Chapter 6

Preparation and Characterization of Cu$_2$SnS$_3$ Powder and Nanoparticles

Direct liquid coating techniques encompass large variety of deposition methods which utilizes precursor “ink” in different forms. These inks may range from true solution to colloidal suspensions to paste or slurry. Accordingly, materials to be deposited can be synthesized in different forms such as powder or nanoparticles. As reviewed in literature section, present routes for synthesis of powder or nanoparticles include multiple or tedious steps and often require special reagents and conditions, which restrict the use of the method on large-scale. In this chapter, two simple different methods for synthesizing Cu$_2$SnS$_3$ powder and nanoparticles has been discussed. Cu$_2$SnS$_3$ powder has been synthesized by solid state reaction of metal salts and thiourea, Cu$_2$SnS$_3$ nanoparticles have been prepared by microwave heating of metal-thiourea precursor complex solution. The products have been characterized for structural, compositional, morphological, optical and electrical properties. Since both the methods utilize metal-thiourea complex as an intermediate, thermal decomposition behaviour and interaction between metal ions and ligand of precursor have also been studied.

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6.1 Preparation and characterization of powder by solid state reaction

6.1.1 Preparation

In search of a method to obtain pure Cu₂SnS₃, five different sulphur sources have been utilized. These are thiourea (TU), thioacetamide (TAA), dimethyl thiourea (DMTU), sodium sulphide (Na₂S) and elemental sulphur (S). Samples of CTS are prepared by solid state reaction between Cu(CH₃COO)₂, SnCl₂.2H₂O and a sulphur source. The metal salts are pulverized and blended with a sulphur source in molecular proportion to yield a homogenous paste. For five different sulphur sources, the samples are labeled as CTS(TU), CTS(TAA), CTS(DMTU), CTS(SS) and CTS(S), respectively. The pastes are then heated in a furnace at 473 K in air for 1 h (Fig. 6.1). On heating, the pastes are converted to black powders. The chemicals used are of analytical grade supplied by Merck Limited, India.

![Image](image)

**Sulphur Sources:**

Thiourea (TU), Thioacetamide (TAA), Dimethyl Thiourea (DMTU), Sodium Sulphide (Na₂S), Sulphur (S)

*Fig. 6.1: Schematic of Cu₂SnS₃ powder synthesis by solid state reaction*

6.1.2 Characterization

6.1.2.1 Composition, Structure and Morphology

6.1.2.1a X-ray Diffraction

Fig. 6.2 shows the X-ray diffraction patterns of (a) CTS (TU), (b) CTS (TAA), (c) CTS (DMTU), (d) CTS (SS) and (e) CTS (S). The X-ray diffractogram of CTS (SS) and CTS (S) show prominent presence of Cu₅S and SnS₂. Whereas, XRD pattern of CTS (TAA) and CTS (DMTU), indicate the presence of Cu₂SnS₃ along with Cu₅S and SnS₂. However, XRD plot of CTS (TU) shows peaks due to tetragonal Cu₂SnS₃ only and no other extra peaks are present implying pure CTS sans Cu₅S and SnS₂ is formed. Hence, further study is conducted on CTS (TU) only (henceforth mentioned as CTS).
**Fig. 6.2:** X-Ray diffractograms of powder samples prepared using metal salts and different Sulphur sources: (a) thiourea (b) thioacetamide (c) dimethyl thiourea (d) sodium Sulphide (e) sulphur via solid state reaction at 473 K in air.

To study the progress of reaction, XRD of the product obtained upon heating the precursor paste is carried out at different time intervals. The XRD patterns of product at each interval are shown in Fig. 6.3. Although, just after 1 hour of thermolysis diffractogram shows peaks only due to CTS, the intensity of peaks keeps on increasing till further two hours. It is inferred that the reaction completes after three hours of synthesis.

**Fig. 6.3:** XRD pattern of CTS during time interval of reaction
The X-ray diffractogram of the final product obtained after 3 hours of heating along with quantitative refinement fit is shown in Fig. 6.4. It consists of sharp peaks at 2θ values of 28.63°, 33.09°, 47.55°, 56.40°, 69.45°, 76.71° and 88.46°; these are found to match well with standard data for Tetragonal Cu₂SnS₃ (JCPDS File: 089-4714) and are identified to be reflections from (112), (102), (204), (312), (008), (316) and (228) planes, respectively. For quantitative phase analysis, full profile Rietveld analysis is carried out using Topas 4.2 software (Fig. 3). The Goodness of Fit (GOF) and R weighted profile (Rwp) values for fitting are 1.13 and 2.63 respectively. Various structural parameters obtained upon refinement are shown in Table 6.1.

![Graph showing X-ray diffraction pattern with peaks labeled (112), (312), (200), (204), (400)(316), (424)](image)

**Fig. 6.4: Rietveld refined X-ray diffraction pattern of pure Cu₂SnS₃ powder obtained from thiourea as Sulphur source**

**Table 6.1: Structural parameters of Cu₂SnS₃ obtained after Rietveld refinement**

<table>
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<th>y</th>
<th>z</th>
<th>occupancy</th>
</tr>
</thead>
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<td>0.25</td>
<td>0.5011</td>
</tr>
<tr>
<td>Cu1B</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.4664</td>
</tr>
<tr>
<td>Sn1A</td>
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<td>0.5</td>
<td>0.25</td>
<td>0.5003</td>
</tr>
<tr>
<td>Sn1B</td>
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<td>0</td>
<td>0.5</td>
<td>0.4773</td>
</tr>
<tr>
<td>Cu2</td>
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<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>S1</td>
<td>0.25</td>
<td>0.25</td>
<td>0.125</td>
<td>1</td>
</tr>
</tbody>
</table>
A unit cell structure depicting the atomic coordination in Cu₂SnS₃ is shown as inset in Fig. 6.4. The product crystallizes with tetragonal stannite type structure (space group: I-42m), where Cu atom is at origin, mixed sites A (56.4 at. % Cu and Sn 43.6 at. %) and B (53.7 at. % Cu and Sn 46.3 at. %) occupy equivalent position as (Fe, Zn), Cu and Sn, in stannite structure, respectively (refer to fractional coordinates of elements: Cu, Sn and S; shown in Table 6.1). The lattice parameters obtained from refinement are \( a = 0.5419 \text{ nm} \) and \( b = 1.0842 \text{ nm} \). Each metal atom site is coordinated to four S atoms forming a tetrahedron. Similarly, each sulphur atom site is linked to one Cu atom site, two A sites and one B site forming a distorted tetrahedron. There is no direct S-S linkage in the structure. All metal - sulphur bond have same lengths and are equal to 0.234 nm. Similarly, all the three tetrahedron about the metal ions sites, Cu, A and B have bond angles in a range of 109.43° – 109.55°, ideal for tetrahedron.

6.1.2.1b Raman spectroscopy

Raman spectrum of CTS powder is shown in Fig. 6.5. On the basis of the results of X-ray Diffraction, the peaks at 335 cm\(^{-1}\) is assigned due to metal-ligand vibrations of tetragonal CTS. The peak at 335 cm\(^{-1}\) concurs with the previous and singular data of Raman spectrum of tetragonal CTS [1]. The Raman data observed for CTS powder synthesized in this investigation is different from Raman peaks for cubic and monoclinic phases of Cu₂SnS₃ and other compositional phases of Cu-Sn-S reported in literature [2]. It is thus concluded that the present route yields to the synthesis of CTS powder with tetragonal structure.

![Fig. 6.5: Raman Spectrum of Cu₂SnS₃ powder](image)
6.1.2.1c X-ray Photoelectron Spectroscopy and Inductively Coupled Plasma-Optical Emission Spectroscopy

The XPS data is shown in Fig. 6.6. Fig. 6(a) shows the core level Cu 2p spectrum of CTS. The observed values of binding energies for Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ are 932.86 and 952.82 eV, respectively. No satellite peaks in the range of 942-43 eV, arising due to presence of Cu$^{+2}$ along with Cu$^{+1}$, are observed. This indicates that sample consists of Cu in Cu$^{+1}$ state only. Similarly, the core level Sn 3d spectrum is displayed in Fig. 6.6 (b). The binding energy for Sn 3d$_{5/2}$ and Sn 3d$_{3/2}$ are 486.65 eV and 495.1 eV, respectively. These values indicate the presence of Sn in +4 oxidation state. The S 2p core level peak appears at 162.88 (Fig. 6.6 (c)). In addition, quantitative analysis is carried out to find the elemental concentrations. The relative concentration of Cu, Sn and S is thus found to be 31.34, 15.87 and 48.77 %, whereas, concentration of C and O is 1.37 and 2.63 %, respectively (Fig. 6.6 d and e). No other major element is detected in XPS data. XPS study thus suggests Cu, Sn and S to be present in +1, +4 and -2 oxidation states, respectively, with slightly Cu deficient stoichiometry. Since XPS provides elemental composition at the surface only, bulk elemental composition is determined using ICP-OES. The atomic ratio of copper to tin from ICP-OES is found to be 1.96, which near to the Cu/Sn ratio calculated from XPS data. Thus ICP-OES also suggests slightly Cu deficient stoichiometry.
Fig. 6.6: X-ray photoelectron spectra for (a) Cu 2p core level, (b) Sn 3d core level and (c) S 2p core level of Cu₂SnS₃
6.1.2.1d Scanning Electron Microscopy

Scanning Electron Micrographs of Cu₂SnS₃ powder is shown in Fig. 6.7. The image depicts formation of large lumps with porous coral like structures. The pores are believed to form during the reaction as vents for evolution of by-product gases. The images show presence of large particles which are irregular in shape and with sizes in micrometer range.

![Scanning electron micrograph of Cu₂SnS₃](image)

*Fig. 6.7: Scanning electron micrographs of a typical CTS*
6.1.2.2 Optical Properties

Diffuse reflectance spectrum of Cu₂SnS₃ in wavelength range 800 to 1800 nm shown in Fig. 6.8 (a). The spectrum shows a significant extinction of the incident light in the wavelength range 1400 to 900 nm. Modified Kubelka-Munk model is employed to extract the value of energy band gap (E_g) from diffuse reflectance data [3]. The modified Kubelka-Munk equation is:

\[
(f(R_o) \, h\nu) = C \, (h\nu - E_g)^{1/2} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (6.1)
\]

where, \( f(R_o) = (1-R_o)^2/2R_o \) is the Kubelka-Munk function, \( R_o = R_{\text{sample}}/R_{\text{standard}} \), (here standard is taken to be BaSO₄) is diffuse reflectivity, \( C \) is a constant. This is similar to the Tauc relation for direct band to band transition, where \( f(R_o) \) behaves as \( \alpha \). The band gap of CTS is determined by plotting \( (f(R_o) \, h\nu)^2 \) versus \( h\nu \) (Fig. 6.8 b) and is found to be 1.1 eV.

![Fig 6.8](image)

**Fig 6.8**: (a) Diffuse reflectance spectrum of Cu₂SnS₃ powder (b) Plot of \( (f(R) \, h\nu)^2 \) versus \( h\nu \) for determination of band gap.

However, there is no report on optical properties of tetragonal CTS, the value of band gap for cubic and monoclinic phase are reported to be 0.93-0.94 eV [14,21] and 0.91
eV [26], respectively. The observed value of $E_g$ in tetragonal CTS is optimal for solar photons absorption.

### 6.1.2.3 Electrical Properties

Electrical conductivity of CTS pellet is 0.01 S/cm. The thermoelectric power (TEP) is measured to be $+173 \ \mu \text{V/K}$. The positive sign of TEP indicates the pellet to have p-type conduction. The electrical conductivity and TEP data are used to calculate hole concentration and hole mobility using the following relation:

$$p = N_v \exp(A_e - e\alpha_h / k)$$

(6.2)

where, $N_v$ is the effective density of state in valence band (= $6.91 \times 10^{17}$ cm$^{-3}$ for Cu$_2$SnS$_3$ at 300 K), $A$ is a constant depending on scattering (= 4 for impurity scattering), $\alpha_h$ is the thermoelectric power, $k$ is the Boltzmann constant (= 86.7 $\mu \text{V/K}$), $e$ is the electronic charge

The mobility of holes is determined from the equation:

$$\mu = \sigma / p.e$$

(6.3)

where, $\mu$ is the mobility and $\sigma$ is the electrical conductivity

The calculated values of holes concentration and mobility are $5.07 \times 10^{18}$ cm$^{-3}$ and 0.012 cm$^2$V$^{-1}$s$^{-1}$ respectively. However, values of carrier mobilities or carrier concentration have not been reported for p-type bulk CTS. Khanauer and Gorochev [4] have have reported electron mobility and concentration to be 0.50 cm$^2$V$^{-1}$s$^{-1}$ and 1.2 $\times \ 10^{20}$ cm$^{-3}$ respectively, for n-type monoclinic CTS crystals using Hall measurements.

Temperature variation of dark electrical conductivity ($\sigma_d$) in the range 333 to 523 K is shown in Fig. 6.9. The carrier transport in polycrystalline semiconductors, near room temperature and above is explained well by thermoionic emission (TE) over grain boundaries (GB), as seen in literature after Seto [5]. In present case as well, the temperature dependence of conductivity is found to follow Seto’s model:

$$\sigma = \frac{\sigma_0}{T^{\alpha}} \exp \left( \frac{-E_a}{kT} \right)$$

(6.4)
$\sigma_0$ is a constant, $k$ is the Boltzmann constant and $E_a$ is grain boundary (GB) barrier energy respectively. As seen in Fig. 6.9, the experimental data fits well to the Eq. 6.4. The grain boundary barrier energy, $E_a$, is found to be 0.27 eV.

Fig. 6.9: Temperature variation of electrical conductivity

6.1.2.4 Analysis of Precursor

6.1.2.4a Thermal degradation of precursor

TGA/DSC of the precursor paste is presented in Fig. 6.10. Thermogravimetric analysis shows number of weight loss steps. The first step in TGA starts at 393 K and continues till 448 K. The weight loss is due to degradation of metal-TU precursor complex to sulphide with evolution of water, HCl, acetic acid and other volatile products. The next step which starts around 523 K shows a weight loss corresponding to oxidation of sulphide in air. The DSC curve show three valleys (endothermic changes), in region below 573 K, with minima at 373 K and 518 K corresponding to loss of water and acetic acid, whereas minima at 453 and 553 K correspond to degradation of metal-TU precursor complex and oxidation of sulphide product, respectively. TGA/DSC reveals that the reaction temperature for formation of sulphide is in the range 453 to 523 K. However, 473 K was chosen for the present study to avoid possible oxidation during processing.
**Fig. 6.10:** Plots showing the thermogravimetry and differential scanning calorimetry for Cu$_2$SnS$_3$ precursor with thiourea.

6.1.2.4b Metal ion-Thiourea bonding interaction

The comparison of FT-IR spectra of TU and metal ions –TU complex is shown in Fig 6.11. The assignment of absorption bands corresponding to different vibrational modes is tabulated in Table 6.2. It has already been stated at chapter 4 that the C=S stretching in thiourea at 740 cm$^{-1}$ shifts to lower frequency when metal binds to sulphur. The presence of C=S frequency at 705 cm$^{-1}$ in this nano material suggests the metal binding to sulphur of C=S. The binding of metal to sulphur lowers the double bond character of C=S, leading to lowering of its stretching frequency. The absorptions at 1470 and 1600 cm$^{-1}$ in thiourea are assigned to coupled vibrations of C-N stretching and NH$_2$ bending. The peak at 1470 cm$^{-1}$ has predominant contribution from C-N stretching and bending of NH$_2$ contributes significantly to the absorption at 1600 cm$^{-1}$. When sulphur (of C=S) bonds to metal, C-N bond order increases because of delocalization of lone pair on nitrogen atom to the bond. The shift of electron density on C-N bond depends on the strength of metal–S bond. Consequently there will be shift of those absorptions in thiourea to higher frequency where C-N stretching contributes. It is satisfying to note that the thiourea peaks at 1470 and 1600 cm$^{-1}$ shift to 1495 and 1630 cm$^{-1}$ in the metal –TU complex, further supporting the formation of metal–S bond. The delocalization of N lone
pair on the C-N bond will give N atom some +ve charge and this may be reflected in the increase of NH\textsubscript{2} stretching frequency in the complexes. The asymmetric and symmetric stretching in thiourea are observed respectively at 3280 and 3160 cm\textsuperscript{-1}; these in the complexes, as expected shift to higher frequencies and are observed at 3185 and 3300 cm\textsuperscript{-1}.

![Infrared spectra of (a) copper-tin-thiourea complex precursor and (b) pure thiourea. Inset shows schematic of metal-TU interaction in the precursor complex](image)

**Fig. 6.11:** Infrared spectra of (a) copper-tin-thiourea complex precursor and (b) pure thiourea. Inset shows schematic of metal-TU interaction in the precursor complex

**Table 6.2:** Assignment of FT-IR Absorption bands of pure thiourea (TU) and copper-tin-thiourea complex precursor

<table>
<thead>
<tr>
<th>Pure Thiourea</th>
<th>Cu\textsubscript{Sn} and TU Precursor complex</th>
<th>Vibrational modes</th>
<th>Shift observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>740</td>
<td>700</td>
<td>C=S stretching</td>
<td>Bathochromic</td>
</tr>
<tr>
<td>1090</td>
<td>1090</td>
<td>NH\textsubscript{2} rocking</td>
<td>-</td>
</tr>
<tr>
<td>1390, 1430,</td>
<td>1390, 1430, 1475</td>
<td>N-C-N stretching</td>
<td>-</td>
</tr>
<tr>
<td>1470, 1590</td>
<td>1490, 1620</td>
<td>Coupled NH\textsubscript{2} bending and C-N stretching</td>
<td>Hypsochromic</td>
</tr>
<tr>
<td>3160</td>
<td>3185</td>
<td>Symmetrical N-H stretching</td>
<td>Hypsochromic</td>
</tr>
<tr>
<td>3280</td>
<td>3300</td>
<td>Asymmetrical N-H stretching</td>
<td>Hypsochromic</td>
</tr>
</tbody>
</table>
The strong direct metal – sulphur bond in the precursor complex results in formation of metal sulphide upon thermolysis, cleaving C-S bond. This results in pure CTS by thermolysis at 200 °C in air. The formation of CTS can be expressed as thermolysis of thiourea complex of Cu and Sn yields by the equation:

\[
\text{[CuSn(CS(NH\textsubscript{2})\textsubscript{2})\textsubscript{n}]^{n-} \xrightarrow{\text{Heat}} \text{Cu}_2\text{SnS}_3 + \text{Volatile matter}} \quad \text{.......................... (6.5)}
\]
6.2 Microwave-assisted rapid synthesis of nanoparticles

6.2.1 Synthesis of CTS nanoparticles

Nanoparticles of Cu₂SnS₃ are prepared from metal-thiourea complex based solution (precursor solution) used earlier to directly deposit thin films of CTS [12]. First, 10 ml of ethylene glycol is added to 40 ml of precursor solution, to make the solution microwave receptive. Then, solution is transferred to a 250 ml round bottom flask fitted with a reflux condenser and heated in a microwave reactor operating at 900 Watts power for 5 minutes (Fig. 6.12). After microwave heating black dispersion of CTS particles is clearly seen. The nanoparticles are first washed with methanol and then with toluene. At each step of washing, the nanoparticles are separated from the liquid by centrifuging at 18000 rpm for 10 minutes. Then washed with toluene using same protocol as for methanol. Finally, obtained nanoparticles are dried at 333 K in a hot air oven after a wash of acetone.

![Diagram of microwave-assisted synthesis of Cu₂SnS₃ nanoparticles](image)

**Fig. 6.12:** Schematic of synthesis Cu₂SnS₃ nanoparticles assisted by microwave irradiation
6.2.2 Characterization

6.2.2.1 Structure and composition

6.2.2.1a X-ray Diffraction

The X-ray diffractionogram of CTS nanoparticles along with quantitative fit is shown in Fig. 6.13. XRD pattern shows peaks at 28.5°, 32.99°, 47.39°, 56.2°, 58.84°, 69.26°, 76.52°, 88.23°, 95.04° 2Theta angles which are found to match well with standard file for tetragonal CTS structure (JCPDS file no.: 089-4717). By comparing the experimental data with standard file the peaks at 28.5°, 32.99°, 47.39°, 56.2°, 58.84°, 69.26°, 76.52°, 88.23°, 95.04° are identified to be reflections from (112), (200), (204), (312), (224), (040), (316), (424) and (512) planes of tetragonal CTS, respectively. The average crystallite size as calculated from the broadening of (204) peak using Scherrer relation, is ~ 12 nm. Various structural parameters are calculated from quantitative Rietveld refinement of XRD data using Topas 4.2 software. The Goodness of Fit (GOF) and R weighted profile (Rwp) values for fitting are 1.13 and 2.63 respectively. The site occupancies of ions along with their fractional coordinates are shown in Table 6.3.

![X-ray diffraction pattern](image)

**Fig. 13:** Rietveld refined X-ray diffraction pattern of pure Cu$_2$SnS$_3$ powder obtained from thiourea as Sulphur source

A unit cell structure depicting the atomic coordination in Cu$_2$SnS$_3$ is shown as inset in Fig. 6.13. The result of crystal structure refinement of Cu$_2$SnS$_3$ nanoparticles is more or less similar to that obtained for Cu$_2$SnS$_3$ powder sample (section no. 6.1.2.1a)
The product crystallizes with tetragonal stannite type structure with I-42m space group, where Cu atom in origin occupy equivalent position as (Fe, Zn) and mixed sites A (57.52 at. % Cu and Sn 42.48 at. %) and B (31.71 at. % Cu and Sn 68.29 at. %) occupy equivalent position as Cu and Sn, respectively, in stannite structure (refer to fractional coordinates of elements: Cu, Sn and S; shown in Table 6.3). The lattice parameters calculated after refinement are a = 0.542 nm and b = 1.085 nm. Each metal atom site is coordinated to four S atoms forming a tetrahedron. Similarly, each sulphur atom site is linked to one Cu atom site, two A sites and one B atom site forming a distorted tetrahedron. There is no direct S-S bond present in the structure. There is no direct S-S bond present in the structure. The bond lengths of Cu-S and Sn-S bonds are 0.23 and 0.25 nm, respectively. All the three tetrahedron about the metal ions sites, Cu, A and B have bond angles in a range of $109.43^\circ - 109.55^\circ$, ideal for tetrahedron.

<table>
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<tr>
<th>Site</th>
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<th>y</th>
<th>z</th>
<th>Occupancy</th>
</tr>
</thead>
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<td>0</td>
<td>1</td>
</tr>
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</tr>
<tr>
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</tr>
<tr>
<td>Sn 2B</td>
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</tr>
<tr>
<td>Cu 2B</td>
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<td>0.5</td>
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</tr>
<tr>
<td>S</td>
<td>0.243</td>
<td>0.243</td>
<td>0.1302</td>
<td>1</td>
</tr>
</tbody>
</table>

6.2.2.1b Raman Spectroscopy

The Raman spectrum of CTS nanoparticles along with the quantitative fit profile is shown in Fig 6.14. On the basis of the results of X-ray diffraction, the peaks at 288 and 336 cm$^{-1}$ are assigned due to metal-ligand vibrations of tetragonal CTS. The spectrum is similar to the earlier one by Guan et al. [6]. Also, the peak at 335 cm$^{-1}$ concurs with the previous data of Raman spectrum of tetragonal CTS [7]. However, as stated in the report the spectrum quality was poor due to amorphous nature of sample [7]. The Raman data observed for CTS nanoparticles synthesized in this investigation is different from Raman peaks for cubic and monoclinic phases of Cu$_2$SnS$_3$ and other compositional phases of Cu-Sn-S reported in literature [8]. It is thus concluded that the present route yields to the synthesis of CTS nanoparticles with tetragonal structure.
6.2.2.1c X-ray photoelectron spectroscopy

The survey scan of XPS of the CTS nanoparticles in binding energy range of 0-1000 eV is shown in Fig. 6.15 a. The Cu 2p, Sn 3d, S 2p core level photoelectron spectra with the fitting profile for quantitative elemental composition determination, is shown in Fig 6.15 b,c,d, respectively. The binding energy of Cu 2p\textsubscript{1/2} and Cu 2p\textsubscript{3/2} peaks are 952.78 eV and 933.32 eV respectively. No shake-up or satellite peaks around 942 eV are found implying the absence of Cu in +2 state. The binding energies for Sn 3d\textsubscript{5/2} and Sn 3d\textsubscript{3/2} are 486.87 eV and 495.32 eV respectively and that for S 2p is 162.16 eV. The X-ray photoelectron spectroscopy indicates that Cu and Sn are present in +1 and +4 oxidation states. Further, quantitative refinement of Cu 2p, Sn 3d, S 2p core level peaks shows the relative concentration of Cu, Sn and S to be 31.03, 15.64, 49.58 %, respectively. Whereas, concentration of C and O is 1.62 and 2.13 %, respectively. No other major element is detected in XPS data. The [Cu]/[Sn] ratio suggests CTS nanoparticles to have slightly Cu deficient and Sn excess stoichiometry. It is gratifying to note that the results of XPS of CTS nanoparticles, powder and films are practically similar, indicating that all the three different types of preparation yield similar product.
Fig. 6.15 X-ray photoelectron spectra of Cu₂SnS₃ thin film (a) Survey Scan and (b) Cu 2p core level (c) Sn 3d core level (d) S 2p core level with fitting profiles (black circles for data, Olive green color line for peak sum, red and blue lines for two different states)
6.2.2.2 Morphology

A general overview of suspended CTS nanoparticles is shown in Fig. 16a. Transmission Electron Micrograph of CTS nanoparticles along with distribution of particle sizes are shown in Fig. 6.16 b and c, respectively. The Fig. 6.16 b shows a general distribution of CTS nanoparticles with size ranging between ~ 2 to 25 nm. The shape of nanoparticles is nearly spherical. The median value of distribution of particle sizes is around 12 nm, which is close to the XRD average crystallite size. The Fig. 6.16 d shows the high resolution TEM of smallest of particles, which is of dimension around 2 nm. The lattice fringes with inter planar distance of 3.1 Å are ascribed to {112} planes. This emphasizes the presence of crystallinity even at such small size. The selective area electron diffraction (SAED) of CTS nanoparticles is shown in Fig. 6.16 e. The diffraction pattern matches well with that of Tetragonal Cu₂SnS₃ (JCPDS No. 089-4714). On basis of the method of relative ratios the diffraction rings have been assigned to (112), (204), (312), (040), (316) and (424) planes. The SAED again confirms the formation of CTS nanoparticles with tetragonal structure.
\[ f(R_\infty) = C (h\nu - E_g)^{1/2} \]
nanoparticles, the value of band gap for cubic and monoclinic phase are reported to be 0.93-0.94 eV [9,10] and 0.91 eV [11], respectively. Thus, it seems the tetragonal CTS has near optimal band gap for maximal solar photons absorption.

![Figure 6.17](image)

**Fig. 6.17** (a) Diffuse reflectance spectrum of Cu$_2$SnS$_3$ powder (b) Plot of $(f(R) h_v)^2$ versus $h_v$ for determination of band gap

### 6.2.2.4 Electrical properties

The electrical conductivity of CTS nanoparticles pellets at room temperature is 0.2 S/cm. The thermoelectric power (TEP) of these pellets is measured to be around $+160$ $\mu$V/K. The positive sign of the TEP indicates p-type conduction behavior of CTS nanoparticles.

The hole concentration is determined from TEP using the following relation:

$$p = N_v \exp(A - e\alpha_e / k)$$ .................................. (6.7)

where, $N_v$ is the effective density of state in valence band ($= 6.91 \times 10^{17}$ cm$^{-3}$ for Cu$_2$SnS$_3$ at 300 K), $A$ is a constant depending on scattering ($= 4$ for impurity scattering), $\alpha_e$ is the thermoelectric power, $k$ is the Boltzmann constant ($= 86.7$ $\mu$V/K), $e$ is the electronic charge.

The mobility of holes is determined from the equation:

$$\mu = \sigma / p.e$$ ........................................... (6.8)

where, $\mu$ is the mobility and $\sigma$ is the electrical conductivity.

The hole concentration and hole mobility thus calculated from these relation using room temperature conductivity and TEP values, is $5.8 \times 10^{18}$ cm$^{-3}$ and 0.22 cm$^2$V$^{-1}$s$^{-1}$.
respectively. Although there is no report of these electrical parameters i.e. carrier concentration and mobility for p-CTS. The carrier concentration and mobility of n-type monoclinic CTS, as reported by Khanafer and Gorochev based on Hall measurements are 1.2 x 10^{20} cm^{-3} and 0.50 cm^2 V^{-1} s^{-1}, respectively [11].

Temperature variation of electrical conductivity in the temperature range of 250 - 425 K is shown in Fig. 6.18. Near room temperature, the transport of carriers in such semiconductors is thermally activated and is well explained by Seto’s model [5]. The conductivity (σ) of a sample according to this model is expressed as:

\[ \sigma = \sigma_0 \frac{T^{\alpha}}{T^{\beta}} \exp \left( \frac{-E_a}{kT} \right) \]  …… (6.9)

where, \( \sigma_0 \) is a constant, \( k \) is the Boltzmann constant and \( E_a \) is intergrain barrier height (also called as activation energy). It is observed from the plot that experimental data obeys well Seto’s model. The activation energy obtained after fitting the experimental data is 0.16 eV.

![Graph showing temperature variation of electrical conductivity of pellets of Cu2SnS3 nanoparticles](image)

**Fig. 6.18:** Temperature variation of electrical conductivity of pellets of Cu2SnS3 nanoparticles
References:


[10] Q. Liu, Z. Zhao, Y. Lin, P. Guo, S. Li, D. Pan, X. Ji, Alloyed (ZnS)$_x$Cu$_{2-x}$SnS$_3$ and (CuInS$_2$)$_x$(Cu$_3$SnS$_4$)$_{1-x}$ nanocrystals with arbitrary composition and broad tunable band gaps, Chemical Communications 47 (2011) 964-966