

THE LUMINESCENCE PROPERTIES AND LATENT FINGERPRINT IDENTIFICATION APPLICATION OF $\text{Gd}_2\text{MoB}_2\text{O}_9\text{:Sm}^{3+}$ PHOSPHOR

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Abstract

Latent fingerprint detection is one of the promising techniques in forensic science. Here, an oxide-based orange-emitting phosphors, $\text{Gd}_2\text{MoB}_2\text{O}_9$ doped with trivalent samarium have been prepared. The structural, spectroscopic properties were studied through XRD, reflections, luminescence and decay time measurements. The structural analysis was characterized with XRD. The reflections spectra reveal seven peaks which are assigned to the transitions from the ground level of $^6\text{H}_{5/2}$ to $^6\text{F}_{11/2}$, $^6\text{F}_{9/2}$, $^6\text{F}_{7/2}$, $^6\text{F}_{5/2}$, $^6\text{F}_{3/2}$, $^6\text{H}_{15/2}$, and $^6\text{F}_{1/2}$ excited energy levels of Sm^{3+} ions. The luminescence properties were studied at room temperature and lifetime measurements were performed to understand the decay curve behavior. Intense orange emission peak at 601 nm was observed due to $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ transitions of Sm^{3+} under the excitation of 404 nm. The observed emission obtained show intense emission for 0.1 mol% Sm^{3+} ion concentration. These results indicate that $\text{Gd}_2\text{MoB}_2\text{O}_9\text{:Sm}^{3+}$ be potential candidate for practical applications in latent fingerprint detection.

Keywords: Latent fingerprint, Sm^{3+} , $\text{Gd}_2\text{MoB}_2\text{O}_9$, phosphors

Introduction

Fingerprint identification technology is one of the most powerful tools which has been widely utilized in forensic science due to its unique pattern which can be used as fingerprint detecting technology for each person's identity. In many cases, latent fingerprints cannot be seen directly by the naked eyes. Thus, it requires to develop the visualization

and scanning techniques. In the literature, various approaches have been established to identify the latent fingerprints such as equipment analysis, chemical staining method, and powder dusting method (Day *et al.*, 2004; Hansen and Joullie', 2005; Song *et al.*, 2012; Wang *et al.*, 2017). However, there are some limitations for each technique. Rare Earth

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(RE) elements in divalent/trivalent state have intense luminescence because of 4f electron transitions (Frindell *et al.*, 2002). Lanthanide ions doped phosphors have been much researched because they can be applied to applications in various fields, such as white light emitting diode (WLEDs), bio imaging, anti-counterfeiting, and latent fingerprint detection (Dhanalakshmi *et al.*, 2018; Shao *et al.*, 2019). To obtain specific fluorescent properties, researchers have been studied for host materials such as aluminates, silicates, phosphates, and orthoborate (Zhang *et al.*, 2018). The gadolinium oxide (Gd_2O_3) is widely investigated because of enormous properties including, crystallographic stability, large mechanical strength, thermal conductivity, and high optical band gap energy (Tamrakar *et al.*, 2014; Huang *et al.*, 2019). The molybdenum trioxide belongs to the transition metal oxides, crystallizes in the orthorhombic structure and has high chemical and thermal stability and interesting physical properties that may be useful in optoelectronic apparatus. Recently, due its attractive electrical properties, the MoO_3 oxide was used in many applications such as optical devices, smart windows, medicine, and agriculture and it was incorporated in transistors, catalysts, electrochemical capacitors, and gas sensors (Ouyang *et al.*, 2012; Munasinghe Arachchige *et al.*, 2018; Zhu *et al.*, 2019) to improve their physical properties. Borate crystals and glasses are the best host materials for use in practical of luminescence and paramagnetic centers. In general, the borate compounds that are undoped and doped with rare earth and transition elements are very promising materials for nonlinear optics, quantum electronics and laser technology, dosimeters, detectors and ionizing radiation transformers for scintillators and thermo luminescence (Sasaki *et al.*, 2000; Xue *et al.*, 2000; Ishii *et al.*, 2004; Zadneprovski *et al.*, 2005; Adamiv *et al.*, 2006; Rojas *et al.*, 2006; Padlyak *et al.*, 2013; Tajuddin *et al.*, 2017; Wantana *et al.*, 2019).

In this work, we synthesized a novel orange-emitting $\text{Gd}_2\text{MoB}_2\text{O}_9:\text{Sm}^{3+}$ phosphors by means of a solid-state method, and the synthesized phosphors are used to detect the latent fingerprints. The structural and morphological analyses were examined by the X-ray diffraction (XRD), measurements. The room-temperature luminescent properties were studied in detail by measuring the photoluminescence (PL) excitation, PL emission spectra, CIE 1931 chromaticity system, and decay curves.

Materials and Methods

$\text{Gd}_2\text{MoB}_2\text{O}_9:\text{xSm}^{3+}$ ($x = 0.00, 0.01, 0.05, 0.10, 0.15, 0.20, 0.40$ mol%), phosphors were synthesized via the solid-state method. Four different oxides (Gd_2O_3 (99.99%), MoO_3 (99.9%), B_2O_3 (99.98%), and Sm_2O_3 (99.9%)) were used for the preparation of these phosphors. The starting materials were prepared by grinding the corresponding stoichiometric composition using ball milling process in a agate mortar for 30 min, until they were fine grounded homogeneously. The materials were pre-sintered under air atmosphere at 900°C for 18 h, the phase structure of samples was analyzed by X-ray diffractometer. The crystallographic phases were identified by comparison with the X-ray patterns of the standard JCPDS database. The reflections spectra were recorded in the UV-VIS-NIR regions in the range of 200-2,500 nm using a UV-3600 Shimadzu UV-VIS-NIR spectrophotometer. The photoluminescence spectra were determined by using Cary Eclipse fluorescence spectrophotometer. The lifetime spectra of the title glasses were measured employing science-tech modular spectrometer using xenon flash lamp as an excitation source ($\lambda_{\text{ex}} = 404$ nm). Color of photoluminescence was evaluated by using CIE 1931 chromaticity system.

Results and Discussion

X-ray Diffraction (XRD) Analysis

The X-ray diffraction (XRD) pattern has been recorded in the range of 10° to 80° . The XRD patterns of the $\text{Gd}_2\text{MoB}_2\text{O}_9:\text{xSm}^{3+}$ phosphors obtained at different samarium ion concentrations ranging from 0.00 to 0.40 mol% are shown in Figure 1. The XRD diffraction peaks of the samples (samarium concentrations ranging from 0.00 to 0.20 mol%) are basically consistent with the $\text{Gd}_2\text{MoB}_2\text{O}_9$ (JCPDS No. 0371099). It should be noted that the intensity of the distribution decreases with increasing the concentration of Sm^{3+} content. The mixed concentration of Sm^{3+} ion greater than 0.20 mol

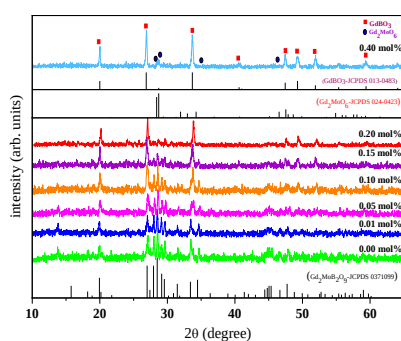


Figure 1. X-ray diffraction (XRD) pattern of $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphor doped with Sm^{3+} ion

shows new phase which is separated between the elements of Gd_2MoO_6 (JCPDS No. 0240423) and GdBO_3 (JCPDS No. 0130483).

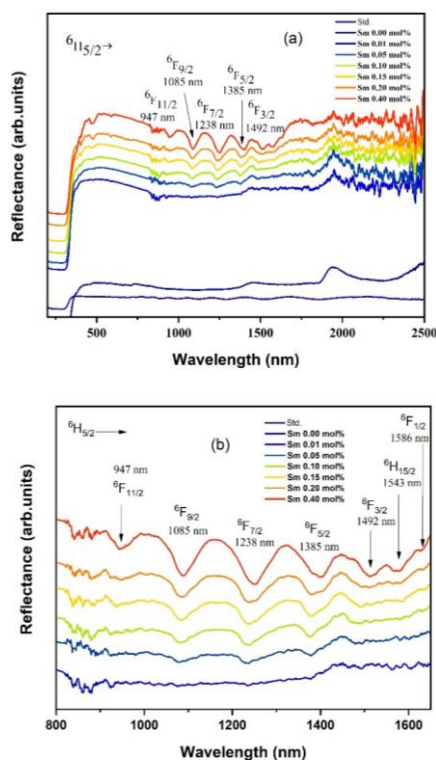


Figure 2. (a-b) The reflections spectra of $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphor doped with Sm^{3+} ion

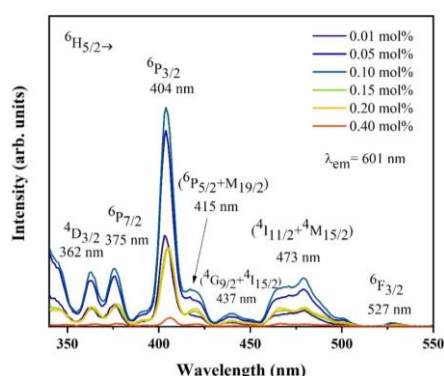


Figure 3. The excitation spectra of $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphor doped with Sm^{3+} ion

Reflections Spectra

The reflection spectra of $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphor in the range 200-2500 nm at room temperature were observed as shown in Figure 2(a). The intensity of reflection peaks increases with increasing in Sm_2O_3 concentration as shown in Figure 2(b). Figure 2(b) shows the peaks corresponding to ${}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{11/2}$ (947

nm), ${}^6\text{F}_{9/2}$ (1,085 nm), ${}^6\text{F}_{7/2}$ (1,238 nm), ${}^6\text{F}_{5/2}$ (1,385 nm), ${}^6\text{F}_{3/2}$ (1,492 nm), ${}^6\text{H}_{15/2}$ (1,543 nm), and ${}^6\text{F}_{1/2}$ (1,586 nm) transitions. The result shows that the peaks of reflections spectra increase with increasing of Sm_2O_3 concentration.

Excitation and Emission Spectra

The excitation spectrum of $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphor doped with Sm^{3+} ion at various concentration ranging from 0.00 to 0.40 mol% obtained by monitoring at 601 nm emission. The excitation spectra of these samples show peaks centered at 362, 375, 404, 415, 437, 473, and 527 nm, corresponding to the transitions from ${}^6\text{H}_{5/2} \rightarrow {}^4\text{D}_{3/2}$ (362 nm), ${}^6\text{P}_{7/2}$ (375 nm), ${}^6\text{P}_{3/2}$ (404 nm), ${}^6\text{P}_{5/2} + \text{M}_{19/2}$ (415 nm), ${}^4\text{G}_{9/2} + {}^4\text{I}_{15/2}$ (437 nm), ${}^4\text{I}_{11/2} + {}^4\text{M}_{15/2}$ (473 nm), and ${}^4\text{F}_{3/2}$ (527 nm) as shown in Figure 3.

The emission spectra, monitored at 404 nm excitation wavelength observed four emission bands centered at 563, 601, 644, and 705 nm which are assigned from excited state ${}^4\text{G}_{5/2} \rightarrow$ ground states of ${}^6\text{H}_{5/2}$ (563 nm), ${}^6\text{H}_{7/2}$ (601 nm), ${}^6\text{H}_{9/2}$ (644 nm), and ${}^6\text{H}_{11/2}$ (705 nm), respectively (Praveena *et al.*, 2008; Sreedhar *et al.*, 2014) as shown in Figure 4.

Both excitation and emission spectra show that the maximum luminescence intensity was observed at 0.10 mol% concentration of Sm_2O_3 . The decrease in emission intensities with the increase of 0.15 mol% of Sm_2O_3 concentration is due to the rise in non-radiative decay channels, which are enhanced due to the concentration quenching effect (Rajaramakrishna *et al.*, 2014; Venugopal *et al.*, 2019; Yasaka *et al.*, 2019; Sangwaranatee *et al.*, 2020). If the concentration of an activator (Sm^{3+}) ion and donor (Sm^{3+}) ion mean distance typically approaches $\sim 15\text{\AA}$ (Rajaramakrishna *et al.*, 2014), then the CR channels activates thereby emission intensity will be decreased. Such process is called concentration quenching.

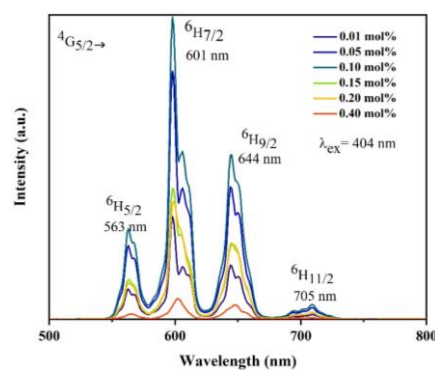


Figure 4. The emission spectra of $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphor doped with Sm^{3+} ion

Decay Curve Analysis

The decay curve for different concentrations of Sm^{3+} ions doped in $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphors are obtained using excitation wavelength 404 nm by monitoring the emission wavelength at 601 nm. And then observing the hypersensitive $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ transition so that the decay time curves can be analyzed which are shown in Figure 5. These decay curves values show decreasing trend with increasing of Sm_2O_3 concentration. The experimental lifetime value is found to be 1.337, 0.967, 0.741, 0.533, 0.507, and 0.446 ms for 0.01, 0.05, 0.10, 0.15, 0.20, and 0.40 mol% of Sm_2O_3 doped in $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphor, respectively. The life time decreases when Sm_2O_3 concentration increases because of the increasing of energy transfer process of Sm^{3+} ions.

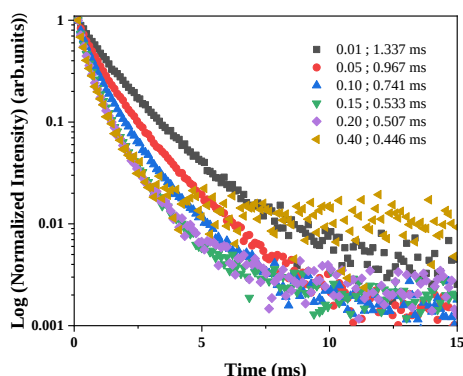


Figure 5. The decay curve of $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphor doped with Sm^{3+} ion

CIE-1931 Chromaticity

In order to quantify the tunability of color emitted by phosphor powder, the variation in the relative intensities of the emission bands has been analyzed in the framework of CIE 1931 (Commission Internationale de l'Eclairage) chromaticity color diagram, which represents all the chromaticity visible to the human eye. The meaning of CIE 1931 color coordinate is defined quantitative number links between emission spectra in the electromagnetic spectrum (in visible), and physiological perceived colors in human color vision. The CIE color coordinates (x , y) of all studied Sm^{3+} -doped $\text{Gd}_2\text{MoB}_2\text{O}_9$ have been calculated and are found to be (0.5970, 0.4022) for all host which is fall on orange region as Figure 6.

Figure 7 shows the observed emission for latent fingerprint under UV excitation. These results indicate that $\text{Gd}_2\text{MoB}_2\text{O}_9:\text{Sm}^{3+}$ be potential candidate for practical applications in latent fingerprint detection.

Conclusions

In summary, the $\text{Gd}_2\text{MoB}_2\text{O}_9:\text{Sm}^{3+}$ phosphors were successfully synthesized via facile solid-state method. The $\text{Gd}_2\text{MoB}_2\text{O}_9:\text{Sm}^{3+}$ phosphors were crystallized in pure hexagonal phase and the XRD patterns were well matched with standard JCPDS card. The PL spectra showed the strong orange emission at 601 nm under UV light excitation. The maximum luminescence intensity was observed at 0.10 mol% of Sm_2O_3 . The CIE color coordinates (x , y) of all studied Sm^{3+} -doped $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphors have been calculated and are found to be (0.5970, 0.4022) which situates on orange region. The experimental lifetime is found to be 1.337, 0.967, 0.741, 0.533, 0.507, and 0.446 ms for 0.01, 0.05, 0.10, 0.15, 0.20, and 0.40 mol% of Sm_2O_3 doped in $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphors, respectively. The life time decreases when Sm_2O_3 concentration increases because of the increasing of energy transfer process of Sm^{3+} ions. The prepared phosphors were used for improving the efficient detection of latent fingerprints regardless surface with any background. Therefore, we believed that $\text{Gd}_2\text{MoB}_2\text{O}_9:\text{Sm}^{3+}$

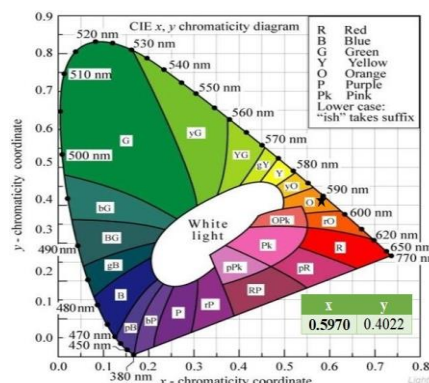


Figure 6. The CIE-1931 Chromaticity of $\text{Gd}_2\text{MoB}_2\text{O}_9$ phosphor doped with Sm^{3+} ion



Figure 7. $\text{Gd}_2\text{MoB}_2\text{O}_9:\text{Sm}^{3+}$ on the aluminum foil surface under UV excitation

phosphors could be promising materials for latent fingerprint technology.

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