

INFLUENCE OF Mn^{2+} CONCENTRATION AND UV IRRADIATION TIME ON THE LUMINESCENCE PROPERTIES OF Mn-DOPED ZnS NANOCRYSTALS

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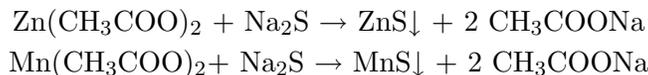
Abstract. *ZnS:Mn were prepared by wet chemical method with Mn doping concentration from 0 at% to 12 at%. The structure and particle size of the obtained powders were measured by X-ray diffraction (XRD) and scanning electron microscopy (SEM) and shown that all samples are single phase with sphalerite crystal structure and average particle size of about 5 - 7 nm. The dependence of Mn^{2+} ions doped concentration, and UV irradiation time on the luminescent intensity of ZnS:Mn nanocrystals was discussed.*

I. INTRODUCTION

Zinc sulphide (ZnS) is an important II-VI semiconducting material with a wide direct band gap of 3.65 eV in the bulk [1]. It has potential application in optoelectronic devices such as blue emitting diodes [2], electroluminescent devices and photovoltaic cells [3]. The optical properties of impurities, such as transition metal ion, doped ZnS have been the focus of several studies; in particular, of Mn^{2+} ions doped in ZnS nanocrystals. ZnS:Mn nanocrystals exhibit an orange luminescence with a high quantum efficiency under the interband excitation of the host crystals by ultraviolet (UV) light. The ${}^4T_1 \rightarrow {}^6A_1$ transition within the $3d^5$ configuration of the divalent manganese ion (Mn^{+2}) has been studied extensively and its orange-yellow luminescence in ZnS is well documented. This luminescence was also observed in nanocrystalline ZnS: Mn^{2+} and applications have already been suggested [4-7]. It has been found that the amount of Mn^{2+} ions affected its luminescence intensity. Also, the PL intensity of ZnS:Mn nanocrystals was founded to increase under UV irradiation [8]. In this paper, we report on the effect of Mn-doped concentration and the dependence of UV irradiation time on the PL intensity of the ZnS:Mn nanocrystals.

II. EXPERIMENTAL

ZnS:MnS nanocrystals were prepared by wet-chemical method. We used $Zn(CH_3COO)_2 \cdot 2H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$, $Na_2S \cdot 9H_2O$ and mix $CH_3OH:H_2O$ as initial chemicals. First, 0.1 mol $Zn(CH_3COO)_2 \cdot 2H_2O$ was dissolved in the buffer acetate CH_3COOH (pH = 3.5), solution contained 0.1 mol Na_2S was added drop by drop in a reaction vessel. The pH level plays importantly in the precipitate of ZnS and ZnS: Mn^{2+} . The reactions were happened as follows:



The theoretical calculation shows that, the precipitation may be happen at $\text{pH} = 3.5$ for ZnS and ZnS:Mn^{2+} in the mixed solution, but does not precipitate of Zn(OH)_2 . This solution was constantly mixed by a homogeneity during the entire process. The precipitate was separated by centrifugation at 2500 rpm and rinsed by mixer $\text{CH}_3\text{OH} : \text{H}_2\text{O}$ (1:1 ratio) for several times. All the rinsed samples were then dried in low pressure (10 mmHg) at 40°C for 48 hours.

The ZnS:Mn^{2+} samples were produced with correlative concentration of Mn^{2+} : 0; 2, 3, 4, 7, 8, 9, 10, 11, and 12 at%. For a qualitative analysis of ZnS, we used optical measurement at $\text{pH} = 6.0$ and test substances of blue methylthimol with maximum absorb wavelength $\lambda = 592$ nm. The results showed that content of ZnS in the samples achieved $> 97\%$ of the total volume.

The structure and crystallinity were characterized and analyzed by X-ray diffraction (SIEMENS D5005), and transmission electron microscope (TEM) and have been reported in Ref. [1]. The photoluminescence spectra were recorded with a fluorescence spectrophotometer HP340-LP370 using laser having excitation wavelength 325 nm at room temperature.

III. RESULTS AND DISCUSSION

Fig. 1 shows the PL spectra of ZnS:Mn nanocrystals with different Mn doping concentration of 0; 2; 3 and 4 at% under UV excitation of 325 nm. As can be seen, for the pure ZnS sample (0 at% Mn), only one very broad emission band with peak at around 2.6 eV was observed. Previously, this UV emission has been studied in pure colloidal ZnS samples and is assigned to a recombination of free charge carriers at defect sites, possibly at the surface, in ZnS nanocrystals [9, 10]. The PL spectrum of Mn-doped samples consists of two emission bands. One is at around 2.7 eV while the other (weaker) is at 2.1 eV. From Fig. 1, it is clearly that intensity of both the 2.7 and 2.1 peaks is increased with increasing Mn doping concentration from 2 to 4 at%. It was interpreted in ref. [9] that the emission band with peak at 2.1 eV was related to a de-excitation of Mn^{2+} ion in the ZnS matrix due to the ${}^4T_1 \rightarrow {}^6A_1$ (in T_d symmetry) transition or $A_1 \rightarrow A_2$ (in C_{3v} symmetry) transition of the Mn^{2+} ion. Thus, we assigned the emission band with peak at 2.1 eV to the well-known orange emission of Mn^{2+} ions in ZnS nanocrystals.

The dependence of the PL intensity on Mn doping concentration is shown in Fig. 2 and Fig. 3 respectively for the Mn doping concentration of 6 and 7 at% (Fig. 2) and of 8, 9, 10, 11, and 12 at% (fig. 3). It is shown that for the orange emission (2.1 eV) the PL intensities reach their maximum at the Mn concentration of about 9 at%. At higher concentration, the intensity of both the PL bands quenched. It is noted that the above mentioned Mn concentration is the calculated based on the starting concentration of Mn in the sample preparation process. The real Mn concentration in the obtained nanocrystals may be less than this number).

To study the effect of UV irradiation time on the PL intensity of the Mn-doped ZnS nanocrystals, the PL measurements were performed in such a way that the PL spectrum was recorded at different time while the UV light was continuously excited on the sample. In our experiment, the irradiation time was selected to be 60, 120, 180, 240, 300 s (second). Samples with different Mn doping concentrations of 6, 9, and 12 at% were subjected to

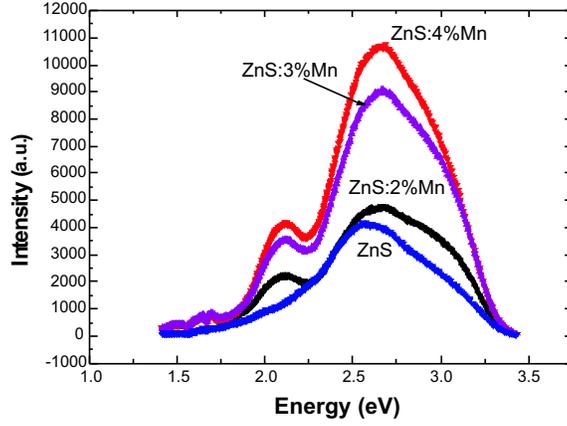


Fig. 1. PL spectra of Mn-doped ZnS samples with Mn doping concentration of 0; 2; 3 and 4 at%; excitation wavelength 325 nm at 300 K

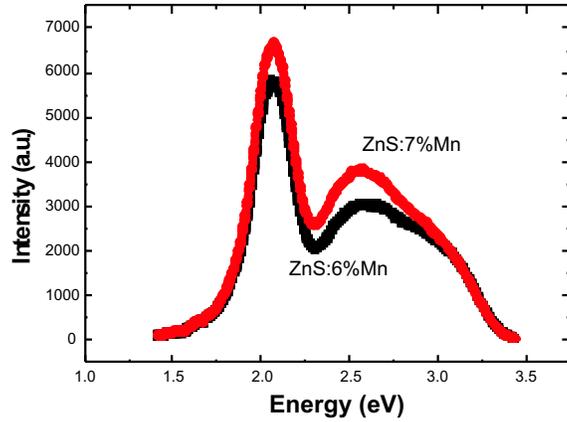


Fig. 2. PL spectra of the Mn-doped ZnS nanocrystals with Mn doping concentration of 6 and 7 at%; excitation wavelength 325 nm at 300 K.

the measurements. The photoluminescence spectra of the ZnS nanocrystals doped with 6 at% Mn is shown in Fig. 4. We can see in Fig. 4 that the PL intensity of the 6 at% Mn-doped ZnS nanocrystals increased when the irradiation time is prolonged. In contrast, the positions of both the 2.1 and 2.7 eV peaks remained unshifted. The UV irradiation time dependence of the PL intensity of the Mn-doped ZnS nanocrystals can be explained using the schematic for the decay of electrons in Mn-doped ZnS nanocrystals as has been reported in ref. [9] and shown in Fig. 5. We can see in the Fig. 5, the efficient energy transfer of the excitation happened from hot semiconductor to the doped Mn sites closer in the ZnS conduction band and Mn-*d*-state. These processes are non-radiative transitions. Their mechanism has been studied by using several experimental methods including photothermal (PT), and photoacoustic (PA) methods. In the PT method, one

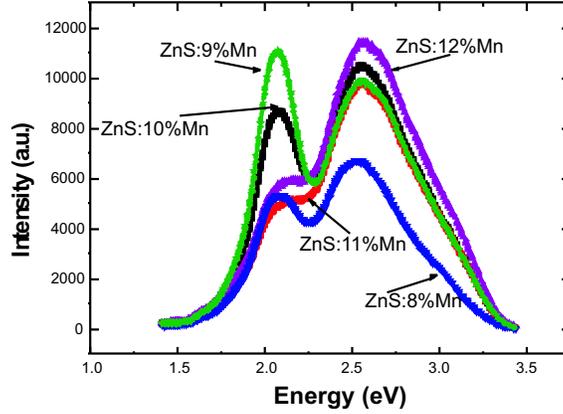


Fig. 3. PL spectra of Mn-doped ZnS nanocrystals with Mn doping concentration of 8; 9; 10; 11 and 12 at%; excitation wavelength 325 nm at 300 K.

detects signal directly proportional to the thermal energy (heat production) induced by the absorbed photons. The photoacoustic (PA) method is a (PT) technique, which detects acoustic energy produced by heat generation due to non-radiative processes in materials [8]. When UV irradiation illuminated on the sample, the optical absorption was happened. This UV irradiation process generates an electron-hole pairs across the band of hot ZnS nanocrystals. This process of optical absorption and the non-radiative transition are the steps in the complex process leading to luminescent of materials.

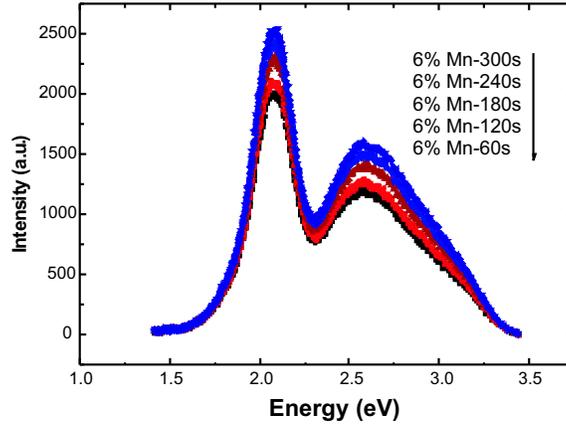


Fig. 4. PL spectra of ZnS:Mn with the Mn doping concentration of 6 at% measured after UV irradiation times of 60, 120, 180, 240, and 300 s.

Similar results are obtained for the ZnS nanocrystal samples doped with 9, and 12 at% Mn. The PL spectra of the samples doped with different Mn doping concentration of 6, 9, and 12 at% and irradiated for 90 s are shown in Fig. 6. One can see that the PL intensity of both the 2.1 and 2.7 eV peaks is highest for the sample doped with 9 at%

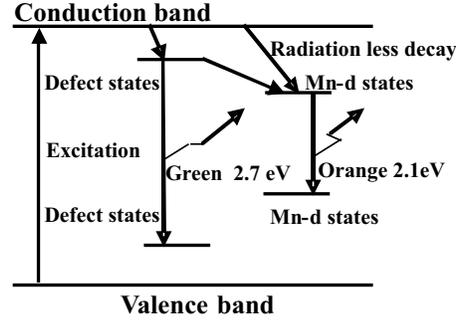


Fig. 5. Schematic for the decay of electrons in Mn doped ZnS nanocrystals, as reported in Ref. [9].

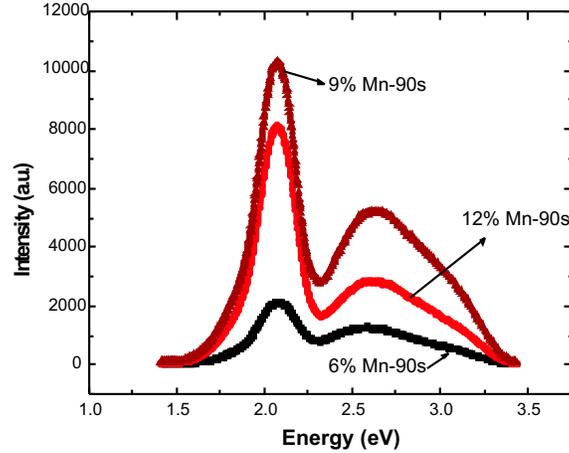


Fig. 6. PL spectra of the ZnS:Mn nanocrystals with Mn doping concentration of 6, 9, and 12 at% measured after UV irradiation for 90 s.

Mn. From all these results, and based on the schematic for the decay of electrons, Fig. 5, it can be attributed the non-radiative transitions to create stronger $d - d$ transitions of Mn^{2+} ions (2.1 eV orange luminescent) when UV irradiation time increased. Due to non-radiative transitions of the excitation happened from hot semiconductor to the doped Mn sites closer in the ZnS conduction band and Mn- d -state, the PL intensity of the 2.1 eV band enhanced stronger than that of the 2.7 eV band as seen in Fig. 3.

Fig. 7 shows the dependence of the PL intensity of the 2.1 eV emission band (orange emission) on the UV irradiation time for ZnS:Mn nanocrystal samples with Mn doping concentration of 6, 9, and 12 at%. As can be seen, these curves have the tendency to saturate with increasing irradiation time. Similar behavior is obtained for the the 2.7 eV band under continuous UV irradiation. These results are in good agreement with those previously reported in Ref. [8].

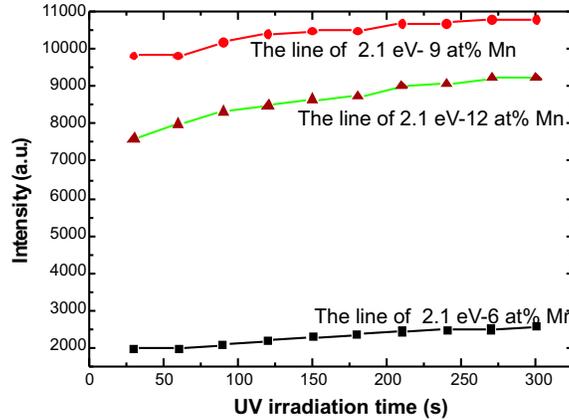


Fig. 7. The dependence of the PL intensity of the 2.1 eV emission band (orange emission) on the UV irradiation time for ZnS nanocrystal samples with Mn doping concentration of 6, 9, and 12 at%.

IV. CONCLUSION

ZnS nanocrystals doped with Mn^{2+} ions were prepared by the wet chemical method. The dependence of Mn^{2+} ions doped concentration, and UV irradiation time on the luminescent intensity of ZnS:Mn nanocrystals was studied. It is shown that the PL intensity of the ZnS:Mn nanocrystals achieved maximum for samples with Mn doping concentration of 9 at%. The PL intensity of both the 2.1 and 2.7 eV emission band is enhanced with increasing UV irradiation time.

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