

Impedance spectroscopy studies of Silver Doped Cadmium Sulphide Nanocrystallites

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Abstract

Using co-precipitation method, cadmium sulphide (CdS) and silver doped cadmium sulphide (CdS:Ag) was prepared. By using energy-dispersive X-ray analysis (EDXA), X-ray diffraction (XRD) and scanning electron microscopy (SEM) to analyse the structural characterization of the prepared samples.

The energy-dispersive X-ray analysis (EDXA) measurement is used to confirm, the presence of elements in prepared samples. There is no peaks of other impurity were detected. The average size of nanoparticles was calculated by scherrer formula. SEM photographs indicate that the nanopowders consist of well dispersed agglomerates of grains with a narrow size distribution, whereas the sizes of the individual particles are between 5 and 12 nm. The synthesized samples have been structurally analysed by X-ray diffraction method. The peaks in the XRD pattern are in good matches with the standard values of JCPDS file and other impurity peaks of crystalline phases were not detected. Scanning electron microscopy (SEM) measurement is used for the morphological studies. Electrical conductivity studies are analysed by Impedance spectroscopy measurement and also calculate the activation energies at low and high temperature for prepared samples.

Keywords: Impedance; conductivity; activation energies; precipitation

1. Introduction

Cadmium sulphide is one of the direct band gap semiconducting materials mainly useful for making optoelectronic devices, sensors etc. Powder sample of silver doped Cadmium sulphide Nano crystallites was prepared in the present work by using the chemical precipitation method. Nano crystallites doping with transition metal like copper, silver, gold etc., exhibit very interesting electronic properties and also have many applications in various field[1]. Cadmium sulphide is one of the II–VI groups of semiconductors, widely used for technological applications. Recently, silver nanoparticles exhibiting antimicrobial activity in medical and industrial applications have been synthesized [2]. Antibacterial activity of the silver-containing materials can be used in medical and dental field. It is



accustomed scale back infections additionally on stop microorganism formation on prostheses, catheters, tube grafts, dental materials, stainless-steel materials and human skin.

The silver nanoparticles act as antibacterial agent due to catalytic properties; play a crucial role in inhibiting bacterial growth in aqueous and solid media. Silver containing materials can be employed to eliminate microorganisms on textile fabrics [2] or they can be used for water purification [2]. Due to the various factors like size, shape and composition, the electrical properties of nano-structured materials are different from those of the bulk form. In the study chemical co-precipitation methodology has been used to prepare CdS:Ag, CdS samples in nano-crystalline kind. Ethylene glycol is used as a capping agent to control the growth of the particles and respective chemical compositions, morphology of the samples are investigated.

2. Materials and Methods

Undoped cadmium sulphide (CdS), Silver doped cadmium sulphide (CdS:Ag) nanocrystallites have been synthesized by precipitation method. The reactants Cadmium Chloride and Sodium Sulphide and also ethylene glycol as the capping agent were used for preparation of samples at room temperature. The precipitation process was carried out over a reflex time of 600 s for 100 ml of reflex volume of each of the reacting solutions. For silver doped cadmium sulphide nanocrystallites, approximately 0.01 mole of silver nitrate was added with cadmium chloride solution during preparation. The precipitates were centrifuged and washed with de-ionized water 3 times and then washed with methanol finally. Then the filtered precipitated samples were dried in vacuum. The dried sample was grinded to obtain fine powder.

XRD Measurements was taken for determination of average particle size. The SEM (Scanning electron microscopy) pictures are used to identify the morphological nature of nanocrystalline materials and the presented elements are confirmed by EDXA patterns.

A pellet of 8.23 mm diameter and 1.52 mm thickness prepared using the prepared sample was placed in between two platinum electrodes and complex impedance (Zn) measurements were carried out as a function of both frequency (from 1 Hz to 1 MHz) and temperature (from 543 to 833 K) using an Impedance/Grain-Phase Analyzer (SOLARTRON 1260) together with a dedicated computer and software to acquire the impedance data. The whole setup of sample compartment inside the furnace was evacuated in order to prevent oxidation of the sample during heating. The heating rate was maintained at 2 K/min. The temperature of the furnace was measured with a resolution of 71 K using a Eurotherm (818 P) PID temperature controller. The data were collected during both heating and cooling cycles. It was found that the data were consistent during both thermal cycles. The dielectric parameter such as complex conductivity was calculated from the raw data from the sample dimension.

3. Results and Discussion

Figure 1 (a) shows three characteristics peaks of the undoped cadmium sulphide of Hexagonal (JCPDS #: 89-2644). Figure 1 (b) shows the X-ray diffraction pattern of Ag doped CdS, the spectrum shows six major diffraction intensity peaks at $[2\theta = 24.80^\circ, 26.50^\circ, 28.30^\circ, 43.8^\circ, 47.80^\circ \text{ and } 52.05^\circ]$. The peaks were identified to originate from (1 0 0), (0 0 2), (1 0 1), (2 0 0), (1 0 3) and (1 1 2) planes of Ag doped CdS (JSPDS #: 89-2644). The XRD patterns could be indexed to the (space group: $P6_{3mc}$ (186), Primitive, Hexagonal structure with cell parameters:

$a = b = 4.114\text{\AA}$, $c = 6.715\text{\AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$. The Average size has been calculated using the Scherer formula [3] and is given in equation (1)

$$\text{Average particle size } D = 0.89\lambda / \beta \cos\theta \dots (1)$$

where D is average particle size in nm, β is the full width at half maximum (FWHM) of X-ray reflection peak expressed in radians and θ is the angle of diffraction at position of the diffraction peaks in the diffractogram. The crystallite size was calculated for maximum intensity peak and the calculated value of prepared sample was found to be 7 nm and 10 nm for CdS and Ag doped CdS samples respectively.

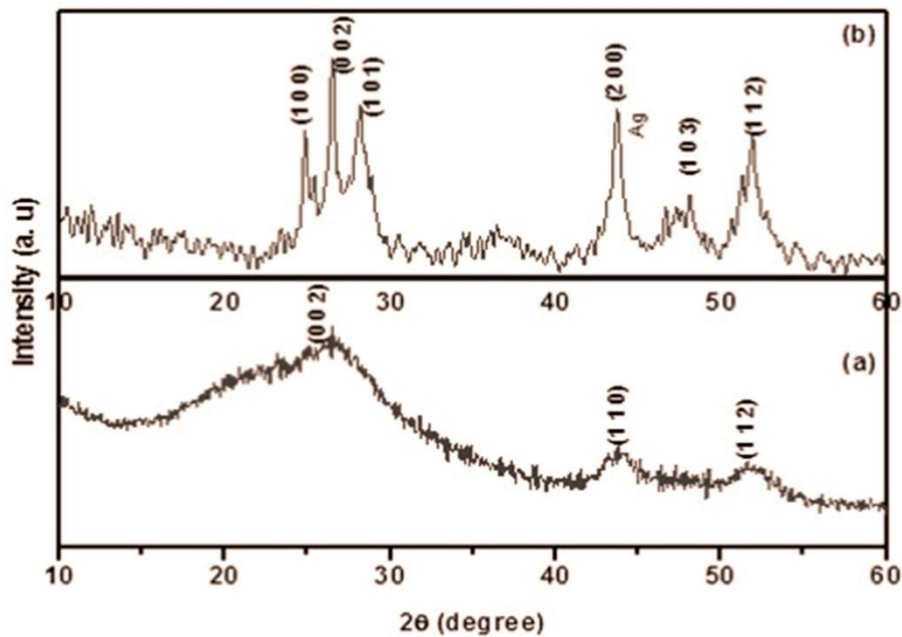


Fig. 1(a) XRD patterns of nanocrystalline (a) undoped CdS and (b) Ag doped CdS

Fig.2 (a-b) shows the Energy dispersive spectroscopy (EDS) for CdS and Ag doped CdS sample. The sample indicates the presence of Cd and S for CdS and Ag, Cd and S for Ag doped CdS. From the EDS spectra results (weight% and atomic % wise) confirm that prepared materials each composition is CdS and Ag doped CdS respectively.

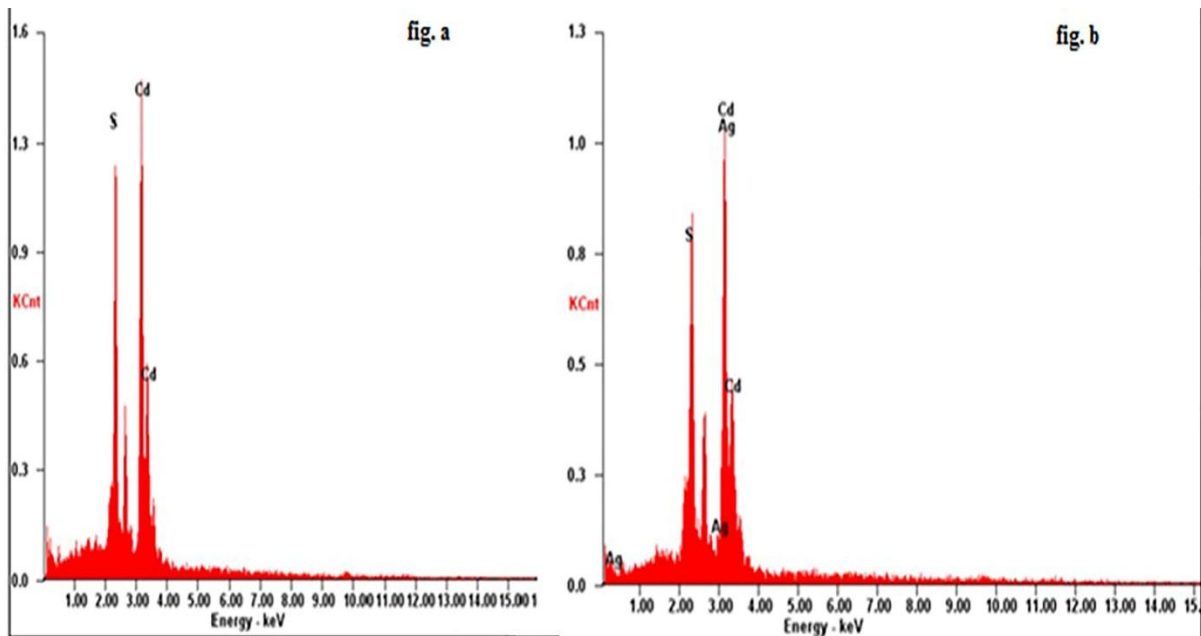


Fig.2 (a-b) shows the Energy dispersive spectroscopy (EDS) for CdS and Ag doped CdS sample.

In Fig.3 (a-b) and (c-d) shows the SEM morphology of CdS and Ag-doped CdS samples respectively. Where CdS is formed in clusters at 1 μm scale (b) and (a) clearly showing the porous nature of the CdS at 500 nm scale and also in Fig.3 (c-d) shows the SEM morphology studies of Ag-doped CdS sample indicating that the silver metal (white colour) is incorporated in the CdS sample at 1 μm scale and also observed very high porosity nature at 500 nm scale.

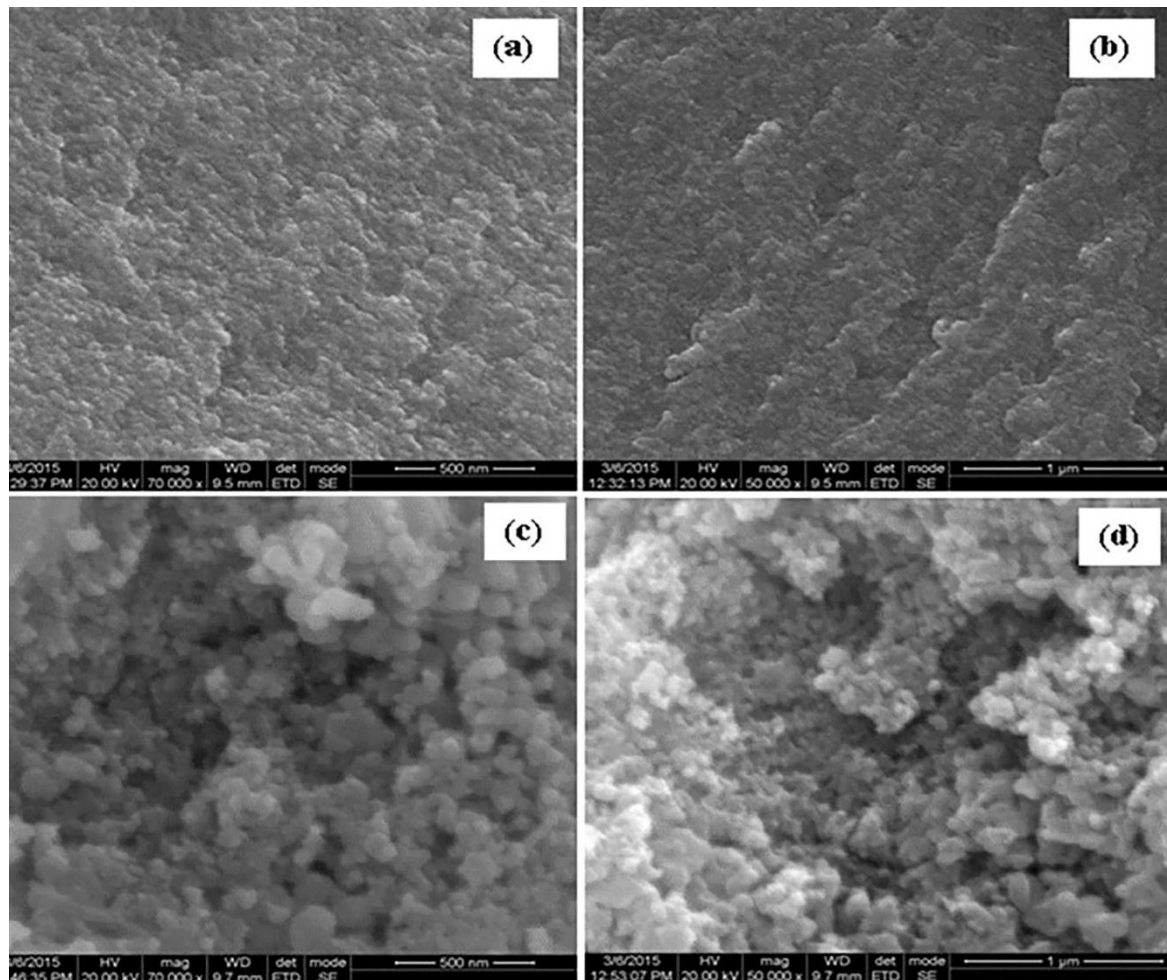


Fig. 3: (a - d) shows the HR-SEM morphology images of CdS and Ag doped CdS, (a) CdS sample at 500nm magnification, (b) CdS sample at 1 μm , (c) Ag doped CdS sample at 500 nm magnification, and (d) Ag doped CdS at 1 μm .

The complex impedance plots measured at different temperatures ranging from 110 $^{\circ}\text{C}$ to 190 $^{\circ}\text{C}$ with the frequency range of 1 Hz – 10^6 Hz for CdS are shown in figure 4 (a). It should be noted from this plot that only two depressed semicircle exists, whose centre is slightly shifted below the real axis (this behaviour is commonly considered to be an indication of a non-Debye relaxation process). At low temperatures and at low measuring frequencies the curve deviates from a perfect semicircle [4]. The impedance plots are fitted with complex non-linear least square fit (CNLLS) to obtain the resistance of the sample. With the geometry of the sample, this resistance value has been converted into conductivity using the relation,

$$\sigma = 1/\rho = l/RA... (2)$$

Here R is the resistance of the sample, A is the area of cross-section and l is the thickness of the pellet.

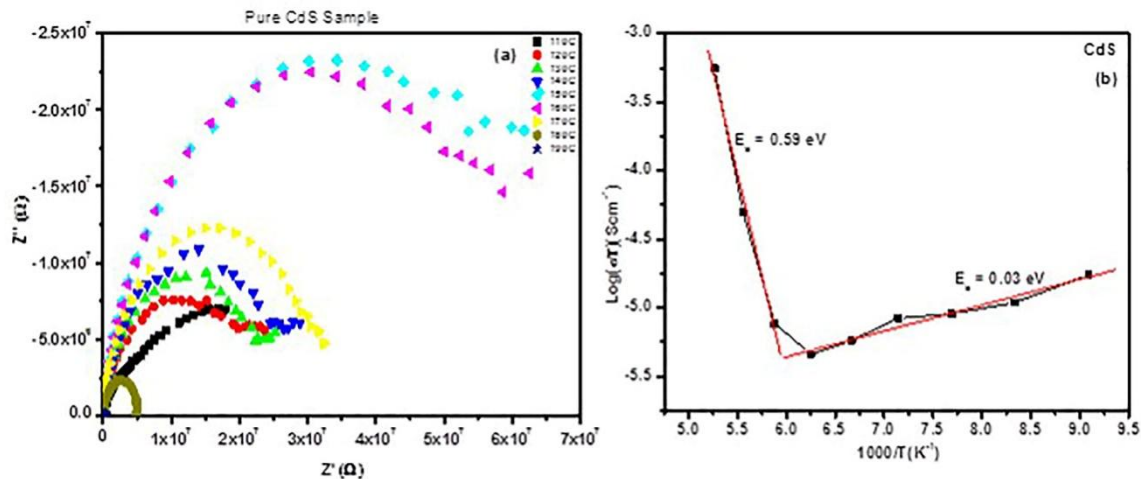


Fig. 4 High temperature Impedance plots of Nanocrystalline CdS Sample:

(a) Different temperature from 110°C to 190°C and (b) The activation energy for nanocrystalline CdS sample.

Figure 4 (b) shows the Arrhenius plot of nanocrystalline CdS sample. Basically, CdS sample is a typical II-VI semiconducting sample with band gap energy of 2.42 eV for bulk. The temperature dependence of the activation energy is expressed as

$$\sigma T = \sigma_0 \exp(-E_a/kBT) \dots (3)$$

Where σ_0 is the pre-exponential factor with dimensions of $\Omega^{-1} \text{cm}^{-1} \text{K}$, E_a is the activation energy for conducting and k_B is the Boltzmann constant.

It is also observed that conductivity increases with temperature in the temperature region from 110°C to 190°C (Resistance also gradually decreases, CdS is known to one of the n-type semiconducting materials).

The plotted data (conductivity against temperature) in figure 4 (b) shows two activation energy values are obtained for the nanocrystalline CdS at lower temperature region in between 110°C to 130°C and another in a higher temperature region between 140°C – 190°C respectively. The corresponding activation energies are 0.59 eV and 0.03 eV respectively. The reason for the first activation energy ($E_a = 0.59 \text{ eV}$) is that CdS being a semiconducting material, the band gap is very large and threshold energy is required to initialize the conduction process is high. The reason for second activation energy ($E_a = 0.03 \text{ eV}$) is that (140°C – 190°C) the lowering of the activation energy indicates the reduction in forbidden gap leading to high electrical conductivity [5].

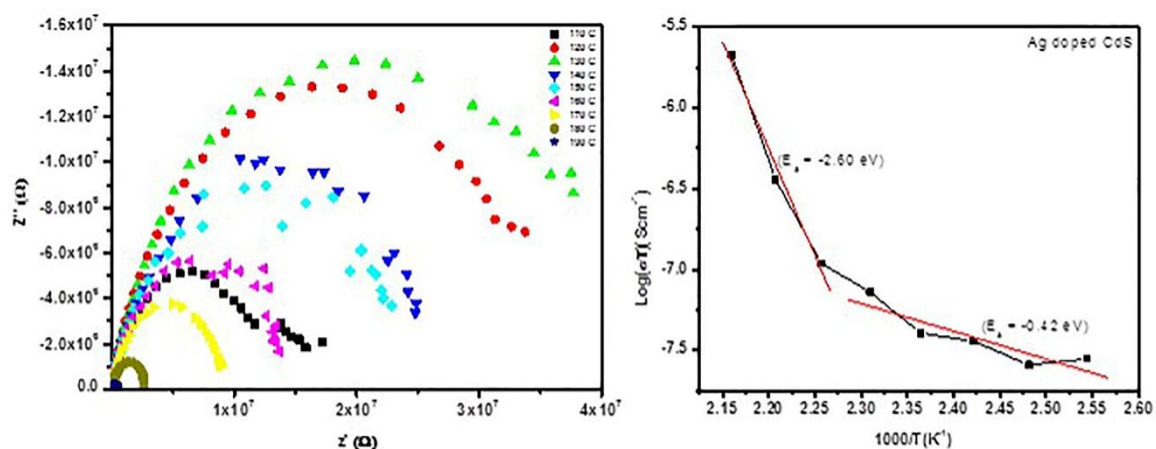


Fig.5 High temperature Impedance plots of Nanocrystalline Ag doped CdS Sample: (a) Different temperature from 110°C to 190°C and (b) The activation energy for nanocrystalline Ag doped CdS.

The complex impedance plots measured at different temperature from 110 °C to 190 °C with the frequency range of 1 Hz – 10⁶ Hz for CdS:Ag are shown in figure 5 (a). It is also observed that conductivity increases with increasing temperature from 110 °C to 190 °C (i.e resistance also gradually decreases due to increasing the temperature, Ag doped CdS acting as semiconducting behaviour). In Fig.5(b) shows the conductivity against temperature plot, from this graph we got two activation energy $E_a = 2.60$ eV and $E_a = 0.42$ eV, first and second activation energy values very higher than compare to pure CdS sample, that is only due to doping effect [6].

4. Conclusion

Nanocrystalline CdS and Ag doped CdS has been prepared using the chemical precipitation method. The structure (pure CdS of Hexagonal $a = b = 4.114\text{\AA}$, $c = 6.715\text{\AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$) formation was confirmed by XRD measurements and the crystallite size was calculated for 100 % intensity peak and the value was found to be 7 nm and 10 nm for CdS and Ag doped CdS samples. Surface morphology was studied using HR-SEM and Elemental composition analysis were made using EDS. The electrical conductivity at high temperature was studied using Impedance spectroscopy. Activation energies were $E_a = 0.59$ and 0.03 eV for CdS and activation energies were $E_a = 2.60$ eV and 0.42 eV for Ag doped CdS sample.

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