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Modifying the electronic and optical properties of nano ZnS via doping with Mn and Fe

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Abstract

5% Fe and Mn-doped nano ZnS ($\text{Zn}_{0.95}\text{A}_{0.05}\text{S}$, A=Fe or Mn) was prepared using the thermolysis technique. The effect of Fe and Mn doping on the lattice parameter, crystallite size, and lattice microstrain was examined applying Rietveld refinement. The analysis showed the incorporation of Fe and Mn substitutionally for Zn ions; a result confirmed by Fourier transforms infrared spectroscopy spectra from the shift in the vibration bands upon doping. The energy of ZnS band gap was reduced by doping, giving ZnS new applications. The different defects inside the different samples were investigated using photoluminescence spectroscopy. The effect of Fe/ Mn doping and incorporation of atmospheric oxygen on the bandgap characteristics, the absorption, optical conductivity, refractive index and the extinction coefficient, reflectance, the real and imaginary parts of the dielectric constant were explored using density function theory calculation (DFT).

Keywords: Nano ZnS; Mn, Fe doping; structure; optical properties; electronic properties.

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1. Introduction

Semiconductor materials with particular characteristics such as appropriate band gap and good adsorption in the visible range can be used in many applications [1]. ZnS (3.72-3.77 eV) is one of the wide-band-gap II–VI semiconductor materials that has been widely studied as an important phosphor material for promising optoelectronic and photonic applications [2]. As the crystallite size of the ZnS nanocrystal decreased below its Bohr excitonic radius, the band structure was changed, and all the optoelectronic characteristics were improved. ZnS has two common crystal structures: Hexagonal wurtzite and cubic zinc blend at room temperature [3]. Furthermore, the absorption edge of ZnS is shorter than 340 nm, which permits only high-energy ultraviolet (UV) light absorption [3]. This light absorption edge can be redshifted upon doping the material with a suitable dopant element [3]. For example, as the semiconductor materials doped with transition metals such as Ni, Co, Mn, Fe..., the formed materials exhibited more exotic characteristics because of spin-spin exchange interactions [4-8]. For instance, doping ZnCdSe/ZnS core/shell quantum dots with Fe, the emission intensity was improved [9]. The energy band gap of nano $\text{Zn}_{1-x}\text{Fe}_x\text{S}$ formed by aqueous synthesis derived was increased as the amount of Fe increased in the matrix due to Burstein-Moss filling effect [4, 10]. Also, the photoluminescence (PL) intensity of orange-red emission was improved by increase in the Fe^{3+} doped amount in the ZnS matrix [4]. On the other hand, the PL intensity in Fe-doped ZnS with wurtzite structure revealed a quenching behavior at a higher Fe-doping amount [11]. Wang et al. showed that the optical band gap of ZnS formed by one-pot hydrothermal procedure was decreased as it doped with Fe [3]. Yu et al. found that Fe:ZnSe transparent ceramics prepared by co-precipitation method and spark plasma sintering have a reddish-brown color and can act as a promising mid-infrared laser material [12]. Mahmood et al. found by applying the first-principle approach that the bandgap of ZnS can be tunable from ultraviolet to visible regions as it doped with iron doping [13]. The energy gap of nano $\text{Zn}_{0.75}\text{Cd}_{0.25}\text{S}$, was reduced upon doping with a small amount of Fe, then it increased with further Fe doping [8]. Also, the emitted colors of Fe doped nano $\text{Zn}_{0.75}\text{Cd}_{0.25}\text{S}$ depended on the excitation wavelengths and the amount of Fe-doping [8]. Furthermore, $\text{Zn}_{0.55}\text{Fe}_{0.2}\text{Cd}_{0.25}\text{S}$ showed weak ferromagnetic characteristics [8]. Scanning tunneling spectroscopy spectra revealed a decrease in the electronic band gap in both CdS and ZnS upon doping with Mn [14]. Mn:ZnS demonstrated a rigid band shift toward higher bias, which is reminiscent of a hole-doping effect while Mn:CdS exhibited no rigid band shift [14]. Barman et al. found that the optical bandgap of Mn-doped ZnS which was prepared at low temperature, revealed a blue shift as compared with the undoped sample and it emitted yellow/red colors [15]. The bandgaps of $\text{Zn}_{1-x}\text{Mn}_x\text{S}$ nanowires exhibited a nonlinear bowing nature against the composition (x) which is important for their better uses in photonics and spintronics [16]. On the other hand, the band gap of Mn-doped ZnS thin films formed by chemical bath deposition technique was increased as the amount of Mn increased in the matrix and the highest photoluminescent yield was detected in 6 at. % Mn-doped sample [17]. Nguyen et al. studied the influence of precursor molar ratio and annealing temperature on the properties of Mn-doped ZnS quantum dots, and they found that the $\text{ZnS}:\text{Mn}^{2+}$ QDs can be especially an appropriate member for biological uses, security ink applications, and electroluminescence devices [18]. Nishimura et al. found that the photoluminescent quantum yield (PL QY) of the ZnSe:Mn QDs synthesized under the optimum conditions reached 20%, which is the highest value ever reported for a water soluble ZnSe:Mn core QD [19]. Furthermore, by introducing a ZnS shell at the surface of the ZnSe:Mn QDs ($\text{ZnSe}:\text{Mn}/\text{ZnS}$ core/shell QDs), the PL QY was increased to 30% [19]. In this work, the influence of 5% Fe or Mn doping on the structure and optical behaviors of nano ZnS were investigated in detail by applying X-ray diffraction (XRD), transmission electron microscope

(TEM), Fourier transforms infrared (FTIR), ultraviolet spectroscopy (UV/VIS) and photoluminescence (PL) techniques. In addition, the electronic performance of the undoped and doped samples was examined by applying Castep program relies on density function theory calculation (DFT).

2. Methods and materials

5% Fe and Mn-doped nano ZnS ($\text{Zn}_{0.95}\text{A}_{0.05}\text{S}$, A=Fe or Mn) was prepared by thermolysis technique using zinc, manganese acetates, iron citrate and thiourea. The required amount of the different salts were mixed, ground and heated in an electric oven at 400 °C (2h). The X-ray diffraction patterns were measured by X'pert MPD Philips ($\text{Cu-K}\alpha$ source, LaB_6 standard for instrumental broadening correction). Different structures and microstructure parameters were extracted using MAUD program which depended on Rietveld profile method [20, 21]. UV-vis spectroscopy (Shimadzu UV-3101PC UV-Vis-NIR scanning spectrometer) was used to determine the optical bandgap of the different samples. The emitted colors from different samples were found using photoluminescence (PL) technique (luminescence spectrophotometer (RF-1501 SHIMADZU, Ltd)). Fourier transforms infrared (FTIR) technique (Bruker Tensor 27 FTIR spectrometer) was used to determine the different vibration bands of the studied materials. The electronic structure's parameters were found using Cambridge sequential total energy package (CASTEP) code based on the first principle calculation [22]. The supercell with $2 \times 2 \times 1$ dimension was used during the calculation for undoped and doped ZnS. An ultra-soft pseudopotential, GGA-PBE and energy cutoff (380 eV) was used in the calculations [23, 24]. In the case of a Fe or Mn-doped ZnS system, one ion of Zn was replaced by either Fe or Mn ion. The influence of oxygen ion on the electronic properties of undoped and doped ZnS with Fe or Mn ions was investigated by replacing one sulfur ion with an oxygen ion. The $3d^{10}4s^2$, $3d^64s^2$, $3d^54s^2$, $3s^23p^4$ and $2s^22p^4$ electrons related to Zn, Fe, Mn, S and O atoms were used for the pseudopotential arrangements, respectively. The absorption coefficient ($\alpha(\omega)$), the refractive index (n), extinction coefficient (k), the real and imaginary dielectric parts (ϵ_1 , ϵ_2) and the optical conductivity ($\sigma(\omega)$) were calculated using the Kramers-Kronig relations [25, 26].

3. Results and discussion

3.1 Structural analysis

X-ray diffraction patterns, Fig. 1, resembled single phase zinc blende cubic structure for all samples. No other phases were found implying the incorporation of Fe and Mn into the ZnS lattice, substitutionally for Zn ions. The effect of Fe and Mn doping on the lattice parameter, crystallite size, and lattice microstrain was examined applying Rietveld refinement and the resulting refined parameters are given in table 1. The lattice parameter increased slightly due to the small doping percentage 5 %; the increase may be ascribed to the difference between the ionic radii for tetrahedral coordination $\text{Zn}^{2+} = 0.6$, $\text{Fe}^{2+} = 0.63$, and $\text{Mn}^{2+} = 0.66$ pm [27]. The crystallite size and lattice strain are almost isotropic and did not change significantly upon doping. The obtained Fe and Mn occupancies, table 1, are very close to the intended doping value, confirming the incorporation substitutionally for Zn ions. Fig.2 shows the Fourier transforms infrared spectroscopy spectra (FTIR) for undoped and doped ZnS doped with Fe and Mn at room temperature in the range of 400–1200 cm^{-1} . The figure revealed that all samples have similar features, but the intensity and wavenumber of different vibration bands affected by the kind of the

doped element. The vibration bands observed at 400–418 cm^{-1} , 612–620 cm^{-1} , and 1020–1150 cm^{-1} are the characteristic bands of ZnS; asymmetric bending, symmetric bending, and asymmetric stretching respectively [28]. It is important to notice the little shift in the wavenumber of bands upon doping, a behavior confirming the incorporation of Fe and Mn substitutionally for Zn ions. The vibration bands of C-S linkage and S-O-C are observed in the range at 701–598 and 1023 cm^{-1} , respectively [29].

3.2. UV absorption analysis

To determine the direct energy gap (E_g) of undoped and doped nano ZnS with Fe and Mn, the following Tauc's relation [30] was applied:

$$(\alpha h\nu)^2 = D(h\nu - E_g)$$

$$\alpha = \frac{2.303A}{t}$$

where D, A and t are a constant, absorbance and thickness of the sample, respectively.

Fig. 4 reveals the graphic relation between $(\alpha h\nu)^2$ and $h\nu$ and from the plot E_g value can be extracted by extrapolating the straight-line portion of the graph on the $h\nu$ axis. The obtained E_g values for ZnS and ZnS doped samples with Fe or Mn are 3.26, 2.83 and 3.12 eV, respectively. The obtained E_g for ZnS samples is compatible with other literature values [31] and less than other ZnS prepared with different methods [32, 33]. It is known the energy gap affected by the size of the sample and the process of formation: for example, ZnS formed using different chemical methods exhibited energy gap values of 3.5, 4.79 and 3.95 eV, which are corresponding to the crystallite size of 4.9, 6.73 and 4.8 nm, respectively [31–33]. Furthermore, the energy gaps of doped materials are less than the undoped ones. Cai et al. found as the amount of Mn-doped ZnS nanowires increased up to 6%, the energy gap of ZnS decreased, and by further doping, the energy gap increased [16]. The optical band gap of Mn-doped ZnS nanoparticles synthesized at 95 °C in basic aqueous solution using the nucleation-doping strategy was reduced as the amount of Mn doping increased in the matrix [34]. Poornaprakash et al. found a similar result as ZnS doped with Mn, where the optical band gap of ZnS was reduced as it was doped with Mn, due to sp–d spin exchange interaction between the band and localized electrons of the transition metal ion substituting the cation [35]. Vineeshkumar et al. found the energy gap of ZnS formed by polyethylene glycol assisted hydrothermal procedure was decreased as it doped with Fe [36]. The optical band gaps of $\text{Fe}_x\text{-ZnS}$ catalysts synthesized by a one-pot hydrothermal process were apparently less than the band gap of ZnS, indicating that Fe doping effectively reduced the bandgap of ZnS catalyst [3]. The reduction in bandgap of ZnS as it doped with Fe can be explained also as the possibility of the present of a small amount of FeS phase which has a smaller bandgap (1.1 eV) as compared with ZnS sample [37], which is not detected from XRD analysis in our case. Conversely, Padmavathi et al. demonstrated that Fe or Mn-doped ZnS exhibited a redshift using spin- polarized first principles calculations method and applying mBJ approximation [38].

3.3. Photoluminescence analysis

Fig. 4 shows the Gaussian fitting of photoluminescence (PL) spectra at an excitation wavelength of 350 nm for ZnS and $\text{Zn}_{0.95}\text{X}_{0.05}\text{S}$ (X= Fe, Mn) samples. It is observed from the figure that the PL intensity of ZnS was reduced as ZnS doped with either Fe or Mn. Peppers et al., revealed that

the excitonic emission of ZnSe crystal is quenched as it doped with Fe ions [39]. On contrary, the PL intensity of Fe-doped ZnS nanorods was increased as the amount of Fe concentration increased in ZnS [11]. The reduction in PL intensity as Fe or Mn-doped ZnS matrix in our case is due to the plying of Fe or Mn ions as quenching centers of fluorescence; Fe or Mn acts as an electron trapping center which out from non-radiative recombination [40]. Furthermore, ZnS, Fe -doped ZnS and Mn-doped ZnS emitted (violet, three blues), (violet, two blues) and (violet, blue, green) colors. Nano ZnS formed using aqueous synthesis method emitted violet and blue colors [4]. Fe-doped ZnS nanorods emitted blue and green emissions [11]. Nano Fe-doped ZnS formed by a refluxing procedure emitted a blue color only and its intensity was reduced as the Fe doped amount increased in the matrix [35]. On the other hand, Fe-doped Nano wurtzite ZnS emitted blue and red colors as it doped with Fe [41]. Fe-doped Nano ZnS prepared by a microwave-assisted co-precipitation process revealed UV, violet and orange colors as it doped with Fe [39]. Fe-doped nano ZnS formed using aqueous synthesis method emitted violet, blue, green, orange and red colors [4]. $\text{Zn}_{1-x}\text{Fe}_x\text{S}$ nanospheres emitted green and yellow colors [36]. Mn-doped ZnS quantum dots prepared by hydrothermal procedure revealed blue and green colors [42]. The violet color may be caused by anion (S^{2-}) vacancy (V_s) which acts as a common electron trap under the conduction band edge, hole traps like cation vacancies (V_{Zn}) and surface states (SS), which are in lower energy states [43]. The blue color caused by the transition from V_s to V_{Zn} [43]. The observed green luminescence emission owes to increase in the lattice defects [44].

3.4. Electronic structure properties analysis

Since the undoped and doped ZnS samples were prepared in air, therefore maybe there is some oxygen enter the lattice. The electronic characteristics of undoped and doped ZnS with Fe or Mn (where one atom of Zn is replaced by a either Fe or Mn atom, $\text{ZnS}/(\text{Fe}, \text{Mn})$) and undoped and doped ZnS with (Fe or Mn) and oxygen (where one atom of Zn is substituted by Fe or Mn atom and one sulfur atom is substituted by one oxygen atom= ZnS/O and $\text{ZnS}/(\text{Fe or Mn}, \text{O})$) was investigated using a unit cell with the zinc-blende unit cell with space group F-43m as an initial model. The lattice parameters obtained from XRD diffraction were used as preliminary values for the DFT calculation. After the geometry relaxation, the obtained lattice parameters are 5.4015, 5.3494, 5.4089, 5.3902, 5.4175 and 5.4093 Å for ZnS, Zn/O, ZnS/Fe, ZnS/(Fe, O), ZnS/Mn and ZnS/(Mn, O), respectively. The lattice parameter of the ZnS/(Fe or Mn) sample is slightly larger than that of the ZnS sample, as a result of replacing the smaller ionic radius ion (Zn) with a bigger ionic radius ion (Fe or Mn) which is in consistence with XRD result. In contrast, the lattice parameter of ZnS/O and ZnS/(Fe or Mn, O) is smaller than the lattice parameter of other samples as a result of replacing of larger ionic radius ion (sulfur) with smaller ionic radius ion (oxygen). Figs.5, 6 show the spin-polarized band structures for ZnS, ZnS/O, ZnS/Fe, ZnS(Fe, O), ZnS/Mn and ZnS/(Mn,O) samples along the high symmetry direction of the first Brillouin zone. The Fermi energy level was located at zero energy. All undoped and doped ZnS samples exhibited a direct band semiconductor characteristic. The calculated energy gap for ZnS sample is 2.148 eV which is smaller than the optical band gap obtained from the UV result [45]. The small value of the calculated bandgap is underestimated because of the accepted limitation of expecting the precise energy band properties [46]. The bandgap of ZnS was decreased as it doped with Fe and/or O, reached 1.853 eV, and both samples exhibited a half-metallic characteristic. On the other hand, Mn and/or O doped ZnS revealed a semiconductor nature and the band gap decreased in both samples as compared with the undoped ZnS sample. A similar effect was achieved by Padmavathi et al. using a Full Potential Linearized Augmented Plane Wave (FP-LAPW) method [38]. Fig.7a,b

show the optical absorption for ZnS, ZnS/O, ZnS/Fe, ZnS/(Fe, O), ZnS/Mn and ZnS/(Mn, O) samples as a function of the photon energy. The absorption spectra for all samples exhibited two peaks which were shifted to higher energy values upon doping with Fe or Mn or/and O. In the visible region ZnS/O has better absorption than ZnS, while in the UV region the situation is reversed. In addition, the absorption was enhanced in the visible region while it reduced in the UV region as ZnS doped with Fe or Mn and/or oxygen. As revealed in Fig.7c, Fe-doped ZnS revealed a higher absorption than Mn-doped ZnS sample. Figs. 8a, b reveal the optical conductivity ($\sigma(\omega)$) of ZnS, ZnS/O, ZnS/Fe, ZnS/(Fe, O), ZnS/Mn and ZnS/(Mn, O) samples. As demonstrated from the figure, the optical conductivity of all samples has two peaks. The intensity of the main peak decreased when Fe or Mn and/or O doped ZnS, whereas the small peak in the UV affected a little with doping. The peaks occurred in the UV region caused by the interband transitions [47]. The reduction in the main peak in the case of Mn-doped ZnS is larger than Fe doped ZnS sample, Fig.8c. Besides, the optical conductivity in the visible range enhanced slightly with doping. The photon energy dependence of the refractive index (n) and the extinction coefficient (k) are demonstrated in Fig.9, where the refractive index was enhanced until reached its highest value at a specific energy range then it decreased with increased photon energy, Figs.9a-c. A small peak has emerged at a higher energy range for all samples. The variation that takes place in the refractive index characteristics may be caused by the dispersion of the light inside the material. Accordingly, many interactions can happen with the different atoms inside the unit cell. The refractive index has high values in the low energy region and its highest value (around 4 eV) reduced as ZnS doped with Fe or Mn and/or O. The extinction coefficient values of all samples revealed as steadily rising as the photon energy value increased until reached the highest value then it reduced with further increased in the photon energy, Figs.9d-f. Also, a small hump occurred in the high energy region for all samples. The extinction coefficient was improved in the visible region as ZnS doped with Fe or Mn and/or O. The extinction coefficient in the visible region in the case of Fe doped is higher than the Mn-doped ZnS sample. The intensity of the maximum peak was decreased as ZnS doped with Fe or Mn and/or O because of the atomic correlation and interactions. The reduction in the highest peak is occurred further in Mn-doped ZnS as compared with Fe doped one.

Fig.10 shows the real and imaginary parts of the dielectric constant as a function of the photon energy for all samples, which demonstrated roughly alike tendency. Additionally, the dielectric constant has negative values in a specific energy range for all samples, established that the materials have a metallic performance in this range [47]. The negative dielectric value was reduced as ZnS sample doped with Fe or Mn and/or O. Additionally, ZnS doped with Fe or Mn and O samples have the highest static dielectric constant among the other undoped and doped samples, sample with Fe and O higher than with Mn and O. The imaginary part of the dielectric constant has two peaks. The higher one is shifted to the high energy region as ZnS doped with Fe or Mn and/or O comparing with undoped one. In energy-loss graph, Fig.11, the maximum peak position, known as the bulk plasma frequency (ω_p), was shifted to a lower energy value as ZnS doped with Fe or Mn and/or O; ω_p occurs when ϵ_2 less than 1 and ϵ_1 nearly became zero [48, 49]. Additionally, the intensity of ω_p was reduced as ZnS doped Fe or Mn and/or O which indicated a fast reduction of the reflectance, Figs. 11d-f.

4. Conclusion

Fe and Mn-doped were obtained as single cubic phase applying thermolysis technique. Applying Rietveld analysis, the lattice parameter increased slightly, and the crystallite size and lattice strain are almost isotropic and did not change significantly upon doping. FTIR spectra confirmed the

incorporation of Fe and Mn substitutionally for Zn ions. The energy gap for ZnS and ZnS doped samples with Fe and Mn are 3.26, 2.83 and 3.12 eV, respectively. The reduction of band gap upon doping is due to the sp–d spin-exchange interaction between the band electrons and the localized electrons of the transition metal ion substituting the cation. The photoluminescence (PL) was reduced upon Fe and Mn doping. The emitted colors are violet, three blues for ZnS, violet, two blues for Fe-doped ZnS and violet, blue, green for Mn-doped ZnS. DFT calculations demonstrated that ZnS, Zn/O, ZnS/Fe, ZnS/(Fe, O), ZnS/Mn and ZnS/(Mn, O) samples exhibited a direct band semiconductor characteristic. Fe and/or O doped ZnS samples exhibited a half-metallic characteristic. The absorption enhanced in visible region while it reduced in UV region as ZnS doped with Fe or Mn and/or oxygen. Fe-doped ZnS revealed a higher absorption than the Mn-doped ZnS sample. The optical conductivity in the visible range enhanced slightly with doping. The refractive index has high values in the low energy region and its highest value (around 4 eV) reduced as ZnS doped with Fe or Mn and/or O. ZnS doped with Fe or Mn and O samples have the highest static dielectric constant among the other undoped and doped samples, sample with Fe and O higher than with Mn and O. The peak intensity of the bulk plasma frequency (ω_p) reduced upon doping with Fe or Mn and/or O indicated a fast reduction of the reflectance.

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Fig.1. Rietveld refinement for undoped and Fe or Mn-doped nano ZnS.

Fig.2. FTIR spectra for undoped and Fe and Mn-doped nano ZnS.

Fig.3. Plots of $((\alpha h\nu)^2)$ vs photon energy ($h\nu$) for undoped and Fe or Mn-doped nano ZnS.

Fig.4. Gaussian fitting for photoluminescence (PL) spectra vs wavelength (λ) for undoped and Fe or Mn-doped nano ZnS.

Fig.5. (a) supercells used in the calculation, yellow (red) and violet (green) balls indicate S (O), Zn (Fe or Mn) and (b) the spin-polarized band structures (up and down) for undoped and Fe-doped nano ZnS.

Fig.6. (a) The spin-polarized band structures (up and down) for Mn-doped nano ZnS.

Fig.7. The absorption spectra for undoped and Fe or Mn-doped nano ZnS.

Fig.8. The conductivity for undoped and Fe or Mn-doped nano ZnS.

Fig.9. (a-c) the refractive index (n) and (d-f) extinction coefficient (k) for undoped and Fe or Mn-doped nano ZnS.

Fig.10. (a-c) real and (d-f) imaginary dielectric parts for undoped and Fe or Mn-doped nano ZnS.

Fig. 11. (a-c) the reflectivity spectra and (d-f) loss function for undoped and Fe or Mn-doped nano ZnS.

Table1. Lattice parameters (a) Å, average crystallite size (nm), strain and occupancy for undoped and Fe / Mn-doped ZnS samples.

		ZnS	ZnS/Fe	ZnS/Mn
a (Å)		5.3364 (1)	5.3500	5.3442
size (nm)	111	25	26	26
	100	21	20	24
strain	111	0.013	0.0068	0.012
	100	0.019	0.012	0.018
Occ.			0.048	0.051

Figures

Figure 1

Rietveld refinement for undoped and Fe or Mn-doped nano ZnS.

Figure 2

FTIR spectra for undoped and Fe and Mn-doped nano ZnS.

Figure 3

Plots of $((\alpha h\nu)^2)$ vs photon energy ($h\nu$) for undoped and Fe or Mn-doped nano ZnS.

Figure 4

Gaussian fitting for photoluminescence (PL) spectra vs wavelength (λ) for undoped and Fe or Mn-doped nano ZnS.

Figure 5

(a) supercells used in the calculation, yellow (red) and violet (green) balls indicate S (O), Zn (Fe or Mn) and (b) the spin-polarized band structures (up and down) for undoped and Fe-doped nano ZnS.

Figure 6

(a) The spin-polarized band structures (up and down) for Mn-doped nano ZnS.

Figure 7

The absorption spectra for undoped and Fe or Mn-doped nano ZnS.

Figure 8

The conductivity for undoped and Fe or Mn-doped nano ZnS.

Figure 9

(a-c) the refractive index (n) and (d-f) extinction coefficient (k) for undoped and Fe or Mn-doped nano ZnS.

Figure 10

(a-c) real and (d-f) imaginary dielectric parts for undoped and Fe or Mn-doped nano ZnS.

Figure 11

(a-c) the reflectivity spectra and (d-f) loss function for undoped and Fe or Mn-doped nano ZnS.