

Room Temperature Ferromagnetism in Cr Doped ZnSe Powders Prepared by Solid State Reaction

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Zn_{1-x}Cr_xSe ($x = 0.00, 0.05, \& 0.10$) powders were prepared by solid state reaction method. The influence of chromium (Cr) doping into ZnSe on structural, optical and magnetic properties Zn_{1-x}Cr_xSe powder samples was studied and reported. All the Zn_{1-x}Cr_xSe powder samples were identified in zinc blende crystal structure. The lattice constant of Zn_{1-x}Cr_xSe samples decreased with increase in Cr concentration. Diffuse reflectance measurements confirmed an increase in the band gap with increase of Cr concentration. The Zn_{1-x}Cr_xSe samples exhibited clear hysteresis loop with enhanced room temperature ferromagnetism.

Keywords: Solid state reaction, X-ray diffraction, Diffuse reflectance, Room temperature ferromagnetism.

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1. INTRODUCTION

The dilute magnetic semiconductors (DMS) which exhibit room temperature ferromagnetism (RTFM) has gained profound interest in recent years appreciating their potential applications in spintronic devices. Spintronic devices hold several advantages such as lower power consumption, non-volatility, higher integration densities and data processing speed over the conventional devices [1]. The unusual spintronic applications of DMS are due to the accommodation of charge and spin degrees of freedom into single matter and their interplay is expected to explore novel physics and new devices [2-5]. With the intention of making these applications practically feasible, it is essential to attain ferromagnetism at or above room temperature. The DMS can be obtained by the incorporation of transition metal or rare earth metal ions such as Mn, Fe, Co, Cr, Ni, Cu, Sm, Er, Dy, Gd in to the core of II-VI, IV-VI and III-V semiconductors. The exchange interaction between the spin of the dopant atoms and the carriers in the semiconductor host is awaited to bring global ferromagnetic order in the complete lattice [6]. In this trail, substantial work has been carried out on transition metal doped Zn based chalcogenides such as ZnS, ZnSe and ZnTe [7-14]. The structure, electronic and magnetic properties of DMS strongly depend on the nature and concentration of the dopant. Several research groups [15-17] have investigated the effect of doping of magnetic transition elements and rare-earth elements into the host semiconductor compounds both theoretically and experimentally. Historical reports on DMS reveal that the II-VI host semiconductor materials when doped with transition magnetic element had greater solubility limit [18]. The ternary

DMS based on II-VI semiconductor compounds such as CdTe, CdSe, CdS, ZnS, ZnSe as host materials have been widely studied [19-25]. Among the binary semiconductors, ZnSe is an important II-VI group semiconductor material, stated to be chemically more stable and technologically better than other semiconductor materials. ZnSe with an energy gap of 2.7 eV is extensively used for the fabrication of blue-light emitting diodes (LEDs), laser diodes (LDs) and non-linear opto-electronic devices and so on [26]. In this manuscript, we made an attempt for the preparation of ZnSe and Cr doped ZnSe powder by solid state reaction. The influence of Cr impurity into ZnSe on its structural, optical and magnetic properties was investigated and the results were discussed.

2. EXPERIMENTAL

Chromium (Cr) doped ZnSe powders (Zn_{1-x}Cr_xSe) were synthesized at high temperatures using solid state reaction. Commercially available pure ZnSe (99.999 %) was used as starting material. Pure Cr and Se (99.99 %, M/S Sigma-Aldrich) were used to prepare CrSe. Stoichiometric amounts of Cr and Se were weighed using microbalance. It is then mixed and ground thoroughly in an agate mortar with a pestle until uniform homogeneity is attained. This solid mixture was loaded tightly into a graphitized quartz tube of length 20 and 0.7 cm diameter. The tube was sealed in a vacuum of 2×10^{-6} torr and it is kept in a horizontal furnace at a firing temperature of 1000 °C for about 2 hours. Later the furnace was cooled slowly to room temperature to get polycrystalline CrSe powder. Then, appropriate quantities of freshly prepared CrSe and ZnSe were mixed and ground

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thoroughly for 18 hours to ensure homogeneity and then sintered at 600 °C for 6 hours under a pressure of 2×10^{-3} mbar. The calcined Cr doped ZnSe powders were investigated for structural, optical and magnetic properties. Structural characterization was carried out with a standard X-ray diffractometer (Bruker, D8 Advance, with monochromatic $\text{CuK}\alpha$ radiation, $\lambda = 0.15406$ nm, operated at 40 kV and 20 mA) in the diffraction angle (2θ) range of 20° - 80° . Optical characterizations were carried out by diffuse reflectance spectroscopy taken in the wavelength range of 200-2500 nm and were recorded using double beam UV-Vis-NIR spectrophotometer (Jasco V-670). Magnetic measurements was examined through magnetic field-dependent magnetization loops (hysteresis loops) up to 1 T magnetic field at room temperature by a calibrated vibrating sample magnetometer, called VSM (Lake Shore 7404). The magnetic field is applied perpendicular to the sample plane, and the magnetization loops of the sample holder were also measured for correction.

3. RESULTS AND DISCUSSION

3.1 Structural Properties

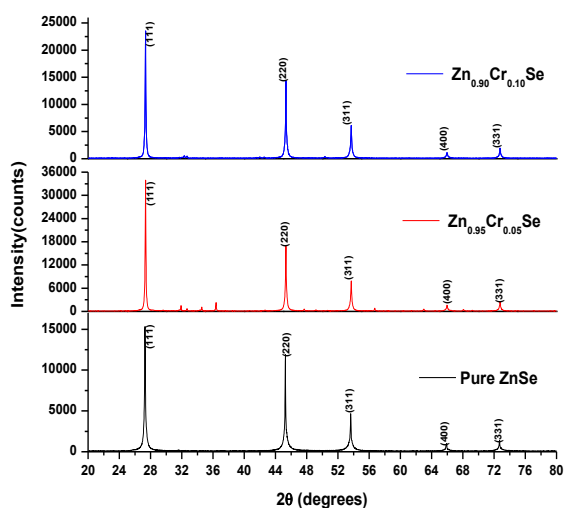


Fig. 1 – XRD patterns of $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$ powder samples

X-ray diffractograms were used to investigate the effect of Cr doping on the structure and the phase composition of the prepared samples. Fig. 1 shows the X-ray diffraction (XRD) patterns of the pure ZnSe and Cr doped ZnSe powder samples. All the characteristic diffraction peaks of the samples were indexed to zinc blende crystal structure of ZnSe, having preferential orientation along (1 1 1) with others peaks (2 0 0), (2 2 0), (3 1 1), (2 2 2) and (4 0 0), which were in good agreement with the JCPDS card (No. 80-0021). Further it is to be noted that the incorporation of Cr ion into ZnSe system retains their crystal structure without altering the structure of host ZnSe. As a matter of fact, no diffraction peaks corresponding to Cr precipitates nor Cr related impurity phase were detected, which further confirmed the formation of $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$ solid solution, indicating that Cr has been doped into the crystal lattice of ZnSe. At higher Cr concentrations from 5 at. % to 10 at. % the intensity of these peaks of

ZnSe reduced significantly. It can be seen from the XRD data that the diffraction peaks of Cr doped ZnSe slightly shift to the higher angle with increasing Cr concentration. This is due to the reason that the Cr atoms occupy Zn sites causing slight peak shift towards higher angle.

It is observed from Fig. 2 that the lattice constant 'a' decreased from 5.655 to 5.645 Å with increase of Cr concentration in ZnSe. This decrease in lattice constant is due to the difference in the ionic radii, as the ionic radii of Cr^{3+} is 0.63 Å which is smaller than the Zn^{2+} ions having the ionic radii as 0.80 Å. Similar results were also observed in Cr doped ZnS:Cr nanoparticles and in Co doped ZnS nanorods [27, 28]. The Table 1 shows the structural parameters of Pure ZnSe and Cr doped ZnSe powder samples.

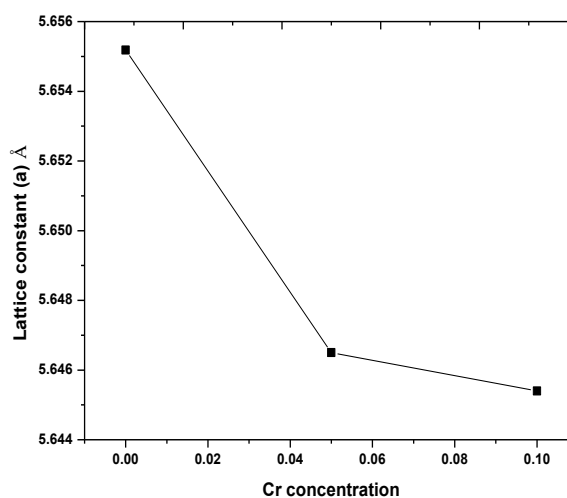


Fig. 2 – Variation of lattice constant (a) with Cr concentration

Table 1 – Variation of lattice parameter with Cr concentration in ZnSe along (111) plane

Cr concentration (x)	Peak position (2θ)	d-spacing (Å)	Lattice constant s (Å) $a = b = c$	Particle size (nm)
0.00	27.292	3.264	5.655	38
0.05	27.388	3.261	5.646	141
0.10	27.184	3.265	5.645	150

3.2 Optical Properties

Room temperature diffuse reflectance spectral (DRS) studies in the UV-vis region were carried out to estimate the optical band gap of pure and Cr doped ZnSe powder samples. Fig. 3 shows the diffuse reflectance spectra as a function of wavelength for pure and Cr doped ZnSe powder samples. All spectra were taken in the range of 200-800 nm. The characteristic absorption edges lie in the range of 400-500 nm. The absorption edges are seen to be shifted towards lower wavelengths/higher energies with increasing Cr content as shown in Fig. 3 indicating that Cr ions replace the Zn ions in the ZnSe lattice and hence the band gap increases with increasing Cr concentration.

The trend of systematic variation of diffuse reflectance near the band edge for the doped samples

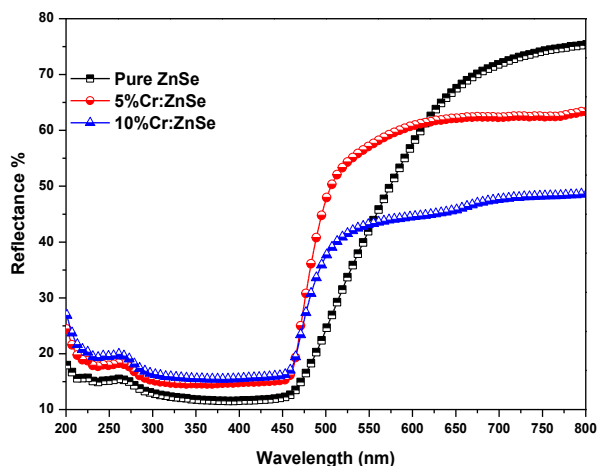


Fig. 3 – Diffused reflectance spectra of pure and Cr doped ZnSe powder samples for different Cr concentrations

compared with the undoped sample is a further indication of the incorporation of Cr ions in the ZnSe lattice. This increase in the band gap of Cr doped ZnSe is obvious due to the large band gap of CrSe (3.7 eV) that of ZnSe [29]. Similar increase in band gap was observed by Krishnaiah et al. in Cr doped ZnTe single crystals [30].

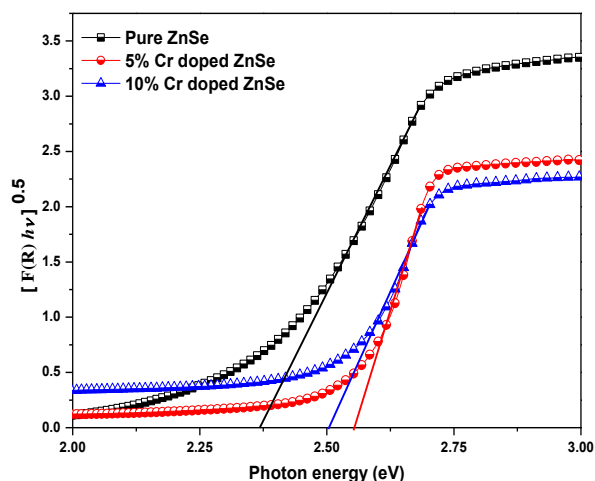


Fig. 4 – Plot between Kubelka-Munk function $F(R)^2$ versus Photon energy

3.3 Magnetic Properties

Fig. 5 shows the field-dependent magnetization ($M-H$) curves of $Zn_{1-x}Cr_xSe$ ($x = 0.05, 0.10$) performed at room temperature using vibrating sample magnetometer in the field range of 0 to ± 12000 G. The magnetization curve of undoped ZnSe indicating diamagnetic behavior can be obtained from the literature [31] with the calculated magnetic susceptibility as $-1.73 \cdot 10^{-6}$ emu/cm³, which agrees with the values reported [32-34]. Hence, from the above literature it is inferred that pure ZnSe is diamagnetic in nature having negative susceptibility and hence ferromagnetism in it is not expected. It is perceived from Fig. 5 that the Cr doped ZnSe powder samples exhibited strong ferromagnetic ordering at room temperature with increasing Cr concentration. In brief,

the observed ferromagnetism in Cr doped ZnSe was attributed to the substitution of Cr for Zn in the ZnSe host lattice providing the necessary unpaired electrons for ferromagnetism rather than the Cr clusters. Thus, the observed intrinsic ferromagnetism in the Cr doped ZnSe samples may arise from the magnetic exchange interaction between localized 'd' spins of the Cr ions and the free delocalized carriers. The possible justifications could be presence of Cr clusters and formation of secondary phases such as Cr oxide impurities like CrO, Cr₂O₃, CrO₂, CrO₃. As chromium is antiferromagnetic in nature, the witnessed ferromagnetism is not due to the presence of metallic chromium clusters as there is no symptom of metal clusters nor impurity phase was observed in Cr doped ZnSe powder samples within the detectable limit of the XRD and UV spectra. Adding up, the RKKY exchange interaction states that, the magnetism is a result of exchange interaction between local spin-polarized electrons and conductive electrons which leads to the spin polarization of conductive electrons. These spin-polarized conductive electrons carry out an exchange interaction with local spin polarized electrons of other Cr ions. So, after the long range exchange interaction, almost all Cr ions show the same spin direction.

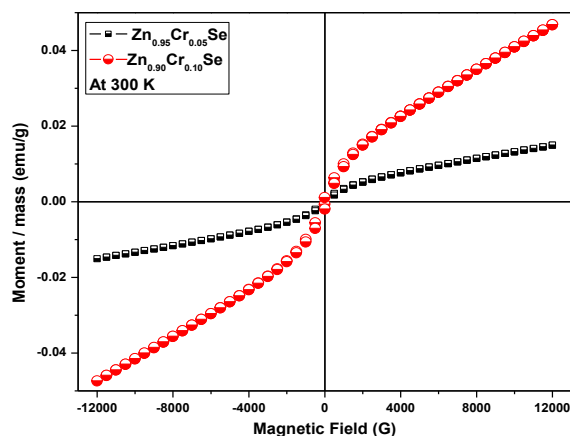


Fig. 5 – Magnetic hysteresis ($M-H$) loops of Cr doped ZnSe powder samples at room temperature

When connecting the aspects like slight shifting of the diffraction peak, decrease of lattice parameter, increase of particle size and increase of band gap energy with Cr doping, authenticates the Cr incorporation into ZnSe and further suggesting the arousal of ferromagnetism from the exchange interaction between local spin-polarized electrons of Cr ions and conductive electrons according to RKKY mechanism rather than Cr oxide impurities. Hence, it may be inferred that the observed ferromagnetic behavior could be ascribed to the substitution of Cr ions for Zn ions in the ZnSe lattice. Similar kind of increase in magnetic behavior with Cr doping was observed by Wang et al. [35] and Kaur et al. [36].

4. CONCLUSION

In conclusion, we report the powder samples of pure and Cr doped ZnSe were synthesized successfully through solid state reaction method. The role of the

dopant concentration on structural, optical and magnetic properties of Cr doped ZnSe powder samples were studied. XRD, studies showed that samples of all compositions crystallized in ZnSe cubic zinc blende structure with the dopant metal atoms entering the lattice as substituents. DRS studies showed a decrease in reflectance with increasing Cr concentration. The band gap increased with increase in Cr content. Band gap values from DRS spectra were in the range of 2.36 eV-2.55 eV which are lower than the bulk ZnSe values. The Cr doped ZnSe powder samples resulted in appreciable enhancement of room temperature

ferromagnetism (RTFM) which is attributed due to the exchange interaction between localized 'd' spins of the Cr ions and the free delocalized carriers.

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