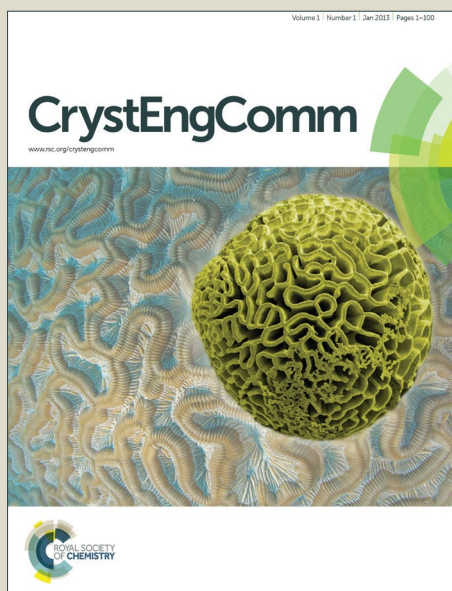


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Synthesis, pair distribution function and diverse properties study on cobalt doped ZnS nanowires†

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Nanowires of undoped and cobalt doped ZnS were synthesized by hydrothermal method. Samples of pure and Co doped ZnS were characterized by ADXRD. Structural parameters were evaluated using ADXRD data. The atomic structure of pure and Co doped ZnS nanowires has been studied using pair distribution function (PDF) analysis. It was confirmed that samples have hexagonal (wurtzite) structure. The interatomic distance was calculated using PDF analysis. The energy band gap of pure and Co doped ZnS nanowires were estimated using UV-Vis spectra and red shift was clearly observed. It was observed that energy band gap goes on reducing as Co content increasing. FTIR spectra indicate that Co substitutes into ZnS lattice. TEM micrographs clearly show growth of nanowires of synthesized samples. Vibrating sample magnetometer (VSM) was used to outline the presence of magnetism in the sample. It was confirmed from VSM that as synthesized pure and Co doped ZnS nanoparticles exhibit weak ferromagnetism at room temperature.

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Introduction

Sulfide diluted magnetic semiconductors (DMS) have attracted more attention due to their potential application in electronics and optoelectronic because of its band gap. ZnS is an important II-VI group DMS materials which have wide band gap of 3.77 eV for wurtzite¹ structure, and 3.72 eV for cubic² structure at 300 K with a large exciton binding energy (~40meV). ZnS has been used as a base materials for cathode ray tube (CRT) and field emission display (FED) Phosphors^{3,4}, electroluminescent device, Light emitting diodes (LEDs)⁵, Infrared (IR) window⁶, Field Effect Transistors (FETs)⁷ and sensors⁸.

Doping of transition metals at the nanoscale level semiconductors have been elaborated to be a feasible method to tune their physical properties such as optoelectronics and further exchange performance of the device^{9,10}.

One dimensional nanomaterial like nanorods^{11,12}, nanowires(NWs)^{13,14}, nanoribbons¹⁵, and nanotube¹⁶ have been synthesized by various techniques such as hydrothermal method¹⁷⁻¹⁹, thermal evaporation method²⁰, pulse laser deposition²¹, electrochemical deposition²², molecular beam epitaxy (MBE)²³,

Microwave assisted technique²⁴, Chemical vapour deposition²⁵ etc. by doping TM (Mn²⁺, Fe²⁺, Ni²⁺, Cr²⁺, Co²⁺ etc.) into ZnS. Recently synchrotron XRD with fast computing methods impact in the area of crystalline as well as amorphous materials of interest. The pair distribution function (PDF) is one of the versatile method, it can be applied to any materials. It has been numerous applications to analyze the structures of nanomaterials for determining crystal phase and unit-cell parameters and for quantifying various types of disorder or defects²⁶⁻²⁸. PDF is the incorporation of a form factor describing nanoparticles size and shape. Also the PDF is one of the special approach has been developed to analyze diffuse (non-Braggs type) XRD patterns. The PDF technique and total-scattering methods, allow both the Bragg and diffuse scattering to be analyzed together without bias, revealing the short and intermediate range order of the material regardless of the degree of disorder²⁹⁻³⁴.

Generally high temperature physical methods have been employed for the synthesis of wurtzite ZnS NWs with the temperature ~1273 K which results larger diameter owing to these materials do not show quantum confinement effect³⁵⁻³⁷. There are less reports available in literature on Co doped ZnS NWs and PDF study on Co doped ZnS NWs are not available yet. Therefore, we have initiated to work on this problem to find various facets by employing different experimental techniques. In this report high crystalline cobalt doped ZnS NWs were synthesized via hydrothermal method at temperature 458 K. The structural analysis of Cobalt doped ZnS NWs was investigated by high energy angle dispersive X-ray diffraction (synchrotron ADXRD). Using PDF data interatomic distances were evaluated as considering total scattering structure function. TEM study candidly outlines ZnS samples exhibit nanowires.

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†Electronic Supplementary Information (ESI) available: Supplemental Fig. 1 shows SXRD patterns, fig. 2, 3 shows TEM image of pure ZnS and 4% Co doped ZnS nanowires with different magnification and fig. 4 shows EDS spectra of samples. Table 1 gives the values of elemental concentration.

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Experimental details

Hydrothermal method was used to synthesis $\text{Zn}_{1-x}\text{Co}_x\text{S}$ nanowires with nominal compositions ($x=0.00, 0.04, 0.08, 0.12$). In typical synthesis 100 ml Teflon-lined stainless steel autoclave was used. All of the chemicals were of analytical grade and used without any further purification. The appropriate amounts of zinc nitrate (1 mM), cobalt nitrate (1- x) mM and thiourea (2 mM) were dissolved in 75ml deionized (DI) water and ethylenediamine (1:1 ratio) solution. Then this solution was stirred for 20 minutes using magnetic stirrer at room temperature and these transparent solutions were transferred to autoclave. Then the autoclave containing solution was sealed and kept in furnace at 185°C temperature for 5 hours then allowed to cool naturally. Then obtained product was centrifuged and washed for several time by ethanol and DI water and filtered. After this, final product was dried in vacuum for 2 hours at 60°C . Angle Dispersive X-ray Diffraction (ADXRD) patterns were recorded from Beam line (BL-11) at INDUS-2, RRCAT Indore, India at room temperature and atmospheric pressure. The synchrotron X-rays patterns of nanowires were produced using wavelength of $0.378377\text{\AA}$ with the energy 32 keV. Transmission electron microscopy (TEM) measurement were undertaken at accelerating voltage 200kV and selected-area electron diffraction (SAED) patterns were carried out with a Tecnai G² 20 at an acceleration voltage at 200 kV. Fourier transform infrared (FTIR) absorption spectra were obtained using Bruker, Germany Model: Vertex 70 spectrometer. UV-Vis absorption spectra were outlined by Perkin Elmer, USA Model: lambda 950 UV-Vis spectrophotometer. Vibrating Samples Magnetometer (VSM) was (14T PPMS VSM) employed to define magnetization of as synthesized samples at room temperature.

Results and discussion

Angle Dispersive X-ray Diffraction study

The Angle Dispersive X-ray Diffraction (ADXRD) patterns of $\text{ZnS}:\text{Co}^{2+}$ ($x = 0.00, 0.04, 0.08, 0.12$) nanowires are shown in fig. 1. The ADXRD measurements have been achieved by monochromatic white synchrotron beam using Si (111) channel cut monochromator. All samples were sealed to kapton foils for further measurement. The two-dimensional (2D) image obtained from ADXRD, was subjected to geometrical corrected integrated and reduced to one dimensional XRD patterns are shown in fig. 1. The full 2θ range of ADXRD was given in ESI† fig. 1.

ADXRD revealed high resolution diffraction for structural refinement. The entire diffraction peak of Co doped ZnS NWs can be readily indexed as wurtzite structure. There are no secondary phases observed in the prepared samples. The ADXRD results are very close to the standard values card no. (JCPDS-80-0007 space group, P6₃mc (186)) with $a = 3.777\text{\AA}$, $c = 6.188\text{\AA}$. The full width at half maxima (FWHM) of the (002) peak stronger and narrowest among all peaks, which indicate that nanowires grown in the (002) direction, it is further demonstrated through TEM analysis. Lattice parameters were calculated using ADXRD data and their values are tabulated in table 1. Verma et al.⁴⁹ has synthesized pure and Co doped ZnS samples and investigated lattice parameters using XRD data. According to his results samples show cubic lattice structure.

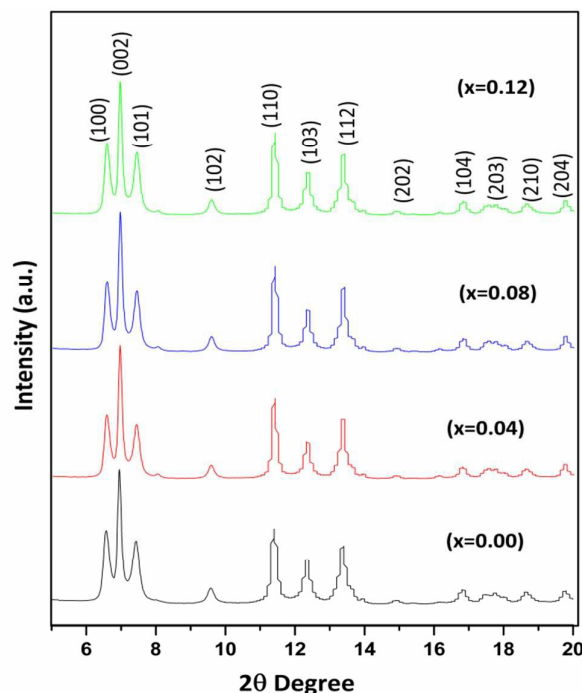


Fig. 1 ADXRD patterns of pure and Co doped ZnS nanowires.

But our ADXRD results evidently confirmed that samples are organized in hexagonal lattice structure. However, there are no alloys or oxide phases were detected as the Co^{2+} concentrations increase. Since that the ionic radius of the Co^{2+} ions ($0.79\text{\AA}$) is larger than that of Zn^{2+} ions ($0.75\text{\AA}$).

PDF Analysis

Angle dispersive X-ray powder diffraction was employed to obtain the PDF from AD/ED-XRD BL-11 beam line at Raja Ramanna Center for Advanced Technology, Indore. Diffraction images were recorded at MAR 345 with imaging plate $50 \times 30\text{ }\mu\text{m}$ (using compound refractive lens). For the purpose of PDF, data were corrected and normalized using the program PDFGETX3-1.1³⁸. Pair distribution function ($G(r)$) was plotted which reveals the probability of finding certain distance ' r ' between atoms.

$$G(r) = 4\pi r [\rho(r) - \rho_0] \quad (1)$$

Where $\rho(r)$ is the atomic pair density, ρ_0 is the average atomic number density and r is the radial distance³⁹. The total scattering technique outlines Bragg's peak with position and intensity gives structure and diffuse scattering with deviation gives perfect lattice. The PDF $G(r)$ is a one dimensional function which oscillates around zero and indicates peak position at distance separation pairs of an atom. The negative valleys in the PDF are corresponding to the real-space vector not having atoms at either of their ends. Owing to this reason PDF resembles Patterson function therefore it is widely applicable for X-ray crystallography study²⁹. Fourier analysis of the total scattering is known as atomic PDF analysis, means PDF is the Fourier transform of the scattering intensity. PDF was obtained using the total scattering structure function $S(Q)$ considering

Table 1 Lattice parameters, volume of unit cell, APF and X-ray density, first, second PDF peak positions and first peak width (FPW) position of pure and Co doped ZnS nanowires.

Samples (x)	Lattice Parameter(nm)		Volume of Unit cell (Å) ³	APF%	X-ray Density (gm/cm ³)	I st PDF Peak(Å)	II nd PDF Peak(Å)	PDF FPW (Å)
	'a'	'c'						
0.00	0.38373	0.60914	77.6807	76.13	4.1675	2.3424	3.8636	0.890
0.04	0.38587	0.605664	78.1003	77.00	4.1440	2.3903	3.8897	1.206
0.08	0.38246	0.61072	77.3684	75.60	4.1821	2.3433	3.8427	0.790
0.12	0.38400	0.60744	77.5741	76.40	4.1699	2.4112	3.8898	0.800

Fourier transformation is given inequation⁴⁰ (2). PDF $G(r)$ is a sine Fourier transformation of the experimentally observable reduced structure function,

$$F(Q) = Q[S(Q) - 1] = \frac{4\pi(\sin \theta)}{\lambda} [S(Q) - 1]$$

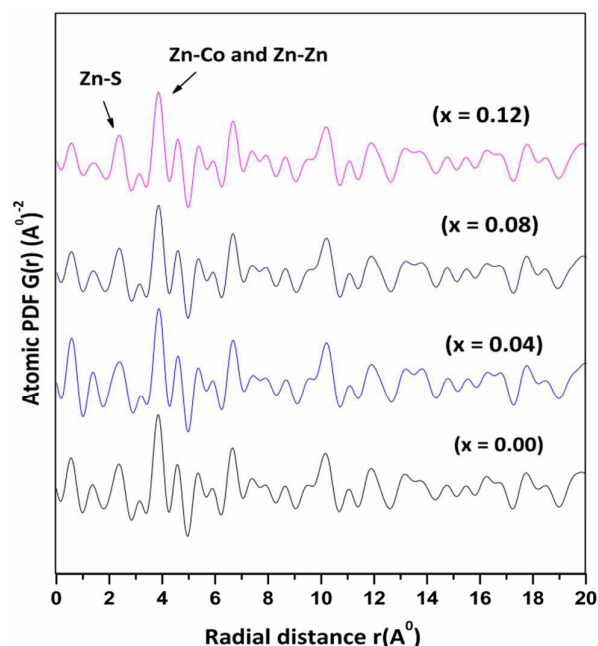
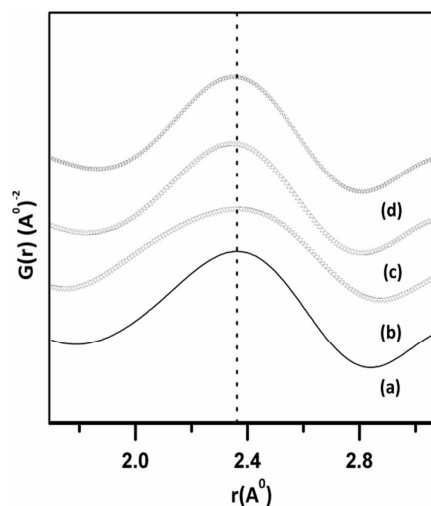
$$G(r) = \frac{2}{\pi} \int_{Q=0}^{Q_{max}} F(Q) \sin(Qr) dQ \quad (2)$$

$$G(r) = \frac{2}{\pi} \int_{Q=0}^{Q_{max}} Q[S(Q) - 1] \sin(Qr) dQ \quad (3)$$

Where Q is the magnitude of the wave vector and is derived from $Q = 4\pi \sin(\theta)/\lambda$, θ is the half scattering angle, λ is the wave length of X-rays^{39,40}. The Faber-Ziman type total structural function $S(Q)$ was related to the diffraction patterns, $I^{coh}(Q)$ and the relation of $S(Q)$ is given below,

$$S(Q) = 1 + \left[I^{coh}(Q) - \sum c_i |f_i(Q)|^2 \right] / \left[\sum c_i f_i(Q) \right]^2 \quad (4)$$

Where $I^{coh}(Q)$ is the coherent scattering intensity per atom in electron units and c_i is the atomic concentration, $f_i(Q)$ is X-ray scattering factor for atomic species type i ³⁹. Here we report $Q_{max} = 10.2 \text{ \AA}^{-1}$ at 32 keV is optimized to avoid large terminal effect and reduce signal to noise ratio. The $G(r)$ gives probability of finding a neighbour atom at distance r . From the PDF patterns hexagonal structure was confirmed with space group P63mc. The sharp and well resolved peaks in PDF suggest high symmetry and a well defined local structure. The PDFs are shown in fig. 2(a) which give the interatomic distance from peaks values. The local bonding of the hexagonal Zn-S, Zn-Zn and Zn-Co was investigated from PDF data. The first and second nearest neighbour distance (r) for pure and Co doped ZnS NWs was estimated using PDF data and values are enlisted in table 1. The first peak reflects the bond length of Zn-S for pure and doped ZnS NWs. The second intense peak reflects metal-metal bonding i.e. Zn-Zn for pure and Zn-Co for Co doped ZnS NWs which reveals covalently bonded pairs. The first position and width which outlined using Gaussian fit are shown in fig. 2(b). The width of PDF peaks corresponding to diameter of nanostructure materials was reported elsevier⁵⁰. The diameter of pure and Co doped ZnS NWs were estimated using PDF data and it was found to 8.9, 12.06, 7.8 and 8 nm respectively.

**Fig. 2(a)** Pair distribution function (PDF) of pure and Co doped ZnS nanowires.**Fig. 2(b)** First PDF peak were fitted using Gaussian fit for pure and Co doped ZnS nanowires.

Optical study

UV-Vis absorption spectra of semiconductor nanoparticles depend on their size whereas absorption minimum increases with the particle size⁴¹. UV-Vis absorption spectra were recorded of samples considering BaSO₄ as background with wavelength 200 to 850 nm. The UV-Visible absorption spectra of Co doped ZnS nanowires are shown in fig. 3. The absorption peaks were observed at 312 nm, 317 nm, 318 nm, 320 nm for pure and Co doped ZnS nanowires respectively. This result shows that band gap decreases due to cobalt doping. The red shift observed of the absorption edge to the smaller wavelength side, it is due to exchange interaction between the outermost d electrons of cobalt ions and the s and p electrons of host electron band. The pure and Co doped ZnS samples show red shift comparable to bulk ZnS¹ (345 nm). This red shift can be attributed to the quantum confinement effect in nanowires. The energy band gap was calculated from Tauc equation⁴² (5) and (6) and it is found to be 3.57, 3.51, 3.45 and 3.40 eV for different x values (0.00, 0.04, 0.08, 0.12) of pure and Co doped ZnS nanowires. Here for pure ZnS NWs the band gap is found to be 3.57 eV and for

$$\alpha h\nu = A(h\nu - E_g)^n \quad (5)$$

cobalt doped ZnS NWs occurs the band gap goes on decreasing. It is well known that ZnS is having direct band gap therefore, the value of n is ½ as transition from valence band to conduction bands direct, therefore equation (5) becomes,

Where α is the absorption coefficient, $h\nu$ is the photon energy, A is

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (6)$$

the constant, E_g is the energy band gap of the sample. Verma et al. has outlined that pure and Co doped ZnS samples show blue shift and energy band gap increases because prepared samples form nanoparticles in nature⁴⁹. But in our case, samples explicitly show red shift and form nanowires and energy band gap goes on decreasing as Co content increases.

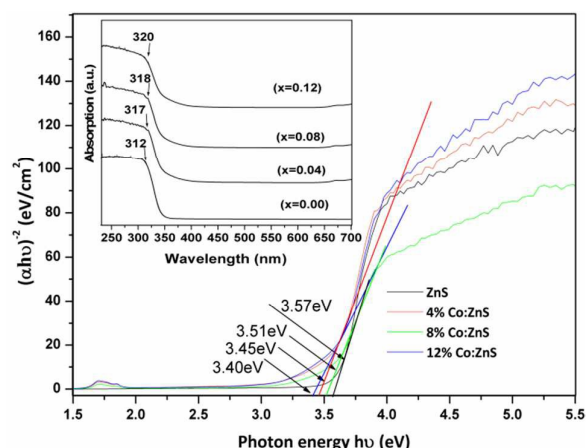
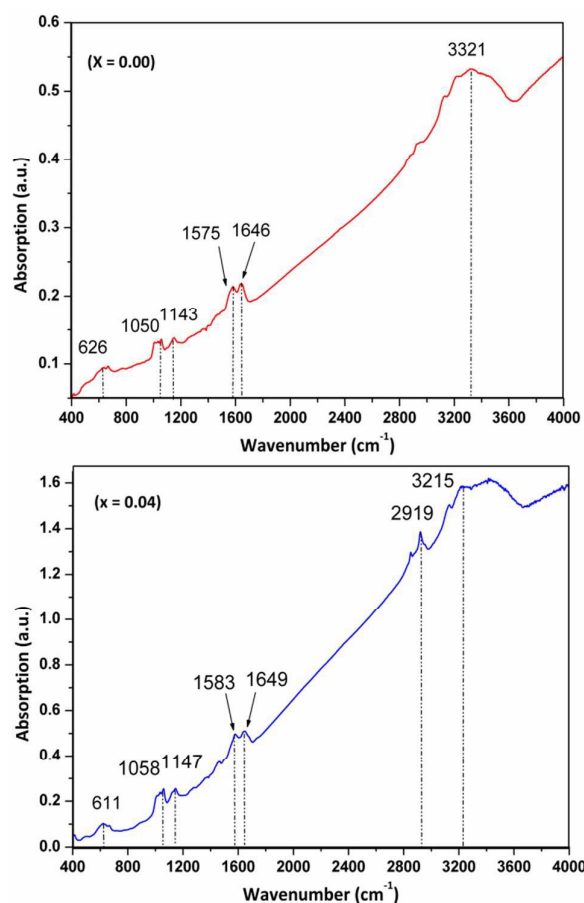


Fig. 3 Band gap and absorption spectra of pure and Co doped ZnS spectra.

FTIR spectroscopic study

FTIR spectrums were employed for the detection of functional groups/chemical species which were presents in the synthesised samples. It is also interpreted that the change in vibrational, absorption band, inter and intra molecular interaction owing to effect of Co doping into ZnS lattice. FTIR spectra for pure and Co doped ZnS samples are shown in fig. 4. The sharp and strong peaks also show the samples were highly crystalline in nature. The backgrounds of KBr and air spectra were eliminated while taking FTIR spectra. In the preparation of pallet the samples of ~5mg were taken in 0.3 gm of KBr powder. There were only few peak observed at 400-4000 cm⁻¹. In the fig. 4, the absorption peak at 500-650 cm⁻¹ indicating Zn and S stretching⁴³. It indicates the formation of cobalt doped ZnS nanowires. The absorption bands at 2912 to 2920 cm⁻¹ attribute to -C-H vibration⁴³ which is observed due to doping of cobalt. From the FTIR spectra at 3215 to 3321 cm⁻¹ indicate OH stretching. The peaks at 1050 to 1147 cm⁻¹ were observed due to the formation of microstructure Co doped ZnS in samples^{44, 47}. The bands at 1575 to 1650 cm⁻¹ are due to -C=O stretching mode arising from the absorption of atmospheric CO₂ on the surface of samples⁴⁵. The band values are in good agreement with the reported literature⁴³⁻⁴⁶.



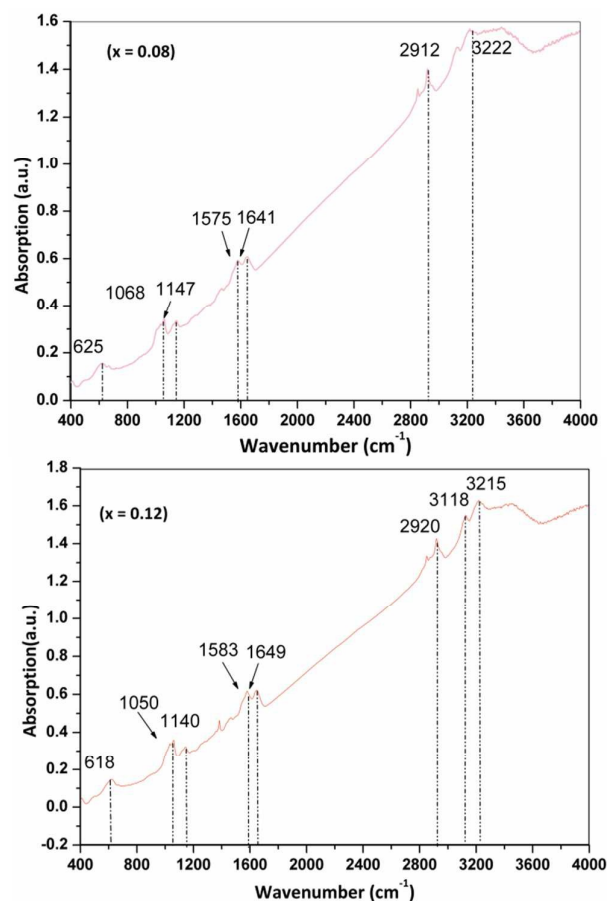


Fig.4 FTIR spectra of Pure and Co doped ZnS nanowires.

Morphological study

Transmission electron microscopy of pure and Co doped ZnS samples are shown in fig.5(a,b) and 5(c,d). TEM micrograph clearly shows that nanowire structures of as synthesized samples. TEM image shows tip of nanowires have triangular shape which shows hexagonal structure of samples. The average diameter and length of undoped and Co doped ZnS NWs were found to be 9 nm, 1.92 μm and 12 nm, 1.52 μm respectively. Selected area electron diffraction (SEAD) patterns also show that the concentric rings which reflect hexagonal structure. TEM micrographs of Co doped ZnS NWs are shown in fig.5(a, b) and 5(c, d) and SEAD patterns of pure and Co doped ZnS NWs samples are depicted in the fig.5(e)

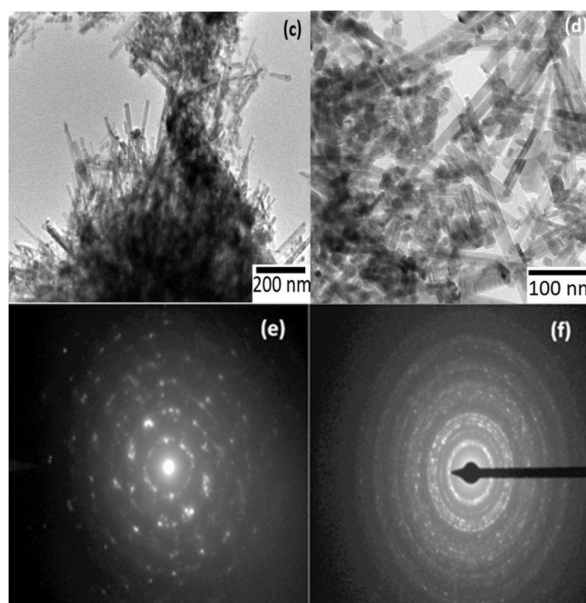
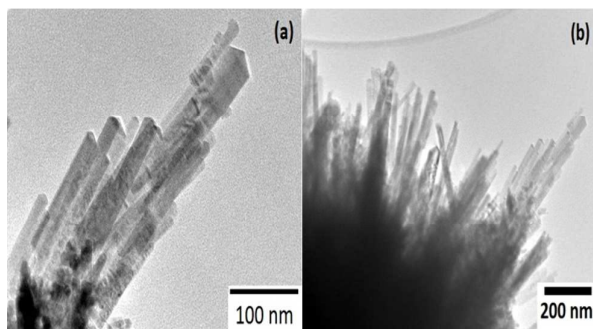


Fig.5(a, b)TEM micrograph of pure, (c, d) for 4% Co doped ZnS nanowires with different magnification respectively and (e), (f) SEAD patterns of pure and 4% Co doped ZnS nanowires respectively.

and 5(f) respectively. The compositional analysis of the pure and Co doped ZnS NWs are performed by EDS which can be shown in ESI† fig. 4. The chemical composition analysis shows the presence of Zn, S and Co signals only, indicating that the nanowires are made up of that element which confirms the high purity of the samples. It is confirmed that the cobalt is present in samples. For pure ZnS structure, qualitative analysis reveals that the atomic ratio of Zn to S is very close to 1:1 stoichiometrically. For 4% Co doped ZnS NWs atomic% of Zn, Co and S was found to be 51.63, 1.66, 46.71 respectively. Whereas for 8% and 12% Co:ZnS NWs the atomic % of the elements of Zn, Co, S was found to be 50.85, 2.44, 46.70 and 47.67, 3.05, 49.29 respectively. The amount of Co element detected is less than those actually added during synthesis. For detail information see ESI† table 1 for weight% and atomic% of pure and Co doped ZnS NWs.

Magnetic study

Magnetic studies of cobalt doped ZnS nanowires have been outlined using vibrating sample magnetometer VSM measurements. Fig.6(a) shows the M-H curves of nanowires with field strength -0.5 T to 0.5 T at 300 K. Magnetic study revealed that cobalt doped ZnS NWs exhibits weak ferromagnetism at room temperature. The magnetization of Co doped ZnS nanowires may arise from the magnetic exchange interaction between Co^{2+} ions⁴⁸. Fig.6(b) shows magnifying image of the magnetic hysteresis loop of 4% Co:ZnS, 8%Co:ZnS and 12%Co: ZnS NWs measured at room temperature. The coercivity (H_c) of NWs were found to be 32.44 Oe for 4% Co:ZnS, 209.33 Oe for 8% Co:ZnS and 99.77 Oe for 12% Co:ZnS NWs. The saturation magnetizations (M_s) are 4.1933, 4.1233 and 4.3933 emu/gm respectively. The remanent magnetizations of samples were found to be 0.026, 0.1202 and 0.1069 emu/gm respectively. The value of coercivity increases for 8% doping of Co

but concentration increases to 12% the coercivity suddenly decreases, it is also observed for retentivity. The saturation magnetization of Co doped ZnS NWs decreases at 8% doping of Cobalt and it also increases for 12% doping of Co. This behaviour clearly indicates that substitution of Co ions in ZnS matrix induces a mixed ferromagnetic and paramagnetic character in the Co doped ZnS NWs. It may be ascribed to the intrinsic coupling between the doped Co ions in to ZnS lattice. Verma et al. shows that the ferromagnetic character is decreased with increased Co ions concentrations due to antiferromagnetic interactions⁴⁹. We have also got the same results of as synthesized samples.

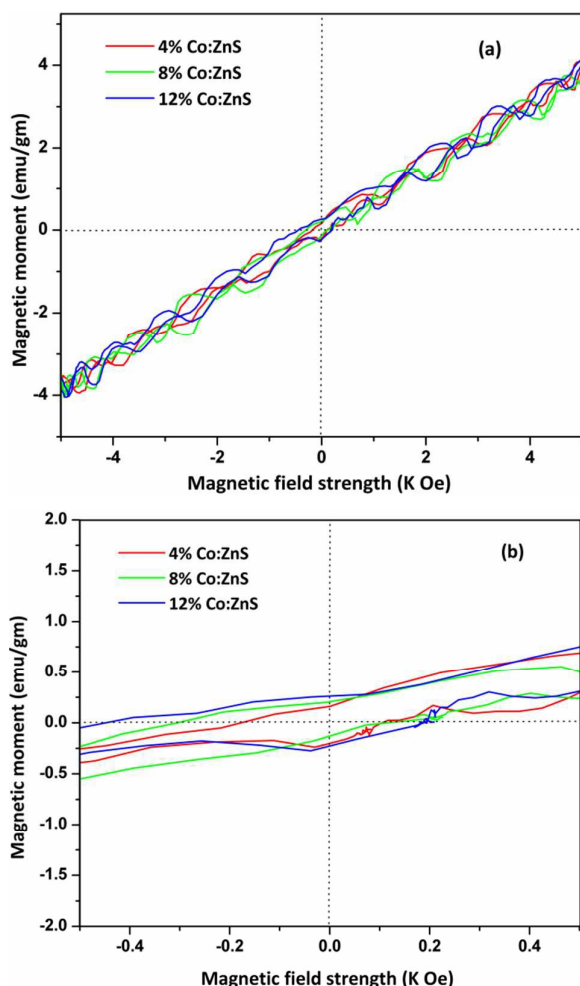


Fig. 6 (a) M-H curves of cobalt doped ZnS nanowires and (b) magnifying images of (a) which clearly reflect the magnetic behaviour of cobalt doped ZnS nanowires.

Conclusions

Pure and Cobalt doped ZnS NWs were successfully synthesized by hydrothermal method. The angle dispersive X-ray diffraction was used for PDF analysis. The PDF was used to address the structure of pure and cobalt doped ZnS NWs. The diameter of the pure and Co

doped ZnS NWs was evaluated using PDF data and it is in good agreement with the diameter values obtained from TEM. The synthesized pure and cobalt doped ZnS NWs having hexagonal (wurtzite) structure. The energy band gap of cobalt doped ZnS samples shows more red shift as compared to the bulk ZnS band gap. It is confirmed from FTIR study cobalt substitutes into ZnS structure. TEM micrograph clearly shows nanowires for pure and Co doped ZnS samples. Samples show weak ferromagnetism at room temperature which was confirmed from VSM. By tuning the properties of pure and Co doped ZnS nanowires could be widely used in optical, electronic and magnetic field. The present investigations open the door for potential applications in the photocatalytic reduction and spintronic devices.

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GRAPHICAL ABSTRACT

Synthesis, pair distribution function and diverse properties study on cobalt doped ZnS nanowires[†]

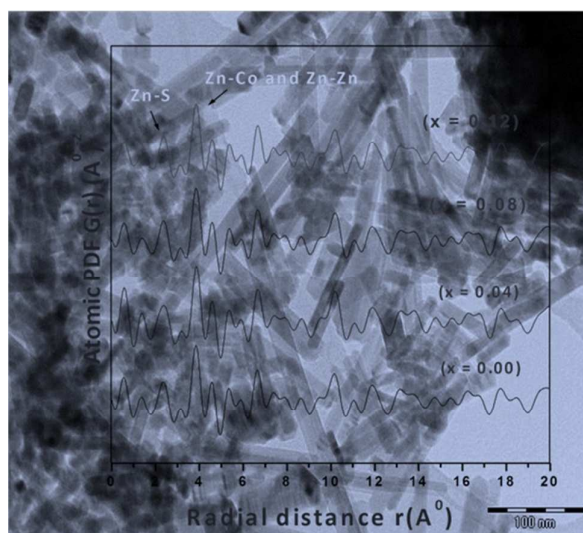
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The fundamental atomic structure of pure and Co doped ZnS nanowires has been studied using pair distribution function (PDF) analysis. It was confirmed that samples have hexagonal (wurtzite) structure. The interatomic distance was calculated using PDF analysis. It was observed that the energy band gap goes on reducing as Co content increasing. TEM micrographs clearly show growth of nanowires of synthesized samples.



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[†] Electronic Supplementary Information (ESI) available: Supplemental Fig. 1 shows SXRD patterns, fig. 2, 3 shows TEM image of pure ZnS and 4% Co doped ZnS nanowires with different magnification and fig. 4 shows EDS spectra of samples. Table 1 gives the values of elemental concentration.

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