Studies on the effect of Ni & Ba co-doping on CdS nano structures

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Abstract— The pure and various metals (Ni and Ba) doped Cadmium Sulphide (CdS) nano particles were successfully synthesized by chemical co-precipitation method using analytical grade Cadmium Chloride and Sodium Sulphide chemicals. The prepared samples were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), and Optical absorption (UV- Vis) studies. The XRD results showed that the all prepared samples were polycrystalline with hexagonal structure. The peaks were identified and compared with JCPDS (File No. 89-2944) values. From the SEM studies, the particles agglomerations are decreased by the addition of metal dopants and the average grain size of the particles are found in the range 500 nm. The optical properties have been characterized. The obtained band gap values are 2.56 eV, 2.54 eV, 2.35 eV and 2.48 eV. The band gap is reduced and the crystallization is increased in the Ni and Ba doped CdS nano particles are more suitable for fabrications of Opto electronic studies.

Keywords— Cadmium Sulphide, Nano particles, X-ray diffraction, Scanning Electron Microscope, Optical studies.

I. INTRODUCTION

Semiconductor nano crystals are of great interests for both fundamental research and industrial development. This is due to their unique size-dependent optical and electronic properties and their exciting utilization in the fields of light-emitting diode [1], electrochemical cells [2], laser [3]. The usual preparation technique of nano crystals are by liquid reaction system at high temperatures for several hours, making those methods either expensive, explosive, moisture sensitive, extreme toxic, and energy consuming. Recently, much attention was paid to develop liquid–liquid approach for synthesis of nano crystal metals, metal oxides and metal sulfides [4, 5]. Particularly, semiconductor nano particles have been attracting much attention because of their characteristic properties resulting from the quantum size effect which are significantly different from those of the corresponding bulk material [6-13]. In particular, sulfides of transitional metals acquired attention for applications such as sensors, optical filters, solar cells, and photovoltaic systems among others because the optical properties characteristic of the size and morphology of the crystal, essentially characterized by the transition phase from the electrical conductivity [14]. CdS (Cadmium Sulphide) particles are II-VI semiconductor materials with the band gap 2.42 eV. They show very good physical and chemical properties thus the nanocrystalline semiconductor materials having wide range band gaps. [15, 16], CdS is an important semiconductor photo catalyzer. In order to explore more suitable

applications or acquire the enhanced properties, different morphological CdS nano materials have been synthesized by sputtering, vapour-phase condensation, sol-gel reaction, micro emulsion reaction, template-assisted reaction, chemical hydrolytic reaction, etc [17,18]. It has also extended applications in light emitting diodes Several methods have been developed to synthesize CdS with divergent morphologies and structures such as solvo thermal method [19], hydrothermal method [20], photochemical method[21], one pot synthesis method [22], chemical precipitation method [23] etc. Among them, chemical precipitation method is a simple, clean and inexpensive technique to obtain CdS nano particles [24]. Nano crystalline CdS, CdTe, CdSe, ZnSe and PbS have been synthesized by a variety of methods including precipitation, sputtering, electrochemical deposition and inverse micelles. A reduction in the particle size strongly influences the crystallinity, melting point and structural stability. In the present work, Ni and Ba co-doped CdS nano particles were prepared via cost effective, facile chemical co-precipitation method at room temperature and the structural, morphological, Optical studies and chemical synthesis of these nano particles were investigated.

II. MATERIALS AND METHODS

In the present work, we have synthesized cadmium sulphide (CdS) nano particles by simple and low cost co-precipitation method using Cadmium Chloride ($CdCl_2.5H_2O$) and Sodium Sulphide (Na_2S) are used as cationic and anionic precursors.

All the chemicals used in the experiment of (A.R) grade without further purification. In typical synthesis, desired molar proportions of Cadmium Chloride (5.829gms, 0.5M) are dissolved in 50 ml ultrapure de-ionized water. Later stirring the solution at 80 ˚C for 80 min, Na_2S solution taken in a burette and was drop wisely added to the solution under constant stirring which was continued for 5 hours to get fine precipitation. The obtained precipitate was washed with de-ionized water several times. Finally, the powders were dried and annealed for 2 hours at 400°C, the orange color CdS powder was obtained. For Ni, Ba co-doped CdS nano particles, the appropriate amount of NiCl2.6H2O (10 %) and $BaCl_2.2H_2O$ (10 %) were added to the cationic precursor solution. Thus undoped and doped CdS nano particles were synthesized by the same procedure. Final CdS nano particles are used to study its micro structural, morphological and optical properties.

III.   RESULTS AND DISCUSSION

The structural studies using XRD patterns obtained for undoped and Ni, Ba and Ni & Ba co-doped CdS nano particles are shown in figure 4.1 and they exhibit hexagonal structure as per the standard JCPDS card no. 89 - 2944. The 2θ values of the diffraction peaks are observed at 24.82º, 26.53º, 28.19º, 36.64 º, 43.69º, 47.87º, 51.85º, 52.81º, 66.80º, 69.28º, 72.42º and 77.89º respectively which corresponds to reflections from (100), (002), (101), (102), (110), (103), (112), (201), (203), (210), (114) and (204) planes for all samples of CdS nano particles. The predominant peak at 28.19º indicates that CdS is preferentially oriented along plane (101). No other diffraction peaks corresponding to doped metal or other impurity phases were observed in diffraction patterns. All the peaks from metal content doped samples have intense sharpness of peaks and is suggested that the good crystalline nature of the pure CdS nano powders.

The enlarged portion of XRD patterns for 2θ values between 26˚ to 29.5˚ is presented in Fig. 4.2. From figure 4.2 (b), the (101) peak position is shifted a little towards higher angles with increase of the Ni content. This could be due to the CdS lattice modification by the Ni (10 at.%) doping because of the difference in radii of Cd (0.98Å) and Ni (0.74Å) which is consist with the earlier reports on Ni – doped CdS systems [25]. This may confirms the formation of pure Ni doped CdS particles.

With increasing Ba concentration, the peak (101) slightly shift to lower angle which indicates the decreased lattice parameter in Ba (10 at.%) doped CdS samples. This is an expected result as the ionic radius of Ba (1.35Å) is larger than Cd (0.98Å). Wang et. al. [26] reported a shift of diffraction peak towards the lower angle indicating the expansion of CdS nano particles with Ba doping. but for Ni

& Ba co-doped CdS does not altered the diffraction peaks as compared pure CdS nano material.

Figure 1 (a-d) shows the typical X-ray diffraction pattern obtained for the undoped and Ni & Ba doped CdS nano particle. The 'd'' (interplanar spacing) value is decreased for Ni (10 at. %) doped CdS and increased for Ba (10 at. %) doped CdS naoparticels but for Ni & Ba co-doped CdS has same compared to the pure CdS nano material. These results implies that Ni^{2+} and Ba^{2+} have been incorporated into the crystal lattice of CdS, thus brings contraction and elongation in the observed 'd' spacing values of doped CdS samples.

The lattice constants 'a' and 'c' values varied with dopants, but (c/a) ratio remain constant. It may assign by the presence of dopant contents (or) it was aroused due to the lattice contraction in nano structure but this lattice constant variation does not altered the crystal structure of CdS. The lattice constant CdS nano particles are calculated using the following formula,

$$\frac{1}{d^2} = \frac{4(h^2+hk+k^2)}{3a^2} + \frac{l^2}{c^2} \qquad \text{----------- (1)}$$

The (c/a) ratio calculated from the lattice constants 'a' and 'c' are found to be has closely constants compared to standard values.

The broad peaks in the sample (a), which indicates that the dimensions of CdS particles has small in size. This is the main reason for the sample (a) has lowest crystallite size compared to the other doping CdS particles of. The observed sharp and high intensity peaks in samples (b), (c) and (d), which indicate the increased crystalline nature by the addition of dopant elements. The average crystallite sizes are calculated using Debye - Scherrer's formula [27],

$$D = \frac{k\lambda}{\beta Cos\theta} \qquad \text{------------ (2)}$$

In Ba doped CdS has highest crystallite size (77nm) which may attribute the largest ionic radius of Ba (1.35Å) compared to the host Cd (0.98Å). Microstrain values are varied due to the increased crystallite sizes [28].

Dislocation density can be evaluated from crystalline size (D) by following relation

$$\delta = \frac{1}{D^2} \qquad \text{------------ (3)}$$

The origin of micro strain is related to lattice misfit which is related to lattice misfit which in turn depend upon the deposition condition. The micro strain (ε) developed in thin films can be evaluated from the relation

$$\varepsilon = \left(\frac{\lambda}{DCos\theta} - \beta\right)\frac{1}{\tan\theta} \qquad \text{----------- (4)}$$

The lattice distortion (LD) developed in thin films can be evaluated from the relation [26]

$$LD = \frac{\beta}{4\tan\theta} \qquad \text{------------ (5)}$$

The stacking fault probability (α) with peak shift $\Delta(2\theta)$ is given by warren Warehouse developed in thin films can be evaluated from the relation

$$\alpha = \frac{2\pi^2}{45\sqrt{3}} \frac{\Delta(2\theta)}{\tan\theta} \qquad \text{------------ (6)}$$

The calculated lattice constant, crystallite size, dislocation density, strain, stacking fault probability and micro structures are presented in Table - 1.
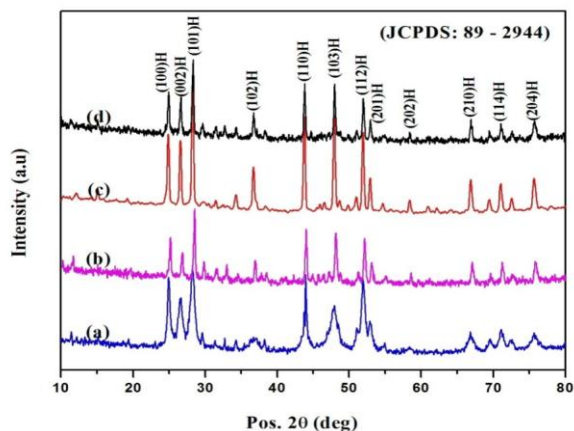

Fig. 1 (a-d). The X-ray diffraction patterns for CdS Nanoparticles

Table – 1: Micro Structural Properties of CdS nanoparticles

Material	CdS	Ni - Doped CdS	Ba - Doped CdS	(Ni & Ba) co - Doped CdS
c/a	1.62	1.62	1.63	1.62
Crystallite Size, D (10^{-9}m)	32.45	49.37	77.03	59.61
Dislocation density, $\delta \times$ (10^{16} lines/m)	9.4967	4.1027	1.6853	2.8143
Micro Strain, $\varepsilon \times$ (10^{-3} Lines^{-2} m^{-4})	0.1054	0.0452	0.07411	0.0597
Lattice Distortion (LD) $\times$ (10^{-3})	8.162	2.881	1.794	2.388

Surface Morphological Studies

Fig. 2. Shows the morphology of undoped, Ni, Ba and Ni & Ba co-doped CdS nanoparticles at 500 nm magnifications. Figures 2(a), (b), (c), and (d) show the SEM images of pure CdS, CdS: Ni_x, Ba_x and Ni_y co-doped Ba_y (x = 10% and y=5%) respectively. SEM images showed the agglomerated nanoparticles of the prepared samples. From Fig. 2(a) the SEM result revealed that the grains are uneven and different in sizes with some void and cracks are found which indicate

that the agglomeration process is highly occurred for undoped CdS samples. But in the Fig 2(b, c and d) the grains are in more or less in spherical shape which indicates that the doping content that is slow down the agglomeration of CdS Nps. The SEM image showed that the agglomeration process is occurred slowly down with the Ba content doped CdS NPs.
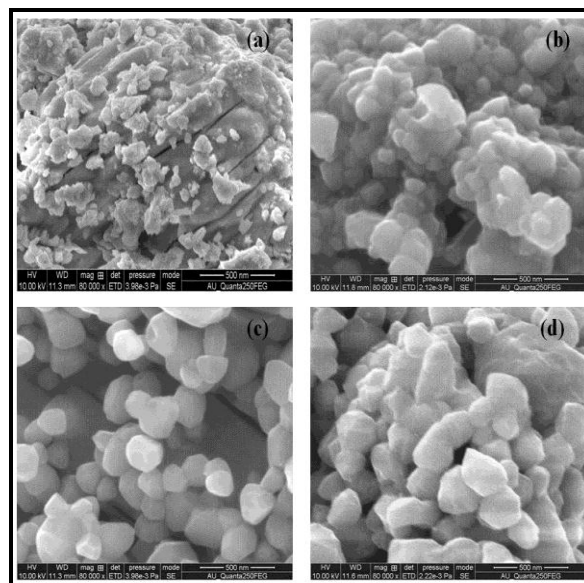

Fig. 2. SEM images of (a) Undoped CdS (b) Ni doped CdS (c) Ba doped CdS (d) Ni & Ba co-doped CdS Nano particles

Optical studies:

The optical absorption spectra of undoped and Ni, Ba and co-doped CdS nanoparticles are recorded by UV - Vis. NIR spectrometer. The absorbance as a function of wavelength is given in fig. 4. The absorbances depict a sharp fall at the band edge implying the good crystal quality of the CdS nanostructure. the absorbance values is around 483 nm for all the CdS nano powders.

The wavelength dependence of the optical transmittance spectra for the pure, Ni, Ba and Ni-Ba co-doped CdS are shown in figure - 3 measured at the room temperature. From the transmittance spectra, the average optical transmissions are achieved at the visible region. The values of m depends upon the type of the transition; which may have values 1/2, 2, and 3/2 corresponding to the allowed direct, allowed indirect, and forbidden direct transitions respectively [29]. It is due to the direct band-to-band transition. The band gaps are found to be 2.56 eV, 2.54 eV, 2.35 eV and 2.48 eV for undoped, Ni doped, Ba doped and Ni & Ba co-doped CdS nanostructure. Development of semiconductor film with controllable energy gap is necessary due to the increased application in solar cell fabrication and opto-electronic devices.
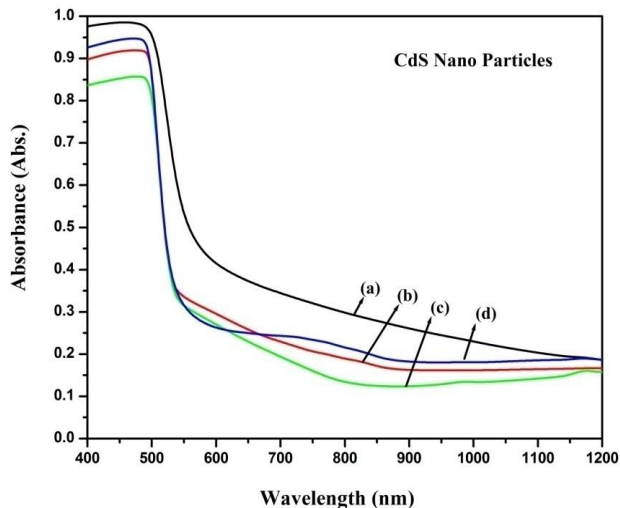
Fig. 4. (i). Absorbance spectra of (a) Undoped,
(b) Ni, (c) Ba and (d) Ni & Ba co-doped CdS Nano particles
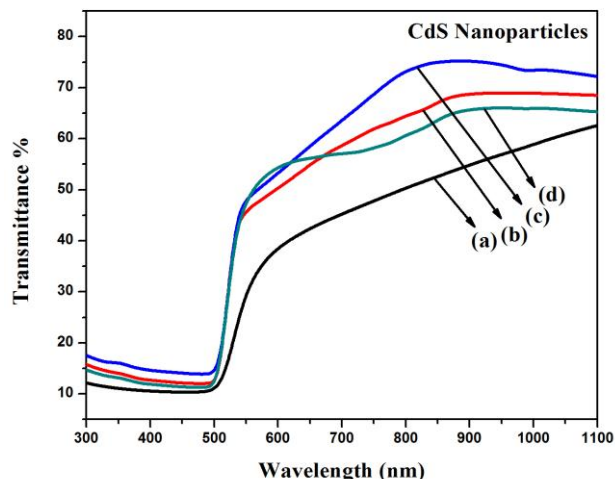

Fig. 4. (ii). Transmission spectra of (a) Undoped, (b) Ni, (c) Ba and (d) Ni & Ba co-doped CdS Nano particles
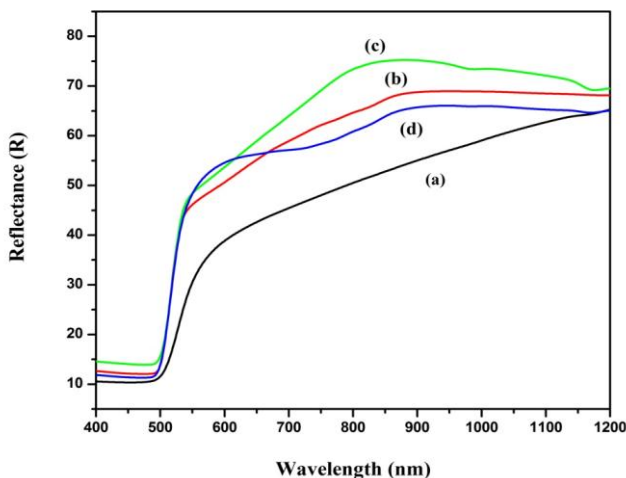

Fig. 4. (iii). Reflectance spectra of (a) Undoped,
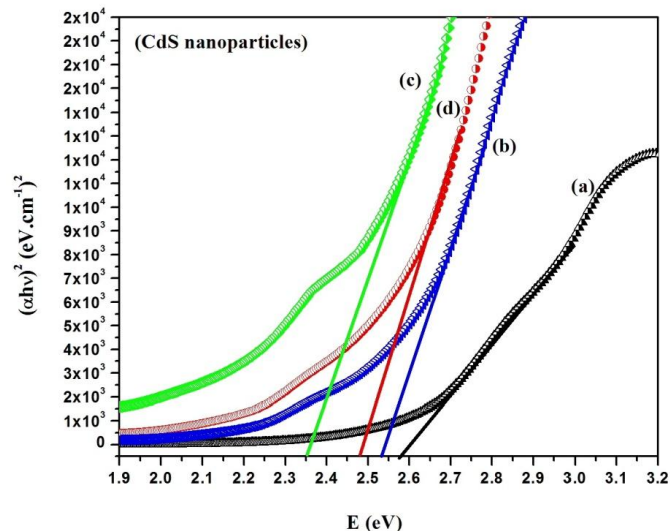(b) Ni, (c) Ba and (d) Ni & Ba co-doped CdS Nano particles

Fig. 4.4 (iv). Tauc's plot of of (a) Undoped, (b) Ni, (c) Ba and (d) Ni & Ba co-doped CdS Nano particles

IV. CONCLUSION

In summary, Ni and Ba co-doped CdS nano particles have been successfully synthesized by chemical co-precipitation method using analytical grade Cadmium Chloride and Sodium Sulphide chemicals. The X-ray diffraction pattern confirms the formation of hexagonal structure (fcc) of CdS and the peaks are identified with the JCPDS (89-2944). The corresponding intensity of peak is increased with increased dopant materials. The peak shift is obtained for both Ni and Ba doped CdS NPs and the crystallite size increased for the sample (c) because the ionic radii is high for Ba to the host CdS. The micro structural parameters were calculated.

The absorbance and transmittance values are high in the visible region and their spectra for all samples have sharp fall edge near to the band edge which indicates the formation of nano size CdS particles. The band gap is small to the Ba doped CdS which exhibit the quantum confinement effect.

The SEM image indicates that the particles are more or less in spherical shape for doped CdS samples. The SEM image showed that the agglomeration process is occurred slowly down with the addition of doping content.

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