 0, 1, 2$) are given in Table 1. It is clear that emission lines from the site of $La_2(MoO_4)_3 : Eu^{3+}$ could not be fully separated because different sites may possibly have energy transfer.

The laser-selective PL excitation spectra of $Gd_2(MoO_4)_3 : Eu^{3+}$ were measured by monitoring the $^5D_0-^7F_2$ emission

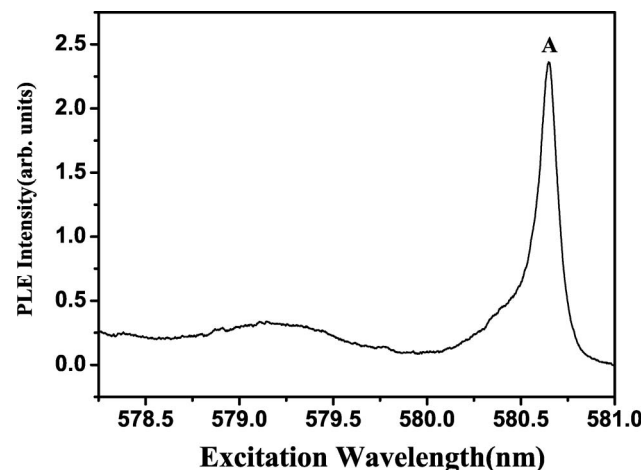Fig. 3. High-resolution emission spectrum of $La_2(MoO_4)_3 : Eu^{3+}$ phosphors for the excitations at (a) 579.69 nm and (b) 579.93 nm, respectively.

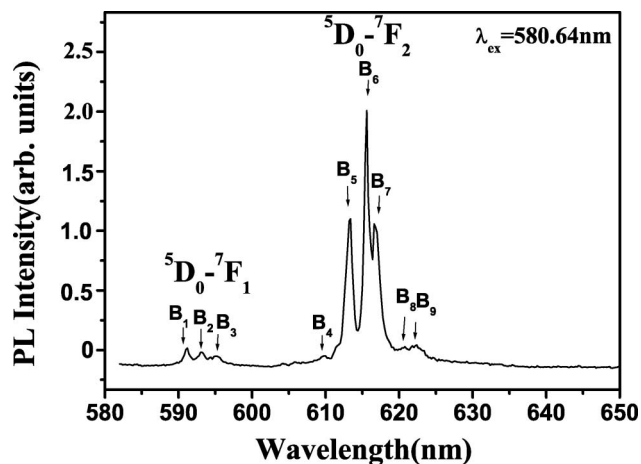Fig. 4. Site-selective PL excitation spectra of $Gd_2(MoO_4)_3 : Eu^{3+}$ phosphors measured by monitoring at 616.50 nm.

Fig. 5.   High-resolution emission spectrum of $Gd_2(MoO_4)_3 : Eu^{3+}$ phosphors for the excitations at 580.64 nm.

at 616.50 nm and displayed in Fig. 4. We observed only one line for $^7F_0$–$^5D_0$ transition recorded at 580.64 nm (site A). The broadband appearing on the higher-energy side of the A excitation line is attributed to a vibronic sideband at room
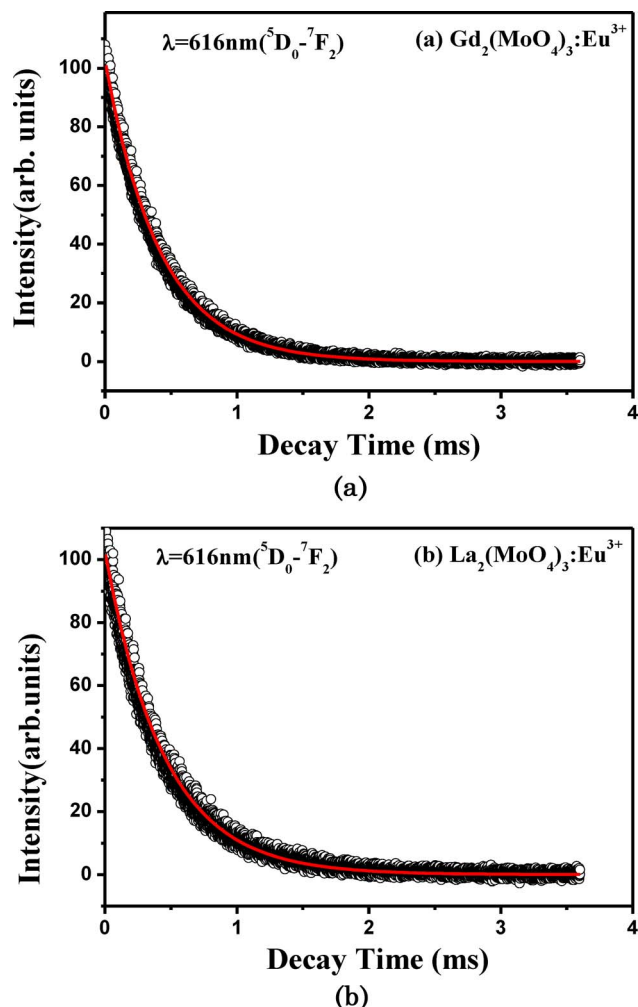

(a)

(b)

Fig. 6.   (Color online) Decay curves for the as-prepared samples: (a) $Gd_2(MoO_4)_3 : Eu^{3+}$ (round circles, experimental data; red solid line, fitting results by $I = I_0 \exp(-t/\tau)$, $\tau = 0.416$ ms) and (b) $La_2(MoO_4)_3 : Eu^{3+}$ (round circles, experimental data; red solid line, fitting results by $I = I_0 \exp(-t/\tau)$, $\tau = 0.448$ ms).

temperature. This was confirmed by the emission spectrum under the excitation at the shoulder (579.25 nm) in which the emission lines were completely matched with those under the excitation at site A (580.64 nm). Brixner *et al.* [15] suggested that since the spectra of Eu^{3+} in $Gd_2(WO_4)_3$ and α-$Gd_2(MoO_4)_3$ are very similar, the two compounds are isostructural. Moreover, Kodaira *et al.* [16] also watched only one line for $^5D_0$–$^7F_0$ transition in the $Gd_2(MoO_4)_3 : Eu^{3+}$ at low temperature, which was in agreement with the structure of $Gd_2(MoO_4)_3$, where the RE occupies only one crystallographic site. Those analogy can explain that the Eu^{3+} ions doped in α-$Gd_2(MoO_4)_3$ may occupy just one crystallographic site of the Gd^{3+} ion. Figure 5 shows the highly resolved emission spectra of $Gd_2(MoO_4)_3 : Eu^{3+}$ upon excitation at 580.64 nm. The $^5D_0$–$^7F_1$ transition splits into three peaks, confirming the existence of a single local low symmetry chemical environment for the Eu^{3+} ion, whereas the hypersensitive $^5D_0$–$^7F_2$ transition split into five bands, which is compatible with a C2 site symmetry.

In order to avoid the superimposition of images and signals, it is well known that the lifetime of phosphors applied in the field of displays and lights should be suitable [17]. The PL decay curves of the as-obtained phosphors were also investigated. The decay curves of the $R_2(MoO_4)_3$ (R = Gd, La) doped with Eu^{3+} powders prepared indicate that all the curves can be well fitted into a single exponential function as $I(t) = I_0 \exp(-t/\tau)$, where I is intensity, I_0 is initial intensity, and τ is decay lifetime. The lifetimes are determined to be 0.448 and 0.416 ms for $La_2(MoO_4)_3 : Eu^{3+}$ and $Gd_2(MoO_4)_3 : Eu^{3+}$ samples, respectively (Fig. 6). The results show that the lifetime is short enough for potential applications in displays and lights.

4. CONCLUSION

From a detailed analysis of the site-selective laser excitation and emission spectroscopy in Eu^{3+}-doped $R_2(MoO_4)_3$ (R = La, Gd), two crystallographic sites in the $La_2(MoO_4)_3$ and one crystallographic site in the $Gd_2(MoO_4)_3$ are assigned. The luminescent properties of the $R_2(MoO_4)_3 : Eu^{3+}$ (R = La, Gd) phosphors were investigated, showing strong absorption at 395 nm and much intense red emission, which indicated they might be applied as the cheap and excellent red component for fabrication of near-UV GaN-based W-LEDs. Moreover, the $La_2(MoO_4)_3 : Eu^{3+}$ phosphors showed a higher emission intensity and better luminescent properties. Further work is underway to study the luminescent properties of the well-prepared samples at a low temperature and the possibility of synthesizing other related materials.

REFERENCES

1. V. Sivakumar and U. V. Varadaraju, "Intense red phosphor for white LEDs based on blue GaN LEDs," J. Electrochem. Soc. **153**, H54–H57 (2006).

2. G. Blasse, "On the Eu^{3+} fluorescence of mixed metal oxides. IV. The photoluminescent efficiency of Eu^{3+}-activated oxides," J. Chem. Phys. **45**, 2356–2360 (1966).

3. Y. R. Do and Y. D. Huh, "Optical properties of potassium europium tungstate phosphors," J. Electrochem. Soc. **147**, 4385–4388 (2000).

4. T. W. Chou, S. Mylswamy, R. S. Liu, and S. Z. Chuang, "Eu substitution and particle size control of Y_2O_2S for the excitation by UV light emitting diodes," Solid State Commun. **136**, 205–209 (2005).

5. X. X. Zhao, X. J. Wang, B. J. Chen, Q. Y. Meng, B. Yan, and W. H. Di, "Luminescent properties of Eu^{3+} doped α-$Gd_2(MoO_4)_3$ phosphor for white light emitting diodes," Opt. Mater. **29**, 1680–1684 (2007).

6. F. Lei and B. Yan, "Hydrothermal synthesis and luminescence of $CaMO_4 : RE^{3+}$ (M = W, Mo; RE = Eu, Tb) submicrophosphors," J. Solid State Chem. **181**, 855–862 (2008).

7. S. Neeraj, N. Kijima, and A. K. Cheethanl, "Novel red phosphors for solid-state lighting: the system $NaM(WO_4)_{2-x}(MoO_4)_x : Eu^{3+}$ (M = Gd, Y, Bi)," Chem. Phys. Lett. **387**, 2–6 (2004).

8. C. F. Guo, T. Chen, L. Luan, W. Zhang, and D. X. Huang, "Luminescent properties of $R_2(MoO_4)_3 : Eu^{3+}$ (R = La, Y, Gd) phosphors prepared by sol–gel process," J. Phys. Chem. Solids **69**, 1905–1911 (2008).

9. E. H. Williams, "The magnetic properties of some rare earth oxides at low temperature," Phys. Rev. **14**, 348–351 (1919).

10. S. Foner, E. J. McNiff, R. N. Shelton, Jr., R. W. McCallum, and M. B. Maple, "Upper critical fields of superconducting rare-earth molybdenum selenides," Phys. Lett. A **57**, 345–346 (1976).

11. Y. S. Cho, D. Kim, Y. J. Lee, H. Yang, and Y. D. Huh, "Preparation and photoluminescence properties of red-emitting $Gd_2(MoO_4)_3 :$ Eu phosphors for a three-band white LED," Bull. Korean Chem. Soc. **31**, 2992–2994 (2010).

12. Z. H. Xu, C. X. Li, G. G. Li, R. T. Chai, C. Peng, D. M. Yang, and J. Lin, "Self-assembled 3D urchin-like $NaY(MoO_4)_2 : Eu^{3+}/Tb^{3+}$ microarchitectures: hydrothermal synthesis and tunable emission colors," J. Phys. Chem. C **114**, 2573–2582 (2010).

13. P. M. Selzer, "Topics in applied physics" in *Laser Spectroscopy of Solids*, W. M. Yen and P. M. Selzer, eds. (Springer, 1981), pp. 141–143.

14. W. Jeitschko, "Crystal structure of $La_2(MoO_4)_3$, a new ordered defect scheelite type," Acta Cryst. **29**, 2074–2081 (1973).

15. L. H. Brixner, P. E. Bierstedt, A. W. Sleight, and M. S. Licis, "Precision parameters of some $Ln_2(MoO_4)_3$-type rare earth molybdates," Mater. Res. Bull. **6**, 545–554 (1971).

16. C. A. Kodaira, H. F. Brito, and O. L. Malta, "Luminescence and energy transfer of the europium (III) tungstate obtained via the Pechini method," J. Lumin. **101**, 11–21 (2003).

17. G. Blasse and B. C. Grabmaier, *Luminescent Materials* (Springer-Verlag, 1994).