Structural, Optical and Magnetic Properties of Co doped ZnSe Powders

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ABSTRACT. Co doped ZnSe nano crystalline powder samples were prepared by solid-state reaction method. Structural, optical and magnetic properties of pure and Co doped ZnSe powders were studied. Both Pure and doped ZnSe samples were in cubic structure. Lattice parameter and band gap of pure and doped ZnSe powders decreased with increase of Co concentration. The Raman shift in the Raman spectra of the samples confirms the Co doping in to the ZnSe lattice. Band gap of the samples decreased with increase of Co concentration. Codoped ZnSe powders exhibited half-metallic ferromagnetism at room temperature with low Co concentration and paramagnetism with high Co concentration.

Introduction. Dilute magnetic semiconductors (DMS) have earned good interest in recent years because of its feasibility to have magnetic and semiconducting properties in the same materials. DMS materials are the traditional non-magnetic semiconductors doped with transition metal or rare earth metal ions at very low concentration. The host material is exhibiting some peculiar properties after doping with suitable transition metal ions [1]. DMS materials find more attention because of their applications in opto-electronics and spintronics devices, which utilizes both the spin and charge of the electrons [2, 3]. Further these find significant role in designing of spin valves, spin light emitting diodes and ultra-fast optical switches [4]. Extensive studies had been carried out on several II-VI DMS compounds. Among all II-VI semiconductors, ZnSe is a potential candidate to fit in various applications as solar cells [5], bio-medical tags [6] and light emitting diodes [7]. ZnSe is a blue-lasing material and can be employed in designing modulated hetero structures and optical wave guides [8]. Doping magnetic ions of +2 oxidation state into II-VI DMS such as CdSe, CdTe and ZnSe is easy. Co is one of the suitable ferromagnetic transition metal to dope in to II-VI semiconductors. Different model or mechanisms such as double exchange, RKKY carrier induced interactions, super-exchange were applied to explain the origin of ferromagnetism in these II-VI DMS compounds [9, 10]. The present work focus on the effect of Co doping concentration on structural, optical and magnetic properties of Co doped ZnSe powders.

Experimental details. Pure and Co doped ZnSe powder samples were prepared with different concentrations of Cobalt by solid state reaction. There sets of powders sample-1: pure ZnSe, sample-2: 5at. % Co doped ZnSe and Sample-3: 10 at. % Co doped ZnSe were prepared. Stoichiometric quantities of ZnSe and freshly prepared Co doped ZnSe were weighed and subjected to continuous mechanical grinding for about 14-16 hours. The powders were sintered at 800°C for 10 hours under a
pressure of $10^{-3}$ mbar. The pure ZnSe and Co doped ZnSe powders were characterized to study their structural, raman, optical and magnetic properties.

**Results and Discussion.**

**Structural analysis.** Fig. 1 shows the X-ray diffraction patterns of the pure ZnSe and Co doped ZnSe powder samples at different Co doping concentrations. The diffraction peaks of all the samples are found to be matched with ZnSe cubic structure pattern having JCPDS data [card no 88-2345]. The crystal structure of the host material has not been altered on increasing dopant concentration. These observations indicate that Co ions were doped in the corresponding metal sites of Zn ions. It is also observed from the XRD studies that the intensity of the peaks increased as the concentration of the dopant ions of cobalt increased from 5% to 10%.

![XRD patterns of pure ZnSe and Co doped ZnSe powders.](image)

**Fig. 1.** XRD patterns of pure ZnSe and Co doped ZnSe powders.

![Variation of lattice parameter of Co doped ZnSe with Co concentration.](image)

**Fig. 2.** Variation of lattice parameter of Co doped ZnSe with Co concentration.

Fig. 2 shows the variation of lattice parameter ZnSe with increase of Co concentration. The lattice parameter increased with increase of Co doping concentration which might be due to substitution doping of Co in Zn metal ion sites in ZnSe host compounds. Similar lattice contraction was observed by Begam et.al. in Co doped CdTe powders[11] and in Co doped CdSe[12]. Fig. 3 presents the typical Raman spectrum of the all samples. The obtained dominant Raman peaks at 138 cm$^{-1}$, 248 cm$^{-1}$ and...
287 cm\(^{-1}\) are attributed to the second transverse acoustic (2TA), transverse optical (TO) and longitudinal optical (LO) phonon modes of ZnSe, respectively. The observations agree well with the reported results for ZnSe nanobelts and nanowires [13]. All the above results further confirm that the as-prepared products present a cubic structure of ZnSe phase. Fig. 4 shows the EDAX spectra and SEM images of Cr doped CdSe powders. EDAX spectra confirm the existence of Cr in the powder samples and SEM images illustrate that the Cr doped CdSe powder are in submicron size.

![Raman spectra of pure ZnSe and Co doped ZnSe powders.](image)

**Fig. 3.** Raman spectra of pure ZnSe and Co doped ZnSe powders.

![EDAX spectra and SEM images of Co doped ZnSe powders with 5% and 10% Co concentration.](image)

**Fig. 4.** (a), (b) EDAX spectra and (c), (d) SEM images of Co doped ZnSe powders with 5% and 10% Co concentration.
Optical properties. Fig. 5 shows the diffused reflectance spectra of pure and Co doped ZnSe powders. The bandgaps for different substitutions of Co ions (x=0.05, 0.10) are calculated using Tauc’s relation as shown in the Fig.6. It can be found that the band gaps of Co doped ZnSe tend to decrease from 2.378 eV (pure ZnSe) to 2.199 eV and 1.835 eV. The red shift in the band gap with increase in Co doping can be explained on account of the sp-d exchange interaction taking place between the conduction band electrons and the localized ‘d’ electrons of Co ions that replace the host Zn ions. Babuet. al. also observed same trend of decrease in band gap with increase of dopant concentration in Mn doped ZnSe thin films up 15 at. wt. % of Mn concentration [14].

Magnetic properties. The M-H curves for Co doped ZnSe powders at room temperature are showed in the Fig.7. Inset of the Fig. 7 shows the M-H curve of pure ZnSe at room temperature. It confirms that ZnSe is diamagnetic in nature. The magnetization values ($M_s$) observed in the present samples for 5at% and 10at% Co concentrations are 0.024088 emu/g and 0.05728 emu/g.

In general the manifestation of ferromagnetic behavior in DMS compounds may be understood from the mutual exchange interaction present between free delocalized charge carriers and d spins of Co ions. But these Co doped ZnSe samples exhibit half metallic ferromagnetism. This type of magnetism is attributed due to polarization of electronic spins.

Benstaali et.al.[15] in Co doped ZnSe, Mohamood et. al.[16] in Ti doped ZnSe and Arifet. al. [17] in Co doped CdSe were reported half metallic ferromagnetism due to polarization of the spin in their theoretical investigation and further suggested these materials are suitable for spintronic materials.

Fig. 5. Diffused reflectance spectra of undoped and Co doped ZnSe powders

Fig. 6. Plots of $(\alpha h\nu)^2Vsh\nu$ of undoped and Co doped ZnSe powders.
Summary. ZnSe powders doped with Co were synthesized by solid state reactions and investigations were carried at different concentrations of Zn$_{1-x}$Co$_x$Se ($x=0.05$ and $x=0.10$) and studied the effect of Co concentration on structural, optical and magnetic properties of the prepared samples. The X-ray diffraction studies and Raman analysis confirmed that all the samples are in cubic structure. Optical studies denote a decrease in band gap with increase in Co compositions. Half metallic ferromagnetism is observed in the present Co doped ZnSe powder samples at room temperature.

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References


Cite the paper