Communications in Physics, Vol. 23, No. 1 (2013), pp. 75-83

INFLUENCE OF REACTION TEMPERATURE ON OPTICAL PROPERTY OF Mn-DOPED ZnS NANOPARTICLES

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Abstract. *The reaction temperature has essential effect on quality of the product synthesized by hydrothermal method. We report here the variation of the optical characteristics of Mn-doped ZnS nanocrystallites prepared by mean of the stated method from* $Zn(CH_3COO)_2.2H_2O$, $Mn(CH_3COO)_2.4H_2O$ *and* $Na_2S_2O_3.5H_2O$ *as the precursors. The reaction temperature was set to vary from 120 °C to 240 °C at a constant reaction time of 15 hours. The XRD patterns showed that, for the reaction temperature range from 120 to 160 °C, the obtained products possessed a cubic* $T_d^2 - F\bar{4}3m$ *and a wurtzite* $C_{6v}^4 - P6_3mc$ *structure, in which the cubic phase was dominant. At the temperature range from 180 to 240 °C, the structures exhibited a cubic phase with the lattice constant increased from 5.41 to 5.43 Å. The photoluminescence spectra showed that with the increase of reaction temperature from 120 to 240 °C the intensity of a blue band around 425 - 500 nm (attributed to both Zn, S vacancies) gradually decreased while the intensity of a yellow-orange band at 585 nm (attributed to the* $^4T_1(^4G)$ - $^6A_1(^6S)$ *transition of* Mn^{2+} *ions) was enhanced and reached maximum at 220 °C. The excitation spectra of the 585 nm band recorded at 160 °C showed a band at 335 nm which should be assigned to the near band-edge absorption. With increasing temperature to 200-240 °C the new bands appeared at 390, 430, 467, 494 nm. The intensity of these bands increased with temperature and achieved the maxima at 220 °C. They should be attributed to the absorption transitions of electrons from ground state* $^6A_1(^6S)$ *to excited states*$^4E(^4D)$; $^4T_2(^4D)$; $^4A_1(^4G)$ - $^4E(^4G)$; $^4T_2(^4G)$ *of* $Mn^{2+}(3d^5)$ *ions, respectively. The bands at 467, 494 nm only exposed clearly in the absorption spectra at 220 °C and 240 °C.*

I. INTRODUCTION

In recent years the Mn-doped ZnS nanomaterials have attracted a lot of attention of scientists for both fundamental and application driven interests due to the raising demands in optoelectronics, biological markers, photocatalysis etc. [1-5]. In order to synthesize this material, there are many different methods such as co-precipitation, hydrothermal, sol-gel, electrodeposition, γ-iradiation . . . The applied precursor chemicals usually include Zn^{2+}, S^{2-}, Mn^{2+}. The S^{2-}source can be created from organic or inorganic compounds such as Na_2S, $Na_2S_2O_3.5H_2O$, $CS(NH_2)_2$ thioglycolic acid $C_2H_4O_2S$ (TGA). Among the listed, there was only a few reports available that were involved with $Na_2S_2O_3.5H_2O$ as the S^{2-} source. K.R.Murali and S.Kumaresan [3] have prepared the deposited ZnS films from $Na_2S_2O_3$ by mean of the brush electrodeposition technique. Their products showed only the weak bands at 420, 480 nm. Xuan Xue and co-workers [4] have also prepared the

ZnS nanoballs with average diameter of 50 - 120 nm by mean of γ-irradiation method. But only Changlong Jiang and co-workers [6] have presented a hydrothermal synthesis of micro-sized spheres and nano-sized hollow spheres ZnS from $Na_2S_2O_3.5H_2O$ (reaction temperature of 200°C and time of 4 hours). Therefore, we present in this paper the results of a study of the effect of reaction temperature on the optical quality of Mn-doped ZnS nanoparticles prepared in the range of reaction temperature from 120 to 240°C from $Na_2S_2O_3.5H_2O$, $Zn(CH_3COO)_2.2H2O$, $Mn(CH_3COO)_2.4H_2O$ and at a constant reaction time of 15 hours.

II. EXPERIMENTAL

The Mn-doped ZnS nanoparticles were prepared as follows. First by dissolving $Zn(CH_3COO)_2.2H_2O$, $Mn(CH_3COO)_2.4H_2O$ and $Na_2S_2O_3.5H_2O$ in the deionized water we created the solutions of $Zn(CH_3COO)_2 0.1M$ (A), $Mn(CH_3COO)_2 0.01M$ (B) and $Na_2S_2O_3$ 0.1M (C). Then by mixing solution A with solution B in the stoichiometric volume ratios we received 30 ml mixture solution D, which was then stirred for 60 minutes. After that, the solution C was slowly dropped into the solution D and stirred further for 60 minutes. We transferred the mixed solution into the teflon-lined stainless steel autoclave, which was sealed and maintained with reaction temperature in the range from 120 to 240°C for 15 hours. The autoclave was then left to cool down to room temperature. In the hydrothermal process discussed above, the Mn-doped ZnS nanoparticles were formed as followed:

$$\begin{aligned} 4Na_2S_2O_3 \quad &\rightarrow Na_2S + 3Na_2SO_4 + 4S \\ Zn(CH_3COO)_2 + Na_2S &\rightarrow ZnS\downarrow + 2CH_3COONa \\ Mn(CH_3COO)_2 + Na_2S &\rightarrow MnS\downarrow + 2CH_3COONa \end{aligned}$$

The resultant containing ZnS:Mn was a white solid powder suspension which was then filted, washed with double distilled water several times, and dried at 60°C for 10 hours in open air. The crystalline structure of samples was examined by using the X-ray diffraction technique on XD8 Advance Bruker Diffractometer equipped with the Cu-K_α radiation ($\lambda = 1.54056$ Å). The surface morphology was studied by mean of Transmission Electron Microscope (JEM-1010 TEM). The photoluminescence (PL), photoluminescence excitation (PLE) and absorption spectra were obtained at 300 K with the excited wavelength at 325 nm from a He - Cd laser, a xenon lamp XFOR - 450, hydro, and halogen lamp and 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 presents the XRD patterns of ZnS:Mn (C_{Mn}= 5 mol%). The patterns show the lines at 28.54, 33.02, 47.47, 56.42, and 69.45° which correspond to (111), (002), (220), (311) and (400) diffraction planes. As seen, the (111) peak has the strongest intensity.

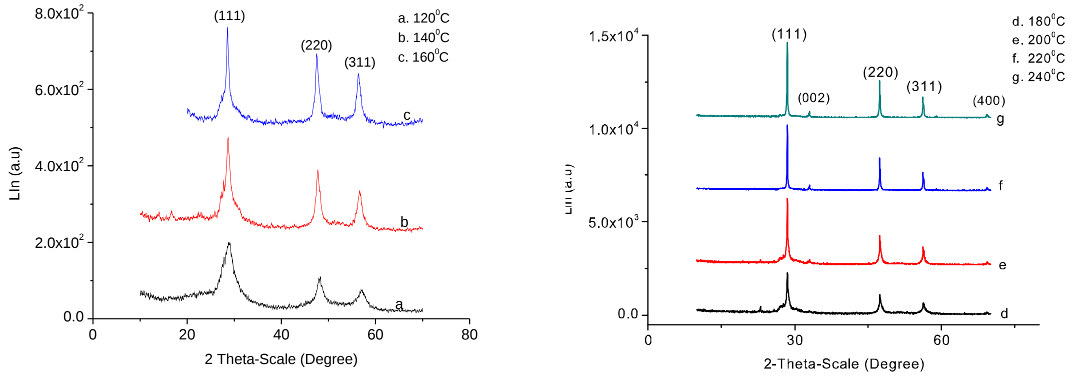
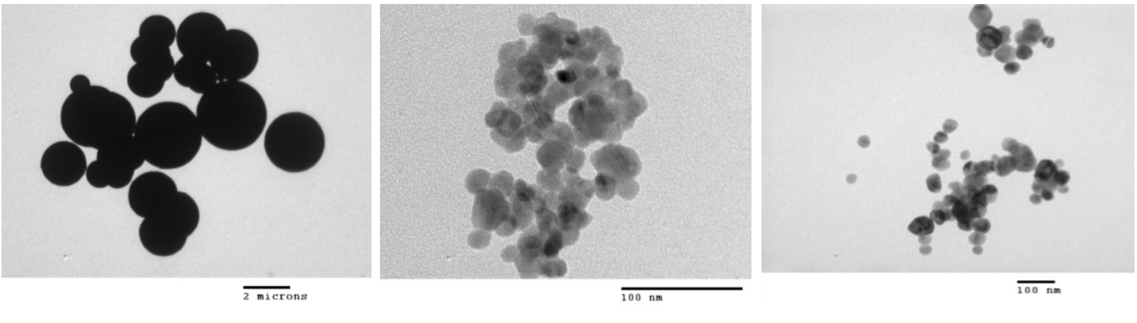


Fig. 1. XRD patterns of ZnS:Mn (C$_{Mn}$= 5 mol%) nanoparticles synthesized for 15 hours at different reaction temperatures

The obtained XRD patterns show that at 120°C (Fig. 1(a)) the material has crystallized in both cubic ($T_d^2 - F\bar{4}3m$) and wurtzite form ($C_{6v}^4 - P6_3mc$), of which the cubic structure (with the lattice constant a = 5.355Å) was prominent. As the reaction temperature increased from 140 to 160°C, the full width of diffraction lines decreased and the finger-prints of a cubic phase appeared more clearly (Fig. 1(b)-(c)). The lattice constant of this phase also increased from 5.385 to 5.408 Å. As temperature reached 240°C the lattice constant expansed further to 5.427 Å (Fig.1(d)-(f)). These values are in good agreement with the JCPDS card no. 05-0566 where a = 5.406 Å. The average crystallite sizes were estimated by the Debye-Scherrer's formular $D = 0.9\lambda/(\beta\cos\theta)$ (where β is the full width at half maximum, θ the diffraction angle and λ the wavelength). The obtained size showed the increase from 7.5 to 13.4 nm according to rising of the reaction temperature from 120 to 160°C, while further increase of temperature from 180 to 240°C seemed to have no effect on the average size which remained unchanged at 16.7 nm. The crystalline structure change as reaction temperature increased may have origin in the kinetics of the complex decomposition reaction: the different decomposition rates at low and high reaction temperature prefer different form of the crystalline structures [7]. The lattice constant change may be due to the different interatomic force in the tetragonal distortion of ZnS nanostructure [5].

Fig. 2 shows the TEM images of ZnS:Mn (C$_{Mn}$ = 5 mol%). As seen, at 120°C they formed the microspheres of 1 - 2 μm diameter (Fig. 2(a)) whereas at 180°C and 220°C they exhibited the form of quasi-spheres with much smaller average size of 20 - 30 nm (Fig. 2(b), (c)). These values are quite consistent with the results obtained from XRD patterns. This situation is however not obvious as the increase in reaction temperature usually induced larger crystallite size. Indeed we have observed a slight increase in particle size when temperature increased above 180°C but the fact that at the temperature higher than 120°C the crystallite size gradually reduced posted a question. We believed that the spheres formed at low temperature were larger due to the bridge-binding of organic water because of the -OH group polarity. The increase in the reaction temperature caused the gradual reduction of bridging water molecules, so preventing the aggregation of nanocrystallites to create the larger particles.



(a) (b) (c)

Fig. 2. TEM images of ZnS:Mn (C_{Mn}= 5 mol%) nanoparticles synthesized for 15 hours at some reaction temperatures: 120 (a), 180 (b), and 220°C (c).

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

Fig. 3 presents the PL spectra of the sample ZnS:Mn (C_{Mn}= 5 mol %). At 120°C, the PL spectrum exhibits a wide asymmetric band with maximum lying in blue region of 425 - 500 nm (Fig. 3(a)). At 140°C, the blue band reduced its intensity while there appeared a yellow-orange band at about 585 nm (Fig. 3(b)). At further increase to 160°C, the intensity of the blue band continuously reduced while the intensity of the yellow - orange band increased rapidly (Fig. 3(c)). This provides a support argument for the interpretation of the blue band as being attributed to the Zn and S vacancies at interstitial sites in ZnS structure [9-14]. As the temperature increased further from 180 to 240°C, the intensity of the yellow-orange continuously increased and achieved the maximum at around 220°C (Fig. 3(d)-(g)). This development demonstrates that the yellow-orange band is attributed to the transitions of Mn^{2+}ions, which is the radiative transition of electrons in the $3d^5$ unfilled shell of $Mn^{2+}[^4T_1(^4G)$ - $^6A_1(^6S)]$ [15,16]. Therefore, the synthesized reaction temperature is an important factor affecting the PL behavior of the ZnS:Mn product. At low temperature, the substitution sites of Mn^{2+} for Zn^{2+} and the vacancies in the ZnS microspheres co-exist to allow both blue and yellow-orange emission bands to occur. But at higher reaction temperature the microspheres were broken into nanocrystallites unloading the interstitial vacancy defects and reducing the interparticle absorption. As a result, we observed the decrease of the blue band emission while the intensity of the yellow-orange band gradually increased. As the reaction temperature reached further to 240°C, a decrease in the emission intensity of the yellow-orange band due to the relaxation effect of Mn^{2+} substitution sites on the defects at surface was observed [17, 18]. The dependence of the intensity of yellow-orange band emission on the reaction temperature is showed in Fig. 4. This observation allows to conclude that the reaction temperature above 220°C reduces the optical quality of ZnS:Mn crystallites due to the probable raising of the number of surface defects.

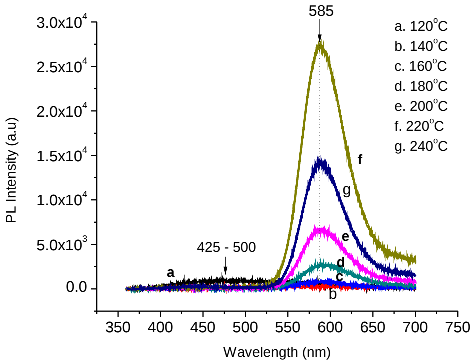


Fig. 3. The PL spectra of ZnS:Mn ($C_{Mn} = 5$ mol%) nanoparticles synthesized for 15 h at difference reaction temperatures

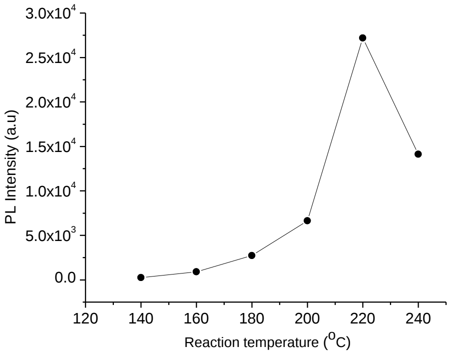


Fig. 4. The dependence of the yellow-orange band intensity at 585 nm on reaction temperature

In order to illustrate the influence of reaction temperature on the optical property of ZnS:Mn nanoparticles, we studied the PLE spectra when monitoring the blue and yellow-orange band. Fig. 5(a) shows the PLE spectrum for a blue band around 425 - 500 nm. There is a main wide band with strong intensity seen at 356 nm. That band can be assigned to the absorption of interstitial Mn^{2+} sites, or of Mn^{2+} sites at the surfaces and of impurities presented [17, 18]. Fig. 5(b)-(g) feature the PLE spectra for the yellow-orange band at 585 nm. As seen, at 140°C there are a small band with weak intensity at 356 nm and a wide band with peaks at 398, 468, 493 nm (Fig. 5(b)). At 160°C, besides the given bands, there appears a new band at 335 nm (Fig. 5(c)). At 180°C, the intensities of all bands increase in comparison with that of 160°C but the positions remain unchanged (Fig. 5(d)).

The band at 335 nm (3.69 eV) can be attributed to the near band edge absorption because the photon energy corresponding to this transition is near the band edge of ZnS (E_g= 3.70 eV) [15,16]. The wide band around 375 - 550 nm can be attributed to absorption of Mn^{2+} ions doping into ZnS structure, or of Mn^{2+} interstitial sites and of Mn^{2+} site at the surfaces.

At 200°C, the intensity of the near band edge absorption at 335 nm increases while a wide band around 375-550 nm divides into 4 bands at 390, 430, 467, 494 nm with lower intensity. Besides, there is a weak band at about 530 nm. These bands are attributed to the absorption transitions of electrons from the ground state ${}^6A_1({}^6S)$ to the excited states ${}^4E({}^4D)$; ${}^4T_2({}^4D)$; ${}^4A_1({}^4G)$ -${}^4E({}^4G)$; ${}^4T_2({}^4G)$, ${}^4T_1({}^4G)$ of Mn^{2+} ions (called Mn^{2+} absorption bands) [1]. For the temperature increased from 180 to 240°C, the intensity ratios of Mn^{2+} absorption bands and the near band edge band increase and reach the maximum at 220°C (Fig. 6) but the near band edge absorption position shifts towards to the longer wavelength (around 345 nm at 220, 240°C), the positions of Mn^{2+} absorption bands remain the same (Fig. 5(d)-(g)). The result presented showed that at the reaction temperature above 200°C the absorption caused by the substituted Mn^{2+} ions completely dominates over the ones of the Mn^{2+} interstitial sites or at the particles surfaces.

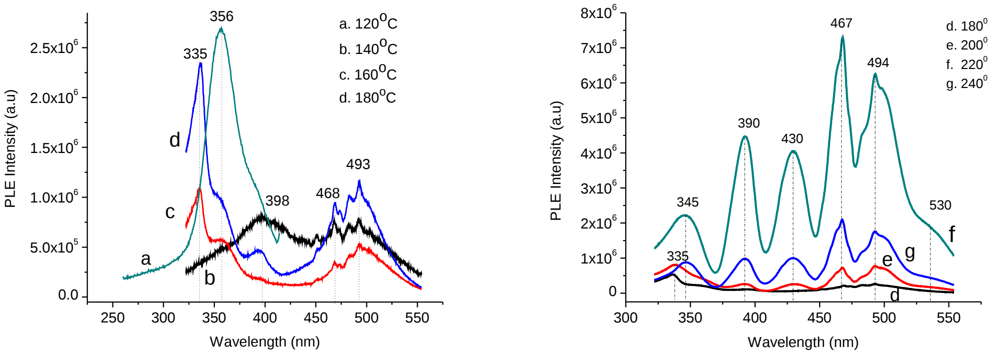


Fig. 5. The PLE spectra of ZnS:Mn (C_{Mn}= 5 mol%) nanoparticles synthesized for 15 h at difference reaction temperatures: (a) monitoring the blue band of ZnS:Mn synthesized at 120°C; and monitoring the yellow-orange of ZnS:Mn synthesized at 140-240°C (b-g)

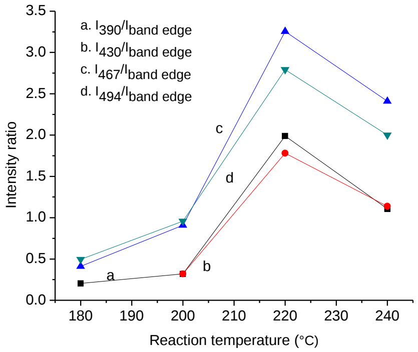


Fig. 6. Intensity ratio of Mn^{2+} absorption bands and near band edge band according to the reaction temperatures in PLE spectra

To futher illustration the absorption near the band edge and Mn^{2+} ions absorption in the bulk, we examined the ZnS:Mn absorption spectra. Fig. 7 presents the absorption spectra. The absorption spectra show a wide band at 335 - 347 nm with strong absorptance. This band is attributed to near the band edge absorption. There are still bands in the range of 375 - 550 nm which attribute to the Mn^{2+} absorption. The appearance of these bands depends on the reaction temperature. At 120°C, the absorption spectra shows a band around 398 nm with weak absorptance. This band does not appear in the form of a clear peak and lies near the foot of band edge absorption. At 140°C, the absorptance of this band increases rapidly, then remains unchanged at 160 and 180°C (Fig. 7(b)-(c)).

When increasing the reaction temperature from 180°C to 240°C, the absorption of this band decreases gradually (Fig. 7(d)-(f)), this proves that the band at 398 nm can

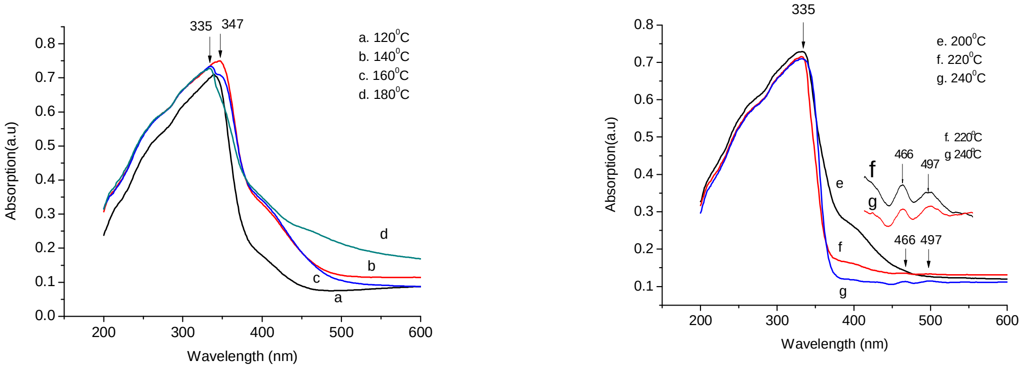


Fig. 7. The absorption spectra of ZnS:Mn (C_{Mn}= 5 mol%) nanoparticles synthesized for 15 h at difference reaction temperatures

be attributed to the absorption of Mn^{2+} doped into the bulk ZnS crystal, the interstitial Mn^{2+}ions and the Mn^{2+} ions occurred at the particles surfaces, in which the more dominance is the absorption of interstitial Mn^{2+} ions and Mn^{2+} ions on the particles surfaces. At 220 and 240°C, the Mn^{2+} absorption bands exhibit a form of a clear band at about 466, 497 nm with weaker absorptance than that of the band near the band edge (Fig. 7(e)-(f)). These bands are attributed to the absorption transitions of electrons from ground state $^6A_1(^6S)$ to the excited states $^4A_1(^4G)$ - $^4E(^4G)$; $^4T_2(^4G)$ of Mn^{2+} ($3d^5$) ions, respectively [1].

In turn, we used the radiations of wavelength 325, 335 - 345, 356, 390, 430, 467, 494 and 530 nm from a xenon lamp (which correspond to the peak positions in the PLE spectra) to excite the ZnS:Mn (C_{Mn}= 5 mol%) nanoparticles, we realized that the bands present in PL spectra depend on the reaction temperature, and at the given reaction temperature the intensity of bands depend on the excited wavelength. At 120°C, there is only blue band at 450 nm as excited by 325 nm radiation (Fig. 8(a)). This fact proves that at this reaction temperature the Mn^{2+} ions were not substituted into the ZnS bulk crystallites. At 140°C and excited by 325, 335 and 356 nm radiation we observed a blue and a yellow-orange bands at 585 nm, for which the blue band intensity was strongest when excited by 356 nm radiation. Its intensity gradually reduced if excited by 325 or 335 nm radiation. Whereas the yellow-orange band intensity achieved the maximum when excited by 325 nm radiation and gradually reduced when excited by 356 and 335 nm radiations (Fig. 8(b)-(d)). This demonstrates at that 140°C was the reaction temperature at which the Mn^{2+} ions began to substitute into ZnS bulk crystallites. At reaction temperatures 160, 200, and 240°C, the PL spectra of ZnS:Mn showed only a yellow-orange band at 585 nm with the position almost unchanged but with the intensity depended on the wavelength of excitation radiation. At 160°C, the intensity gradually increased when excited by 325, 335, and 356 nm radiations which possess the photon energy nearly the same as of the band gap (Fig. 9). At 200°C, the intensity was strongest when excited by 335 nm radiation, then it reduced when excited by the radiations of 325, 494, 467, 390, 430, and 530 nm

(Fig. 10). At 240°C, the intensity was strongest when excited by 467 nm radiation, then reduced when excited by 390, 494, 335, 430, 325 and 530 nm radiations (Fig. 11).

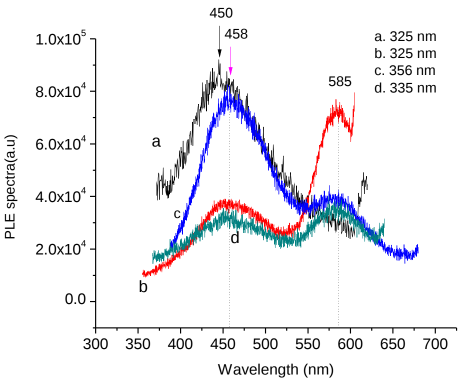


Fig. 8. The PL spectra of ZnS:Mn (C_{Mn}= 5 mol%) nanoparticles synthesized at 120°C (a) and 140°C (b, c, d) as excited by difference radiations

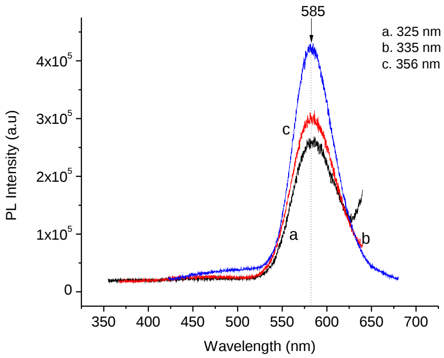


Fig. 9. The PL spectra of ZnS:Mn (C_{Mn}= 5 mol%) nanoparticles synthesized at 160°C as excited by difference radiations

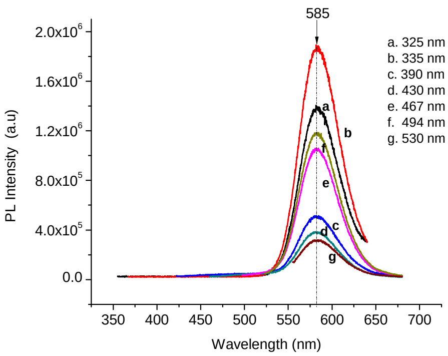


Fig. 10. The PL spectra of ZnS:Mn (C_{Mn}= 5 mol%) nanoparticles synthesized at 200°C as excited by difference radiations

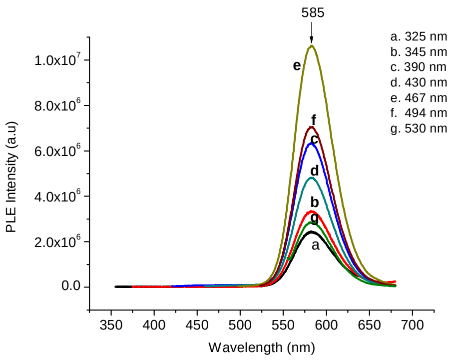


Fig. 11. The PL spectra of ZnS:Mn (C_{Mn}= 5 mol%) nanoparticles synthesized at 240°C as excited by difference radiations

The results presented showed that in there may be two excitation mechanisms of $3d^5$ electrons of Mn^{2+} ions: an indirect and direct excitation. In our opinion, the excitation by radiations of 325, 335, 356 nm wavelength possesses the photon energy nearly equal to the band gap of ZnS is indirect excitation, whereas the excitation by radiations of 390, 430, 467, 494, 530 nm possesses the photon energy smaller than that of the band gap of ZnS is direct excitation. In addition, indirect excitation is dominant for ZnS:Mn nanoparticles synthesized at 180, 200°C; while the ones synthesized at 220, 240°C prefer the direct excitation.

IV. CONCLUSION

The ZnS:Mn (C_{Mn}= 5 mol%) nanoparticles have been synthesized from the solutions of $Zn(CH_3COO)_2$ 0.1M, $Mn(CH_3COO)_2$ 0.01M and $Na_2S_2O_3$ 0.1M in a determined volume ratio by the hydrothermal method at varying the reaction temperature from 120 to 240°C. The XRD patterns, TEM images, absorption, PL, PLE spectra as monitored for the yellow-orange band at 585 nm showed that the increase of reaction temperature from 120°C to 220°C enhanced the cubic phase quality and the band at 585 nm should be attributed to the radiative transition of Mn^{2+} ions while the bands at 390, 430,467, 494, 530 nm were characterized for the absorption of Mn^{2+} ($3d^5$) ions in ZnS crystal. The constant position of the yellow-orange band at 585 nm in PL spectra as excitation radiations varied and the increase of the emission intensity as reaction temperature varied are the important evidences for the $Mn^{2+}(3d^5)$ ions substitution for $Zn^{2+}(3d^{10})$ ions in the ZnS:Mn structure.

ACKNOWLEDGMENTS

The authors would like to thank Hanoi University of Science project (code TN.12 - 04 project) for financial support.

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Received 20 October 2012.