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Optical and electrical properties of CuS nanorods

M. Annie Freeda[a]*, C. K. Mahadevan[a], S. Ramalingom[b]

[a]*Physics Research Centre, S.T.Hindu College, Nagercoil, India*
[b]*Department of Physics, Vivekananda College, Agastheeswaram, India*

ABSTRACT

CTAB capped copper sulphide nanorods of size 6-8nm width and 40-60nm length has been synthesized by a simple aqueous co-precipitation method at room temperature. Powder X-ray diffraction pattern suggests the product obtained is pure hexagonal phased CuS(Covellite). The material exhibits very low optical transmittance in the UV region but more than 50% in the Visible and NIR regions. The photoluminescent reflectance decreases from UV region to visible region and increases drastically above 500nm. The AC electrical parameters, viz. dielectric constant, dielectric loss factor and AC electrical conductivity increase with the increase in temperature. Also, a higher dielectric constant and a lower AC electrical conductivity were observed. Results obtained indicate that quantum sized CuS nanorods with useful optical and electrical properties can be prepared by the simple method adopted in the present study.

Key Words: Electronic materials, semiconductors, solar energy materials, nanomaterials, optical materials and properties, electrical properties.

INTRODUCTION

Crystals of size in the order of a few nanometers in at least one dimension are nanocrystals. It has been proved that as particles become smaller in size, they may take on different chemical and physical properties. The nanocrystals exhibit higher chemical reactivity than conventionally prepared samples [1-3]. Semiconductor nanoparticles are currently an active subject of research [4] in nanoscience and nanotechnology. Copper mono sulphide is one of the important semiconductor transition – metal chalcogenides. It has gained more attention in material science because of its excellent optical, electronic and other physical and chemical properties [5]. They have potential applications in solar radiation observer [6], coating on polymer surface to increase its conductivity [7], high capacity cathode material in lithium secondary batteries [8], nanoscale switches [9], optical filters, photo electric transformers, sensors , super ionic materials [10] and catalyst [11]. It shows metallic conductivity and transform into a super conductor at 1.6K [12]. It is an important p-type semiconductor which belongs to Wurtzite structure [13] with copper vacancies within the lattice [14]. Many approaches have been proposed to synthesize CuS nanocrystals in various methods including thermolysis [15], microwave irradiation, hydrothermal or solvothermal method [16].

In the present study, an attempt has been made to prepare quantum sized CuS nanorods at room temperature by a simple aqueous co-precipitation method using CTAB (cetyl trimethyl ammonium bromide) as the capping agent. The prepared nanorods were characterized chemically, structurally, optically and electrically. The details are presented in this paper.

MATERIALS AND METHODS

All chemicals used in the present study were of analytical reagent (AR) grade. Copper acetate and thiourea were used as the Cu^{2+} and S^{2-} precursors respectively. NaOH was used to adjust the pH value of the solution. CTAB was used as surfactant. Acetone was used for washing purpose.

1M copper acetate and 5wt% CTAB were dissolved in 250ml distilled water with constant stirring. 1M thiourea was dissolved in 50ml and 5 wt% sodium hydroxide was dissolved in 10ml distilled water. First thiourea solution was added with copper acetate slowly with constant stirring. Then NaOH solution was added to the original solution drop by drop to maintain a pH value of 7. The solution was constantly stirred for 30 min and left without disturbance for 24 hrs at room temperature (30°C). The colloidal solution obtained was centrifuged, washed sequentially with distilled water and acetone several times. The sample was annealed at 60°C for 1hr to improve ordering.

X-ray powder diffraction measurements (PXRD) were carried out on the prepared sample by using an automatic X-ray powder diffractometer (Bruker AXS D8 Advanced diffractometer). The optical properties were determined by making UV-Vis-NIR transmittance (using Varian, Cary 5000 Spectrometer) and photoluminescence (PL) reflectance (using Centaurms 10X Microscope) spectral measurements in the wavelength range 200-1000nm. The electrical properties were determined by making AC electrical measurements using an Agilent 4284A Precision LCR meter at various temperatures ranging from 40-120°C with five different frequencies, viz. 100Hz, 1kHz, 10kHz, 100 kHz and 1MHz in a way similar to that followed by Mahadevan and his co-workers [17,18].

RESULTS AND DISCUSSION

The PXRD pattern (see Figure 1) corresponds to typical CuS (covellite) with hexagonal structure. The estimated lattice parameters are a=3.806 and c=16.544Å which are in good agreement with those reported in the literature (JCPDS file no: 06-0464) for covellite. The broad peaks observed indicate the reduced crystallite size of the prepared sample. A rough estimate of the average crystallite size using the Scherrer formula gives a value of 3nm.

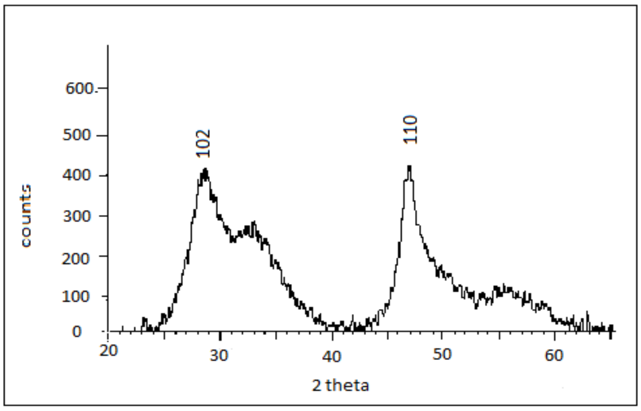
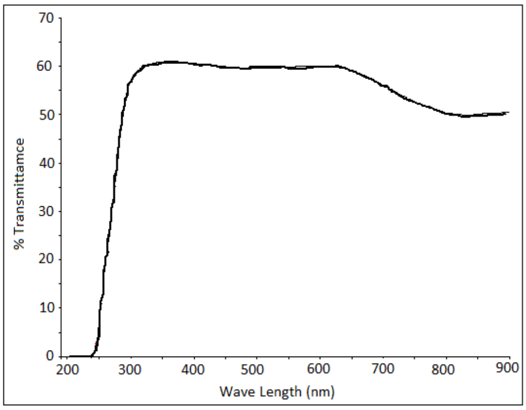


Figure 1 : PXRD pattern of CuS nanorods

The UV-Vis –NIR transmittance spectrum (see Figure 2(a)) shows that the CuS nanorods have varying transmittance, 0-60% in the wavelength region studied. The transmittance increases from UV region to Visible region and decreases at the- NIR region. The 60% transmittance in the wavelength region 300-650nm observed for CuS nanorods is very high compared to the transmittance of CuS film (17%) [11]. The architectural use of CuS nanorods prepared may be used in spectrally selective window coatings. Also, as it is 60% transparent in the Visible region and 50% in the IR region, it can be used for coating eyeglasses for protection from sunburn caused by UV radiation. In addition, it can be used for coating of poultry roof and walls which could protect young chicks from UV radiation as they have not developed protective thick feather [19]. Figure 2(b) shows that the PL reflectance decreases from UV region to Visible region and increases drastically above 500nm.



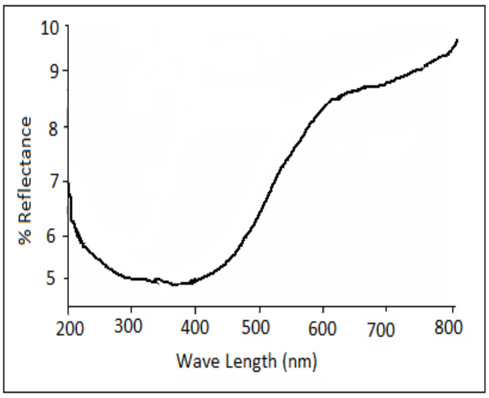


Figure 2(a) **Figure 2(b)**

Figure 2(a): UV-Vis –NIR transmittance spectrum, 2(b) : PL reflectance of CuS nanorods

The dielectric parameters observed, viz. dielectric constants (ε_r), dielectric loss factors (tan δ) and AC electrical conductivities (σ_{ac}) are shown in Figure 3. The dielectric parameters are found to increases with the increases in temperature. The ε_r and tan δ values decrease whereas the σ_{ac} value increase with the increase in frequency.

The average crystallite size obtained for the system studied is small and hence the polarization mechanism in the nanocrystal considered can be understood as mainly due to the space charge polarization. Thus, it can be understood that the space charge contribution plays an important role in the charge transport process and polarizability in CuS nanorods prepared in the present study.

The electrical conductivity of nanocrystalline material is lower than that of both conventional coarse grained polycrystalline materials and alloys. If the crystal size is smaller than electron mean free path, grain boundary scattering dominates and hence electrical conductivity is decreased. The AC conductivity values observed for CuS nanorods in the present study (see Figure 3(c)) are at the order of 10^{-5} mho/m. This agrees with the above theory. The values of dielectric constant, AC electrical conductivity and crystallite size observed in the present study indicate that the CuS nanorods studied exhibit the possible occurrence of nano-confined states.

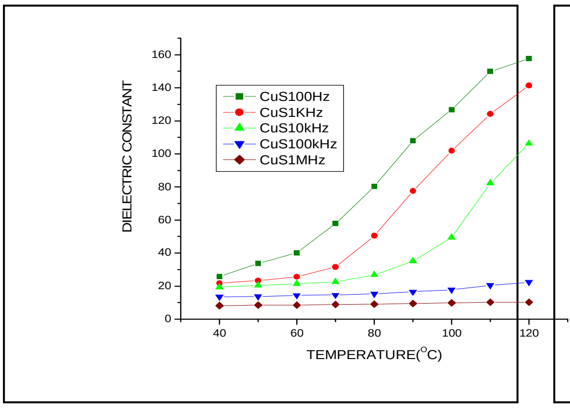


Figure 3(a)

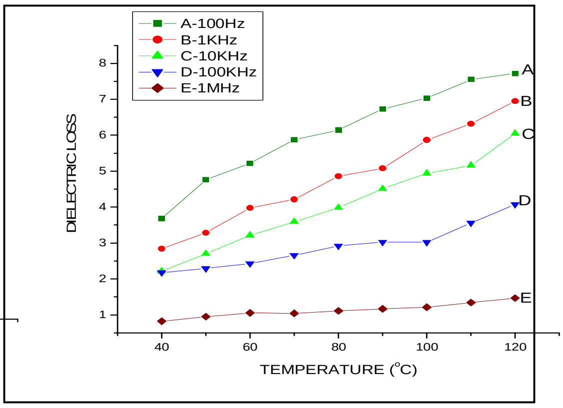


Figure 3(b)

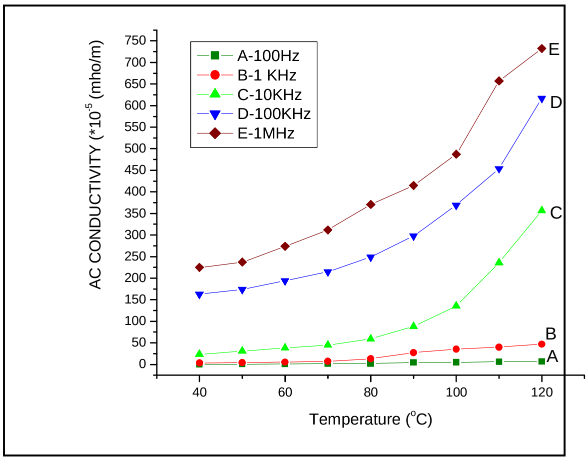


Figure 3(c)

Figure 3 : (a)The dielectric constants, (b) The dielectric loss and (c) The AC electrical conductivity of CuS nanorods

Krityk et al [20] have found a giant linear electro-optic (Pockel's) effect upto 17pm/V for wavelengths around 435nm in ZnO crystalline films doped with fluorine and deposited on bare glass. This was explained to be due to the presence of ZnO. Also, it is a known fact that the electro-optic coefficient is directly proportional to the dielectric constant of the material. We have observed significantly higher dielectric constants (see Figure 3(a)) for the CuS nanorods which indicate a higher electro-optic coefficient for them. Also, it is found that the ε_r value is very high at higher temperatures.

Results obtained, in effect, indicate that quantum sized CuS nanorods with useful optical and electrical properties can be prepared with high purity by the simple method adopted in the present study.

CONCLUSION

Quantum sized CuS nanorods could be prepared with high purity by the reaction of copper acetate with thiourea in the presence of NaOH and CTAB at 30^oC for 24 hrs. The method of preparation is found to be inexpensive, simple and environmental friendly. The observed optical properties indicate the possible occurrence of nano-confined states. The higher dielectric constants observed indicate a higher electro- optic coefficient for the CuS nanorods prepared. The higher optical transmittance in the Visible and NIR regions indicate the utility in spectrally selective window coatings.

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