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Effect of Mn low concentration on the optical properties of ZnO nanocrystals

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ABSTRACT

ZnO and ZnO:Mn nanocrystals synthesized via reverse micelle method. The size, band gap, Urbach energy, optical constants and penetration depth of nanocrystals were calculated by UV-vis spectroscopy data. The surface morphology was studied with the use of scanning electron microscope (SEM). Moreover the samples exposed to Gama ray source of ^{60}Co and their thermoluminescence properties were also investigated.

Keywords: *ZnO; Nanocrystals; Reverse micelle; Optical properties*

INTRODUCTION

Zinc oxide, a typical II–VI compound semiconductor, with a direct band gap of 3.37 eV at room temperature and 60meV as exciton binding energy, is a very good luminescent material used in displays, sensors, ultraviolet and visible lasers and solar cells components. The physical properties of ZnO have been intensively investigated focused mainly on the characterization of its optical and electrical properties [1]. Doping is a widely used method to improve the electrical and optical properties of semiconductors [2]. In this work, we indicate the synthesis of ZnO and ZnO:Mn nanocrystals that obtained via reverse micelle method and their optical properties were compared.

EXPERIMENTAL

Preparation

ZnO nanocrystals were fabricated through the mixture of two micro emulsion systems. In micro emulsion (I) hexane as oil, AOT as surfactant and zinc acetate (or zinc acetate and manganese acetate for ZnO:Mn nanocrystals) and water as aqueous phase were used in solution.

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Micro emulsion (II) has similar mixture but instead of previous aqueous solution, the potassium hydroxide and water were used as aqueous media. The two micro emulsion solutions (I) and (II) were mixed vigorously with a magnetic stirrer. Then centrifugation took place and the precipitation was kept at 250 ^{o}C for 3 hours, till ZnO and ZnO:Mn nanocrystals were fabricated.

Characterization

The products were analyzed by UV-Vis spectrometer (PERKIN ELMER, Lambda 45), scanning electron microscopy (Philips-XL30) and TLD reader (HARSHAW 4500).

RESULTS AND DISCUSSION

Optical study

The optical characteristic of the samples are investigated by the absorption and the transmittance measurements in the range of 200 – 700 nm. Figure 1 shows the UV–Vis absorption and transmittance spectra of ZnO nanocrystals. The excitonic absorption peak is observed due to the ZnO and ZnO:Mn nanocrystals at 347 and 355 nm, which lies much below the band gap wavelength of 388 nm of bulk ZnO[3].

The following equation derived using the effective mass model describes the particle size as a function of peak absorbance wavelength (λ_p) for ZnO nanocrystals.[3]

$$r(nm)=\frac{-0.3049+\sqrt{-26.23012+\frac{1024072}{\lambda_p(nm)}}}{-6.3829+\frac{2483.2}{\lambda_p(nm)}} \qquad (1)$$

Our prepared ZnO and ZnO:Mn nanocrystals show peak absorbance at 347 and 355 nm which corresponds to the average particle size of 3.8 and 4.2 nm. The transmission spectrum decreases in ultra violet region rapidly, until receive the minimum value, shows the strong interaction between light and electrons and it is higher for doped sample. Samples are much transparent at visible wavelength.

Absorption coefficient (α) associated with the strong absorption region of the sample was calculated from absorbent (A) and the sample thickness (t). It is calculated by relation (2) [4]:

$$\alpha = 2.3026\frac{A}{t} \qquad (2)$$

And extinction coefficient (k) was calculated by absorption coefficient (α) using the relation [5]:

$$k=\frac{\alpha\lambda}{4\pi} \qquad (3)$$

Where λ is the wavelength of absorption spectra. The absorption coefficient (α) and the extinction coefficient (k) as function of photon energy are shown in Figure 2.

We can calculate the optical band gap using the following relation [6]:

$$\alpha h\nu = B(h\nu - E_g)^n \qquad (4)$$

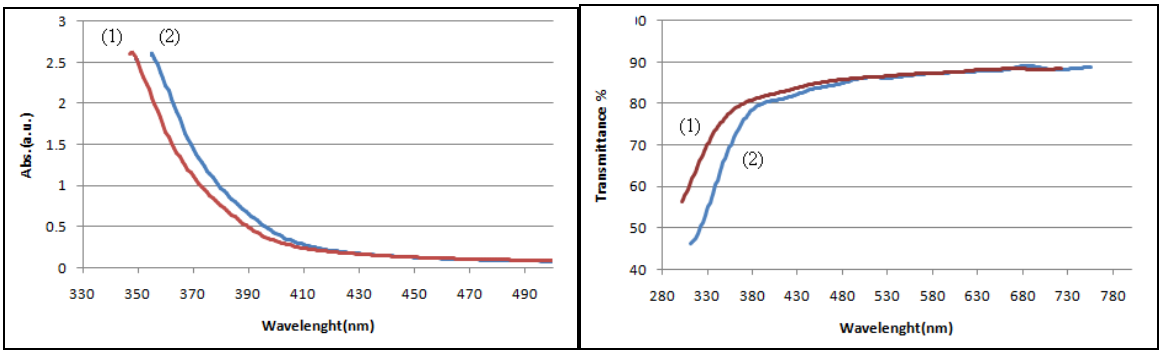

Fig.1. UV-Vis absorption and transmission characteristics of ZnO (1) and ZnO:Mn (2) nanocrystals.

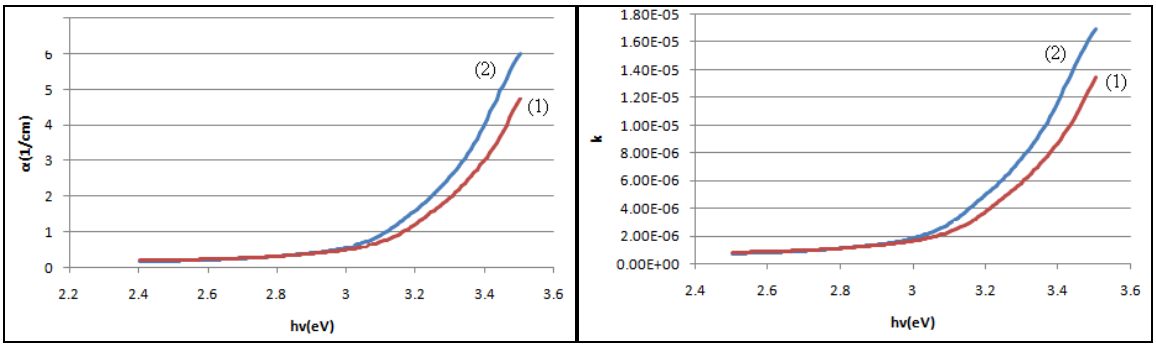

Fig.2. absorption coefficient (α) and extinction coefficient (k) as function of photon energy of ZnO (1) and ZnO: Mn (2) nanocrystals.

Where B is a constant and E_g is the optical band gap of the material. n value depends on the type of the transition which may have values 1/2, 2, 3/2 and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. But in the nanocrystalline sample, there may be some deviation from the bulk like transition. From the above equation, it is clear that, plot of $(\alpha h\nu)^2$ vs. hν will indicate a divergence at an energy value, E_g , where the transition takes place. The band gap value is depend on the nature of the transition (i.e., the n value) is determined. The estimated band gap from the plot of $(\alpha h\upsilon)^2$ versus hυ for ZnO nanocrystals can be seen in Figure 3. The band gap 'E_g' is determined by extrapolating the straight portion to the energy axis at α=0. The linear part shows that the mode of transition in these nanocrystals is direct nature. The calculated band gap value of the ZnO and ZnO:Mn were 3.4 and 3.34 eV. The ZnO:Mn nanocrystals band gap values are lower than bulk value of ZnO because the magnetic properties of ZnO:Mn nanocrystals increase by doped manganese and interaction potential become stronger in comparison with ZnO nanocrystals [7].

To calculate the width of the energy tail, ΔE, of the density of states, the model proposed by Urbach is presented and the following relation is valid [8]:

$$\ln(\alpha) = C + h\nu/\nabla E \qquad (5)$$

Where C is a constant and ΔE is the Urbach energy and is calculated by the inverse slope of the ln(α), vs. hυ plot (Figure 4). The Urbach energy was used to characterize the degree of disorderness (which would depend on the thermal history of the samples) in amorphous and crystalline systems. Materials with larger Urbach energy would have greater tendency to convert weak bonds into defects. Consequently, the defect concentration could be estimated by the measure of Urbach energy. The Urbach energy of ZnO and ZnO:Mn nanocrystals are 0.18 and 0.2 eV. It shows doping increases defects in nanocrystals.

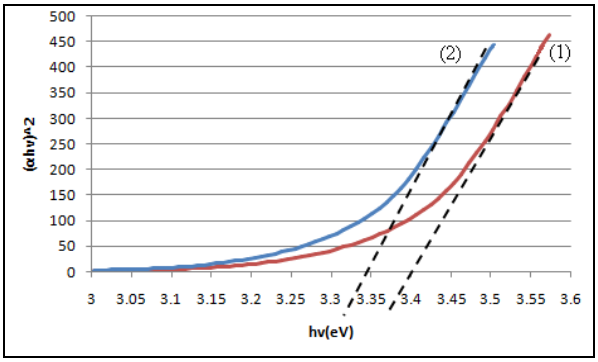

Fig.3. The plot of $(\alpha h\upsilon)^2$ versus hυ of ZnO (1) and ZnO:Mn (2) nanocrystals.

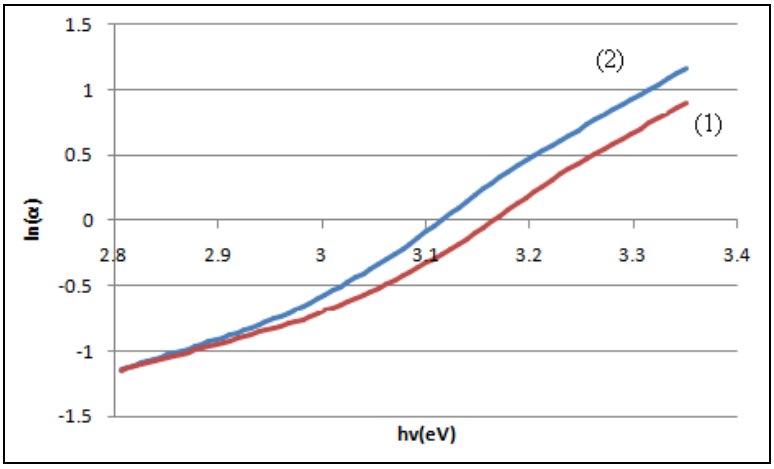

Fig.4. The variation of the ln(α) with hυ for ZnO (1) and ZnO:Mn (2) nanocrystals.

In order to evaluate the threshold wavelength (λ_s) value, UV–Vis spectra has been analyzed according to the following equation [9]:

$$(\frac{A}{\lambda})^2 = K(\frac{1}{\lambda} - \frac{1}{\lambda_s}) \qquad (6)$$

Where A, λ, and K are absorbance, wavelength, and an empirical constant, respectively. Plotting $(A/\lambda)^2$ vs. $1/\lambda$ from spectrum, the λ_S value was obtained from the intersection of the tangent drawn to the inflection point with the baseline; (Figure 5). It has been calculated that the threshold wavelengths (λ_s) are 367 and 374 nm for ZnO and ZnO:Mn nanocrystals.

One of important parameters in quantification optical properties of materials is penetration depth which is shown in Figure 6. Penetration depth is more for doped samples in visible wavelength and corresponds in ultra violet wavelength for samples. It can be useful application for optical equipments.

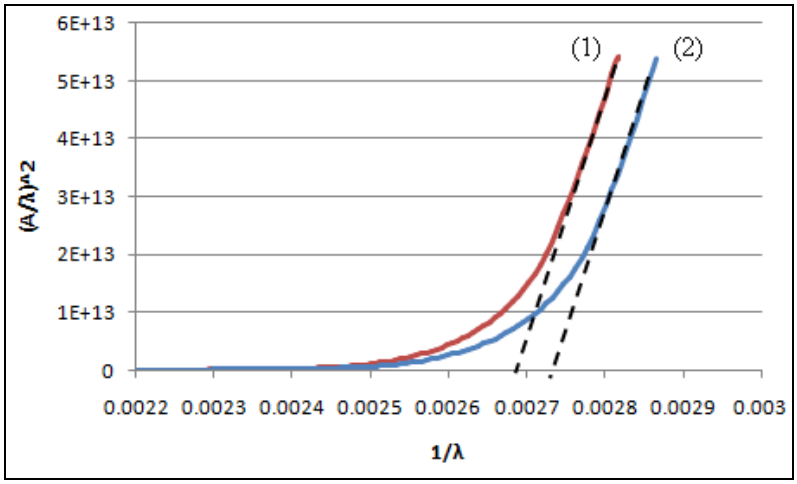

Fig.5. Typical $(A/\lambda)^2$ vs. $1/\lambda$ plot for ZnO (1) and ZnO:Mn (2) nanocrystals.

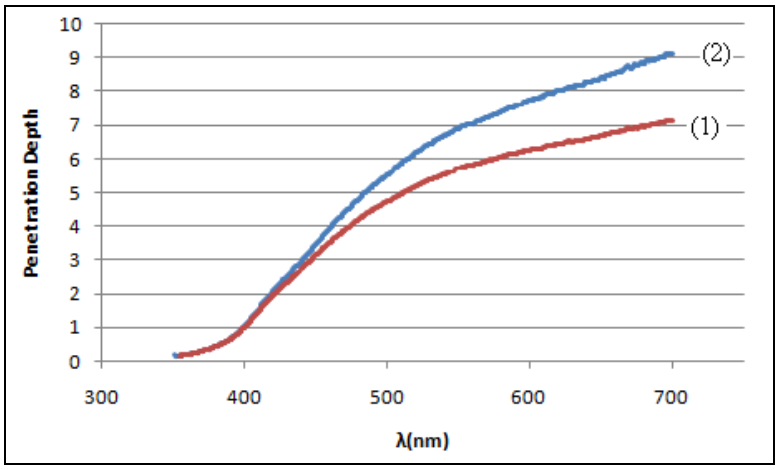

Fig.6. penetration depth for ZnO (1) and ZnO:Mn nanocrystals.

SEM studies

As observed in the experiments, nanocrystals were made within the first few minutes, but after a few minutes, because of their large surface to volume ratio the particles were aggregated and their size grew larger. In fact, due to the increase in the surface area to volume ratio, without coating of surfactant on the particles, the attractive force between the nanocrystals will increase, and the particles will agglomerate as well. Thus, the particle size becomes larger (Figure 7). SEM provides imaging of individual crystallites and the development of a statistical description of the size and shape of the particles in samples. SEM images of ZnO and ZnO:Mn nanocrystals are shown in Figure 7. It is worth mentioning that the ZnO aggregated particles were composed of much smaller crystallites. It is envisaged that the micron size particles as seen by SEM consist of large number of primary nanocrystallites which are detected by UV–Vis spectra.[10]

Thermoluminescence study

Figures 8 and 9 show the intensity of thermoluminescence of ZnO and ZnO:Mn nanocrystals exposed to Gama ray source of ^{60}Co. The study of thermoluminescence shows doping ZnO nanocrystals by manganese cause the improving of thermoluminescence and increases the sensitivity for Gama ray. Thus doping causes the improving of crystalline luminescence.

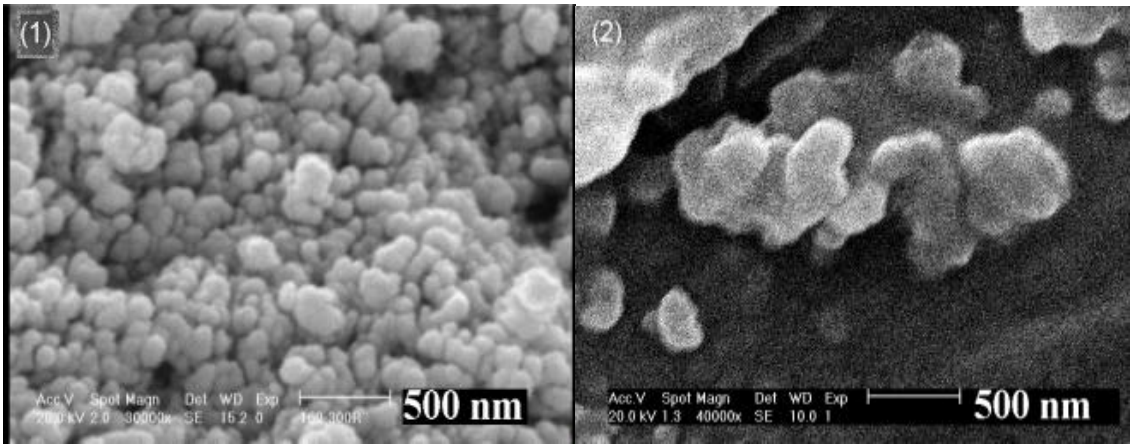

Fig.7. SEM micrograph of ZnO (1) and ZnO:Mn (2) nanocrystals at high magnification.

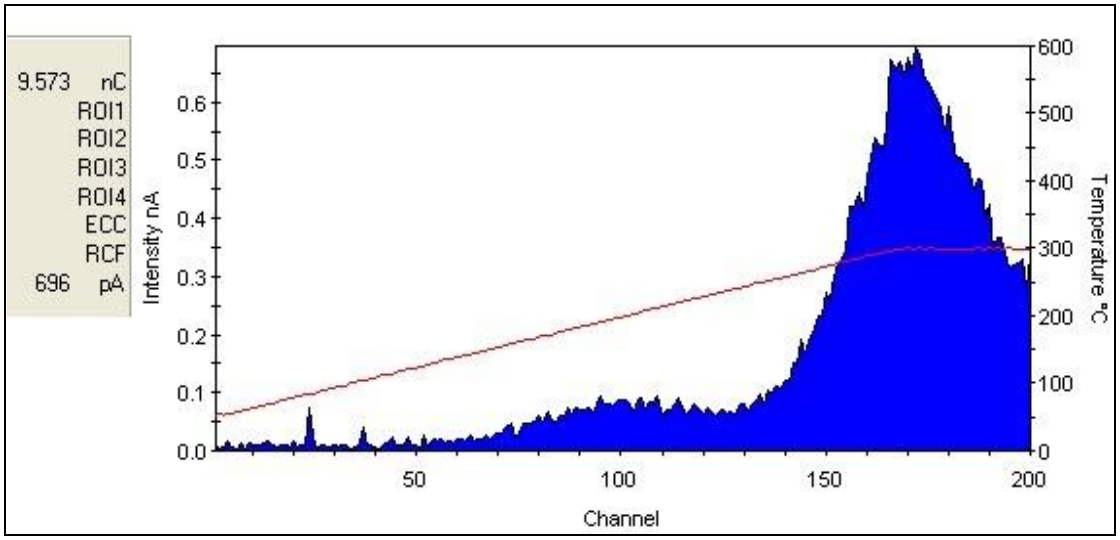

Fig.8. TL glow curves of ZnO nanocrystals.

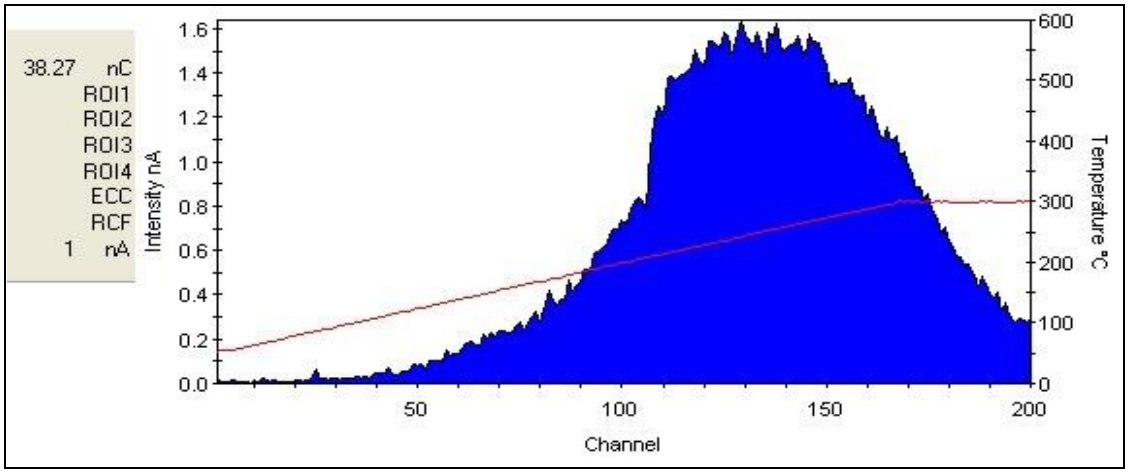

Fig.9. TL glow curves of ZnO:Mn nanocrystals.

CONCLUSION

ZnO and ZnO:Mn nanocrystals have been synthesized by the reverse micelle method using AOT as surfactant. The UV-vis studies revealed that their optical band gap energy is 3.4 and 3.34 eV, their Urbach energy is 0.18 and 0.2 eV and their threshold wavelength is 367 and 374 nm for ZnO and ZnO:Mn. Also, doping ZnO nanocrystals by manganese improves the thermoluminescence property and increases the sensitivity for Gama ray.

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