For a semiconductor intended to be used for optoelectronic applications, it is imperative to have knowledge of optical and electrical properties. Thus this chapter deals with optical and electrical properties of the layer-by-layer deposited Cu$_2$SnS$_3$ films. In specific effect of thickness and annealing has been studied in detail. The chapter is divided into two parts, each of which discusses optical and electrical properties separately. For the study of optical properties, transmittance and reflectance spectrum of films of different thickness and annealed at different temperatures is collected. These data has been utilized to derive different parameters like absorption coefficient, band gap, refractive index, dielectric constant and energy loss functions. Dispersion of refractive index is also analyzed using two approaches – Wemple-Didomenico and Spitzer-Fan models. The charge transport is studied with aid of conductivity and thermoelectric power measurements carried out under illuminated and dark conditions in the temperature range of 120 to 273 K. The primary data is used to extract more relevant physical quantities – carrier concentration and mobility and their variation with thickness and annealing is discussed. A qualitative model has been also proposed to explain the observations.
5.1.1 *Optical properties of Cu$_2$SnS$_3$ thin films*

Transmittance spectra of Cu$_2$SnS$_3$ films of different thickness is shown in Fig. 5.2 (a) (b) (c). Increase in thickness of the films is found to considerable decrease the overall transmittance of films. The plots show significant decrement in transmittance starting around 1100 nm which continues till 600 nm. This decrease in the transmittance is caused by absorption due to fundamental band to band transition. It is however difficult to point the absorption edge in spectrum due to presence of interference fringe near the absorption. Fig. 5.1 shows the transmittance spectrum of a CTS thin film collected after placing the film sample in optical path at different angles. It is clear from the figure that changing by angle between the incident light and film surface, an apparent change in the absorption edge is observed. This deviation should be irrespective of fundamental absorption; therefore it is believed that such change is caused by the presence of fringes.

The reflectance spectra of Cu$_2$SnS$_3$ films of different thickness is shown in Fig. 5.4 (a) (b) (c). It is noticed that number of fringes in a spectrum increases with the number of CTS layers. Secondly, the fringes are found to appear after the absorption edge. It is proposed to explain that each layer behaves independently and acts as a reflecting surface. Individual layer thin enough to absorb the incident light completely (after absorption edge) allows the light to pass through the next layer. Thus, partially reflected light from two more surface interfere to produce such fringe pattern.

![Transmittance spectrum](image)

*Fig. 5.1: Transmittance spectrum of ~ 300 nm taken by orienting the sample at different angles in optical path*
Fig. 5.2: Transmittance spectra of CTS films of different thickness (a) ~150 nm, (b) ~300 nm and (c) ~450 nm

Fig. 5.3: Transmittance spectra of CTS films annealed at different temperatures (a) 523 K, (b) 623 K and (c) 673 K
Fig. 5.4: Reflectance spectra of CTS films of different thickness (a) ~150 nm, (b) ~300 nm and (c) ~450 nm

Fig. 5.5: Reflectance spectra of CTS films annealed at different temperatures (a) 523 K, (b) 623 K and (c) 673 K
Similarly, the transmittance and reflectance spectra of CTS films annealed at different temperature of 473 K, 573 K and 623 K are shown in Fig. 5.3 (a), (b), (c) and Fig. 5.5 (a), (b), (c), respectively. The transmittance and reflectance spectra of the films remain more or less similar after annealing, though fringe pattern in the reflectance spectrum tend to coalesce by annealing at higher temperature.

The transmittance and reflectance data is used to calculate the absorption coefficient of CTS films using the relation:

\[
\alpha = \frac{1}{t} \ln \left( \frac{T}{(1-R)^2} \right) \\
\text{(5.1)}
\]

The Plots of variation in absorption coefficient with wavelength for CTS films of different thickness and annealed at different temperature are shown in Fig. 5.6 (a), (b), (c) and Fig. 5.7 (a), (b), (c), respectively.

In general, it is found that the absorption coefficient is greater than \(10^4 \text{ cm}^{-1}\) and for wavelengths less than \(\sim 600 \text{ nm} \) remain higher than \(> 10^5 \text{ cm}^{-1}\). The band gap of the films is determined using Tauc’s relation for direct band to band allowed transitions:

\[
\alpha h \nu = A (h \nu - E_g)^n \\
\text{(5.2)}
\]

The values of band gap determined for different samples are tabulated in Table 5.1.

<table>
<thead>
<tr>
<th>Types of films</th>
<th>Different thickness</th>
<th>Annealed at different temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>~150 nm</td>
<td>~300 nm</td>
</tr>
<tr>
<td>Band gap (eV)</td>
<td>1.1</td>
<td>1.1</td>
</tr>
</tbody>
</table>

It is observed that band gap remains nearly constant for the CTS films of different thickness. The found value of band gap of \(~1.1 \text{ eV}\), which is similar to the values reported for tetragonal CTS in literature [1,2]. However, there is a slight variation in band gap and it decreases with annealing temperature. This may be due to the transition of tetragonal CTS to a mix of tetragonal and cubic. Cubic CTS have been reported to have a band gap of \(~0.95 \text{ eV}\) i.e. slightly less than the tetragonal less [1]. Thus, films after annealing (at 573 and 623 K) with mix phase of Cubic and Tetragonal CTS is found to have slightly less band gap than pure tetragonal films.
5.1.2 Refractive index

Refractive index is the most critical optical constant of a semiconductor and its relationship with wavelength of incident light is known as dispersion. An electromagnetic wave while traversing through a lossy medium experiences attenuation i.e. loss in its energy via number of phenomena such as generation of phonons, free carrier absorption, scattering and photogeneration. In such a case the refractive index is expressed as \( n + ik \), i.e. a complex function of wavelength with \( n \) and \( k \) being the real and imaginary refractive index, respectively. \( k \) is also called as extinction coefficient as it indicates the total optical loss caused by transmittance and scattering. The real and imaginary refractive indices can be calculated from the following relations [3]:

\[
k = \frac{\alpha \lambda}{4\pi} \quad \ldots (5.3)
\]

\[
n = \left( \frac{1+R}{1-R} \right) - \frac{4R}{\sqrt{(1-R)^2 - k^2}} \quad \ldots (5.4)
\]

where, \( \alpha \) is the absorption coefficient and \( R \) is reflectance.

The variation of refractive index, \( n \) with wavelength for CTS films of different thickness and annealed at different temperature are shown in Fig. 5.8 (a), (b), (c) and Fig. 5.9 (a), (b), (c), respectively. In general, the refractive index of CTS films lies between \(~1.8\) to \(~2.5\) in the wavelength range of 2400 to 400 nm. All the plots show similar behaviour i.e. refractive index, \( n \) first increases with decrease in wavelength with a peak at around fundamental absorption and thereafter decreases. The change in thickness causes no apparent change in the values of refractive index although the transition near the absorption edge becomes sharper with increasing thickness. It is seen that with increasing the annealing temperature the refractive index of films increases slightly. This may be due to the fact that refractive index is dependent on the atomic mass of components and the density of material. Thus, as annealing temperature increases the grain growth takes place and density thus the refractive index of films increases.
Fig. 5.6: Variation of absorption coefficient with wavelength for CTS films of different thickness (a) ~150 nm, (b) ~300 nm and (c) ~450 nm

Fig. 5.7: Variation of absorption coefficient with wavelength for CTS films annealed at different temperatures (a) 523 K, (b) 623 K and (c) 673 K
The variation of extinction coefficient, \( k \), with wavelength for CTS films of different thickness and annealed at different temperature are shown in Fig. 5.10 (a), (b), (c) and Fig. 5.11 (a), (b), (c), respectively. The extinction coefficient ranges between the extremes of 0.1 and 1.3 for all the samples in the wavelength range of 400 to 2400 nm. The behaviour of curves seems to be similar which the value of \( k \) first decreases, with decreasing wavelength, to a then rises at end, forming a valley near the absorption edge. As \( k \) is directly proportional to the absorption coefficient and as the absorption coefficient of the films of different thickness and annealed at different temperatures is more or less unchanged; so is the extinction coefficient. In fact, the variation follows the same trend as absorption coefficient. Also, as the absorption of the CTS films is quite high (\( >10^4 \text{ cm}^{-1} \)), so is the value of \( k \).
Fig. 5.10: Variation of extinction coefficient with wavelength for CTS films of different thickness (a) ~150 nm, (b) ~300 nm and (c) ~450 nm

Fig. 5.11: Variation of extinction coefficient with wavelength for CTS films annealed at different temperatures (a) 523 K, (b) 623 K and (c) 673 K
5.1.3 Dielectric constants

Fundamental electronic transition in semiconductor thin film is intimately related to the wavelength dependent complex dielectric constant, expressed as \( \varepsilon_1 + i\varepsilon_2 \). The real and imaginary parts of the dielectric constant can be calculated from the refractive index and extinction coefficient using the following relations [3]:

\[
\varepsilon_1 \ (or \ \varepsilon_r) = n^2 - k^2 \quad \ldots \ldots \quad (5.5)
\]

\[
\varepsilon_2 \ (or \ \varepsilon_i) = 2nk \quad \ldots \ldots \quad (5.6)
\]

Physically, real part of dielectric constant related to slowing down of speed of light in the medium, whereas, the imaginary part of dielectric constant can be correlated with interaction of matter with electric field vector, thus causing the absorption of light.

Fig. 5.12 (a), (b), (c) and Fig. 5.13 (a), (b), (c) show the dependence of real part of dielectric constant and Fig. 5.14 (a), (b), (c) and Fig. 5.15 (a), (b), (c) show dependence of imaginary part of dielectric constant on wavelength for CTS films of different thickness and annealed at different temperatures, respectively.

It can be observed that variation of real part of dielectric constant is governed by the character of variation in the refractive index, whereas, the imaginary part of dielectric constant is by character of variation in extinction coefficient. In general, the value of \( \varepsilon_r \) varies between extremes of 2 to 6 and in visible region on average \( \sim 4 \) to 5. For CTS films of different thickness \( \varepsilon_n \), remains same, with films of \( \sim 150 \) nm showing maximum variation. However, the value of \( \varepsilon_i \) increases slightly with increasing annealing temperature. Also, the nature peak in variation of \( \varepsilon_i \) becomes sharper with increasing the annealing temperature.

The imaginary part of dielectric constant, \( \varepsilon_n \), varies between the limits of \( \sim 1 - 5.5 \) for films of different thickness and annealed at different temperatures and specifically 1-2 in the visible region. While, \( \varepsilon_i \) remains similar for films of different thickness, the \( \varepsilon_n \) increases marginally with increasing the annealing temperature. The ratio of real and imaginary parts of dielectric constant, known dissipation factor, mathematically defined as:

\[
\tan \delta = \frac{\varepsilon_2}{\varepsilon_1} \quad \ldots \ldots \quad (5.7)
\]
Fig. 5.12: Variation of real part of dielectric constant with wavelength for CTS films of different thickness (a) ~150 nm, (b) ~300 nm and (c) ~450 nm

Fig. 5.13: Variation of real part of dielectric constant with wavelength for CTS films annealed at different temperatures (a) 523 K, (b) 623 K and (c) 673 K
Fig. 5.14: Variation of imaginary part of dielectric constant with wavelength for CTS films of different thickness (a) ~150 nm, (b) ~300 nm and (c) ~450 nm.

Fig. 5.15: Variation of imaginary part of dielectric constant with wavelength for CTS films annealed at different temperatures (a) 523 K, (b) 623 K and (c) 673 K.
This constant quantifies the dissipation of energy of electromagnetic radiation in the medium. Fig. 5.16 (a), (b), (c) and Fig. 5.17 (a), (b), (c) show the dependence of dissipation factor, \( \tan \delta \) on wavelength for CTS thin films of different thickness and annealed at different temperatures, respectively. The values of \( \tan \delta \), vary from 0.05 to 2, for wavelengths between 400 and 2400 nm. However, dissipation factor remains less than unity for wavelengths less than 1600 nm, while increases rapidly when moving towards IR region.

While, the loss of energy of electromagnetic radiation in the medium is expressed by \( \tan \delta \), the loss of energy of a fast moving electron in a medium is given in terms of volume energy loss function (VELF) and surface energy loss function (SELF). VELF and SELF define the loss of energy of fast moving electron via characteristic plasma excitation when traveling through bulk and surface of the material, respectively. VELF and SELF can be calculated from the real and imaginary parts of dielectric constants using the following relation [4]:

\[
VELF = \frac{\varepsilon_2}{(\varepsilon_1^2 + \varepsilon_2^2)} \quad \ldots \ldots \quad (5.8)
\]

\[
SELF = \frac{\varepsilon_2}{[(\varepsilon_1 + 1)^2 + \varepsilon_2^2]} \quad \ldots \ldots \quad (5.9)
\]

Fig. 5.18 (a), (b), (c) and Fig. 5.19 (a), (b), (c), show change in SELF as a function of wavelength for CTS films of different thickness and annealed at different temperature, respectively.

The variation of VELF with wavelength for films of different thickness and annealed at different temperature, respectively shown in Fig. 5.20 (a), (b), (c) and Fig. 5.21 (a), (b), (c). The nature of variation of SELF and VELF is similar i.e. with increasing wavelength the function first goes to minimum around the fundamental absorption, thereafter increasing and tending to saturate at the end. The values of SELF and VELF typically range between the limits of 0.02 to 0.2. It is noticed that the values of function whether SELF or VELF, tend to limit to a maximum value earlier than the annealed sample. Also, increasing the annealing temperature causes slight increase in the values of SELF and VELF, especially in the IR region.
**Fig. 5.16**: Variation of tan delta loss with wavelength for CTS films of different thickness (a) ~150 nm, (b) ~ 300 nm and (c) ~ 450 nm.

**Fig. 5.17**: Variation of tan delta loss with wavelength for CTS films annealed at different temperatures (a) 523 K, (b) 623 K and (c) 673 K.
Fig. 5.18: Variation of surface energy loss function with wavelength for CTS films of different thickness (a) ~150 nm, (b) ~300 nm and (c) ~

Fig. 5.19: Variation of surface energy loss function with wavelength for CTS films annealed at different temperatures (a) 523 K, (b) 623 K and (c) 673 K
Fig. 5.20: Variation of volume energy loss function with wavelength for CTS films of different thickness 
(a) ~150 nm, (b) ~300 nm and (c) ~450 nm

Fig. 5.21: Variation of volume energy loss function with wavelength for CTS films annealed at different 
temperatures (a) 523 K, (b) 623 K and (c) 673 K
5.1.4 Dispersion energy parameters

Dispersion energy parameters are of vital significance in designing optoelectronic devices on a material. In first part the dispersion of refractive index is analyzed using Wemple-Didomenico’s single oscillator model (WD model) [5]. This model describes wavelength dependence of dielectric constan in terms of single oscillator picture. Important to this model are the parameters E_d and E_o where E_d is the dispersion energy parameter related to the average strength of inter band optical transition and E_o is the average oscillator energy (an average of optical band gap). It is also related to the optical band gap as 2E_o ≈ E_o. WD model examines the dispersion of refractive index below the inter-band absorption edge, where normal dispersion of optical dielectric constant of a material and energy dependence of refractive index obey Sellmeier equation i.e. [3]:

\[ n^2 - 1 = \frac{E_d E_o}{E_o^2 - (hv)^2} \quad \ldots \ldots \quad (5.10) \]

The values of E_o and E_d can be obtained from the slope and intercept of the straight line plot between \((n^2-1)^\dagger\) and \((hv)^2\). This plot also yields other important parameter such as static refractive index, n(0), which gives an indication about structure and density of material and \(\varepsilon_{\infty}\), the high frequency dielectric constant. Various such parameters have been listed in Table 5.2.

It is seen that E_d increases slightly with increasing thickness while increase noticeably with increasing annealing temperature. Similar trend thus follows for n(0) and \(\varepsilon_{\infty}\). The value of E_o remains roughly twice the optical band gap obtained from the Tauc plot.

Imaginary part of dielectric constant \(\varepsilon_{\infty}\) can be related to E_o and E_d and is expressed as moments of \(\varepsilon_{\infty}\) as [5]:

\[ E_d^2 = \frac{M_{-3}}{M_{-3}} \quad \ldots \ldots \quad (5.11) \]

\[ E_o^2 = \frac{M_{-3}^3}{M_{-3}} \quad \ldots \ldots \quad (5.12) \]

Further analysis of optical data, is done using Spitzer-Fan model [6], especially the contribution of free carrier susceptibility to real part of dielectric constant.

\[ \varepsilon_r = \varepsilon_{\infty} - \left[ \frac{e^2}{\pi c^2} \right] \left( \frac{N}{m^*} \right) \lambda^2 \quad \ldots \ldots \quad (5.13) \]
where, ε₀ is the high frequency dielectric constant, N/m* is the free carrier concentration to the effective mass ratio, e is the electronic charge and c is the speed of light. By plotting ε₁ versus λ² and fitting to straight line yield the values for ε₀ and N/m* from the intercept and slope, respectively (listed in Table 5.2). It is seen that the N/m* remains constant for films of different thickness, whereas, increases upon increasing the annealing temperature. ε₀ as determined from the Spitzer-Fan model are similar to the values obtained from WD model and follow the same trend. The N/m* is used to calculate the plasma resonance frequency, ω₀, which is characteristic frequency at which the material changes from a metallic to dielectric response (the values are listed in Table 5.2). It is mathematically expressed as:

\[ \omega_0^2 = \frac{e^2 N}{m^* \varepsilon_0} \]  \hspace{1cm} (5.14)

Also, the free carrier susceptibility can be calculated from the N/m* using the relation and the value are listed in Table 5.2.

\[ \chi_c = -\frac{e^2 N}{m^* \varepsilon_0^2} \]  \hspace{1cm} (5.15)

Table 5.2: Different dispersion energy parameters deduced from the optical data

<table>
<thead>
<tr>
<th>Types of films</th>
<th>Different thickness</th>
<th>Annealed at different temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>~150 nm</td>
<td>~300 nm</td>
</tr>
<tr>
<td>Wemple-Didomenico model</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E_d (eV)</td>
<td>4.17</td>
<td>4.34</td>
</tr>
<tr>
<td>E_0 (eV)</td>
<td>2.15</td>
<td>2.16</td>
</tr>
<tr>
<td>\varepsilon_0</td>
<td>2.94</td>
<td>2.95</td>
</tr>
<tr>
<td>n (0)</td>
<td>1.71</td>
<td>1.73</td>
</tr>
<tr>
<td>M_1</td>
<td>1.93</td>
<td>1.95</td>
</tr>
<tr>
<td>M_3 (eV)²</td>
<td>0.417</td>
<td>0.418</td>
</tr>
<tr>
<td>Spitzer-Fan model</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N/m* (10¹⁴ cm⁻³)</td>
<td>0.4</td>
<td>0.35</td>
</tr>
<tr>
<td>\varepsilon_0</td>
<td>3.95</td>
<td>3.82</td>
</tr>
<tr>
<td>\omega_0 (10¹² s⁻¹)</td>
<td>1.53</td>
<td>1.01</td>
</tr>
<tr>
<td>\chi_c (10⁻²)</td>
<td>0.17</td>
<td>0.07</td>
</tr>
</tbody>
</table>
5.2 Carrier transport in Cu$_2$SnS$_3$ films using thermoelectric and conductivity measurements

Unlike controlled environments of vacuum deposition systems, solution processing may yield films with unpredictable carrier transport due to inherent proclivity of gettering defects during processing. Thus understanding the nature of carrier transport in these films becomes crucial from basic and application perspective. This will suggest the ways of improvement for fabricating better thin film solar cells. Thermoelectric and photothermoelectric power analysis have been employed reliably for seeking insight into carrier transport in semiconducting thin films [7,8]. Here, an in-depth analysis of temperature dependence of basic semiconducting thin film parameters such as carrier concentration and mobility, derived from conductivity and thermoelectric power measurements, is presented. The experiments have been performed for layer by layer solution processed CTS films of different thickness and after annealing, under dark and illumination to provide information relevant to solar cells. At the end, a qualitative physical model for understanding the influence of deposition and post-deposition work-up parameters on carrier migration in these films is proposed.

The electrical characterization of Cu$_2$SnS$_3$ films are performed in a custom designed and indigenously fabricated cryostat (discussed in chapter 3). To check the validity of results, a preliminary measurement is first carried out at the user facility at UGC-CSR Indore. This study included temperature variation of electrical conductivity of a ∼ 550 nm thick CTS in the temperature range of 5 to 290 K. The data is analyzed for different transport behaviours in different temperature range and results are discussed below. Detail measurements and analysis is later carried for the CTS films of different thicknesses and annealed at different temperatures for elucidation of carrier transport in layer-by-layer deposited CTS films.

5.2.1 Preliminary studies in temperature range of 5-290 K

Fig. 5.22 shows the plot of variation of dark electrical conductivity (σ) of the films with temperature from 5 to 290K. In general, σ increases as T increases and variation can be expressed by the equation:

$$\sigma = \sigma_0 \exp\left(-\frac{E_1}{kT}\right) + \sigma_{02} \exp\left(-\frac{E_2}{kT}\right) + \frac{\sigma_{03}}{T^n} \exp\left(-\frac{E_3}{kT}\right) \quad \ldots \ldots \quad (5.16)$$
Where, $\sigma_{01} = 3e^2 v_\mu \left( \frac{N_{E_F}}{8\pi \alpha k T} \right)^{1/2}$, $v_\mu$ is the Debye frequency, $T_o = \frac{\lambda \alpha^3}{kN_{E_F}}$ is the Mott characteristic temperature, $N_{E_F}$ is the density of states at Fermi energy ($E_F$), $\lambda$ is a dimensionless constant, $\alpha$ is the wavefunction decay length, $\sigma_{02}$ is a constant, $E_2$ is nearest activation energy, $\sigma_{03}$ is a constant and $E_3$ is grain boundary (GB) barrier energy. The first, second and third term of the Eq. 5.16 represents: Mott variable range hopping (M-VRH), nearest neighbour hopping (NNH) and thermoionic emission (TE) over GB barriers, respectively.

![Fig. 5.22: Temperature variation of electrical conductivity of a typical CTS film (black circles for data points and red line for model fit)](image)

As can be seen, the experimental data fits well to the Eq. 5.16 over the entire temperature range. The conductivity of CTS films can be approximately divided into three temperature regions of 5-50 K, 50-150 K and 150-290 K. In the range 5-50 K the carrier transport has prominent contribution from M-VRH, as $T_o/T >> 1$ and a fit to Arrhenius plot yields insignificant activation energy. The electrical conductivity behaviour of polycrystalline films near room temperature has been found to follow TE over GB as seen in literature after Seto [9]. In particular, Seto’s model with the exponent $n = 0.5$ (to minimize the errors due to model assumptions [10]) is used here to explain the conductivity in the temperature range of 150 to 290 K. However, the conductivity for intermediate temperatures ($> 50$ K and $< 150$ K) cannot be accounted solely due to M-VRH or TE over GB and an additional transport mechanism is required. In earlier reports
NNH type conduction is found to be operative along M-VRH with increasing temperatures [27]. The electrical conduction in CZTS films has also been explained satisfactorily using such model [10]. The NNH activation energy ($E_2$) and GB barrier energy ($E_3$) for the prepared films are found to be 236 and 37 meV, respectively.

5.2.2 Detailed measurements and analysis for CTS thin films

5.2.2a Variation of conductivity with temperature

In the previous study, the temperature variation of CTS films was studied in the temperature range of 5 – 290 K. Analysis of the data suggested presence of three different transport mechanisms: (i) from 5-50 K: variable range hopping, between 150 to 290 K: thermoionic emission over grain boundaries and the intermediate range (50 – 150 K) shows a transition between the two behaviors, and expected to follow nearest neighbour hopping type conduction.

In the detailed study, the temperature range considered for elucidation of carrier transport is 120 – 273 K. General behaviour of variation in conductivity with temperature shows existence of two different slopes at extremes of the temperature range considered. As in the preliminary, in the present case too; observed data for variation of conductivity with temperature can be explained by amalgamation of two different conduction mechanisms i.e.: in temperature range of 120-160 K carrier conduction is due to nearest neighbour hopping whereas between 160-273 K conductivity is governed by thermoionic emission over grain boundaries. The quantitative contribution of each of the behavior can be obtained by fitting the experimental data to the following equation:

$$\sigma = \sigma_{01} \exp \left( \frac{-E_1}{kT} \right) + \frac{\sigma_{02}}{T^n} \exp \left( \frac{-E_2}{kT} \right) \quad \ldots \ldots \quad (5.17)$$

where, $\sigma_{01}$ is a constant, $E_1$ is nearest neighbor hopping activation energy, $\sigma_{02}$ is a constant and $E_2$ is grain boundary (GB) barrier energy. The first and second term of the Eq. 5.17 represents: nearest neighbour hopping (NNH) and thermoionic emission (TE) over GB barriers, respectively. The electrical conductivity behaviour of polycrystalline films near room temperature has been found to follow TE over GB as seen in literature after Seto [9]. Again, Seto’s model with the exponent $n = 0.5$ (to minimize the errors due to model assumptions [10]) is used here to explain the conductivity in the temperature range of 160 to 273 K. In the temperature range of 120-160 K the first term dominates i.e. nearest neighbor hopping. The occurrence of NNH type conduction is indicative of some extent
of disorder, which leads to localized states near band edges [10]. It is expected due to the fact that as the synthesis is carried out at a relatively low temperature of 473 K in air, which may not be sufficient to form a thermodynamically more stable structure, thus leading to a disordered lattice. There is possibility of accumulation of these localized states which make NNH carrier transport feasible.

Overall conductivity increases with thickness (Fig. 5.23). The values of $E_1$ and $E_2$ for the temperature variation of conductivity of samples of different thicknesses are tabulated in Table 5.3, it is seen with the thickness, activation energy decreases.

![Graph showing the variation of conductivity with temperature for Cu$_2$SnS$_3$ films of different thicknesses. The graph indicates that as the thickness increases, the conductivity decreases.](image)

**Fig. 5.23:** Plot of variation in conductivity with temperature of Cu$_2$SnS$_3$ films of different thicknesses (with a thickness increment of ~ 75 nm). Red curves indicate data under illumination and Black curves indicate data under dark

The variation in conductivity with temperature for films of different thicknesses under illumination is also subjected to the same theoretical fit (similar to preliminary study: 5.2.1) and values of the activation energies for samples of different thickness are given in Table 5.3. A similar trend of decrease in activation energy with thickness is observed. However, the activation energies ($E_1$ and $E_2$) are comparatively lower under illumination than in dark.
Table 5.3: Nearest neighbour hopping, $E_1$ and grain boundary barrier energy, $E_2$ for Cu$_2$SnS$_3$ films of different thickness and after annealing at different temperatures, under dark and illumination conditions

<table>
<thead>
<tr>
<th>Samples</th>
<th>$E_1$ (meV) dark</th>
<th>$E_2$ (meV) dark</th>
<th>$E_1$ (meV) light</th>
<th>$E_2$ (meV) light</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness variation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>~ 75 nm</td>
<td>305</td>
<td>63</td>
<td>287</td>
<td>52</td>
</tr>
<tr>
<td>~ 150 nm</td>
<td>289</td>
<td>57</td>
<td>264</td>
<td>45</td>
</tr>
<tr>
<td>~ 225 nm</td>
<td>273</td>
<td>52</td>
<td>249</td>
<td>41</td>
</tr>
<tr>
<td>~ 300 nm</td>
<td>264</td>
<td>46</td>
<td>247</td>
<td>37</td>
</tr>
<tr>
<td>~ 375 nm</td>
<td>256</td>
<td>41</td>
<td>235</td>
<td>28</td>
</tr>
<tr>
<td>~ 450 nm</td>
<td>243</td>
<td>37</td>
<td>221</td>
<td>24</td>
</tr>
</tbody>
</table>

Annealing Temperature

| 523 K       | 180              | 26               | 159               | 22                |
| 623 K       | 167              | 22               | 148               | 19                |
| 673 K       | 153              | 19               | 138               | 12                |

An overall rise in conductivity is observed with increasing annealing temperature (Fig. 5.24). Activation energies obtained after fitting the experimental data with Eq. 5.17 are listed Table 5.3. It is seen that activation energies for conduction in dark, for samples annealed at different temperatures remains constant. However, under illumination a decrease in activation energy is seen.

![Graph showing conductivity vs. annealing temperature](image)

Fig. 5.24: Plot of variation in conductivity with temperature of Cu$_2$SnS$_3$ films (thickness: ~500 nm) after annealing at different temperatures. Red curves indicate data under illumination and Black curves indicate data under dark.
5.2.2b Variation of thermoelectric power (TEP) with temperature:

The variation of TEP with temperature, for films of different thicknesses and films annealed at different temperatures, is shown in Fig. 5.25 and 5.26, respectively. The variation of TEP with temperature for all samples is found to be linear. The dS/dT values are seen to be positive and constant within the temperature range studied. It can be inferred that (i) samples behave in non-metallic fashion and (ii) $E_F$ within the studied range remains constant and variation in TEP depends on T as $E_F/KT^2$ [11]. Thus, in this case when $E_F$ remains constant, TEP of non-degenerate p-type semiconductor is given by:

$$S = \frac{k}{e} \left( A + \frac{E_F}{kT} \right)$$

\[ \ldots \ldots \quad (5.18) \]

where, $k$ is the Boltzmann constant, $e$ is the electronic charge, $E_F$ is the Fermi energy level from the top of the valence band and $A$ is a dimensionless constant that varies from 0 to 4 depending on type of scattering process. Thus by plotting $S$ vs. $1/T$, values of $A$ and $E_F$ can be obtained from the intercept and slope of line. The values of $A$ for samples with different thickness lie in a short range of 3.8 to 4, which indicates the presence of scattering due to ionized impurity [8,11]. This is expected, as the method of synthesis involves solution, it may impart impurities due to non-stoichiometric proportions and native impurity of initial reagents. Moreover, thermolysis of precursor films in air may also incorporate atmospheric impurities. Similar features have been reported earlier in case of chemical deposited thin films [7,8]. The values of $E_F$ vary from 0.031-0.026 eV, with increasing thickness of films. This indicates that with increasing the thickness, the extent of doping or population of majority carrier increase, slightly.

Increasing the annealing temperature results in decreased TEP. From the plot of $S$ vs. $1/T$, scattering constant $A$ is again found to be 4. Fermi level rises above valence band maxima from 0.026 to 0.033 eV with annealing temperature (from 523 to 673 K) indicating a decrement in hole density.

The variation of TEP with temperature under light is also found to be linear and there is an overall increase in values of TEP of all the samples under light than in dark.
**Fig. 5.25:** Plot of variation in Thermoelectric Power (TEP) with temperature of Cu$_2$SnS$_3$ films of different thicknesses (with a thickness increment of ~75 nm). Red curves indicate data under illumination and Black curves indicate data under dark.

**Fig. 5.26:** Plot of variation in Thermoelectric Power (TEP) with temperature of Cu$_2$SnS$_3$ films after annealing at different temperatures. Red curves indicate data under illumination and Black curves indicate data under dark.
5.2.2c Variation of carrier concentration with temperature:

Majority carrier density can be calculated from TEP at each temperature using the following relation [8]:

\[ p = N_v \left[ A + \frac{S(\text{TEP})}{k/e} \right] \quad \ldots \ldots \quad (5.19) \]

where, \( p \) is hole concentration, \( S(\text{TEP}) \) is the thermoelectric power in units of \( \mu \text{V/K} \). \( A \) is constant due to scattering, here 4, due to ionized impurity scattering, \( N_v \) is the effective density of state for valence band and is given as:

\[ N_v = 2 \left( \frac{2\pi m^*_h k T}{\hbar^2} \right)^{3/2} \quad \ldots \ldots \quad (5.20) \]

where, \( m^*_h \) is the effective mass of hole (0.1\( m_e \)), \( k \) is the Boltzmann constant, \( \hbar \) is the Planck’s constant.

![Graph](image)

**Fig. 5.27:** Plot of variation in hole concentration \((p)\) with temperature of \(\text{Cu}_2\text{SnS}_3\) films of different thicknesses (with an thickness increment of ~75 nm). Red curves indicate data under illumination and Black curves indicate data under dark.

The plot of hole concentration versus 1000/T for samples of different thickness is shown in Fig. 5.27. In general, for any thickness, the majority carrier density remains almost independent of temperature. The carrier concentration throughout for all thickness is of order \(10^{18} \text{ cm}^{-3}\). For each increment in thickness, there is increase in carrier
concentration. Similarly, the films annealed at different temperatures the carrier concentration remains almost constant with varying temperature. Increasing the annealing temperature results in a small increment in carrier density.

Under illumination the majority carrier concentration decreases in comparison to respective dark values for the samples of different thickness. However, the change in $\Delta p$ (change in hole concentration) also decreases with increase in thickness, meaning that there is not much change in majority carrier density under illumination.

For samples annealed at different temperature majority carrier concentration in dark remains almost constant with varying temperatures (shown in Fig. 5.28). After annealing (referring temperature in increasing fashion i.e. 523, 623 and 673 K) there is only slight increase in majority carrier concentration. The carrier density of these samples under light is found to be slightly higher than in dark. The values of change in hole concentration, $\Delta p$ (i.e. $p_\text{T}-p_\text{d}$, where $p_\text{T}$ is the hole concentration under illumination and $p_\text{d}$ is the hole concentration under dark) increase with increase in annealing temperature.

![Graph](image)

**Fig. 5.28:** Plot of variation in hole concentration $(p)$ with temperature of Cu$_2$SnS$_3$ films (thickness: ~500 nm) after annealing at different temperatures. Red curves indicate data under illumination and Black curves indicate data under dark.
5.2.2d Variation of hole mobility with temperature:

The hole mobility for CTS thin films can be readily calculated from the values of conductivities and carrier densities using the simple relation:

\[ \mu = \sigma/(pe) \quad \ldots \quad (5.21) \]

It is observed that mobility of samples (under dark and light) for each thickness vary linearly with temperature (Fig. 5.29). The mobilities of the samples tend to decrease with increasing thickness. For annealed samples, increasing the annealing temperature results in increase of mobility (Fig.5.30). In presence of light, the change in mobility with temperature follows the same behaviour as in dark. Although in comparison to dark mobility in presence of light decreases. For the annealed samples the mobility under illumination is same for all the cases and becomes almost constant.

![Graph showing variation of hole mobility with temperature](image)

*Fig. 5.29: Plot of variation in hole mobility (\(\mu\)) with temperature of Cu₂SnS₃ films of different thicknesses (with an thickness increment of ~ 75 nm). Red curves indicate data under illumination and Black curves indicate data under dark*
Fig. 5.30: Plot of variation in hole mobility ($\mu$) with temperature of Cu$_2$SnS$_3$ films (thickness: ~500 nm) after annealing at different temperatures. Red curves indicate data under illumination and Black curves indicate data under dark.

5.2.3 Discussion

5.2.3a Recapitulation of results and preliminary inferences

Before discussing the specific aspects of results, it is important to summarize the key points of the experimental results for the determination of the transport mechanism:

1. Conductivity in dark or in light is in general found to be cumulative effect of NNH and thermoionic emission over grain boundaries in temperature range of 120-273 K.
2. Dark conductivity of the films increases with increasing thickness as well as after annealing the films at different temperatures.
3. In presence of light, the conductivity of the films whether of different thickness, or obtained after annealing at different temperatures increases compared to that in dark.
4. TEP of all film samples varies linearly with temperature, indicating scattering of charge carriers is due to ionized impurities.
5. With increasing thickness and annealing temperature, TEP increases by a constant value.
6. Hole mobility in films, decreases with increasing thickness and increases after annealing.

7. Under illumination, there is marginal decrease in the hole concentration, while hole mobility increases as thickness of films increases.

8. Samples after annealing show an increase in carrier concentration and, a reduction and saturation of mobility under light compared to dark.

The change in conductivity ($\Delta \sigma$) whether in dark or light can be attributed to change in carrier concentration ($\Delta p$) or change in mobility ($\Delta \mu$) or their combination, and is expressed as:

$$\Delta \sigma = \Delta p \mu + \rho e \Delta \mu \quad \ldots \ldots \quad (5.22)$$

A combination of both seems to be responsible for final change in conductivity in the present investigation.

For films with increasing thickness, the change in hole concentration is positive whereas, change in mobility is negative. Thus the overall increase in the conductivity under dark is due to increase in hole concentration which overrides the effect of decreasing mobility. However, the change in $\Delta p$ and $\Delta \mu$ becomes lesser with increasing thickness. Thus it is inferred that simultaneous contributions from change in mobility as well as change in hole concentration are responsible for the observed variation in conductivity. The change in hole concentration becomes significant for increase in conductivity, with increasing thickness. Whereas under illumination the change in carrier concentration is insignificantly negative and the change in the mobility is positive. Thus, the increase in conductivity under light is governed by change in mobility.

For films annealed at different temperatures (referring in ascending fashion), a positive change in both carrier concentration as well as mobility is observed. Thus both, increasing carrier concentration as well as mobility results in increasing conductivity. However, for each sample the contribution from the mobility or carrier concentration varies with temperature. The change in carrier concentration contributes more at 523 K and change in mobility contributes more at 623 K and 673 K.

Under illumination, there is an increment in carrier concentration which solely accounts for increase in conductivity since the mobility remains same for films annealed at different temperature and its magnitude is less than that under dark.
5.2.3b Temperature dependence of mobility

In general, for all samples (films of different thickness or films annealed at different temperatures), with change in temperature there is almost no change in the carrier concentration (order of magnitude is same). Thus, variation in conductivity with temperature is due to temperature dependence of mobility of a particular sample. This generally expressed as [11]:

\[ \mu = \mu_0 \exp (-\phi/kT) \] (5.23)

where, \( \mu \) is mobility, \( \phi \) is intergranular barrier height and the preexponential factor \( \mu_0 \), a term which is dependent on the mean free path. There are two possibilities for multicrystalline system: (i) the mean free path is equal to or greater than grain size and (ii) the mean free path is less than the grain size. In former, the restriction to the movement of the carrier will only be present at the grain boundaries and thus the change in mobility with temperature will only be dependent on intergranular barrier height. If latter is the case then the motion of carriers will be impeded within the grain, implying the presence of defects (impurities or native) in the grains. In such cases, the preexponential factor is expressed as \( \mu_0(T) \), which has its own temperature dependence and is inversely proportional to ionized impurity concentration.

The values of \( \mu_0 \) and \( \phi \), under dark and light, for different samples of different thickness and after annealing are tabulated in Table 5.4. The intergranular barrier height decreases with increasing thickness. The film of \( \sim 450 \) nm thickness has the least \( \phi \) value amongst films of different thickness, after annealing \( \phi \) decreases and remains almost same for films annealed at different temperatures. In presence of light there is decrease in values of \( \phi \) by a constant with respect to dark. However, these changes in values of \( \phi \) do not correlate with change in the mobility of films, i.e. the mobility do not increase with thickness as \( \phi \) goes down.
Table 5.4: Intergranular barrier height, $\phi$ and preexponential factor, $\mu_o$, for hole mobility of Cu$_2$SnS$_3$ films of different thickness and after annealing at different temperatures, under dark and illumination conditions

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\phi$ (eV) dark</th>
<th>$\mu_o$ dark</th>
<th>$\phi$ (eV) light</th>
<th>$\mu_o$ light</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness variation</td>
<td>0.106</td>
<td>9.62</td>
<td>0.058</td>
<td>same as dark</td>
</tr>
<tr>
<td>~ 75 nm</td>
<td>0.089</td>
<td>7.58</td>
<td>0.046</td>
<td></td>
</tr>
<tr>
<td>~ 150 nm</td>
<td>0.078</td>
<td>6.35</td>
<td>0.039</td>
<td></td>
</tr>
<tr>
<td>~ 225 nm</td>
<td>0.065</td>
<td>5.41</td>
<td>0.034</td>
<td></td>
</tr>
<tr>
<td>~ 300 nm</td>
<td>0.0559</td>
<td>4.77</td>
<td>0.027</td>
<td></td>
</tr>
<tr>
<td>~ 375 nm</td>
<td>0.0478</td>
<td>4.58</td>
<td>0.022</td>
<td></td>
</tr>
<tr>
<td>~ 450 nm</td>
<td>0.0423</td>
<td>4.3</td>
<td>0.019</td>
<td></td>
</tr>
<tr>
<td>Annealing Temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>523 K</td>
<td>0.041</td>
<td>9.17</td>
<td>0.017</td>
<td>4.27</td>
</tr>
<tr>
<td>623 K</td>
<td>0.039</td>
<td>13.56</td>
<td>0.015</td>
<td>5.31</td>
</tr>
<tr>
<td>673 K</td>
<td>0.043</td>
<td>15.23</td>
<td>0.018</td>
<td>5.92</td>
</tr>
</tbody>
</table>

Although, for a particular sample the variation in mobility with temperature is governed by $\phi$, it is the preexponential factor which dictates the change in the mobility with respect to the change in thickness and annealing temperature. Dependence on $\mu_o$ suggests presence of defects, affecting the mean free path of the carrier. The variation of $\mu_o$ with thickness and annealing temperature, indicate change in the concentration and distribution of defect, altering the mean free path of holes [11].

5.2.4 Qualitative model for carrier transport

Considering the changes occurring in transport behavior of films as presented above, a qualitative model, the origin of which lies in process of deposition, is proposed as follows:

As the deposition of films is done layer by layer, it is natural to believe that in such deposited (i.e. without annealing) film each layer act as a separate channel for electrical conduction.

After dip-coating, every time the precursor film is thermolysed in air at 473 K for conversion to CTS. This gives a possibility of incorporation oxygen impurities at the surface. At the time of next deposition these impurities get embedded with in structure at boundaries and diffuse slightly (as thermolysis temperature is just 473 K). Thus increasing the layers (or thickness), allows accumulation of higher concentration of impurity. Consequently, $\mu_o$, (known to depend inversely on impurity concentration) drops down with increasing concentration; this explains the lowering of mobility with increasing thickness. In presence of light same trend continues along with fact that the intergranular barrier decreases, thus there is slight increase in mobility under illumination.
as compared to dark. However, under light, ionization of these electron donor type defects results in increased recombination with the holes produced within grain, as a result carrier density lowers down under illumination.

Annealing the films under nitrogen atmosphere is thought to affect the concentration and distribution of impurities. Chemical potential of oxygen impurities inside the material becomes less under annealing condition, thus resulting in lowering of concentration of defects within the films. Secondly, annealing at higher temperature for hour long, results in more homogenous distribution of impurities. This explains the slight increase in mobility with the annealing temperature. This change in concentration of impurities with annealing temperature releases more free holes. Thus an increment in hole concentration is observed under dark.

The incorporation of defects during deposition and change in their concentration and distribution with varying thickness and annealing temperature is schematically summarized in Fig. 5.31.

**Fig. 5.31:** Schematic representation of accumulation and change distribution of defects under deposition and post deposition processing

### 5.2.5 Anomalous mobility of annealed films under illumination

From anomalous behavior of mobility of the annealed samples under light, it is inferred that the variation of mobility is independent of temperature and defect concentration, as it is seen that the intergranular barrier height for different annealed samples under light is same and their magnitude is very low. Under such condition tunneling of carriers becomes important. Transmission coefficient for tunneling of carriers can be calculated as a function of barrier height as [11]:

\[ \mu = C \exp \left( -\frac{2\beta \eta \phi}{e} \right) \quad \ldots \ldots \quad (5.24) \]

Where,

\[ \beta = \left[ \frac{e m^*}{h^2 (N_D - N_A)} \right]^{1/2} \quad \ldots \ldots \quad (5.25) \]
η is a numerical factor, 0 < η < 1, C is a constant independent of V, N_D-N_A is free carrier density. Fitting for equations it is found that β ranges between 500-700 V⁻¹. An empirical fit of calculated effective mobilities matches with that of experimental data, with η ranging between 0.11-0.12.

Thus, photoexcitation of annealed samples is controlled by tunneling of carrier through intergranular barriers.
References:


Chapter 6

Preparation and Characterization of \( \text{Cu}_2\text{SnS}_3 \) 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 \( \text{Cu}_2\text{SnS}_3 \) powder and nanoparticles has been discussed. \( \text{Cu}_2\text{SnS}_3 \) powder has been synthesized by solid state reaction of metal salts and thiourea, \( \text{Cu}_2\text{SnS}_3 \) 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 Cu$_2$SnS$_3$, five different sulphur sources have been utilized. These are thiourea (TU), thioacetamide (TAA), dimethyl thiourea (DMTU), sodium sulphide (Na$_2$S) and elemental sulphur (S). Samples of CTS are prepared by solid state reaction between Cu(CH$_3$COO)$_2$, SnCl$_2$.2H$_2$O 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.

![Schematic of Cu$_2$SnS$_3$ powder synthesis by solid state reaction](image)

**Sulphur Sources:**

- Thiourea (TU), Thioacetamide (TAA), Dimethyl Thiourea (DMTU), Sodium Sulphide (Na$_2$S), Sulphur (S)

**Fig. 6.1:** Schematic of Cu$_2$SnS$_3$ 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 Cu$_x$S and Sn$_y$S$_z$. Whereas, XRD pattern of CTS (TAA) and CTS (DMTU), indicate the presence of Cu$_2$SnS$_3$ along with Cu$_x$S and Sn$_y$S$_z$. However, XRD plot of CTS (TU) shows peaks due to tetragonal Cu$_2$SnS$_3$ only and no other extra peaks are present implying pure CTS sans Cu$_x$S and Sn$_y$S$_z$ 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.

![Rietveld refined X-ray diffraction pattern of pure Cu₂SnS₃ powder obtained from thiourea as Sulphur source](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>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1A</td>
<td>0</td>
<td>0.5</td>
<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>
<td>0</td>
<td>0.5</td>
<td>0.25</td>
<td>0.5003</td>
</tr>
<tr>
<td>Sn1B</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.4773</td>
</tr>
<tr>
<td>Cu2</td>
<td>0</td>
<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 Cu$_2$SnS$_3$ 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 $a = 0.5419$ nm and $b = 1.0842$ 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 $109.43^\circ - 109.55^\circ$, 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 Cu$_2$SnS$_3$ 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 Cu$_2$SnS$_3$ powder](image-url)
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.
(b) Sn 3d

Intensity (arb. unit)

Binding Energy (eV)

$b_{3d_{5/2}}$

$b_{3d_{3/2}}$

(c) S 2p

Intensity (arb. unit)

Binding Energy (eV)

$b_{2p}$
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 Cu$_2$SnS$_3$.
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.

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 (E₉) from diffuse reflectance data [3]. The modified Kubelka-Munk equation is:

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

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 \( \hbar \nu \) (Fig. 6.8 b) and is found to be 1.1 eV.

![Figure 6.8](image)

**Fig 6.8:** (a) Diffuse reflectance spectrum of Cu₂SnS₃ powder (b) Plot of \( (f(R) \ h \nu)^2 \) versus \( \hbar \nu \) 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:

$$p = N_v \exp(A - e\alpha_h / k) \quad \text{.......................... (6.2)}$$

where, $N_v$ is the effective density of state in valence band ($= 6.91 \times 10^{17} \ \text{cm}^{-3}$ 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:

$$\mu = \sigma / p.e \quad \text{.......................... (6.3)}$$

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

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

$$\sigma = \frac{\sigma_0}{T^{0.7}} \exp\left(-\frac{E_a}{kT}\right) \quad \text{.......................... (6.4)}$$
\( \sigma_0 \) 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.

![Graph](image)

**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$_2$ stretching frequency in the complexes. The asymmetric and symmetric stretching in thiourea are observed respectively at 3280 and 3160 cm$^{-1}$; these in the complexes, as expected shift to higher frequencies and are observed at 3185 and 3300 cm$^{-1}$.

![Infrared spectra](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$_2$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$_2$ 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$_2$ 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:

\[
[CuSn((\text{CSN}_{2})_{n})_{\text{mr}} \xrightarrow{\text{Heat}} \text{Cu}_2\text{SnS}_3 + \text{Volatile matter}} \quad (6.5)
\]
6.2 Microwave-assisted rapid synthesis of nanoparticles

6.2.1 Synthesis of CTS nanoparticles

Nanoparticles of Cu$_2$SnS$_3$ 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 Cu$_2$SnS$_3$ nanoparticles](image)

**Fig. 6.12:** Schematic of synthesis Cu$_2$SnS$_3$ 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 diffractogram 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 Cu2SnS3 powder obtained from thiourea as Sulphur source

A unit cell structure depicting the atomic coordination in Cu2SnS3 is shown as inset in Fig. 6.13. The result of crystal structure refinement of Cu2SnS3 nanoparticles is more or less similar to that obtained for Cu2SnS3 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 6.3: Structural parameters of Cu\textsubscript{2}SnS\textsubscript{3} obtained after Rietveld refinement**

<table>
<thead>
<tr>
<th>Site</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu 1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Cu 2A</td>
<td>0</td>
<td>0.5</td>
<td>0.25</td>
<td>0.5752</td>
</tr>
<tr>
<td>Sn 2A</td>
<td>0</td>
<td>0.5</td>
<td>0.25</td>
<td>0.4248</td>
</tr>
<tr>
<td>Sn 2B</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.6829</td>
</tr>
<tr>
<td>Cu 2B</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.3171</td>
</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\textsubscript{2}SnS\textsubscript{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 2p1/2 and Cu 2p3/2 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 3d5/2 and Sn 3d3/2 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 Cu$_2$SnS$_3$ 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. 6.16b and c, respectively. The Fig. 6.16b 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. 6.16d 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. 6.16e. 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.
Fig. 6.16 (a) Overview image of dispersed Cu_{2}SnS_{3} nanoparticles. (b) Transmission Electron Micrograph (TEM) showing general distribution and (c) Plot showing the particle size distribution as calculated from TEM, (d) High Resolution Transmission Electron Micrograph of a smaller CTS particle and (e) Selective area electron diffraction, of Cu_{2}SnS_{3} nanoparticles via microwave assisted route.

6.2.2.3 Optical properties

Diffuse reflectance spectrum of CTS nanoparticles in the wavelength range of 300 – 2400 nm is shown in Fig. 6.17 a. The spectrum shows a major decrement step in diffuse reflectance starting at 1500 nm till 900 nm, corresponding to fundamental absorption due to band to band transitions. The large wavelength range of this transition is also suggestive of nanoparticles with wide distribution of sizes. To determine the value of bandgap (E_{g}), modified Kubelka-Munk function is employed [3]. Modified Kubelka-Munk function (f(R_o)) can be expressed as:

\[
(f(R_o) \cdot h \nu) = C \cdot (h \nu - E_g)^{1/2}
\] ............................ (6.6)

where, \( f(R_o) = (1-R_o)^2/2R_o \) is the Kubelka-Munk function, \( R_o = R_{sample}/R_{standard} \), (here standard is taken to be BaSO_4) is diffuse reflectivity, \( C \) is a constant. This equation behaves similar to as Tauc relation, and \( f(R_o) \) is analogous to \( \alpha \). The value of band gap is evaluated by plotting \( f(R_o) \cdot h \nu \) versus \( h \nu \) and then extrapolating the linear portion of the curve to x-axis (Fig. 6. 17 b). The value of band gap for CTS nanoparticles is so found to be 1.1 eV. This value matches with that reported for tetragonal CTS thin films [7]. However, there are no reports on band gap of tetragonal CTS in powder, crystal or
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.

Fig. 6.17 (a) Diffuse reflectance spectrum of Cu$_2$SnS$_3$ powder (b) Plot of $(f (R) h\nu)^2$ versus $h\nu$ 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 \( \mu \text{V/K} \). 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:

\[
p = N_v \exp(A - \alpha_n/k)
\]

where, \( N_v \) is the effective density of state in valence band (= 6.91 x 10\(^{17}\) cm\(^{-3}\) for Cu$_2$SnS$_3$ at 300 K), \( A \) is a constant depending on scattering (= 4 for impurity scattering), \( \alpha_n \) 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:

\[
\mu = \sigma / p.e
\]

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 x 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 $1.2 \times 10^{20}$ 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 ($\sigma$) of a sample according to this model is expressed as:

$$\sigma = \sigma_0 \frac{T^{0.5}}{T} \exp \left( \frac{-E_a}{kT} \right) \quad \ldots \quad (6.9)$$

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](image_url)

Fig. 6.18: Temperature variation of electrical conductivity of pellets of Cu$_2$SnS$_3$ nanoparticles
References:


[10] Q. Liu, Z. Zhao, Y. Lin, P. Guo, S. Li, D. Pan, X. Ji, Alloyed (ZnS)$_x$(Cu$_2$SnS$_3$)$_{1-x}$ 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