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A near-UV-converted $LiMgBO_3$:Dy^{3+} nanophosphor: Surface and spectral investigations

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ABSTRACT

A near-ultra violet (UV) converted $LiMgBO_3$:Dy^{3+} nanophosphors have been synthesized by the combustion method. The structural, spectral and optical properties were examined by powder X-ray diffraction, fluorescent spectrophotometry and UV–vis spectroscopy. The excitation spectra of the phosphors contain sharp peaks at 294, 323, 348 and 385 nm due to the 4f–4f transition of the Dy^{3+} ion. The phosphor is efficiently excited by near-UV chips. Upon near-UV excitation the phosphor emits intense blue and yellow with a weak red band centered at 484, 573 and 669 nm respectively, ascribed to the transition of Dy^{3+} ion from ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$, ${}^6H_{13/2}$, ${}^6H_{11/2}$. The diffuse reflectance spectra of the phosphors were consistent with the excitation spectra and were used to calculate the band gap of the material, approximated to be 5.4 eV. The calculated CIE coordinates (0.45, 0.46) under 348 nm excitation were found to be in the white spectrum region. For surface investigation, X-ray photoelectron spectroscopy was used which confirms the presence of all the elements on the surface of the material.

1. Introduction

Recently, the studies on spectral properties of alkali–alkaline based oxide materials ($MNBO_3$, A = alkali, B = alkaline) have generated interest in research community, because of their good thermal and chemical properties [1–2]. These materials have high melting points, capability to accommodate defects, high thermal expansion coefficient, low thermal conductivity and strong absorption in the near-ultraviolet region, makes them a strong candidate for the solid state lighting, display devices, optoelectronic devices and light-emitting diodes (LEDs) [3–7]. Today, the investigation of oxide based light emitting materials for white light-emitting diodes (w-LEDs) applications have generated interest due to the advantages such as long lifetime, low energy consumption, high luminescence efficiency and environmental friendliness [8]. WLEDs produced by downconverting the blue light from InGaN using suitable color converters, such as YAG:Ce (cerium-doped yttrium aluminum garnet) has certain demerits, such as halo effect, low color rendering index (CRI) and re-absorption of the blue emission which limits its applicability [9–11]. Therefore, in order to overcome these limitations, another approach has been suggested in which tricolor (red/green/blue) phosphors have been excited by a near-ultraviolet light to produce white light with high color tolerance and high conversion efficiency with excellent optical and thermal stability [12,13]. Hence, the potential application of near-UV converted phosphors for white WLED is expected to increase considerably. Therefore, the phosphors excited by near-UV light are highly desirable and could be explored for their potential applications in lighting.

Among the rare earth ions, Dy^{3+} is of much interest because of the existence of two characteristic emission bands in the blue (∼480 nm) and yellow (∼570 nm) regions, which correspond to the magnetic dipole transition (${}^4F_{9/2} \rightarrow {}^6H_{15/2}$) and the hypersensitive electric dipole transition (${}^4F_{9/2} \rightarrow {}^6H_{13/2}$) of Dy^{3+} [14,15]. In addition, the intensity of the yellow emission is strongly affected by the crystal field environment of the host lattice and the radial integral of *4f* and *5d* electrons [16]. Hence, the white light could be produced by tailoring the yellow to blue (Y/B) intensity ratio. Research on alkali–alkaline based oxide phosphors has been carried out extensively and the materials are explored for their potential applications in the lighting industry [17–20]. However, there are only few reports available on rare earth doped $LiMgBO_3$ phosphors [21–23]. Moreover, there is lack of reports on the surface

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properties of the $LiMgBO_3:Dy^{3+}$, as the surface of the material plays an important role in the luminescent processes.

In this present work, $LiMgBO_3:Dy^{3+}$ nanophosphors were synthesized by combustion method and their photoluminescence (PL) and optical properties were explored. In addition, the chemical states of the phosphors were determined on the surface of the material due to the surface sensitivity to luminescence emission.

2. Experimental details

Dy^{3+} doped $LiMgBO_3$ phosphors were synthesized by combustion method using urea as a fuel. The concentration of the activator (Dy^{3+}) varied from 0.5 to 2.5 mol.%. The lithium nitrate anhydrous [$LiNO_3$], magnesium nitrate [$Mg(NO_3)_2$], dysprosium oxide [Dy_2O_3] (99.99%) and boric acid [H_3BO_3] were used as precursors. In a typical preparation, all the reactants were taken according to the balanced reaction (Eq. 1) and dissolved, stoichiometrically, in a few drops of distilled water with vigorous stirring until a thick paste was formed. The thick paste was transferred into the crucible and was kept in a preheated muffle furnace at 550 °C. Initially, the paste gets boiled followed by dehydration and finally decomposed with the evolution of the large amount of gases such as CO_2, N_2 and H_2O. The final foamy product was cooled to room temperature and were grounded well using a pestle and mortar to get a fine powder. The powder was annealed in air at 800 °C to improve its crystallinity.

$$\begin{aligned}&LiNO_3 + (1-x)Mg(NO_3)_2\cdot 6H_2O + xDy_2O_3 + 2.5NH_2CONH_2\\&\quad + H_3BO_3 \rightarrow LiMg_{1-x}Dy_xBO_3 + 12.5H_2O + 2.5CO_2 + 4N_2 \qquad (1)\end{aligned}$$

The crystalline phase of the synthesized samples were identified by X-ray powder diffractometer (XRD) (Bruker Advance D8 X-ray diffractometer), operating at 40 kV and 40 mA using Cu Kα radiation ($\lambda = 1.5406$ Å). The photoluminescence (PL) measurements of the phosphors were done on a Cary-Eclipse Spectrofluorometer equipped with a 150 W xenon discharge lamp as an excitation source. For optical properties, the diffuse reflectance spectra of the powder samples were recorded using a UV–vis-2600 double beam spectrophotometer; attached with an ISR (integrating sphere assembly). To study the surface and the chemical states of the nanophosphors, the X-ray photoelectron spectroscopy (XPS) was performed on a PHI 5000 versa probe spectrometer using monochromatic Al Kα radiation. The details for measuring the high-resolution spectra were described in a previous report [24].

3. Results and discussion

3.1. XRD studies

Fig. 1 shows the XRD pattern of $LiMgBO_3:Dy^{3+}$ (2 mol.%) nanophosphor along with the standard JCPDS (00-079-1996) pattern of $LiMgBO_3$. The XRD pattern is consistent with the standard pattern and depicts that the pattern belongs to the pure monoclinic phase with space group C2/c. The diffraction peaks are indexed according to the JCPDS file (00-079-1996). Also, it has been observed that the addition of small amounts of Dy^{3+} (activator), did not alter the crystal structure of the host lattice, which suggested that the activator ion is fully incorporated in the host lattice. The calculated lattice parameters were approximated to be $a = 5.168$ Å, $b = 8.887$ Å, $c = 9.916$ Å, $\beta = 91.20°$ and $V = 455.322$ Å. The average crystalline size of the nanophosphors was calculated from the full width half maxima of the diffraction peaks by using Scherrer's equation [25] and is approximated to be 35 nm.

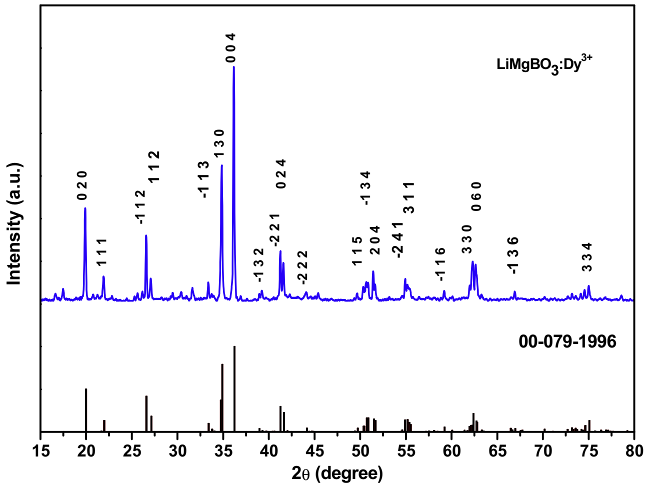

Fig. 1. XRD pattern of the $LiMgBO_3:Dy^{3+}$ nanophosphor.

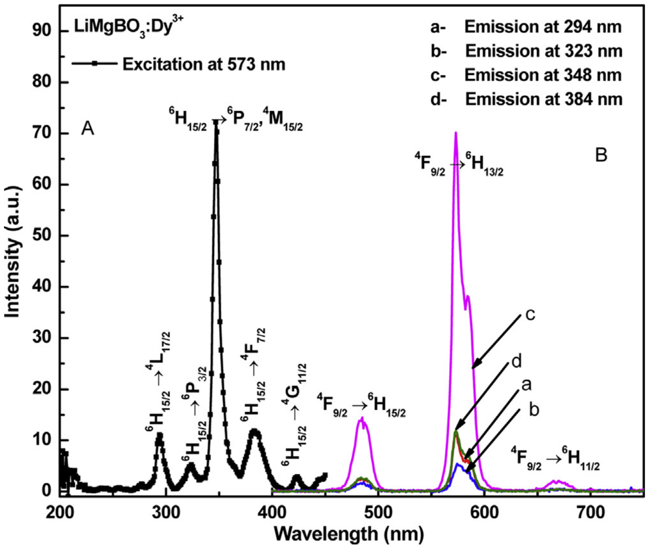

Fig. 2. PL excitation (A) and emission (B) spectra of the $LiMgBO_3:Dy^{3+}$ (2 mol.%) nanophosphor.

3.2. Spectral properties

3.2.1. Photoluminescence

The excitation (Fig. 2(A)) and the emission spectra (Fig. 2(B)) of $LiMgBO_3$: Dy^{3+} (2 mol.%) nanophosphor are shown in Fig. 2. The excitation spectrum was measured when monitoring the emission wavelength at 573 nm. The spectrum consists of sharp peaks at 294 nm ($^6H_{15/2}\rightarrow{}^4L_{17/2}$), 323 nm ($^6H_{15/2}\rightarrow{}^6P_{3/2}$), 348 nm ($^6H_{15/2}\rightarrow{}^6P_{7/2}$, $^4M_{15/2}$), 384 nm ($^6H_{15/2}\rightarrow{}^4F_{7/2}$) and 423 nm ($^6H_{15/2}\rightarrow{}^4G_{11/2}$), which correspond to the characteristic 4f–4f transitions of the Dy^{3+} [26]. Under different excitation (294, 323, 348, and 385 nm), the emission spectra of the nanophosphors show two main emission bands at 484 nm and 573 nm corresponding to the $^4F_{9/2}\rightarrow{}^6H_{15/2}$ magnetic dipole transition, which is much less sensitive to the coordination environment of the host lattice and the hypersensitive $^4F_{9/2}\rightarrow{}^6H_{13/2}$ electric dipole transition of Dy^{3+}. The force electric dipole transition ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) is allowed only when the Dy^{3+} ion is located at the local sites with non-inverted center symmetry. Since, the electric dipole transition (yellow band) is much more intense than the magnetic dipole transition (blue band), suggesting that the Dy^{3+} ion occupied more than one non-centrosymmetric site in the host lattice. The emission spectra also