Communications in Physics, Vol. 22, No. 2 (2012), pp. 167-173

THE OPTICAL PROPERTY OF MN- DOPED ZnS NANOPARTICLES SYNTHESIZED BY A CO-PRECIPITATION METHOD

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Abstract. *By a co-precipitation method, we have synthesized Mn-doped ZnS nanoparticles with the Mn contents of 2-12 mol% from solutions* $Zn(CH_3COO)_2$ *0.1M,* $Mn(CH_3COO)_2$ *0.1M and* Na_2S *0.1M. XRD patterns, TEM images show these nanoparticles possess cubic crystalline structure with average size about of 3-4 nm. Photoluminescence spectra of samples present a broad yellow-orange band of 603 nm, its intensity increases with the increasing of Mn content from 2 mol% to 8 mol % when the excitation power density increases from 0.06 W/cm*^{2} *to 0.21 W/cm*^{2}*. However, while the intensity increases with the increasing of Mn content its position is almost unchanged. This band is attributed to the radiative transition of electron in 3d*^{5} *unfulfilled shell of* Mn^{2+} *ions* [$^4T_1(^4G)\to{}^6A_1(^6S)$*. The absorption spectra show main bands at 308-328 nm with strong intensity related to absorption near band edge of ZnS crystal. These bands related to* Mn^{2+} *absorption also appeared with weaker intensity. The photoluminescence excitation spectra monitored at the yellow-orange band exhibited a band at 354 nm with strong intensity and bands at 432, 466, 497 nm with weaker intensity. The band of 354 nm is attributed to the absorption near band edge. Simultaneously, the bands of 432, 466, 497 nm are attributed to the absorption transitions of electrons from ground state* $^6A_1(^6S)$ *to excited states* $^4T_2(^4D)$, $^4A_1(^4G)$ - $^4E(^4G)$, $^4T_2(^4G)$ *of* Mn^{2+} *ions in ZnS crystal, respectively.*

I. INTRODUCTION

The prominent characteristic of ZnS, Mn-doped ZnS nanomaterial is a wide band gap energy, direct transition, strong luminescence in vissible range and high luminescence efficiency. Therefore, those materials have been widely applied in opto-electronics as light, television screen, computer, laser sensor, photocatalysis, bio-label... [1-3]

The Mn-doped ZnS nanoparticles possessing a high luminescence efficiency can be prepared by a physical method as the cathode sputtering, laser ablation and as well as chemical methods as the sol-gel, hydrothermal, co-precipitation... in which the co-precipitation method is a quite simple, can prepare nanoparticles at room temperature [2,4-6]. In this paper, we present synthesis results of Mn-doped ZnS nanoparticles with Mn content of 2-12 mol% by a co-precipitation method from $Zn(CH_3COO)_2.2H_2O$, Na_2S, $Mn(CH_3COO)_2.4H_2O$ and study on some optical properties. The results give information about absorption, radiation, excitation of Mn^{2+} ions in ZnS crystal and the influence of particle size effect on the photoluminescence spectra.

II. EXPERIMENTAL

The nanoparticles Mn-doped ZnS with Mn content of 2-12 mol% was synthesized by a co-precipitation method as following: dissolve $Zn(CH_3COO)_2.2H_2O$, $Mn(CH_3COO)_2.4H_2O$ and Na_2S in two-times distilled water in order to create solution of $Zn(CH_3COO)_2$0.1M (A), $Mn(CH_3COO)_2$0.1M (B) and Na_2S(C), then stirring this solutions for 30 minutes. The solution A and B were mixed in a certain volume proportion. Then an additional amount of CH_3COOH was droped into abovemixed solution to produce a solution (D) with a pH = 3.5 and stirred for 30 minutes. After that, the solution D was slowly droped into the solution C and stirred continuously for 30 minutes. The ZnS and MnS precipitations were created by reaction equations as following:

$$Zn(CH_3COO)_2 + Na_2S \rightarrow ZnS\downarrow + 2CH_3COONa$$

$$Mn(CH_3COO)_2 + Na_2S \rightarrow MnS\downarrow + 2CH_3COONa$$

These precipitations were washed by two-times distilled water, separated by centrifuge with speed of 2500 rpm, then they were dried at 80° for 10h and annealed at 120^{o}C for 10h in the air atmosphere. The crystalline structure of samples was studied through X-ray deffraction patterns on a XD8 Advance Buker system using Cu-K_α (λ= 1.5046Å). The surface morphology of samples were seen on TEM images which was taken on the TEM system JEM-1010. The photoluminescence (PL), photoluminescece excitation (PLE) and absorption spectra at 300K were excited by 325 nm radiation of He-Cd laser, a xenon lamp XFOR-450 and have been measured on Oriel-Spec MS-257, FL3-22 and JASCO-V670 spectrometers, respectively.

III. RESULTS AND DISCUSSION

III.1. The structure and morphology of Mn-doped ZnS nanoparticles

Fig. 1 shows the XRD patterns of ZnS,Mn-doped ZnS nanoparticles of samples with Mn content of 2-12 mol%. These XRD patterns include three diffraction peaks corresponded to (111), (220) and (311) planes, in which the peak (111) has the largest intensity. The XRD patterns show that ZnS nanoparticles are in the single phase, $T_d^2 - F\overline{4}3m$ symmetry cubic structure with the lattice constant of $a = 5.3795$Å. Generally, with the increase of Mn content of $2 - 12$ mol%, the position of diffraction peaks are nearly unchanged butthe lattice constant increase slightly. This increasing of lattice constant can be induced by the bigger radius of Mn^{2+} ion in high spin(0.97Å) than that of Zn^{2+} ion (0.88Å)[7]. From XRD patterns and using Debye-Scherrer's formular $D = \frac{0.9\lambda}{\beta\cos\theta}$, the average size of Mn-doped ZnS nanoparticles have been estimated about of 3-4 nm.

Fig. 2 shows TEM image of Mn-doped ZnS nanoparticles (C_{Mn} = 8 mol%). The TEM image shows the quite disperse Mn-doped ZnS nanoparticles with average size aboutof 3-5 nm.

III.2. The optical properties of Mn-doped ZnS nanoparticles

Fig. 3 presents PL spectra of the ZnS and Mn-doped ZnS nanoparticles recorded at 300K with different Mn contents as excited by 325 nm radiation of He-Cd laser. The PL spectra of ZnS nanoparticles show a wide blue band around 450 nm(Fig.3a). This band is

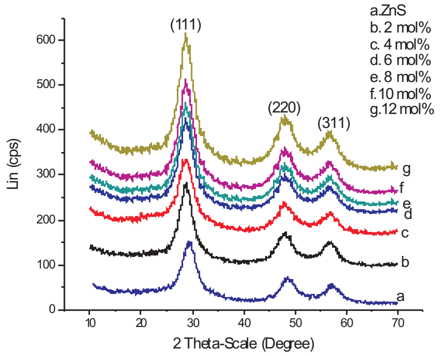

Fig. 1. The XRD patterns of ZnS, Mn-doped ZnS nanoparticles with diferent Mn contents

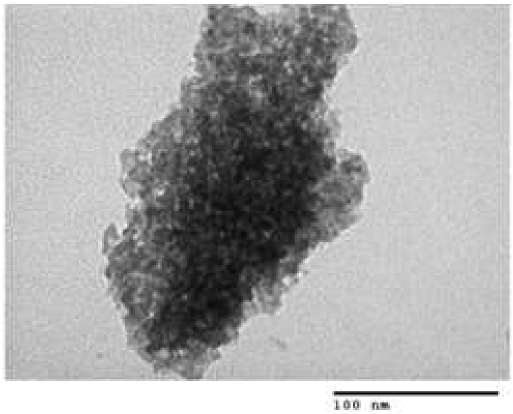

Fig. 2. The TEM image of Mn-doped ZnS nanoparticles (C_{Mn} = 8 mol%)

attributed to vacancies of Zn, S, their interstitial atoms and surface states (called the self activated band) [8-12]. When Mn is introduced into ZnS with the Mn content of 2 mol%, the blue band is almost quenching, a yellow-orange band at 600 nm with wide band width appears (Fig. 3b). When increasing the Mn content from 2 mol% to 12 mol%, the yellow-orange band intensity gradually increases (Fig. 3c, Fig. 3d) and reaches the maximum value at the Mn content of 8 mol%(Fig. 3e), the PL shift towards the longer wavelength from 600 nm for Mn content of 2-6 mol% to 603 nmfor Mn content of 8-12 mol%.This proves the yellow-orange band is attributed to the radiative transitions of electrons in $3d^5$ un fullfilled configuration of Mn^{2+} ions $[^4T_1(^4G)\rightarrow{}^6A_1(^6S)]$ [1].

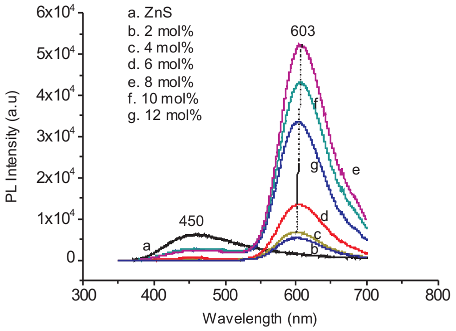

Fig. 3. The PL spectra of ZnS, Mn-doped ZnS nanoparticles with different Mn contents

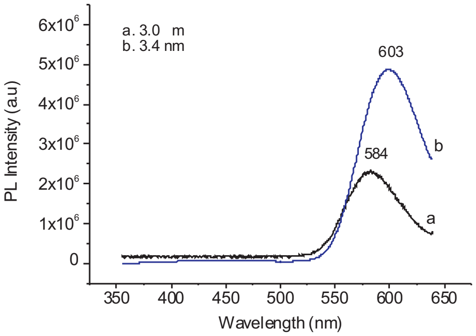

Fig. 4. The PL spectra of Mn-doped ZnS prepared by a solid reaction method (C_{Mn} = 0.8 mol%) (a) and a co-precipitation method (C_{Mn} = 8 mol%) (b).

As increasing the Mn content, the Mn^{2+}ions substituted Zn^{2+} ions and their vacancies increase, so the intensity of the yellow-orange band increases. With a higher Mn content, the photoluminescence intensity reduces, this is possibly due to interact between

Mn^{2+} ions and ions of crystalline lattice and between Mn^{2+} ions mutually [5]. The PL spectra of Mn-doped ZnS prepared by the solid state reaction method (C_{Mn}= 0.8 mol%) and prepared by the co-precipitation method (C_{Mn}= 8 mol%) with the particle size of 3 μm, 3.4 nm, respectively, show that the yellow-orange band shifts towards the longer wavelength about 9 nm (Fig. 4). This is attributed to the quantum confinement effect when grain size reduces [3,13].

Figures 5 and 6 show the PL spectra of ZnS, Mn doped ZnS nanoparticles (C_{Mn}= 8 mol%) with some excitation power densities. When increasing the excitation power density of He-Cd laser radiation from 0.06 W/cm^2 to 0.21 W/cm^2, the self-activated centers and Mn^{2+} ions joining in radiation increase, so the intensity of the blue band, the yellow-orange band increase while theirs peak positions are almost unchanged. Their intensities are increased obey to the exponential law, $I_{PL} = J_{Ex}^{n}$, with n $\approx$ 1.1 for the blue band and n$\approx$1.0 for the yellow-orange band. Those are quite in agreement with reference [14].

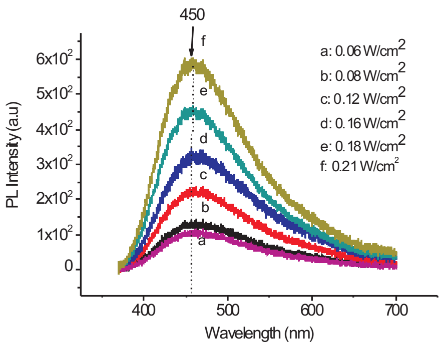

Fig. 5. The PL spectra of ZnS nanoparticles with different excitation power densities.

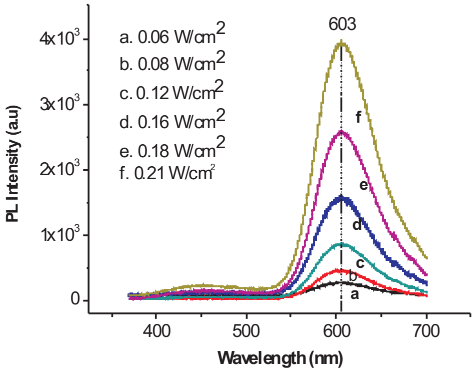

Fig. 6. The PL spectra of Mn-doped ZnS nanoparticles (C_{Mn} = 8 mol%) with different excitation power densities.

To clarify the radiation nature of the yellow-orange band, we have studied on absorption and PLE spectra of Mn-doped ZnS nanoparticles. Fig. 7 is the absorption spectra of ZnS, Mn-doped-ZnS nanoparticles with different contents. In absorption spectra of ZnS, there is a wide band around 308 nm with strong intensity (Fig. 7a) attributed to absorption transition near the band edge of ZnS [9,15]. When Mn content increases from 2 mol% to 12 mol%, the right side of this band denegenates gradually and the maximum peak shifts towards to the longer wavelength due to Mn^{2+} ions absorption contribution. At the Mn content of 6, 8 mol%, the Mn^{2+}ions absorption present clearly at 466, 497 nm band (Fig. 7d, 7e). At the Mn content of 10, 12 mol%, those bands combine into one band and a band around 390 nm on the right side band attributed to Mn^{2+} appears. The absorption near the band edge and Mn^{2+} ions absorption of Mn-doped ZnS exhibite more clearly in PLE spectra.

Fig. 8 presents the PLE spectra monitoring at 450 nm and 603 nm of ZnS, Mn-doped ZnS nanoparticles with different Mn contents, respectively. In the PLE spectra monitoring

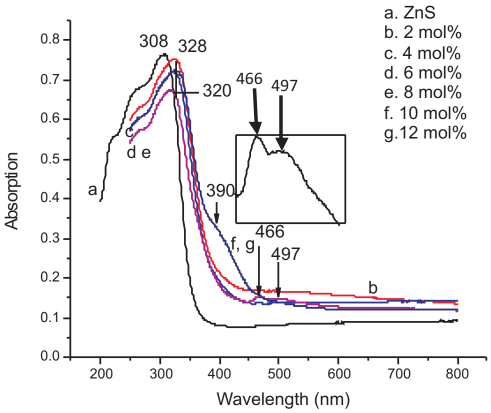

Fig. 7. The absorption spectra of ZnS, Mn doped ZnS nanoparticles with different Mn contents.

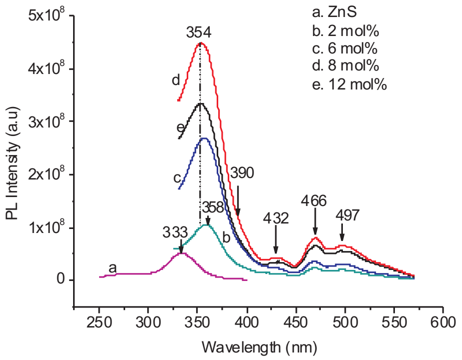

Fig. 8. The PLE spectra of ZnS, Mn-doped ZnS nanoparticles with different Mn contents.

at 450 nm of ZnS, there is a wide band with maximum at about 333 nm (3.6946 eV) (Fig. 8a). This value is quite similar with the band gap energy of ZnS crystal [13], therefore, we have proposed that 333 nm band is attributed to the absorption transition near the band edge of ZnS crystal. In the PLE spectra monitoring at 603 nm of Mn-doped ZnS (C_{Mn}= 2 mol%), the absorption band near the band edge shifts towards to the longer wavelength (at 358 nm), there are also bands at 432, 466, 497 nm with weaker intensity. Those are assigned to absorption transitions of electrons from$^6A_1(^6S)$ ground state to excited states $^4T_2$ (^{4}D), $^4A_1(^4G)$- $^4E(^4G)$, $^4T_2(^4G)$ [15]. As increasing the Mn content from 2 mol% to 8 mol%, intensity of the near band edge absorption increases and reaches the maximum at 8 mol%, after that the intensity decrease gradually, the position shifts towards to the shorter wavelength from 358 nm for 2 mol% to 354 nm for 12 mol% (Fig.8b-8e). Intensity of Mn^{2+} absorption band increases while its position is unchanged. This proves that Mn^{2+} ions substituted Zn^{2+} ions, vacancies and produced the yellow-orange band in PL spectra.

Using in turn radiation 325, 354, 432, 466, 497 nm of xenon lamp to excite Mn-doped ZnS nanoparticles (C_{Mn}=8 mol%), we obtaina yellow-orange band at 603 nm. The position of this band is almost unchanged but the intensity depends on the excitation radiations (Fig. 9). The intensity is strong as exciting by 325, 354 nm raditions, that decreases gradually as exciting by 466, 497, 432 nm although the intensity of 325, 354 nm radiations are weaker. From the results of absorption, PLE spectra monitoring at 603 nm and the unchanging of this band position as exiting by 325,354, 432, 466, 497 nm radiations showed that there possibly occur the near band edge absorption of ZnS host crystal and Mn^{2+} absorption with more efficiency of near the band edge absorption in Mn-doped ZnS nanoparticles. We think that, excitation by the radiations of 325, 354 nm with photon energy estimate the band gap energy of ZnS crystal is the indirect excitation of $3d^5$ Mn^{2+} ions. Under the effect of radiations, unbalance electron-hole pairs generated can be bound with Mn^{2+} ions, these pairs nonradiative recombination and transfer energy to $3d^5$ electrons of Mn^{2+} ions. Excitation by the radiations of 432, 466, 497 nm with photon energy smaller than band gap energy of ZnS crystal is the direct excitation of $3d^5$ Mn^{2+} ions[3].Electrons in $3d^5$ unfullfilled shell of Mn^{2+} ions absorb photons, they transfer from ground state $^6A_1(^6S)$ into excited states$^4E(^4D)$, $^4T_2(^4D)$, $^4A_1(^4G)$, $^4E_1(^4G)$, $^4T_2(^4G)$, after that, nonradiative transition into $^4T_1(^4G)$ state and finally transfer into ground state $^6A_1$ (^6S) to emit the yellow-orange band at 603 nm. The absorption, radiative transitions of electrons in $3d^5$unfulfilled shell of Mn^{2+}ions and the mechanism of excitation energy trasferring in Mn-doped ZnS crystal is illustrated in Fig. 10.

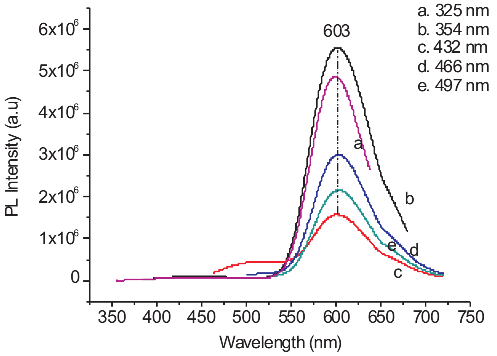

Fig. 9. The PL spectra of Mn-doped ZnS nanoparticles (C_{Mn} = 8 mol%) with different excitation radiations.

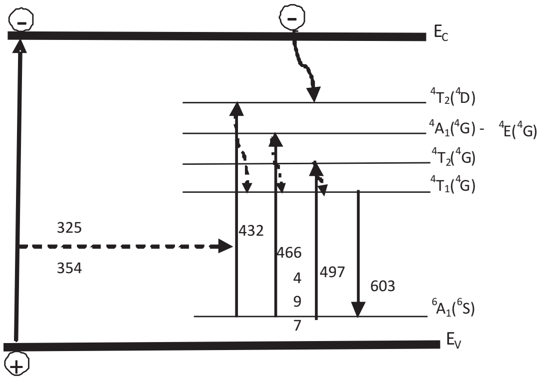

Fig. 10. The diagram of energy levels and absorption, radiative transitions of Mn^{2+} in Mn- doped ZnS crystal.

IV. CONCLUSION

Mn-doped ZnS nanoparticles with Mn contents of 2 - 12 mol% from solutions $Zn(CH_3COO)_2$ 0.1M, Na_2S 0.1M and $Mn(CH_3COO)_2$0.1M by a co-precipitation method have not changed significantly in microstructure of ZnS but changed significantly in the optical properties. Mn^{2+} ions in ZnS crystal caused 432, 466, 497 nm bands in absorption and PLE spectra and the yellow-orange band at about 600-603 nm in PL spectra. Those bands attribute to the absorption, radiative transitions of electrons in $3d^5$unfulfilled shell of Mn^{2+}ions in ZnS crystal, respectively. When decreasing Mn content, excitation power density and changing the excitation wavelengths, the position of the yellow-orange band is unchanged while their intensity is changed. This proves that Mn^{2+}ions substituted Zn^{2+}ions and induced vacancies in ZnS crystal. The decreasing of Mn-doped ZnS particle size from 3 μmto 3.4 nm cause the quantum confinement effect. The yellow-orange band characterizing to Mn^{2+} shifts towards to the longer wavelength about of 9 nm.

ACKNOWLEDGMENTS

The authors would like to thank Vietnam National University project (code QG.11.07 project) for financial support.

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Received 26 April 2012.