Improvement in luminescence of Dy³⁺ doped ZnMoO₄ single ingredient white light emitting phosphor

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Single-component phosphors for white-light emission are gaining interest among researchers. This paper presents a cost-effective synthesis of Dy^{3+} doped and un-doped ZnMoO₄ by environment-friendly and auto-combustion process. The Dy^{3+} doped ZnMoO₄ phosphor is well suited for single ingredient white-light emitting phosphor. The X-ray diffraction (XRD) pattern reflects a triclinic phase of un-doped and Dy^{3+} doped ZnMoO₄ phosphor. The UV-Vis absorption analysis of Dy^{3+} doped ZnMoO₄ depicts a blue shift in the absorption peak. A broadband photoluminescence (PL) emission was observed due to the charge transfer band from O²⁻ to Mo^{6+/} Dy³⁺. Broad PL emission was de-convoluted in the form of three intense emission peaks at 484 nm, 574 nm, and 661 nm for Dy³⁺ doped phosphor, correlated with Dy^{3+} transitions ${}^{4}F_{9/2} \rightarrow {}^{6}H_{j}$ (j = 15/2, 13/2, and 11/2). Mechanism of energy transfer between [MoO₄]²⁻ to Dy³⁺ energy states discussed based on different transitions.

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1. Introduction

Light Emitting Diodes with white emission have gained popularity over other light sources because of their unique qualities, which include sustainable environmental effect, a long life span, higher optical power, and electrical energy savings [1]. Industrial white emissive LEDs (w-LEDs) are commonly use Ce^{3+} doped (Y, Ga)₃(Al, Ga)₅O₁₂ yellow emitting phosphors on InGaN blue chips [2]. Another method for w-LED is prepared by combining multiple phosphors with different emission such as red, blue, and green. However, this technique has shown drawbacks related to color ratio adjustment, and color re-absorption [3]. The potential solution to resolve these hindrances belongs to find a single-constituent phosphor that may emit better white light.

Metal molybdates are gaining interest in the scientific community because of their remarkable optical characteristics. $ZnMoO_4$ is a phosphor without an activator for the broad emission between 400 nm to 700 nm centered at 518 nm under near-UV excitation [4]. The $ZnMoO_4$ phosphor can be synthesized using various methods (solid-state, auto-combustion, solgel, sol/hydro thermal, etc. [4-6]) with good chemical and thermal stability. The simplicity and affordability of the auto-combustion method make it superior in compare to others. The emitted color of the $ZnMoO_4$ phosphor may be improved and adjusted by doping in it with different rare-earth elements due to varied 4f orbital electron configurations of rare-earth ions. The Dy^{3+} ion is a

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unique rare-earth element due to its spectroscopic property of being extremely sensitive to the chemical environment. Therefore, the Dy^{3+} ion is successfully utilized as a dopant for various applications such as white light emission, sensing applications, photo-catalysis etc [1, 7, 8].

Hence, this study is planned to prepare a series of Dy^{3+} ion doping in ZnMoO₄ phosphor. The Dy^{3+} ion usually results in three emission transitions lies in the visible spectrum to form white light. Dy^{3+} concentration is used as key parameter to optimize the white luminescence. The CIE coordinates and color purity are discussed by varying Dy^{3+} concentration to build a good understanding for the development of single component phosphor to achieve excellent white emission.

2. Synthesis method and characterization

Varied concentration of Dy^{3+} (x = 0, 1, 2, 3, 4) doped ZnMoO₄ samples were synthesized via a urea-based combustion process, indexed with code-name D0, D1, D2, D3, and D4, respectively. Required precursors used for synthesis were metal nitrates (Zn(NO₃)₂, Dy(NO₃)₃ with assay correction) and ammonium molybdate hydrate ((NH₄)₆Mo₇O₂₄*xH₂O with assay correction). Fig. 1 shows the complete process of synthesis with the pictorial view of different steps of synthesis.



Fig. 1. Steps of synthesis process for D0, D1, D2, D3, and D4 phosphors.

The XRD spectra were obtained from the Rigaku-Mini Flex system. The Fourier-Transform IR spectra of prepared samples were fetched from JASCO FT/IR 4600 spectroscopy. The absorbance study was featured using the JASCO V770 spectrophotometer. We have obtained both excitation as well as emission spectra of photoluminescence with a Horiba Fluorolog-3 spectrophotometer.

3. Result and discussion

3.1. X-ray diffraction measurement

The structure pattern has been analyzed by X-ray diffraction (XRD) patterns for the prepared phosphors. The XRD patterns of samples D0 and D3 in Fig. 2,which confirm the triclinic crystalline phase with the space group P1(2) of α -ZnMoO₄ being verified by JCPDS file #35-0765 [4]. The Bragg's position of peak (120) for the D3 sample shifts to a lower 20 value from 24.32° to 24.16°, indicating that the greater ionic radii (0.91 Å) Dy³⁺ ions are successfully occupied in the place of lower ionic radii (0.74 Å) Zn²⁺ ions [10]. The unit cell volume and lattice parameters with the doping of Dy³⁺ found continuously increased due to the greater ionic radii of the Dy³⁺ ions.

The crystalline size of the phosphors was evaluated by the well-known Debye-Scherer formula [11];

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where, λ is the excitation wavelength of the X-rays (1.54 Å), and β is the full width at half maximum (FWHM) of the XRD features at peak position 2 θ . The evaluated crystallite sizes of D0, D1, D2, D3, and D4 samples are 67 nm, 66 nm, 69 nm, 77 nm, and 74 nm, respectively. The crystallite size with Dy³⁺ doping continues to increase up to the D3 sample with the improvement in the crystallinity. This improved crystallinity is responsible for the enhancement of the luminescence of phosphor, further discussed in photoluminescence measurement.



Fig. 2. X-ray diffraction pattern of (a) $ZnMoO_4$, (b) $3\% Dy^{3+}$ doped $ZnMoO_4$, and (c) (120) peak shift observed after Dy^{3+} doping.

3.2. FTIR measurement

FTIR spectroscopy of the synthesized phosphors is plotted and analyzed in the form of different vibration bands in Fig. 3. The observed bands at 432 cm⁻¹ and 778 cm⁻¹ are accredited to the Mo–O bending vibration and O–Mo–O stretching vibration in the $[MoO_4]^{2-}$ tetrahedron, respectively [9]. These observed bands are expected to support the formation of the tetragonal structure. Some additional bands are also observed at nearly 1740 cm⁻¹ and 2360 cm⁻¹ due to a vibration band of C=O group bond and CO₂, respectively [12].



Fig. 3. Vibrational bands of D0 and D3 phosphors.

3.3. Absorption measurement

Fig. 4(a) reflects the absorption spectra for the synthesized phosphors. A absorption band centered at 270 nm is observed for the D0 sample in Fig. 4(a), which reflects the O^{2-} to Mo^{6+} charge transfer band [13]. As seen in Fig. 4(a), this absorption band for Dy^{3+} doping is shifted to higher energy at 260 nm (for D3 sample) due to increase in optical bandgap. Simultaneously, another band is observed for D3 at 366 nm, which corresponds to the ${}^{6}H_{15/2} \rightarrow {}^{4}M_{19/2}$ transition of Dy^{3+} ions [14].

The optical bandgap (E_q) of phosphors has been evaluated by Tauc expression [9,13];

$$(\alpha h\nu)^{\frac{1}{n}} = A(h\nu - E_a) \tag{2}$$

where, hv is energy of incident photons, α and A are known as absorbance and proportion constant respectively. The direct transitions are quite favorable in ZnMoO₄, therefore ½ value of exponent n has been considered. The optical bandgap of D0 sample calculated as 4.01 eV. After Dy³⁺ doping, optical bandgap gets increased to 4.16 eV, as shown in Fig. 4(b) for D3 sample. This increment in bandgap is observed due to formation of abundant carrier concentration, resulting in Burstein-Moss shift [15].



Fig. 4. (a) Absorption spectra and (b) Tauc plot for D0 and D3 phosphors.

3.4. Photoluminescence measurement

Photoluminescence (PL) excitation spectra for all synthesized phosphors are plotted in Fig. 5(a). These PL excitation spectra were recorded for emission transition of Dy^{3+} ion at 574 nm. The PL excitation spectra provide an excitation band centered at 297 nm for all phosphors due to charge transfer band from ligand to metal [9,16].



Fig. 5. (a) PL excitation spectra and (b) PL emission spectra for all Dy^{3+} doped ZnMoO₄ phosphors.

The intensity of this band found to be increased consistantly with the increment in concentration of Dy^{3+} doping and maximed for D3 sample, as shown in Fig. 5(a). The excitation spectra for Dy^{3+} samples also hold peaks at 353 nm, 367 nm, 388 nm, 427 nm, 454 nm and 476 nm, which correspond to ${}^{6}H_{15/2} \rightarrow {}^{6}P_{7/2}$, ${}^{6}P_{5/2}$, ${}^{4}I_{13/2}$, ${}^{4}G_{11/2}$, ${}^{4}I_{15/2}$, and ${}^{4}F_{9/2}$ transitions of Dy^{3+} ion respectively. These excitation peaks for Dy^{3+} doped phosphors have already been reported by Kaur *et al.* [17].

Photoluminescence (PL) emission spectra were recorded with the excitation of 297 nm, shown in Fig. 5(b). PL emission spectra show a broad band in the visible region centered at 500 nm for all synthesized samples, which was resulted with the energy transfer from the excited level of $[MoO_4]^{2-}$ ion to ground level. For Dy³⁺ doped phosphors, prominent three peaks at 487 nm, 574 nm, and 661 nm are observed, which correspond to the transitions ${}^{4}F_{9/2} \rightarrow {}^{6}H_{i}$ (j = 15/2, 13/2, and 11/2) of Dy^{3+} ion respectively [17]. With the increase in doping concentration of Dy^{3+} ions, decrease in intensity of the broad emission band and increase in the intensity of the Dy³⁺ emission peak were observed. This decrease in broadband intensity and increase in Dy³⁺ emission intensity indicates energy transferring from $[MoO_4]^{2-}$ to Dy^{3+} excited levels, shown in Fig. 7(a). The intensity of Dy³⁺ doped emission is maximzed for D3 sample. Thereafter, with the increase in doping concentration, quenching occurs in the intensity of Dy3+ emission. The quenching phenomenon is mainly due to the overlapping of wave functions of Dy³⁺ ions or the exchange of energy by the electric multipolar transition of Dy^{3+} ions [18]. The critical distance between Dy^{3+} ions for the overlap of their interaction functions should not exceed 0.5 nm, this possibility will be less for low concentrations of Dy³⁺ ions. Hence, the intensity quenching may be due to electric multipolar interaction.

The multipolar interaction can be investigated by logarithmic conversion of Dexter's expression [19], which is as follows;

$$\log\left(\frac{I}{c}\right) = A - \frac{Q}{3}\log(c) \tag{3}$$

where, c (1%, 2%, 3%, and 4%) represents the percentage of doping concentration of Dy^{3+} ions and I represents the intensity of the electric transition peak of Dy^{3+} ion. Parameter Q value are considered as 6, 8, and 10 for dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions of multipolar interaction respectively. Value of Q (~5.64) for Dy^{3+} emission transition analysed through the plot of log(I/x) versus log(x). The log(I/c) vs. log(c) plot is shown in Fig. 6. Hence, the multipolar interaction responsible for the quenching achieved in Dy^{3+} doped ZnMoO₄ is the dipole-dipole interaction.



Fig. 6. The plot log(I/c) versus log(c).

The intensity of Dy^{3+} emission observed to be increase with increment in concentration of Dy^{3+} ions and maximized for the D3 sample as seen in Fig. 5(b). The enhancement in PL emission intensity of Dy^{3+} transitions has been achieved up to 3% concentration of Dy^{3+} doping. The possible reason for the enhancement in the emission intensity by Dy^{3+} doping could be an increase in the asymmetricity between the electric dipole transition and magnetic dipole transition of Dy^{3+} ions. The electric dipole transition of Dy^{3+} ions is strongly affected by surrounding ions; however magnetic dipole transition shows immunity for it [20]. For the D3 phosphor, maximum enhancement is observed in ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ peak. The asymmetricity around Dy^{3+} ions is calculated by the area ratio of the electric dipole transition (${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$) and magnetic dipole transition (${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$) peaks [20];

$$Asymmetricity = \frac{Area under the intensity peak of 4F_9 \rightarrow 6H_{13}of Dy^{3+} transition}{Area under the intensity peak of 4F_9 \rightarrow 6H_{15}of Dy^{3+} transition}$$
(4)

The asymmetry ratios for D1, D2, D3, and D4 phosphors after calculation are 2.42, 2.79, 3.11, and 3.0 respectively. The increased asymmetry indicates facilitation for the energy transfer between Dy^{3+} and O^{2-} ions because of favorable ions surrounding for electric dipole transition of Dy^{3+} . This phenomenon results an increment in the interaction strength of Dy^{3+} ions with the ZnMoO₄ host, which maximizes the emission intensity for the D3 sample.

3.5. Chromaticity diagram

The colors quality based on photoluminescence emission spectra of all Dy^{3+} doped phosphors are shown in Fig. 7(b) through the chromaticity diagram by using CIE coordinates. The calculated CIE coordinates are listed in Table 1. The CIE coordinates of the D0 sample are (0.219, 0.324), near the natural white light area. With the increase in Dy^{3+} doping, it is further shifted towards center of white illuminated point, finally CIE coordinate (0.332, 0.379) for D3 sample is close to it. The Correlated color temperature (CCT) and color purity (%) of all Dy^{3+} doped phosphors are also calculated and listed in Table 1. The color purity (CP) of a phosphor represents mono-chromaticity. The color purity (CP) computed by given expressions [21];

$$CP(\%) = \frac{\sqrt{(x-x_0)^2 + (y-y_0)^2}}{\sqrt{(x_d-x_0)^2 + (y_d-y_0)^2}} \times 100$$
(5)

where, the coordinates of the white illumination point (0.3101, 0.3162) of the 1931 CIE Standard Source are (x_o, y_o) and the CIE coordinates of the produced phosphor are (x, y). The (x_d, y_d) coordinates can determine by extending the straight line from (x_o, y_o) and (x, y) to the CIE diagram's perimeter. The low color purity (10 % - 14 %) of the D1, D2, and D3 samples shows the overall emission of these phosphors in the white light zone. There are many Dy^{3+} doped phosphors already reported for white light emitting application such as $Ca_2MgSi_2O_7$: Dy^{3+} [22], $LiSr_4(BO_3)_3$: Dy^{3+} [23], Sr_2SiO_4 : Dy^{3+} [24], $CaGd_2ZnO_5$: Dy^{3+} [25], $Ba_3Y(PO_4)_3$: Dy^{3+} [26] etc. The color purity and CIE index of all these phosphors are quite different from the white light index. While the color purity and CIE index for D3 sample are nearest to the perfect white light emission. Thus, D3 phosphor might be a potentially alternative as a single component white light emitting phosphor.



Fig. 7. (a) Energy transfer diagram [MoO₄]²⁻ to Dy³⁺ levels.
(b) Chromaticity diagram for all Dy³⁺ doped phosphor.

Sample code	CIE coordinates	CCT (in K)	Color purity (%)
D0	(0.219, 0.324)	More than 10000	39.3
D1	(0.302, 0.385)	6603	10.7
D2	(0.317, 0.383)	6058	11
D3	(0.332, 0.379)	5526	13.5
D4	(0.343, 0.390)	5172	20

Table 1. Chromaticity parameters for all Dy^{3+} *doped phosphors.*

4. Conclusion

 Dy^{3+} doping in ZnMoO₄ white light emitting single component phosphors have successfully synthesized by urea based self-combustion process. Different samples by tuning Dy^{3+} doping have been examined by using XRD, FTIR, UV-Vis and PL measurements and compared with un-doped ZnMoO₄ phosphors. Absorbance analysis represented the enhancement in optical bandgap after Dy^{3+} doping. The excitation/emission PL spectrum have used successfully to explain the energy transfer mechanism between $[MoO_4]^{2-}$ to Dy^{3+} . The PL emission spectra are used to calculate the CIE coordinates and further processed to calculate the color purity revealed. Moreover, the overall emitted spectra are used to deconvolute the actual contribution of different optical transitions, known as 487 nm, 574 nm, and 661 nm. Role of increasing concentration of Dy^{3+} has been discussed against the possible reason behind it for increasing and quenching phenomenon of luminescence. Significant good color purity of 13.5% with (0.332, 0.379) CIE coordinates has been achieved for 3% Dy^{3+} doping for close to natural white light.

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