

AC IMPEDANCE SPECTROSCOPY STUDIES ON Ni DOPED CdS NANOPARTICLES PREPARED BY CHEMICAL CO-PRECIPITATION METHOD

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In the present work, pure CdS and Ni doped CdS nanoparticles have been synthesized by chemical co-precipitation method using thiophenol as a capping agent. The frequency dependent dielectric dispersion of pure CdS and Ni doped CdS nanoparticles are investigated at room temperature in the frequency range of 100 Hz - 1 MHz by impedance spectroscopy. The dielectric properties and ac conductivity (σ_{ac}) of the samples were measured as a function of frequency. The plots of Z' vs Z'' (Z' is the real part of impedance and Z'' is the imaginary part) for Ni doped CdS were recorded at room temperature over the frequency ranges. All samples have a semicircle arc originating at the origin point. This indicates that each composition can be described by one bulk resistance and one bulk capacitance both connected parallel. The centre below the real axis indicates the relaxation behaviour of the system.

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1. Introduction

Transition metal (TM) (Mn, Fe, Co, Ni, etc.,) doped CdS has drawn considerable attention as it offers a great opportunity to integrate electrical, optical and magnetic properties into a single material, which makes it an ideal candidate for nonvolatile memory, magneto-optical and future spintronic devices [1,2]. Fe and Ni doped CdS diminishes yields in the visible and near-band-gap region by acting as a quenching or killer centres for fluorescence and photoconduction, and results in short carrier lifetimes useful in fast optoelectronic devices [3-5]. These findings have opened additional avenues to step further towards the development of advanced devices based on TM doped CdS. Different techniques such as electrodeposition, coevaporation, chemical vapour deposition, spray pyrolysis and other chemical routes [6-8] have been used to synthesize TM doped CdS.

Dielectric measurements and ac conductivity have been reported for a wide variety of chalcogenide semiconductors in order to understand the mechanisms of conduction processes in these materials and the types of polarization. In nanostructured materials, the surface to volume ratio of atoms is higher than their bulk counterparts. Hence we expect the grain boundary effects to play a significant role in determining the dielectric properties of these materials. The electrical conductivity and dielectric behaviour of nanocrystalline materials depend on chemical compositions, preparation conditions and grain size. Studies on the effect of temperature, grain

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size and frequency on the dielectric behaviour and ac electrical conductivity offer valuable information about conduction phenomenon based on localized electric charge carriers in nanostructured materials.

The structural and optical properties of Ni doped CdS nanoparticles are reported in our previous work [9, 10]. A complete systematic study of various dielectric parameters of Ni doped CdS nanoparticles in a wide frequency range are still lacking. In this paper we have studied systematically the dielectric properties of Ni doped CdS synthesized by a chemical co-precipitation method in the frequency range of 100 Hz - 1 MHz by impedance spectroscopy.

2. Experimental

DMS nanoparticles of CdS: Ni²⁺ were prepared by colloidal chemical co-precipitation method using Cadmium acetate, Sodium sulfide and Nickel acetate as starting compounds. Appropriate quantities of these were weighed in microbalance (M/s SICO, India) according to the stoichiometry to obtain 2, 4, 6, 8 and 10 at% target dopant concentrations and dissolved in 100 ml of methanol to make 0.1M solutions. The stoichiometric solution was taken in a burette and was added in drops with continuous stirring to a mixture of Na₂S(0.1M) + 50 ml of H₂O + 1.1 ml of thiophenol + 100 ml of methanol until fine precipitate of CdS and CdS:Ni was formed. After complete precipitation, the solution in conical flask was constantly stirred for about 20 hours. A single step chemical reaction is given below for the precipitation of the CdS and Ni doped CdS nanoparticles. Then the precipitates were filtered out separately and washed thoroughly with de-ionized water. Finally these samples are subjected to sintering process. The green coloured nanocrystalline CdS and CdS: Ni²⁺ powders were obtained. These powders were mixed with organic binder of 1wt.% polyvinyl alcohol (PVA). Pellets of 12 mm in diameter and 2-3 mm thickness were uniaxially pressed at 2 tons. These pellets were calcined at 300 °C / 2 hours in vacuum. Impedance measurement was carried out using the frequency impedance analyzer (Model HIOKI LCR Hi Tester 3532-50 JAPAN) in the frequency range from 100 Hz to 1 MHz at room temperature.

3. Results and discussion

Impedance spectroscopy is a powerful method of characterizing many of the electrical properties of materials and their interfaces with electronically conducting electrodes. A great strength of impedance spectroscopy is that, with appropriate data analysis, it is often possible to characterize the different electrically active regions in a material by demonstrating their existence and by measuring their individual electric properties [11, 12]. The frequency dependent properties of a material are normally described in terms of any of the formalism expressed as

$$\text{Complex impedance: } Z^* = Z' - jZ'' = R_s - \frac{j}{\omega C_s} \quad (1)$$

$$\text{Complex admittance: } Y^* = Y' + jY'' = \frac{1}{R_p} + j\omega C_p = G(\omega) + jB(\omega) \quad (2)$$

$$\text{Complex permittivity: } \epsilon^* = \epsilon' - j\epsilon'' \quad (3)$$

and

$$\text{Complex modulus: } M^* = (\epsilon^*)^{-1} = M' + jM'' = j\omega C_0 Z'' \quad (4)$$

where subscripts p and s refer to equivalent parallel and series circuit components, $\omega = 2\pi f$, angular frequency, C_0 is capacitance of the cell in vacuum (Z' , Y' , E' , M') and (Z'' , Y'' , ϵ'' , M'') are the real and imaginary components of impedance, admittance, permittivity, and modulus, respectively, G: conductance, B: susceptance, and $\tan \delta$: dielectric loss.

Fig. 1(a) and 1(b) shows the variation of real and imaginary part of impedance (Z' and Z'') with frequency at different concentrations of Ni doped CdS. The decrease in the value of Z' and Z'' with the increase in frequency indicates the effect of space charge polarization. Since the space charge polarization is reduced with increasing frequency, all the curves appear to merge at higher frequencies. The magnitude of Z' and Z'' is maxima for 4% Ni doped CdS and minima for 2% Ni doped CdS.

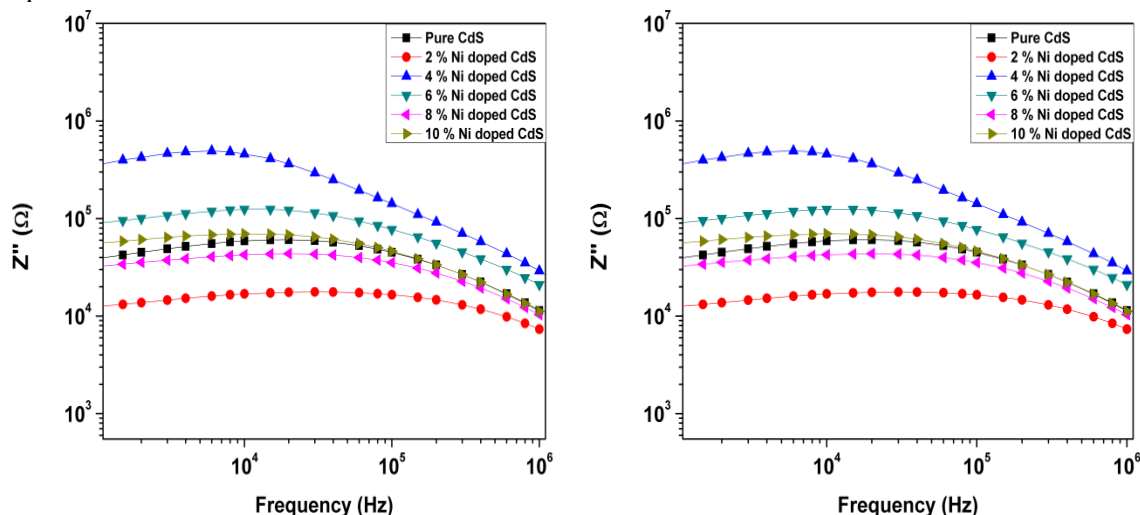


Fig. 1 Frequency dependence of (a) real part of impedance (Z') and (b) imaginary part of impedance (Z'')

The ac impedance data also provides information on relaxing dipoles of the materials in terms of real and imaginary complex dielectric permittivity using the relation

$$\epsilon' = \frac{Z''}{\omega C_0 (Z'^2 + Z''^2)} \quad \text{and} \quad \tan \delta = \frac{\epsilon'}{\epsilon''} = \frac{Z'}{Z''} \quad (5)$$

The variation of real and imaginary part of dielectric constant (ϵ' and ϵ'') with frequency is shown in Fig. 2(a) and 2(b). Decrease in real and dielectric part of dielectric constant is observed with increase in frequency. The decrease of ϵ' and ϵ'' with increasing frequency were due to extermination of the atomic and electronic polarization at low frequency. It is believed that the values of ϵ' and ϵ'' decrease at a certain frequency because of the orientation polarization and space charge polarization, which agrees with the Debye equation [13,14]. At low frequencies, the maximum value of dielectric constant is obtained for 4% Ni doped CdS where as the minimum value is obtained for 6% Ni doped CdS. The high values of dielectric constant at lower frequency can also be explained on the basis of space charge polarization. The exponential decrease of dielectric loss with frequency is shown in Fig. 3. At low frequencies the dielectric constant values are high because under the influence of applied electric field the charge carriers existing in the dielectric film can migrate for some distance. When such carriers are blocked at the electrodes, a space charge region results. This leads to a substantial increase in $\tan \delta$ towards low frequencies [15]. The dielectric loss decreases with increase of frequency and Ni concentration in CdS. The low dielectric loss with high frequency implies that the samples possess good optical quality with lesser defects.

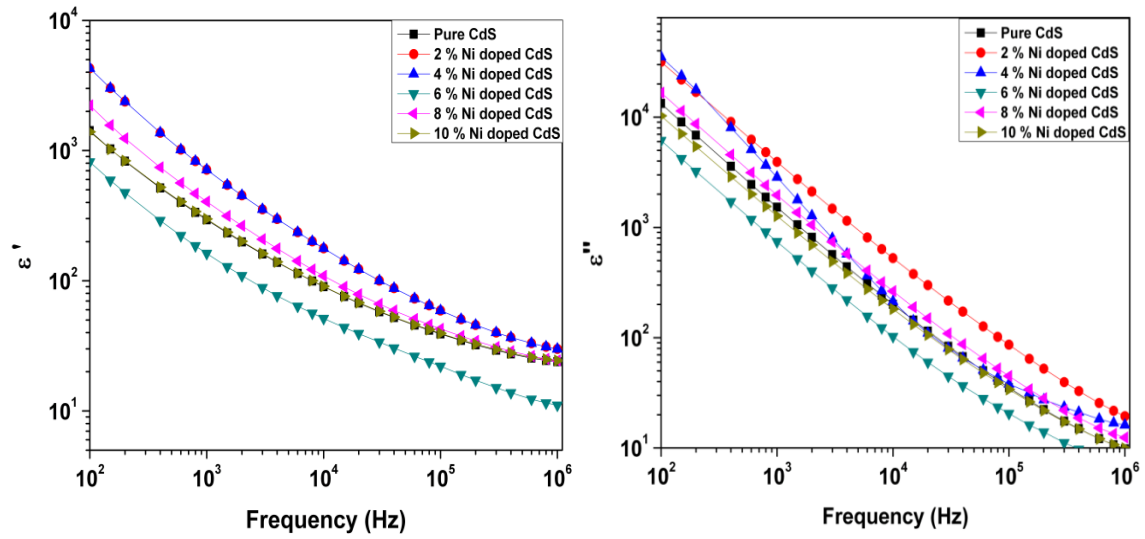


Fig. 2 Variation of (a) real part of dielectric constant (ϵ') and (b) imaginary part of dielectric constant (ϵ'') with frequency

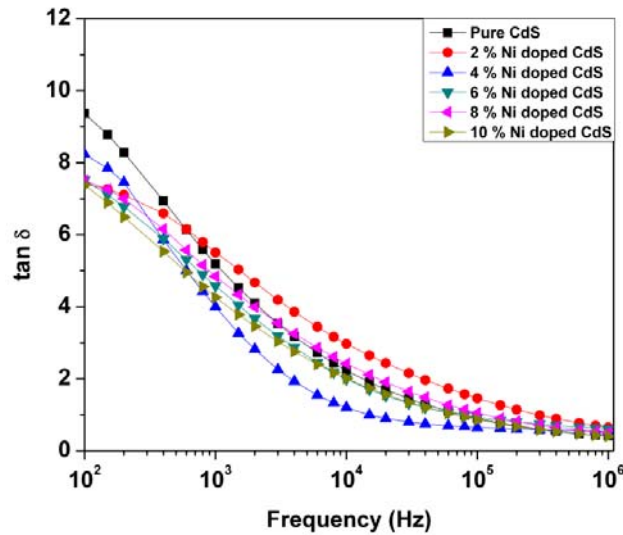


Fig. 3 Frequency dependence of dielectric loss ($\tan \delta$) for pure CdS and Ni doped CdS

The variation of ac conductivity with frequency at different concentrations of Ni doped CdS is shown in Fig. 4 in log-log scale. The ac conductivity is determined from the relation

$$\sigma_{ac} = \omega \epsilon_0 \epsilon' \tan \delta \quad (6)$$

The conductivity increases with increase of frequency but decreases with increase of Ni concentration in CdS. The maximum σ_{ac} is found for 2% Ni doped CdS whereas the minimum conductivity is found for 6% Ni doped CdS. Frequency independent behaviour of the conductivity in the low frequency region is observed but that become sensitive at high frequency region, which generally known as hopping frequency. The high frequency variation of σ_{ac} found to obey universal Jonscher's power law behaviour, $\sigma_{ac} = K\omega^s$ [16], with $0 \leq s \leq 1$, where ω is angular frequency of ac field, in the frequency sensitive region. The dielectric constant (ϵ'), dielectric loss ($\tan \delta$) and ac conductivity (σ_{ac}) values at 1 MHz are tabulated in Table 1.

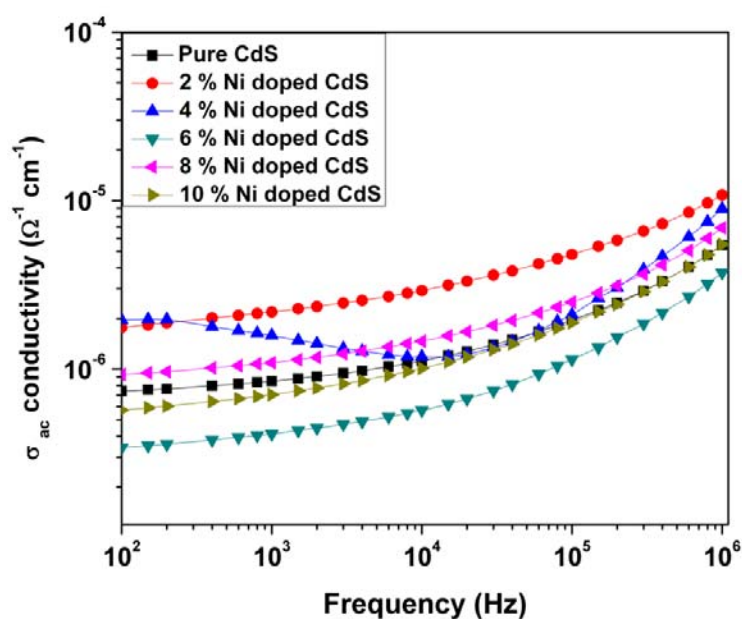


Fig. 4 Frequency dependence of ac conductivity (σ_{ac}) for pure CdS and Ni doped CdS

Table 1. Dielectric parameter values of pure and Ni doped CdS at a frequency of 1 MHz

S.No	Compound Name	Dielectric constant (ϵ')	Dielectric loss ($\tan \delta$)	ac conductivity σ_{ac} ($\Omega^{-1} \text{ cm}^{-1}$)
1	Pure CdS	23.87	0.41	5.44×10^{-6}
2	2% Ni doped CdS	29.94	0.65	1.08×10^{-5}
3	4% Ni doped CdS	26.14	0.54	8.96×10^{-6}
4	6% Ni doped CdS	27.32	0.60	3.73×10^{-6}
5	8% Ni doped CdS	24.41	0.51	6.90×10^{-6}
6	10% Ni doped CdS	24.37	0.40	5.50×10^{-6}

Contribution of individual micro-structural element to bulk admittance (Y') was evaluated using the relation

$$Y' = \frac{Z'}{Z'^2 + Z''^2} \quad (7)$$

Where Z' and Z'' are real and imaginary impedance of individual micro-structural element obtained from the impedance plots. Bulk admittance was simulated using equation (7) as shown in Fig. 5 with the help of brick-layer model [17]. According to brick layer model the electrical properties are determined by series combination of individual microstructural impedances.

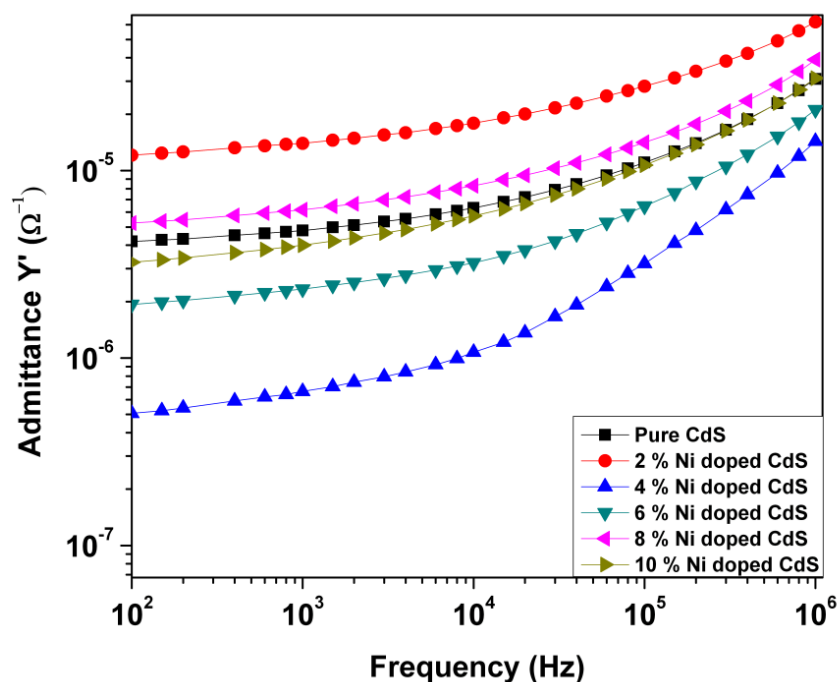


Fig. 5 Frequency variation of the admittance for pure CdS and Ni doped CdS

When a Cole-Cole plot is considered, the impedance response commonly shows a semicircular form. The real part (Z') vs. imaginary part (Z'') of impedance curves of pure CdS with 2, 4, 6, 8 and 10% Ni doped CdS shows clearly a semicircle (Fig. 6) which indicates the effect of the grain. While the data for real homogeneous dielectrics actually fit an arc of a circle with the centre below the real axis and described by an RC-equivalent circuit (shown in Fig. 6), for the polycrystalline material with electrodes, a more complex model is appropriate, in which different groups of RC-circuits describe: (a) the grain (high frequency, close to the axis origin of the Cole-Cole plot) (Fig. 6), (b) the grain boundaries (in the middle part of the Cole-Cole plot), (c) the electrode interfaces (for low frequencies, at high values of ϵ'). The intercept of the semicircle on the real axis (Z') gives the resistance of the corresponding component contributing towards the impedance of the samples.

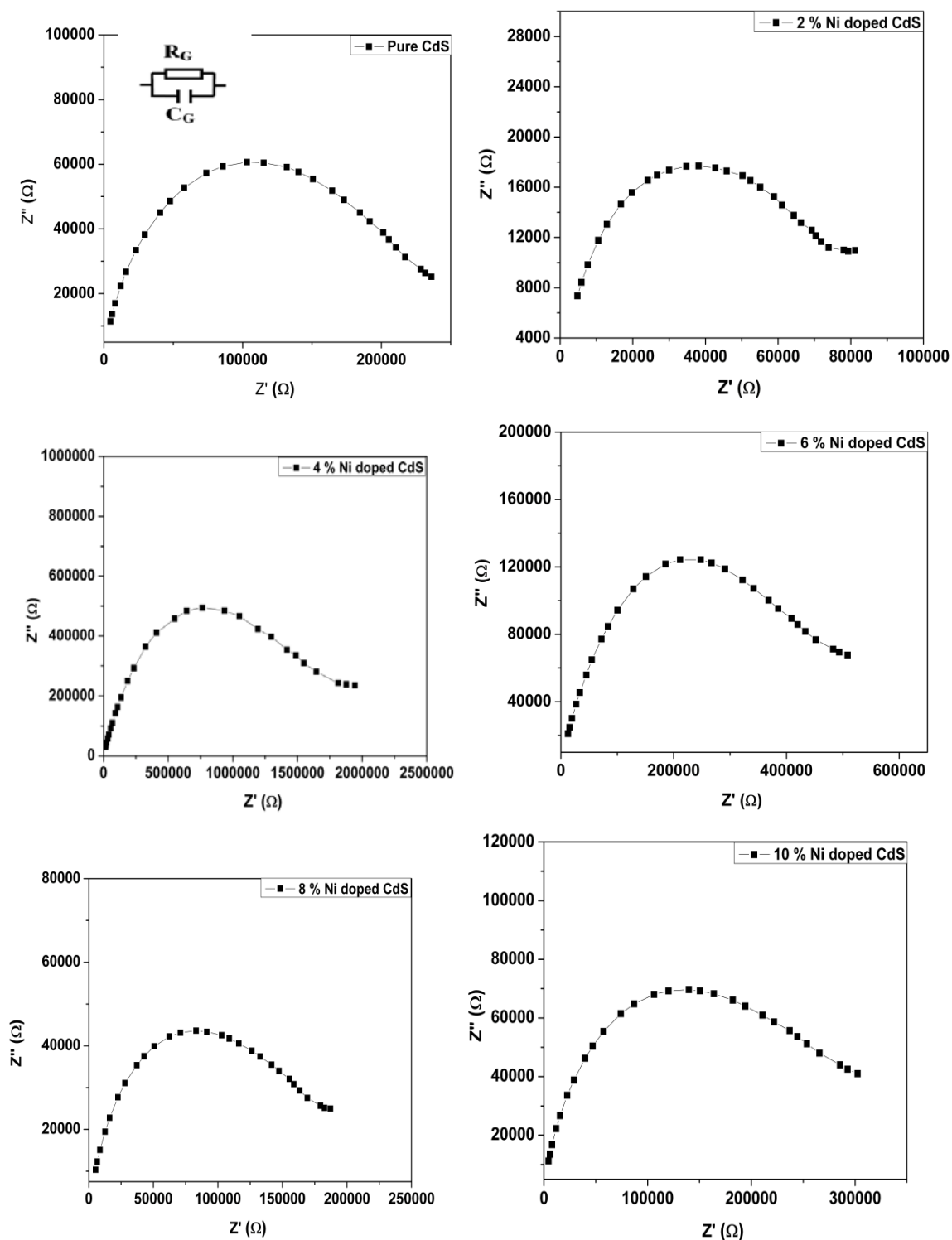


Fig. 6 Cole-Cole plots for pure CdS and Ni doped CdS

The high frequency semicircle represents the bulk grain property of the materials arising due to the parallel combination of bulk resistance and bulk capacitance of the material. The capacitance of the values can be evaluated from the experimental semicircles, using the relation $\omega RC = 1$ for all the samples. The values of bulk grain resistance (R_G) and bulk grain capacitance (C_G) are calculated from the equivalent circuit and tabulated in the Table 2.

Table 2. Resistance and capacitance values calculated from the equivalent circuit

S.No	Compound Name	$R_G (\Omega)$	$C_G (F)$
1	Pure CdS	2.76×10^5	5.76×10^{-10}
2	2% Ni doped CdS	9.62×10^4	1.65×10^{-9}
3	4% Ni doped CdS	2.42×10^6	6.57×10^{-11}
4	6% Ni doped CdS	6.42×10^5	2.50×10^{-10}
5	8% Ni doped CdS	2.30×10^5	7.00×10^{-10}
6	10% Ni doped CdS	3.98×10^5	4.00×10^{-10}

4. Conclusions

The frequency dependent dielectric properties of pure CdS and Ni (2, 4, 6, 8 and 10 %) doped CdS nanoparticles, synthesized by chemical co-precipitation method, are investigated at room temperature in the frequency range of 100 Hz - 1 MHz. Analysis of the real and imaginary part of complex impedance with frequency were performed assuming a distribution of relaxation times as confirmed by Cole-Cole plot. It was found that the impedance plots were single semicircular arcs with their centres in the high frequency region. All samples are represented by bulk grain resistance R_G connected in parallel with a bulk grain capacitance C_G .

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