SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF CdS NANOCRYSTALS ADDED WITH Pb^{2+}

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Abstract

For the past few years, the prepration and characterization of nanocrystals of materials have become an interesting area in the research activity. CdS (Cadmium Sulphide) is a well known semi conducting material which finds applications in optical devices. In the present study, we have made an attempt to investigate the effect of Pb^{2+} as impurity on the properties of CdS nanocrystals. The samples were prepared by using simple domestic microwave assisted solvothermal method with ethylene glycol as solvant. The samples prepared were annealed to have good ordering. X-ray diffraction measurements were carried out for all the smples. The grain size, lattice parameter and yield were determined. The colour before and after annealing was noted. EDX and SEM analyses were also done. The prepared samples were electrically characterized by making dielectric measurements on the prepared pellets. The present study indicates that the polarization mechanism in the nano crystals considered is mainly contributed by the space charge polarization.

Keywords: *Semiconducting II –IV materieals, Cadmium sulphide, XRD patterns, solvothermal method, electrical measurements*

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1. INTRODUCTION

Semiconductor nanocrystals exhibit a wide range of electrical and optical properties which particularly depend on both size and shape [1, 2]. Cadmium sulphide is an important II – VI semiconducting compound having a typical wide band gap of 2.42 eV at room temperature and exhibiting excellent optical properties and various luminescence properties such as photoluminescence (PL) and electroluminescence (EL). Its wide applications involve laser light emitting diodes, solar cells and other optical devices based on its nonlinear properties [3,4]. Moreover it finds potential application in the field of Bio imaging [5,6]. It is well known that those fantastic properties of nanoscale semi conductive materials are dependent on size, shape and crystallinity. Various routes have been developed to prepare the nano scaled semi conductive materials, particularly group II-VI semi conductive nano materials and their optical and opto electrical properties have been investigated intensively [7,8]. As CdS nanocrystals are an important II-VI semiconductor material, quite different approaches have been applied to achieve one dimensional CdS nano crystal with controlled morphology and size.

Those approaches include solvothermal route [9,10], liquid crystal template [11], irradiation technique [12,13], polymer controlled growth [14], electrodepositing porous plate [15] and wet chemical routes [16]. Recently new methods have also been developed for the preparation of CdS nano crystals. In the present study, we have made an attempt to prepare pure and Pb^{2+} doped CdS by Mahadevan's method (the simple microwave assisted solvothermal method) using a domestic microwave oven [17]. The grain sizes of the samples were determined by using the X-ray powder diffraction data. The AC electrical measurements were carried out.

2. EXPERIMENTAL DETAILS

The Cadmium acetate (AR grade) and thiourea (AR grade) in 1:3 molecular ratio were mixed and dissolved in 200ml ethylene glycol and kept in domestic microwave oven operated with frequency of 2.45 GHz and Power 800W. Microwave irradiation was carried out until the solvent gets evaporated. The colloidal precipitate was washed several times with double distilled water. The sample was washed with acetone 3 or 4 times. Again the sample was dried in atmospheric air and collected as the yield. Thus the pure CdS nanocrystals was prepared. To prepare CdS doped with Pb^{2+} (5wt. % and 10 wt. %) we have added lead acetate to cadmium acetate and the same procedure was repeated. The required amount of substance (A) was estimated by using the formula,

$$A = \frac{M \times X \times V}{1000} \text{ (in gram units)}$$

Where M is the molecular weight of the substance, X is the concentration in molar units and V is the required volume of solution.. The colour of the nanopowders produced was noted. The yield percentage for all the samples were calculated by the formula,

$$\text{Yield percentage} = \frac{\text{Total product mass}}{\text{Total reactants mass}} \times 100.$$

Using an automated X-ray powder diffractometer (PANalytical) with monochromated CuK_α radiation (λ = 1.54056Å) the powder X-Ray diffraction (PXRD) data were collected for the 3 samples. Using the Scherer formula [18] the grain sizes were determined. The prepared nanocrystals were palletized using a hydraulic press (with a pressure of about 5 tons) and used for the AC electrical measurements. The flat surfaces of the cylindrical pellets were coated with good quality graphite to obtain a good conductive surface layer. Using a traveling microscope the dimensions of the pellets were measured.

The capacitance (C_c) and the dielectric loss factor (tan δ) were measured using the conventional parallel plate capacitor method using an LCR meter (Agilent 4284A) for the 3 samples with a fixed frequency of 1 kHz at various temperatures ranging from 40 - 100°C. The observations were made while cooling the sample. The temperature was controlled to an accuracy of ± 1°C. Air capacitance (C_a) was also measured for the thickness equal to that of the pellet. The area of the pellet in contact with the electrode is same as that of the electrode. The air capacitance was measured only at room temperature because the variation of air capacitance with temperature was found to be negligible[19].

The dielectric constant of the pellet sample was calculated using the relation,

$$\varepsilon_r = C_c / C_a.$$

The AC electrical conductivity (σ_{ac}) was calculated using the relation,

$$\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega \tan \delta.$$

Here, ε_0 is the permittivity of free space (8.85×10^{-12} C^2 N^{-1} m^{-2}) and ω is the angular frequency ($\omega = 2\pi f$, where f is the frequency).

3. RESULTS AND DISCUSSION

Figure 1 contains the photograph of the prepared samples along with the corresponding pellets .The preparation time, colour and the yield percentage are given in Table 1. The colour of Pure CdS nanocrystals observed is yellow and that of doped with 5 wt % and 10 wt % Pb^{2+} is green and light green respectively. The yield percentage is also significantly high. The results obtained indicate that the solvothermal method is a considerable one for the preparation of CdS nanocrystals.

Table 1: Colour, yield percentage, preparation time and observed average grain size

Sample	The reaction time [min]	Yield percentage [%)]	Colour
Pure CdS	37	36.51	Yellow
CdS doped with 5 wt % Pb^{2+}	37	26.25	Green
CdS doped with 10 wt % Pb^{2+}	28	33.25	Light green

Fig. 1 :Samples produced: From the left
(i)Pure CdS
(ii) CdS doped with 5 wt % Pb^{2+}
(iii) CdS doped with 10 wt % Pb^{2+}

The X-ray powder diffraction (PXRD) patterns obtained in the present study are shown in figure 2. They were indexed using the JCPDS files and they were hexagonal in structure. The estimated grain (crystallite) sizes and lattice parameters are given in Table 2. The broadening of peaks in the PXRD patterns indicates that the samples prepard in the present study are nanostructured particles. Variation of particle size due to Pb^{2+} doping is small. Also the doping doesnot distort the crystal lattice of CdS which is evidenced by the observed lattice parameters.

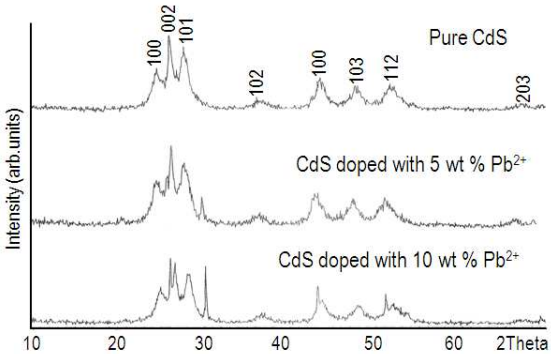

Fig.2: XRD pattern for doped and pure CdS

Table 2: Particle size and lattice parameters

Sample	Particle size (nm)	Lattice Parameters	
		a(Å)	c(Å)
Pure CdS	6.1	4.14	6.69
CdS doped with 5 wt % Pb^{2+}	5.52	4.17	6.69
CdS doped with 10 wt % Pb^{2+}	6.27	4.18	7.75

The EDX spectra and the SEM photographs for the pure and Pb^{2+} doped CdS samples are shown in Figure 3 and 4 respectively.The SEM pictures shows clearly the surface morphology of the samples. The EDX spectra indicates that the Pb^{2+} impurity has entered into the crystal matrix of the CdS. This is also confirmed by the change of colour due to doping.

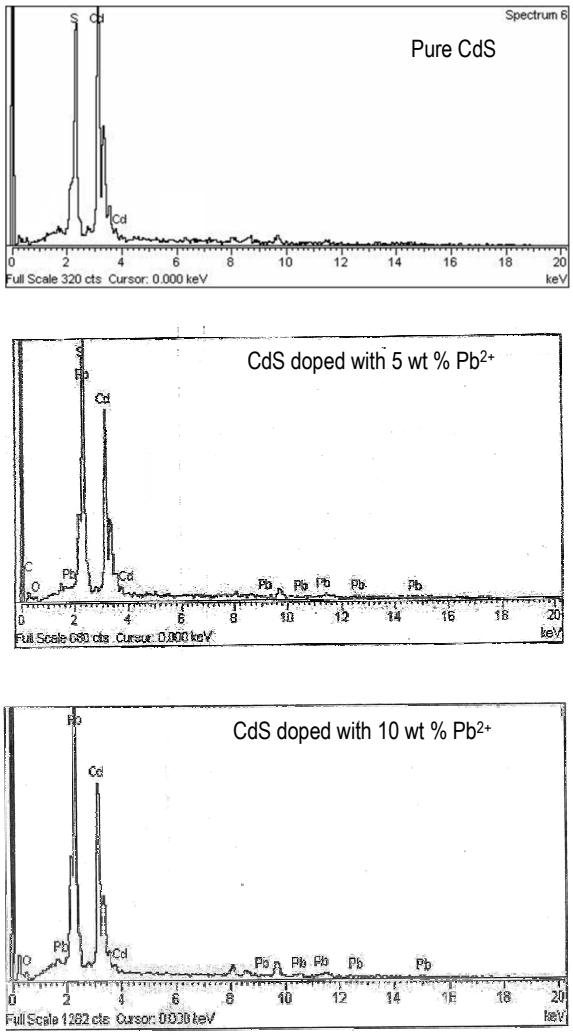

Fig.3: EDX spectra for doped and pure CdS

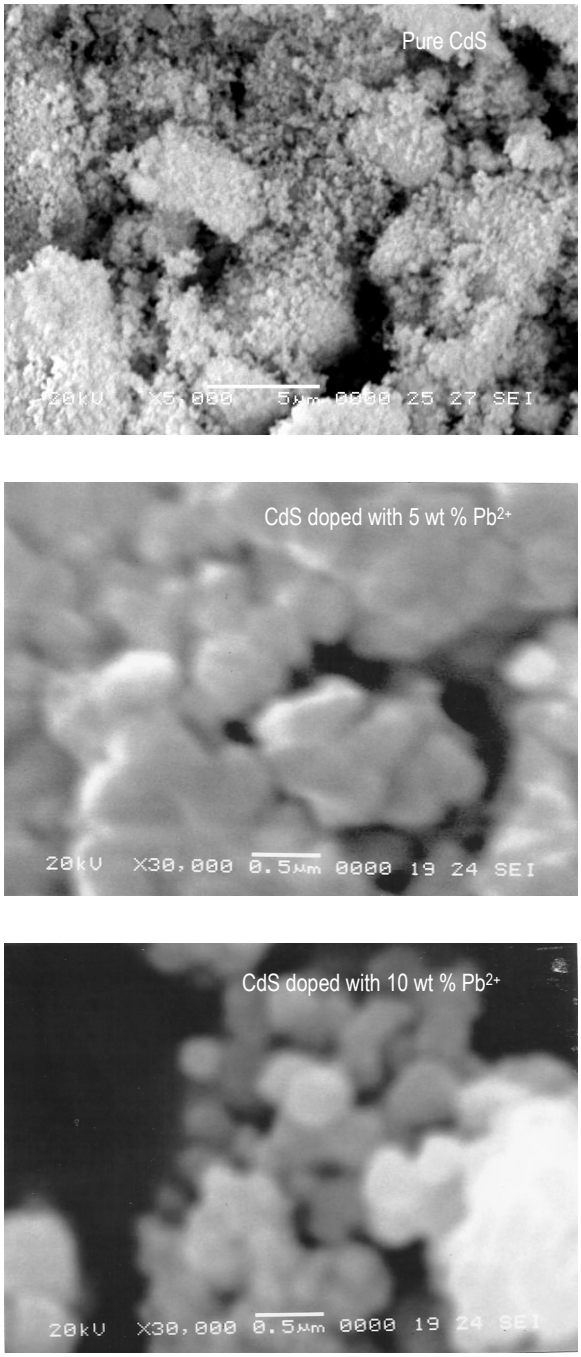

Fig.4: SEM images for pure and Pb^{2+} doped CdS

The dielectric parameters viz. ε_r, tan δ and σ_{ac} observed are shown in Figures 5-7. All the three dielectric parameters increase with increase in temperature. The variation in AC conductivity with temperature indicates that all the three nanocrystals prepared are semiconductor. Pb^{2+} doping do not change the dielectric parameters systematically.

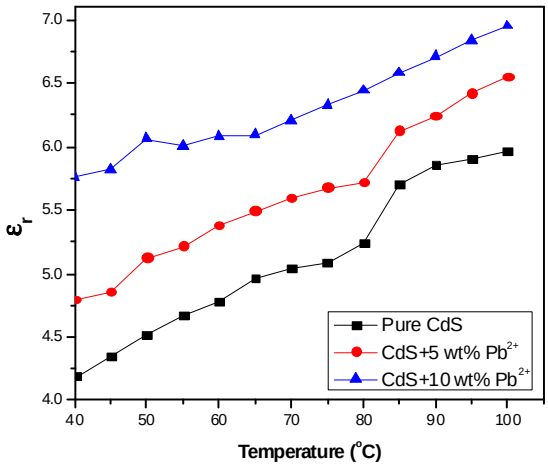

Fig.5: Dielectric constants for pure and Pb^{2+} doped CdS

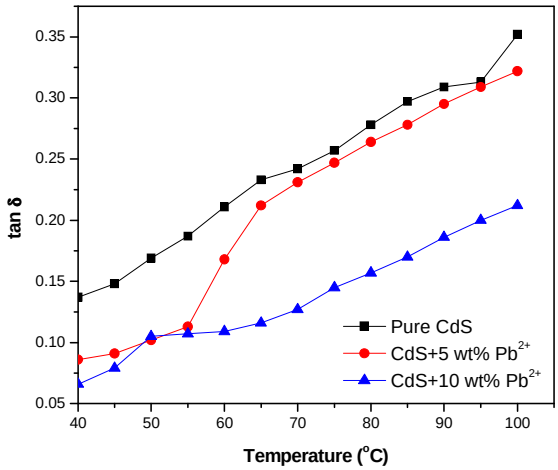

Fig.6: Dielectric loss factor for pure and Pb^{2+} doped CdS

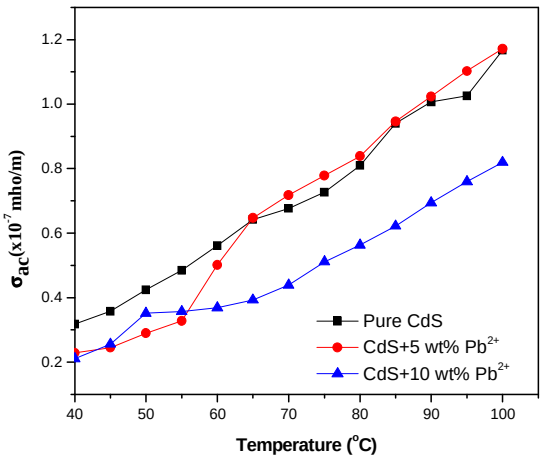

Fig.7: AC electrical conductivities for pure and Pb^{2+} doped CdS

Normally the dielectric constant is attributed to four types of polarizations. They are space charge, dipolar, ionic and electronic [20]. Even though all four types of polarizations contribute at lower frequencies, the dielectric constant rapidly increases mainly due to space charge and dielectric polarizations, which are strongly temperature dependent[20,21]. The space charge polarization is due to the accumulation of charges at the grain boundary. An increase in space charge polarization results as more and more charges accumulate at the grain boundary with the increase in temperature. Beyond a certain temperature, the charges acquire adequate thermal energy to overcome the resistive barrier at the grain boundary and conduction takes place resulting in decreasing of polarization. This interfacial polarization occurs up to frequencies of around 1 kHz with possibly some contribution from the dipolar polarization also as the temperature increases. The average grain size observed for the three systems considered in the present study are less than 7 nm. As the observed grain size is small, the polarization mechanism is mainly contributed by the space charge polarization.

Nanoparticles lie between the infinite solid state and molecules. The electrical resistivity of nanocrystalline material is higher than that of both conventional coarse grained polycrystalline materials alloys. The magnitude of electrical resistivity and hence the conductivity in composites can be changed by altering the size of the electrically conducting component the magnitude of electrical resistivity and the conductivity in composites can be changed. The observed AC electrical conductivities in the present study are very small. When the grain size is smaller than the electron mean free path, grain boundary scattering dominates and hence electrical resistivity is increased. Thus the space charge contribution plays an important role in the charge transport process and polarizability in the case of all the systems considered in the present study.

4. CONCLUSION

Pure and Pb^{2+} doped CdS were prepared by Mahadevan's method using a domestic microwave oven and they were structurally and electrically characterized. The yield percentage and the observed grain size indicates the suitability of the method adopted. The AC electrical parameters increase with increase in temperature. The results obtained indicate that the space charge contribution plays an important role in the charge transport process and polarizability.

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