Study on structure and luminescence properties of LaBMoO₇:Dy³⁺ phosphor for photonic material applications

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Received date: 24 May 2018
Revised date: 17 June 2018
Accepted date: 31 August 2018

Abstract

Phosphor powder of LaBMoO₇: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 LaBMoO₇ 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 LaBMoO₇ 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 (⁴F₉/₂ → ⁶H₁₃/₂) and magnetic dipole (⁴F₉/₂ → ⁸H₅/₂) 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 (⁴F₉/₂ → ⁶H₁₃/₂) and yellow (⁴F₉/₂ → ⁸H₅/₂) emission which can also intercept to be white light [3-7]. Therefore, there were many researches of Dy³⁺ doped phosphor such as Ca₃SiO₄: Dy³⁺ [3], KSrPO₄: Dy³⁺ [4], BaKWO₄: Dy³⁺ [5], Ba₅La₃PO₁₂: Dy³⁺ [6], ZnWO₄:Dy³⁺ [7] for white light emitting devices and NaLaMgWO₄:Dy³⁺ [8], PbGdB₃O₁₁: 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, BO₃ 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\(_2\)O\(_3\) 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\(_2\)O\(_3\), MoO\(_3\), H\(_3\)BO\(_3\) and Dy\(_2\)O\(_3\). The Dy\(_2\)O\(_3\) doped concentration was varied as 0.00, 0.10, 0.50, 1.50 and 2.00 mol\% that replaced in a part of La\(_2\)O\(_3\) 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\(_\alpha\) 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\(_2\)O\(_3\) 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 20 centered around 26.19\(^\circ\), 30.31\(^\circ\) and 28.82\(^\circ\), respectively. The overall diffraction peaks exhibit the similar pattern for all phosphor sample because of small difference in Dy\(_2\)O\(_3\) concentration between phosphor samples. However, there is an excess diffraction peak at 20 around 28.05\(^\circ\) (a symbol) matched with diffraction of (1 1 0) atomic plane in cubic La\(_2\)O\(_3\) structure of JCPDs 00-040-1284 database [14]. This diffraction peak of La\(_2\)O\(_3\) is degraded with increasing of Dy\(_2\)O\(_3\) concentration. It is an evidence that addition of Dy\(_2\)O\(_3\) by replacing La\(_2\)O\(_3\) results to the reduction of excess La\(_2\)O\(_3\) structure in LaBMoO\(_6\):Dy\(^{3+}\) phosphors. Moreover, atomic plane of Dy\(_2\)O\(_3\) and other Dy composition was not observed in XRD due to low doping Dy\(_2\)O\(_3\) concentration.

**Figure 1.** XRD result of LaBMoO\(_6\):Dy\(^{3+}\) phosphors doped with 0.00, 0.50 and 2.00 mol\% Dy\(_2\)O\(_3\) 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 band in UV region. Dy$^{3+}$ ion can absorb photon with 452, 475, 760, 810, 912, 1106, 1299 and 1704 nm wavelength under transition from $^6$H$_{15/2}$ ground state to $^4$I$_{15/2}$, $^6$F$_{9/2}$, $^6$F$_{5/2}$, $^6$F$_{7/2}$, $^6$F$_{9/2}$, $^6$H$_{11/2}$ and $^6$H$_{15/2}$ state, respectively [15,16]. The strongest band at 1299 nm represents the hypersensitive $^6$H$_{15/2}$ → $^6$F$_{11/2}$ 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$_2$O$_3$ 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, $[F(R) \cdot h\nu]^2$ values as a function of h\nu were plotted in Figure 3 which corresponds to the allowed direct electronic transitions. The linear portion is extrapolated until $[F(R) \cdot h\nu]^{-1} = 0$ (example as green strength line) and the intersection point on h\nu 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$_2$O$_3$ 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 rise up from $^6$H$_{15/2}$ to $^4$I$_{15/2}$ under excitation, it non-radiative relaxed (NR) down to $^4$F$_{9/2}$ luminescence level. The radiative transitions then occurred from $^4$F$_{9/2}$ to $^6$H$_{15/2}$, $^6$H$_{13/2}$, $^6$H$_{11/2}$ and $^6$F$_{11/2}$ resulting to emission with 480, 570, 657 and 748 nm, respectively [15-17]. The strongest emission belongs to photons with 570 nm wavelength ($^4$F$_{9/2}$ → $^6$H$_{15/2}$). The emission intensity increases with increment of Dy$_2$O$_3$ concentration from 0.00 to 0.50 mol% after that intensity decreases with Dy$_2$O$_3$ 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$_2$O$_3$ 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 other Dy$^{3+}$ doped phosphor such as 1.33, 2.40 and 2.72 of Ca$_2$SiO$_4$:Dy$^{3+}$ [3], BaKWO$_4$:Dy$^{3+}$ [5] and PbGdB$_2$O$_13$: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$_2$SiO$_4$:Dy$^{3+}$ but lower than BaKWO$_4$:Dy$^{3+}$ and PbGdB$_2$O$_13$:Dy$^{3+}$ phosphor.

![Figure 4](image_url)

**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 $^6$H$_{15/2}$ ground state to $^6$P$_{1/2}$, $^6$P$_{3/2}$, $^4$P$_{1/2}$, $^4$D$_{3/2}$, $^4$F$_{7/2}$, $^4$G$_{11/2}$, $^4$H$_{11/2}$ and $^4$F$_{9/2}$ 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 $^4$F$_{9/2}$ luminescence level and then emit the 570 nm photons by $^4$F$_{9/2} ightarrow ^6$H$_{13/2}$ transition. However, the strongest excitation for 570 nm emission belongs to photon with 452 nm wavelength corresponding to the emission spectra.

![Figure 5](image_url)

**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.
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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 $^4$F$_{9/2}$,$^6$H$_{15/2}$ → $^6$H$_{5/2}$,$^2$F$_{5/2}$, $^4$F$_{9/2}$,$^6$H$_{15/2}$ → $^2$F$_{5/2}$,$^2$H$_{9/2}$ and $^4$F$_{9/2}$,$^6$H$_{15/2}$ → $^2$H$_{15/2}$,$^2$F$_{5/2}$, 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.

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 ($^4$F$_{9/2}$ → $^6$H$_{13/2}$) 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

The authors wish to thank Center of Excellence in Glass Technology and Materials Science
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