Study on structure and luminescence properties of LaBMoO₆:Dy³⁺ phosphor for photonic material applications

Eakgapon KAEWNUAM[1,*], Nuanthip WANTANA[2,3], Sasithorn SAIKAEW[4], Hong Joo KIM[5], and Jakrapong KAEWKHAO[2,3]

[1]*Physics Program, Faculty of Science and Technology, Muban Chombueng Rajabhat University, Ratchaburi, 70150, Thailand*
[2]*Physics Program, Faculty of Science and Technology, Nakhon Pathom Rajabhat University, Nakhon Pathom, 73000, Thailand*
[3]*Center of Excellence in Glass Technology and Materials Science (CEGM), Nakhon Pathom Rajabhat University, Nakhon Pathom 73000, Thailand*
[4]*Center for Science and Applied Science, Faculty of Science and Technology, Muban Chombueng Rajabhat University, Ratchaburi, 70150, Thailand*
[5]*Department of Physics, Kyungpook National University, Daegu, 41566, Republic of Korea*

*Corresponding author e-mail: Eakgapon@mcru.ac.th

Abstract

Phosphor powder of LaBMoO₆:Dy³⁺ were prepared to investigate the structure, absorption and luminescence properties. The influence of Dy₂O₃ concentration on these properties were also studied. XRD characterization represents the main structure of phosphor as monoclinic from LaBMoO₆ host matrix. From the reflection spectra, Dy³⁺ in phosphor can absorb more amount of visible light and near infrared radiation with increasing of Dy₂O₃ concentration. The energy band gap of LaBMoO₆ compound was expanded after doping with Dy₂O₃ which results to the blue shift of absorption edge. The emission spectra perform the strong yellow and blue light emitting under Dy³⁺ electric dipole ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) and magnetic dipole ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) transition, respectively. Fitting the luminescence decay curve results to Dy³⁺ emission life time in millisecond. This phosphor performs the potential for using as photonic materials in display/screen and LED devices.

1. Introduction

Photonic devices such as light source, display/screen, light emitting diode (LED), detector and electromagnetic wave converter are integrated with the high efficiency luminescence materials. Since small particle, luminescence powder called "phosphor" is one type of luminescence materials which are suitably and easily contained in mentioned photonic devices. In phosphor component, it consists of the host matrix compound and doped luminescence ion. Lanthanide ions (Ln³⁺) had been often used as luminescence center because of their strong emission from intra 4f-4f transition [1] which can be enhanced by non-centrosymmetric field from surround asymmetric ligands [2]. Dysprosium ion (Dy³⁺) possess the signature luminescence properties, strong blue ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) and yellow ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) emission which can also intercept to be white light [3-7]. Therefore, there were many researches of Dy³⁺

doped phosphor such as Ca₂SiO₄:Dy³⁺ [3], KSrPO₄:Dy³⁺ [4], BaKWO₄:Dy³⁺ [5], Ba₃Lu(PO₄)₃:Dy³⁺ [6], ZnWO₄:Dy³⁺ [7] for white light emitting devices and NaLaMgWO₆:Dy³⁺ [8], PbGdB₇O₁₃:Dy³⁺ [9] for yellow light emitting devices. Since asymmetric environment around Dy³⁺ can enhance the photo-emission under 4f-4f transition, Dy³⁺ should be doped into host lattice with non-centrosymmetric site. Lanthanum boron molybdenum oxide (LaBMoO₆) is an interesting option for using as Dy³⁺ host material because it performs the asymmetric lattice from monoclinic system [10]. Its three-dimensional network composes of one-dimensional LaO₇, BO₂ and MoO₄ chains along the b-axis interconnected via corner- and edge-sharing. Recently, LaBMoO₆ structure was used to promote the strong red emission of Eu³⁺ [11] and green emission of Tb³⁺ [12] but for blue, yellow and integrated white light emission of Dy³⁺, they have still not been investigated. Moreover, LaBMoO₆ absorbed photon of near-ultraviolet (near-UV)

which can be transfer the energy to excite some Ln^{3+} such as Eu^{3+} and Tb^{3+} resulting to the visible light (VIS) emission [11,12]. Hence, $LaBMoO_6$ doped with Dy^{3+} perhaps can also convert the radiation from near-UV to VIS.

In this work, Dy^{3+} doped $LaBMoO_6$ phosphor ($LaBMoO_6:Dy^{3+}$) were prepared to study the crystal structure, absorption and luminescence properties. The effect of Dy_2O_3 concentration doped in $LaMoBO_6$ powder on these properties were also studied to determine the optimum condition of phosphor for photonic applications.

2. Experimental

2.1 Sample preparation

$LaBMoO_6:Dy^{3+}$ phosphors were prepared by the solid-state reaction with high purity chemical composition of La_2O_3, MoO_3, H_3BO_3 and Dy_2O_3. The Dy_2O_3 doped concentration was varied as 0.00, 0.10. 0.50, 1.50 and 2.00 mol% that replaced in a part of La_2O_3 content. $LaBMoO_6:Dy^{3+}$ phosphor samples then consist of Dy0.00, Dy0.10, Dy0.50, Dy1.50 and Dy2.00. Raw chemicals were weighted under stoichiometry with total mass as 10 g and mixed thoroughly in agate mortar. Mixtures were then pressed with 20 tons by hydraulic press machine to make a circle tablet for comfortable measurement. All tablets were annealed with 700°C for 10 h in electrical furnace to make the phosphor nucleation.

2.2 Sample measurement

Obtained $LaBMoO_6:Dy^{3+}$ phosphors were studied the crystalline structure by using x-ray diffractometer (XRD-6001, Shimadzu) with CuK_α radiation (0.154 nm wavelength). Photon absorption of phosphor was monitored through the reflection spectra by UV-VIS-NIR spectrophotometer (Shimadzu, UV-3600). Emission spectra and decay curve were investigated the luminescence properties of phosphors. Commission of International de L'Eclairage (CIE) 1931 chromaticity was used to evaluate the emission color of phosphors and McCamy's approximate formula was used to calculated the correlated color temperature (CCT) of emission. Finally, Inokuti-Hirayama (IH) model was used to analyse the Dy^{3+}- Dy^{3+} energy transfer from non-single exponential decay curve.

3. Results and discussion

3.1 Crystal structure

XRD results of $LaBMoO_6:Dy^{3+}$ phosphors with Dy_2O_3 concentration as 0.00, 0.50 and 2.00 mol% are shown in Figure 1. The XRD patterns of all phosphor samples correspond with JCPDs 00-060-0869 database [13] that confirms the monoclinic structure with $P2_1$ space group of $LaBMoO_6$ composition. The top three dominant atomic planes (h k l) in this crystal structure consist of (1 0 2), (-1 0 3) and (0 1 2) which make the strong x-ray diffraction at 2θ centered around 26.19°, 30.31° and 28.82°, respectively. The overall diffraction peaks exhibit the similar pattern for all phosphor sample because of small difference in Dy_2O_3 concentration between phosphor samples. However, there is an excess diffraction peak at 2θ around 28.05° (α symbol) matched with diffraction of (1 1 0) atomic plane in cubic La_2O_3 structure of JCPDs 00-040-1284 database [14]. This diffraction peak of La_2O_3 is degraded with increasing of Dy_2O_3 concentration. It is an evidence that addition of Dy_2O_3 by replacing La_2O_3 results to the reduction of excess La_2O_3 structure in $LaBMoO_6:Dy^{3+}$ phosphors. Moreover, atomic plane of Dy_2O_3 and other Dy composition was not observed in XRD due to low doping Dy_2O_3 concentration.
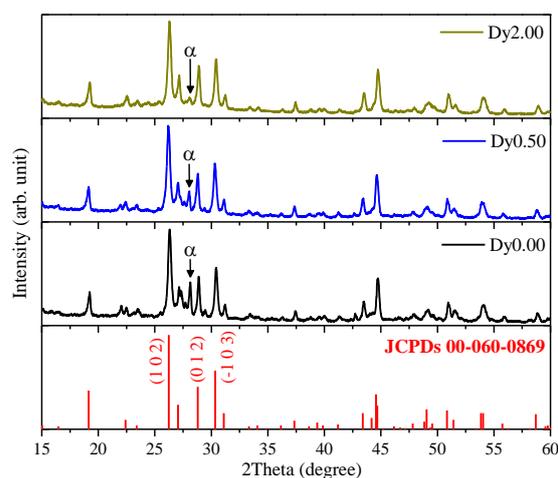

Figure 1. XRD result of $LaBMoO_6:Dy^{3+}$ phosphors doped with 0.00, 0.50 and 2.00 mol% Dy_2O_3 compared with XRD pattern from JCPDs 00-60-0869 database.

3.2 Absorption property

Absorption property of $LaBMoO_6$:Dy^{3+} phosphors are performed as reflection spectra in Figure 2. The absorption bands centered at each bottom point in reflection spectra consist of Dy^{3+} ion's eight sharp bands in VIS - NIR region and $LaBMoO_6$ host's board band in UV region. Dy^{3+} in phosphor can absorb photon with 452, 475, 760, 810, 912, 1106, 1299 and 1704 nm wavelength under transition from $^6H_{15/2}$ ground state to $^4I_{15/2}$, $^4F_{9/2}$, $^6F_{3/2}$, $^6F_{5/2}$, $^6F_{7/2}$, $^6F_{9/2}$, $^6F_{11/2}$ and $^6H_{11/2}$ state, respectively [15,16]. The strongest band at 1299 nm represents the hypersensitive $^6H_{15/2} \rightarrow {}^6F_{11/2}$ transition, following by selection rule, $|\Delta S| = 0$, $|\Delta L| \leq 2$, $|\Delta J| \leq 2$. This transition is dramatically effected which Dy^{3+} local environment [16,17]. Furthermore, these eight photons are more absorbed with increasing of Dy_2O_3 concentration.
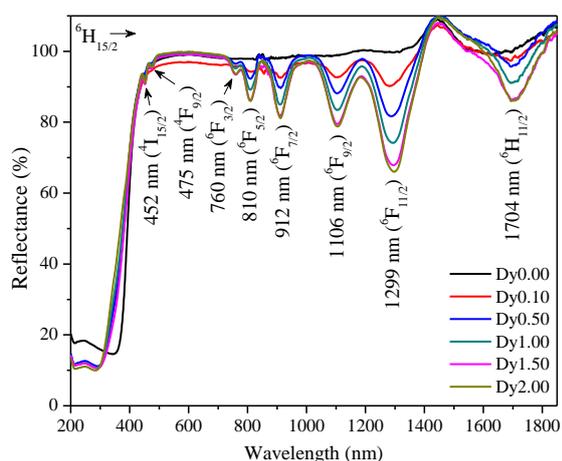

Figure 2. Reflection spectra of $LaBMoO_6$:Dy^{3+} phosphors.

For $LaBMoO_6$ absorption in UV region, the absorption edge of Dy0.10 – Dy2.00 samples are shift to shorter wavelength (higher energy, blue shift) compared with Dy0.00 sample. To analyze this blue shift, the reflection spectra were taken to evaluated the Kubelka-Munk function (F(R)) following the literatures [5,18]. Then, $[F(R) \cdot h\upsilon]^2$ values as a function of $h\upsilon$ were plotted in Figure 3 which corresponds to the allowed direct electronic transitions. The linear portion is extrapolated until $[F(R) \cdot h\upsilon]^{\frac{1}{m}} = 0$ (example as green strength line) and the intersection point on $h\upsilon$ axis is claimed to be the energy band gap, E_g, of phosphors. The obtained band gap of Dy0.00, Dy0.10, Dy0.50, Dy1.00, Dy1.50 and Dy2.00 phosphor is 3.26, 3.76,

3.78, 3.74, 3.72 and 3.87 eV, respectively. This can be explained that adding Dy^{3+} into the undoped $LaBMoO_6$ compound results to the expansion of energy band gap in crystalline structure. However, the effect of Dy_2O_3 concentration between 0.10 – 2.00 mol% on phosphor band gap shows the unclear relation. The Dy2.00 phosphor possesses the largest band gap.

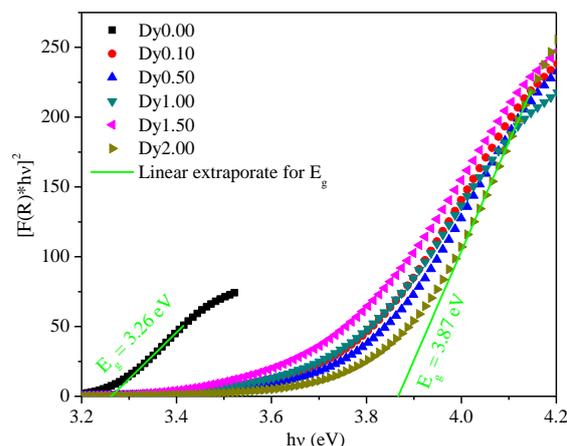**Figure 3.** Kubelka-Munk function plot of $LaBMoO_6$:Dy^{3+} phosphors.

3.3 Luminescence property

3.3.1 Emission spectrum

$LaBMoO_6$:Dy^{3+} phosphors were excited by photons with 453 nm to study the emission spectra as shown in Figure 4 (a) and the corresponded energy transition of Dy^{3+} are shown in Figure 4 (b). After Dy^{3+} energy state rised up from $^6H_{15/2}$ to $^4I_{15/2}$ under excitation, it non-radiative relaxed (NR) down to $^4F_{9/2}$ luminescence level. The radiative transitions then occurred from $^4F_{9/2}$ to $^6H_{15/2}$, $^6H_{13/2}$, $^6H_{11/2}$ and $^6F_{11/2}$ resulting to emission with 480, 570, 657 and 748 nm, respectively [15-17]. The strongest emission belongs to photons with 570 nm wavelength ($^4F_{9/2} \rightarrow {}^6H_{13/2}$). The emission intensity increases with increment of Dy_2O_3 concentration from 0.00 to 0.50 mol% after that intensity decreases with Dy_2O_3 from 0.50 to 2.00 mol% due to concentration quenching effect. The photon re-absorption between Dy^{3+} those getting close together causes this phenomenon. The yellow emission (Y) at 570 nm corresponds with the electric dipole transition (ED), while blue emission (B) at 480 nm corresponds with the magnetic dipole transition (MD). ED can be enhanced by the

asymmetric environment surrounding Dy^{3+} but MD is not. Therefore, intensity ratio between yellow and blue emission (Y/B ratio) is often used to brief the condition of Dy^{3+} environment in each host matrix. Y/B ratio of $LaBMoO_6$:Dy^{3+} phosphors doped with 0.50 mol% Dy_2O_3 is about 1.50 (higher than 1) which performs the asymmetric arrangement of most ligands surrounding Dy^{3+} in this phosphor. This value is compared with Y/B ratio of the other Dy^{3+} doped phosphor such as 1.33, 2.40 and 2.72 of Ca_2SiO_4:Dy^{3+} [3], $BaKWO_4$:Dy^{3+} [5] and $PbGdB_7O_{13}$:Dy^{3+} [9], respectively. It can be said that the asymmetric degree of Dy^{3+} environment in $LaBMoO_6$:Dy^{3+} phosphors is higher than Ca_2SiO_4:Dy^{3+} but lower than $BaKWO_4$:Dy^{3+} and $PbGdB_7O_{13}$:Dy^{3+} phosphor.
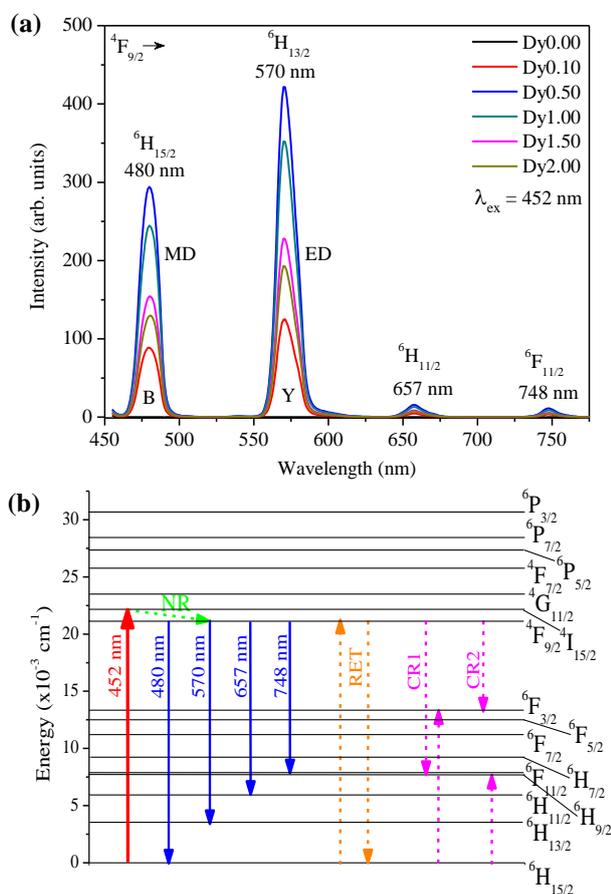

Figure 4. (a) Emission spectra of $LaBMoO_6$:Dy^{3+} phosphors under 452 nm excitation wavelength and (b) energy transition diagram of Dy^{3+} emission.

3.3.2 Excitation spectrum

To confirm and check the excitation wavelength that can induce the strongest emission with 570 nm of $LaBMoO_6$:Dy^{3+} phosphor, the excitation spectra then were monitored and shown in Figure 5. There

are seven sharp excitation-bands between near-UV and VIS region such as 326, 352, 366, 388, 427, 452 and 474 nm which can excite Dy^{3+} to emit 570 nm photon. These seven photo-excitations correspond to Dy^{3+} energy transitions from $^6H_{15/2}$ ground state to $^6P_{3/2}$, $^6P_{7/2}$, $(^4P,^4D)_{3/2}$, $^4F_{7/2}$, $^4G_{11/2}$, $^4I_{11/2}$ and $^4F_{9/2}$ excited state, respectively [15,16]. Furthermore, there is some part of small board excitation-band around 200 – 280 nm wavelength. It perhaps represents the transfer of near-UV energy absorbed by $LaBMoO_6$ host to Dy^{3+} for 570 nm emission. After direct excitation or energy transfer from host, Dy^{3+} non-radiative relaxed to $^4F_{9/2}$ luminescence level and then emit the 570 nm photons by $^4F_{9/2} \rightarrow$ $^6H_{13/2}$ transition. However, the strongest excitation for 570 nm emission belongs to photon with 452 nm wavelength corresponding to the emission spectra.
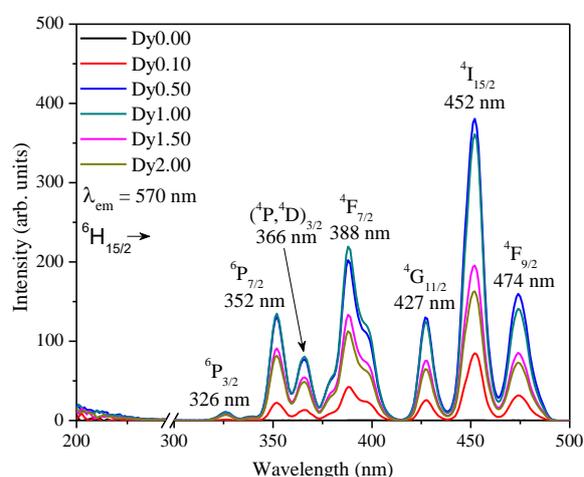

Figure 5. Excitation spectra of $LaBMoO_6$:Dy^{3+} phosphors under 570 nm emission wavelength.

3.3.3 Color prediction

The emission spectrum of Dy0.50 phosphor with 452 nm excitation wavelength was brought to evaluate the color of emission by CIE 1931 chromaticity. Obtained color coordinate (x, y) of emission is (0.36, 0.41) plotted as blue star symbol in white region of CIE 1931 diagram in Figure 6. This indicates the white light emission of $LaBMoO_6$:Dy^{3+} phosphor under 452 nm excitation. Then, color coordinate was taken to evaluate CCT by using McCamy's approximate [16] and the value was 4841 K. This temperature value is higher than white light of fluorescent tube (3935 K), but lower than day light (5500 K). Therefore, $LaBMoO_6$:Dy^{3+} phosphor can be applied in the white light photonic applications i.e. light bulb, white-LED and display.

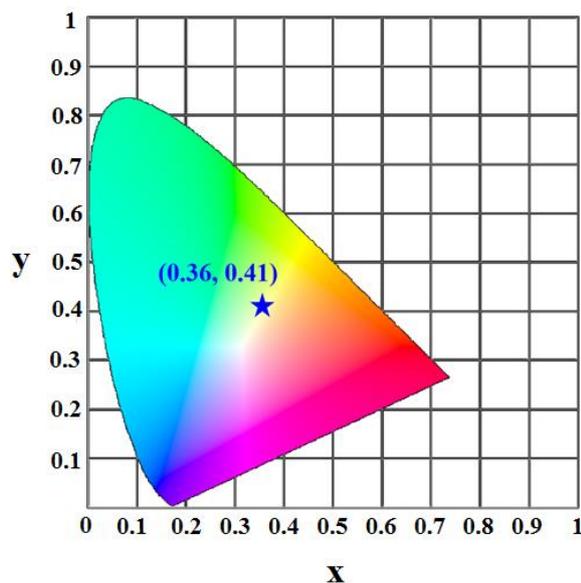**Figure 6.** CIE 1931 chromaticity diagram of LaBMoO$_6$:Dy^{3+} phosphors [19].

3.3.4 Decay curve

The luminescence decay curves for 570 nm emission of LaBMoO$_6$:Dy^{3+} phosphor under 452 nm excitation were plotted in Figure 7. From decay curve, obtained luminescence life time (τ) of Dy0.10, Dy0.50, Dy1.00, Dy1.50 and Dy2.00 phosphor is 0.50, 0.43, 0.40, 0.39 and 0.38 ms, respectively. The decay curves perform the non-single exponential behavior which is more dominant in higher Dy$_2$O$_3$ doped phosphor. The reduction of life time and more non-single exponential with increment of Dy$_2$O$_3$ concentration indicates the Dy^{3+} - Dy^{3+} energy transfer. This can be analyzed by fitting the decay curve with IH model by using relation from literature [16,17]. From model, the IH parameter (S) can be 6, 8 and 10 which represents the type of energy transfer between donor and acceptor ions as dipole - dipole, dipole - quadrupole and quadrupole - quadrupole interaction, respectively. Since S = 6 made the best fitting with decay curves in this work, the type of energy transfer between Dy^{3+} donor and Dy^{3+} acceptor is dipole – dipole interaction. Such energy transfers occurred under cross relaxation (CR1 and CR2) and resonance energy transfer (RET) process. The channel of CR1, CR2 and RET is $^4F_{9/2}$,$^6H_{15/2}$ → $^6H_{9/2}$,$^6F_{3/2}$, $^4F_{9/2}$,$^6H_{15/2}$ → $^6F_{3/2}$,$^6H_{9/2}$ and $^4F_{9/2}$,$^6H_{15/2}$ → $^6H_{15/2}$,$^6F_{92}$, respectively [16,17] as shown in figure 4 (b). The result of IH fit (S = 6) with decay curves gives the energy transfer parameters (Q) which represents the probability of energy transfer between donor and acceptor ions. In this work, Q value is 0.19, 0.28, 0.30 and 0.34 for Dy0.50, Dy1.00, Dy1.50 and Dy2.00 phosphor, respectively. Rising of Q value exhibits the enhanced probability of CR1, CR1 and RET process with increment of Dy$_2$O$_3$ amount in phosphor.
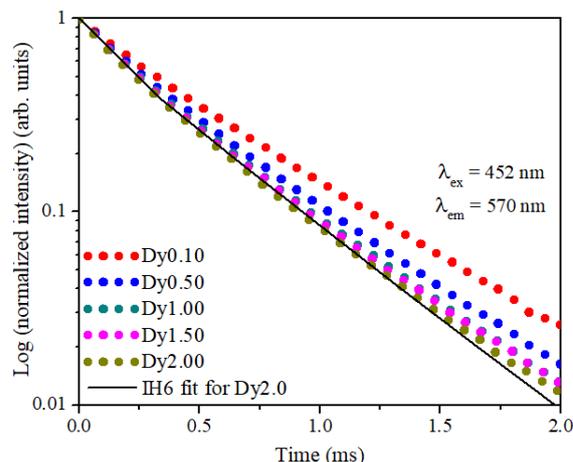

Figure 7. Decay curve of LaBMoO$_6$:Dy^{3+} phosphors.

4. Conclusions

LaBMoO$_6$:Dy^{3+} phosphors possess the main crystal structure of monoclinic with P2$_1$ space group. The excess La$_2$O$_3$ structure is reduced with increasing of Dy$_2$O$_3$ concentration. More number of photons in VIS and NIR region are absorbed with increment of Dy^{3+} amount in phosphor. The strongest emission of Dy^{3+} belongs to photons with 570 nm ($^4F_{9/2}$ → $^6H_{13/2}$) under 452 nm excitation. The emission intensity rises with increasing of Dy$_2$O$_3$ concentration from 0.0 to 0.5 mol%, over than that it decreases due to concentration quenching. The overall emission color of phosphor under 452 nm excitation is white. The UV radiation can also excite phosphor to emit the 570 nm photon in low intensity via host – Dy^{3+} energy transfer. Luminescence life time of phosphor is in millisecond reduced via Dy$_2$O$_3$ increment due to CR and RET under dipole-dipole interaction. LaBMoO$_6$:Dy^{3+} phosphor performs a good potential for application in display/screen, white-LED and other white light source.

5. Acknowledgements

(CEGM), Nakhon Pathom Rajabhat University and Center of Science and Applied Science, Muban Chombueng Rajabhat University for research facilities.

References

[1] B. G. Wybourne, *Spectroscopic properties of rare earths*. USA: Interscience Publishers, 1965.

[2] B. M. Walsh, "Judd-Ofelt theory: Principles and practices," in *Advances in spectroscopy for lasers and sensing*, Di Bartolo, Baldassare, Forte, Ottavio, eds, Netherlands: Springer, 2006, pp. 403-433.

[3] L. Lakshmi Devi, C. Basavapoornima, V. Venkatramu, P. Babu, and C. K. Jayasankar, "Synthesis of $Ca_2SiO_4:Dy^{3+}$ phosphors from agricultural waste for solid state lighting applications," *Ceramics International*, vol. 43, pp. 16622-16627, 2017.

[4] Z. Zhang, A. Song, S. Song, J. Zhang, W. Zhang, and D. Wang, "Synthesis and luminescence properties of novel $KSrPO_4:Dy^{3+}$ phosphor," *Journal of Alloys and Compounds*, vol. 629, pp. 32-35, 2015.

[5] A. K. Kunti, N. Patra, S. K. Sharma, and H. C. Swart, "Radiative transition probability enhancement of white light emitting Dy^{3+} doped and K^+ co-doped $BaWO_4$ phosphors via charge compensation," *Journal of Alloys and Compounds*, vol. 735, pp. 2410-2422, 2018.

[6] Y. Zaifa, S. Yumei, X. Qiguang, and S. Jiayue, "Preparation and photoluminescence properties of Dy^{3+}-doped $Ba_3Lu(PO_4)_3$ phosphors," *Journal of Rare Earths*, vol. 33, pp. 1251-1255, 2015.

[7] Z. Yongqing, L. Xuan, L. Jia, and J. Man, "A novel white-emitting phosphor $ZnWO_4:Dy^{3+}$," *Journal of Rare Earths*, vol. 33, pp. 350-354, 2015.

[8] B. Han, Y. Dai, J. Zhang, and H. Shi, "Luminescence properties of a novel yellow-emitting phosphor $NaLaMgWO_6:Dy^{3+}$," *Materials Letters*, vol. 204, pp. 145-148, 2017.

[9] J. Zhao, S. Huang, D. Zhao, J. Chen, Y. Tian, Q. Zong, Y. Fan, C. Nie, and B. Liu, "Synthesis and luminescence of a new yellowish phosphor $PbGd_{1-x}B_7O_{13}:xDy^{3+}$," *Optik*, vol. 161, pp. 342-347, 2018.

[10] Y. Yu, L. Li, Z. Lin, and G. Wang, "Growth, structure and optical properties of a nonlinear optical crystal α-$LaBMoO_6$," *Cryst Eng Comm*, vol. 15, pp. 5245-5249, 2013.

[11] Z. W. Zhang, D. Q. Ma, Y. Yue, M. Z. Ma, and R. P. Liu, "Wide-band excited $LaBMoO_6:Eu^{3+}$ red phosphor for white-light-emitting diode," *Journal of Alloys and Compounds*, vol. 636, pp. 113-116, 2015.

[12] E. Kaewnuma, N. Wantana, and J. Kaewkhao, "Comparative luminescence study of $LaBMoO_6:Tb$ phosphor under VIS and near-UV excitation for green photonic applications," *Materials Today: Proceedings*, vol. 5, pp. 13940-13947, 2018.

[13] V. Kroutko, G. Lysanova and M. Komova, *JCPDS 00-060-0869*, Institute of General and Inorganic Chemistry, RAS, Moscow, Russian Federation, ICDD Grant-in-Aid, 2009.

[14] P. Aldebert, *JCPDs 00-040-1284*, Institut de Recherche Fondamentale, France: Private Communication, 1988.

[15] W. T. Carnall, P. R. Fields, and K. Rajnak, "Electronic energy levels in the trivalent lanthanide aquo ions. I. Pr^{3+}, Nd^{3+}, Pm^{3+}, Sm^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, and Tm^{3+}," *The Journal of Chemical Physics*, vol. 49, pp. 4424-4442, 1968.

[16] N. Vijaya, K. Upendra Kumar, and C. K. Jayasankar, "Dy^{3+}-doped zinc fluorophosphate glasses for white luminescence applications," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 113, pp. 145-153, 2013.

[17] E. Kaewnuam, N. Wantana, H. J. Kim, and J. Kaewkhao, "Development of lithium yttrium Borate glass doped with Dy^{3+} for laser medium, W-LEDs and scintillation materials applications," *Journal of Non-Crystalline Solids*, vol. 464, pp. 96-103, 2017.

[18] S. Raya, P. Tadge, S. Dutta, T.M. Chen, G.B. Nair, and S. J. Dhoble, "Synthesis, luminescence and application of $BaKYSi_2O_7:Eu^{2+}$: A new blue-emitting phosphor for near-UV white-light LED," *Ceramics International*, vol. 44, pp. 8334-8343, 2018.

[19] S. Gage, D. Evans, M. W. Hodapp, and H. Sorensen, *Optoelectronics applications manual*. New York: McGraw Hill, 1977