Preparation, photoluminescence and time-resolved luminescence of ZnS:Mn$^{2+}$ nanophosphors

Nguyen Vu$^1$, Pham Thi Minh Chau$^2$, Dinh Xuan Loc$^1$, and Tran Kim Anh$^1$

$^1$ Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Road, Cau Giay Dist., Hanoi, Vietnam
$^2$ Institute of Geography, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Road, Cau Giay Dist., Hanoi, Vietnam

E-mail: nguyenvu@ims.vast.ac.vn

Abstract. Nanocrystals of ZnS:Mn$^{2+}$ were prepared by chemical synthesis. The samples were characterized by scanning electron microscopy, photoluminescence, and time-resolved luminescence measurements. The emission spectra of ZnS:Mn$^{2+}$ nanoparticles under 325-nm excitation consist of an intense broad band at 585 nm, ascribed to the $^4T_1-^6A_1$ transition of the Mn$^{2+}$ ions. No emission in the blue spectral region (about 425 nm) from the ZnS host is observed. The dependence of PL intensity on Mn$^{2+}$ concentration has been investigated.

Keywords: Photoluminescence, time-resolved, nanophosphor, ZnS:Mn.

1. Introduction

In the past 20 years, nanostructure materials have been widely studied [1-5]. Application of nanometer phosphors for display has gathered great interest, since Bhargava et al. reported the optical properties of ZnS:Mn$^{2+}$ nanocrystals with high quantum efficiency in 1994 [2]. ZnS is a typical II-VI semiconductor. It has been commercially used as a phosphor as well as in thin film electroluminescent devices, especially if doped with divalent manganese ions [6]. Recent years, Mn-doped ZnS nanocrystals have attracted much attention in many groups for preparation, physical properties and potential applications [7-11]. ZnS:Mn$^{2+}$ nanocrystals have possibility to enhance reliability of organic electroluminescent devices due to the stability of ZnS:Mn$^{2+}$ which has been established already in commercial use as an inorganic electroluminescent device [7, 8]. Mohagheghpour [9] reported on synthesis and characterization of Mn-doped ZnS nanoparticles which could be used with avidin bioconjugated antibodies. Luminescence kinetics and time-resolved luminescence of ZnS:Mn$^{2+}$ nanocrystals were also discussed [8, 10]. In time-resolved luminescence measurements, the photo luminescence intensity corresponding to each spectral component which is detected at a certain moment delayed from the start of the excitation laser pulse provides a real intensity in the dynamic regime.

Red and green nanophosphors were successfully synthesized in our group [12, 13]. Many different techniques such as, co-precipitation, sol–gel, hydrothermal, sonochemical... have been used in preparation of ZnS:Mn$^{2+}$ nanoparticles. In the present work, we describe our procedure concerning the synthesis of ZnS:Mn$^{2+}$ nanoparticles (orange nanophosphors) using the wet chemical method. Structural phase and micro image of nanoparticles are presented. Photoluminescence (PL) and time-resolved luminescence properties of ZnS:Mn$^{2+}$ nanoparticles are reported.
2. Experimental

2.1. Synthesis of ZnS:Mn$^{2+}$ nanocrystals

The ZnS:Mn$^{2+}$ nanocrystals were synthesized using the wet chemical method, involving a propagation step of ZnS which was terminated by the adsorption of thiolate on nanoparticle surface. The crystal size is controlled by the relative rates of the propagation and termination reaction of initiating (sulphide) and terminating (thiolate) species.

Five stock solutions were prepared: (I) 20 vol.% 0.1 M succinic acid (C$_4$H$_6$O$_4$) in 80 vol.% methanol (solvent 1); (II) 0.1 M S$^2$ from Na$_2$S in methanol and de-ionized water; (III) 0.1 M Zn$^{2+}$, and 0.1 M Mn$^{2+}$ were dissolved by Zinc acetate with stoichiometric calculated concentration and Manganese (II) chloride with concentrations 0.5, 1.5, 2 mol.% in solvent 1 (solution A); (IV) 0.1 M thiosemicarbasite (CH$_5$N$_3$S) in methanol; (V) Mixture of the 50 ml (II) with 50 ml (IV) (solution B). To form nanoparticles, the solution A was added drop-wise during continuous stirring. A white cloudy solution was stirred for one hour then washed by methanol then centrifuged (5000 rpm, 10 min). The sedimentation was dried in vacuum oven at 105°C for one hour, and then calcimined at 500°C in vacuum for 30 min.

2.2. Characterizations

The ZnS:Mn$^{2+}$ powder was analyzed by the X-ray diffractometer (XRD, Siemens, D-5000) with Cu K$\alpha$ radiation. The morphology of ZnS:Mn$^{2+}$ was observed by using a transmission electron microscopy (TEM, JEM-1010) and field emission scanning electron microscopy (FESEM, Hitachi, S-4800). The photoluminescence measurements were performed at room temperature by using a cw He-Cd laser (325 nm) as the excitation source, a Spectrapro 2300i monochromator (Acton) as the dispersive unit, and a Pixis 256 CCD (Acton) as the detector. Time-resolved emission spectra were recorded by using a HRD1 monochromator (Jobin-Yvon) as the dispersive unit, a pulsed nitrogen laser (337 nm) and a fast photomultiplier (Hamamatsu model H733) as the excitation source and the detector, respectively. Averaging the multi-pulses at each spectral point using a 1.5 GHz digital oscilloscope (LeCroy 9362) strongly improved the signal-to-noise ratio.

3. Results and discussion

The powder XRD pattern of typical ZnS:Mn$^{2+}$ nanoparticles is given in figure 1. It is noted that all of the diffraction peaks could be well indexed to the zinc blende crystal structure, having prominent (111), (220), and (311) $d$-spacings. In this Mn-doped sample no additional phase was observed, indicating that manganese has been successfully doped in the ZnS crystalline lattice. However, the width of the diffraction lines is broadened because of the small size of the crystallites. The full width at half maximum (FWHM) of the diffraction peak at $2\theta = 8.487^\circ$ is 3.6218°. The XRD patterns also
agree with that of the ZnS:Mn$^{2+}$ nanoparticles reported by Mohagheghpour [9].

Figure 2 shows typical TEM and FE-SEM images of the as prepared ZnS:Mn$^{2+}$ nanoparticles. From the image, one can see that the mean size of the Mn-doped ZnS is about 20 - 30 nm. These images also reveal the possibility of powders in somewhat agglomerated forms.

![TEM and FE-SEM images of ZnS:Mn$^{2+}$ nanoparticles](image)

**Figure 2.** TEM (left) and FESEM (right) images of the as prepared ZnS:Mn$^{2+}$ nanoparticles.

Figure 3 shows the PL spectra of ZnS:Mn$^{2+}$ (0.5, 1, and 2 mol.%) nanoparticles upon 325-nm excitation. The spectra consist of a very intense emission Gaussian broad band with a maximum at 585 nm, ascribed to the $^{4}T_1 - ^{6}A_1$ transition of Mn$^{2+}$ [2]. This result is consistent with the emission of Mn$^{2+}$ in ZnS nanoparticles [2-4]. But no emission in the blue spectral region (~ 425 nm), which ascribed to radiative recombination at defects in the ZnS nanoparticles [10], is observed. It was reported that in Mn$^{2+}$-activated ZnS nanocrystals in which the Mn$^{2+}$ ions are distributed outside the ZnS nanocrystals, the PL is totally different from that of ZnS:Mn$^{2+}$ nanocrystals in which the Mn$^{2+}$ is incorporated within the nanocrystals. When the Mn$^{2+}$ is incorporated within the nanocrystals, both the 435-nm blue emission of ZnS and the orange Mn$^{2+}$ emission at 590 nm are observed [3]. However, in the Mn$^{2+}$-activated ZnS nanocrystals in which the Mn$^{2+}$ ions are distributed outside the ZnS nanocrystals, no orange emission at 590 nm is observed; a new peak at ~350 nm appears and the blue 435-nm emission of ZnS is quenched considerably and shifted to 390 nm. Comparison of these observations with our own suggests that in our material the Mn$^{2+}$ ions are incorporated within the ZnS nanoparticles.

![PL spectra of ZnS:Mn$^{2+}$](image)

**Figure 3.** PL spectrum of ZnS:Mn$^{2+}$ (2 mol.%) nanoparticles upon 325-nm excitation.

Inset: PL intensity (at 585 nm) of ZnS:Mn$^{2+}$ nanoparticles with different Mn$^{2+}$ concentrations.
In order to study the Mn-concentration dependence of the luminescence, we prepared a series samples with different concentration ratios of Mn$^{2+}$ (0.5, 1, and 2 mol.%) to Zn$^{2+}$ in the precursor solution under the same conditions. Figure 3 (inset) presents the relative PL intensity (at 585 nm) of ZnS:Mn$^{2+}$ nanoparticles as a function of the manganese concentration. This shows the maximum intensity at a 2 mol.% Mn concentration. Some researchers [3, 13] also observed the highest intensity peak for 2 mol.% doping.

![Figure 3](image1.png)

**Figure 4.** Time-resolved emission spectra of the ZnS:Mn$^{2+}$ (2 mol.%) nanoparticles, upon 337-nm excitation, with variable time delays.

![Figure 5](image2.png)

**Figure 5.** PL decay curve of ZnS:Mn$^{2+}$ (2 mol.%) nanoparticles at 583.4 nm, upon 337-nm excitation. This curve was recorded at room temperature.

Figure 4 presents the room temperature time-resolved emission spectra of the ZnS:Mn$^{2+}$ (2%) nanoparticles upon 337-nm excitation and with variable time delays. The maximum intensity correspond to the $^{4}T_{1} - ^{6}A_{1}$ transition of Mn$^{2+}$ is observed in a time delays of 0.4 ms. As the time delays increases from 0.4 ms the emission intensity correspond to the $^{4}T_{1} - ^{6}A_{1}$ transition of Mn$^{2+}$ decreases. This is due to the fact that the decay time of the $^{4}T_{1} - ^{6}A_{1}$ transition of Mn$^{2+}$ ion is in the ms range. The decay curve at 583.4 nm of the ZnS:Mn$^{2+}$ (2 mol.%) nanoparticles is shown in figure 5. The obtained decay curve can be fitted by a exponential function as $I = I_{0} \exp(-t/\tau)$ (where $I_{0}$ is the initial intensity at $t = 0$, $\tau$ is the 1/e lifetime). For the 2 mol.% Mn$^{2+}$-doped sample, the 1/e decay time is about 1.2 ms which is attributed to $^{4}T_{1} - ^{6}A_{1}$ transition of Mn$^{2+}$ in ZnS:Mn$^{2+}$.
4. Conclusions
The Mn$^{2+}$-doped ZnS nanoparticles were prepared by chemical synthesis. The mean size of the Mn$^{2+}$-doped ZnS is about 20 - 30 nm. The emission spectra of ZnS:Mn$^{2+}$ nanoparticles upon 325-nm excitation consists of a very intense emission broad band at 585 nm, ascribed to the $^4T_1 \rightarrow ^6A_1$ transition of Mn$^{2+}$ ions. The maximum PL intensity of ZnS:Mn$^{2+}$ nanoparticles was observed in the case of 2 mol.% Mn-doped sample. The room temperature time-resolved emission spectra of the ZnS:Mn$^{2+}$ nanoparticles upon 337-nm excitation and with variable time delays indicates that the $1/e$ decay time is about 1.2 ms for the 2 mol.% Mn$^{2+}$-doped sample.

References
[1] Nalwa H S 1999 Handbook of Nanostructured Materials and Nanotechnology (New York: Academic Press)
[2] Bhargava R N, Gallagher D, Hong X, and Nurminikko A 1994 Phys. Rev. Lett. 72 416
[3] Sooklal K, Cullum B S, Angel S M, Murphy C J 1996 J. Phys. Chem. 100 4551
[4] Chen W, Li G, Malm J O, Huang Y, Wallenberg R, Hanb H, Wang Z., Bovin J O 2000 J. Lumin. 91 139
[5] Anh T K, Benalloul P, Barthou C, Giang L T K, Vu N, and Minh L Q 2007 J. of Nanomaterials Vol. 2007 Article ID 48247
[6] Shionoya S, Yen W M 1999 Phosphor Handbook (CRC Boston-London-New York-Washington, D.C, CRC. Press LLC)
[7] Hwang J M, Oh M O, Kim I, Lee J K, Ha C S 2005 Curr. Appl. Phys. 5 31
[8] Mahlik S, Zalewska M, Grinberg M, Klonkowski A M, Godlewski M 2008 J. Lumin. 128 921
[9] Mohagheghpour E, Rabice M, Moztarzadeh F, Tahiri M, Jafarbeglou M, Bizari D, Eslami H 2009 Mater. Sci. and Eng.: C In Press
[10] Donega C de Mello, Bol A A, Meijerink A 2002 J. Lumin. 96 87
[11] Yang P and Bredol M 2008 Res. Lett. in Mater. Sci. Vol. 2008 Article ID 506065
[12] Vu N, Anh T K, Yi G C, and Strek W 2007 J. Lumin. 122-123 776
[13] Vu N, Quan N H, Anh T K, Khoi N T and Liem N Q 2008 J. Korean Phys. Soc. 52 1514
[14] Sohling U, Jung G, Saenger D U, Lu S, Kutsch B and Menning M 1998 J. Sol-Gel Sci. Technol. 13 685

Acknowledgments
This work is supported in part by Vietnam Academy of Science and Technology (VAST). A part of the work was done in the National Key Laboratory for Electronic Materials and Devices, Institute of Materials Science, VAST. We would like to thank MSc. Tran Quang Huy, MSc. Do Hung Manh, and MSc. Tran Dang Thanh for their helps on TEM, SEM, and XRD measurements, respectively.