PHASE TRANSITION IN CuS NANOPARTICLES

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Copper sulfide nanoparticles were synthesized by solvothermal method.The as-synthesized nanoparticles annealed at 50^0 C temperature was characterized by X ray diffraction, scanning electron microscopy and atomic force microscope to confirm the crystal structure, morphology and size. The DC electrical resistance was measured in the temperature range 310K-485K. Resistance measurements on copper sulfide nanoparticles shows a phase transition around 470 K , not previously reported. Resistance measurements made on copper sulfide nanoparticles prepared by precipitation method confirms this phase transition. A jump in electrical band gap energy was also observed in the two samples after phase transition. The band gap energies calculated from resistance measurements agree with the band gaps obtained from UV-VIS spectra, FTIR spectrum PL spectrum and previously reported values.

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1.Introduction

Copper sulfide is an important semiconductor used in solar cells[1], photo electric transformers,room temperature ammonia gas sensors ,optical filters and as super ionic materials[2]. Various kinds of structures of CuS have been synthesied recently such as nanoparticles,nanodisks [3],nanotubes[4],nanorods[5] and nanowires[6].There are various methods for the preparation of copper sulfide in nanoscale such as polyol method[7],wet chemistry[8] ,precipitation technique[9] and Sonochemical method[10]. Herein we report the synthesis of CuS nanoparticles by microwave assisted solvothermal route.

CuS has a direct band gap of 2.5eV for bulk hexogonal wurtzite structure[11].The samples of CuS nanocrystals have a wide range of optical absorption from 360nm(3.4eV) [9] to 900 nm(1.4eV) [8] as like silver sulfide [12,13] which undergoes a phase transition at 452K [14]. Studies related to band gap energy from electrical resistance measurements of the CuS nanoparticles are not yet done unlike silver sulfide which gave information about the phase transition[15]. In the present work DC electrical resistance of CuS nanoparticles were measured at different temperatures and from this measurements band gap energies are calculated and are compared with band gap energies obtained from UV-VIS spectra,FTIR spectrum and PL spectrum.

2. Experimental details

2.1Synthesis of CuS nanoparticles by solvothermal method

To prepare CuS nanoparticles by microwave assisted solvothermal route, copper(11) acetate and thiourea were taken as the starting precursor materials in 1:3 molar ratio. The precursor materials were dissolved in ethylene glycol and stirred well. The well mixed solution was taken in a bowl and it was kept in a domestic microwave oven. The solution was subjected to microwave irradiation of 800W for 20 minutes. The cooled substance was washed several times using doubly

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distilled water and then with acetone to remove the organic impurities if any present in the sample. The un annealed sample was finally annealed at 50^0 C for 1 hour to get phase pure CuS nanoparticles.

2.2 Synthesis of CuS nanoparticles by precipitation method

50 gram of copper carbonate was dissolved in dilute HCl and stirred well till the solution turns green in colour. After heating the solution H_2S gas was passed through it. The product was then cooled to room temperature and filtered. The filtrate was washed with water several times and dried in atmospheric air. The sample made was annealed at 50^0 C for one hour.

2.3 Instrumentation

X-ray diffraction patterns of all the samples were recorded on a X-ray diffractometer with with Cu K_α radiation of wavelength 1.541 A^0. The scanning electron microscope was used to study the surface morphology. Optical absorption spectrum of the samples were recorded on UV-VIS spectrometer in the wavelength range 200nm-900nm. FTIR analysis was carried out using a Carey 630 FTIR spectrometer. The PL measurement was performed on a RF-5301PC spectrophotometer. The resistance of the pellet form of the samples were measured by the four probe technique.

3.Results and discussion

3.1Structural studies

Fig 1(a) shows the indexed XRD pattern of the CuS nanoparticles synthesized by solvothermal method . Fig 1(b) shows the indexed XRD pattern of the CuS nanoparticles synthesized by precipitation method. Comparing to the JCPDS file no.78-0876 they were the hexagonal CuS structure.

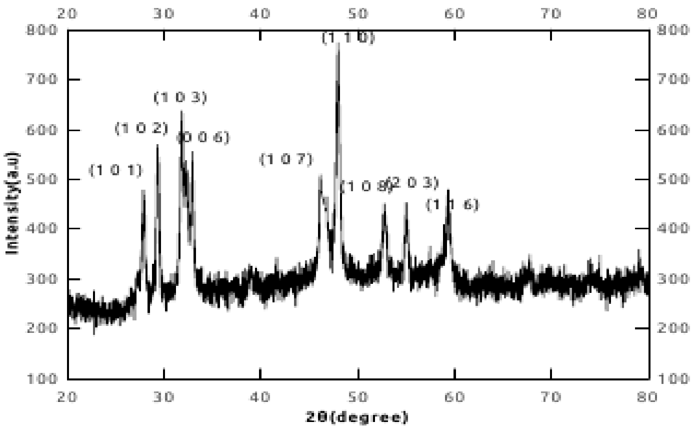

Fig 1(a) Indexed XRD pattern of CuS nanoparticles synthesized by solvothermal method .

The peaks of the XRD patterns of the samples synthesized by solvothermal method were fitted to Gaussian using a c++ program and from the width of the Gaussian particle sizes were calculated using Scherrer method [16]. The average particle size calculated for CuS nanoparticles is 16nm . Fig 2 shows the Gaussian fittted (1 1 0) peak of fig 1(a). The SEM image of the powered sample(fig 3) shows the uniform distribution of copper sulfide nanoparticles . AFM image of the sample (fig 4) synthesized by solvothermal method confirms the nano size of the particles. Fig 1(c) shows the indexed XRD pattern of the pellet of CuS used for resistance measurements synthesized by solvothermal method. Fig 1(d) shows the indexed XRD pattern of the CuS pellet synthesized by precipitation method.

The above two pellets were repeatedly heated and cooled . The XRD pattern of the repeatedly heated and cooled samples show only small changes. One of the reason is resistance measurements shows that it is not brought above the transition temperature in all trials.

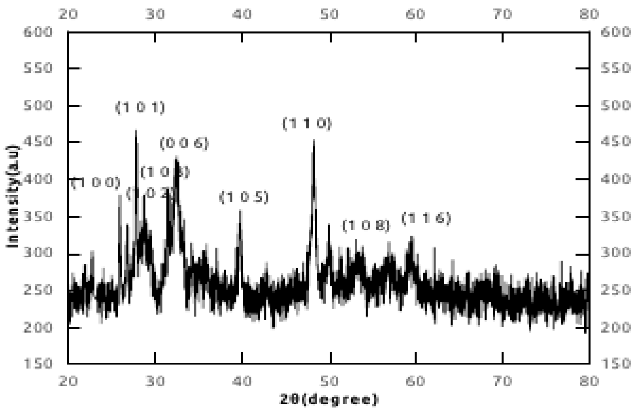

FIg 1(b) Indexed XRD pattern ofCuS nanoparticles synthesized by precipitation method.

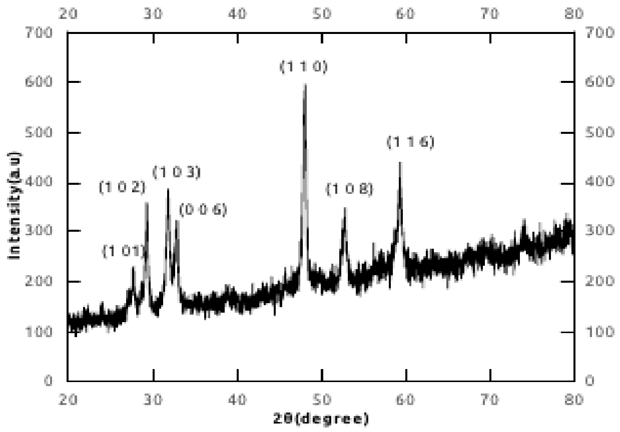

Fig 1(c) Indexed XRD pattern of CuS pellet synthesized by solvothermal method.

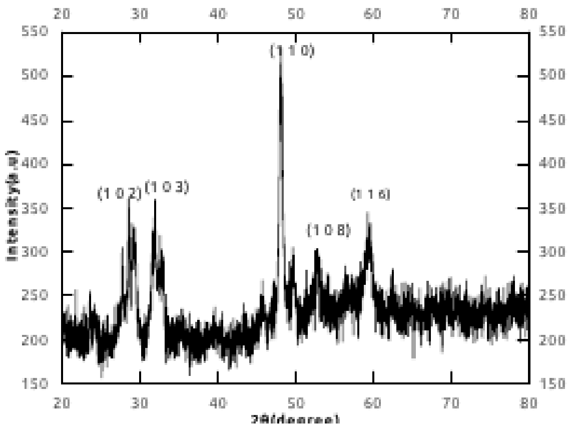

Fig 1(d) Indexed XRD pattern of CuS pellet synthesized by precipitation method. (λ=1.54 A^0)

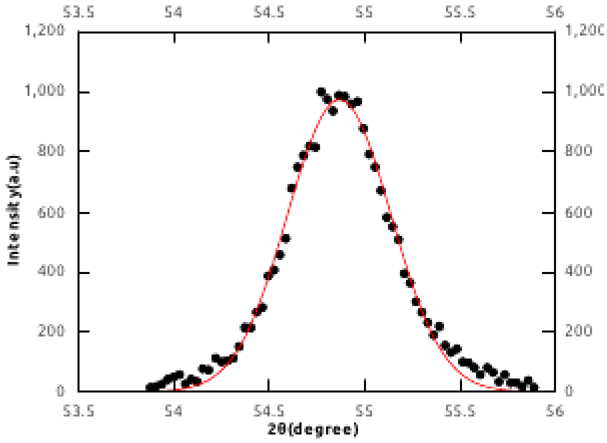

Fig 2. Gaussian fitted (1 1 0) peak of copper sulfide nanoparticles.

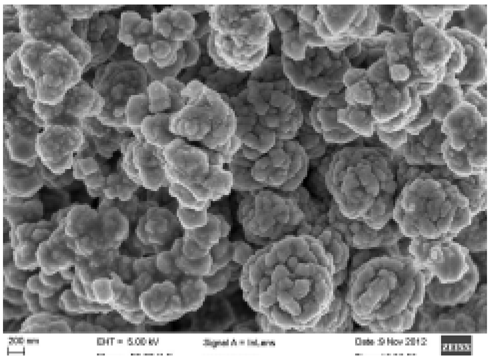

Fig 3. SEM image of copper sulfide nanoparticles synthesized by solvothermal method.

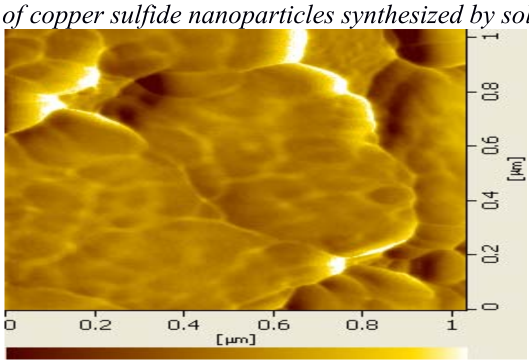

Fig 4. AFM image of copper sulfide nanoparticles synthesized by solvothermal method.

3.2.Optical studies

Fig 5. shows optical absorption spectrum of copper sulfide nanoparticles synthesized by solvothermal method.There is an absorption band with edge at 380nm(3.25 eV) and another with edge at 900nm (1.3 eV). Fig 6 shows optical absorption spectrum of copper sulfide nanoparticles prepared by precipitation method. It also consists of two absorption bands, one with edge at 525nm(2.4eV) and another again at 900nm. The P.L spectrum of CuS nanoparticles synthesized by solvothermal method is shown in fig(7). It absorbs 3.2 eV (380nm) energy and emits 2.4eV(520 nm) energy. So there exists an level above .8 eV from the valance band. The maximum emission wavelength of 523nm in the PL spectrum was also obseved by F.Li and J.F.Wu for CuS[17]. The absorption emission energy level diagram is shown in fig (8). Fig (9) shows the FTIR spectrum of CuS nanoparticles synthesized by solvothermal method. It shows absorptions around 1050cm-1 and 1600 cm-1. Even though reports say that CuS is not IR- active ,absorption around 1100cm-1 and 1600cm-1 were obtained by H.T Boey and W.L.Tan, Guang-YiChen and Bin Deng and Jin-Zhong Xu etal[18,19,20].

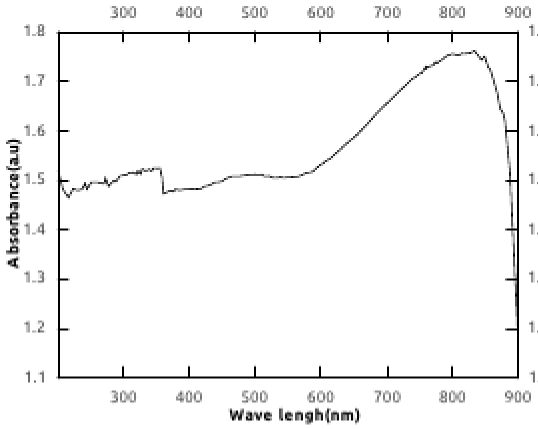

Fig 5. Optical absorption spectrum of copper sulfide nanoparticles synthesized by solvothermal method.

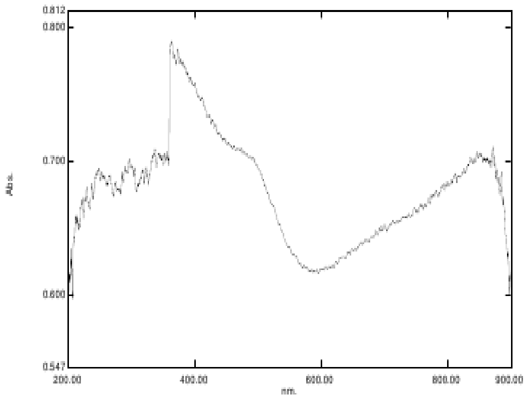

Fig 6. Optical absorption spectrum of copper sulfide nanoparticles synthesized by precipitation method.

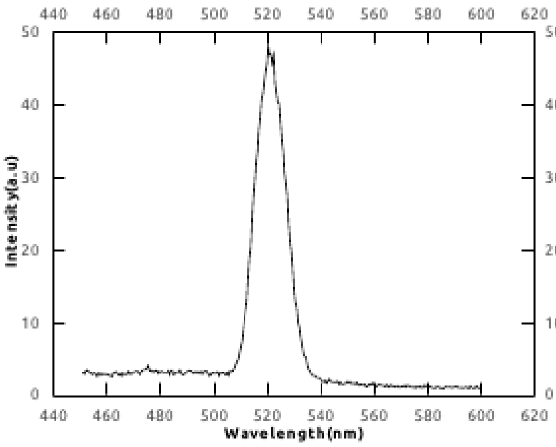

Fig 7.P.L. spectrum of copper sulfide nanoparticles synthesized by solvothermal method.

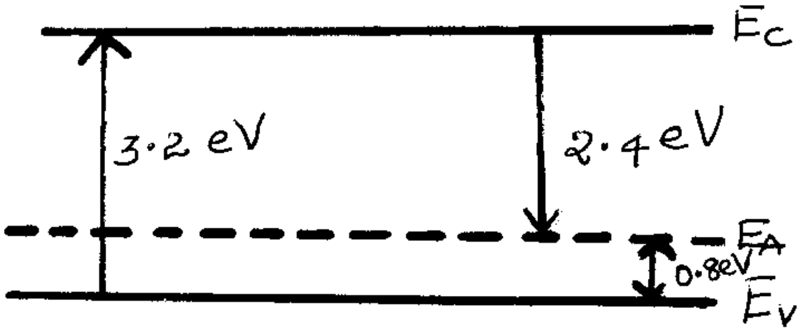

Fig 8Emission absorption energy level diagram of copper sulfide nanoparticles synthesized by solvothermal method.

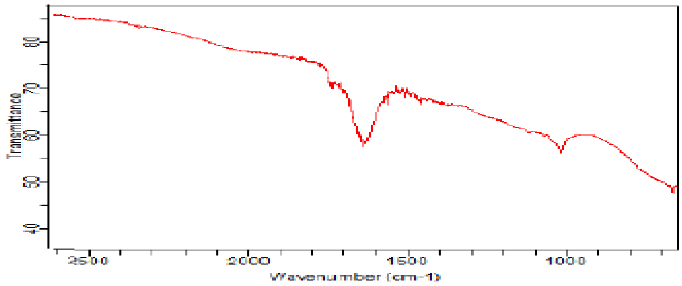

Fig 9 FTIR spectrum of copper sulfide nanoparticles synthesized by solvothermal method.

3.3Electrical studies

Assuming that mobilities of holes and electron are independent of temperature the electrical conductivity of an intrinsic semiconductor is given by [21]

$$\sigma=\sigma_0 T^{-3/2} \exp(-E_g/2kT)$$

Resistivity

$$\rho=\rho_0 T^{-3/2} \exp(E_g/2kT)$$

Resistivity = Resistance*area/thickness
On using the same pellet area and thickness of the sample are constants.
Resistance(R) α Resistivity (ρ)

$$R=R_0 T^{-3/2} \exp(E_g/2kT) \quad (1)$$

E_g is the intrinsic band gap energy and σ_0, ρ_0 and R_0 are constants ,k and T are Boltzman constant and absolute temperature respectively.

The D.C electrical resistance of the pellet form of the samples were measured in the temperature range 310 K-485K .Fig 10(a) shows the variation of resistance with temperature of copper sulfide nanoparticles synthesized by solvothermal method. During the first trial plot “a” was obtained. Upto 400K on increasing the temperature there is slow decrease in resistance showing the behaviour of a semiconductor with small band gap. On increasing the temperature above 400K the resistance increases and the pellet behaves as a conductor and this behaviour of the sample exists upto 450 K. Further increasing the temperature above 450K it again regain its semiconducting behavior. On repeating the experiment second time using the above pellet after cooling it to room temperature plot “b” was obtained . It takes the same path but the transitions takes place at slightly higher temperatures .Since the form of plot “b” is same as plot “a” and there are no new peaks in the XRD pattern of the pellet after using it for resistance measurements ,there is no change in the composition of the pellet during the first trial and since there are slight increase in the transformation temperatures there may be slight change in the structure after the first trail. Since there is no change in composition we may conclude that there is a phase transformation above 450K. The conducting behaviour may be its behavior in the vicinity of phase transformation.

To confirm this phenomena resistance measurements were also made on copper sulfide nanoparticles synthesized by precipitation method. Fig 10(d) shows the variation of resistance with temperature of the copper sulfide nanoparticles prepared by precipitation method during the first and second trials. The behaviour is similar to the nanoparticles synthesized by solvothermal method.

The measured resistances at various temperatures were fitted to equation(1) using a nonlinear curve fitting c++ program developed using least square principle. For the sample synthesized by solvothermal method the best fit for the first semiconducting region (310 K-390 K) was obtained for R0=0.61 and Eg=0.13eV. The measured resistances and the curve for $R=0.61T^{-3/2}$ exp(0.13 /2kT) for plot "a" in the region 310K-390K is shown in fig 10(b).The best fit for the second semiconducting region was obtained for $R0=3.7 *10^{-18}$ and Eg=3.38 eV. The measured resistances and the curve for $R=3.71*10^{-18}T^{-3/2}$ exp(3.38/2kT) for plot "a" in the region 460K-485K is shown in fig 10 (c).

For the sample synthesized by precipitation method the best fit for the first semiconducting region (310 K-380 K) was obtained for R0=0.00045 and Eg=0.7eV. The measured resistances and the curve for $R=0.00045*T^{-3/2}$ exp(0.69 /2kT) for plot "c" in the region 310K-380K is shown in fig 10(e).The best fit for the second semiconducting region was obtained for $R0=6.25*10^{-12}$ and Eg=2.4 eV. The measured resistances and the curve for $R=6.25*10^{-12}T^{-3/2}$ exp(2.39/2kT) for plot "c" in the region 460K-485K is shown in fig 10 (f).

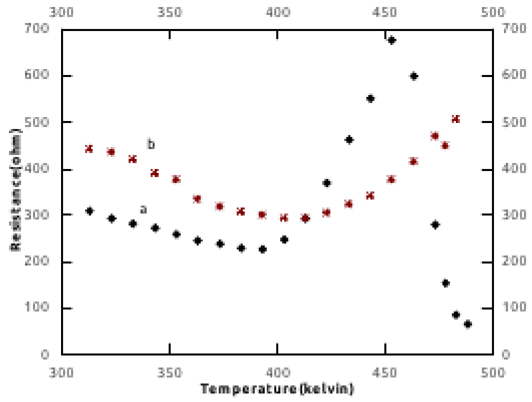

Fig 10(a) Variation of resistance with temperature of copper sulfide nanoparticles synthesized by solvothermal method.

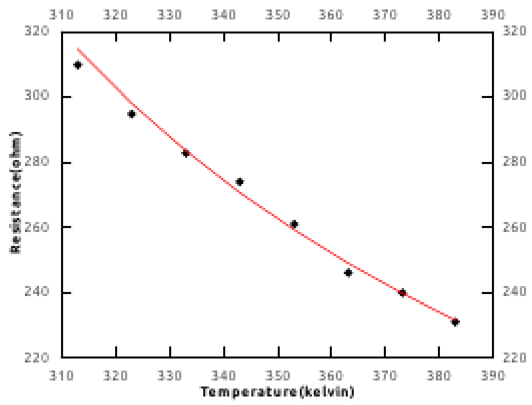

Fig 10(b) Variation of resistance with temperature inthe region 310K-390K. Experimental pints and fitted curve for plot "a".

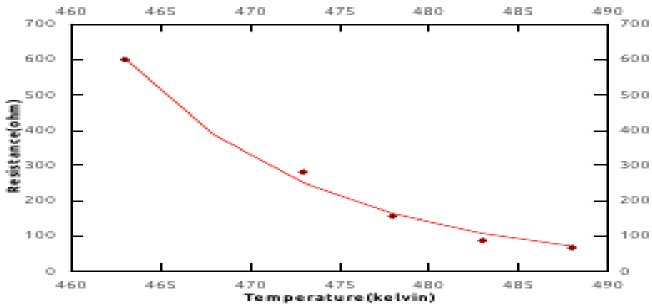

Fig 10(c) Variation of resistance with temperature inthe region 460K-490K. Experimental pints and fitted curve for plot "a".

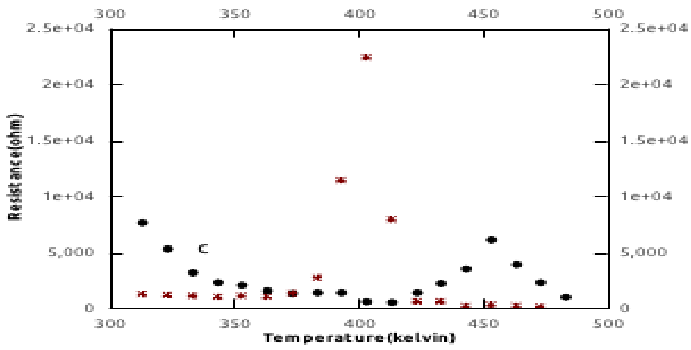

Fig 10(d) Variation of resistance with temperature of copper sulfide nanoparticles synthesized by Precipitation method.

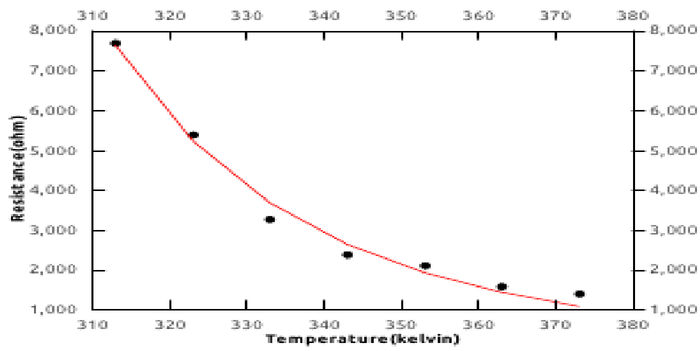

Fig 10(e) Variation of resistance with temperature inthe region 310K-398K. Experimental pints and fitted curve for plot "c".

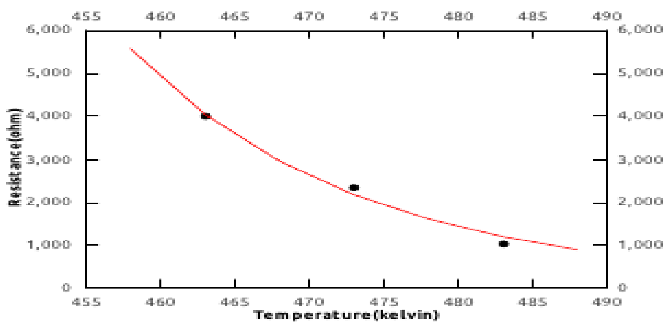

Fig 10(f) Variation of resistance with temperature inthe region 460K-490K. Experimental pints and fitted curve for plot "c".

3.4Comparison of electrical and optical studies

Hence for CuS nanoparticles synthesized by solvothermal method there is a first semiconducting behavior between temperature 310^0 C and 390^0 C which has a band gap energy of 0.13 eV which agrees with the absorption energy 1050 cm-1 in the FTIR spectrum(fig 9) and a second semiconducting region between temperature 460^0 C and 490^0 C corresponds to band gap energy of 3.4 eV which agrees with the first absorption edge of the UV-VIS spectrum of the same sample 360nm(fig 5) and in between there is a conducting region. For CuS nanoparticles prepared by precipitation method there is a first semiconducting behavior between temperature 310^0 C and 380^0C which has a band gap energy of 0.7eV which agrees with the energy EA in the emission absoption energy level diagram(fig8) and second semiconducting region between temperature 460^0C and 490^0 C corresponds to band gap energy of 2.4 eV which agrees with the first absorption edge of the UV-VIS spectrum of the same sample 525nm(fig 6) and is also the band gap energy of bulk CuS[11] and in between there is a conducting region.

So we may conclude that as like silver sulfide nanoparticles due to phase transition there is a jump in band gap energy from 0.13 eV to 3.4 eV for CuS nanoparticles synthesized by solvothermal method and from 0.7eV to 2.4eV for CuS nanoparticles synthesized by precipitation method[15]. Such a sudden increase in band gap energy with annealing temperature around 200^0 C was also reported by J.Santos Cruz and Mayen Hernandez for CuS thin films [22].

A similar plot for variation of resistance with temperature was also observed by M.Ramya and S.Ganesan for Cu_2S thin films where the transition temperature is around 380k [23].This is the temperature around which transition from monoclinic to hexagonal Cu_2S takesplace[14]. During this transiton there in no much change in the XRD pattern. Some low intense peaks disappeared.Only slight shift in the angles of the high intense peaks [24]. A similar curve was also observed by D.Chakravorty and S.Basu for PbS nanocomposites where the transition temperature observed was above 300K while cooling from 673K[25]. It was reported that diffraction pattern of PbS films changes with increasing temperature in the temperature range 300K-475K and S.I Sandovinko and A.I. Gusev reported this transition as a weak transition[26]. A structural phase transition through metal to semiconductor transition was also observed by Tao Wu and Trevor A Tysar for Ca3Co4O9 where anomalies in some of the lattice parameters were observed at the transition temperature[27].

Hence we conclude that this is also a weak transition causing only slight changes in the diffraction pattern as in fig 2(c) and 2(d) observed in nano materials. On comparing fig 2(b) total no of peaks are considerably redued in fig 2(d).(1 0 5) peak at 40^0 disappeared. Intensity of (1 1 6) peak at 59^0 has increased. As like Cu_2S transforms from hexagonal to f.c.c at temperature above 700K CuS also may transform from hexagonal to f.c.c at a slightly lower temperature around 500K. So we may expect that the structure after phase transition may be f.c.c with lattice parameter 5.2 A whose peak angles for the allowed diffractions (1 1 1) ,(2 0 0), (2 2 0) and (3 1 1)are at 29.7^0,34^0,49.6^0 and 58^0 as in fig 2(d).

4.Conclusion

Copper sulfide nanoparticles with an average particle size of 16nm were synthesized by solvothermal method. Resistance measurements on copper sulfide nanoparticles shows a phase transition around 470 K , not previously reported. Resistance measurements made on copper sulfide nanoparticles prepared by precipitation method confirms this phase transition. A jump in electrical band gap energy was also observed in the two samples after phase transition. The band gap energies calculated from resistance measurements agree with the band gap energies obtained from UV-VIS spectra,FTIR spectrum PL spectrum and previously reported values.

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