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Synthesis of ZnS:Tm³⁺ Nanoparticles by the Polyol Method

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Abstract

In this work, the synthesis of undoped and Tm-doped ZnS nanoparticles is successfully carried out by the polyol method. From XRD analyses, it was confirmed that both types of particles possess the cubic zinc blend structure of the ZnS, and that the structure is not altered by doping. The crystallite size computed by the Scherrer equation is about 9 ± 1 nm. From photoluminescence analyses, the results show that the excitation spectrum has two excitation peaks at 304 nm and 356 nm; by exciting at 304 nm, a strong blue emission is observed at 420 nm, while exciting at 356 nm the characteristic Tm transition $^1G_4 \rightarrow {}^3H_6$ is observed at 417 nm. By doping with Tm ions, the emission color changes from pure blue to sky according to the change in CIE coordinates from $x = 0.15$, $y = 0.015$ to $x = 0.18$, $y = 0.17$, respectively.

Keywords

Luminescence, Zinc Sulfide, Blue Emission

1. Introduction

Zinc sulfide (ZnS) is a semiconductor which in the size range of nanoparticles (1 - 100 nm), exhibits photoluminescent properties when it is excited by ultraviolet radiation, where the color emission is directed related to the size particle [1]. The unique properties of these nanoparticles, such as photoluminescence and electroluminescence, make these nanoparticles important for many technological applications, for example, light emitting diodes (LEDs), sensors, displays, lasers, solar cells, and for biomedical applications [2] [3] [4] [5].

During the last decade, a special emphasis has been put on the synthesis of high monodispersed semiconducting nanoparticles, with stability for a long period of time, control of the nanocrystal size and morphology [6] [7], which are very important factors to influence the optical properties of ZnS and their appli-

cations. Different methods have been reported for the synthesis of ZnS, for example, hydrothermal [8], sol-gel [9], solid state reaction [10] and polyol method [11]. Among them, the polyol method is considered a green synthesis method because no toxic chemicals are used; it only needs a glycol source such as ethylene glycol, polyethylene glycol, glycerol, etc. Besides, in many cases, temperatures below 150°C are required in the synthesis, giving as result chemical stability, biocompatibility, and low toxicity homogeneous materials [12].

On the other hand, it can be found that doping ZnS nanoparticles with other ions, for instance Mn^{2+}, produce a catalysis-assisted CL emission [13]. However, the doping with rare earth trivalent ions is very difficult by conventional methods because the difference in valence number and the higher ionic radius avoids the lanthanide ions enter to the ZnS crystal structure [14], however, the polyol method allows the incorporation of lanthanide ions into the ZnS structure. In this regard, this article shows the results of the effect of Tm ions on the ZnS nanoparticles, regarding the crystal structure and photoluminescent properties.

2. Experiment Details

The synthesis of Tm^{3+} doped ZnS nanoparticles was carried out by the polyol method. The precursors: Thulium nitrate ($Tm (NO)_3$), Thiourea (NH_2CSNH_2) and Zinc acetate ($ZnC_4H_6O_4$) were purchased at Sigma Aldrich. Ethylene glycol and ethanol were used as solvents.

For the synthesis, 3 mmol thiourea and 3 mmol zinc acetate precursors were dissolved in 20 mL ethylene glycol under vigorous stirring at room temperature for 20 minutes. Then an adequate volume of $Tm(NO)_3$ dissolved in ethanol $C_2H_6O_2$ was added to keep 3 and 5 at % with respect to ZnS. In addition, an undoped ZnS sample was synthesized for comparison purposes. After that, the temperature of the solution was increased up to 120°C under stirring for 2.5 h. Then, the resulting white precipitate was separated from the final solution and washed with distilled water three times by centrifugation at 4000 rpm. Finally, the obtained product was dried in an oven at 80°C by 24 h.

The crystal structure of Tm doped ZnS powders was analyzed by XRD, conducted in reflective mode in a Bruker D8 ADVANCE eco diffractometer with Cu $K\alpha_1$ radiation ($\lambda = 0.15406$ nm), in the range of 10° - 60°. With the aim to know the powders morphology, it was used a scanning electron microscopy JEM-2200FS model operating at 80 keV. For luminescence analysis, excitation and emission spectra were obtained by using a Horiba Jobin-Yvon Flourolog 3 - 22 spectrofluorometer equipped with a 450 W ozone-free Xe lamp for the steady state mode and a pulsed Xe lamp.

The nanoparticle size was determined by dynamic light scattering by using a Zetasizer Nano ZS90 device (Malvern Instrument) equipped with a He-Ne laser and avalanche photodetectors. The hydrodynamic radius is obtained from acumulant analysis of the intensity correlation function measured at 90° and the

reported values are the mean of different measurements performed with different samples.

3. Results and Discussion

3.1. Structural Analyses

Figure 1 shows the XRD patterns of (a) undoped ZnS and (b) Tm-doped ZnS nanoparticles, respectively. As can be observed, Tm ions do not modify the crystal structure of ZnS. The reflections (111), (220) and (311) can be indexed to the cubic blend ZnS structure according to the JCPDS card No. 05-0566 [15]. From the patterns, the crystallite size was computed by using the Scherrer equation:

$$D = (0.9\lambda)/\beta \cos\theta \tag{1}$$

where D is the average crystallite size, K is a constant with a value close to unity, λ is the X-ray wavelength (CuKα = 0.15418 nm), β is the Full Width at Half Maximum (FWHM), and θ is the half diffraction angle of the centroid of the peak 3. The computed crystallite size was about 9 ± 1 nm.

Figure 2 shows the SEM images of the ZnS:Tm (5 at. %), the image reveals agglomerated spherical particles with an average size of 90 ± 5 nm. The agglomeration of these nanoparticles is due to their high surface energy, and the presence of van der Waals attractive forces.

3.2. Dynamic Light Scattering Measurements

The mean hydrodynamic diameter measured by dynamic light scattering is (245 ± 14) nm for the undoped Zns nanoparticles. For the doped nanoparticles the hydrodynamic diameter increases up to (280 ± 18 nm) and (550 ± 30 nm) in case of ZnS:Tm (3 at. %) and (5 at. %), respectively. Here, the uncertainty is estimated as the standard error of the mean.
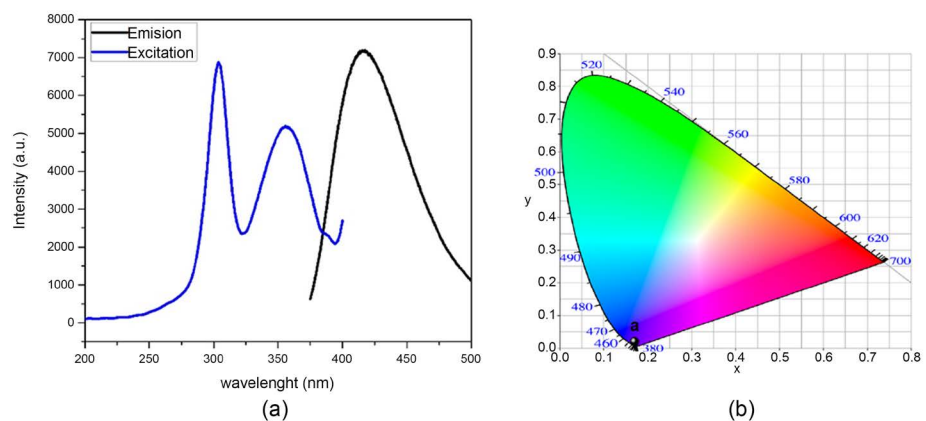
3.3. Photoluminescence Results

Figure 3(a) depicts the excitation and emission spectra of the ZnS nanoparticles.
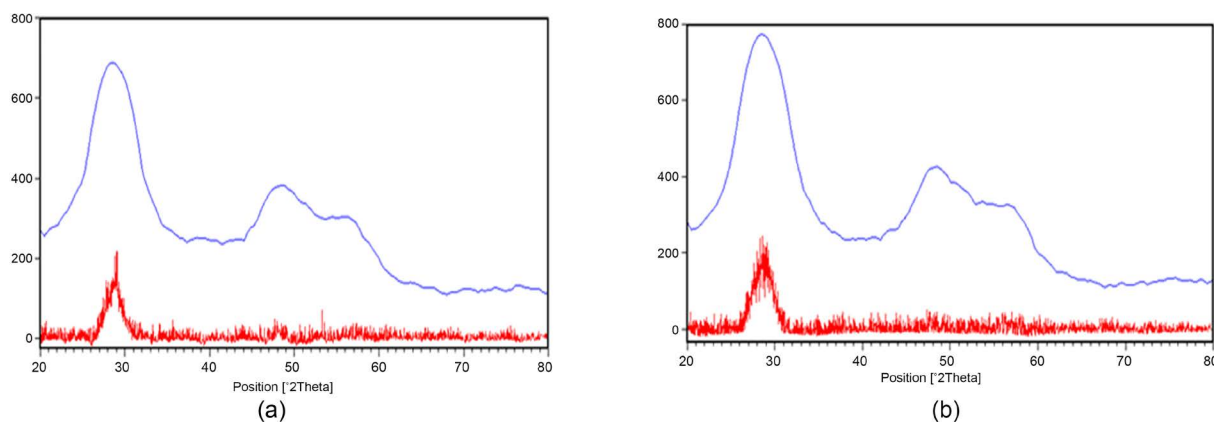
Figure 1. X-ray diffraction patterns of (a) undoped and (b) ZnS:Tm nanoparticles.
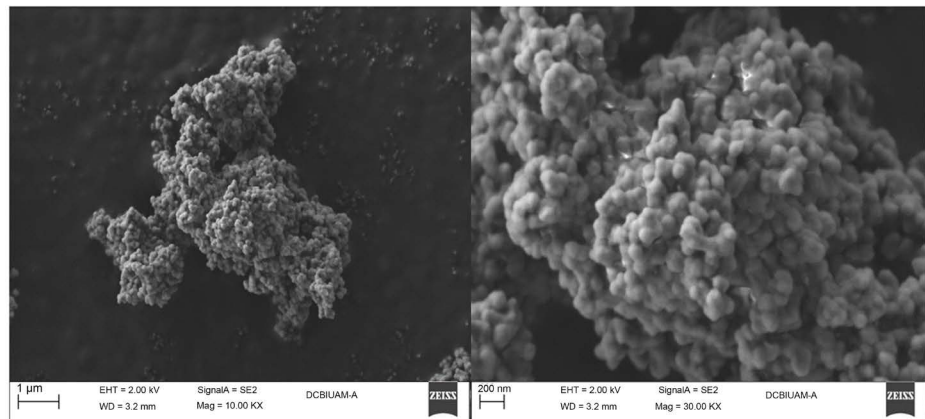
Figure 2. SEM images of ZnS:Tm (5 at. %) nanoparticles at different magnifications.


(a)   (b)

Figure 3. (a) Excitation and emission spectra of undoped ZnS nanoparticles; (b) CIE coordinates of the undoped ZnS.

The excitation spectrum (blue line) shows that zinc sulfide has two excitation peaks at 304 and 356 nm. On the other hand, the emission spectra (black line) show a broad blue emission centered at 420 nm by exiting the sample at 304 nm. From the emission spectra, the CIE coordinates were computed as $x = 0.15$, $y = 0.015$. **Figure 3(b)** displays the highly blue emission in the CIE map.

Figure 4(a) shows the emission spectra of Tm-doped ZnS QDs at 3 at. % and 5 at. % by exciting at 304 nm. As can be seen, these spectra are similar to those obtained for the undoped ZnS sample, with the difference that the emission intensity is increased due to the higher Tm content (5%). Besides, by doping with Tm ions, the CIE coordinates (see **Figure 4(b)**) are shifted slightly to the sky blue color region with the next CIE coordinates: $x = 0.15$, $y = 0.055$.

On the other hand, when the samples are excited at 356 nm (see **Figure 5(a)**), the luminescent intensity increases and a peak at 417 nm emerges, corresponding to the electronic transition of Tm ($^1G_4 \rightarrow {}^3H_6$) [16]. Besides, the spectra show a shoulder at 500 nm which is absent in case of samples that are not doped. This contribution makes the CIE coordinates shift to the green region, obtaining new CIE coordinates about as $x = 0.18$ $y = 0.17$ (**Figure 5(b)**).
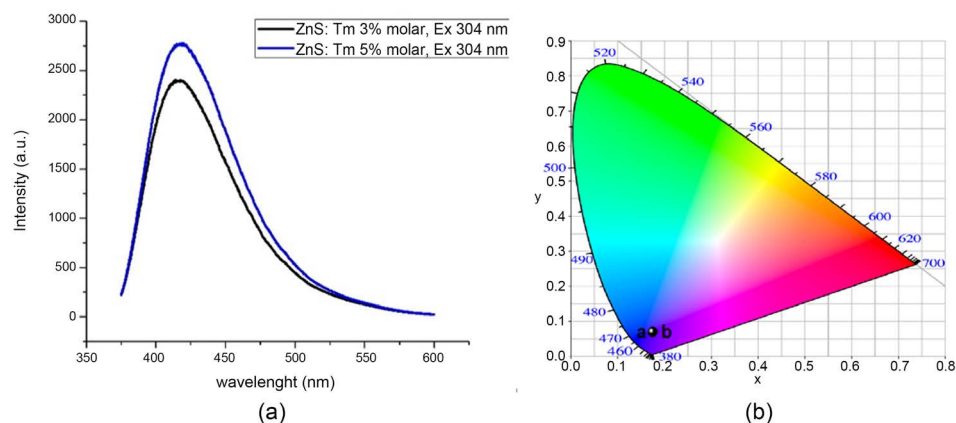
Figure 4. (a) Emission spectra of the ZnS:Tm^{3+} 3 - 5 at. %, excited to 304 nm; (b) CIE coordinates of ZnS:Tm^{3+}.
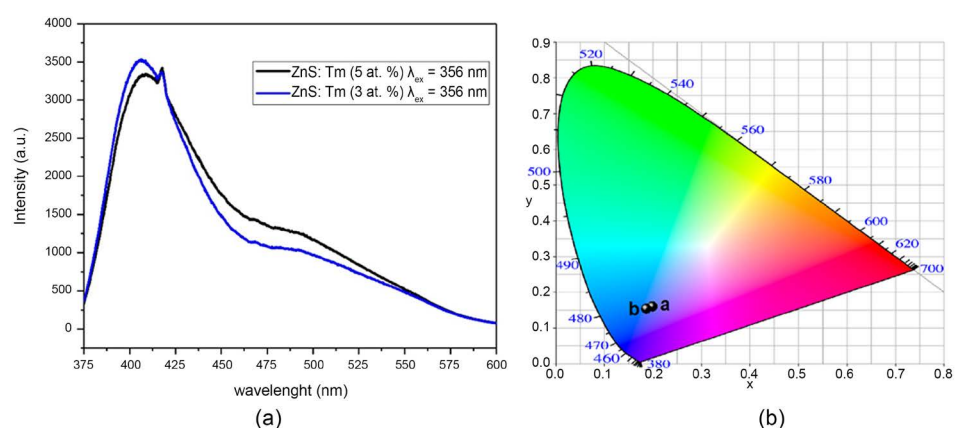
Figure 5. (a) Emission spectra of the ZnS:Tm^{3+} 3 - 5 at. %, excited to 354 nm; (b) CIE coordinates of ZnS:Tm^{3+}.

4. Conclusion

Luminescent undoped and Tm-doped ZnS powders were successfully synthesized by the polyol method, from which crystalline ZnS structure indexed to the pure blend cubic form was obtained. The light emission was dependent on the Tm content and the excitation wavelength. When the sample is not doped, a broad blue emission centered at 420 nm was observed by exciting at 304 nm. By doping the samples at 3 and 5 at. % with Tm ions and exciting at 304 nm, quite similar emission spectra of the undoped sample are obtained. However, by exciting at 354 nm, the typical Tm^{3+} transition $^1G_4 \to {}^3H_6$ was identified at 417 nm and this peak is accompanied by a shoulder centered at 500 nm which changes the color emission according to the computed chromatic coordinates as $x = 0.15$, $y = 0.055$ and $x = 0.18$, $y = 0.17$ for the sample doped at 5 at. % Tm excited at 304 and 354 nm, respectively.

Acknowledgements

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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