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Influence of Reaction Time on Optical Property of ZnS:Mn Nanoparticles Synthesized by a Hydrothermal Method

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Abstract: ZnS:Mn (C_{Mn} = 5 %mol) nanoparticles have been synthesized by a hydrothermal method from solutions of $Zn(CH_3COO)_2$ 0.1 M, $Na_2S_2O_3$ 0.1 M and $Mn(CH_3COO)_2$ 0.01 M at 220°C for different reaction time. The result showed that increasing reaction time from 3 to 30h almost does not change cubic crystalline structure, peak positions attributed to Mn^{2+} ions at 585 nm in photoluminescence spectra and 392, 430, 463, 468, 492 nm in photoluminescence excitation spectra when monitoring the 585 nm band of ZnS:Mn nanoparticles but only slight increases lattice constant, the average particle size and changing their intensity. As increasing the reaction time from 3 to 10h, intensity of bands attributed to Mn^{2+} ions also increase, reaches the maximum at 15h and then decreases as increasing reaction time to 30 h. Cause of these phenomena have been investigated and reported.

Keywords: Nanoparticles, photoluminescence, photoluminescence excitation.

1. Introduction

With the prominent features wide band gap, direct transition, strong luminescence in the yellow-orange region, ZnS:Mn nanomaterial has been widely applied in optoelectronic devices, bio-label, photo-catalyst…[1-3]. ZnS:Mn nanoparticles may be prepared by some methods such as chemical vapor deposition, microwave, hydrothermal,… [4], in which, by hydrothermal method, the morphology and particle size can be controlled by changing the reaction time and temperature. Therefore, some optical properties of them will be changed. In this paper, ZnS:Mn nanoparticles with the Mn content of 5 %mol have been prepared by the hydrothermal method at 220°C for reaction time varying from 3 to 30 h and studied influence of the reaction time on crystalline structure and optical property.

2. Experimental

The Mn-doped ZnS with Mn content of 5 %mol nanoparticles were synthesized by a hydrothermal method according to the following process. The initial solutions of $Zn(CH_3COO)_2$ 0.1M (A),

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$Mn(CH_3COO)_2$ 0.1M (B) were mixed together in the specified molar ratios to obtain 30 ml solution (C) and stirring for 60 minutes. Then, $Na_2S_2O_3$ 0.1M solution (D) with the volume of 30 ml was slowly dropped into solution (C) at continuous stirring for 60 minutes. This final mixture was put into the teflon-lined chamber steel vessel with enclosed lid, after that they annealed at 220^0C for reaction time varying from 3 to 30 h and cooled down to room temperature, naturally. In the hydrothermal process, the Mn-doped ZnS nanocrystals were formed as follows:

$$4Na_2S_2O_3 \rightarrow Na_2S + 3Na_2SO_4 + 4S$$

$$Zn(CH_3COO)_2 + Mn(CH_3COO)_2 + 2\,Na_2S \rightarrow (ZnSMnS)\downarrow + 4CH_3COONa$$

(ZnSMnS) precipitation is Mn-doped ZnS nanoparticles (denoted as ZnS:Mn nanoparticles).

The crystal structure was studied by X-ray diffraction pattern (XRD) on the XD8-Advance Buker system with Cu-Kα radiation (λ = 1.54056 Å). The surface morphology was examined using Transmission Electron Microscope (TEM) JEM-1010. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were recorded at 300K using the 325 nm excitation radiation of a He-Cd laser, radiation of XFOR-450 xenon lamp on the Oriel-Spec MS-257, FL3-22 spectrometers, respectively.

3. Result and discussion

Figure 1 present XRD pattern of ZnS:Mn (C_{Mn} = 5 %mol) nanoparticles synthesized at 220°C for different reaction time. Even at 3h, nanoparticles have possessed $T_d^2 - F\bar{4}3m$ cubic crystalline structure with characteristic diffraction peaks of (111), (220) and (311) in which (111) peak have strongest intensity (Fig. 1.a). As increasing the reaction time from 5 to 30h, the cubic structure becomes more perfect (Fig 1.b-g). It is manifested in: when increasing the reaction time, positions of these peak are not unchanged but their intensity increase. Meanwhile, the lattice constant increases slightly from 5.402 to 5.421 Å, is closer to the lattice constant standard (JCPDS card No.05-0566, a = 5.411 Å). From XRD patterns and using Debye-Scherrer's formula, the average crystalline size was calculated about of 15.5 to 17.5 nm.

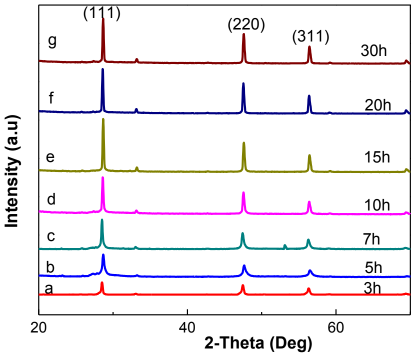

Fig. 1. XRD patterns of ZnS:Mn nanoparticles synthesized at 220^oC for different reaction time.

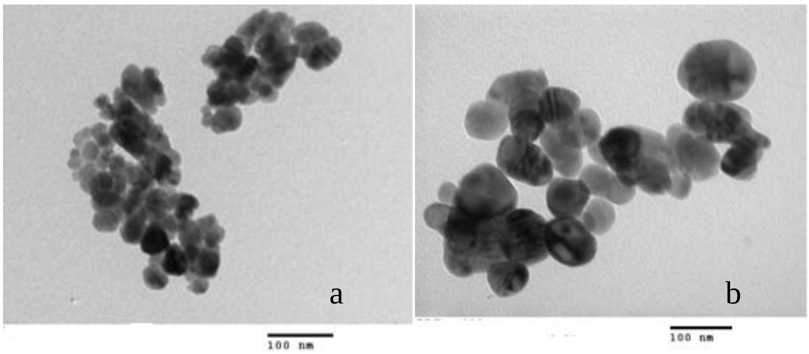

Fig. 2. TEM images of ZnS:Mn nanoparticles synthesized at 220^oC for reaction time: a.5h b. 15h

Figure 2 are TEM images of ZnS:Mn (C_{Mn} = 5 %mol) nanoparticles synthesized at 220°C for 5h and 15h. TEM images show that nanoparticles are in the form of quasi-sphere, quite homogeneous distribution and the particle size increases gradually with the reaction time: 28.5 nm (for 5h) and 34.6 nm (for 15h). When increasing the reaction time, the grain boudaries become more clearly and these particles separate better because of Ostwald ripening mechanism [5]. The above obtained results are a little bigger than the calculated results from XRD patterns and Debye-Scherrer's formula by the aggregation of nanoparticles [5-7].

Figure 3 presents the PL spectra of ZnS:Mn(C_{Mn} = 5 %mol) nanoparticles synthesized at 220°C for different reaction time when exciting by 325 nm radiation of He-Cd laser. For 3h, there is an yellow-orange band at 585 nm with weak intensity and wide full width at half maximum (Fig 3.a). This band is attributed to the radiation transition of electrons in $3d^5$ unfulfill shell of Mn^{2+} ions [$^4T_1$ (^4G)- $^6A_1$ (^6S)] in ZnS crystal [8].

As increasing the reaction time from 5 to 30h, the intensity of that band increases, reaches the maximum value at 15h, then decreases gradually but its position is nearly unchanges (Fig 3.b-g). When raising up the reaction time, the number of Mn^{2+} ions replaced Zn^{2+} ions in ZnS lattice increases, so, intensity of the yellow-orange band increases. Long reaction time makes up a large amount of Mn^{2+} ions doped into the ZnS crystal lattice, leading to interaction between Mn^{2+} ions and lattice ions and between Mn^{2+} each other, therefore, the intensity of this band decreases as the reaction time is longer than 15h [9, 10]. The dependence of yellow-orange band intensity on reaction time is illustrated in the insert of Fig. 3.

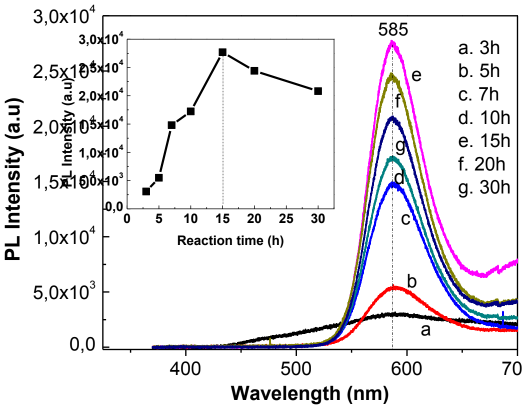

Fig.3. PL spectra of ZnS:Mn nanoparticles synthesized at 220°C for different reaction time.

The influence of reaction time on PLE spectra of ZnS:Mn (C_{Mn}= 5 %mol) nanoparticles synthesized at 220°C when changing reaction time from 3 to 30 h is given in Fig.4. For 3h, there appear bands attributed to near band-edge absorption at 336 nm, defect absorption at 363 nm and Mn^{2+} absorption at 392, 430, 468 and 492 nm, in which band at 336 and 392 nm does not exhibit clearly and the 363 nm band have the strongest intensity (Fig 4.a). Bands at 392, 430, 463, 468 and 492 nm are assigned to absorption transitions of electrons from ground state $^6A_1$(^6S) to excited states ^4E(^4D); $^4T_2$(^4D); $^4A_1$(^4G); ^4E(^4G) and $^4T_2$(^4G) of Mn^{2+} ions in ZnS crystal, respectively [11, 12]. When raising reaction time to 5h, intensity of these bands almost increases, simultaneously the near band - edge absorption at 336 nm exhibits clearly with strongest intensity besides, there is strong intensity band at about of 356 nm(Fig.4b),. This band might be attributed to defects in ZnS crystal [13]. For 7h, intensity of these bands almost increase, although, the near band-edge absorption shifts toward to the longer wavelength at about of 345 nm, and positions of Mn^{2+} absorption bands are almost unchanged (Fig.4c). When increasing the reaction time from 7 to 15 h, intensity of these bands increases, get the maximum for 15 h, then reduces when the reaction time increases to 30h but their positions are almost unchanged (Fig.4 c-g). The dependence of PL intensity of some bands attributed to Mn^{2+} absorption transitions in ZnS:Mn nanoparticles on reaction time is given in Fig.5.

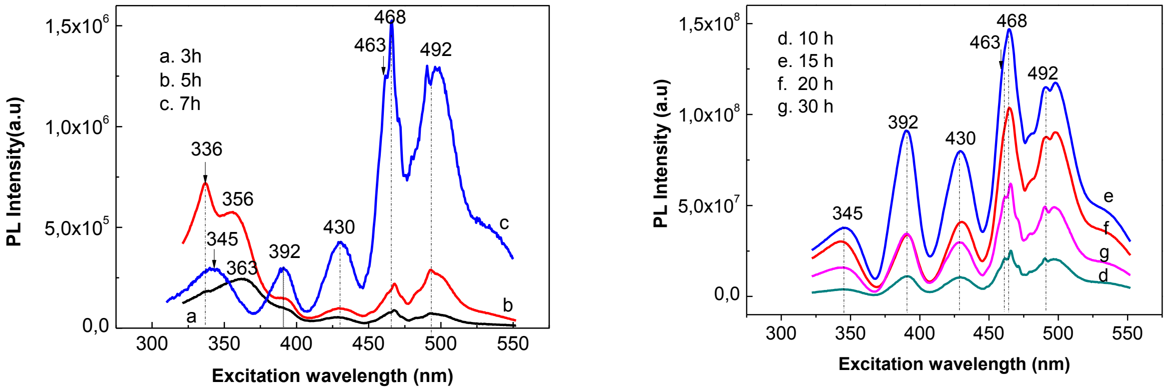

Fig.4. PLE spectra when monitoring the yellow-orange band at 585 nm of ZnS:Mn nanoparticles synthesized at 220°C for different reaction time.

The appearance of bands assigned to Mn^{2+} ions in PL and PLE spectra with strong intensity and the intensity increasing with the increasing of reaction time from 3 to 15h is improved the substituted of Mn^{2+} ions into positions of Zn^{2+} ions in ZnS crystal. Under the effect of ZnS cubic crystalline field, energy levels of free Mn^{2+} ions are separated to energy multilevel. The absorption and radiation transitions of $3d^5$ electrons between energy multilevel of Mn^{2+} ions in ZnS crystal are illustrated in Fig.6.

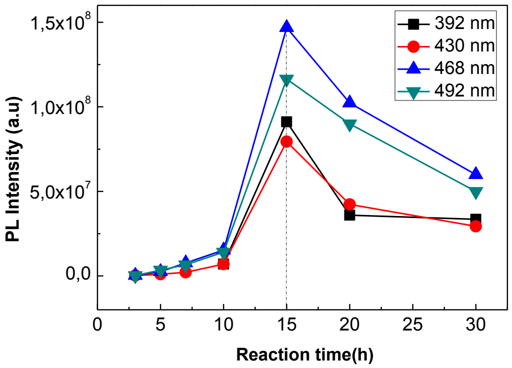

Fig.5. The dependence of PL intensity of some bands attributed to Mn^{2+} absorption transitions in ZnS:Mn.

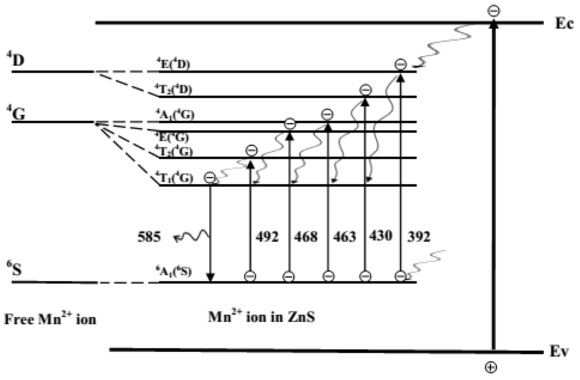

Fig.6. Schema for some absorption and radiation transitions of Mn^{2+} ions in ZnS crystal.

4. Conclusion

By the hydrothermal method, ZnS:Mn nanoparticles have been synthesized at 220°C for reaction time from 3 to 30h, in which, for 15h, the nanoparticles possess the best quality for both crystal and optical property. The reaction time increasing from 3 to 15h cause slightly increasing the lattice constant, averaged crystalline size of nanoparticles and the number of Mn^{2+} ions doping into ZnS crystal. This lead to increasing the intensity of bands attributed to Mn^{2+} ions in PL and PLE spectra but their positions are almost unchanged.

Acknowledgments

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