Room temperature ferromagnetism in Ni doped ZnS nanoparticles

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Ni doped ZnS (Zn1–xNi xS) nanoparticles with Ni concentration x = 0.01, 0.03 and 0.05 were synthesized by the chemical co-precipitation technique. Powder X-ray diffraction (XRD) reveals that Ni incorporates into the ZnS crystal lattice with a cubic structure. Transmission electron microscopy (TEM) measurements show that the average size of these nanoparticles is in the range 2–3 nm. Micro-Raman and photoluminescence (PL) studies also confirm the incorporation of Ni in the lattice. X-ray absorption spectroscopy (XAS) reveals that Ni replace the Zn atoms in the host lattice without forming second phases. The ZnS nanoparticles with lower Ni concentration exhibit saturated hysteresis loop at room temperature indicating ferromagnetism where as samples having higher Ni concentrations did not show such saturation confirming the intrinsic nature of the ferromagnetism at smaller doping.

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1. Introduction

Discovery of a new class of spintronics devices based on room temperature ferromagnetism (RTFM) has stimulated intensive research in the synthesis of materials showing RTFM [1]. Dilute magnetic semiconductors (DMS) having RTFM, have attracted the curiosity of researchers, because of the exchange interactions between the spins of the dopant atoms and the carriers in the semiconductor host, as they are expected to bring global ferromagnetic order in the entire lattice at room temperature [2]. However, transition metal doping in DMS materials leads to some problems such as formation of secondary phases or clusters, and the mechanism of ferromagnetism in these materials is still unclear, making them undesirable for device applications. A lot of work has been reported on RTFM particularly in wide band gap semiconductor host materials such as ZnO [3–6], TiO2 [7–9], SnO2 [10–13], AlN [14–16], GaN [17,18] doped with a few percent of 3d transition-metal ions.

Among the various host materials investigated for DMS, ZnS is one of the prospective candidate for device applications because of its wide band gap (3.68 eV), large Bohr exciton radius (2.5 nm), large exciton binding energy (40 meV), high index of refraction (2.27) [19]. ZnS has been recognized as an outstanding host semiconductor for sustaining room-temperature ferromagnetism when doped with a variety of 3d transition metal ions. Various reports are available on room-temperature ferromagnetism in ZnS doped with Mn [20], Co [21], Cr [19] and Fe [22] etc. However, ZnS doped with Ni has been the least investigated with few reports available [23,24] and they concern mainly the photo catalytic properties. Nickel has been chosen as the dopant for our present investigation because of the above reasons such as (i) Ni is an important transition-metal element having ionic radius close to crystal lattice and substitutes for Zn2+ in the lattice, (ii) Ni metal is ferromagnetic having high magnetic moment, (iii) theoretical research also supports the prospect of producing ferromagnetism in nickel based ferromagnetic semiconductors [25,26] and (iv) reports on room-temperature ferromagnetism in Ni doped ZnS nanoparticles are not available.

2. Experimental

All the chemicals used were of Analytical Reagent grade (Sigma Aldrich chemicals), without further purification. Zinc acetate, sodium sulfide and nickel acetate were used as source materials for Zn, S and Ni, respectively, with double distilled water as solvent. Ni-doped ZnS nanoparticles have been synthesized using the soft chemical approach, known as chemical co-precipitation technique, [18,20] by mixing nickel acetate of different concentrations with zinc acetate aqueous solution. Sodium sulfide aqueous solution was also added to this solution drop-by-drop followed by thioglycerol, to prevent agglomeration of the particles. The precipitates so formed were washed and dried to remove the last adherent. The undoped and Ni-doped ZnS nanoparticles, so obtained, were finally crushed to the powder form for further investigations.

The structural properties of Zn1–xNi xS nanoparticles were investigated using “Panaanalytical Xpert Diffraclometer”. The particle size determination and structure confirmations were made using a JEOL High Resolution Transition Electron

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Microscopy (HR-TEM) coupled with an energy dispersive X-ray analysis (EDX) accessory. Photoluminescence and Raman spectroscopy measurements were carried out using a Horiba Jobin Yvon HR-800 UV micro-PL Raman setup. The 325 nm line of a He–Cd laser was used as the excitation source with a 2400 grooves/mm grating in the backscattering geometry. Magnetic measurements were made using a Quantum Design Vibrating Sample Magnetometer (VSM). The X-ray absorption spectroscopy (XAS) measurements were performed at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan operated at 1.5 GeV with a maximum stored current of 200 mA. The hard X-ray measurements were recorded with a spacing of 0.3 eV for the XANES in the fluorescence yield (FY) mode using a Lytle detector at room temperature, using a Si(111) double crystal monochromator in BL01C and BL17C beamline. All spectra were normalized to a unity step height in the absorption coefficient from well below to well above the edge. Standard samples of ZnO, ZnS, NiO, and the foils of Zn and Ni were used for energy calibration and also for comparing the different electronic valence states.

3. Results and discussion

XRD patterns of Zn$_{1-x}$Ni$_x$S nanoparticles are shown in Fig. 1 and are fitted to the cubic (zinc blende) phase of ZnS and indexed. Additional peaks are not observed indicating that no impurity phases are formed during the preparation process. Broadening of the diffraction peaks indicates the nanocrystalline nature of the sample. The average crystallite size is calculated from the full width at half maximum (FWHM) of the XRD peaks (calculated using the Debye Scherrer formula; $D = k \lambda / \beta \cos \theta$, where $\theta$ is the diffraction angle, $\beta$ is the FWHM of the diffraction peak, $k$ is the geometric factor and $D$ is the mean crystallite size) is found to be 2.8 nm, 1.86 nm and 1.4 nm for 1%, 3% and 5% Ni doped ZnS nanoparticles, respectively. The size observed is thus in the strong charge confinement regime.

The FWHM of any diffraction peak can be expressed as a linear combination of the contribution from lattice strain and small grain size (using Hall and Williamson relation $(\beta \cos \theta) / \lambda = 1 / D + \eta \sin \theta / \lambda$, where $\eta$ is the effective strain). Fig. 2 represents the plot between $(\beta \cos \theta) / \lambda$ and $\sin \theta / \lambda$. The graph has a positive slope indicating a tensile strain. From the XRD patterns, it is observed that peak positions shift towards higher 2$\theta$ value with increasing Ni doping indicating a decrease in the lattice parameters ($5.36–5.28$ Å). This is due to the smaller ionic radius of Ni$^{2+}$ (0.83 Å) compared to that of Zn$^{2+}$ (0.88 Å). This confirms that Ni is entering the Zn lattice substitutionally replacing Zn ions in the ZnS matrix. Fig. 3 shows typical HR-TEM image of Zn$_{1-x}$Ni$_x$S nanoparticles illustrating that the average size of the nanoparticles is in the range 2–3 nm in agreement with the XRD data above. Clear lattice fringes (circled for clarity) observed in the images in Fig. 3 confirm the crystalline nature of Zn$_{1-x}$Ni$_x$S of the individual nanoparticles. Inset of Fig. 3 presents the selected area electron diffraction (SAED) pattern confirming the cubic structure of Zn$_{1-x}$Ni$_x$S nanoparticles. The diffused rings in the SAED pattern indicate that the particles are small in size [27].

The Raman spectra of ZnS polytypes have been described by Schneider and Kirby [28]. Nilsen et al. [29] reported the one- and two-phonon Raman spectra of bulk cubic ZnS. For bulk cubic ZnS, the transverse optical (TO) and longitudinal optical (LO) zone-center phonons have been observed near 271 and 352 cm$^{-1}$ respectively. Room temperature Raman spectra of the Zn$_{1-x}$Ni$_x$S nanoparticles are presented in Fig. 4. The peaks observed near 263 and 346 cm$^{-1}$ may therefore be assigned to TO and LO phonon modes respectively. The observed broadening of the Raman peaks and their shifting towards lower energy as compared to the bulk values indicate quantum confinement effects in Ni doped ZnS nanoparticles. The position of the TO mode is slightly different for 3% Ni doped ZnS. This may be due to two reasons, first may be due to small amount of compressive strain and second may be due to large number of sulfur (S) vacancies. It is seen from the PL spectra that the intensity of the 412 nm peak in the 3% Ni doped ZnS is higher compared to others, which indicates that the 3% Ni doped ZnS has more number of S vacancies.

One additional weak mode (shoulder) near 312 cm$^{-1}$ is also observed in the Raman spectra which may be connected with surface vibrations and may be attributed to a surface phonon mode. Such modes have been reported in II–VI nanocrystalline semiconductors in the literature [30–32]. In nanoparticles, since the surface-to-volume ratio is much higher, there is an increase in the number of atoms on the surface compared to the number of atoms inside the particles. The vibrational frequency of the surface atoms is lower than that of the interior atoms as they are bound by weaker force. The surface mode is predictable since: (a) the surface-to-volume ratio increases, with decreasing crystallite size, therefore, the peak intensity of the surface phonons would enhance. (b) the surface mode should be positioned between the TO and LO modes [33]. Cumulative effect of phonon confinement and tensile strain given above may be the reason for the red shift of LO Raman peak in our sample.

The room temperature PL spectra of Zn$_{1-x}$Ni$_x$S nanoparticles with concentrations of $x = 0.01$, 0.03 and 0.05 shown in Fig. 5(a)–(c) are broad and asymmetric. Gaussian fitting of these curves resulted in deconvolution into three peaks and the details of their analysis are presented in Table 1. The first two peaks correspond to blue emission and third one is identified in the green region. It is well reported that Schottky defects are dominating in cubic ZnS [34]. Borse et al. [35] reported emission peak around 425 nm in ZnS nanoparticles corresponding to sulfur vacancies. Lu et al.
also reported one peak around 422 nm attributed to sulfur vacancies. On the basis of these reports, the peak observed in the range 409–414 nm have been assigned to sulfur vacancies i.e. to the recombination of electrons at the sulfur vacancy with holes in the valence band. With increase in Ni doping 420 nm peak is blue shifted indicating the increase in energy responsible for this transition.

The origin of the emission peak observed in the range 453–465 nm has been reported [37]. In our case this peak does not result from impurity states related with Ni dopant, but originated from native defect states. Similar PL peak was observed around this wavelength range and was attributed to emission from trap states in ZnS that are related to the native zinc vacancy [38–40]. The green emission peak observed in the range 511–530 nm may be a result of the recombination between the shallow donor level (S vacancy) and the t2 level of Ni$^{2+}$ ions that replaced the Zn$^{2+}$ ions in the ZnS matrix [37,40]. The green emission peak is steadily shifted to longer wavelength with increase in Ni concentration. The energy level corresponding to S vacancy remains same relative to valence band in spite of the variation in Ni concentration. So it can be suggested that the t2 energy level of Ni$^{2+}$ ions is farther from the valence band with increasing Ni$^{2+}$ concentrations [40].

Fig. 6 shows the Zn K-edge XAS spectra obtained on the Zn$_{1-x}$Ni$_x$S nano-particles along with the ZnO and ZnS bulk standards that are normalized at the photon energy around 100 eV from the absorption edge at $E_0 = 9661.6$ eV. The inset of the figure shows the first derivative plots of these spectra. These multi-feature absorption spectra between 9658 and 9667 eV correspond to the transitions from Zn 1$s$ to the empty 4$p$ states with various overlapping electronic orbital states. The energy position of maximum of the peak does not change with increasing $x$ indicating that the valence of Zn is not changed but maintained in the divalent state. The spectra of the ZnS series (nano-particle) are slightly different from the ZnS bulk. Owing to different orientations of the 4$p$ orbitals in the crystal symmetry of Zn–S, the $p_x(p_y)$ and $p_z(p_x)$ bands. The size effect (particle size) would influence the atomic geometry and electron–orbital interaction and therefore would influence the spectra. The main feature of the Zn$_{1-x}$Ni$_x$S samples appears broad with a shoulder features at 9663 eV which is enhanced as $x$ is increased indicating the presence of the orbital hybridization in Zn 4$p$ and Ni 3$d$ states, which means a change in the atomic structural geometry (structure distortion) through a change in the bond length (Zn–S) or bond angle (S–Zn–S) with the Ni doping.

The transition metal Ni K-edge XAS spectra are mostly related to the partial density of Ni 4$p$ states at the Zn site. However, the unoccupied states of the 3$d$ (due to quadrupled transition) and 4$p$ bands are sensitive to the local structure and the type of the green emission peak observed in the range 511–530 nm may be a result of the recombination between the shallow donor level (S vacancy) and the t2 level of Ni$^{2+}$ ions that replaced the Zn$^{2+}$ ions in the ZnS matrix [37,40]. The green emission peak is steadily shifted to longer wavelength with increase in Ni concentration. The energy level corresponding to S vacancy remains same relative to valence band in spite of the variation in Ni concentration. So it can be suggested that the t2 energy level of Ni$^{2+}$ ions is farther from the valence band with increasing Ni$^{2+}$ concentrations [40].

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nearest neighbors and the valence states are also observed. Fig. 7 presents the Ni K-edge spectra of these samples along with NiO film and the Ni metal foil. These spectra of $x = 0.01–0.05$ are noisy due to the lower concentration of the Ni in the crystals. The spectra can still be interpreted to characterize the effect of Ni substitution in the ZnS nano-particles as compared to the standards. No energy shift is observed in the main absorption peaks in the Ni K-edge spectra for different Ni concentration indicating that the Ni valence remains the same i.e. $2^+$ by a comparison with the divalent Ni standard in NiO. The spectra in the high energy region (8350–8367 eV) are dissimilar to the NiO (rocksalt structure) indicating that no NiO cluster or Ni impurity is present in the system. Since the spectral line shapes do not show any large change and also different from the NiO it is concluded that Ni replaces Zn sites in the $\text{Zn}_{1-x}\text{Ni}_x\text{S}$ nanoparticles in conformity with the XRD and Raman measurements above.

The magnetization ($M$) vs. magnetic field ($H$) curves recorded on the $\text{Zn}_{1-x}\text{Ni}_x\text{S}$ nanoparticles with $x = 0.01, 0.03$ and $0.05$ are presented in Fig. 8. The hysteresis loops with perceptible coercivity values of 82 Oe, 73 Oe and 50 Oe and remnant magnetization ($M_r$) of $22 \times 10^{-3}$ emu/g, $20.7 \times 10^{-3}$ emu/g and $16.7 \times 10^{-3}$ emu/g, respectively, are observed for $x = 0.01, 0.03$, and $0.05$. These results indicate that Ni substitution in the ZnS matrix can be utilized for magnetic applications.
have been observed respectively for 1%, 3% and 5% Ni doped ZnS nanoparticles (as shown in inset of Fig. 8). Thus the observed ferromagnetism is mainly due to the Ni ions substituting for Zn in the ZnS host lattice and not due to Ni metal cluster like phases as confirmed by the XRD and XAS studies. It is speculated that the ferromagnetism in the Ni-doped ZnS samples may be a result of the exchange interaction between localized ‘d’ spins on the Ni ions and the free delocalized carries.

The hysteresis loop for 1% Ni doped ZnS nanoparticles exhibit saturation which is not observed at higher concentrations of Ni. Bi et al. [27] have observed that the distance between the Co atoms decide the type of magnetic interaction (ferromagnetic or antiferromagnetic) in Co doped ZnS. Due to very small size of Ni doped ZnS nanoparticles (2–3 nm), surface to volume ratio anticipated to be very high which means that the surface related properties are thought to be noticeably pronounced. For higher doping of Ni, the number of Ni ions residing on the surface is expected to be large as compared to lower doping. The present result may also be explained to be a result of reduced Ni–Ni distance and may strengthen anti-ferromagnetic interaction resulting in the non-saturation of hysteresis loop.

The ferromagnetic behavior at lower doping of Ni in ZnS may be attributed to the existence of small magnetic dipoles positioned at the surface of the nanoparticles which interact with their nearest neighbors inside the particles. The exchange energy in these magnetic dipoles force other neighboring dipoles to be aligned in the same direction. Since the surface to volume ratio is very high in case of the nanoparticles, the population of magnetic dipoles oriented in the same direction will be enhanced at the surface [41]. As a result, the surface of nanoparticles will be more ferromagnetically ordered. Gao et al. [42] and Zhu et al. [43] reported room temperature ferromagnetism in undoped ZnS nanoparticles and ZnS nanowires, respectively. But we observed higher value of magnetization as compared to undoped ZnS nanoparticles and ZnS nanowires, may be due to doping of ferromagnetic Ni having high magnetic moment.

4. Conclusions

In the present study, Ni doped ZnS (Zn1-xNi,xS) nanoparticles with x = 0.01, 0.03, 0.05 have been synthesized successfully through chemical co-precipitation method using thioglycerol as the capping agent. Structural analysis indicates that the Ni doped ZnS nanoparticles crystallize in a cubic structure without forming other secondary phases. The substitution of Ni ions at Zn sites is also confirmed through XAS studies of Zn and Ni K-edge. Raman studies show the quantum confinement effects in Zn1-xNi,xS nanoparticles. The room temperature M–H curves indicate that Zn1-xNi,xS nanoparticles exhibit RTFM. The non-saturation in M–H curve with increasing Ni content demonstrates that observed ferromagnetism at room temperature is an intrinsic property of Zn1-xNi,xS nanoparticles. The present studies demonstrate that very small doping of Ni in ZnS nanoparticles gives rise to room-temperature ferromagnetic ordering which may be useful for spintronic applications.

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