

Enhancement of Blue Emission in Novel ZnWO₄:Ce³⁺ Nanophosphors for Solid State Lighting Applications

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Abstract. In the present work, highly efficient blue emitting Ce³⁺ doped ZnWO₄ nanophosphors were successfully synthesized by simple hydrothermal technique. The nanophosphors were then characterized by using the X-ray powder diffraction (XRD), Rietveld refinement of XRD, Field Emission Scanning Electronic Microscopy (FESEM), High resolution transmission electron microscopy (HRTEM) and Photoluminescence spectroscopy (PL). The as prepared nanophosphors display intense blue emission having a broad peak with maxima at 464 nm under 283 nm UV excitation which enhances by Ce³⁺ doping. Color purity of the samples are also enhanced due to the doping of the rare earth activator in the ZnWO₄ matrix. Obtained results prove that this nanophosphor is suitable to compete in the rapidly growing field of solid-state lighting and field emission display devices.

INTRODUCTION

The rising necessity of efficient and useful lighting devices and high resolution displays now a days has lead researchers to develop new phosphors with increased brightness and color purity. Several important features of the phosphors expedite their use in different applications like light emitting diodes (LEDs), field emission displays (FEDs), and plasma display panels (PDPs).¹ Phosphor converted white LEDs (PC-WLED) are the ultimate crest among them for application in solid state lighting devices. The main mechanism of a PCWLED is to convert the ultraviolet (UV) light generated from the InGaN LED chip to visible white light by utilizing a phosphor or combination of phosphors. The well-known method to get white light is to mix tricolor phosphors (i.e., red, green and blue) in proper proportion. However, due to lack of efficiency and color rendering index of the red phosphors WLEDs display higher color temperature which is not suitable for lighting purposes and also harmful to human eyes. To put an end to this problem, development of several types of phosphors are investigated which can perform under long-wavelength UV and have higher efficiency.

As the host matrix, tungstates have several advantages such as high average refractive index, good chemical and thermal stability, and long afterglow² etc. ZnWO₄ is a type of self-activating phosphors which shows a broad blue–green emission band under UV excitation, which is due to the W⁶⁺– O²⁻ charge transfer (CT).² To enhance the blue emission we have successfully doped Ce³⁺ in the host matrix ZnWO₄ by simple hydrothermal method and studied the luminescence properties which has not been reported earlier to the best of our knowledge. PL properties were investigated extensively. Addition of Ce³⁺ increases the PL emission intensity, color coordinates and also the brightness of the phosphor. The observed characteristics implies that the nanophosphor is a potential candidate for solid state lighting and field emission display devices.

EXPERIMENTAL SECTION

Synthesis of the $\text{ZnWO}_4 \cdot \text{Ce}^{3+}$ nanophosphors

Powder samples of $\text{Zn}_{(1-x)}\text{WO}_4 \cdot \text{Ce}_x$ ($x=0.01, 0.03$) were prepared by simple hydrothermal method. At first 5 mmol $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck 99.9%) and 5 mmol $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (Merck 99.9%) and 5 mmol $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich 99.9%) were dissolved in 20 ml, 15 ml and 5 ml deionized water respectively to obtain the corresponding solutions. All of the materials were analytical reagent. The solutions were then stirred in magnetic stirrers for 30 mins. Later $\text{Ce}(\text{NO}_3)_3$ solution was added to the $\text{Zn}(\text{NO}_3)_2$ solution with vigorous stirring. After that Na_2WO_4 solution was slowly drop casted over the mixed solution to form the white precipitate. Next the solution was poured into a Teflon-lined stainless steel autoclave of 50.0 mL capacity. The autoclave was then kept at 160°C for 8 h in an oven. After that step the autoclave was cooled down to room temperature steadily. The formed white precipitate was then washed with deionized water and ethanol twice. The filtrated solid was then dried overnight at 80°C to obtain the white powders the resultant sample was then sintered in a tube furnace at 700°C for 4 h under a reducing atmosphere of 90% N_2 and 10% H_2 to get the powder nanophosphor.

Characterization

The structural parameters and phase purity of the as synthesized nanophosphors were investigated using X-ray diffraction (XRD) patterns, with a Rigaku-Ultima-III X-Ray powder diffractometer with monochromatic $\text{Cu } k_\alpha$ radiation ($\lambda = 1.5404\text{\AA}$). The surface morphologies of the nanophosphors were investigated by FESEM Hitachi S-4800. Lattice image of the nanophosphors were obtained with high resolution transmission electron microscopy (JEOL JEM 2100). The room temperature photoluminescence spectra were recorded on a JASCO FP-8300 with 283 nm UV excitation.

RESULTS AND DISCUSSION

The XRD patterns of the $\text{ZnWO}_4 \cdot \text{Ce}^{3+}$ nanophosphors are presented in Fig.1 (a). The peak positions are in good agreement with the JCPDS card no. 15-0774 and are indexed as (010), (100), (011), (110), (111), (021), (200), (121), (112), (211), (022), (220), (130), (202), (113), (311), (041). No impurity peaks are present in the XRD pattern which confirms the formation single phase monoclinic structures with space group P2/c. Looking closely to the (111) XRD peak (Fig.1 (b)) the lower angle shifting of the diffraction peak can be observed with the increase in Ce^{3+} concentration. Usually, Ce^{3+} occupies the position of Zn^{2+} in the ZnWO_4 lattice. Since the ionic radius of Zn^{2+} and Ce^{3+} is 0.74 and 1.01 \AA , respectively, the expansion of the unit cell resulted by this substitution is the cause behind the observed lower angle peak shifting.

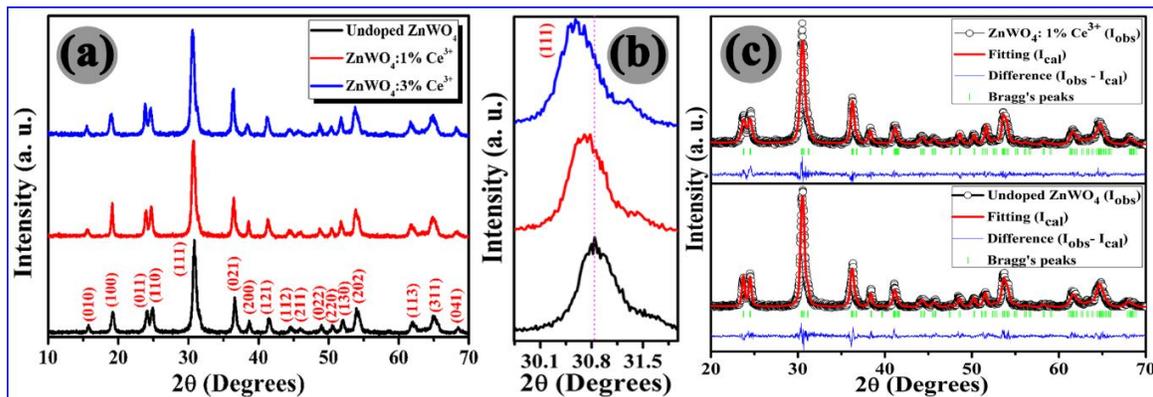


FIGURE 1. (a) XRD pattern of undoped ZnWO_4 and $\text{Zn}_{(1-x)}\text{WO}_4 \cdot x\text{Ce}^{3+}$ ($x=0.01, 0.03$) nanophosphors. (b) Lower angle shifting of the (111) peak with increase in Ce^{3+} concentration. (c) Rietveld refinement of XRD pattern of the undoped ZnWO_4 and 1% Ce^{3+} doped ZnWO_4 nanophosphors.

To further understand the doping, typical Rietveld refinement of XRD is carried out of the undoped ZnWO₄ and ZnWO₄:1% Ce³⁺-doped samples using Fullprof software (Fig.1 (c)). Rietveld analysis reveals the expansion in the unit cell volume and also the change in the lattice parameters in ZnWO₄:1% Ce³⁺ nanophosphors compared to the undoped ZnWO₄ host.

The crystallite size of the as prepared phosphors are in the range between 15 to 20 nm which proves the formation of ZnWO₄: Ce³⁺ nanoparticles within the nano regime. The average crystallite size was calculated by Scherrer's equation using the full width at half maximum (FWHM) of the most intense peak of the (111) plane. As stated in the literature,³ Scherrer's equation is described as follows:

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

where D is the average crystallite size, λ is the X-ray wavelength (0.154 nm), θ is the Bragg angle, and β is the FWHM of the diffraction peak associated with the (111) plane.

TABLE 1. Obtained parameters from Rietveld refinement with errors.

Sample name	Parameters	Refined Values (Standard errors)
Undoped ZnWO ₄	a(Å)	4.687(1)
	b(Å)	5.740(1)
	c(Å)	4.943(1)
	V(Å ³)	133.018(5)
	ρ (g/cm ³)	7.022
ZnWO ₄ :1% Ce ³⁺	a(Å)	4.697(8)
	b(Å)	5.730(9)
	c(Å)	4.950(8)
	V(Å ³)	133.253(4)
	ρ (g/cm ³)	7.028

The surface morphologies of the ZnWO₄: 3% Ce³⁺ nanophosphors have been investigated by FESEM (Fig.2 (a)). The shape of the particles are nearly spherical with average diameters of 40 to 45 nm and the distribution of particle size is mostly uniform. Particularly, nanophosphors with non-agglomerated condition and spherical (< 2 μ m) morphology are of great significance, as they offer lower scattering of light, higher packing density and brighter luminescent performance.⁴

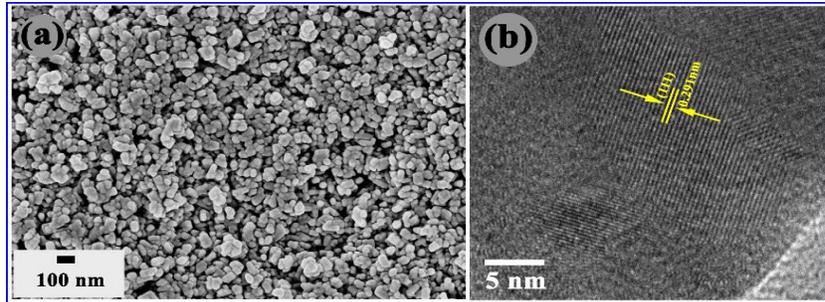


FIGURE 2. (a) FESEM and (b) HRTEM image of the ZnWO₄:3% Ce³⁺ nanophosphors.

The typical HRTEM image (Fig.2(b)) distinctly shows well-resolved lattice fringes with approximated interplanar spacing of 0.291 nm that is consistent with the (111) plane of Ce³⁺ doped ZnWO₄ nanophosphors with monoclinic structure.

The excitation spectra of the pure and Ce³⁺ doped ZnWO₄ samples show a broad band from 240 to 320 nm with a maximum at around 283 nm which corresponds to the W⁶⁺ \rightarrow O²⁻ charge transfer (CT) transition (Fig.3 (a)). Under 283 nm UV-light irradiation, the PL emission spectra of the Ce³⁺ doped ZnWO₄ nanophosphors exhibit not only the ZnWO₄ emission band at 464 nm but also the Ce³⁺ emission band at around 420 nm (Fig.3 (b)), so that the emission band is very broad. The emission at 420 nm occurs due to the transition from the lowest energy crystal field splitting component of the 5d level to the 4f ground state of Ce³⁺ incorporated in the ZnWO₄: Ce³⁺ lattice⁵. The

PL emission intensity increases with the doping concentration of Ce^{3+} due to the enhancement in defect states within the band gap of ZnWO_4 matrix. The color coordinate and the digital image of the samples under 283 nm UV lamp is shown in Fig 3(c & d) which shows brighter blue emission of the $\text{ZnWO}_4: 3\% \text{Ce}^{3+}$ sample than the undoped ZnWO_4 sample.

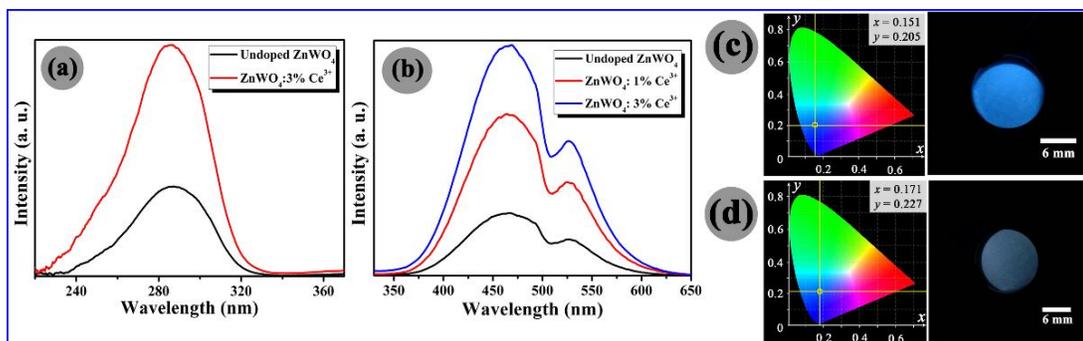


FIGURE 3. (a) PL excitation spectra and (b) PL emission spectra of the undoped ZnWO_4 and Ce^{3+} doped samples. (c) Color coordinates and the optical image of the 3% Ce^{3+} doped ZnWO_4 sample under 283 nm UV excitation. (d) Color coordinates and the optical image of the undoped ZnWO_4 sample under 283 nm UV excitation.

To get high brightness in solid condition entails a significant property for a good nanophosphor. It becomes clear from the optical images of the nanophosphors that enhancing the Ce^{3+} concentration dominates the problems related to the enhanced surface states and increases PL brightness. By increasing Ce^{3+} concentration, the color coordinates of the prepared nanophosphors reach to the extreme blue region for the National Television Standard Committee (NTSC) system with good color saturation.

CONCLUSION

In summary, we have successfully synthesized the Ce^{3+} doped ZnWO_4 nanophosphor by a cost-effective hydrothermal method. The developed nanophosphors enhances the emission of the tungstate host to a brighter blue emission due to the overlapping of the emissions coming from the host and the activator under UV irradiation. Color purity is also higher for the doped samples due to the lowering of the nonradiative transition centers in it. Finally, the obtained outcomes strongly show that $\text{ZnWO}_4:\text{Ce}^{3+}$ nanophosphors could be a promising candidate for use in solid-state lighting as well as field emission display devices.

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