

Synthesis and Structural Characterization of Cr doped CdS Nanoparticles

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Abstract : Pure CdS and Cr doped CdS nanoparticles were synthesized via surfactant assisted simple chemical co precipitation method. XRD pattern reveals the cubic zincblende structure and nanoscale regime of the synthesized nanoparticles. Particle size was found to be in the range 2-3nm. Dopant related shift of XRD peaks supports the substitution of Cd²⁺ ions with Cr²⁺ ion and lattice contraction in doped samples. Agglomerated clusters of nanoparticles were noticed through SEM image.

IndexTerms – Chemical co precipitation, Nanoparticles, Zincblende, Lattice contraction.

I. INTRODUCTION

Due to their applications in high capacity communication networks, optoelectronics and bio-photonic devices, wide band gap II–VI compounds with high refractive indices and multi-photon absorption properties have received much interest for the last two decades [1–3]. Cadmium Sulphide (CdS) is one of the wide bandgap II-VI semiconductors with wide range of applications like photo resistors, X-ray detectors, hybrid sensitized solar cells, hetero junction light emitting diodes, photo catalysts, gas detectors, bio sensors and address decoders [4-11]. Doped semiconductors have attracted extensive research interest due to their unique optical, magnetic and other potential applications. Doping with proper element is widely used as an effective method to tune surface states, energy levels, electrical, optical and magnetic properties of semiconducting materials. Large number of reports are available with TM doped CdS other than Cr. Particularly doping of CdS with Cr is attractive because Cr is an important transition metal and it has ionic radius (0.63 Å) lesser than that of Cd²⁺ (0.96 Å) which means that Cr can easily substitute Cd²⁺ in the host lattice. Effect of Cr-doping on the structural and optical properties of CdS nanoparticles prepared by chemical precipitation method was studied by Thambidurai et.al and Sivakumar et.al [12- 13]. Room-temperature ferromagnetic and optical properties of Cr-doped CdS nanoparticles via a solvothermal method reveals that intensity of magnetism increases with increasing Cr dopant from 0 to 0.394% [14]. Recently photovoltaic properties of Cr doped CdS quantum dots was examined by Sabit Horoz et.al [15]. Magic-sized pure and Cr-doped CdS DMQDs have been synthesized by Srivathsava et.al with solution phase chemistry (lyothermal method). Structural, optical, and magnetic investigations suggest an intrinsic nature of ferromagnetism with highly quantum-confined system [16]. Chemical co precipitation method is a simple and inexpensive alternative to more complex chemical vapour deposition (CVD) and physical techniques. Compared to the physical methods colloidal chemical method offers a good control of size. Here surfactant is used to passivate the surface atoms, eliminate the energy levels inside the gap and decrease the particle size. In view of this, in the present study an attempt has been made to synthesize Cd_{1-x}Cr_xS nanoparticles with x = 0.00, 0.001, 0.03, 0.05 and 0.07 by the chemical route using 2-mercaptoethanol as surface capping agent.

II. EXPERIMENTAL

Pure CdS and Cr doped CdS [Cd_{1-x}Co_xS (x = 0, 0.01, 0.03, 0.05 and 0.07)] nanoparticles capped with 2-mercaptoethanol were synthesized by simple co precipitation method at room temperature. The chemical co-precipitation method has been found to have a number of advantages including easy processing ability at ambient conditions, possibility for doping different kinds of impurities with high doping concentration even at room temperature, good control over the chemistry of doping, easiness of surface capping with a variety of different steps involved in the synthesis process of nanoparticles. All chemicals ((Cd(CH₃COO)₂·2H₂O, Cr(CH₃COO)₂·2H₂O and Na₂S) used in the present study are of AR grade and used without further purification. Cadmium acetate, sodium sulfide and chromium acetate were used as source materials for Cd, S and Cr respectively with double distilled water as solvent. Freshly prepared aqueous solutions of the chemicals were used for the synthesis of nanoparticles at room temperature. The source materials were weighed according to the stoichiometry as per the target compositions and were dissolved in distilled water to make 0.2 M solutions. These precursor solutions were stirred for 30 minutes each and kept ready for the further procedure. The anionic pre cursor solution was taken in a burette and the mixture of cationic precursor solutions and 0.5 ml surfactant (2-mercaptoethanol) was taken in a conical flask or beaker. Anionic precursor solution in the burette is added drop wise to the conical flask containing cationic precursor solutions and surfactant under continuous vigorous stirring. The reaction was continued for 8 hours until a fine precipitate was formed. Later the precipitate was washed several times with double distilled water to remove the last adherent. Surfactant 2-mercaptoethanol acts as template in the synthesis procedure. Similar steps were followed to prepare Cd_{1-x}Cr_xS (x= 0, 0.01, 0.03, 0.05 and 0.07), nanoparticles. Finally, the washed particles were filtered and dried at 60 °C for 12 hrs in an oven. The dried flakes were separated from the filter paper and made in to fine powders in order to examine with various characterization tools. Crystal structure of the synthesized nanoparticles was determined using Serifert 3003 TT X-ray diffractometer with Cu-Kα radiation with a wavelength of 1.540 Å. Surface morphology of the samples was analysed using scanning electron microscope (CARL-ZESIS EVO MA 15).

III. RESULTS AND DISCUSSION

X-ray diffraction patterns of Cd_{1-x}Cr_xS (x = 0, 0.01, 0.03, 0.05 and 0.07) nanoparticles are shown in Fig. 1. Two broad peaks observed for all the samples can be indexed to (111) and (220) planes of the cubic zincblende structure according to the JCPDS card number 02-0549. In the synthesis of nanoparticles, particle size and the structure of the prepared nanoparticles are also influenced by the surfactant [17-18]. The capping agent (2-mercaptoethanol or 2ME) which we have used in our investigations can greatly reduce the particle size but this organic capping agent could not provide a net work in which CdS nanoparticles get trapped giving rise to order structure with different

set of planes [17]. Hence this two peak XRD pattern is usually obtained for CdS nanoform when 2-mercaptoethanol is used as surfactant [17-18]. As dopant concentration increases, peak positions in the X-ray diffraction pattern were shifted to higher 2θ values which can be attributed to the smaller ionic radii of Cr^{2+} (0.63 Å) when compared to Cd^{2+} (0.96 Å). This result supports the substitution of Cd^{2+} ion by the Cr^{2+} ion in the as synthesized Cr doped CdS nanoparticles. The increase in diffraction angle is obviously a result of lattice contraction expected to occur because of higher surface to volume ratio in nanoparticles. The average crystallite size of the nanoparticles was calculated using Scherrer formula [19]

$$D = 0.89\lambda/\beta \cos\theta$$

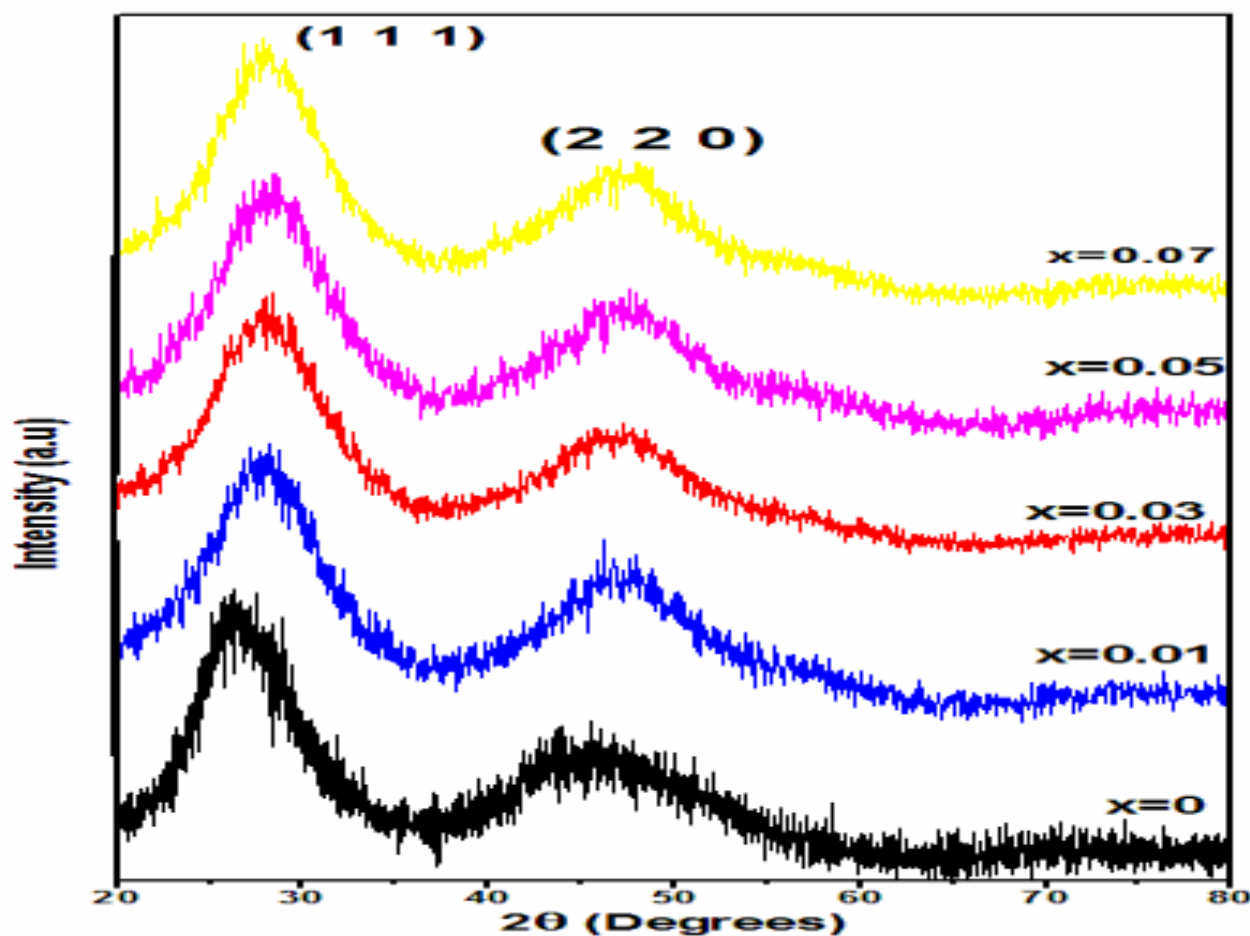


Fig. 1. XRD patterns of $\text{Cd}_{1-x}\text{Cr}_x\text{S}$ ($x = 0, 0.01, 0.03, 0.05$ and 0.07) nanoparticles

where D is the average crystallite size, λ is the wavelength of Cu-K α radiation, β is the full width at half maximum intensity of the diffraction peak and θ is the diffraction angle. From the XRD studies, calculated diameters of the particles are found to be in the range 2-3 nm. The calculated values of crystallite size and lattice parameters of cubic CdS:Cr samples of all compositions are shown in Table 1. The lattice parameter values obtained from the XRD data of $\text{Cd}_{1-x}\text{Cr}_x\text{S}$ nanopowders appear to decrease in a narrow range of 5.8-5.5 Å with increasing Cr content. Furthermore, the presence of any secondary phase corresponding to Cr clusters could not be detected in the XRD patterns of present samples. This indicates the clear substitution of Cd^{2+} by Cr^{2+} in the synthesized $\text{Cd}_{1-x}\text{Cr}_x\text{S}$ nanoparticles.

Table 1. Crystallite size and lattice parameters of $\text{Cd}_{1-x}\text{Cr}_x\text{S}$ nanoparticles

Composition (x)	Crystallite size (D) nm	Lattice parameter (a) (Å)
0.00	2.54	5.80
0.01	2.78	5.58
0.03	2.81	5.53
0.05	2.84	5.51
0.07	2.97	5.50

Scanning electron microscopy (SEM) is a powerful tool to study the surface morphology especially by observing the top and the cross-sectional views. Figs. 2 shows the SEM image of $\text{Cd}_{1-x}\text{Cr}_x\text{S}$ ($x = 0.03$) nanoparticles. In our synthesis, formation of agglomerated clusters of nanoparticles was noticed from the SEM micrograph.

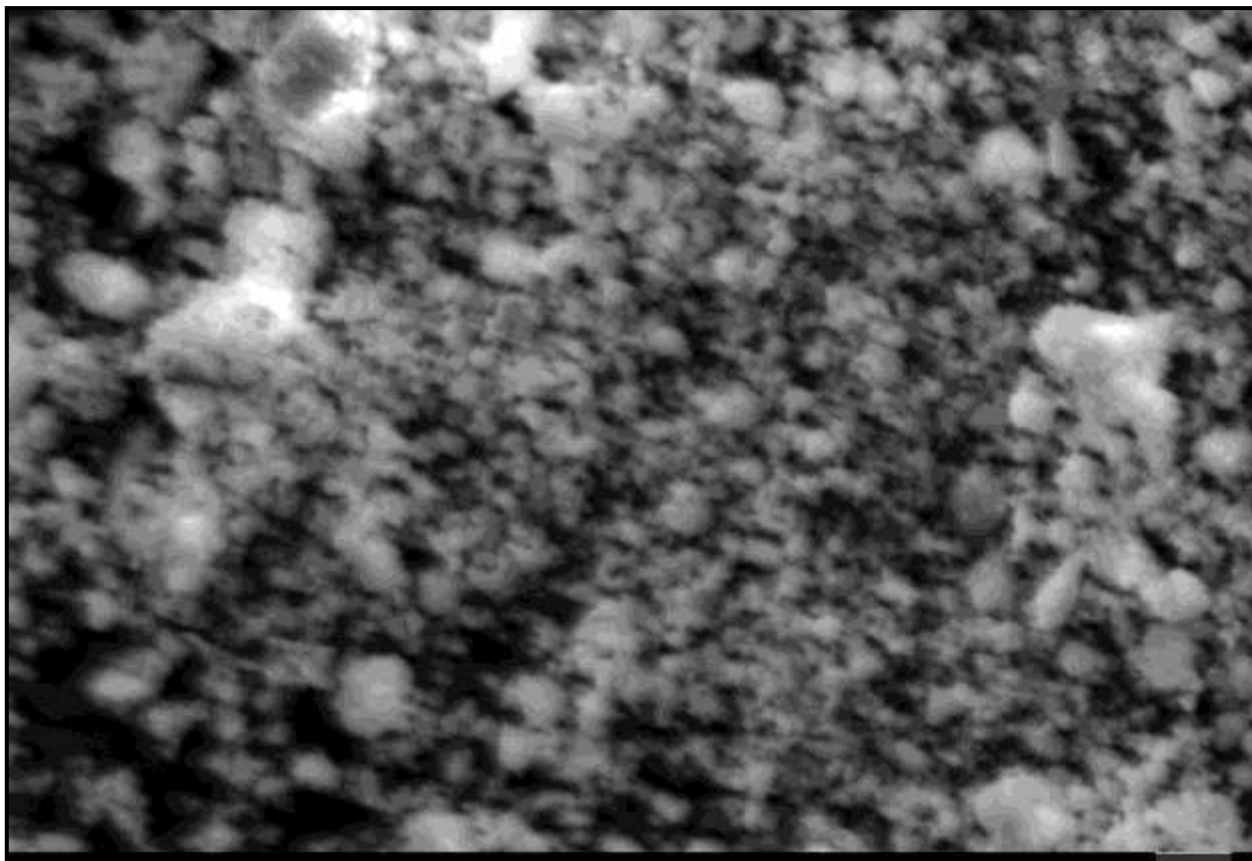


Fig. 2. SEM image of $\text{Cd}_{1-x}\text{Cr}_x\text{S}$ ($x=0.03$) nanoparticles.

IV. CONCLUSIONS

We successfully synthesized $\text{Cd}_{1-x}\text{Cr}_x\text{S}$ ($x = 0, 0.01, 0.03, 0.05$ and 0.07) nanoparticles of size range 2-3nm with surfactant assisted chemical bottom up route. For all samples, dopant independent cubic zincblende structure is evident from XRD analysis. Lattice contraction and shift of XRD peaks to higher 2θ values with increasing dopant concentration was noticed. SEM image further confirms the nanoform of the prepared particles.

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