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Dielectric and Optical Properties of Fe doped ZnS Nanoparticles

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Abstract—The optical and dielectric properties of ZnS:Fe nanoparticles have been investigated at room temperature. X-ray diffraction analysis confirms that pure and Fe doped ZnS nanoparticles transform into cubic phase and impurities such as iron clusters are absent. Band-gap energy increases with Fe doping in ZnS nanoparticles. Photoluminescence spectra show that defects increase with increase in concentration of Fe as dopant. Further, dielectric measurement shows the maximum value of dielectric constant at particular concentration of Fe in ZnS nanoparticles. Enhancement in dielectric constant is due to space charge polarization that is due to presence of higher oxidation state of Fe in ZnS nanoparticles.

Index Terms— Dielectric Constant, Nanoparticles, Photoluminescence, Polarization, Rietveld, X-ray, ZnS.

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1 Introduction

In recent years, semiconducting nanostructured and multi-functional materials have attracted research interests [1]. The electrical, optical as well as magnetic properties of these semiconducting nanostructures can be controlled by incorporating suitable amount of defects and/or impurities [2]. Zinc sulphide (ZnS) is II-VI semiconductor with its large band gap (3.7 eV) has many applications in light emitting diodes, UV sensors, field effect transistors and in opto-electronic devices [3]. ZnS has been doped with various metals, transition metals and rare earth metals to control its electrical, optical and magnetic properties [4], [5], [6], [7]. For example, ZnS doped with lead, gives interesting optical and dielectric properties [8]. Magnetic properties in ZnS have been achieved by incorporating transition metals (Co, Cr, Ni, Fe etc.) in ZnS [5], [6], [9]. Semiconducting nanostructures exhibit larger band-gap when compared with bulk material. Owing to their larger band-gap these nanostructures can find application as a dielectric medium. ZnS doped with Fe gives good optical and magnetic properties as reported in literature [9]. So it is interesting to find the change in dielectric properties of ZnS when doped with Fe. The study of dielectric properties of nanomaterials is useful for technological application as high value dielectric materials can be used in filters, capacitors, resonant, metal cavities and miniature devices [8].

In this article, we report the synthesis of pure and Fe doped ZnS nanoparticles at room temperature using chemical precipitation method. Further, we discuss the structural, optical and dielectric properties of Fe doped ZnS nanoparticles.

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2 Experiment Details

2.1 Synthesis

Fe (0, 2 and 4%) doped ZnS nanoparticles were prepared by using chemical precipitation method at room temperature. Zinc acetate dihydrate [Zn $(CH_3COO)_2$. $2H_2O$], ferric nitrate nonahydrate [$Fe_2No_3.9H_2O$] and sodium sulphide [(Na_2S)] were used as precursors and were dissolves in double distilled water to prepare solutions. A required amount of ferric nitrate was mixed with aqueous solution of zinc acetate and after 3 hours, aqueous solution of sodium sulphide was added. Precipitations were formed and filtered. The collected precipitates were washed using ethanol and water and then dried in oven at 60°C. Pallets were made form powder samples to perform dielectric studies and silver paste was coated on adjacent faces of these pallets.

2.2 Characterization

Bruker D8 focus X-ray diffractometer (40 kV, 30 mA) having Cu-K_α (1.54 Å) as radiation source, was used to study structural properties of pure and Fe doped ZnS nanoparticles. To find optical properties of all these samples Shimadzu UV-2450 spectrophotometer (UV-Vis-NIR) and Perkin Elmer LS55 fluorescence spectrometer were used. Dielectric properties of these nanoparticles were studied at room temperature using Hioki 3532−50 LCR HiTester.

3 Results and Discussions

3.1 X-Ray Diffraction

The X-ray diffraction pattern of Fe doped ZnS nanoparticles are shown in Fig.1. Three peaks are obtained in all samples which correspond to (111), (220) and (311) planes of cubic structure of ZnS (JCPDS no. 80−0020). The obtained peaks are relatively broadened due to finite size of nanoparticles. No extra peak related to dopant is observed, indicates that the Fe dopant replaced Zn ions in the lattice. The lattice constant 'a'

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for all samples is calculated using Rietveld refinement software listed in Table 1.

TABLE 1
LATTICE CONSTANT AND GOODNESS OF FIT (GOF) OF PURE AND FE DOPED ZNS SAMPLES.

Fe Content (%)	Lattice Constant a(Å)	GoF
0	5.364 ± 0.0013	1.16
2	5.357 ± 0.0019	1.14
4	5.354 ± 0.0021	1.10

From Table 1. lattice constant decrease with increase in doping of Fe in ZnS. This lattice contraction occurs due to smaller ionic radius of Fe ions as compared to Zn ions. The inter-atomic distance decreases when Zn is replaced by Fe in ZnS lattice.

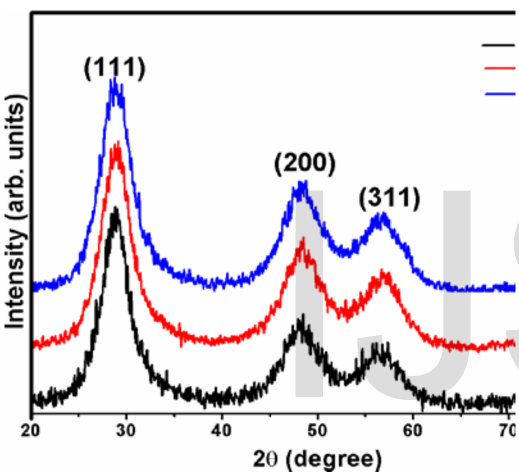

Fig.1. XRD patterns of pure and Fe doped ZnS nanoparticles.

3.2 UV-Vis Analysis

Fig. 2 displays the absorption spectra of the nanoparticles measured at room temperature. In pure ZnS nanoparticles, the absorption peak appears at 278 nm and while in doped nanoparticles, it is shifted to 275 nm. This blue shift with Fe doping is due to quantum confinement effect as reported earlier [9]. The other peak obtained at 374 nm is due to bulk ZnS.

The band-gap is calculated from the photons which are absorbed between the different energy transitions. Tauc plot for determination of band-gap energy is shown in inset of Fig. 2. The value of energy gap is calculated from the relation:

$$\alpha h\nu = A\,(h\nu - E_g)^{(1\backslash n)} \qquad (1)$$

where, α is absorption coefficient, A is constant, h is Planck constant, ν is photon frequency and E_g is the optical band gap, n= 1/2 for direct band gap material. The band gap energy varies from 4.00- 4.70 eV. The band gap increases for 2% Fe and then decrease for 4% Fe in ZnS nanoparticles. The decrease in value of band gap at higher concentration of Fe is due to sp-d interaction [10].

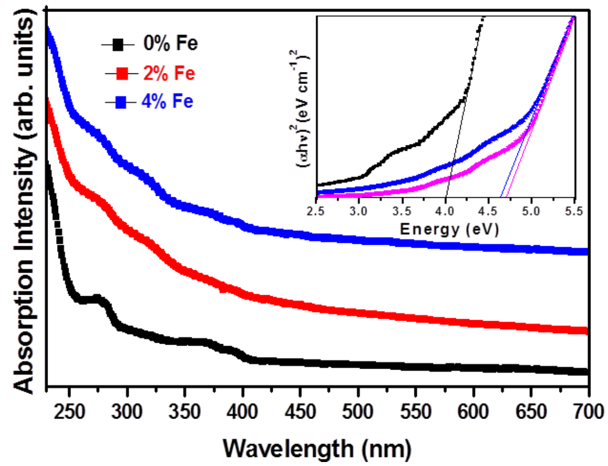

Fig.2. UV-Visible absorption spectra of ZnS:Fe nanoparticles. Inset shows Tauc plot of ZnS:Fe nanoparticles for band gap estimation.

3.3 Photoluminescence Analysis

The photoluminescence (PL) spectra of pure and Fe doped ZnS nanoparticles are displayed in Fig. 3. The PL spectra have been obtained using excitation wavelength of 325 nm at room temperature. From this spectrum, it is clear that emission intensity quenches with addition of Fe in ZnS nanoparticles. The quenching might arise due to electron trap center formed by the dopant.

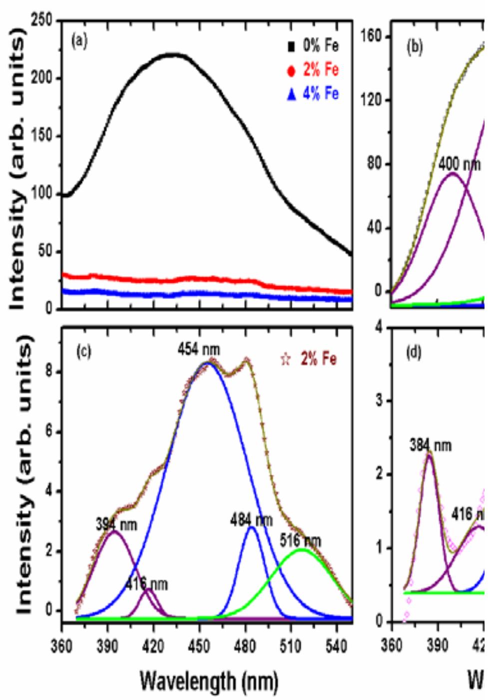

Fig.3. **(a)** PL spectra of pure and Fe doped ZnS nanoparticles, (b-d) Gaussian deconvulated spectra of (b) 0, (c) 2 and (d) 4% Fe doped ZnS

Further, Gaussian de-convolution of these obtained peaks for ZnS:Fe are shown in Fig.3 (b-d). The obtained values of these peaks are listed in Table. 2.

TABLE 2
LATTICE CONSTANT AND GOODNESS OF FIT (GOF) OF PURE AND FE DOPED ZNS SAMPLES.

Fe Content (%)	Violet emission (nm)	Blue emission (nm)	Green emission (nm)
0	400	442, 480	503
2	394	418, 454, 484	516
4	384	416, 451, 483	509, 526

In case of pure nanoparticles, four peaks are appeared at 400, 442, 480 and 503 nm. The peaks obtained at 385−400 are attributed to deep traps and 440−454 nm is corresponding to interstitial zinc vacancies [10]. The peak observed at 480 nm is due to self−activated centers [12], while the peak at 503−516 nm is due to electron transition between sulphur and zinc vacancies [10], [11]. With addition of Fe in ZnS nanoparticles, defects are increased, more peaks are observed in PL spectra. The peak at 416 nm is ascribed to interstitial sulphur defects while peak at 525 nm confirms that the lattice sites are occupied by iron dopants [9], [13].

3.4 Dielectric Study

The dielectric measurements have been performed on pure and Fe doped ZnS nanoparticles in frequency range from 10 kHz to 1 MHz at room temperature. The variation in the value of dielectric constant with frequency is shown in Fig. 4(a). All samples display the exponential behavior i.e. first dielectric constant decreases with increase in frequency and at very high frequency it becomes constant which is well explained using Maxwell−Wagner Model [2]. According to Maxwell−Wagner Model, dielectric medium is made of poorly conducting grain boundaries separates the well conducting grains. When external field is applied, the charge carriers present in material can accumulate at grain boundaries but easily migrate through grains, results in large polarization and high value of dielectric constant. With increase in frequency, polarization decreases and becomes constant at higher value of frequency because beyond a certain value of frequency, the hopping of electrons of different metal ions (Zn^{2+}, Fe^{2+} and Fe^{3+}) cannot follow the alternate field. In case of 2% Fe doped ZnS nanoparticles, the value of dielectric constant is quite high as compared to pure sample but with further increase in concentration of Fe i.e. at 4% Fe the dielectric constant decreases. The enhancement in dielectric constant is due to Fe that exists in higher oxidation state to balance charge of zinc vacancies/defects at surface of nanoparticles which results in formation of space charge polarization. But with further increase in concentration of dopant, electrical conductivity improves that leads to decrease in value of dielectric constant [1].

Fig.4(b) shows the variation of tanδ with frequency which informs that dielectric loss decreases with Fe doping in ZnS nanoparticles.

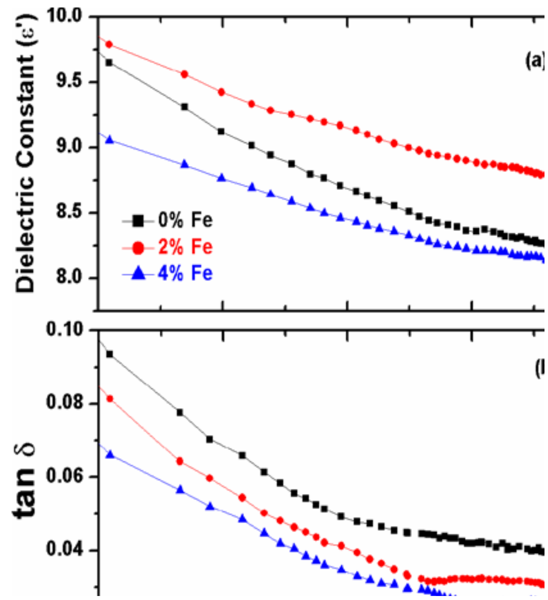

Fig. 4. Plot of (a) Dielectric constant and (b) tanδ as a function of frequency for pure and Fe doped ZnS nanoparticles.

4 CONCLUSION

XRD pattern of ZnS:Fe nanoparticles confirms the cubic structure of synthesized nanoparticles without the presence of any impurity. Optical studies show that the value of band gap energy and intensity of photoluminescence peaks decreases with increase in concentration of Fe in ZnS nanoparticles. Enhancement in the value of dielectric constant is observed at the specific concentration of Fe in ZnS nanoparticles i.e. by adding suitable amount of dopant, value of dielectric constant can be tuned.

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