Comparative study between pure and manganese doped copper sulphide (CuS) nanoparticles

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Abstract
The pure CuS and Mn2++ doped CuS nanoparticles are synthesized by wet chemical route. The CuS phase and hexagonal crystal structure is confirmed by the powder X-ray diffraction and Raman analysis. The vibrational bonds present in the respective synthesized samples are confirmed by Fourier transformed infra-red spectroscopy. The spherical shapes of the nanoparticles are validated by the electron diffraction in scanning and transmission mode. The thermal analysis showed the Mn2++ doped CuS nanoparticles to be more stable than pure CuS nanoparticles. The thermal parameters determined using Coats-Redfern relation stated thermal activation energy and enthalpy change values are highest in the higher temperature range. The Seebeck coefficient variation with temperature and ambient condition Hall effect measurements showed the synthesized nanoparticles to be semiconducting and p-type in nature. The magnetic properties study by Gouy method showed the nanoparticles to be paramagnetic.

1. Introduction

Magnetic and electrical transport properties of dilute magnetic semiconductor (DMS) materials have received more attention for their spintronic and opto-electronic device applications. To tailor properties of DMS material for more potential application needs doping by transition metal ions. Doping enhances contribution to the carrier charges as well as spin by the application of magnetic and electric field [1, 2]. Recently many researchers are working on doping of magnetic ions (transition metals like Co, Ni, Fe, Mn) in semiconductor compounds leading to DMS applications [3–16].

The semiconductor copper compounds found much interest due to its prospective properties and characteristics [17–21]. The other advantages of semiconductor copper compounds are the precursor elements being benign and amply available making them environment friendly and cost effective. Of the semiconductor copper compounds, the copper sulfide (CuS) is one of the potential compound for various applications in optoelectronic devices, super capacitor [22, 23], lithium batteries, energy storage [24, 25], gas sensor [26], catalysis [27] and biomedical field [28]. It has been observed that photo catalytic activity enhances in CuS due to doping with Co [29], Ni [30] and Fe [31] while high efficiency is achieved in quantum dot synthesized solar cell by doping with Mn2+ ions [32]. Also Mn doped various materials are showing results leading to potential applications in the field of ultra-sensitive latent fingerprint detection and in vivo bio-imaging [33], as humidity sensors [34], in LED [35, 36], as biomarkers [37], in solar energy conversion [32, 38, 39], in optical fiber communication [40], in solid state lasers [40], in solar water heaters [40], in spintronics [41, 42], etc Sensing the importance of Mn doped materials, the authors got inspired to study the structural, thermal, electrical transport and magnetic properties of pure CuS and Mn2++ doped CuS nanoparticles. An attempt is made to do a comparative study of the different properties between these two compounds.
2. Experimental

In the synthesis of pure and Mn$^{2+}$ doped CuS nanoparticles, copper(II) chloride (CuCl$_2$·2H$_2$O), manganese (II) chloride (MnCl$_2$·4H$_2$O), triethanolamine (TEA) (C$_6$H$_{15}$NO$_3$), ammonia solution (NH$_4$OH), sodium hydroxide pellets (NaOH) and thiourea (TU) (NH$_2$CSNH$_2$) are used. The chemicals are of analytical grade and used directly without any processing. Here copper(II) chloride, manganese(II) chloride and thiourea are the sources for Cu$^{2+}$, Mn$^{2+}$ and S$^{2-}$ ions, respectively. Triethanolamine and sodium hydroxide are the complexing agents, whereas ammonia solution is used to adjust pH of solution to achieve alkaline medium. Brief step by step synthesis process employed in present study is given below [43]. Here all addition of solution in steps is done under continuous magnetic stirring. The stirring after each addition is of 10 min. The solutions and all reactions in the complete synthesis processes are carried out with double distilled water (DDW).

For pure CuS nanoparticles,

$$1M \text{CuCl}_2\cdot2\text{H}_2\text{O} (5 \text{ ml}) + 3.7M \text{C}_6\text{H}_{15}\text{NO}_3 (4 \text{ ml}) + 2M \text{NH}_4\text{OH} + 1M \text{NaOH} (10 \text{ ml}) + 1M \text{NH}_2\text{CSNH}_2 (6 \text{ ml}) + \text{DDW (65 ml)}$$

For Mn doped CuS nanoparticles,

$$1M \text{CuCl}_2\cdot2\text{H}_2\text{O} (5 \text{ ml}) + 0.15M \text{MnCl}_2\cdot4\text{H}_2\text{O} (5 \text{ ml}) + 3.7M \text{C}_6\text{H}_{15}\text{NO}_3 (4 \text{ ml}) + 2M \text{NH}_4\text{OH} (10 \text{ ml}) + 1M \text{NaOH} (10 \text{ ml}) + 1M \text{NH}_2\text{CSNH}_2 (6 \text{ ml}) + \text{DDW (60 ml)}$$

On final addition and next 10 min stirring, the final solution becomes greenish black. Stirring is stopped and the solution is kept ideal at ambient condition. After few hours, the sediment precipitates are filtered using Whatmann filter paper Grade 5. The final nanoparticles are given multiple wash by DDW followed by methanol to remove impurities. The particles are dried in oven at 373K for 2 h to obtain pure and Mn$^{2+}$ doped CuS nanoparticles yield.

The chemical compositions and surface topography of the as-synthesized CuS and Mn doped CuS nanoparticles are studied with the help of energy dispersive analysis of X-rays (EDAX) and scanning electron microscopy (SEM) using LEO 1430 VP. Both the synthesized nanoparticles are structurally characterized by powder X-ray diffraction (XRD) and Raman spectroscopy. The XRD are recorded by Philips X-ray Diffractometer Xpert MPD with CuK$\alpha$ radiation in the 2$\theta$ range of 3$^\circ$ and 95$^\circ$. The ambient condition Raman spectra is recorded in backscatter geometry by Jobin Yvon Horiba LabRam, HR800 single monochromator having Peltier cooled charge coupled device with 488 nm argon laser excitation. The Fourier transform infrared spectroscopy (FTIR) of the synthesized nanoparticles is done by incorporating the samples in KBr as base material. The FTIR spectra are recorded in the wave number range of 4000 and 400 cm$^{-1}$ with a resolution of 0.15 cm$^{-1}$ employing Perkin Elmer Spectrum GX FTIR. The JEOL JEM 2100 high resolution transmission electron microscopy (HRTEM) is employed for shape-size analysis of the synthesized nanoparticles. The selected area electron diffraction (SAED) patterns are recorded using Philips, Technai-20 transmission electron microscope using CCD with electron source as LaB6, having accelerating voltage of 200 kV. The thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) curves are recorded of the synthesized nanoparticles by Seiko SII-EXSTAR TG/ DTA-7200 thermal analyzer. The thermocures are recorded in the temperature range of ambient and 1173 K for heating rate of 10 K min$^{-1}$ in inert N$_2$ atmosphere. The electrical transport properties study is carried out on the synthesized nanoparticles. The measurement is done on pellets prepared from the nanoparticles by hydraulic pressing. The variation of thermoelectric power ‘S’ as a function of temperature in the temperature range of 308 K and 393 K maintaining a
temperature gradient of 5 K are measured on thermoelectric power measurement setup Model-TPSS-200, Scientific Solution, Mumbai, India. The Hall Effect measurement at room temperature using van der Pauw technique are measured on the Hall set-up Model-DHE-22 using constant current source Model-DPS175 developed by SES Instruments Pvt. Ltd, Roorkee, India. The magnetic properties of both the synthesized, pure CuS and Mn$^{2+}$ doped CuS nanoparticles are measured by Gouy balance method.

3. Results and discussion

The chemical composition of wet chemical synthesized pure CuS and Mn doped CuS nanoparticles are determined by EDAX technique. The obtained spectra are shown in figure 1. Only copper and sulphur peaks are observed in the pure CuS nanoparticles, figure 1(a). In the Mn doped CuS nanoparticles, figure 1(b), manganese peaks are also observed along with copper and sulphur. The observed EDAX weight percentage values along with standard values are tabulated in table 1. The data shows the synthesized pure CuS nanoparticles are slightly sulphur rich but are near stoichiometric.

Similarly the Mn doped CuS nanoparticles data shows presence of Mn, thus confirming doping to have happened in the CuS nanoparticles. The dopant Mn$^{2+}$ ions replaces Cu$^{2+}$ ions in CuS, reason being the ionic radii of Mn$^{2+}$ (0.83 Å) matches well with ionic radii of Cu$^{2+}$ (0.87 Å) [43].

The XRD patterns of pure CuS and Mn$^{2+}$ doped CuS nanoparticles are shown in figure 2(a). The XRD patterns are indexed by Powder-X software. The indexing of all the peaks showed them to possess CuS phase with hexagonal unit cell structure. The obtained lattice parameters are; $a = b = 3.79$ Å and $c = 16.34$ Å. The unit cell structure and the lattice parameters matched with the standard JCPDS File No. 06-0464 of CuS phase. The XRD analysis showed no extra peaks or excess peaks corresponding to any other phase due to doping. The minute analysis of the XRD showed slight shift in the peaks of Mn$^{2+}$ doped CuS from the pure CuS peak positions. This is due to Vegard’s law [44] which states the minor doping does not generate phase involving dopant but shifts the host materials peak position. The determined average crystallite sizes using Scherrer’s equation [45] came out to be 4.01 and 4.52 nm for CuS and Mn$^{2+}$ doped CuS nanoparticles, respectively.

The Raman spectra, figure 2(b), showed both the nanoparticles had single peak positioned at 470 cm$^{-1}$. The peak position matches the reported data which arises due to hexagonal CuS crystalline $P6_{3}/mmc$ space group.

| Element | Standard (Wt%) | CuS | Mn doped CuS |
|---------|---------------|-----|--------------|
| Cu      | 66.47         | 65.21 | 64.43        |
| S       | 33.53         | 34.79 | 31.90        |
| Mn      | —             | —    | 3.67         |

Figure 2. The (a) XRD patterns and (b) Raman spectra of synthesized nanoparticles.

Table 1. The EDAX data.
It has primitive unit cell consisting of 12 atoms, 6 each of copper and sulphur. The XRD and the Raman analysis showed the synthesized nanoparticles are single phase CuS.

The FTIR spectra of pure CuS and Mn$^{2+}$ doped CuS nanoparticles are shown in figure 3. The observed FTIR peaks of pure CuS and Mn$^{2+}$ doped CuS are tabulated in Table 2. The peaks are assigned the functional vibrational bonds [46, 47]. The majority bonds are owing to impurities from the chemicals used during synthesis. The Mn$^{2+}$ doped CuS showed Mn-O bond positioned at 426 cm$^{-1}$ clearly stating doping of Mn into CuS [49].

The SEM images of as synthesized pure CuS and Mn$^{2+}$ doped CuS nanoparticles are shown in figures 4 (a), (b). The SEM image of pure CuS nanoparticles, figure 4(a), shows them to be spherical in shape with uniform

| Peaks Wavenumber (cm$^{-1}$) | CuS     | Mn doped CuS | Assignment                                           |
|-----------------------------|---------|--------------|-----------------------------------------------------|
| 3438                        | 3436    | N–H and O–H stretching mode of vibration due to NH$_4$OH/H$_2$O [50, 51] |
| 2923, 2852                  | 2923, 2852 | C–H symmetric and asymmetric stretching mode due to C$_6$H$_{15}$NO$_3$(TEA) [51] |
| 1631                        | 1632    | O–H bending mode due to H$_2$O [50]                          |
| 1458                        | 1458    | C–H bending mode [52]                                      |
| 1125                        | 1120    | C–O stretching mode due to CH$_3$OH [53]                   |
| 1017                        | 1063, 1018 | C = S stretching mode of vibration due to NH$_2$CSNH$_2$(TU) [54] |
| 675, 619 (600 – 700)        | 671, 616 | C = S stretching mode of vibration due to NH$_2$CSNH$_2$(TU) [54] |
| 465                         | 466     | Cu–O vibration [55]                                       |
| —                           | 426     | Mn–O wagging mode of vibrations [49]                      |

Figure 3. The FTIR spectra of pure CuS and Mn$^{2+}$ doped CuS nanoparticles.

Figure 4. The SEM images of (a) CuS and (b) Mn doped CuS nanoparticles.

Table 2. The FTIR data of the as synthesized CuS and Mn$^{2+}$ doped CuS nanoparticles [50–55, 49].
distribution. The figure 4(b) is the SEM image of Mn$^{2+}$ doped CuS nanoparticles, they shows spherical shape particles similar to CuS along with platelets. Doping of Mn leads to platelet formation is reported in literature [56–59].

The TEM images of the pure CuS and Mn$^{2+}$ doped CuS nanoparticles are shown in figures 5(a), (b). The figure 5(a) is TEM image of pure CuS nanoparticles, which shows the particles to be spherical in shape.
Figure 5(b) is the TEM image of Mn$^{2+}$ doped CuS nanoparticles; it shows spherical shapes along with platelet. These TEM observations substantiate the observation of SEM analysis.

The figures 5(c), (d) are the particle size distribution of pure CuS and Mn$^{2+}$ doped CuS nanoparticles respectively. The analysis shows Mn$^{2+}$ doping changes the morphology leading to enhanced size.

The HRTEM images of pure CuS and Mn$^{2+}$ doped CuS nanoparticles are shown in figures 5(e), (f). The interplaner spacing ($d$) value of pure CuS is 0.319 nm and of Mn$^{2+}$ doped CuS is 0.327. The observed $d$ values are in match with the $d$ spacing value of the XRD lattice plane (102) [43].

The SAED patterns of CuS and Mn$^{2+}$ doped CuS nanoparticles are shown in figure 6. The pattern clearly shows rings, substantiating polycrystallinity of both the samples. After recording the diffraction pattern, the planes are indexed by evaluating the ‘$d$’ spacing using the standard equation,

$$d_{hkl} = \frac{\lambda}{R}$$

Where R is the distance from the central bright spot to corresponding rings, L is the camera length between specimen and photographic film and $\lambda$ is the wavelength of the electron beam based on the accelerating voltage. The planes are indexed as (1 0 7), (2 0 3) and (3 0 0) for CuS. While (1 0 7), (1 0 8), (2 0 3) and (3 0 0) planes indexed for Mn$^{2+}$ doped CuS nanoparticles.

The TG, DTG and DTA curves of the synthesized pure CuS and Mn$^{2+}$ doped CuS nanoparticles are shown in figures 7(a)–(c). The TG curves, figure 7(a), show the total weight loss between ambient and 1173 K is ~42% in case of pure CuS nanoparticles, while in case of Mn doped CuS nanoparticles the weight loss is ~38%. It clearly indicates that the decomposition of Mn doped CuS nanoparticles is ~4% less than pure CuS nanoparticles. This
observation states, Mn$^{2+}$ doping into CuS enhances the stability. Reason of such observation may be due to melting point of Mn, 1519 K, is much higher to melting point of Cu, 1358 K.

The first derivatives of the TG for both the samples are given in figure 7(b) known as DTG curves. The figure shows presence of good number of peaks in both the curves, stating large decomposition steps in TG. The comparison between both the DTG curves states the peak numbers are more in case of pure CuS compared to Mn$^{2+}$ doped CuS. This observation states less decomposition steps in Mn$^{2+}$ doped CuS compared to pure CuS, meaning the Mn$^{2+}$ doping thermally stabilizes CuS.

The DTA curves for both the pure CuS and Mn$^{2+}$ doped CuS nanoparticles shows them to be of endothermic nature since the curves lies below zero level base line all through the analyzed temperature range. The endothermic nature of the curves states heat absorption by the samples. The heat absorption leads to decomposition being reflected by weight loss in the corresponding TG curves.

The thermal activation energy ($E_a$) values are calculated from the TG curves employing standard Coats-Redfern (C-R) method [60, 61]. The C-R method is employed since it is easy and simple to use with data obtained from the TG. The C-R plots for both the samples for the different decomposition steps as per DTG peak numbers are shown in figures 8(a), (b).

The important thermal parameters such as, activation enthalpy change ($\Delta H$) and activation entropy change ($\Delta S$) for both pure CuS and Mn$^{2+}$ doped CuS nanoparticles are evaluated using TG data by below equations [62].

![Figure 8. The C-R plots of (a) pure CuS and (b) Mn doped CuS nanoparticles.](image)

| Sample      | Steps | Temp. range (K) | DTG Peak (K) | Weight Loss (Wt %) | $E_a$ (kJ·mol$^{-1}$) | $\Delta H$ (kJ·mol$^{-1}$) | $\Delta S$ (J·K$^{-1}$·mol$^{-1}$) | $r$  |
|-------------|-------|-----------------|--------------|--------------------|----------------------|---------------------------|---------------------------------|------|
| CuS NPs     | 1     | 363–413         | 393          | 2.31               | 102.89               | $7.88 \times 10^{12}$   | 99.63                          | −0.32 | 0.99 |
|             | 2     | 498–573         | 553          | 12.47              | 131.71               | $4.58 \times 10^{11}$   | 127.11                         | −26.80 | 0.99 |
|             | 3     | 574–653         | 605          | 11.36              | 265.79               | $1.47 \times 10^{12}$   | 260.76                         | 173.62 | 0.99 |
|             | 4     | 693–763         | 731          | 2.76               | 352.17               | $2.42 \times 10^{14}$   | 346.99                         | 214.49 | 0.99 |
|             | 5     | 993–1093        | 1050         | 4.54               | 526.95               | $2.72 \times 10^{15}$   | 518.22                         | 231.57 | 0.99 |
| Mn doped CuS NPs | 1     | 498–573         | 529          | 4.27               | 113.48               | $2.66 \times 10^{10}$   | 109.08                         | −50.10 | 0.98 |
|             | 2     | 623–703         | 671          | 8.52               | 180.26               | $1.79 \times 10^{13}$   | 174.68                         | 2.05  | 0.99 |
|             | 3     | 873–963         | 931          | 9.96               | 384.50               | $6.21 \times 10^{15}$   | 376.76                         | 143.70 | 0.99 |
|             | 4     | 1083–1153       | 1128         | 3.70               | 768.97               | $6.75 \times 10^{14}$   | 759.39                         | 410.86 | 0.99 |
Here, $E_a$ is the thermal activation energy, $R$ is gas constant, $A$ is Arrhenius constant, $K_B$ is Boltzmann constant, $h$ is Planck’s constant and $T$ is temperature of DTG peaks. The evaluated parameters are tabulated in table 3.

The obtained thermal activation energy $E_a$ values in different temperature ranges states the magnitude value of $E_a$ is maximum in the highest temperature ranges (Step—5 for pure CuS and Step—4 for Mn$^{2+}$ doped CuS). This behavior is observed in case of both the nanoparticles. The highest $E_a$ values states maximum decomposition of the samples to takes place in the highest temperature ranges.

The $\Delta H$ values are positive in all the temperature ranges stating absorption of heat by the sample. The heat absorption leads to decomposition of the sample being substantiated by weight loss observed in simultaneous TG curves. In both the samples $\Delta H$ values are maximum in the highest temperature ranges (Step—5 for pure CuS and Step—4 for Mn$^{2+}$ doped CuS) stating entire sample decomposition in this respective temperature ranges. This maximum $\Delta H$ observation agrees with the maximum values of $E_a$ in the highest temperature ranges.

The obtained $\Delta S$ values states the value to be negative in the initial temperature range for both the samples and in higher temperature ranges the values are positive. The negative $\Delta S$ values in the initial temperature range states ordering to happen before becoming positive $\Delta S$ values, stating decomposition and leading to disorder. The $r$ values are in the range of ~ 0.99 stating the thermal parameters calculations are to the best of correct values.

The electrical transport properties studies are carried out on the pellets prepared from the nanoparticles by hydraulic pressing. The pellets of pure CuS and Mn$^{2+}$ doped CuS nanoparticles are prepared by hydraulic pressing of uniformly loaded 1gm of CuS nanoparticles and Mn doped CuS nanoparticles in die (pelletizer) to a pressure of 0.9GPa for 30 min. The obtained pellets are of 1.4 cm diameter and 240 $\mu$m thickness. The electrical contacts on the pellets for transport properties measurements are taken by silver paste and copper wires. The variation of thermoelectric power $S$ as a function of temperature in the temperature range of 308 K and 393 K maintaining a temperature gradient of 5 K is measured on pellets prepared from CuS and Mn$^{2+}$ doped CuS nanoparticles. The $S$ variation as a function of inverse of temperature ($1000/T$) for CuS and Mn$^{2+}$ doped CuS nanoparticles pellets are shown in figure 9. The plots show that the absolute value of $S$ increases with temperature in line with the semiconducting behavior in both the nanoparticles pellets [63]. The p-type semiconducting natures of the samples are confirmed by the positive sign of the absolute values of $S$ for the CuS and Mn$^{2+}$ doped CuS nanoparticles. The Fermi energy ($E_f$), scattering parameter ($s$) of CuS and Mn$^{2+}$ doped CuS nanoparticles are calculated using standard expression [64],

$$ S = \frac{K_B}{e} \left[ \frac{A}{e} + \frac{E_f}{K_B T} \right] $$  \hspace{1cm} (4)

Here $K_B$ is the Boltzmann constant, $e$ is the electronic charge, $A$ is the constant determined by dominant scattering process and $E_f$ is the separation of Fermi level from the top of the valence band. The value of $E_f$ is determined from the slope of the best fitted straight line by least squares analysis and scattering constant $A$ is determined from the intercept of figure 9. The value of scattering parameters ($s$) is given by $s = 5/2 - A$. The

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**Figure 9.** Plots of Seebeck coefficient $S$ versus $1000/T$ of CuS and Mn doped CuS nanoparticles pellets.
Magnetic susceptibility of as-synthesized pure CuS and Mn$^{2+}$ doped CuS nanoparticles.

| Sample                  | $\chi_s$ (emu gm$^{-1}$) | $\chi_M$ (emu mol$^{-1}$) | $\mu_{\text{eff}}$ |
|-------------------------|--------------------------|---------------------------|-------------------|
| CuS                     | $0.18 \times 10^{-6}$    | $1.73 \times 10^{-3}$    | 2.06              |
| Mn$^{2+}$ doped CuS     | $0.48 \times 10^{-6}$    | $4.63 \times 10^{-3}$    | 3.32              |

obtained values are tabulated in table 4. The Fermi energy ($E_f$) value is small in case of Mn doped CuS nanoparticles. The dopant Mn$^{2+}$ which possesses higher oxidation state compared to the host anion Cu$^{2+}$, pushes the Fermi level nearer to valence band due to larger carrier concentration [65, 66]. The scattering parameter ($s$) is negative for both, the pure CuS and Mn$^{2+}$ doped CuS nanoparticles suggesting that the scattering mechanism arises due to carrier scattering by acoustic phonon assuming a single parabolic band model [67].

The Hall Effect parameters such as Hall coefficient ($R_H$), Hall mobility ($\mu_{\text{Hall}}$) and carrier concentration ($p$) of the CuS and Mn$^{2+}$ doped CuS nanoparticles pellets are evaluated using standard relations [67],

$$R_H = \frac{\rho}{\Delta}$$

$$\mu_{\text{eff}} = \frac{R_H}{\rho}$$

$$p = \frac{1}{R_H e}$$

Here $t$ is the thickness of the pellet, $V_H$ is Hall voltage, $I_x$ is the applied current, $B_z$ is applied magnetic field, $\rho$ is the resistivity and $e$ is the electric charge.

The value of $R_H$ is 41700 cm$^{-3}$ C$^{-1}$ and 6000 cm$^{-3}$ C$^{-1}$ for pure CuS and Mn$^{2+}$ doped CuS nanoparticles, respectively. The positive value of $R_H$ for both the nanoparticles pellets indicates the $p$-type conductivity of the samples which substantiates the Seebeck coefficient results of $p$-type semiconductor samples. The obtained carrier concentrations $p$ values are $1.49 \times 10^{14}$ cm$^{-3}$ and $1.04 \times 10^{15}$ cm$^{-3}$ for CuS and Mn$^{2+}$ doped CuS nanoparticles, respectively. The range of the carrier concentrations $10^{14} - 10^{15}$ cm$^{-3}$ confirms that both the samples are semiconductors [68]. The values of $\mu_{\text{eff}}$ obtained are 1981.93 cm$^2$ V$^{-1}$ sec$^{-1}$ for CuS and 0.025 cm$^2$ V$^{-1}$ sec$^{-1}$ for Mn$^{2+}$ doped CuS nanoparticles. The small value of $\mu_{\text{eff}}$ in Mn$^{2+}$ doped CuS nanoparticles is due to Mn$^{2+}$ ions incorporation into CuS nanoparticles.

The magnetic properties study of as synthesized pure CuS and Mn$^{2+}$ doped CuS nanoparticles at room temperature are carried out by employing 0.4 tesla magnetic field employing Gouy method. The magnetic susceptibility such as gram susceptibility ($\chi_g$), molar susceptibility ($\chi_m$) and effective magnetic moment ($\mu_{\text{eff}}$) are calculated by standard Gouy method relation [69]. Gram susceptibility of the sample is calculated using equation,

$$m\chi_g - \chi_V V = \tau(\Delta - \delta)$$

Here $V = (W_5 - W_1)/d$, $\delta = W_2 - W_1$, $\Delta = W_4 - W_3$, $m = W_3 - W_1$, $V$ is the calibration standard of the tube, $d$ is density of water in gm ml$^{-1}$ at $T$, $W_1$ is weight of empty tube in gm when field is off, $W_2$ is weight of empty tube in gm when field is on, $W_3$ is weight of filled tube in gm when field is on and $W_4$ is weight of filled tube in gm when field is on (applied) and $W_5$ is weight of water filled tube in gm. The volume susceptibility ($\chi_V$) of air is taken as $0.029 \times 10^{-6}$ per ml.

Molar susceptibility ($\chi_m$) and effective magnetic moment ($\mu_{\text{eff}}$) are calculated using equations,

$$\chi_m = \chi_g \times M$$

$$\mu_{\text{eff}} = 2.84(\chi_g \times T)^{1/2}$$

Here $M$ is molecular weight and $T$ is the room temperature. The values of evaluated parameters are tabulated in table 5.
The positive sign of gram susceptibility and molar susceptibility of pure CuS and Mn\(^{2+}\) doped CuS nanoparticles indicates paramagnetic nature. The observed paramagnetic nature of pure CuS and Mn\(^{2+}\) doped CuS nanoparticles matches the observation of Freeda et al.\(^{70}\). The data shows the magnitude values of parameters are greater in case of Mn\(^{2+}\) doped CuS compared to pure CuS nanoparticles. The enhanced localized 3d electron in Mn atoms increases the paramagnetic nature of Mn\(^{2+}\) doped CuS nanoparticles\(^{71, 72}\). Consequently the effective magnetic moment increases in case of Mn\(^{2+}\) doped CuS nanoparticles compared to pure CuS nanoparticles. The study of magnetic properties of pure CuS and Mn\(^{2+}\) doped CuS nanoparticles reveal that both nanoparticles are not preferable for spintronic application due to paramagnetic nature.

4. Conclusion

The pure CuS and Mn\(^{2+}\) doped CuS nanoparticles are synthesized by wet chemical route at ambient temperature. The elemental content of the samples are determined by EDAX analysis, stating the samples to be near stoichiometric. The XRD and Raman analysis stated the synthesized nanoparticles to possess hexagonal unit cell structure. The peaks of FTIR spectra are assigned to different vibrational bond. The FTIR proved doping of Mn\(^{2+}\) ions into CuS. The SEM analysis showed the synthesized nanoparticles to be spherical in shape with additional platelets present in Mn\(^{2+}\) doped CuS nanoparticles. The spherical shapes of both the synthesized nanoparticles along with platelets in case of Mn\(^{2+}\) doped CuS is further confirmed by TEM analysis. The TEM showed pure CuS nanoparticles size to be in the range of 6 to 30 nm and of Mn\(^{2+}\) doped CuS to be in range of 5 to 30 nm. The lattice spacing in HRTEM matched with the (102) crystal plane of hexagonal structured CuS. The thermal analysis establishes that Mn\(^{2+}\) doped CuS nanoparticles are more stable than pure CuS nanoparticles. The determined thermal parameters using C-R model stated decomposition to be maximum in the higher temperature range. The Seebeck coefficient variation with temperature and Hall effect study on nanoparticles pellets showed the pure CuS and Mn\(^{2+}\) doped CuS to be semiconducting and of p-type nature. The values of Fermi energy is less in Mn\(^{2+}\) doped CuS nanoparticles compared to pure CuS nanoparticles. The magnetic properties like gram and molar susceptibility suggests that, the pure CuS and Mn\(^{2+}\) doped CuS nanoparticles are paramagnetic in nature. The effective magnetic moment increases in Mn\(^{2+}\) doped CuS nanoparticles compared to pure CuS nanoparticles. These results conclude that Mn\(^{2+}\) doped CuS nanoparticles are not suitable for spintronic application due to enhanced paramagnetism.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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