Structural, Optical and Magnetic Properties of Cr Doped CdSe Powders Prepared by Solid State Reaction

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ABSTRACT. As the key factor to study dilute magnetic semiconductors (DMS) for spintronic applications is the potential to harvest high-quality-single-phase dilute magnetic semiconductors. In this paper, we report the room temperature ferromagnetism (RTFM) in Cr doped CdSe powders synthesized through solid state reaction. The structural, optical and magnetic properties of Cd₁₋ₓCrₓSe (x = 0.00, 0.04 and 0.08) powders at room temperature has been investigated. X-ray diffraction (XRD) studies confirmed the chromium (Cr) incorporation into the CdSe crystal lattice without disturbing the hexagonal (wurtzite) structure. The lattice parameters are found to be increased with increased Cr concentration in CdSe lattice. The band gap of Cd₁₋ₓCrₓSe powders has been found to be red shifted as compared to pure CdSe. Magnetic hysteresis (M-H) loops at room temperature reveal the persistence of ferromagnetism in Cd₁₋ₓCrₓSe powders. The saturation magnetization values increased with increase of ‘x’ in Cd₁₋ₓCrₓSe. The observed RTFM might due to carrier mediated exchange interactions present in the system.

Introduction. The novel combination of material properties such as room temperature ferromagnetism and semiconducting behavior has spawned interest in spin current injection for storage devices. Dilute magnetic semiconductors (DMS) are traditional semiconductors in which magnetic transition metal impurities with partially filled ‘d’ states and lanthanide series elements with partially filled ‘f’ shell electrons replace cations of the host semiconducting materials. DMS are assumed to be potential resources for practical spintronic based devices [1-3]. It is an exciting field of research wherein both the charge and spin are used for transportation, storage and processing of information in a single spintronic device [4]. Room temperature ferromagnetism (RTFM) is an essential property for DMS materials. In order to acquire RTFM in DMS materials, transition metal (Fe, Ni, Co, Mn, Cr) has been doped in different semiconductors such as ZnO [5], GaN [5], TiO₂ [6], CdS [7], CdSe [8] and SnO₂ [9]. II-VI and III-V DMS offer unique combination of structural, electronic and magnetic properties, which strongly depends on the nature and concentration of the dopant. The transition metals find greater solubility in II–VI compound semiconductors, when compared with III–VI semiconductors[10]. Till date extensive reports are available on nitride, oxide and chalcogenide DMS with different theories and mechanisms explaining the interactions such as double exchange, super-exchange and RKKY type in both the theoretical and experimental aspects with conflicting results on room temperature ferromagnetism. Yet, the origin of observed magnetism in DMSs is still a topic of debate[11, 12]. Apart from this, various reasons for the observed magnetism...
are contaminants, metal clusters, structural changes and defects present in pure and doped DMS materials [13, 14]. Among II–VI semiconductors, cadmium selenide (CdSe) is a well-known semiconductor, crystallizing in either the wurtzite or the zinc blende structure [15-20]. It has suitable properties for applications in electronics and optoelectronic devices such as laser diodes, high efficiency solar cells, sensors and biomedical imaging devices [21-23]. In present investigation, we have synthesized Cr doped CdSe powders via solid state reaction by varying the chromium concentration.

**Experimental.** Cr doped CdSe powders were synthesized at high temperatures by using a solid state reaction method. Commercially available pure CdSe, Cr and Se (99.99 %, M/S Sigma-Aldrich) were used as starting materials. To prepare CrSe, stoichiometric amount of Cr and Se were weighed and were physically grounded thoroughly in an agate mortar with a pestle until physical homogeneity is attained. These solid mixtures were packed tightly into a graphitized quartz tube of length 20 and 0.7 cm diameter. The tube was sealed in a vacuum of $2 \times 10^{-6}$ mbar and it is kept in a horizontal furnace and fired at 1000 °C for about 2 hours. Later the furnace was cooled slowly to room temperature to get good polycrystalline CrSe powder. Then, appropriate quantities of freshly prepared CrSe and CdSe were mixed and ground thoroughly for 18 h to ensure homogeneity and then sintered at 600°C for 6 hours under a pressure of $10^3$ mbar. The calcined Cr doped CdSe powders were investigated to study structural, optical and magnetic properties.

**Results and discussions.**

**Structural Properties.** The X-ray diffraction patterns of the pure and Cr doped CdSe samples were shown in Fig.1. All the diffraction peaks perfectly matches with the standard JCPDS data (00-77-2307) for CdSe system exhibiting wurtzite structure. No traces of chromium metal clusters or oxides were observed in XRD patterns. The lattice constants ‘a’ and ‘c’ of the Cd$_{1-x}$Cr$_x$Se powders were calculated from XRD data. The lattice constants are found to be increased with increasing Cr concentration as shown in Fig.2. These results imply that the Cr$^{2+}$ has been incorporated into the crystal lattice of CdSe by replacing Cd in CdSe lattice, which produces a strain in the host lattice. Similar variation of lattice constant with dopant was observed by the authors in Cu doped CdSe [24] and Cr doped ZnTe [25]. Fig. 3 shows the EDAX spectra and SEM images of Cr doped CdSe powders. EDAX spectra confirms the existence of Cr in the powder samples and SEM images illustrate that the Cr doped CdSe powder are in submicron size.

**Optical properties.** The optical properties of pure and Cr doped CdSe powders have been studied by recording diffuse reflectance at room temperature. Diffused reflectance spectra and the band gap estimation plots of pure and Cr doped CdSe powders were shown in Fig.4. Pure CdSe powder samples exhibited a band gap of 1.65 eV, whereas Cr 4 at.% and Cr 8 at.% doped CdSe samples have band gap of 1.675 and 1.689 eV, respectively. It is clearly seen from the spectra that the absorption edge shifts towards lower wavelength with increasing chromium concentration. Hence an increase in optical band gap was observed. This may be due to the increase in the carrier concentration by the inclusion of chromium ions and creation of defect levels in the band gap.
Fig. 1. XRD pattern of pure and Cr-doped CdSe powders.

Fig. 2. Deviation of lattice parameter of Cr doped CdSe powders with Cr concentration.
Fig. 3. (a), (b) EDAX spectra and (c), (d) SEM images of Cd$_{1-x}$Cr$_x$Se powders with $x = 0.04$ and $0.08$.

Fig. 4. (a) Diffuse reflectance spectra and (b) band gap estimation plots of pure and Cr doped CdSe powders.

**Magnetic properties.** Fig. 5 shows the field depended magnetization of Cd$_{1-x}$Cr$_x$Se powders with $x = 0.00$, $0.04$ and $0.08$ measured by vibrating sample magnetometer at room temperature. The inset of Fig. 5 shows the M-H loops of Cr doped CdSe. The pure CdSe showed diamagnetic nature as its
magnetic susceptibility is negative \((\chi) = -2.25 \times 10^{-7} \text{emu g}^{-1} \text{Oe}^{-1}\) [26] and hence ferromagnetism was not expected and Cr is antiferromagnetic in nature. But, as the Cr doping concentration is increased from 4 to 8 at.% the magnetic moment increased showing clear hysteresis loops. A ferromagnetic behaviour with weak magnetic moment was observed for 4 at.% Cr doped CdSe. It is evident that the diamagnetic dominating characteristic is responsible for reduced magnetic moment in the case of lower chromium ions doped CdSe. Whereas for 8 at.% Cr doped CdSe, the S-type hysteresis loop was observed with a significant impact of high magnetic moment. The hysteresis loops observed in the present study display a characteristic pattern of soft magnetic materials. It can be interpreted that this RTFM might be due to creation of spin-split impurity band at the fermi level, below the conduction band due to the hybridization between the charge carriers of chromium and cadmium. In the present investigations, neither trace of metal clusters nor impurity phases were detected in the XRD measurement, which confirms the substitution of Cr ions into the CdSe host lattice. It is also seen that the wurtzite structure is unaltered even after the substitution of \(\text{Cr}^{2+}\) ions for \(\text{Cd}^{2+}\) ions, resulting in ferromagnetic behavior. In addition to that, as Cr ions are antiferromagnetic in nature[10], probability of inducing an extrinsic ferromagnetism due to Cr ions is not possible. Therefore, it is clear that the observation of ferromagnetism may be ascribed to the exchange interaction between free delocalized carriers and localized ‘d’ spins of Cr ions[27]. Similar kind of trend was observed in Cu doped CdSe powders [24] and Cr doped CdSe nanoparticles [28]. In contrast to the case of Ni doped CdSe nanorods[29], the magnetic moment has been found to be decrease with increased Ni concentration due to direct coupling between \(\text{Ni}^{2+}\) ions.

**Fig. 5. Vibrating sample magnetometer analysis curves of pure, 4% and 8% Cr doped CdSe powders.**

**Summary.** Cd\(_{1-x}\)Cr\(_x\)Se powders at x= 0.00, 0.04 and 0.08 were prepared using solid state reaction method and the role of dopant concentration on the structural, optical and magnetic properties of the Cd\(_{1-x}\)Cr\(_x\)Se powder samples were investigated. Structural analysis indicated that the pure CdSe and Cr doped CdSe powder samples were hexagonal in structure, and no other secondary phases were found in the samples indicating that Cr ions are substituted at the Cd sites. Diffuse reflectance spectra has shown blue shift in the band gap. Ferromagnetic strength increases with Cr concentration in Cd\(_{1-x}\)Cr\(_x\)Se powder samples. Such ferromagnetism is attributed to the intrinsic nature of the samples rather than any secondary magnetic phases.

**References**


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Cite the paper