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Synthesis, spectral and surface investigation of novel $CaMgB_2O_5:Dy^{3+}$ nanophosphor for UV based white LEDs

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ABSTRACT

This paper reports the surface, spectral and luminescent properties of Dy^{3+} doped $CaMgB_2O_5$ phosphor synthesized by combustion method. X-ray diffraction (XRD) was used to characterize the phase structure. X-ray photoelectron spectroscopy (XPS) was used to investigate the surface elemental composition and chemical states of the synthesized phosphor. The luminescent properties of $CaMgB_2O_5:Dy^{3+}$ phosphor was investigated by using photoluminescence emission, excitation and reflectance spectra. The excitation spectra under 576 nm emission consist of charge transfer band (CTB) and a series of 4f-4f transition states of Dy^{3+} ion. The emission spectra of $CaMgB_2O_5:Dy^{3+}$ phosphor recorded at 349 nm excitation shows sharp peaks at 485 nm, 576 nm and 665 nm assigned to ${}^4F_{9/2} \rightarrow {}^6H_{J/2}$ ($J = 15$, 13, and 11) transitions of Dy^{3+} ion. The CIE chromaticity color coordinates (0.38, 0.40) of $CaMgB_2O_5$: Dy^{3+} phosphor falls in the yellowish white region of the horse shoe plot of color gamut. The band gap of the material was calculated to be 5 eV. The phosphor decay curve was also determined. The results show that $CaMgB_2O_5$: Dy^{3+} phosphor might be potential phosphors for n-UV-based white light-emitting diodes.

1. Introduction

The first commercial white emitting LED was developed in 1997 [1] after the fabrication of a blue-emitting GaN light emitting diode LED in 1993 by Nakamura et al. [2] after that more and more interest was focused on GaN-based white-emitting LEDs (W-LED). The white light can be obtained by a variety of methods such as by combining blue InGaN LED with a broadband yellow-emitting phosphor, *e.g.*, YAG: Ce^{3+} [3]. In addition to this, white light can also be produced by the combination of UV-LED with blue, green and red phosphor and by the combination of blue, green and red LED's. Among them for white light the use of tricolor (red, green and blue) LEDs has potential high efficiencies and flexible user controlled color. It is well known that photoluminescent (PL) properties of Dy^{3+} doped phosphors have been widely studied because of the different optical energy levels of Dy^{3+} which shows light emitted in the white regions because of the existence of two intense emission band in, blue (${}^4F_{9/2} \rightarrow {}^6H_{15/2}$) and yellow (${}^4F_{9/2} \rightarrow {}^6H_{13/2}$) region and a weak red (${}^4F_{9/2} \rightarrow {}^6H_{13/2}$) region. The yellow ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition is a hypersensitive forced electric dipole transition ($\Delta J = 2$) and is very sensitive to the coordination environment of the host. However blue (${}^4F_{9/2} \rightarrow {}^6H_{15/2}$) transition is a host insensitive magnetic dipole transition ($\Delta J = 3$) [4,5]. Thus we can obtain white light with doping of Dy^{3+} ion into the host materials by changing the yellow to blue (*Y/B*) ratio.

The borate based phosphor materials show excellent luminescent properties as host matrix due to their large band gap, low synthesizing temperature and high chemical and physical stability [6]. A large verity of borate phosphors doped with rare earth ions has been reported in the literature for their applications in solid state lighting, TL personal dosimetry, field emission display panels (FDP) *etc.* [7–9]. Among these borate materials, alkaline earth borates are good candidates as a host structure due to their low synthetic temperature, easy preparation, and high luminescent brightness [10]. In this family the luminescence properties of $Sr_2B_2O_5$ doped with different rare earth ions has been reported as good host material for LEDs [11–13]. The luminescent properties of mixed alkaline borate phosphors doped with different rare earth/transition metal ions such as $Ba_2Ca(BO_3)_2:Ce^{3+}$, $Ba_2Mg(BO_3)_2:Eu^{2+}$, Mn^{2+} and $M_2Mg(BO_3)_2$: Sm^{3+} (M: Sr and Ba) have been reported for the applications of LED [14–16]. The crystal structure of $CaMgB_2O_5$ host was reported by Yakubovich et al. (1976) and Simonov et al. (1980) [17] which show two stable phases; orthorhombic below

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400 °C and monoclinic above 400 °C. To best our knowledge, no report is available on the photoluminescence and optical studies of Dy^{3+} doped $CaMgB_2O_5$ phosphor.

In the present work, a noble yellowish-white emitting $CaMgB_2O_5:Dy^{3+}$ phosphors have been synthesized by the combustion method and its optical and photoluminescence (PL) properties have been investigated. In PL studies, the effects of Dy^{3+} concentration on luminescent properties and the mechanism for concentration quenching have been reported. In addition, the decay curve and optical energy band gap of $CaMgB_2O_5:Dy^{3+}$ phosphors also have been investigated.

2. Experiment

The $CaMgB_2O_5:Dy^{3+}$ phosphors were synthesized by combustion method using urea as fuel. Calcium nitrate [$Ca(NO_3)_2{\cdot}4H_2O$], magnesium nitrate [$Mg(NO_3)_2{\cdot}6H_2O$], boric acid [H_3BO_3], urea [CH_4N_2O] and dysprosium oxide [Dy_2O_3] of (AR) grade from Merck chemical were used as starting materials. The samples were synthesized by varying the concentration of dopant Dy^{3+} from 0.5 to 3.0 mol% according to the complete chemical reactions shown below:-

$$(1\text{-}x)Ca\ (NO_3)_2{\cdot}4H_2O + Mg\ (NO_3)_2{\cdot}6H_2O + 2H_3BO_3 + 3.34CH_4N_2O + 0.5xDy_2O_3 \rightarrow Ca_{(1-x)}\ MgDy_xB_2O_5 + 11.67H_2O + 3.34CO_2 + 5.34N_2 \quad (1)$$

For complete combustion, the oxidizer/fuel ratio should be equal to unity in order to have the maximum energy release [18]. All the reactants were taken according to the balanced Eq. (1) and mixed together according to the stoichiometric ratio in an agate mortar pastel up to 40 min, until the mixture turns into a thick viscous paste. The thick paste was then transferred to a beaker and then introduced into a preheated muffle furnace at 600 °C to produce the phosphors by undergoing a flaming combustion. The whole process was completed within 4 min. The mixture experienced rapid dehydration and foaming followed by decomposition and evolution of combustible gasses. After some time a volumetric combustion occurs, with a yellow flame yielding a white porous solid foamy product 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 was ground to obtain a fine powder. The fine powder was then annealed at 900 °C temperature for three hours to improve crystallinity.

The phosphors were characterized by using X- ray powder diffractometer of **Rikagu-Miniflex,** operated at 45 kV and 100 mA and using CuK_α radiation ($\lambda = 1.5406$ Å). The XRD patterns were recorded in the range of $10^\circ \leq 2\theta \leq 60^\circ$ with step size of 0.02° (2θ). The lattice parameters of the phosphor were calculated by using the UnitCellWin program [19]. The photoluminescence excitation and emission spectra were recorded by using a Cary–Eclipse Spectrofluorometer equipped with a 150 W Xenon lamp as an excitation source with slit width of 5 nm. The decay curve for this phosphor is recorded by using excitation at 349 nm and emission at 578 nm with slit width of 5 nm. The diffuse reflectance spectra of the powder samples were recorded on a Shimadzu UV–VIS –2600 double beam spectrophotometer attached to the ISR (Integrating Sphere Assembly) using $BaSO_4$ as a standard powder for measurement. To study the surface and the chemical states of the phosphors, the XPS was conducted on a PHI 5000 versa probe spectrometer using monochromatic Al K_α radiation ($h\nu = 1486.6$ eV) generated by a 25 W, 15 kV electron beam. For high resolution spectra, the Hemispherical Analyzer pass energy was maintained at 11 eV. Measurements were performed using either a 1 eV/step (45 min acquisition times) binding energies for survey scans from 0 to 1400 eV or 1 eV/step and 20–30 min times for the high-resolution scans. The X-ray beam size used for the XPS measurements is 10 μm.The pressure during acquisition was less than 1.3×10^{-9} Torr. A low energy electron beam was used to achieve charge neutrality on the sample surface. All the absolute binding energies of the photoelectron spectra were corrected with C 1s signal at 284.6 eV.

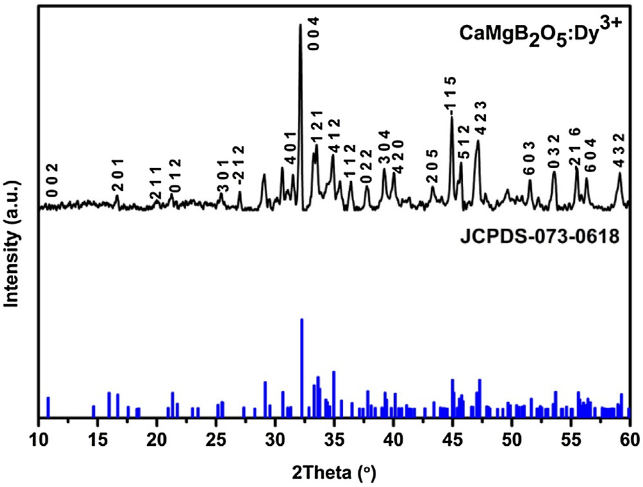

Fig. 1. XRD pattern of $CaMgB_2O_5:Dy^{3+}$ nanophosphor.

3. Results and discussions

3.1. XRD studies

Fig. 1 represents the X-ray diffraction (XRD) pattern of $CaMgB_2O_5:Dy^{3+}$ (1.5 mol%) phosphor. It can be observed from Fig. 1 that the diffraction peaks matched with the standard card of $CaMgB_2O_5$ (JCPDS–0 73–0618) indicating the single phase of the prepared phosphor. It shows the monoclinic phase structure with space group P21/b. In addition the lattice parameter calculated by using UNITCELLWIN software found to be close to the reported in the JCPDS card shown in Table 1. The average crystallite size of the particles was estimated from the line broadening of the XRD peaks by the well-known Debye -Scherrer's equation [20] and found to be 30 nm.

3.2. Spectral properties

Fig. 2 shows the excitation (a) and emission (b) spectrum of $CaMgB_2O_5:Dy^{3+}$ (1.5 mol%) phosphor monitored at 576 nm emission wavelength. The excitation spectrum of $CaMgB_2O_5:Dy^{3+}$ phosphor shows a charge-transfer (CT) band extending from 190 nm to 230 nm. The CT band corresponds to an electron transfer from an oxygen 2p orbital of O^{2-} to an empty 4f orbital of Dy^{3+} [21]. The sharp peaks are located at 293, 323, 349, 364, 384, 425, 452 and 472 nm belongs to the intrinsic 4f–4f transitions of Dy^{3+}. They are assigned to transition from the ground $^6H_{15/2}$ state to the excited $^4L_{3/2}$, $^4L_{19/2}$, $^6P_{7/2}$, $^6P_{5/2}$, $^4I_{13/2}$, $^4G_{11/2}$, $^4I_{15/2}$ and $^4F_{9/2}$ states respectively [22]. The strongest 349 nm excitation peak corresponds to the ($^6H_{15/2} \rightarrow {}^6P_{7/2}$) transition state. Since Dy^{3+} ($^6H_{15/2} \rightarrow {}^6P_{7/2}$) (349 nm) wavelength falls in the n-UV range. This phosphor is suitable to be used for white lighting devices based on GaN LEDs. The PL emission spectrum of $CaMgB_2O_5:Dy^{3+}$ phosphor recorded at 349 nm excitation shown in Fig. 2(b). The emission spectrum consists of three peaks centered at 484 nm (blue), 576 nm (yellow) and 662 nm (red) which corresponds to the transitions of Dy^{3+} from the excited state $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ respectively [23]. The weak blue emission at 484 nm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) corresponds to the magnetic