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Comparative luminescence study of LaBMoO$_6$:Tb phosphor under VIS and Near-UV excitation for green photonic applications

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Abstract

La$_{(1-x)}$BMoO$_6$:Tb$_x$ phosphors were synthesis to study structure, absorption and luminescence properties. XRD results show monoclinic structure (P2$_1$ space group) LaBMoO$_6$ host composition. This phosphor can absorb photon in near-UV, VIS and NIR region observed from reflectance spectra. VIS light with 487 nm and near-UV with 259 nm excitation resulted to strong green emission from Tb^{3+} in phosphor. VIS excitation via 4f-f4 transition generated stronger emission than near-UV excitation via 4f-5d transition. From decay curve results, luminescence life time of phosphor is in millisecond order and energy transfer between Tb^{3+} with dipole-dipole interaction was found in this under VIS excitation. The optimum composition of this phosphor for luminescence excited by VIS and near-UV is La$_{0.96}$BMoO$_6$:Tb$_{0.04}$ and La$_{0.84}$BMoO$_6$:Tb$_{0.16}$, respectively. La$_{0.96}$BMoO$_6$:Tb$_{0.04}$ perform a good potential for using as green emitting powder in display and LED device, while La$_{0.84}$BMoO$_6$:Tb$_{0.16}$ is suitable for applying in near-UV to VIS converter.
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Keywords: Phosphor; Terbium; Molybdenum

1. Introduction

Nowadays, luminescence materials have became more role in human life, especially in activity related with artificial light. These materials can be prepared in form of liquid, bulk, fiber and powder. Phosphor is luminescence

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powder which has been used in the important photonics applications such as light source, display, light emitting diode (LED), detector and electromagnetic wave converter. Inside powder, it composes of host matrix composition and luminescence activator. Lanthanide ions had been often used as activator because of its strong emission from intra 4f-4f transition [1] which can be enhanced by non-centrosymmetric field from surround ligands [2]. Terbium ion (Tb^{3+}) is one of lanthanide group that $^5D_4 \rightarrow {}^7F_5$ transition can generate the visible light (VIS) with green color. Therefore, it was doped in various phosphor, such as $Bi_2ZnB_2O_7$:Tb^{3+} [3], $Li_2Ca_{0.4}Sr_{0.6}SiO_4$:$Tb^{3+}$ [4], BiOCl:Tb^{3+} [5], $Gd_3A_{l5}O_{12}$:Tb^{3+} [6] and $KMgLa(PO_4)_2$:Tb^{3+} [7], for development in green emitting applications. Since strong emission requirement from Tb^{3+}, this ion needs to be surrounded by asymmetric ligand arrangement in host lattice. Lanthanum boron molybdenum oxide ($LaBMoO_6$) with monoclinic structure is very interesting to be doped with Tb^{3+} for green emission. From non-centrosymmetric site of $LaBMoO_6$ structure [8], it can encourage the 4f-4f transition of Tb^{3+} leading to strong green emission. Some display devices and LED need to be coated or contained green emitting powder like this one. The asymmetric site in $LaBMoO_6$ structure was only used to promote the strong red emission of Eu^{3+} [9] but for green emission of Tb^{3+}, it has still not been reported. Moreover, molybdenum in this host matrix are coordinated by five oxygen with distorted trigonal-bipyramidal formation which can be absorbed photon in near-ultraviolet (near-UV). This absorbed UV can be transfer to some lanthanide doped ion such as Eu^{3+} by charge transfer and generate the photoluminescence from UV-excitation [9,10]. It gives a chance to study UV-excitation of Tb^{3+} in this phosphor for UV-VIS converter application.

In this paper, Tb^{3+} doped $LaBMoO_6$ phosphor were synthesized to study crystal structure, absorption and luminescence properties. The influence of Tb^{3+} amount in $LaMoBO_6$ phosphor on these properties were also investigated to find out the best condition of powder for green photonic applications.

2. Experiment

$La_{(1-x)}BMoO_6$:Tb_x phosphor were prepared by solid state reaction with x = 0.004, 0.020, 0.040, 0.080, 0.120, 0.160, 0.200 and 0.240 mol. The high purity chemicals such as La_2O_3, MoO_3, H_3BO_3, Tb_2O_3 were weighted totally for 15 g and mixed thoroughly in agate mortar. Mixtures were then pressed with 20 tons by hydraulic press machine to make as a circle pellet for comfortable measurement. After that, all samples were annealed with 700 °C for 10 hr in electrical furnace. Obtained phosphors were studied the crystalline structure by using x-ray diffractometer (XRD-6001, Shimadzu) with CuKα radiation (wavelength 0.154 nm). Photon absorption of phosphor was evaluated from reflectance spectra via UV-VIS-NIR spectrophotometer (Shimadzu, UV-3600). The luminescence properties were monitored from excitation spectra, emission spectra and decay curve. The decay curve were analyzed the energy transfer behavior by using Inokuti-Hirayama (IH) model. The emission color of phosphor was studied by method of Commission of International de L'Eclairage (CIE) 1931 chromaticity.

3. Results and discussion

3.1. Structure characterization

XRD results of all $La_{(1-x)}BMoO_6$:Tb_x phosphors exhibit the crystalline structure of $LaBMoO_6$ as monoclinic with space group $P2_1$. This pattern matches precisely via JCPDs 00-60-0869 database [8]. Three main atomic plane (h k l) in compound are (1 0 2), ($\bar{1}$ 0 3) and (0 1 2) which center at 2θ about 26.23, 30.35 and 28.79, respectively. The XRD result of $La_{0.96}BMoO_6$:$Tb_{0.04}$ and $La_{0.84}BMoO_6$:$Tb_{0.16}$, including, JCPDs database are shown in Fig. 1. However, it was found an intermediate atomic plane at 2θ about 28.05 at α symbol. It is probably belong to (1 1 0) plane of La_2O_3 with cubic structure corresponding to JCPDs 00-040-1284. This plane is degraded with increasing of Tb^{3+} amount in phosphor. Since La^{3+} and Tb^{3+} particle has closely radius (R_{La} = 1.10 Åand R_{Tb} = 0.98 Å for coordination number as 7) [11], adding Tb_2O_3 via replacing La_2O_3 make the basis substitution of La^{3+} by Tb^{3+}. This results to reduction of La_2O_3 plane. However, Tb-composition plane was not observed because of low doping concentration.
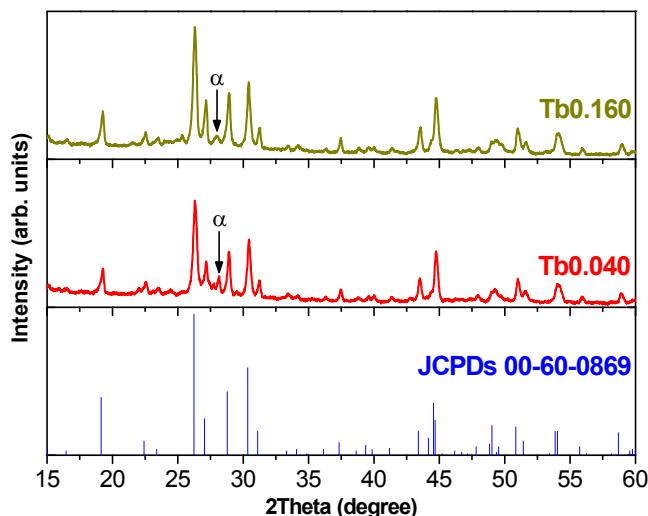
Fig. 1. XRD result of $La_{(1-x)}BMoO_6:Tb_x$ (x = 0.04 and 0.16 mol) and XRD pattern from JCPDs 00-60-0869 database.

3.2. Absorption properties

The reflectance spectra of all $La_{(1-x)}BMoO_6:Tb_x$ phosphors are shown in Fig. 2. Part of deflated curve in spectra performs the absorption ability of phosphor. It was found that VIS light with 487 nm and near-infrared (NIR) with 1995 and 2276 nm were directly absorbed by Tb^{3+} with 4f-4f transition from $^7F_6$ ground state to upper state such as, $^7F_6 \rightarrow {}^5D_4$, $^7F_6 \rightarrow {}^7F_{0,1}$ and $^7F_6 \rightarrow {}^7F_3$, respectively [12]. Moreover, near-UV radiation in 200 - 400 nm region was also absorbed by host matrix and Tb^{3+} with 4f-5d transition [13] as will be mentioned in next chapter. The absorption ability of phosphor in VIS region clearly increases with increasing of Tb^{3+} concentration. However, it was found some fluctuation for NIR absorption with higher amount of Tb^{3+} but can still be observed the increasing trend.
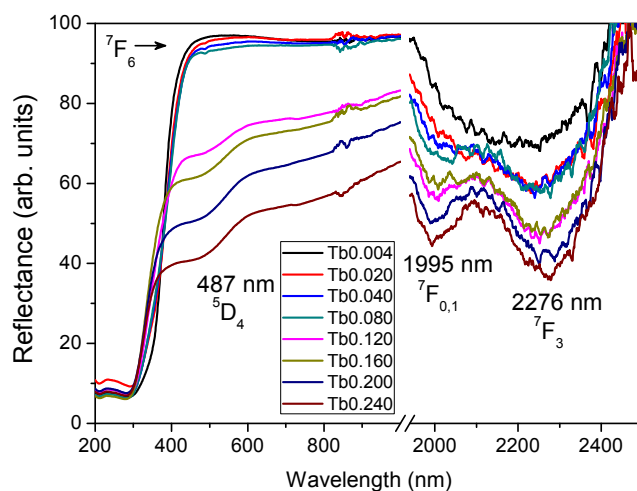

Fig. 2. Absorption spectra of $La_{(1-x)}BMoO_6:Tb_x$ phosphor.

3.3. Luminescence properties

Since goal of this work focus on the green emission of Tb^{3+}, the excitation spectra with 544 nm emission wavelength of $La_{(1-x)}BMoO_6:Tb_x$ phosphor were then monitored as show in Fig. 3. The result shows that phosphor can be emitted photon with 544 nm if it were excited by near-UV radiation with 259, 353, 369 and 378 nm and by VIS light with 487 nm. All these excitation, except with 259 nm, correspond to inner 4f-4f transition of Tb^{3+} such as $^7F_6 \rightarrow ^5L_9$, $^7F_6 \rightarrow ^5L_{10}$, $^7F_6 \rightarrow ^5G_6$ and $^7F_6 \rightarrow ^5D_4$, respectively [5,12,14]. For board excitation band centered at 259 nm wavelength, it relates with inter 4f-5d transition as $4f^8 \rightarrow 4f^8 5d^1$ [4,5,13,15]. Not like behavior in Eu^{3+} doped phosphor [9,16], this board band cannot be assigned as $O^{-2} \rightarrow Tb^{3+}$ charge transfer band (CTB) because this electron transfer need energy higher than 5d level of Tb^{3+}, around 60,000 cm-1 comparable with 167 nm of photon [13,17]. After Tb^{3+} climbed up to several excited states by those excitations, they all decayed down to same state, $^5D_4$, without light emitting by non-radiative relaxation (NR). Then, Tb^{3+} emitted 544 nm photon by $^5D_4 \rightarrow ^7F_5$ transition. Energy transition process of excitation spectra are shown in Fig. 5. There were various trend of relation between spectra intensity and Tb concentration, it is better to explain this solution in emission spectra.
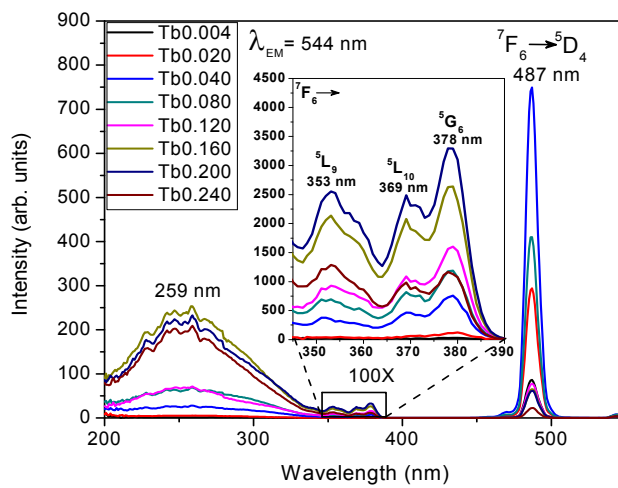

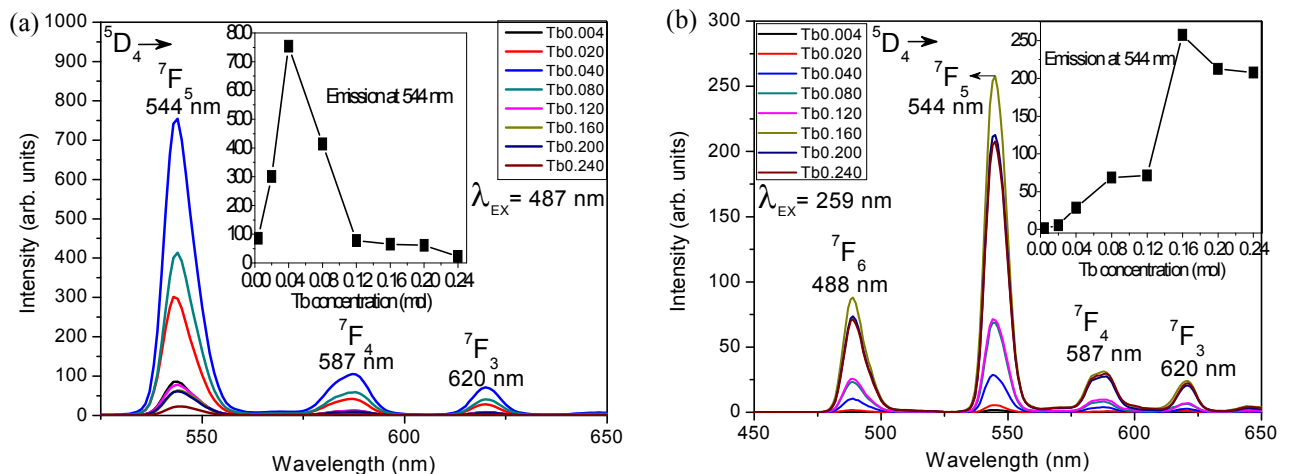Fig.3. Excitation spectra with 544 nm emission wavelength of $La_{(1-x)}BMoO_6:Tb_x$ phosphor.

Fig. 4. (a) Emission spectra with 487 nm excitation wavelength of $La_{(1-x)}BMoO_6:Tb_x$ phosphor, (b) Emission spectra with 259 nm excitation wavelength of $La_{(1-x)}BMoO_6:Tb_x$ phosphor, both inset pictures show 544 nm emission intensity as a function of Tb concentration.
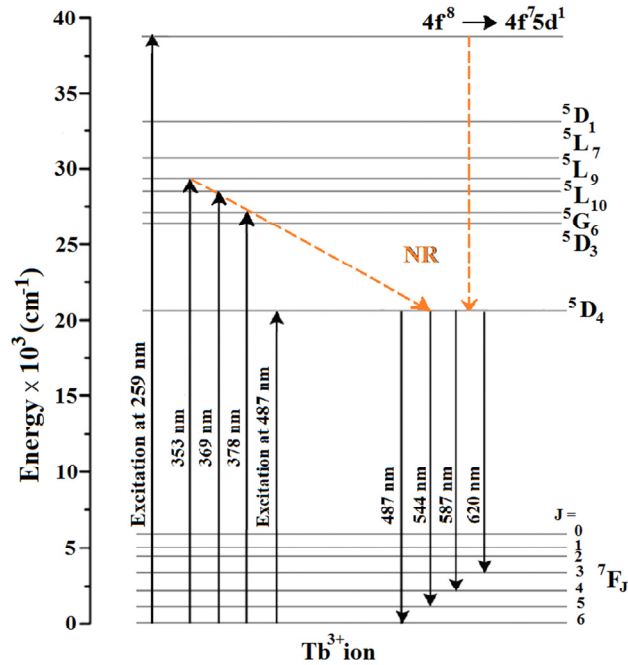
Fig.5. Tb^{3+} energy transition diagram for excitation and emission spectra of $La_{(1-x)}BMoO_6$:Tb_x phosphor [22].

Since photon with 487 nm and 259 nm can strongly excited Tb^{3+} in phosphor, both wavelength then were used to study the emission spectra as show in Fig. 4(a) and Fig. 4(b), respectively. For VIS excitation with 487 nm, energy state of Tb in phosphor change to $^5D_4$ and the photon with 544, 587 and 620 nm then were emitted via state transition from excited $^5D_4$ such as $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$, $^5D_4 \rightarrow {}^7F_3$, respectively [4,5,12,14]. In near-UV excitation with 259 nm, electron configuration of Tb^{3+} were changed to $4f^8 \rightarrow 4f^8 5d^1$ resulting to the 4f-5d energy transition. After that, electron configuration came back to $4f^8$ and Tb^{3+} energy state decay down to $^5D_4$ by NR. The emission then occurred in the same process with 487 nm excitation, but it had the extra emission with 488 nm from $^5D_4 \rightarrow {}^7F_6$ transition [4,5,13,15]. The strongest emission in both excitations is belonged to 544 nm ($^5D_4 \rightarrow {}^7F_5$) which is dominant for green emission and excitation by 487 nm give stronger emission than 259 nm excitation. All energy transition process of emission spectra are shown in Fig. 5. Moreover, the emission intensity as a function of Tb^{3+} concentration performed in different ways as show in the inset picture of Fig. 4(a) and Fig. 4(b). The emission intensity with 487 nm excitation increases with increasing of Tb^{3+} content from 0.004 to 0.040 mol after that it decreases. For 259 nm excitation, the emission intensity increases in the range of 0.004 to 0.160 mol after that it also decreases. The reduction of emission intensity after maximum at 0.020 mol (for 487 nm excitation) and 0.160 mol (for 259 nm excitation) are result from concentration quenching. This phenomena is the energy transfer between activator ion, when it get close together in range of critical distance and make total emission intensity decreases. From strong band of emission spectra, this kind of Tb^{3+} phosphor performs a good potential for using as luminescence material in photonics application especially, $La_{0.96}BMoO_6$:$Tb_{0.04}$ for display and LED, while $La_{0.84}BMoO_6$:$Tb_{0.16}$ for near-UV to VIS converter.

The emission spectrum of $La_{0.96}BMoO_6$:$Tb_{0.04}$ phosphor with 487 nm excitation and $La_{0.84}BMoO_6$:$Tb_{0.16}$ with 259 nm excitation were taken to evaluate the color of luminescence via CIE 1931 chromaticity system [18]. In Fig. 6, the coordinate of emission color with 487 nm excitation and 259 nm excitation were plotted at (0.35, 0.64) (red star symbol) and (0.31, 0.60) (blue circle symbol) in diagram, respectively. Both excitations create the bright green light coming out from phosphor. This is confirmation that $La_{0.96}BMoO_6$:$Tb_{0.04}$ and $La_{0.84}BMoO_6$:$Tb_{0.16}$ powder can be coated or contained in display and LED devices which require the green light emitting.
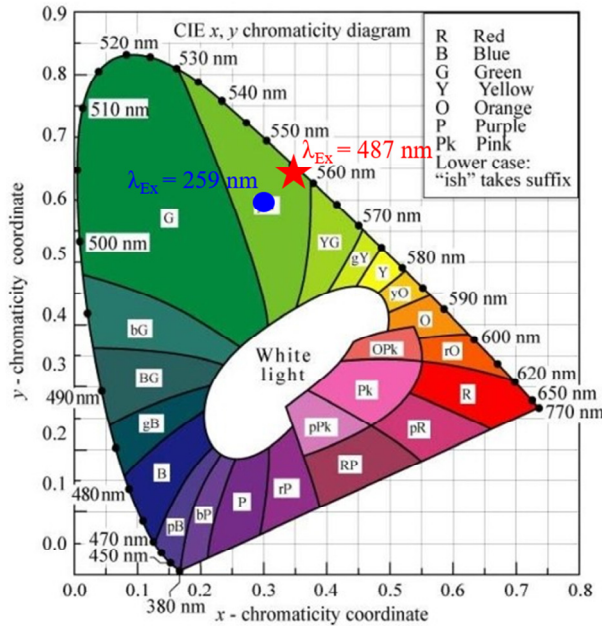
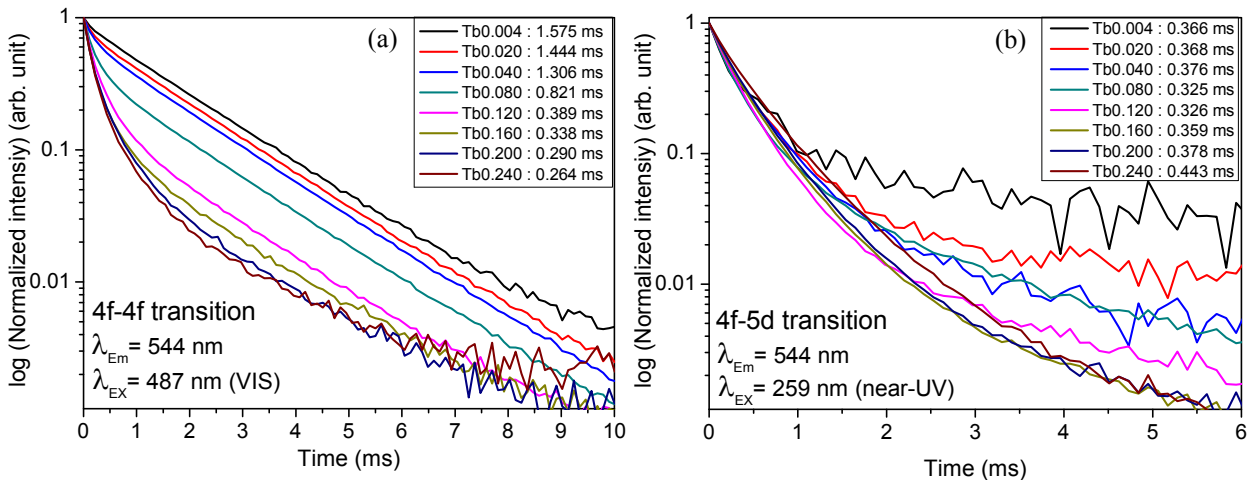Fig 6. CIE 1931 chromaticity diagram of $La_{0.96}BMoO_6:Tb_{0.04}$ with 487 nm excitation and $La_{0.84}BMoO_6:Tb_{0.16}$ with 259 nm excitation [19].

Fig. 7. (a) Decay curve of 544 nm emission from $La_{(1-x)}BMoO_6:Tb_x$ phosphor excited by VIS with 487 nm; (b) Decay curve of 544 nm emission from $La_{(1-x)}BMoO_6:Tb_x$ phosphor excited by near-UV with 259 nm.

The luminescence decay curve with VIS (487 nm) and near-UV (259 nm) excitation of all $La_{(1-x)}BMoO_6:Tb_x$ sample were investigated and shown in Fig. 7(a) and Fig. 7(b), respectively. Decay behavior between two excitations is clearly distinct. For 487 nm excitation, curve exhibit almost single exponential decay in low Tb concentration phosphor and it becomes to be more non-single exponential with higher Tb content. Along that decay behavior change, obtained life time value decrease from 1.575 to 0.264 ms. This simultaneousvariation indicate the energy transfer between Tb^{3+} donor and acceptor which can be explained by Inokuti-Hirayama (IH) model [20,21]. The decay curves in Fig. 7(a) were then fitted with the expression:

$$I(t) = I_0 exp\left\{-\frac{t}{\tau_0} - Q\left(\frac{t}{\tau_0}\right)^{3/S}\right\} \tag{1}$$

where I_0 is a maximum intensity at start of emission, t is time, τ_0 is life time of phosphor with lowest concentration of activator ion, Q is energy transfer parameter and S can be 6, 8 and 10 for dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interaction, respectively. From fitting with IH model by using S = 6, Q value is obtained such as 0.301, 0.460, 1.111, 1.844, 2.228, 2.265 and 2.394 for phosphor doped with Tb 0.020, 0.040, 0.080, 0.120, 0.160, 0.200 and 0.240 mol, respectively. All fitting show R^2 value are not lower than 0.986. Since S = 6 and fitted Q value increase with increasing of Tb concentration, the energy transfer between Tb^{3+} via dipole-dipole interaction can occur more effectively. It results from shorter distant between Tb^{3+} in phosphor structure. For decay curve with near-UV, 259 nm excitation, it has not found an obviously trend of changing between single to non-single exponential behavior. The variation of life time also cannot be identified the exact trends with Tb concentration. The reason of this fluctuation probably come from 4f-5d transition with near-UV excitation. It is not transition between sub-states inner 4f shell like VIS excitation so, excitation and emission, including energy transfer between Tb^{3+} can be effective perturbed by ligand field. From all decay curve result, the life time of green emission for $La_{(1-x)}BMoO_6:Tb_x$ is in millisecond. This phosphor is so suitable for using in display and LED which need continuously emission of green light.

4. Conclusion

$La_{(1-x)}BMoO_6:Tb_x$ phosphors were prepared by solid state reaction. Structure of this compound is monoclinic with $P2_1$ space group. Small site of La_2O_3 intermediate in phosphor structure but it was degraded by Tb_2O_3 replacement. Tb^{3+} and host matrix combination in this phosphor can absorb photon in near-UV, VIS and NIR region. The strong green emission of Tb^{3+} can be generated by VIS excitation with 487 nm and near-UV excitation with 259 nm, former give the stronger emission. The main mechanism of Tb^{3+} for emission with those VIS and near-UV excitation is based on 4f-4f and 4f-5d transition, respectively. Energy transfer between Tb^{3+} with dipole-dipole interaction was found in this phosphor with VIS excitation. The optimum composition of this phosphor for luminescence excited by VIS and near-UV is $La_{0.96}BMoO_6:Tb_{0.04}$ and $La_{0.84}BMoO_6:Tb_{0.16}$, respectively. From strong emission spectra with green color and life time in millisecond, $La_{0.96}BMoO_6:Tb_{0.04}$ perform a good potential for using as green emitting powder coated in display and LED device, while $La_{0.96}BMoO_6:Tb_{0.04}$ is suitable for applying in near-UV to VIS converter.

Acknowledgements

References

[1] B.G. Wybourne, Spectroscopic Propertiesof Rare Earths, John Wiley & Sons. Inc., New York, 1965.
[2] B.G. Wybourne, in:B. Di Bartolo, O. Forte (Eds.), Advances in Spectroscopy for Lasers and Sensing, John Wiley & Sons. Inc., New York, 1965, pp. 403–433.
[3] E. Erdoğmuş, E. Korkmaz, Optik 125 (2014) 4098–4101.
[4] X. Li, D. Zhang, Y. Chen, C. Chang, Ceram. Int. 43 (2017) 1677–1681.
[5] X. Huang, B. Li, H. Guo, J. Alloy.Compd. 695 (2017) 2773–2780.
[6] X. Teng, J. Li, G. Duan, Z. Liu, J. Lumin. 179 (2016) 165–170.
[7] Z. Yang, Q. Bai, T. Li, S. Xu, H. Dong, Z.Wang,P. Li, Optik 127 (2016) 9338–9343.
[8] V.Kroutko, G.Lysanova, M. Komova,Inst. of General and Inorganic Chemistry, RAS, Moscow, Russian Federation. ICDD Grant-in-Aid, 2009.
[9] Z.W. Zhang, D.Q. Ma, Y. Yue, M.Z. Ma, R.P. Liu, J. Alloy. Compd. 636 (2015) 113–116.
[10] Y. Yu, L.Y. Li, Z.B. Lin, G.F. Wang, Cryst. Eng. Comm. 15 (2013) 5245–5249.
[11] R. D. Shannon, Acta Cryst. 32 (1976) 751–767.
[12] C.R. Kesavulu, H.J. Kim, S.W. Lee, J. Kaewkhao, E. Kaewnuam, N. Wantana, J. Alloy. Compd. [in press] (2017).
[13] G. Annadurai, M. Jayachandiran, S. Masilla Moses Kennedy, V. Sivakumar, Mat. Sci. Eng. B 208 (2016) 47–52.
[14] Li Yang, Yingpeng Wan, Yanlin Huang, Cuili Chen, Hyo Jin Seo, J. Alloy. Compd. 684 (2016) 40–46.
[15] Neharika, V. Kumar, J. Sharma, V. K. Singh, O.M. Ntwaeaborwa, H.C. Swart, J. Electron Spectrosc.206 (2016) 52–57.
[16] V. Jubera, J.P. Chaminade, A. Garcia, F. Guillen, C. Fouassier, J. Lumin. 101 (2003) 1–10.

[17] L.J. Nugent, R.D. Baybarz, J.L. Burnett, J.L. Ryan, J. Phys. Chem. 77 (1973) 1528–1539.
[18] K.V. Krishnaiah, K.U. Kumar, C.K. Jayasankar, Mater. Express 3 (2013) 61–70.
[19] S. Gage, D. Evans, M.W. Hodapp, H. Sorensen, Optoelectronics Applications Manual, McGraw Hill, New York, 1977.
[20] N. Vijaya, K. Upendra Kumar, C.K. Jayasankar, Spectrochim. Acta A 113 (2013) 145–153.
[21] K. Linganna, Ch. Srinivasa Rao, C.K. Jayasankar, J. Quant. Spectrosc. Ra. 118 (2013) 40–48.
[22] M. Reza Dousti, R. Junaid Amjad, J. Nanophoton. 9(1) (2015) 093068.