

Optical Properties of Fe²⁺ Ion Doped ZnS Nanoparticles Synthesized Using co-Precipitation Method

(Ciri-ciri Optik Ion Fe²⁺ Terdop Dalam Zarah Nano ZnS Disintesis Menggunakan Kaedah Pemendakan)

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ABSTRACT

Nanoparticles of Zn_{1-x}Fe_xS (x = 0.0, 0.1, 0.2 and 0.3) were prepared by chemical co-precipitation method from homogenous solution of zinc and ferum salt at room temperature with controlled parameter. These nanoparticles were sterically stabilized using Sodium Hexamethaphosphate (SHMP). Here, a study of the effect of Fe doping on structure and optical properties of nanoparticles was undertaken. Structure, elemental analysis and optical properties have been investigated by X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Fourier-Transform-Infrared spectroscopy (FT-IR), X-Ray Fluorescence (XRF), UV-Visible Spectroscopy and photoluminescence (PL) spectrophotometer. FT-IR and XRF results confirmed the incorporation of ion dopants into ZnS crystal structure, and XRD results showed that Zn_{1-x}Fe_xS (x = 0.00 and 0.10) nanoparticles crystallized in a zinc blende structure without any impurity. The particle size of all of samples ranged from 2 nm to 3 nm, as calculated by the Debye-Scherrer formula. The optical absorption spectra indicate a blue shift of the absorption edge with increasing Fe-content. The luminescence of nanoparticles excite at about 370 nm with an emission peak at around at 452 nm, 490 nm and 550 nm.

Keywords: Nanoparticles; ZnS:Fe²⁺; Sodium Hexamethaphosphate; luminescence

ABSTRAK

Partikel zarah nano Zn_{1-x}Fe_xS (x = 0.0, 0.1, 0.2 dan 0.3) telah disediakan dengan menggunakan kaedah pemendakan kimia dari larutan homogen zink dan garam ferum pada suhu bilik dengan parameter terkawal. Partikel zarah nano ini telah distabil menggunakan bahan penstabil Sodium Hexamethaphosphate (SHMP). Satu kajian telah dijalankan untuk mengkaji kesan unsur doping ion ferum terhadap struktur dan optik partikel zarah nano ZnS. Struktur, unsur dan optik telah dianalisis oleh pengukuran pembelauan sinar-X (XRD), Mikroskopi imbasan elektron peralihan (TEM), Infamerah Transformasi Fourier (FT-IR), X-Ray pendarfluor (XRF), spektrometer UV-Vis dan photoluminescence (PL) spectrophotometer. Pengukuran FTIR dan XRF mengesahkan kehadiran ion didalam struktur kristal ZnS. Analisis XRD menunjukkan partikel nano Zn_{1-x}Fe_xS (x = 0.00 and 0.10) terbentuk dalam kristal zink tanpa menunjukkan kehadiran benda asing. Saiz partikel yang dihasilkan adalah dalam lingkungan 2 nm kepada 3 nm seperti mana yang telah dikira dengan menggunakan formula Debye-Scherrer. Ciri-ciri optikal spektrum penyerapan menunjukkan anjakan biru dengan peningkatan kuantiti ion Fe. Ciri-ciri pendarkilau daripada nanopartikel teruja pada spektrum 370 nm dengan puncak pemancaran di sekitar 452 nm, 490 nm dan 550 nm.

Kata kunci: Partikel zarah nano; ZnS:Fe²⁺; Sodium Hexamethaphosphate; pemancaran

INTRODUCTION

During recent decades, investigation into the synthesis and characterization of nanoparticles continues to remain an active area of research (Brian et al. 2004; Enyong et al. 2011; Kanemitsu et al. 2006). The potential for exploitation of these fine particles have produced a great number of researches in fabricating novel material. The characteristics of nanoparticles depend directly on their size and shape. The synthesis of controlled shape and size of nanoparticles are of great importance to their application (Zhang et al. 2004; Amaranatha et al. 2011). By decreasing the size of the particles, it will increase the surface area to volume ratio. Particles with extremely high surface area

will increase the surface specific activity sites for chemical reactions and photon absorption to enhance the reaction and absorption efficiency (Muragados et al. 2010; Grieve et al. 2000). Among those area of research, Luminescence II-IV semiconductor like ZnS, CdS, CdSe nanocrystal are still in the great tract of research due to their unique properties and potential application in various devices such as sensor, solar cells, lasers, photocatalysts and etc (Sharma et al. 2012; Liua et al. 2011; Beaulac et al. 2008). Among these, ZnS has the largest energy band gap II-IV semiconductor (3.6 eV), direct transition type and non toxic (Zang et al. 2011).

Recently, many research reports that doping ZnS semiconductor with transition metal reveals a new class of luminescent materials due to the formation of dopant

levels within the band gaps and the modification of the band structure (Fang et al. 2011). These impurities affect the physical and chemical characterization of host materials. Incorporating suitable dopants is an approach to enhancing the potential of ZnS semiconductor as a phosphor. However, there are lacks of systematical studies on the optical properties of the Fe²⁺ ion doped ZnS nanoparticles (Hu & Zang 2006; Sambasivam et al. 2008).

The development of wide variety technique such as solvent thermal process (Yang et al. 2005), microemulsion method (Li et al. 2011) and co-precipitation (Eryong et al. 2011) are rapidly used among researchers to producing nanoparticles. However, most of the previous researches mainly focus on the production of nanoparticles with passivating agent to stop it from agglomeration (Naskar et al. 2006). This is due to that the majority of the system will undergo aggregation without passivation of the surface (Sakthi et al. 2012; Sambasivam et al. 2009). Unfortunately a lot of passivator agent are toxic and will pollute the environment and not suitable for industry scale (Xie et al. 2011). Therefore, in this study, we used Sodium Hexamethaphosphate (SHMP) as a passivator agent which was reported as non toxic, low cost and good enhancement in photoluminescence intensity (Saravanan et al. 2010; Warad et al. 2005). In the present work, Fe²⁺ ion doped ZnS nanoparticles were synthesized at room temperature by chemical co-precipitation method using SHMP as the capping agent. More emphasis was laid on the influence of Fe²⁺ ion doping on structure and optical properties of ZnS nanoparticles. All the samples were annealed at 300°C to induce crystallinity.

METHOD AND MATERIALS

The Zn_{1-x}Fe_xS nanoparticles with $x = 0.00, 0.10, 0.20$ and 0.30 were synthesized in a water-ethanol solution mixture by the co-precipitation method at room temperature. All the chemical reagents in the experiment were analytical grade purity. Zinc acetate (Zn(CH₃COO)₂·2H₂O) (R&M Chemicals), Iron acetate (Fe(C₂H₃O₂)₂·2H₂O) (R&M Chemicals), Sodium Sulfide (Na₂S) (R&M Chemical) and Sodium Hexamethaphosphate (SHMP) (NaPO₃)₆ (ALDRICH). Those chemical are used are of Zinc acetate and iron acetate as starting materials were weighed according to the stoichiometry $x = 0.0, 0.1, 0.2, 0.3$ and were dissolved in 100 ml of water-ethanol solution to make 0.5 M solution. The stoichiometric solution was taken in a burette and added in drops with continuous stirring for half an hour to a mixture of Na₂S (0.5 M) and 4 g of Sodium Hexamethaphosphate (SHMP) until fine precipitates are formed.

After complete precipitation, the solution was then centrifuged at 4,000 rpm for 5 minutes. The precipitated particles were filtered, washed several times using double distilled water and dried in vacuum oven at 40°C for 24 hours. Finally, the obtained powder will be annealed at 300°C in nitrogen atmosphere in horizontal furnace.

CHARACTERISATIONS

The X-ray diffraction (XRD) patterns of the powdered samples were obtained using a D8 Advance AXS X-ray diffractometer at diffraction patterns that ranged from 20° to 80°. The crystal size was estimated using Scherrer equations $(0.9\lambda)/(\beta\cos\theta)$ at full width half maximum (FWHM) of the XRD peaks. Fourier transform-infrared (FT-IR) spectra were obtained using a NICOLET 6700 FT-IR spectrophotometer to determine chemical interaction. XRF analysis using Philips PW 1480 fully automated X-Ray fluorescence system (XRF) to determine the element and quantitative analysis. The optical absorption spectra of all samples in ultra-pure H₂O were obtained using an AMBDA 35 ultraviolet (UV) spectrometer. The fluorescence measurements were performed on a photoluminescence (PL) SP920 spectrophotometer.

RESULTS AND DISCUSSION

STRUCTURE ANALYSIS

The influence of Fe²⁺ ion in ZnS crystal structure can be discussed by observing the results of the X-ray diffraction pattern for these samples of Zn_{1-x}Fe_xS ($x = 0.00, 0.10, 0.20, 0.30$) nanoparticles. The diffraction patterns were recorded over the range of 20° – 80°. Figure 1 shows the XRD patterns of undoped ZnS and Fe²⁺ doped ZnS ($x = 0.10$), these are three diffraction peaks at 2θ value 28.5°, 48.3° and 56.5° which corresponding to the (1 1 1), (2 2 0) and (3 1 1) planes. These peaks matched very well with the cubic zinc blended structure (JCPDS No. 05-0566), confirming the purity of the synthesized ZnS. No impurity peak was observed, which indicated the formation of high-purity ZnS nanoparticles. Moreover, the broadening of XRD pattern showed the formation of nanosized particles. Based on the FWHM, the most intense peak corresponded with the (111) plane, the substitution of Zn²⁺ ion with Fe²⁺ ion resulted in a large decrease (~50%) in the lattice constant of ZnS. Lattice contraction was believed to be due to the differences in ionic radii among ions. The ionic radii of Zn²⁺ is 0.74 Å compare to 0.645 Å of Fe²⁺ ionic radii. Therefore, adding small amounts of these ion dopants affected the internal pull force of ZnS molecule and caused nanoparticles to shrink. Furthermore, the broadening of peaks suggests the small size of nanocrystal.

In addition, further increasing the amount of ion doping ($x = 0.20$ and $x = 0.30$) the XRD patterns showed additional peaks at 20° and 37°. The XRD peaks for $x = 0.2$ and 0.3 , which indicate that the sample is nearly amorphous, are too weak to be calculated. Noticeably, the intensity of the main peaks decreases with the increase of Fe concentration, indicating the degeneration of the crystalline quality. It is believed that the Fe doping can reduce crystallinity. However, crystallite size can be calculated according to the Debye-Scherrer formula (Uekawa et al. 2010).

$$D = k\lambda / \beta \cos \theta \quad (1)$$

Where $k = 0.89$, D represent coherent length, λ is the X-ray wavelength and β is the Full Wave Half Maximum (FWHM) of diffraction peak and θ is the diffraction angle. Based on the FWHM of the most intense peak (1 1 1), the average crystalline sizes were estimated to be 2.18 nm for

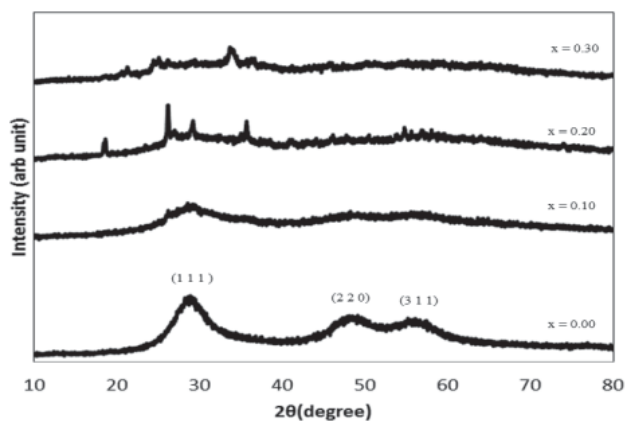


FIGURE 1. XRD scan of $Zn_{1-x}Fe_xS$ ($x = 0.0, 0.1, 0.2, 0.3$) annealed at $300^\circ C$

undoped ZnS and 2.04 nm for $Zn_{0.9}Fe_{0.1}S$. Decreasing the sizes of the particles indicate that Fe^{2+} ion occupied with the ZnS crystal structure. The particle size was also obtained using TEM.

As shown in the TEM image in Figure 2(a)-2(d), undoped ZnS had uniformly distributed spherical nanoparticles (<50 nm). The images provided indirect evidence of successful capping on the sample surface by SHMP for undoped ZnS. However, the image of a sample doped with ZnS showed a crosslinked polymeric structure on TEM. The matrix, being too dense to allow penetration of the incident electron beam with some nanoparticles, was not directly observed. Therefore, nanoparticles were embedded within the matrix, referring to the undoped ZnS image of TEM.

ELEMENT ANALYSIS

The passivation of surface of $Zn_{1-x}Fe_xS$ nanoparticles by the stabilizing agent of SHMP can be inferred from the FTIR spectroscopy. FTIR spectra of undoped ZnS and Fe^{2+} ion doped ZnS nanoparticles were recorded in the range $400 - 4000\text{ cm}^{-1}$ as shown in Figure 3. The FTIR samples exhibited ZnS characteristic peaks at 1084 cm^{-1} and 537 cm^{-1} with the new

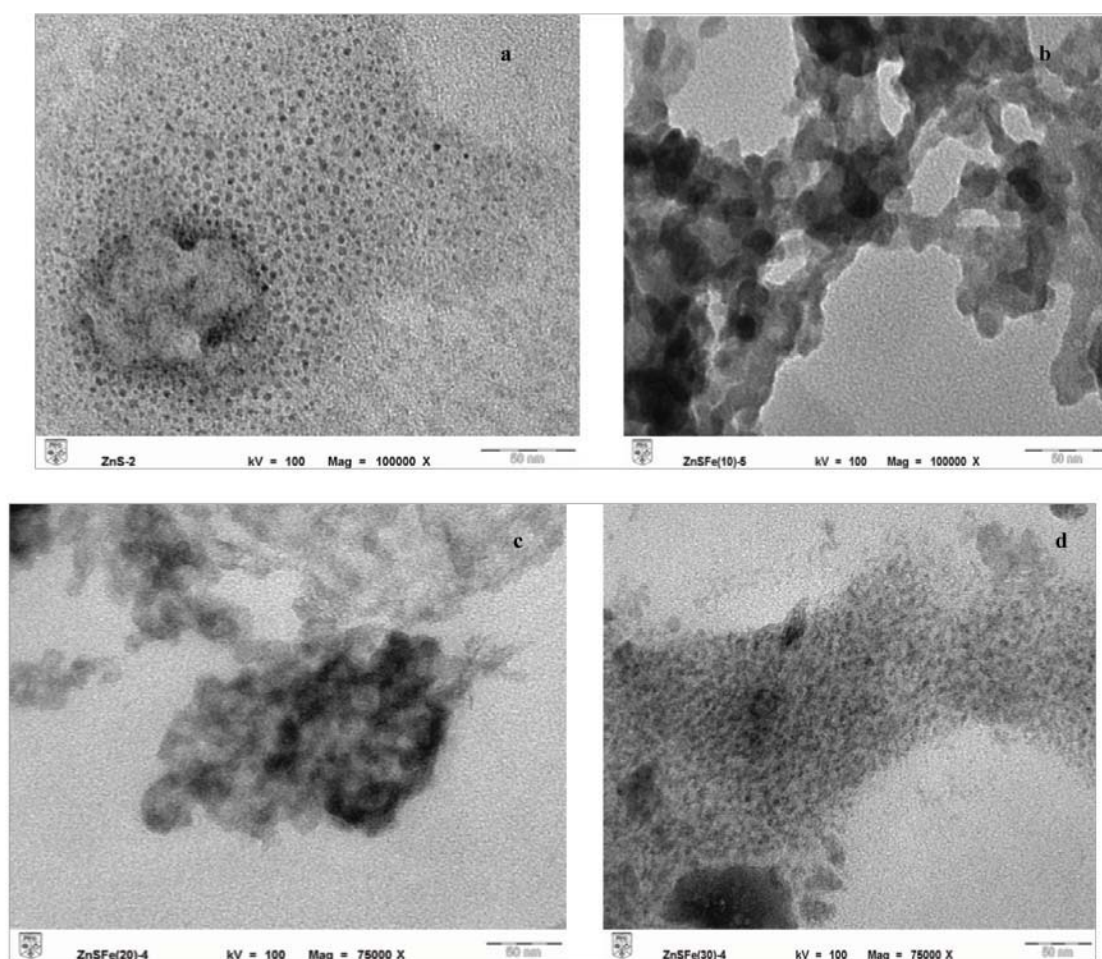


FIGURE 2. Transmission electron microscopy (TEM) analysis (a) undoped ZnS (b) $Zn_{0.9}Fe_{0.1}S$ (c) $Zn_{0.8}Fe_{0.2}S$ (d) $Zn_{0.7}Fe_{0.3}S$

peaks arise at 1020 cm^{-1} and 877 cm^{-1} for Fe^{2+} doped ZnS ($x = 0.10$) were due to Fe-S vibration. This observation suggested that Fe^{2+} ion were embedded in the ZnS nanostructure. The FTIR spectra also showed peak at 1612 cm^{-1} , representing the nitrogen–hydrogen interaction while The FT-IR broad absorption peaks ranging from 3000 cm^{-1} to 3600 cm^{-1} , corresponded with the $-\text{OH}$ group, indicated the presence of water absorbed on the nanoparticle surface. These suggested that some of Zn^{2+} ions had been replaces by Fe^{2+} ions in the cationic side of ZnS particles.

However, to further confirm the present of ion Ferum in ZnS nanoparticles structure as prepared in the experiment, XRF analysis was applied to determine the element and quantitative analysis. Table 1 presents the results of element contents in the samples. The major elements of all samples are Zn and S, while the minor element is Fe and it's approaching the doping value in the experiments. The results from XRF give the confirmation of using co-precipitation method to achieve the appropriate of amount substitution of ion Fe^{2+} in ZnS nanoparticles structure.

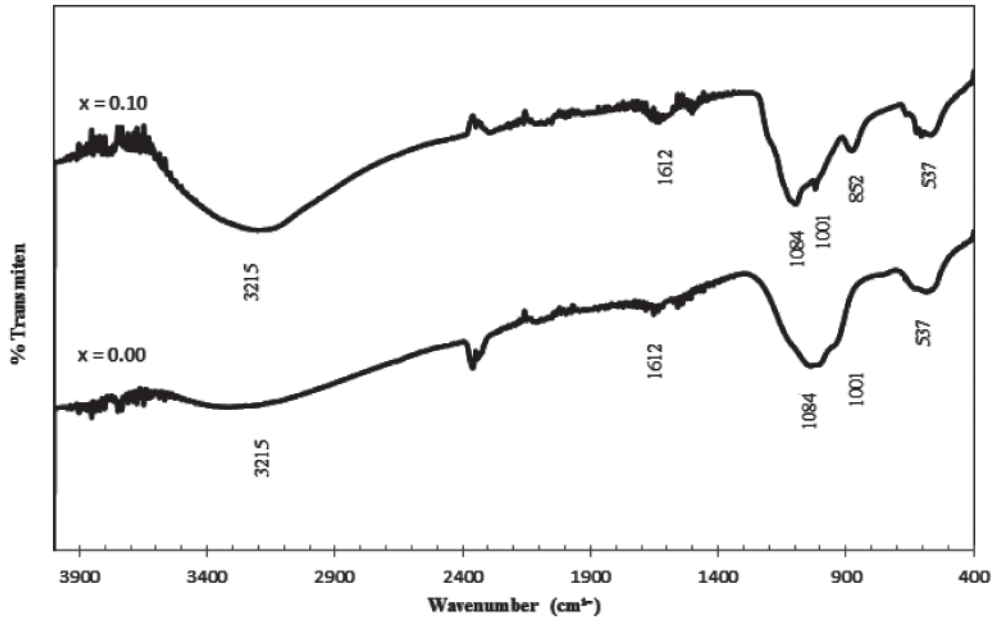


FIGURE 3. FTIR spectra of SHMP cap of ZnS and $\text{Zn}_{0.9}\text{Fe}_{0.1}\text{S}$ nanoparticles

TABLE 1. XRF value as a function of composition (x) in $\text{Zn}_{1-x}\text{Fe}_x\text{S}$ nanocrystals

Composition (x)	Doping value (%)	XRF value (%)
0.10	10	6.8
0.20	20	17.8
0.30	30	27.9

OPTICAL ABSORPTION AND OPTICAL BAND GAP

UV-Vis spectroscopy is a simple and useful tool for the characterization of ZnS nanoparticles, since the nature of the spectrum is dependent on the size of the nanoparticles due to the quantum confinement effect (Sen et al. 2010). Absorption of electromagnetic by a semiconductor results in the excitation of the electron from the valance to the conduction band and being displayed by UV-Vis spectra interval. Figure 4 have showed the absorption threshold was observed to lie at 240 nm for undoped ZnS. However, for doped ZnS nanoparticle, we can witness the dramatic change on UV-visible spectra which being shifted to the lower value to 220 nm ($x = 0.10$) and 230 nm ($x = 0.3$). While for $x = 0.2$,

the UV-visible spectra showing the differences of absorption threshold. The maximum absorption edge showed at 260 nm while the minimum absorption edge showed at 340 nm . The differences of absorption spectrum were due to the different size of nanoparticles appear. This implies UV-Vis spectrum can give a direct estimation of the semiconductor bang-gap (E_g), (Calandra et al. 1999).

The relation between absorption coefficients (α) and incident photon energy ($h\nu$) can be written as (Calandra et al. 1999).

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (2)$$

where E_g is the material band gap, A is a constant, and the exponent " n " depends on transition type. The values of " n " may be $1/2$, 2 , $3/2$, and 3 , and these values corresponded with allowed direct, allowed indirect, forbidden direct and forbidden indirect transition, respectively. The direct band gap with $n = 1/2$ was obtained by extrapolating the straight portion of the plot of $(\alpha h\nu)^2$ versus $h\nu$ on $h\nu$ axis at $\alpha = 0$. Figure 5 shows the band gap value for undop ZnS and doped ZnS. The changes of band gap corresponding with the absorption edge as showed in Figure 4. The band gap energy

value was in the range of 3.9–5.7 eV. The blue shift of doped ZnS is attributed to the quantum confinement effect.

When particles size is smaller than 3 nm, high quantum confinement is observed where the crystallite size is smaller than the Bohr radius (Kripala et al. 2010). In theoretical, the activation energy for conduction is smaller in smaller particles and increasing of the band gap cause the increasing in the conductivity (Zhu et al. 2010). While compared to bulk ZnS, which gave absorption, peak at 340 nm with band gap of 3.6eV (Chen et al. 2005). So that, the activation energy for conduction is higher in these samples compare to bulk ZnS.

This phenomena can be explained on the basic of Ostwald ripening (Steitz et al. 2008). During the onset of nucleation, the surface energy of the particles are of the highest level, thus the surface is passivated by adsorption of anion in the solution (Ac^{-1} and S^{2-}). The accumulation of anions in turn attracts cations (Zn^{2+} , Fe^{2+} and Na^{2+}) towards the surface of the particles. Ion Zn^{2+} and Fe^{2+} react with the S^{2-} which are more reactive than Ac^{-1} and get incorporated into the crystal lattice.

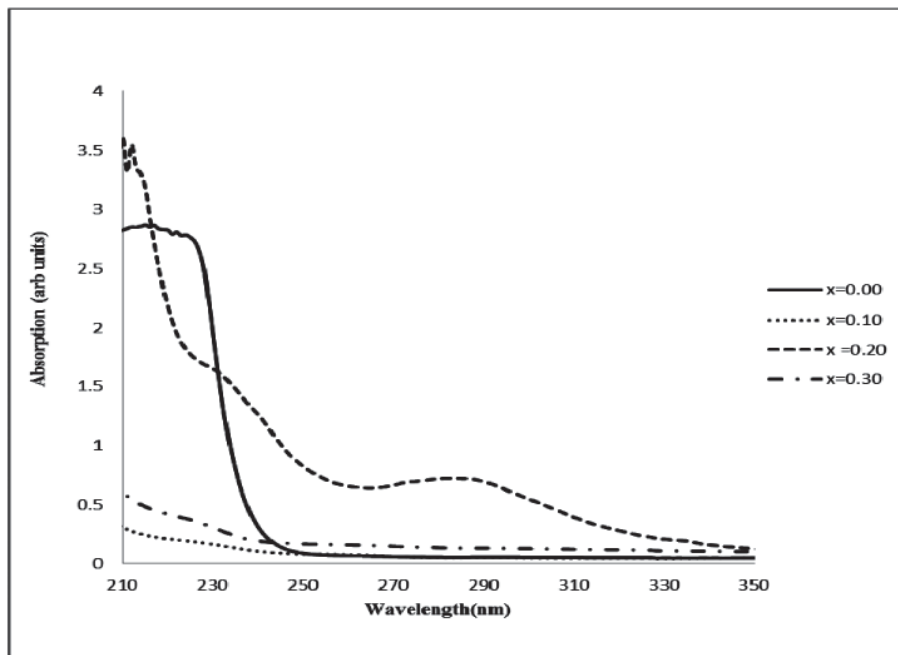


FIGURE 4. Optical absorption spectra of $Zn_{1-x}Fe_xS$ with $x = 0.00, 0.10, 0.20$ and 0.30 nanoparticles

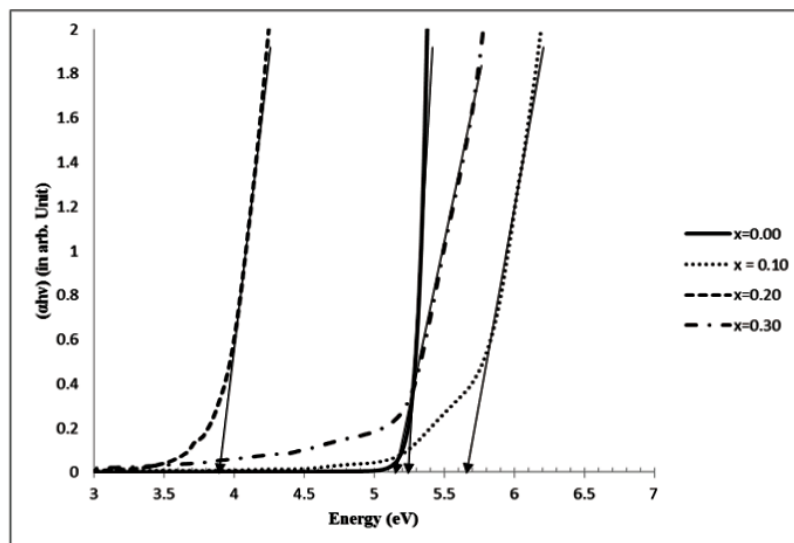


FIGURE 5. Optical band gap of $Zn_{1-x}Fe_xS$ with $x = 0.00, 0.10, 0.20$ and 0.30 nanoparticles

PHOTOLUMINESCENT STUDIES

The excitation spectra of undoped and Fe²⁺ doped ZnS nanocrystals in the wavelength range 320–420 nm are shown in Figure 6. However, only excitation spectrum for Zn_{1-x}Fe_xS with ($x = 0.1$) is only shown for doped ZnS. The excitation spectrum of ZnS appears broader with a high intensity maximum at 370 nm. This observation suggests the presence of defect bands. The excitation spectrum of Zn_{0.9}Fe_{0.1}S also exhibits at 370 nm peak with decrease intensity of the spectrum indicating the suppression of defect band on Fe-

doping. The emission spectra of Zn_{1-x}Fe_xS with ($x = 0.0, 0.1, 0.2$ and 0.3) are shown in Figure 7. The emission for $x = 0.00$ and 0.10 occurs similarity at 440 nm, 452 nm, 468 nm, 500 nm, and 550 nm. The presence of multiple peaks indicated the involvement of different PL centers in the radiation process. Again, the emission intensity for Fe doped ZnS is less than the ZnS host. However, for Zn_{1-x}Fe_xS ($x = 0.02$ and 0.03), there is showed slightly emission at 452 nm and 550 nm. Hence, in all Zn_{1-x}Fe_xS nanocrystals, the iron size acts to quench the fluorescence emission of host. For $x = 0.1$, there is less decrease in the emission intensity; while for higher x , there

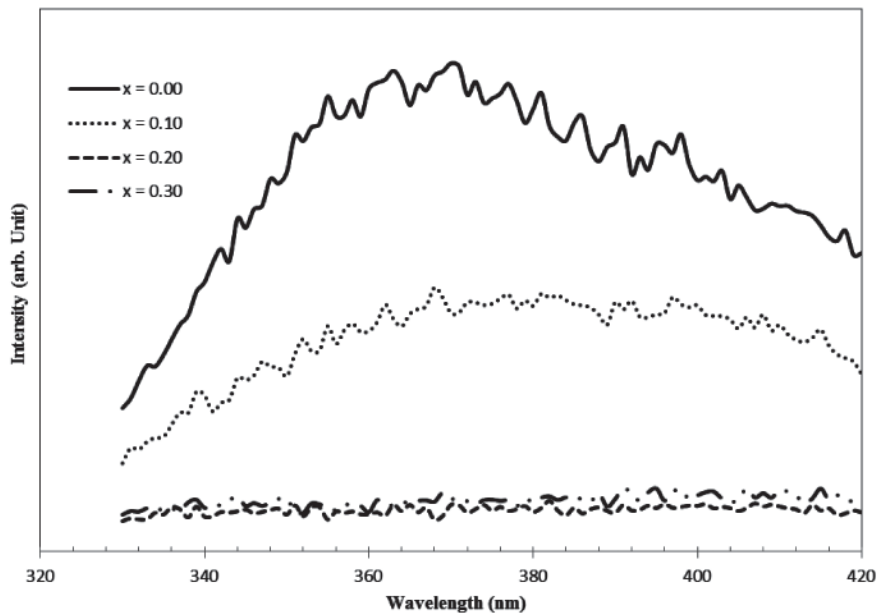


FIGURE 6. Photoluminescence excitation spectra of Zn_{1-x}Fe_xS with ($x = 0.0, 0.1, 0.2, 0.3$)

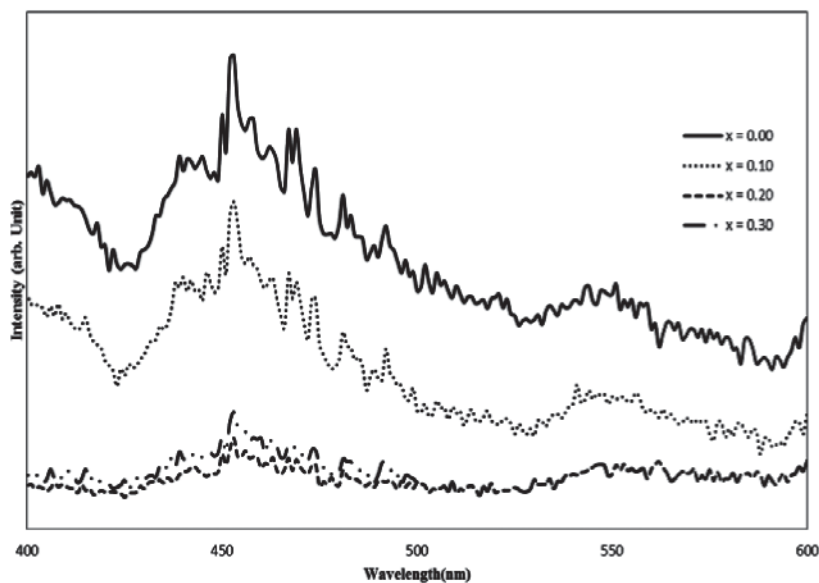


FIGURE 7. Photoluminescence emission spectra of Zn_{1-x}Fe_xS with ($x = 0.0, 0.1, 0.2, 0.3$)

is much more decrease in intensity. The similar quenching effect in Fe doped ZnS nanoparticles have been observed consistent with the data of excitation spectra in Figure 6 (Sambasivam et al. 2009). Fe²⁺ ion seem to act as quenching centers of fluorescence. These results are consistent with the data of excitation spectra in Figure 6.

These results showed that defects were due to uncontrolled particle nucleation and growth during chemical synthesis using the co-precipitation method. Furthermore, the solubility of ZnS ($K_{sp} = 10^{-25}$) was less than that of FeS (8×10^{-19}); thus, the successful rate for ion Fe²⁺ replacing ion Zn²⁺ was higher despite with the small amount of doping ratio. This finding revealed that particle growth was controlled during chemical synthesis. PL spectra provided an excellent and precise representation of a growing ion dopant in the host of ZnS nanoparticle formation thus provided an excellence method of studying the formation of Fe²⁺ doped ZnS nanoparticles during chemical synthesis.

CONCLUSION

Nanoparticles of Ferum ion doped Zinc Sulphide have been successfully synthesized by co-precipitation method. Enhanced quantum confinement effect operates in the presence of the capping agent and annealing process. In this study, the band gap has increased tremendously when compared to bulk ZnS with decreasing size to 2.04 nm. The particles distribution show higher uniformity for Zn_{0.9}Fe_{0.1}S nanocrystals corresponding with the increasing in the absorption values in UV-Vis spectra and band gap energy. The optical absorption spectra indicate a blue shift of the absorption edge with increasing Fe-content. The luminescence of nanoparticles excite at about 370 nm with an emission peak at around at 452 nm, 490 nm and 550 nm.

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