Structural and Dielectric Properties of Cobalt Disulphide Synthesized In Polymer Matrix

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Abstract - Amorphous nano powders of cobalt disulphide and its polymer composite were synthesized using the simple hydrothermal technique. The as-prepared samples were characterized by X-Ray powder Diffraction, Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy, EDAX, dielectric studies and conductivity studies. The crystal structure was confirmed and particle size of the materials was obtained from XRD analysis. The functional groups of the as synthesized sample were analyzed using FTIR. The protective layer formed by polymer over cobalt disulphide nano powder was seen from SEM images. EDAX analysis recorded the elemental composition of the synthesized nanopowders.

Keywords - CoS_2, polymer, hydrothermal technique, XRD, FTIR, SEM, EDAX, grain size.

I. INTRODUCTION

The physical properties of the material get enhanced as it is scaled to nanometer size from macroscopic size. Nanotechnology is the design, characterization, production and application of structures, devices and systems in the nano scale. On Controlling the particle size band gap of semiconductor nanomaterials can be tuned up and so catalytic efficacy of catalyzing agents can be enhanced. Lowering the particle size and narrowing the size distribution leads to high specificity of the excited states in the energy ladder, and the photonic energy increases to induce transitions between these states [1].

Catalytic, electrical and magnetic properties of cobalt disulphide (CoS_2) nanoparticles have made researchers to turn towards them in recent years. The metal sulphide nano powders are so fragile and so polymers are employed as steric stabilizers and as a means of control parameter in the synthesis of metal sulphide nano powders [2].

In this article, poly vinyl pyrrolidone (PVP) has been chosen as protective colloid, with water as solvent and in the presence of some additional organic coordinating solvent, cobalt disulphide nanoparticles were successfully prepared. The structural, optical, conductivity and elemental composition features of the cobalt disulphide nanoparticles were determined with X-ray powder diffraction (XRD), FTIR, SEM, EDAX, dielectric studies and conductivity studies.

II. MATERIALS AND METHODS

A. Materials

Cobalt chloride hexa hydrate ($CoCl_2.6H_2O$), thiourea (NH_2CSNH_2), PVP $(C_6H_9NO)_n$, Ethylenediamine, hydrazine hydrate and anhydrous alcohol. All the chemicals used are of analytical reagent grade.

B. Sample Preparation

In room temperature, 0.05M Cobalt Chloride Hexahydrate was dissolved in 150 ml of water and stirred well for 5 minutes. To this solution 3g of PVP was added and then stirred for 1 hour at 90ºC. Then 0.05M thiourea and 2ml of Ethylenediamine were added and stirred for half an hour. The solution was then centrifuged at the rate of 500rpm for 30 minutes. The solution was then transferred to an autoclave and heated at 160ºC for 24 hours. The resulting solution was filtered and the precipitate was washed with water and ethanol. The sample was collected after filtering and dried in vaccum at 160ºC for 3 hours. The synthesized sample was characterized by XRD, FTIR, FESEM, EDAX, and dielectric and conductivity studies.

III. RESULT AND DISCUSSION

A. XRD Analysis of cobalt disulphide

The powder XRD analysis was carried out using Rich Seifert diffract meter with CuKα (λ=1.5406 Å) radiation. The intensity versus 2θ values was recorded between the ranges 10-70°. The fig.1 shows the X-ray diffraction spectrum of cobalt disulphide nanoparticle and cobalt disulphide nanoparticle in polymer matrix. It is observed that, the peaks in the XRD patterns match well with those of the CoS_2 (hexagonal) reported in the JCPDS Powder Diffraction file no 42-0826. From JCPDS the structures of pure CoS_2 and CoS_2 in polymer matrix were confirmed and the crystal system was found to be hexagonal [4]. The lattice parameters of pure CoS_2 and CoS_2 in polymer matrix obtained using UNITCELL software are given in table 1. The PXRD spectra for the as prepared samples are shown in Fig. 1. The average crystallite size (d) was calculated using the Debye Schrrer formula, $\mathbf{d = k\,\lambda\,/\beta\,\cos\theta}$, Where, **λ** is the wavelength of copper Kα line (1.546 Å), **θ** is the diffraction angle, **β** is the full width at half maximum value [4].

Table 1

Nanopowder	Unit cell parameters						average crystallite size (nm)
	a(nm)	b(nm)	c(nm)	α (°)	β (°)	γ (°)	
CoS_2	3.352	3.352	5.194	90	90	120	13.86
CoS_2 in polymer matrix	3.357	3.357	5.151	90	90	120	35.916

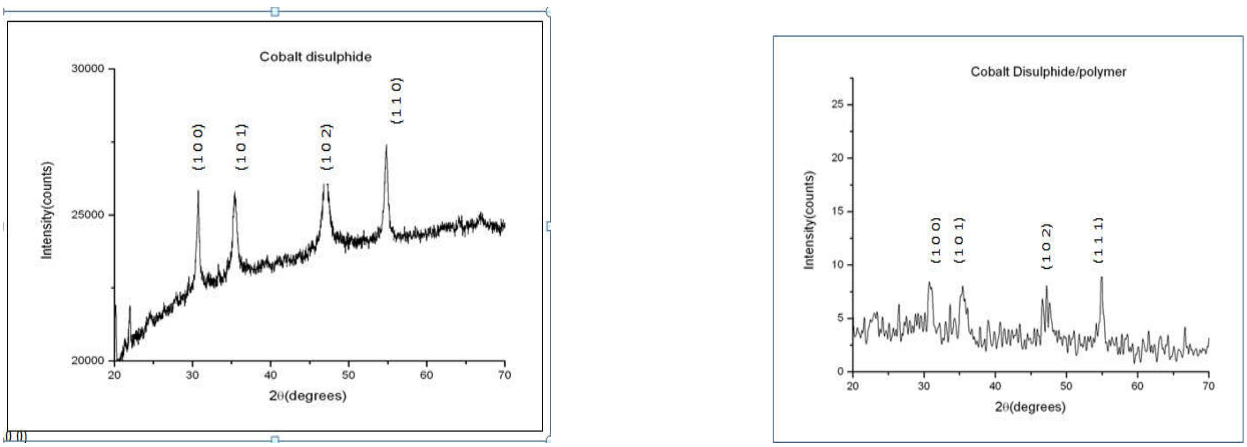

Fig. 1. XRD pattern of pure CoS_2 and CoS_2 in polymer matrix nanoparticles

B. FTIR Analysis of cobalt disulphide

The FTIR spectra were observed for both pure cobalt disulphide and its polymer composite. The fig.2 shows the FTIR spectrum of cobalt disulphide nanoparticle and cobalt disulphide nanoparticle in polymer matrix. The presence of a strong band from 900 – 1300 cm^{-1} is the evidence of the presence of formed cobalt disulphide which is observed in both the spectrums. The frequency band at 619cm^{-1} and 621cm^{-1} in both the spectrums are attributed to the presence of sulphide. The broad band positioned between 2700 – 3400cm^{-1} corresponds to O – H stretching mode of H_2O. The presence of the polymer is very less when compared to the metal sulphide, so its structural transformation in the spectra are not clearly visible [5].

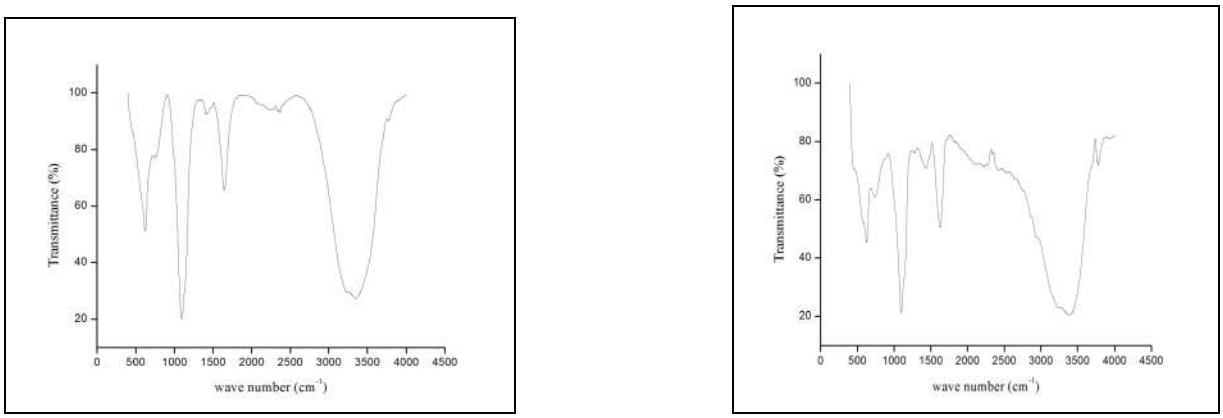

Fig. 2. FTIR spectra of pure pure CoS_2 and CoS_2 in polymer matrix nanoparticles

C. SEM Analysis of cobalt disulphide

The surface morphology of CoS_2 reveals the presence of agglomerates with a flake like structure. The morphology can be controlled by further adjusting the temperature and time of the synthesis. It is confirmed from the SEM image that when PVP forms a protective solid film like structure over the agglomerated cobalt disulphide particles [6]. The SEM images for the as prepared samples are shown in Fig. 3.

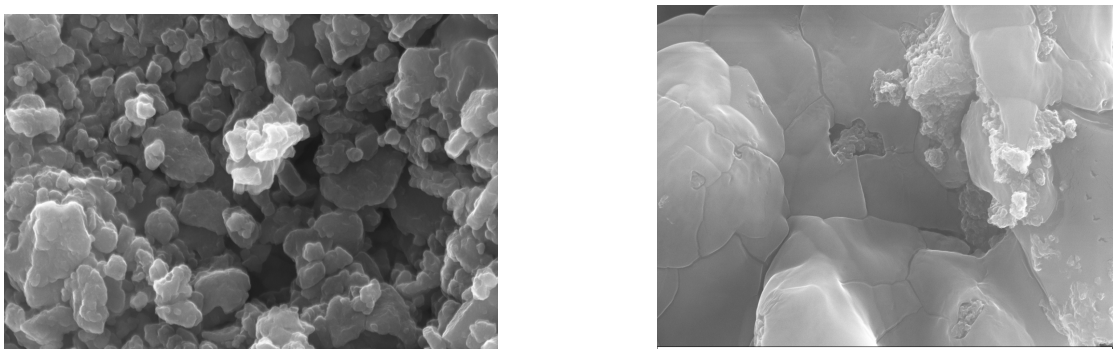

Fig. 3. SEM image of pure CoS_2 and CoS_2 in polymer matrix nanoparticles

D. EDAX Analysis of cobalt disulphide

The EDAX spectrum for the as prepared samples are shown in Fig. 4. From the presented spectrum one can clearly see six peaks located between 0 keV and 8 keV. The maximum is directly related to the Sulphur characteristic line. The peaks located at around1keV and between 6 keV and 8 keV show the presence of cobalt characteristic lines. The maximum located on the left part of the spectrum at 0.2 kV clearly comes from carbon. The hardly visible maximum located at 0.5 keV is connected with the oxygen characteristic line [7]. The detected elements of Co, O, N and S in the spectra are related to CoS_2 and PVP polymer nanoparticles.

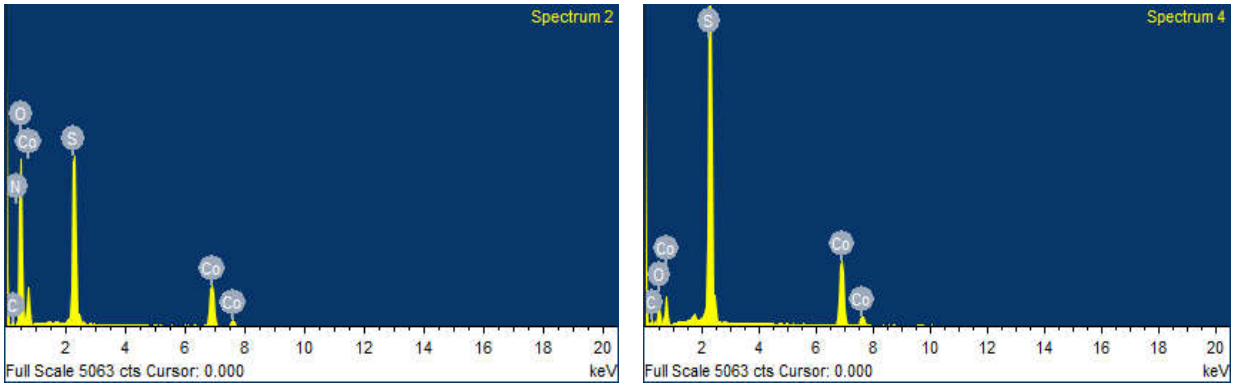

Fig. 4. EDAX spectra of pure CoS_2 and CoS_2 in polymer matrix nanoparticles

E. Dielectric Studies

The dielectric constant of the cobalt disulphide sulphide pellet was measured using HIOKI 3532 LCR Hi TESTER in the frequency range from 50 Hz to 5 MHz. The samples were mounted between the two electrodes. The capacitance of the parallel plate capacitor formed by the electrodes, with the sample as a dielectric medium was measured. The variation of capacitance was recorded in the frequency range 50Hz to 5MHz at different temperatures. The dielectric constant ($\mathcal{E}_r$) of the material was calculated for different frequencies from the measured capacitance values. The plot of the dielectric constant versus log f for both the pure and polymer composite of cobalt disulphide are shown in Fig. 5. It is observed that the dielectric constant has high value in the low frequency region and thereafter decreases with the applied frequency. The high value of $\mathcal{E}_r$ at low frequencies may be due to the presence of all the four polarizations namely space charge, orientation and, electronic and ionic polarization and the low values at higher frequencies may be due to the loss of significance of these polarizations gradually. The variation of dielectric loss with frequency for both the pure and polymer composite of cobalt disulphide are shown in Fig. 6. The AC electrical conductivity was determined using the relation $\sigma ac = \omega \mathcal{E}_0 \mathcal{E}_r \tan \delta$ ($\omega = 2\pi f$, f is the frequency). Also the variation of AC conductivity with frequency for both the pure and polymer composite of cobalt disulphide are shown in Fig. 7. From Fig. 7. The high AC resistance shows that the space charge polarization plays an important role in the electrical property of the sample [8].

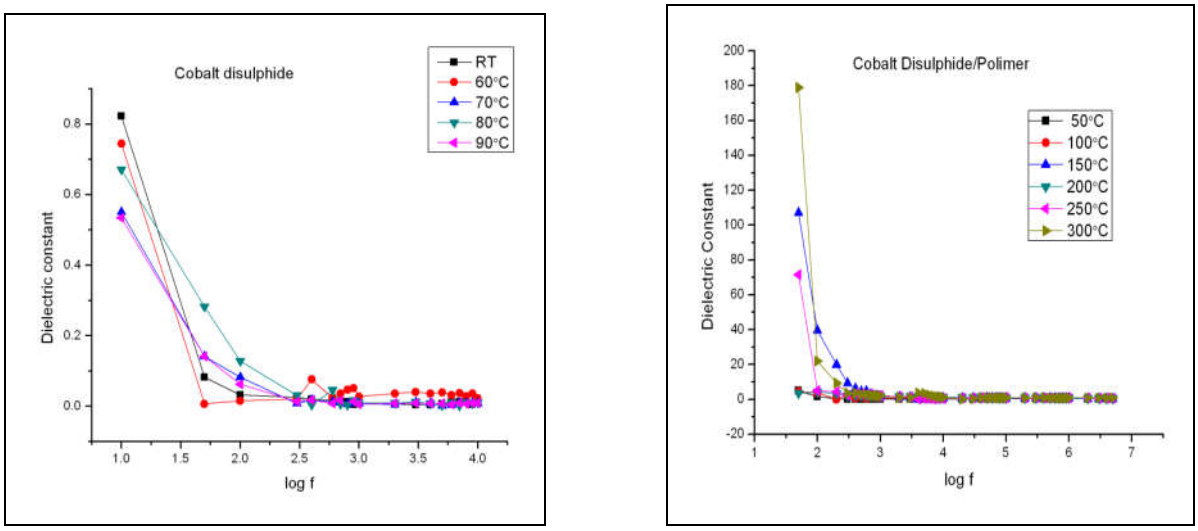

Fig. 5. log f versus Dielectric constant for pure CoS_2 and CoS_2 in polymer matrix nanoparticles

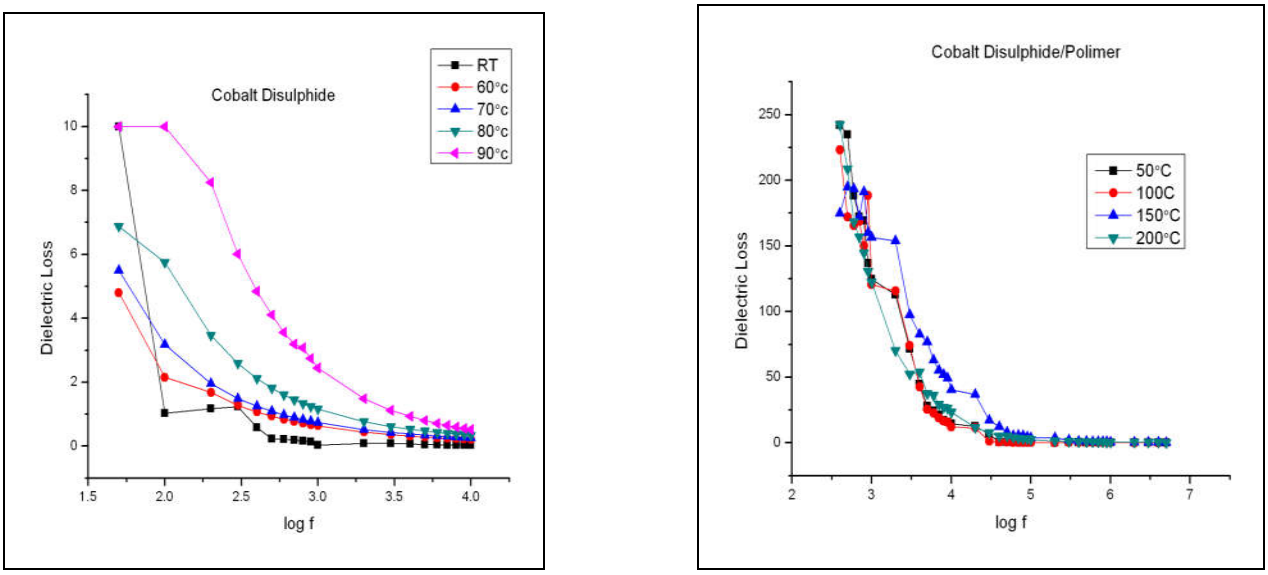

Fig. 6. log f versus Dielectric Loss for pure CoS_2 and CoS_2 in polymer matrix nanoparticles

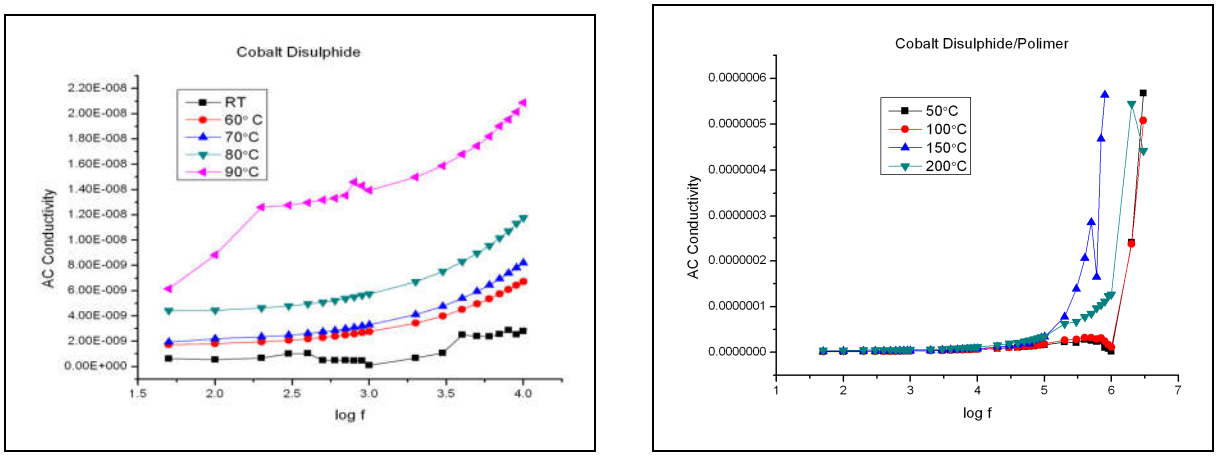

Fig. 7. log f versus Ac conductivity for pure CoS_2 and CoS_2 in polymer matrix nanoparticles

F. Conductivity Studies of cobalt disulphide

The photoconductivity experiment was performed at room temperature using the Keithley 6514 electrometer. Dark conductivity of the sample was studied by connecting the sample in series to a DC power supply and the Keithley meter. The DC input was increased from 1 to 5 volts in steps and the corresponding dark current was noted from the electrometer. For measuring the photocurrent, the sample was illuminated with an incandescent light bulb (40 W). The DC input was increased in the same range as done in the previous case and the corresponding photocurrents were measured. The variation of photocurrent (I_p) and dark current (I_d) with applied field are shown in Fig. 8. Both photo and dark currents of CoS_2 increases linearly with applied field. It is observed from the plot that the photo current is less than dark current, suggesting that CoS_2 exhibits negative photoconductivity. This phenomenon can be attributed to generation of mobile charge carriers caused by absorption of photons. The negative photoconductivity of the sample may be due to the reduction in the number of charge carriers to reveal the dielectric nature of the material [9].

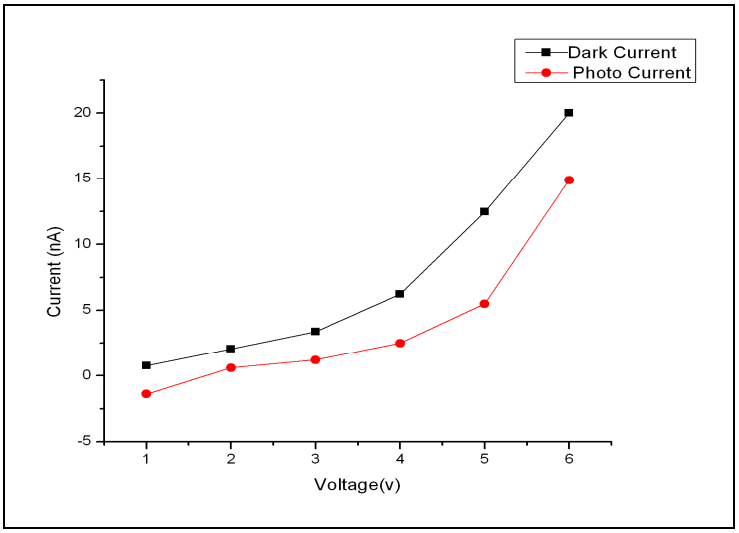

Fig. 8. Voltage Vs Current for CoS_2

IV. CONCLUSIONS

In this article, nano powders of cobalt disulphide and polymer protected cobalt disulphide polymer composite were synthesized using the simple hydrothermal technique and their structural, morphological, electrical and elemental composition features were discussed. XRD studies revealed that the grain size has increased in CoS_2 in polymer matrix. The formation of a protective solid film like structure by the polymer over the agglomerated cobalt disulphide particles was confirmed from SEM analysis. No other impurity peak was seen from EDAX spectrum which confirmed the purity of the as-prepared samples. Conductivity studies suggest that CoS_2 exhibits Negative Photoconductivity.

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