

OPTICAL PROPERTIES OF $\text{Gd}_2\text{MoB}_2\text{O}_9$ Tb^{3+} PHOSPHORS FOR FORENSIC APPLICATIONS

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Received: January 23, 2021; Revised: March 25, 2021; Accepted: March 28, 2021

Abstract

The $\text{Gd}_2\text{MoB}_2\text{O}_9$: Tb^{3+} phosphors were prepared by a solid-state reaction method with various concentration of Tb^{3+} ions as well as sintered at 900°C temperature with different milling time. The photoluminescence properties were studied. The phosphors were investigated by X-ray diffraction (XRD), diffuse reflectance spectroscopy, photoluminescence, energy level scheme and decay curves studies. The phosphors were excited at a wavelength of 484 nm, the emission of the optimized phosphor at 542 nm was observed that corresponds to the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of Tb^{3+} ions. The $\text{Gd}_2\text{MoB}_2\text{O}_9$: Tb^{3+} phosphors have potential applications in forensic science for latent fingerprint identification.

Keywords: Photoluminescence; $\text{Gd}_2\text{MoB}_2\text{O}_9$; phosphor; fingerprint technology

Introduction

The fingerprints are mainly found in crime scenes which are invisible fingerprint or latent fingerprint. Therefore, suitable method will bring about appearance of fingerprints and ridge characteristics on different surface of evidences such as cyanoacrylate fuming, ninhydrin method, and powder dusting method (Yang and Lian, 2014; Errington *et al.*, 2016; Khuu *et al.*, 2016). The powder dusting technique is the simplest and most commonly used procedure for detecting latent fingerprint that can be carried out both at the crime scene or in the laboratory (Sodhi and Kaur, 2001). The luminescent powder containing the rare earth

ions doped materials have been interesting for latent fingerprint detection in forensic science due to high efficiency, sharp and stable luminescence, such as Pr^{3+} (Yeshodamma *et al.*, 2019), Eu^{3+} (Park and Yang, 2017), Nd^{3+} (Dhanalakshmi *et al.*, 2018) Sm^{3+} (Darshan *et al.*, 2016) Ce^{3+} (Wang *et al.*, 2017) and Tb^{3+} (Ashwini *et al.*, 2019) doped and co-doped host materials of phosphors. Green luminescence corresponds to main $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of Tb^{3+} . The quite intense and efficient luminescence bands located at about 543 nm were observed for Tb^{3+} ions in phosphors.

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The Tb^{3+} doped gadolinium molybdenum borate ($\text{Gd}_2\text{MoB}_2\text{O}_9$) phosphors have not been reported widely. In the present work, the $\text{Gd}_2\text{MoB}_2\text{O}_9:\text{Tb}^{3+}$ phosphors were synthesized by conventional solid-state reaction method and evaluated its optical properties for potential latent fingerprint identification in forensic applications.

Materials and Methods

Tb^{3+} doped gadolinium molybdenum borate ($\text{Gd}_2\text{MoB}_2\text{O}_9$) phosphors were prepared by the solid-state reaction method. The gadolinium (III) oxide (Gd_2O_3), molybdenum trioxide (MoO_3), terbium (III) oxide (Tb_2O_3) and boric acid (H_3BO_3) were weighed in a proper stoichiometric ratio and mixed materials thoroughly using ball mill for about 30 min. The concentration of Tb was varied from 0 to 0.40 mol%. The host materials were sintered at different temperature from 800, 900, and 1,000°C. The $\text{Gd}_2\text{MoB}_2\text{O}_9:\text{Tb}^{3+}$ phosphors were sintered at optimized temperature for 18 h. After that, the phosphors were fine powdered by Rock labs ring mill at different time intervals ranging to 3, 6, 9, 12, 15, and 18 min.

The structural properties of the powder samples were examined by X-ray diffractometer (Shimadzu XRD-6100) with operating at 40 kV and 30 mA. The diffractometer was performed in the 2θ range from 10° to 70° at a rate of $5^\circ/\text{min}$. The diffuse reflectance spectra were recorded using the Shimadzu UV-VIS-NIR spectrophotometer in the wavelength range of 350–2,500 nm. The photoluminescence emission, photoluminescence excitation spectra and luminescence decays were carried out on a Cary Eclipse Fluorescence spectrophotometer at room temperature using xenon lamp.

Results and Discussion

Variation in Tb^{3+} Ion Concentration

The study of $\text{Gd}_2\text{MoB}_2\text{O}_9$ doped with Tb^{3+} phosphors were synthesized by the solid-state reaction method for forensic application. Solid state route was convenient and efficient method to prepare phosphor. The $\text{Gd}_2\text{MoB}_2\text{O}_9$ as host material was sintered at 800, 900, and 1,000°C temperature. The crystalline structure was analyzed for phase purities of $\text{Gd}_2\text{MoB}_2\text{O}_9$ using X-ray diffraction (XRD). The patterns of XRD for $\text{Gd}_2\text{MoB}_2\text{O}_9$ at 900°C sintering temperatures were well indexed to the standard data of GdBO_3 JCPDS card No. 13-483 and standard JCPDS File No. 371099 (Ruengsri *et al.*, 2017). The XRD patterns of the 0.01 to 0.40 mol% Tb^{3+} doped $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphors were synthesized

at 900°C sintering temperatures shown in Figure 1. The 0.01–0.20 mol% Tb^{3+} doped $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphors are similar to phase of $\text{Gd}_2\text{MoB}_2\text{O}_9$ which are in accord with the standard JCPDS card. While 0.4 mol% of Tb^{3+} ion concentration shown the corresponding to phase of GdBO_3 and Gd_2MoO_6 . The diffuse reflectance spectra are used to study the opaque solid samples hence it is used to analyze the for the undoped and Tb^{3+} doped $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphors in the present work. As shown in Figure 2, the spectra assigned characteristic peaks at 1,894, 1,953, and 2,210 nm were ascribed to $^7\text{F}_6 \rightarrow ^7\text{F}_1$, $^7\text{F}_6 \rightarrow ^7\text{F}_2$, and $^7\text{F}_6 \rightarrow ^7\text{F}_3$ transitions of the Tb^{3+} ions, respectively.

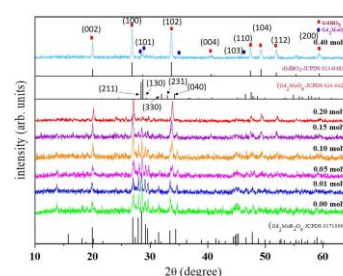


Figure 1. XRD patterns of undoped and Tb^{3+} doped $\text{Gd}_2\text{MoB}_2\text{O}_9$

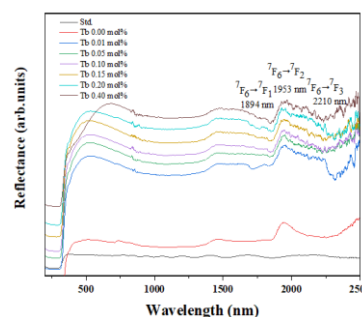


Figure 2. Diffuse reflectance spectra of undoped and Tb^{3+} doped $\text{Gd}_2\text{MoB}_2\text{O}_9$

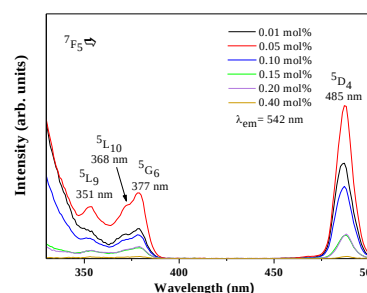


Figure 3. Excitation spectra of Tb^{3+} doped $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphors monitored at 542 nm emission

The photoluminescence properties of the $\text{Gd}_2\text{MoB}_2\text{O}_9:\text{Tb}^{3+}$ (0.01-0.40 mol%) phosphors sintered at 900°C temperatures. The photoluminescence excitation spectra of the Tb^{3+} ions exhibited in the wavelength region at 351, 368, 377, and 484 nm, respectively. As shown in Figure 3, the electronic transitions of the Tb^{3+} ions correspond to $^7\text{F}_5 \rightarrow ^5\text{L}_9$, $^7\text{F}_5 \rightarrow ^5\text{L}_{10}$, $^7\text{F}_5 \rightarrow ^5\text{G}_6$, and $^7\text{F}_5 \rightarrow ^5\text{D}_4$, respectively.

Figures 4(a) and 4(b) shows the emission spectra of Tb^{3+} doped $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphors at different concentration of Tb^{3+} from 0.01 to 0.40 mol% with 484 nm excitation and their intensity dependent with concentration respectively. The emission peaks located around 542, 584, and 622 nm that are assigned to the $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$, and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ transitions of the Tb^{3+} ions (Kumar *et al.*, 2014), respectively as shown in Figure 5 of energy level diagram. The photoluminescence emission intensity of the Tb^{3+} doped phosphors increase with increase in concentration of Tb^{3+} ions and reach a maximum at 0.05 mol% then decrease due to concentration quenching effect that is attributed due to results of non-radiative energy transfer between the donor Tb^{3+} ions to adjacent acceptor Tb^{3+} ions (Zeng *et al.*, 2016).

The luminescent properties of rare-earth ions in gadolinium molybdenum borate ($\text{Gd}_2\text{MoB}_2\text{O}_9$) that the concentration quenching was weak (Meng *et al.*, 2012). The decay curves of Tb^{3+} emission for $\text{Gd}_2\text{MoB}_2\text{O}_9:\text{Tb}^{3+}$ phosphors were displayed in

Figure 6. The decay time were calculated to be 1.210, 1.189, 1.123, 1.034, 0.942, and 0.779 ms for 0.01-0.40 mol% Tb^{3+} concentration, respectively. The increase in Tb^{3+} ion concentration showed decrease in its decay time.

Effect of Milling Period

To investigate milling effect of $\text{Gd}_2\text{MoB}_2\text{O}_9:\text{Tb}^{3+}$ phosphors the work was carried out on choosing 0.05 mol% of Tb^{3+} ion doped $\text{Gd}_2\text{MoB}_2\text{O}_9$ due to high emission intensity as observed in (Figure 4(a)). Hence the analysis was focused to understand their effect on structural and optical phenomenon for various milling period.

Figure 7 demonstrates the XRD patterns of 0.05 samples are single phase indexed to the

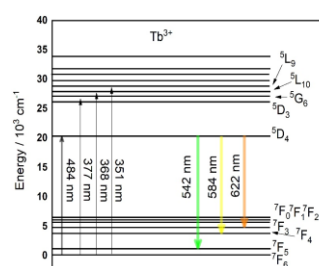
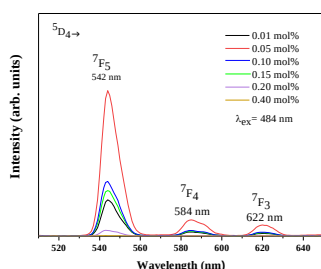
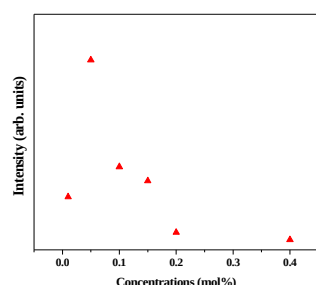


Figure 5. Energy level scheme of Tb^{3+} (0.05 mol%) doped $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphors



(a)



(b)

Figure 4. (a) Emission spectra of Tb^{3+} (0.01-0.40 mol%) doped $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphor excited under 484 nm (b) Photoluminescence emission intensity with different Tb^{3+} concentration

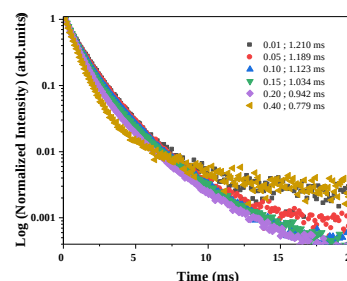


Figure 6. The luminescence decay profiles of $\text{Gd}_2\text{MoB}_2\text{O}_9:\text{Tb}^{3+}$ phosphors

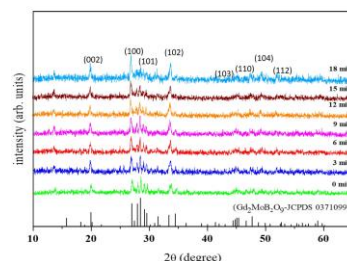


Figure 7. XRD pattern of 0.05 mol% of Tb^{3+} doped $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphors at different milling time

standard data of GdBO_3 JCPDS card No. 13-483 and $\text{Gd}_2\text{MoB}_2\text{O}_9$ using standard JCPDS cards No. 0371099.

The diffuse reflectance spectra of 0.05 mol% Tb^{3+} doped $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphors exhibited characteristic peaks as similar to Figure 2 showing peaks at 1,894, 1,953, and 2,210 nm of different milling time as shown in Figure 8. The excitation spectra of the $\text{Gd}_2\text{MoB}_2\text{O}_9:\text{Tb}^{3+}$ (0.05 mol%) samples with different milling time at 542 nm emission wavelength. As shown in Figure 9, the peaks at 351, 368, 377, and 484 nm are ascribed to the $^7\text{F}_5 \rightarrow ^5\text{L}_9$, $^7\text{F}_5 \rightarrow ^5\text{L}_{10}$, $^7\text{F}_5 \rightarrow ^5\text{G}_6$, and $^7\text{F}_5 \rightarrow ^5\text{D}_4$ transitions, respectively and energy level as demonstrated in Figure 5. While the photoluminescence emission spectra of 0.05 mol% Tb^{3+} doped $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphors at different milling time with 484 nm excitation as shown in Figure 10. It is observed that the doping of Tb^{3+} in $\text{Gd}_2\text{MoB}_2\text{O}_9$ after milling at 3, 6, 9, 12, 15, and 18 min decreases with increase in milling time. The $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transitions are dominant in the emission spectra (Kesavulu *et al.*, 2017) that the intensity of Tb^{3+} emission at 542 nm in green emission (Panse *et al.*, 2018; Singh *et al.*, 2018) representing the electric dipole transition which is strongest. Among various milling period sample with 0 min of milling time

showed highest emission peak intensity than other samples with different milling time.

Luminescence spectra of Tb^{3+} in $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphor were recorded under excitation by 484 nm line (Figures 10 and 5). Three luminescence bands are observed, which correspond to the $^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 3, 4, 5$) transitions of Tb^{3+} . The main emission band is located at 542 nm and it is due to $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of Tb^{3+} ions. The $^5\text{D}_4$ state of Tb^{3+} in $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphor is excited by 484 nm line. The three luminescence lines originating from $^5\text{D}_4$ state were observed in the energy level diagram Figure 5. This phenomenon was due to a large separation (above $15,000 \text{ cm}^{-1}$) between the $^5\text{D}_4$ state and the next lower-lying $^7\text{F}_0$ state and the relative high phonon energy of the host ($\sim 1,300 \text{ cm}^{-1}$). Figure 11 shows the decay curves of Tb^{3+} emission for $\text{Gd}_2\text{MoB}_2\text{O}_9:\text{Tb}^{3+}$ phosphors at different milling time from 0, 3, 6, 9, 12, 15, and 18 min are calculated to be 1.189, 1.233, 1.236, 1.269, 1.271, 1.273, and 1.316 ms, respectively. The increase in milling time shows increase in its decay time.

Conclusions

The optical properties of Tb^{3+} doped $\text{Gd}_2\text{MoB}_2\text{O}_9$

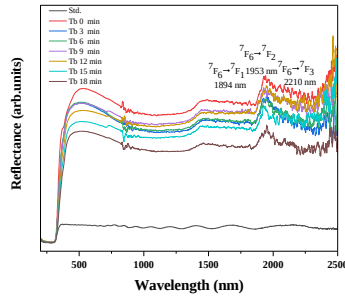


Figure 8. Diffuse reflectance spectra of Tb^{3+} (0.05 mol%) doped $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphors at different time of milling

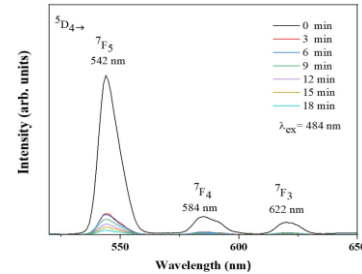


Figure 10. Emission spectra of Tb^{3+} (0.05 mol%) doped $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphors excited under 484 nm at different milling time

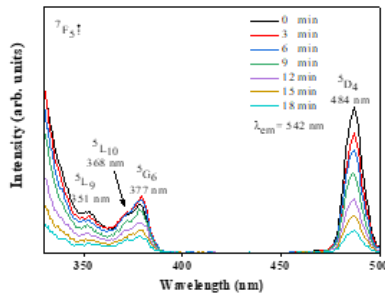


Figure 9. Excitation spectra of Tb^{3+} (0.05 mol%) doped $\text{Gd}_2\text{MoB}_2\text{O}_9$ at different milling time

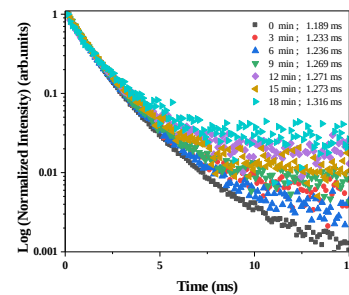


Figure 11. The decay curves of Tb^{3+} (0.05 mol%) doped $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphors at different milling time

phosphors for latent fingerprint detection have been prepared by the solid-state reaction method. The $\text{Gd}_2\text{MoB}_2\text{O}_9:\text{Tb}^{3+}$ phosphors (0.01-0.40 mol%) were sintered at 900°C temperature that the emission spectra of phosphors are assigned by the $^5\text{D}_4 \rightarrow ^7\text{F}_j$, ($j = 5, 4, 3$) transitions of the Tb^{3+} ions. The most intense emission of the Tb^{3+} ions is indicated for the transition at 542 nm under the excitation at 484 nm. Decay time of $\text{Gd}_2\text{MoB}_2\text{O}_9:\text{Tb}^{3+}$ phosphors were displayed in the range 0.779-1.210 ms. The emission intensity showed highest for 0.05 mol% Tb^{3+} ion concentration and for 0 min milling period. The increase in Tb^{3+} ion concentration showed decrease in its decay time whereas decay time increases with increase in milling time. The photoluminescence properties of phosphors can potentially apply for fingerprint powders for forensic applications.

Acknowledgements

The authors thank to the Center of Excellence in Glass Technology and Materials Science (CEGM), Faculty of Science and Technology, Nakhon Pathom Rajabhat University for supporting research facilities. Noppadon Chamchoi and Onanong Chaemlek would like to thank Faculty of Science, Silpakorn University for supporting this research. Narong Sangwanateee would like to thanks Suan Sunandha Rajabhat University (SSRU) (Program in Forensic Science), Thailand.

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