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Dielectric relaxation, complex impedance and modulus spectroscopic studies of mix phase rod like cobalt sulfide nanoparticles

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ABSTRACT

The Cobalt sulfide (CoS) nano-particles were synthesized using microwave assisted route. Powder XRD exhibited mixed phase of Co_3S_4 and CoS. The average crystallite size is found to be 58.28 nm from the Scherrer's formula and 54.41 nm from the Williamson and Hall (W-H) method. Rod like morphology is observed in nano-particles by HRTEM. The EDAX spectrum confirmed the presence of cobalt and sulphur. The impedance spectra were recorded in the range from 10 Hz to 10 MHz at various temperatures from 323 K to 373 K. The complex impedance spectra, i.e., Nyquist plots, were composed of two semicircles indicating the presence of grain and grain boundary contributions of nanoparticles. From the Jonscher's power law plots the Correlation Barrier Hopping (CBH) mechanism was found to prevailing for conduction in CoS nanoparticles. The electrical modulus spectroscopy suggested the temperature dependant relaxation process within CoS Nanoparticles. The results are discussed.

1. Introduction

Chalcogenide nanoparticles are widely studied due to their important applications and size dependent changes in Physico-chemical and optoelectronic properties [1–3]. Metal chalcogenides such as molybdenum sulfide, vanadium sulfide, nickel sulfide and cobalt sulfide have been studied for application in electro chemical supercapacitors [4–7]. Chalcogenide nano particles are synthesized by using various routes such as Microwave irradiation, co-precipitation, and sublimation [8–12]. The uniformly dispersed and stabilized Chalcogenide nanoparticles are successfully achieved by using capping agents and surfactants [13–16].

Cobalt sulfide a semiconductor material from group II–IV finds several potential applications, for example, supercapacitors [17], in solar selective coatings [18], as a catalyst for electrochemical and photo electrochemical hydrogen generation from water [19], as counter electrode in dye sensitized solar cells [20], catalysts for hydrodesulphurization and dehydrodearomatization [20] and exhibit weak ferromagnetic phase at 5.0 K temperature [21]. Due to complex stiochiometric nature cobalt sulfide crystallizes in a variety of phases like CoS, CoS_2, Co_3S_4, etc. [22]. There is reports available pertaining to the existence of mixed phases of Co_3S_4 and $Cos_{1.097}$ nanoparticles [23] as well as mix phases of CoS_2, Co_9S_8 and CoS nanoparticles [24].

Complex impedance spectroscopy is capable to study electrical properties of materials because it can throw light deep inside the phases of nanocrystalline materials like grain, grain boundary and electrode interface under the influence of applied frequency range. So far the knowledge of the present author is concerned no significant reports are available on impedance spectroscopy study, dielectric study and ac conductivity mechanism of CoS nanoparticles in a wide temperature range. However, electrochemical impedance spectroscopy study is reported on CoS_x compound [25].

In present study, the CoS nanoparticles were synthesized using microwave assisted method and characterized by using powder XRD, HRTEM and EDAX. Owing various applications of CoS in electrode and super-capacitor the present authors aimed to carry out the impedance spectroscopy, modulus spectroscopy and dielectric studies.

2. Experimental technique

2.1. Synthesis of CoS nanoparticles

The cobalt sulfide (CoS) nanoparticles were synthesised by using microwave irradiation method. Sodium sulphide (Na_2S) and

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cobalt chloride ($CoCl_2$) were taken as starting materials. 1 M Na_2S and 1 M $CoCl_2$ solutions were prepared in 100 ml distilled water in separate beakers. The capping agent 0.4gm (0.001 M) Polyvinyl-pyrrolidone (PVP) was added in the Na_2S solution and stirred well at 70 °C for 3 h as well as $CoCl_2$ solution was stirred at 40 °C stirred for 3 h. The $CoCl_2$ solution was then poured in to glass burette and added in a drop wise manner to the Na_2S and PVP solution under constant stirring, which resulted in to dark red precipitates. After the span of 4 h the colloidal solution was filtered using Watmann filter paper no.1 and washed with distilled water and dried. The dried samples in glass crucible were irradiated by microwave for 10 min in domestic microwave oven (Kenstar model) with input power set at 64 kW. The irradiated sample was crushed using mortar and pestle for further characterization.

2.2. Characterization techniques

The powder XRD pattern was recorded on PHILIPS X'PERT MPD using Cu K_α radiation. The data were analyzed by soft ware powder-X. The HRTEM images were recorded using Tecnai G2, F30 at 300 kV potential. The samples were prepared for HRTEM by dispersion in acetone solvent and followed sonication at 20 KHz for 30 min/h. The complex impedance spectra were recorded for palletized sample in frequency range of 10 Hz to 10 MHz in a temperature range of 323 K to 373 K using HIOKI 3532 LCR HITERSTER meter. The pelletized samples were applied with silver paint for making conductive surface to place in the sample holder and temperature was varied by using suitable resistive furnace. The Nyquist plots obtained from the impedance data were fitted with equivalent circuits by computer software Z-view and resistance and capacitance data were evaluated.

3. Results and discussions

3.1. Powder XRD study

Fig. 1 shows powder XRD pattern of cobalt sulfide (CoS) nanoparticles. The careful analysis of the powder XRD pattern indicates the presence of mixed phase. The majority of diffraction peaks are matched with the face centred cubic Co_3S_4 phase [JCPDS 75-1561] and the two peaks at diffraction angle 2θ = 30.632° and 73.728°, marked by *, are matched with the primitive hexagonal CoS phase [JCPDS 75-0605]. Previously Yin et al. [22] obtained CoS_2, CoS and Co_3S_4 mixed of nanoparticles by taking DMSO and ethanol (volume ration of 7:3) as a sulphur source, while Krishnamoorthy et al. [23] obtained Co_3S_4 and $CoS_{1.097}$ mixed phases of synthesized nanoparticles by taking thiourea as a sulphur source. It is important to note that it is difficult to obtained pure cobalt sulfide phase Co_mS_n due to complex stiochiometry of various cobalt sulphides [21,26].

The average crystallite size was estimated for highest intensity diffraction peak using Scherrer's equation as follows [27],

$$D = \frac{K\lambda}{\beta\psi o\sigma\theta} \quad (1)$$

Where, D = Average crystallite size, K = Constant = 0.9, λ = X-ray Wavelength, β = Full Width Half Maximum of high intensity diffraction peaks.

The average crystallite size for CoS mixed nanoparticles is found to be 58.28 nm.

Using Williamson-Hall method one can calculate the average crystallite size and the strain by following expression [28],

$$\beta\cos\theta = \frac{K\lambda}{L} + \eta\sin\theta \quad (2)$$

Where, β = Full Width Half Maximum of high intensity diffraction peaks, η = Strain, L = Crystallite size, λ = X-ray Wavelength and K = Constant = 0.9.

The intercept on Y-axis and a slope of linear fitted plot drawn between βcosθ and sinθ, as shown in Fig. 2, for different high intensity peaks gives crystallite size and strain, respectively. The average crystallite size and strain found to be L = 54.41 nm, η = 0.000254, respectively. The average crystallite size obtained from Scherer method and Williamson-Hall method corresponds well. Small variation in average crystallite size obtained from Scherer's equation and W-H equation may due to fact that the W-H equation consist of strain correction factor and that leads to obtain less crystallite size compare to Scherer's equation [29,30]. Further, the low value of micro strain indicates strain free and narrow size of the nanoclustures [31].

3.2. HRTEM study

Fig. 3(a–b) shows HRTEM images of cobalt sulfide (CoS) nanoparticles, which exhibits rod shaped morphology. The minimum and maximum particle size observed is 27 nm and 76 nm, respectively, which confirms the nano-structure nature. Generally, synthesis method, pH, temperature and concentration of precursor greatly affect the morphology of the synthesized particles. Surfactants provide general types of well organized

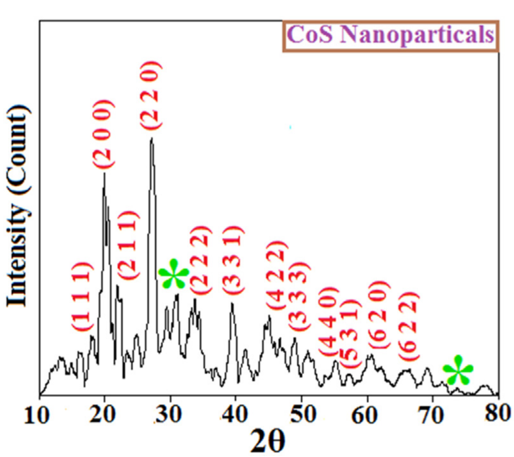

Fig. 1. Powder XRD pattern.

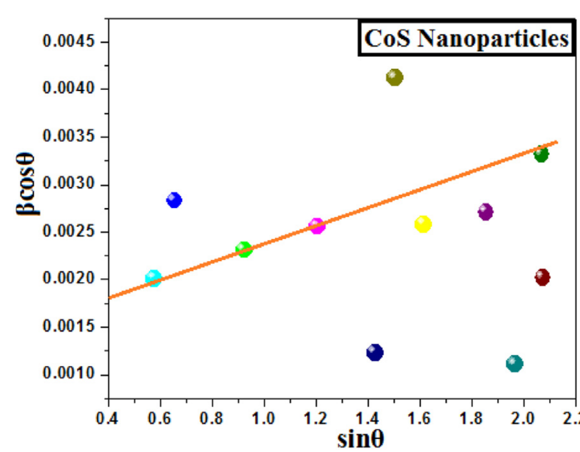

Fig. 2. Williamson – Hall plot.