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Luminescence properties of nano and bulk ZnWO₄: Eu³⁺ phosphors for solid state lighting applications

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Abstract

Rare earth Eu³⁺ doped ZnWO₄ bulk and nanophosphors were synthesized using solid state and hydrothermal reaction methods. Structural, morphological and microstructural characterizations of the as-prepared phosphors were done by using X-ray diffractometer (XRD), Fourier transform infrared spectroscopy (FTIR), Field emission scanning electron microscope (FESEM) and High resolution transmission electron microscope (HRTEM). Their optical properties such as photoluminescence (PL) emission, thermal quenching and lifetime decay were investigated at 394 nm near UV excitation with respect to dimension which shows better outcome for the nanophosphor than the bulk one. The nanophosphors display homogeneous particles with much smaller dimension compared to the bulk phosphors which in turn intensifies the red emission and also increases the thermal stability.

1. Introduction

Rare earth (RE) ion doped phosphors are the topics of utmost interests to the researchers nowadays because of their significant potential in reduction of power consumption, fast response, eco-friendliness etc [1]. Most widely used mechanism to produce white light in light emitting diodes (LEDs) is to incorporate commercial YAG:Ce³⁺ phosphor (yellow-emitting) with blue emitting LED chip. But, main drawback of this combination is the absence of red-emitting part leading to reduced color-rendering index value (CRI < 80) as well as excess colour temperature (>4500 K) [2]. To overcome these drawbacks red, green, and blue emitting phosphors are combined together with a near UV emitting LED chip for obtaining warm white light having higher CRI value.

RE doped phosphors are convenient for applications in white LEDs because their partly filled 4f orbitals are shielded by 5s and 5p orbitals from adjacent chemical environment which gives rise to sharp emission lines corresponding to 4f → 4f transitions [3]. Due to its ⁵D₀ → ⁷F₂ characteristic transition, Eu³⁺ (trivalent europium) ion is mostly utilized in solid state lighting (SSL) [4] among the various RE ions.

As RE ions shows ultimate performance when combined with a suitable host, the selection of the host material is significant. Metal tungstates are used extensively due to their potential applications in technological areas such as high-energy physics applications, scintillator crystal, potential phosphor, electro-optic devices and optical fibers [5, 6]. ZnWO₄ is a potential candidate as a host matrix in phosphor materials for its good thermal and chemical stability, large bandgap, wolframite structure [7].

The optical behaviour of a material changes hugely with reducing the size of the crystal. Nanophosphors have higher interaction with the incident UV light due to their large number of surface atoms than their bulk counterparts. Additionally, the nanophosphors are more suitable for making homogeneous films than the bulk one [2]. A uniform and regular surface texture is also important for a nanophosphor to excel in the field of SSL.

Various methods, i.e. solvothermal, hydrothermal, sol-gel and room temperature co-precipitation techniques etc, are followed to synthesize the nanophosphors [5, 8]. Among those methods, in hydrothermal method the uniformity in morphology can be well regulated. Several reports are available on Eu³⁺ doped ZnWO₄ phosphors which describes the advantage of charge compensation phenomena [5, 7], codoping of other
rare earth ion along with Eu\(^{3+}\) ion \([6, 9]\), effects of annealing temperature on luminescence properties \([10]\) and also Eu\(^{2+}\)-Eu\(^{3+}\) double doping on ZnWO\(_4\) \([8]\). Wang \textit{et al} compared the luminescence properties of nano and bulk phosphors of ZnWO\(_4\) \([11]\). But to the best of our knowledge no works have been reported hitherto on the comparison of nano and bulk Eu\(^{3+}\) doped ZnWO\(_4\) phosphors discussing their photoluminescence as well as thermal quenching properties. Considering all these factors in this work, we have synthesized nano and bulk 1% Eu\(^{3+}\)-activated ZnWO\(_4\) phosphors, by solid-state reaction and hydrothermal methods, to compare their morphological, structural as well as optical properties.

# 2. Materials and methods

Solid-state and hydrothermal reaction methods were used, respectively, for synthesis of Zn\(_{(1-0.01)}\)WO\(_4\): Eu\(_{0.01}\) bulk and nano phosphors.

## 2.1. Synthesis of bulk phosphor

To prepare the bulk phosphors, stoichiometric amounts (0.03 moles each) of zinc oxide [ZnO (Merck, \(\geq 99.0\%\)), tungsten oxide [WO\(_3\) (Sigma Aldrich, 99.9\%)] and europium oxide [Eu\(_3\)O\(_3\), Sigma Aldrich, 99.99\%)] were taken as initial precursors without any further purification. All of them were mixed and grinded uniformly for 1 h using mortar & pestle. Grinded mixture was then kept in an alumina boat and sintered for 10 h at 1100 °C in a box furnace. Finally calcined material was ground thoroughly again to get the resultant fine bulk phosphor for various measurements.

## 2.2. Synthesis of Nanophosphor

Powder samples of Zn\(_{(1-0.01)}\)WO\(_4\): Eu\(_{0.01}\) were synthesized by facile hydrothermal method. First of all, stoichiometric amounts (0.005 mole each) of Zn(NO\(_3\))\(_2\).6H\(_2\)O (Merck 98\%), Na\(_3\)WO\(_4\).2H\(_2\)O (Sigma Aldrich 99\%) and Eu(NO\(_3\))\(_3\) (made by dispersing Eu\(_2\)O\(_3\) into nitric acid (Merck, 69\%)) were taken as initial precursors without further purification. All of the materials are analytical grade reagent. Zn(NO\(_3\))\(_2\).6H\(_2\)O was then carefully dissolved into 20 ml of deionized (DI) water to prepare solution I and Eu(NO\(_3\))\(_3\) solution is gradually added into to it. To prepare solution II, Na\(_3\)WO\(_4\).2H\(_2\)O was also dissolved into 20 ml of DI water. Afterwards, these two solutions were stirred vigorously for 15 min using magnetic stirrers and then solution I is slowly drop casted into solution II to make a white precipitate. Next the resultant solution was stirred for 30 min and poured into a Teflon container with 50.0 ml capacity, covered by a stainless-steel jacket. After that, the autoclave was kept into a preheated oven for 8 h at 160 °C temperature. It was then left for natural cooling to normal room temperature. Final white precipitate was then washed by centrifugation for 5 min at 12000 rpm with DI water and ethanol twice. To get rid of the surplus water from the filtrated solid, it was put into a drying oven at 80 °C overnight. At last, to obtain the nanophosphor, the dried powder was annealed for 1 h in the box furnace at 700 °C temperature.

## 2.3. Characterization

To investigate the phase purity of Zn\(_{(1-0.01)}\)WO\(_4\): Eu\(_{0.01}\) bulk and nanophosphors, powder XRD was done with a Rigaku Miniflex X-Ray powder diffractometer with scanning speed of 0.5° cm\(^{-1}\) & 0.02° step-size by Cu K\(\alpha\) radiation (\(\lambda = 1.5404 \) Å). Morphology and microstructure of both samples were analyzed by FESEM (ZEISS Sigma) and HRTEM (JEOL-JEM 2100) respectively. The Fourier transform infrared (FTIR) spectra were monitored in 4000–500 cm\(^{-1}\) (mid-IR) wavenumber range by a Shimadzu IRPrestige-21 spectrometer. UV-visible diffuse reflectance spectra (DRS) were monitored using BaSO\(_4\) as standard for reflectance by Shimadzu UV 3600 UV–vis–NIR spectrophotometer. The steady-state PL spectra were acquired in JASCO FP-8300 luminescence spectrometer (Xenon lamp of 150 Watt as incident light source), while time-resolved PL measurements were done in an Edinburgh FLSP-980 spectrofluorometer where the source of excitation is 60 W μs flash lamp.

# 3. Results and discussions

## 3.1. Structural and morphological analysis of phosphors

Powder patterns of Zn\(_{(1-0.02)}\)WO\(_4\): Eu\(_{0.02}\) nanophosphors and Zn\(_{(1-0.01)}\)WO\(_4\): Eu\(_{0.01}\) nano and bulk phosphor were shown in figure 1(a). All of the peaks and their intensities were well matched with the ICDD PDF card no.-15-0774. There is no additional impurity peak in the PXRD pattern, confirming single phase of the phosphor and also monoclinic structure having space group P2\(\bar{1}\)c. Debye–Scherrer equation was used to evaluate the nanophosphor’s average crystallite size (D), expressed as \[12\]:
$D = \frac{0.9 \lambda}{\beta \cos \theta}$

where $\lambda$ is 1.5404 Å, the wavelength of the Cu-Kα line, $\beta$ is FWHM of highest intensity XRD peak associated with the plane (111), and $\theta$ is angle of diffraction associated to corresponding peak. Calculated average crystallite size for ZnWO$_4$: Eu nanophosphor was about 20 nm and for the bulk phosphor it was found to be 120 nm which is much higher compared to the nanophosphors.

Due to larger particle and grain size, length of coherence is appreciably high for bulk samples for all the planes. Hence diffraction peaks appear more intense in this case indicating high degree of crystallinity. Whereas for nanostructures, the grain size decreases remarkably causing decrement in coherence length resulting in broadened and low intensity XRD peaks showing lower crystallinity. This can also be noticed from the full width at half maximum (FWHM) values of the samples calculated from the XRD patterns; 0.42 for the ZnWO$_4$: 1% Eu$^{3+}$ nanophosphor and 0.072 for the bulk phosphor.

For further understanding the crystal structure, Rietveld analysis of XRD pattern was done by Fullprof software for the ZnWO$_4$: 1% Eu$^{3+}$ bulk and nanophosphors and ZnWO$_4$: 2% Eu$^{3+}$ nanophosphors as presented in figures 1(b)–(d) respectively. All of the starting parameters were acquired from the previous literature [13] for Rietveld refinement analysis. The calculated (I$_{calc}$) and the observed (I$_{obs}$) patterns were defined by solid red line and black dots respectively in figures 1(b)–(d) whereas the Bragg diffraction positions of the calculated pattern were shown by green vertical line. The blue line at the bottom signifies the difference among the observed and calculated patterns. All related atomic positions, thermal vibration parameters and fraction factors were converged and refined. All the reflection patterns of the materials were explicitly classified to be originated from (ZnWO$_4$) monoclinic phase (COD database #15-0774, space group P2$1/c$) and indexed accordingly. The pristine monoclinic structure formation was confirmed by the absence of any reflection from any secondary phase segregation or from any other precursors [14]. The output results of Rietveld analysis are shown in table 1. Errors in obtained lattice parameters and the cell volumes are given under parentheses, calculated by using the Fullprof software. The structure of the unit cells are well matched with the theoretical results and observed XRD patterns.

From the Rietveld analysis the values of the lattice parameters for the 1% Eu$^{3+}$ doped ZnWO$_4$ nanophosphors are obtained as $a = 4.6955$ Å, $b = 5.7270$ Å, $c = 4.9428$ Å and for the bulk phosphor the values are $a = 4.6916$ Å, $b = 5.7184$ Å, $c = 4.9254$ Å. The lattice parameter values of the nanophosphors are larger.
than that of the bulk phosphors due to the substitution of relatively larger Eu$^{3+}$ (Shannon ionic radius $= 1.066\ \text{Å}$) ions in the place of smaller Zn$^{2+}$ ions (Shannon ionic radius $= 0.74\ \text{Å}$). Zn$^{2+}$ ions are more favourable to be replaced by the RE Eu$^{3+}$ ions because the ionic radius of Zn$^{2+}$ ion is much closer to the Eu$^{3+}$ ion than the W$^{6+}$ (0.42 Å) ions in the lattice. From table 1, it can be clearly observed that with increase in dopant concentration for the nanophosphors there is a little change in the value of lattice parameter $a$ with gradual increase in the values of $b$ and $c$ and also in crystal volume proving the effective substitution of Zn$^{2+}$ ions by Eu$^{3+}$ ions.

| Parameters | ZnWO$_4$: 1% Eu$^{3+}$ (Bulk) | ZnWO$_4$: 1% Eu$^{3+}$ (Nano) | ZnWO$_4$: 2% Eu$^{3+}$ (Nano) |
|-----------|-------------------------------|-------------------------------|-------------------------------|
| $a$ (Å)   | 4.6916(1)                     | 4.6955(7)                     | 4.6951(6)                     |
| $b$ (Å)   | 5.7184(2)                     | 5.7270(6)                     | 5.7463(6)                     |
| $c$ (Å)   | 4.9254(1)                     | 4.9428(6)                     | 4.9473(6)                     |
| $\beta$ (°) | 90.642(1)                     | 90.584(8)                     | 90.693(6)                     |
| $V$ (Å$^3$) | 132.136(8)                   | 132.91(3)                     | 133.46(2)                     |
| $\rho$ (g cm$^{-3}$) | 7.873                         | 7.827                         | 7.794                         |

The monoclinic ZnWO$_4$ unit cell was modeled by the VESTA$^{\text{TM}}$ program using the values of the atomic positions and lattice parameters shown in figures 2(a) & (b) which clearly demonstrates O–Zn–O and O–W–O bonds. Each zinc atom is surrounded by six oxygen atoms, constructing octahedral clusters of [ZnO$_6$] having P2/c symmetry. Thus, the Eu$^{3+}$ doping in the site of Zn$^{2+}$ ion is confirmed by looking closely to the [EuO$_6$] clusters which have same electronic coordination alike the [ZnO$_6$] clusters [15].

From the FESEM images of ZnWO$_4$: 1% Eu$^{3+}$ bulk and nanophosphors presented in figures 3(a) & (b), respectively, it can be distinctly noticed that the surface morphology and overall structures differ hugely. The surface of the bulk phosphors are hugely non-uniform in nature and also shows some random distortions which behaves like surface defects in turn quenching the PL efficiency. However, the surface morphology of the ZnWO$_4$: 1% Eu$^{3+}$ nanophosphors are very much uniform in shape and size. The average particle size of the nanophosphor is around 20–30 nm, shown in figure 3(b) which is similar to the formerly evaluated value of the crystallite size from XRD data. Cube-like microstructures of the nanophosphors can be confirmed from the TEM image in figure 3(c). Visible lattice images with inter-planar d-spacing of 0.33 nm agreeing to the (111) plane of Zn$_{(1–0.01)}$WO$_4$: Eu$_{0.01}$ nanophosphor are shown in the HRTEM image in figure 3(d).
The FT-IR spectrum of ZnWO₄ nano and bulk phosphors are shown in figure 4. The bands at 460 cm⁻¹ and 580 cm⁻¹ are assigned to the bending vibrations and at 690 cm⁻¹ and 790 cm⁻¹ are assigned to the stretching vibrations of W–O, respectively. Band for bending and stretching vibrations of Zn–O–W can be observed at 870 cm⁻¹ [16]. Three bands at 1384 cm⁻¹, 1630 cm⁻¹ and 3587 cm⁻¹ are ascribed to the O–H stretching and the H–O–H bending vibrations [17]. Two weak bands at 2850 cm⁻¹ and 2920 cm⁻¹ arises due to C–O vibration coming from atmospheric CO₂ [18]. The characteristic bands of the ZnWO₄ in the range of 460 to 870 cm⁻¹ indicates formation of pure phase of ZnWO₄.
3.2. Spectroscopic analysis

The diffuse reflectance spectra (DRS) of both Zn_{1-0.01}WO_4: Eu^{3+} bulk and nanophosphors are shown in figure 5(a). The two bands at 394 nm and at 464 nm appear because of the f-f transitions of Eu^{3+}. Absorption band at 464 nm is only confirmed in the diffuse reflectance spectra of nanophosphors but the other f-f transition peak at 394 nm band and the Eu-O and W-O charge transfer band (CTB) at 283 nm is found in both the bulk and the nanophosphors. The reflectance value is larger (~95%) at higher wavelengths for both the phosphors which firmly shows the excellence of the as prepared material.

From the reflectance spectra optical band gaps were estimated using the Kubelka- Munk functions for the Zn_{1-0.01}WO_4: Eu_{0.01} bulk and nanophosphors [19] and the plots are shown in figures 5(b) & (c). Kubelka-Munk equation for any wavelength is defined as:

\[ F(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} = \frac{K}{S}, \]

Here, S & K are scattering and the absorption coefficients respectively and absolute reflectance R_{\infty} is defined as,

\[ R_{\infty} = \frac{R_{\text{Sample}}}{R_{\text{Reference}}} \]

For direct allowed transition of a material linear absorption coefficient (\( \alpha \)) and bandgap (E_g) is related by Tauc relation as [20]:

\[ \alpha \nu = C_1 (\nu - E_g)^{1/2} \]

Where \( \nu \) is energy of a photon and C_1 is a constant. The diffuse reflectance spectra can be transformed to Kubelka- Munk function, replacing \( \alpha \) by F(R_{\infty}),

\[ [F(R_{\infty})h\nu]^2 = C_2(\nu - E_g) \]

The bandgap (E_g) of the materials shown in figures 5(b) and (c) may be estimated by extrapolating the linear slope to the equation \([F(R_{\infty})h\nu]^2 = 0\) from \( h\nu \) versus \([F(R_{\infty})h\nu]^2\) plot. The measured bandgaps are 4.48 and 3.83 eV of the Zn_{1-0.01}WO_4: Eu_{0.01} nano and bulk phosphors, respectively. Significant enhancement to the
The value of the bandgap establishes the production of phosphor in nanoscale regime [8]. All the bandgaps for the samples are above 3.2 eV, i.e., a significant feature of a potential phosphor because due to higher bandgap the possibility of reabsorption of the emission is lesser [21].

In figure 5(d), the PL excitation spectrum is shown for the ZnWO4:1 %Eu3+ nanophosphors, which is in well agreement with reflectance spectra. PL emission peak at 614 nm is choosen to be the monitoring wavelength for measuring the excitation spectra. Noticeable broad band starting from 260 nm to 320 nm having the highest peak wavelength at 283 nm, refers to charge transfer band (CTB) due to the combined contributions of the charge transfer between O2− → Eu3+ & O2− → W6+. The sharp peaks of Eu3+ transition lines at 362 nm (7F0 → 5D4), 384 nm (7F0 → 5L7), 394 nm (7F0 → 5L6), 415 nm (7F0 → 5D3) and 464 nm (7F0 → 5D2) arises due to f-f transitions to different higher energy states of Eu3+ ions from the 7F0 absorption.

The plausible luminescence mechanism in the ZnWO4:1% Eu3+ phosphor is illustrated in the energy-level diagram corresponding to Eu3+ ion in figure 6. In ZnWO4, conduction band is formed by Zn2+ and W6+ and O2− constructs the valance band. A charge transfer band (CTB) is formed between the bandgap due to the electronic charge transfer from the valence band to the 4f orbital of Eu and W. The excitation of electrons can happen in two ways: either by jump of the electrons from the valance band to the CTB (283 nm) or by directly getting excited to the higher energy levels of Eu3+ (394 nm). Excited electrons then jump to the lowest excited state 5D0 of Eu3+ giving rise to nonradiative transitions, and after that there are five possible ways for them to transit to ground state which leads to five spectral lines in the emission spectra 578 nm, 590 nm, 614 nm, 655 nm and 708 nm.

The PL emission spectra for nano and bulk phosphors at room temperature were presented in figure 7(a). At 394 nm UV excitation, PL emission spectra, having the sharp peaks at 578 nm, 590 nm, 614 nm, 655 nm, 708 nm which are ascribed to 5D0 → 7F0, 5D0 → 7F1, 5D0 → 7F2, 5D0 → 7F3, and 5D0 → 7F4 transition lines of Eu3+ ion, belongs to characteristic 5D0 → 7FJ (J=0,1,2,3,4) transitions. In Eu3+ ion the electrons of outermost 4f shell are segregated by 5 s and 5p electrons, for this reason sharp lines arise in PL emission spectra of Eu3+-doped phosphors. Among these transition lines, 5D0 → 7F1 appear owing to magnetic dipole (MD) transitions, while electric dipole (ED) transitions gives rise to 5D0 → 7F2 lines. Although, site symmetry of trivalent europium ions in ZnWO4 host lattice does not affect the MD transition, but the ED transition is very much sensitive to it which consequently influences emission intensity. Also, it is renowned that ED transition plays significant role in the

![Figure 6. Energy level diagram presenting possible luminescence mechanism in the ZnWO4:1% Eu3+ phosphors.](image-url)
PL spectra if Eu$^{3+}$ ions occupy the non-inversion symmetric sites of host lattices [22]. Actually, in ZnWO$_4$ the distorted WO$_6$ octahedral network around Zn sites creates huge structural asymmetry [15]. Thus parity selection rule breaking and non-inversion symmetry in ZnWO$_4$ host lattice makes $^5D_0 \rightarrow ^7F_2$ ED transition dominant among other transitions which results in 614 nm peak becoming prominent emission in all the synthesized phosphors [23].

### 3.2.1. Judd-Ofelt analysis and quantum efficiency calculation

The relationship between relative intensities and hypersensitive transitions of Eu$^{3+}$ ion can be explained using JO intensity parameters $\Omega_\lambda (\lambda = 2, 4, 6)$ [24, 25]. These parameters ($\Omega_\lambda$) were calculated from the emission spectra for Eu$^{3+}$ by utilizing electric-dipole transitions $^5D_0 \rightarrow ^7F_\lambda (~\lambda = 2, 4, 6)$ and keeping magnetic dipole transition $^5D_0 \rightarrow ^7F_1$ as reference, as expressed in the following equation:

$$A_{0 \rightarrow \lambda} = \frac{4\pi^2 \omega^3}{3hc\gamma} \sum_{\lambda=2,4} \Omega_\lambda \left( \langle D_0 \parallel U^\lambda \parallel F_\lambda \rangle \right)^2$$

where $A_{0 \rightarrow \lambda}$ is the experimental coefficient of spontaneous emission, $A_{0 \rightarrow 1}$ is the Einstein’s coefficient of spontaneous emission between energy levels $^5D_0$ and $^7F_1$, which can be calculated as:

$$A_{0 \rightarrow 1} = 0.31 \times 10^{-11} (n_0)^2 (\nu_{0 \rightarrow 1})^3,$$ having the value of approximately 50 s$^{-1}$, $\omega$ is angular frequency of the transition, $e$ is the elementary electronic charge, $c$ is velocity of light, $h$ is Planck’s constant, $\gamma$ is the Lorentz local field correction which can be described as:

$$\gamma = \frac{n (n^2 + 2)^2}{9}$$

where $n$ is the refractive index of the host ($n \sim 2.2$ for ZnWO$_4$) [26].

The values of $\Omega_2$, $\Omega_4$, $\Omega_6$ by can be measured by calculating $A_{0, \lambda}$ directly using the luminescence spectra by taking [25]:

$$\langle D_0 \parallel U^2 \parallel F_2 \rangle = 0.0032, \langle D_0 \parallel U^4 \parallel F_4 \rangle = 0.0023 \text{ and } \langle D_0 \parallel U^6 \parallel F_6 \rangle = 0.0002$$

But in the emission spectrum the $^5D_0 \rightarrow ^7F_6$ transition is not observed so the related term ($\Omega_6$) can be excluded from calculation. The average lifetime ($\tau$), Radiative transition rate ($A_{\text{rad}}$) and non-radiative transition rate ($A_{\text{nrad}}$) are related as

\[ A_{\text{rad}} = \text{Rate of radiation} \]
\[ A_{\text{nrad}} = \text{Rate of non-radiation} \]
\[ \tau = \frac{1}{A_{\text{rad}} + A_{\text{nrad}}} \]
Table 2. Judd-Ofelt intensity parameters ($\Omega_2$, $\Omega_4$), fluorescence lifetime ($\tau$), transition rates ($A_{\text{rad}}$, $A_{\text{rad}} + A_{\text{rad}}$), quantum efficiency ($\eta$) of the ZnWO$_4$: 1% Eu$^{3+}$ nano and bulk phosphors under 394 nm excitation calculated from the corresponding PL emission spectra.

| Sample                              | $\Omega_2$ ($10^{-20}$ cm$^2$) | $\Omega_4$ ($10^{-20}$ cm$^2$) | $\tau$ (ms) | $A_{\text{rad}}$ ($s^{-1}$) | $A_{\text{rad}} + A_{\text{rad}}$ ($s^{-1}$) | $\eta$(%) |
|-------------------------------------|---------------------------------|---------------------------------|-------------|-------------------------------|---------------------------------------------|-----------|
| ZnWO$_4$: 1% Eu$^{3+}$ nano-phosphor| 5.71                            | 0.19                            | 0.35        | 253.8                         | 2857.1                                      | 88.55     |
| ZnWO$_4$: 1% Eu$^{3+}$ bulk-phosphor| 0.41                            | 0.02                            | 0.31        | 230.7                         | 3225.1                                      | 71.54     |

$$A_{\text{tot}} = \frac{1}{\tau} = A_{\text{rad}} + A_{\text{rad}}$$

where ($A_{\text{rad}}$) is the sum of each $^5D_0 \rightarrow ^7F_J$ ($J = 1-4$) transition rate,

$$A_{\text{rad}} = \sum_j A_{0-\text{j}}$$

As quantum efficiency of $^5D_0$ energy level of Eu$^{3+}$ ion can be written as [24]

$$\eta = \frac{A_{\text{rad}}}{A_{\text{rad}} + A_{\text{rad}}} = \tau \sum_j A_{0-\text{j}}$$

The quantum efficiency ($\eta$) and Judd-Ofelt intensity parameters ($\Omega_2$, $\Omega_4$) of 1% Eu$^{3+}$ doped ZnWO$_4$ nano and bulk phosphors are shown in table 2. Since the J-O intensity parameter $\Omega_2$ relates hypersensitivity of $^5D_0 \rightarrow ^7F_2$ transition as it is dependent on the symmetry of local environment surrounding the site of Eu$^{3+}$ ion [24, 27], the results from the calculations ($\Omega_2 > \Omega_4$) suggests higher asymmetry around Eu$^{3+}$ for the individual phosphors and also nanophosphors have larger asymmetry than the bulk ones. Asymmetry ratio (R) can be defined as the intensity ratio between $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ transition [28], which was calculated by integrating the area under the peak of 614 and 590 nm emission spectra respectively. The values of R for ZnWO$_4$: 1% Eu$^{3+}$ nanophosphors and bulk phosphors are 4.1 and 3.6 respectively. Higher value of R suggests lower symmetry of the local environment around Eu$^{3+}$ ion due to distortion of bonds between Eu$^{3+}$ ion and surrounding anions [27]. The emission quantum efficiency is higher for the nanophosphors ($\eta = 88.55\%$) than in bulk phosphors ($\eta = 71.54\%$) which signifies that the nanophosphors have the features to be a good luminescence material compared to their bulk counterparts.

It is clearly evident from figure 7(a), that the intensity of the emission peak at 614 nm of nanophosphor is more prominent than bulk phosphor which is responsible for brighter red emission of the nanophosphor. This statement can also be validated utilizing morphological observations related to both the phosphors. The bulk phosphors have inhomogeneous surface textures which increases nonradiative transitions giving rise to the quenching in PL efficiency whereas the homogeneous surface and regular cube-like shapes of nanophosphors enhances the PL emission.

Electronic surface states can also be modified by reducing the crystallite size from bulk to nanoregime which in turn hugely changes the optical properties. As the intensity of scattering is directly proportional to the particle diameter by sixth of power, nanosizing can reduce the scattering loss significantly which can be realised from the equation described below [29, 30]:

$$I_r = \frac{8\pi^4 N_n a^6}{\lambda^2 \tau^2} \left( \frac{m^2 - 1}{m^2 + 2} \right) \left( 1 + \cos^2 \theta \right) I_i$$

where $I_r$ is Rayleigh scattering intensity per particle, $m = N_p/N_m$ ($N_p$ & $N_m$ are refractive index of particle and medium respectively), $I_i$ & $\lambda$ are intensity and wavelength of incident light, a is diameter of the particle, $r$ is distance between nanoparticle and the viewing point, $\theta$ is angle of scattering. As a result of the quantum size effect [11] in nanophosphors, they usually possess wider bandgap for which they do not reabsorb the emitted light making the emission loss a lot lesser compared to the bulk phosphors which is another reason behind the enhancement of the PL emission intensity in the nanophosphors. Also films made by nanophosphors exhibit higher transmittance than those made by bulk phosphors which is an important reason for the nanophosphors to diminish the scattering loss significantly by increasing the luminescence.

The colour coordinates of corresponding 614 nm PL emission of Zn$_{1.01}$WO$_4$: Eu$_{0.01}$ bulk and nanophosphors in Commission international del’éclairage (CIE) diagram is shown in figure 7(b). In the case of Zn$_{1.01}$WO$_4$: Eu$_{0.01}$ nanophosphor, the value of x coordinate enhances while the value of y coordinate decreases simultaneously, signifying the hike in PL emission. The colour purity of the Zn$_{1.01}$WO$_4$: Eu$_{0.01}$ bulk and nanophosphor is calculated by the following expression [31]:

$$...
Colour purity \( = \frac{\sqrt{(x_s - x_i)^2 - (y_s - y_i)^2}}{\sqrt{(x_d - x_i)^2 - (y_d - y_i)^2}} \times 100\% \) \( (6) \)

Here \((x_s, y_s)\) are coordinates of sample, \((x_i, y_i)\) are coordinates of illuminate points, and \((x_d, y_d)\) are dominant wavelength coordinates. Taking dominant wavelength at 614 nm \((x_d, y_d) = (0.67, 0.32)\), illuminate point \((x_i, y_i) = (0.310, 0.316)\), the colour purities of the \( \text{Zn}_{1-0.01}\text{WO}_4: \text{Eu}^{3+}\) bulk and nanophosphors are calculated to be 91.9% and 95.44%, respectively. Remarkable increase in colour purity and greater colour saturation of the nanophosphor validates it as a superior material for display applications.

For a better demonstration of the PL enhancement, digital images of the \( \text{Zn}_{1-0.01}\text{WO}_4: \text{Eu}^{3+}\) nano and bulk phosphors under 394 nm near-UV irradiation are represented in figures 7(c) & (d) respectively. A strong red emission covering a large portion of the material can be found for the nanophosphor compared to its bulk counterpart.

The PL decay profiles at 394 nm excitation were investigated for the \( \text{Zn}_{1-0.01}\text{WO}_4: \text{Eu}^{3+}\) bulk and nanophosphors depicted in figures 8(a) and (b), to distinguish the radiative and nonradiative mechanisms associated with \( ^5D_0 \rightarrow ^7F_2 \) (614 nm) transition. Lifetime decay curves of both \( \text{Zn}_{1-0.01}\text{WO}_4: \text{Eu}^{3+}\) bulk and nanophosphors were well fitted by a bi-exponential function, defined by the following equation:

\[
I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)
\]

Here, \(A_1, A_2\) and \(\tau_1, \tau_2\) are weighting parameters and decay components of lifetime, respectively. For bi-exponential lifetime decay, average lifetime \(\tau_{\text{avg}}\) is written as \(2\):

\[
\tau_{\text{avg}} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}
\]

The measured average lifetime of the \( \text{Zn}_{1-0.01}\text{WO}_4: \text{Eu}^{3+}\) bulk and nanophosphor is found as 0.31 and 0.35 ms, respectively. PL decay time is always proportional to the radiative transitions; hence, greater lifetimes are always justified for the applications in solid state lighting. The nanophosphors have higher decay times due to their structural homogeneity which makes them superior as a phosphor material than the bulk one.

### 3.2.2. Thermal stability

Thermal stability of a phosphor material has a significant contribution in steady working of LEDs as the increase in temperature between the interface of phosphor and UV LED chip influences not only the output light but also the lifetime of the device hugely [32]. Emission spectra for both nano and bulk phosphors, up to certain higher temperatures, were taken for comparing the thermal stability as shown in figures 9(a) and (b). For both the cases, a temperature quenching phenomenon takes place with increase in temperature from 303 K to 483 K, consequently decreasing the emission intensity.

A careful observation shows that at 210 °C the photoluminescence emission intensity decays down to 23% and 29% from initial intensity for the \( \text{Zn}_{1-0.01}\text{WO}_4: \text{Eu}^{3+}\) bulk and nanophosphors, respectively. As, during operation, temperature of phosphor-UV LED chip interface can be elevated up to 150 °C, it is significant to observe its performance at this temperature. The PL emission intensity decreases down to 18% and 17% from...
initial intensity at 150 °C for Zn\(_{1-0.01}\)WO\(_4\):Eu\(^{3+}\) bulk and nanophosphors, respectively. These decrease both the phosphors is due to the increase in lattice vibration which leads to the enhancement in nonradiative transitions [33]. In the bulk phosphor, the nonradiative transition rate is much higher at high temperatures because of the irregular surface and large size of the phosphor. This comparison of temperature quenching behaviour proves that the nanophosphor is thermally more stable than its bulk counterpart.

The thermal quenching behaviour can be resisted up to a certain level in a phosphor material which defines the activation energy of that particular material. Relation between emission intensity (\(I_T\)) and activation energy (\(E_a\)) at a certain temperature T can be evaluated by using modified Arrhenius equation [34]:

\[
I_T = \frac{I_0}{1 + Ce^{-E_a/K_B T}}
\]

Figure 9. (a) & (b) Temperature dependent emission spectra and (c) & (d) plot of activation energy of 1% Eu\(^{3+}\)-doped ZnWO\(_4\) bulk and nanophosphors.

4. Conclusive remarks

In summary, solid-state and hydrothermal reaction methods were employed to successfully synthesize the Zn\(_{1-0.01}\)WO\(_4\):Eu\(^{3+}\) nano and bulk phosphors. Rigorous observation on the PL emission characteristics of both the phosphors were done in comparison with the morphological studies. The developed nanophosphors show brighter red emission than the bulk phosphor under 394 nm near UV irradiation. The nanophosphors exhibit reduction in nonradiative loss at higher temperature due to the fact that intensity of PL emission drops to only 17% at 150 °C temperature. For the the nanophosphors, colour purity, excited state lifetime and quantum efficiencies are better than the bulk ones owing to their homogeneous and regular surface morphologies. Finally, the acquired outcomes firmly suggest that ZnWO\(_4\):Eu\(^{3+}\) phosphor in nano form is a superior candidate applied in white light LED devices compared to their bulk counterparts.
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