Nano-Structures & Nano-Objects 6 (2016) 59–66

Contents lists available at ScienceDirect

Nano-Structures & Nano-Objects

journal homepage: www.elsevier.com/locate/nanoso

Synthesis and luminescence properties of ZnS: Ce^{3+}, Li^{+}, Mn^{2+} nanophosphors

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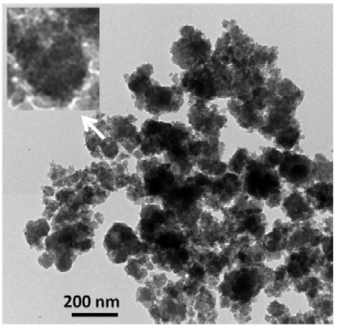
HIGHLIGHTS

- The ZnS: Ce, Li, Mn nanophosphors were synthesized by simple chemical method at room temperature.
- The synthesized nanophosphors crystallized in zinc-blende crystal structure.
- It shows the defect emission in the blue region and Mn^{2+} emission in the orange region.
- The orange emission was due to the $[^4T_1(^4G) - {}^6A_1(^6S)]3d^5$ transition of Mn^{2+} ion.
- The ZnS: Ce^{3+}, Li^{+}, Mn^{2+} nanophosphors show white light, as confirmed by the CIE value (0.374, 0.332).

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 July 2015
Accepted 1 March 2016

Keywords:
Nanophosphors
Semiconductor
Chemical method
X-ray diffraction
Transmission electron microscopy
Photoluminescence

ABSTRACT

The $Zn_{(1-(2x+y))}S$: $Ce^{3+}_{x=0.001}Li^{+}_{x=0.001}Mn^{2+}_{(0.001\leq y\leq 0.03)}$ nanophosphors were prepared using simple chemical ionic mixing method at room temperature. The X-ray diffraction studies on the undoped and doped samples confirmed the formation of zinc-blende structure. As the codopant concentration was increased the band gap energy gradually decreased from 3.92 eV to 3.86 eV. The $Zn_{0.999}S : Ce^{3+}_{0.001}$ nanophosphor showed the defect emission in the blue and green region with the peak positions at 429 nm, and 539 nm and 564 nm respectively. The $Zn_{(1-(2x+y))}S$: $Ce^{3+}_{x=0.001}Li^{+}_{x=0.001}Mn^{2+}_{(0.001\leq y\leq 0.03)}$ samples showed a defect emission at 400 nm along with the Mn^{2+} emission at 590 nm. The orange emission was due to de-excitation of electrons from $[^4T_1(^4G) - {}^6A_1\ (^6S)]3d^5$ unfilled shell of Mn^{2+} ions in ZnS host lattice. The ZnS: Ce^{3+}, Li^{+}, Mn^{2+} nanophosphors show white light, as confirmed by the CIE chromaticity coordinates (0.374, 0.332).

1. Introduction

The optical properties of semiconductor nanocrystals have been studied extensively in recent years because of their potential applications in opto-electronic devices namely LED, solar cell, cathode ray oscilloscope, fluorescence lamp etc. [1–5]. The physical properties of nanocrystalline semiconductors are quite different from that of bulk semiconductors due to quantum confinement effect and large surface-to-volume ratio [6,7]. The size of the particle was reduced to nanolevel with increase in percentage of atoms located at the surface, which significantly affected the electrical, dielectric and optical properties etc. These properties were sensitive to particle size, shape, crystal structure, and the type of defects [8]. In specific, the surface defects of the compound semiconductor nanostructures provided a visible luminescence which is useful for the

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http://dx.doi.org/10.1016/j.nanoso.2016.03.001
2352-507X/

fabrication of optical devices [9–11]. The intrinsic vacancies of Zn and S in ZnS nanostructures lead to defect emission in the visible region of electromagnetic spectrum [12].

ZnS is a potential material for opto-electronic applications particularly in light-emitting diodes, laser diodes of shorter wavelength and photodetectors [13–15]. The luminescent properties of ZnS host materials have been tuned by doping with various transition metals and rare-earth metals [16–19]. The ZnS was activated with transition metals (TM) (viz. Mn and Cu) and rare earth (RE) (viz. Ce^{3+}, Eu^{3+}, and Tm^{3+} etc.) elements along with charge compensators (like Li^{+}, Na^{+}, and Al^{3+}). It exhibited intense emission in the visible region containing narrow and broad band spectrum which are applied to various optical devices [20]. ZnS has an excellent optical transmission property with high index of refraction (2.27 at 1 μm), and it serves as a potential application in novel photonic crystal devices operating in the visible-to-near IR region [21]. Various techniques that were adapted to synthesis ZnS nanoparticles are solid state method [22], microwave assisted synthesis [23, 24], hydrothermal method [25], ultrasonic radiation method [26], etc., to tune their physical, chemical and luminescence properties.

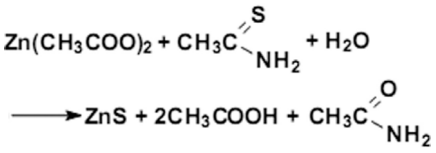
Okamoto et al. [27] investigated the effect of coactivators namely Y^{3+}, La^{3+}, Al^{3+}, Ga^{3+} and In^{3+} on luminescence properties of the ZnS: Ce phosphor. Kawai et al. [28] studied the photoluminescent properties of ZnS: Ce, Li at the liquid nitrogen (LN_2) temperature. It was identified that the noble metal ions and other Ia elements are not as efficient compensator as Li^{+} for Ce^{3+} luminescence. The trivalent rare earth ions in II–VI compounds are associated with various ligand configurations, in compensation with difference in ionic charge and volume between the RE^{3+} and host ions. The luminescent properties of ZnS: Ce^{3+} is unclear due to their structure less broad emission band and the powder form of the samples. The nature of Ce^{3+} emission spectrum also changes with respect to the excitation wavelength, due to the multiple structures of the Ce^{3+} centres in ZnS. Manhas et al. [29] reported the effect of alkali metal ions (Li^{+}, Na^{+} and K^{+}) on the luminescence properties of $CaMgB_2O_5$: Sm^{3+} nanophosphor. The alkali metal ions (Li^{+}, Na^{+} and K^{+}) were used as the charge compensator for Sm^{3+} ion. The emission spectra showed that Li^{+} ion codoped $CaMgB_2O_5$: Sm^{3+} nanophosphor exhibits the highest emission intensity compared to the Na^{+} and K^{+} ions codoped $CaMgB_2O_5$: Sm^{3+} nanophosphor. Yang et al. [30] reported the preparation and characterization of ZnS: Mn, Ce phosphor that showed yellow emission. Hossu et al. [31] reported the enhancement of Mn^{2+} emission by co-doping Eu^{2+} in ZnS phosphor. Ma et al. [32] reported the optical properties of ZnS: Mn nanoparticles. However, the present study focus on the room temperature synthesis of ZnS: Ce^{3+}, Li^{+}, Mn^{2+} nanophosphors by low cost simple chemical ionic mixing method and the investigation of their photoluminescent properties.

2. Experimental

The undoped and Ce^{3+}, Li^{+}, Mn^{2+} doped ZnS nanophosphors were synthesized by simple chemical ionic mixing method at room temperature. The molecular formula $Zn_{(1-(2x+y))}S : Ce^{3+}_{x=0.001} Li^{+}_{x=0.001} Mn^{2+}_{(0.001\le y\le 0.03)}$ was used as nomenclature. The starting materials such as zinc acetate [$(CH_3COO)_2Zn.2H_2O$], thioacetamide [C_2H_5NS], lithium acetate [$CH_3COOLi.2H_2O$], cerium acetate [$(\mathbf{CH_3COO)_3Ce.H_2O}$] and manganese acetate [$(\mathbf{CH_3COO)_2 Mn.4H_2O}$] were used for synthesis. The Li^{+} ion was used as the charge compensator for Ce^{3+} ion. Lithium acetate [$CH_3COOLi.2H_2O$], cerium acetate [$(CH_3COO)_3Ce.H_2O$] and manganese acetate [$(\mathbf{CH_3COO)_2Mn.4H_2O}$] were taken in the composition range $x = 0.001$ mol and $y = 0.001$ mol, 0.01 mol and 0.03 mol respectively.

For the synthesis of undoped ZnS nanophosphors, 2.1949 g of zinc acetate, 0.7513 g thioacetamide were taken and grounded well using mortar to obtain homogeneous mixture. Then 100 ml of deionized water was added in to the homogeneous salt mixture and transferred into the glass beaker. The white precipitate of ZnS nanophosphor dispersed in the aqueous solution was obtained. The precipitate was then separated from the reaction mixture by centrifugation for 10 min at 5000 rpm and was then washed with water. This procedure was repeated for several times until the formation of a neutral paste. Then the wet precipitate was allowed to dry in room temperature for further analysis.

The chemical process can be described by the following chemical equation



The $Zn_{0.998-y}S$: $Ce_{0.001}Li_{0.001}Mn_{(0.001\le y\le 0.03)}$ nanophosphors were synthesized via the above mentioned method by using (2.1883 g ($y = 0.001$ mol), 2.1685 g ($y = 0.01$ mol), 2.1246 g ($y = 0.03$ mol)) of zinc acetate, 0.7513 g of thioacetamide, 0.0031 g of cerium acetate, 0.0010 g of lithium acetate and (0.0024 g ($y = 0.001$ mol), 0.0245 g ($y = 0.01$ mol), 0.0735 g ($y = 0.03$ mol)) of manganese acetate respectively.

The characterization studies such as X-ray diffraction (Philips Xpert, USA), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR – JASCO International Co./Japan – Model FTIR-6300), Diffuse reflectance spectroscopy (DRS—USB 2000, Ocean Optics, USA), and fluorescence spectroscopy (Fluorolog spectrophotometer (JASCO Japan)) studies were performed to check the phase purity, surface morphology, particle size, various functional group, absorption, and photoluminescence (PL) excitation and emission spectra respectively. All the optical measurements were carried out at room temperature.

3. Results and discussions

3.1. Phase analysis of undoped and doped ZnS nanophosphor

In order to examine the phase formation of the synthesized nanophosphors, X-ray diffraction studies were performed. The Fig. 1 shows the XRD patterns of ZnS, $Zn_{0.999}S:Ce_{0.001}$, $Zn_{0.998}S:Ce_{0.001}Li_{0.001}Mn_{(0.001\le y\le 0.03)}$ nanophosphors along with the reference pattern (JCPDS: 800020). The diffraction peaks were well matched with the reference pattern and the spectral peak broadness whose full width half maximum (FWHM) confirms the formation of nanocrystalline phosphor. There are three intense peaks observed corresponding to (111), (2 2 0) and (311) planes of cubic zinc blend structure with lattice constant $a = 5.361$ Å and a space group of F43m. No reflections corresponding to dopant elements viz. Ce^{3+}, Li^{+} and Mn^{2+} ions were identified because of the low dopant concentration and the X-ray detection limit since X-ray source cannot detect elements less than 2 atomic percentage.

3.2. SEM analysis

In order to study the surface morphology of the synthesized nanophosphors, the SEM analysis was carried out. Fig. 2(a), (b) and (c), (d) shows the SEM image of the ZnS and $Zn_{0.968}S:Ce_{0.001}Li_{0.001}Mn_{0.03}$ nanophosphors with different magnification. The undoped and Ce^{3+}, Li^{+}, Mn^{2+} doped ZnS show small and large spherical shaped particles with agglomeration. It is known that the spherical shaped particles show better emission due to the minimum scattering loss which increases the screen brightness of the display [33].