Chapter 2

Literature Review

The chapter surveys the published reports on Cu₂SnS₃. This has been broadly categorized in two sections: Cu₂SnS₃ in thin films and other solid forms. Thin films have been deposited via different physical, chemical or physico-chemical routes. Apart from films, Cu₂SnS₃ have been prepared in other solid forms such as single crystals, polycrystalline powder and nanoparticles using variety of techniques. In general, it is found that the reported methods are quite cumbersome and require special conditions or equipments. Also, there is a lack of detailed study on fundamental physical properties such as, optical and electrical. There are some reports on solar cells of Cu₂SnS₃ which are contemporary to the period of this work. Thus it is indicative that there is much scope to develop newer low-cost route for processing and detailed characterization including photovoltaic properties.
Cu₂SnS₃, known as Mohite was discovered as a mineral in Uzbekistan [1] in the year 1982. It is named after Gunther Moh who first synthesized the compound in about 1975. Also, in 1974, single crystal of Cu₂SnS₃ was found to be semiconducting by Khanafer et al. [2]. However, it was Kuku and Fakolujo [3] in 1987, who were first to deposit thin films and demonstrate solar cells.

CTS have been produced in various forms, such as, thin films, bulk single crystals, polycrystalline and nanocrystalline solid forms. However, the literature shows sparse reports. Although the history of CTS is almost four decades old, only recently it has received some attention. Since purview of this thesis is solution processed route for deposition of CTS thin films. It will be worth to review all the reports on the synthesis whether intended for the thin films or other solid forms i.e. monocristalline, polycrystalline or nanocrystalline. In the first part, the reports on the deposition of CTS thin films are discussed whereas in later half synthesis of CTS in other solid forms is reviewed. At end of this chapter, tabulated summary of the reports on CTS is presented.

### 2.1 Crystal Structure

Structural parameters of CTS/Se prepared in different forms are given in Table 2.1.

<table>
<thead>
<tr>
<th>Cell Shape</th>
<th>Symmetry</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>E₉ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTS</td>
<td>Monoclinic</td>
<td>6.65</td>
<td>11.54</td>
<td>6.67</td>
<td></td>
</tr>
<tr>
<td>CTS</td>
<td>Triclinic</td>
<td>6.66</td>
<td>11.48</td>
<td>20.03</td>
<td>0.95</td>
</tr>
<tr>
<td>CTS</td>
<td>Cubic</td>
<td>5.43</td>
<td></td>
<td></td>
<td>1.15</td>
</tr>
<tr>
<td>CTS</td>
<td>Cubic</td>
<td>5.43</td>
<td></td>
<td></td>
<td>0.98</td>
</tr>
<tr>
<td>CTS</td>
<td>Tetragonal</td>
<td>5.41</td>
<td></td>
<td>10.82</td>
<td></td>
</tr>
<tr>
<td>CTS</td>
<td>Tetragonal</td>
<td>5.41</td>
<td></td>
<td>10.81</td>
<td>1.35</td>
</tr>
<tr>
<td>CTS</td>
<td>Hexagonal</td>
<td>3.90</td>
<td></td>
<td>17.27</td>
<td>0</td>
</tr>
<tr>
<td>CTS/Se</td>
<td>Monoclinic</td>
<td>6.95</td>
<td>12.05</td>
<td>6.97</td>
<td>0.84</td>
</tr>
<tr>
<td>CTS/Se</td>
<td>Cubic</td>
<td>5.73</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The monoclinic structure has 24 atoms in its primitive cell. All the cationic positions in the structure are tetragonally surrounded by S anions as in the zinc blende structure. The structure consists of (111) atomic layers linked by via perpendicular bonds, as in the case of zinc blende. Thus the monoclinic Cu₂SnS₃ structure can be
described as the superstructure of zinc blende. Monoclinic primitive cell can be described in terms of the basis vectors of zinc blende as follows

\[
\begin{pmatrix}
\tilde{a} \\
\tilde{b} \\
\tilde{c}
\end{pmatrix} = \begin{pmatrix}
-0.5 & 0.5 & 1.0 \\
1.5 & 1.5 & 0.0 \\
0.5 & -0.5 & 1.0
\end{pmatrix} \begin{pmatrix}
\tilde{e}_x \\
\tilde{e}_y \\
\tilde{e}_z
\end{pmatrix}
\]

where, \( \tilde{e}_x, \tilde{e}_y, \tilde{e}_z \) are the basis vectors of the zinc blende structure. The tetragonal phase is an intermediate of the two. The X-ray Diffraction pattern of all the forms thus is quite similar. Moreover, the structure of kesterite \( \text{Cu}_2\text{ZnSnS}_4 \) (CZTS) is also similar to zinc blende (ZnS). Consequently, CZTS, CTS, and ZnS cannot be differentiated by XRD especially, when crystallinity is low.

### 2.2 Cu$_2$SnS$_3$ thin films

The deposition routes of Cu$_2$SnS$_3$ (CTS) thin films can be broadly be divided into physical, chemical and physico-chemical methods. Either the entire deposition has been carried out using single source or in parts i.e. different components have been deposited by same or different techniques and then reacted to give Cu$_2$SnS$_3$ film.

Physical methods used during the deposition include vacuum evaporation, e-beam evaporation, sputtering, while chemical methods include chemical bath deposition, electrodeposition and spray pyrolysis. An overview of different methods employed in synthesis of Cu$_2$SnS$_3$ is depicted in Fig. 2.1.

![Fig. 2.1: Overview of different methods adopted for preparation of Cu$_2$SnS$_3$ films](image-url)
2.2.1 Physical Methods

The first report on the deposition of Cu₂SnS₃ thin films was documented by Kuku and Fakoluje [3] in 1987. The thin films were prepared by evaporation of Cu₂SnS₃ ingots. Synthesis of ingots consisted of melting together pure elements Cu, Sn and S in an evacuated quartz ampoule. Films obtained by evaporation of as-prepared ingots were found to be Cu deficient. Other set of samples were prepared by evaporation of ingots in Cu rich environment at 1373 K for compensation of copper. All the films were grown maintaining a substrate temperature of 473-573 K. However, X-ray diffractograms (XRD) of the films were not presented, electron microprobe analysis (EPMA) suggested, the films deposited as such were highly Cu deficient (Cu₀.₄₀₆SnS₁.₀₇) and when the deposition is carried out in Cu rich atmosphere the films were slightly Cu rich (Cu₂₁Sn₂₄). The optical measurements showed two set of band gaps: 1.065 eV (indirect) and 1.658 eV (direct) for Cu deficient films and 1.510 eV (indirect) and 1.770 eV (direct) for near stoichiometric films, respectively. The electrical measurements show films to have p-type conduction with resistivity of 1.7 Ohm.cm. The article also demonstrates Schottky barrier solar cell with device structure: soda lime glass (SLG)/Al/CTS/In/Ag (70% Transmittance). The metal films (Al, In, Ag) were deposited by thermal evaporation. The In/CTS solar cell displayed a photoconversion efficiency of 0.11 % with V_OC, J_SC and FF of 170 mV, 0.3 mA and 0.48, respectively. It was concluded that the poor performance of cell was due to poor collector ohmic contact (70 % transmitting Ag film => too thin).

This particular report is not only is the attempt of deposition of CTS thin film, but also established the potential of CTS for solar cell application.

2.2.2 Chemical Methods

The next report on the deposition CTS film is quite recent in 2009 i.e. after almost 22 years. This report by Bouaziz et al. [5] describes the deposition of Cu₂SnS₃ films via sequential deposition of CuₙS and SnS₂ by spray pyrolysis. The stacked binary sulfides were annealed in vacuum at 550 °C for 2 hrs., under S environment to yield Cu₂SnS₃ films. The X-ray Diffraction of Cu₂SnS₃ films show peaks that match with standard data for cubic Cu₂SnS₃. However, apart from assigned peak for Cu₂SnS₃, an extra peak probably due to CuₙS is observed. The morphology of the films as studied by atomic force microscopy (AFM) showed the presence of blob like structures formed due to the droplets from spray. This resulted in formation of patchy films with high roughness (rms roughness: 118 nm). The optical study revealed a direct band gap of 1.15 eV and an
absorption coefficient $> 10^4$ cm$^{-1}$. Further analysis of transmittance and reflectance data suggests reflectance data in range of 2.2-2.8 for the wavelength range 400-1800 nm.

Avallenda et al. [6] reports the synthesis of Cu$_2$SnS$_3$ films via on substrate solid state reaction of chemically bath deposited (CBD) SnS-CuS stacks. The chemical bath for depositing SnS and CuS consisted aqueous solution of metal salts (CuCl$_2$ or SnCl$_2$), triethanolamine (TEA) as chelating agent, liquor ammonia (aq. NH$_3$) and thioacetamide as sulphur source. To increase the thickness beyond the terminal thickness achieved during the CBD, the cycle were repeated with fresh solution. Such deposited stacks of CuS and SnS (SnS at Top) were heated at 350 °C under vacuum for 1 hour. The X-ray diffraction of films was found to have peaks due to Cu$_2$S as well along with Cu$_2$SnS$_3$. The observed peaks for Cu$_2$SnS$_3$ are assigned due to reflections from triclinic Cu$_2$SnS$_3$. The grazing incidence XRD (GIXRD) of the films suggest inhomogeneity in composition with thickness. A direct band gap of 0.95 eV and absorption coefficient of $10^4$ cm$^{-1}$ was ascertained for Cu$_2$SnS$_3$ films. The films are found to be p-type in nature with hole concentration and mobility of $>10^{18}$ cm$^{-3}$ and 80 cm$^2$V$^{-1}$s$^{-1}$, respectively as determined from Hall measurement. The temperature variation of conductivity from room temperature to 10 K, indicated thermally activated current transport near room temperature with activation energy of 0.45 eV.

Adelifard et al. [7] deposited CTS films by spray pyrolysis of a precursor solution containing copper (II) acetate, tin (II) chloride and thiourea. The ratio of Cu and Sn Salts were varied in the solution resulting in different Cu/Sn composing films. The best composition of Cu and Sn salt resulted in formation of monoclinic Cu$_2$SnS$_3$ phase along with Cu$_x$S phase. The estimation of Cu rich composition was verified with EDAX data. The films have rough topography with globular structures resulting in inhomogenous films with cracks and voids. A direct band gap of 1.68 eV and absorption coefficient $> 10^5$ cm$^{-1}$ was calculated from optical data. The films were p-type with resistivity approaching degenerate behaviour.

Meanwhile, Berg et al. [8] reported preparation of Cu$_2$SnS$_3$ films by annealing electrodeposited Cu and Sn film on Molybdenum (Mo) substrate under S and SnS environment at 550 °C for 2 hrs. Finally, films were etched with KCN solution to remove undesired Cu$_x$S phases. As deposited films were found to have monoclinic Cu$_2$SnS$_3$ with slightly Cu poor and S rich composition (Cu/Sn = 1.9 and [S]/([Cu]+[Sn])) as determined from EDAX. Electron micrographs of the films showed the formation of rough and patchy consisting pinholes. The band gap of the films was determined from 0.95 eV
(direct) with absorption coefficient $> 10^4$ cm$^{-1}$. The article is a first report on fabrication of CTS based heterojunction with device structure: Glass/Mo/CTS/CdS (CBD)/i-ZnO/ZnO:Al (RF sputtering)/Ni-Al (vacuum evaporation). The solar cell displayed an photo-conversion efficiency of 0.54 % with open circuit voltage ($V_{oc}$), short circuit current ($J_{sc}$) and fill factor (FF) of 104 mV, 17.1 mA/cm$^2$ and 30.4 %, respectively. Device showed an external quantum efficiency (EQE) of up to 60 %.

Koike et al. [9] reported synthesis Cu$_2$SnS$_3$ films by sulfurization of electrodeposited Cu/Sn stacked film on molybdenum substrates. The chemical bath conditions were different from that used by Berg et al. Sulfurization of the stacked metal films were done in S atmosphere only (unlike Berg et al., using SnS and S environment) at 580 K for 2 hrs. Different thickness of Cu and Sn layers yielded films of different stoichiometry as confirmed by X-ray Fluoroscence (XRF) and the reflections in XRD are found match with the standard data for tetragonal CTS. Morphology of the films also varied with the Cu/Sn ratio. In general, SEM of the films show presence of voids. The extent of inhomogeneities were observed to increase with annealing at higher temperature which is believed due to the reevaporation of Sn as SnS. Heterojunction thin film solar cell with device architecture: glass/Mo/CTS/CdS (CBD)/ZnO:Al (RF sputtering)/Al has been fabricated. The best performing cell delivered a photo-conversion efficiency of 2.84 % with $V_{oc}$, $J_{sc}$ and FF of 249 mV, 29.3 mA/cm$^2$ and 0.39, respectively. The cell also displayed an EQE of above 70 %.

Mathews et al. [10] used electrodeposition to deposit SnS and Cu films on the SnO$_2$:F substrates. These were then sulfurized to yield Cu$_2$SnS$_3$ films at 350 °C, though still consisted traces of Cu$_2$S. Together XRD and Raman spectroscopy confirmed the formation of monoclinic CTS as the primary phase (along with Cu$_{2-x}$S, as shown by Raman spectrum peak at 475 cm$^{-1}$). SEM and STEM techniques showed the presence of platelet like structure and selective area electron diffraction again confirmed the formation of monoclinic CTS. XPS confirmed the presence of Cu in +1 state only and stoichiometry of Cu:Sn:S was found to be 1.9:1:2.85. From the optical measurement a direct band gap with value 1.05 eV was determined. The films were found to be p-type in nature with dark conductivity of $4 \times 10^{-3}$ S/cm and were photo-conducting.

Guan et al. [11] deposited CTS film by successive ionic layer adsorption and reaction (SILAR) from solution containing SnCl$_2$, CuCl$_2$, and Na$_2$S as Sn, Cu and S source. The films were annealed at 653 K and 673 K resulting in CTS films with tetragonal and cubic phase, respectively (confirmed from XRD and Raman spectroscopic
data). The Cu/Sn ratio in the film varied as a function of temperature and as the
temperature increased the films became more Cu rich and Sn deficient. The topography of
the films was rough consisting of small grains as indicated by SEM. The band gap of
films was determined to be 1.05 eV and 1.19 eV for the films annealed at 380 and 400 °C,
respectively with absorption coefficient $> 10^4$ cm$^{-1}$.

### 2.2.3 Physico-chemical Methods

Amlouk et al. [12] utilized hybrid method for the deposition of Cu$_2$SnS$_3$ films. First SnS$_2$ films were deposited by spray pyrolysis of aqueous solution containing SnCl$_4$
and thiourea. In the next step, Cu films are deposited on to this by vacuum evaporation
and finally these bilayers were heated to react under S environment at 823 K for 2 hrs.
The resulted films consisted of numerous peaks in XRD not belonging to Cu$_2$SnS$_3$,
showing the presence of undesired binary phases such as Cu$_x$S and SnS$_y$. The peaks due
to Cu$_2$SnS$_3$, however are assigned to cubic phase. The Cu/Sn ratio in the films as
determined from energy dispersive analysis of X-rays (EDAX) is 0.53, which is off-
stoichiometric. As observed before for spray pyrolysis deposited films, the morphology of
these films was found to be perturbed and consisted of large rounded aggregates. A direct
band gap of 1.75 eV was determined by UV-Vis spectroscopy. Apart from compositional
and optoelectronic characterization of the films, mechanical properties of the films were
also analyzed. A mean micro hardness of 950 Hv (Vickers scale) was found for Cu$_2$SnS$_3$
which is even higher than that for CuInS$_2$ films deposited by similar route.

Femandes et al. [13] reported a detailed study on Cu$_2$SnS$_3$ films. The deposition
of CTS films involved sulfurization of d.c. magnetron sputtered stack of Cu/Sn layers.
Different sulfurization temperatures of 623 K, 673 K and 793 K have been used. Finally,
after deposition the films are etched with aq. KCN solution to eliminate undesired phases
of Cu$_x$S. All the three types of the samples deposited at three different temperatures are
studied throughout for compositional, structural and optical properties. The structural
analysis using XRD and electron back scattering techniques revealed formation of three
different phases at three different temperatures. In particular tetragonal Cu$_2$SnS$_3$ at 623 K,
Cubic Cu$_2$SnS$_3$ at 673 K and orthorhombic Cu$_2$SnS$_4$ at 793 K. Apart from the the peaks
due to desired phases, peaks due to Cu$_{2-x}$S are also observed in the diffraction pattern. On
the basis of structural confirmation from the diffraction, peaks in Raman spectrum have
been assigned as: 295, 318, 348 cm$^{-1}$ for orthorhombic, 303 and 355 cm$^{-1}$ peaks for cubic
Cu₂SnS₃ and feeble peaks at 336 and 351 cm⁻¹ due to tetragonal. Along with these, peak indicating the presence of Cu₂₋ₓS have also been observed. The composition of the films have been analyzed using inductively coupled plasma-optical emission spectroscopy (ICP-OES) and EDAX measurements and showed the samples to be slightly Cu rich. It is concluded that formation of Cu rich is result of loss of SnS during annealing at high temperature. Scanning electron micrographs of the films indicate formation of rough films with voids and cracks. The optical studies show an absorption coefficient of > 10⁴ cm⁻¹ for all samples, with direct band gap of 0.96, 1.35, 1.60 eV for tetragonal Cu₂SnS₃, Cubic Cu₂SnS₃ and orthorhombic Cu₃SnS₄, respectively. All the samples show p-type semiconducting behaviour with resistivity of the of 10⁻² Ohm.cm for Cu₂SnS₃ and of 10⁻⁴ Ohm.cm⁻¹ for Cu₃SnS₄ films.

Bouaziz et al. [14] deposited CTS films by annealing thermally evaporated Cu/Sn/Cu/Sn... stack under sulphur atmosphere at 803 K for 6 hrs. The X-ray diffraction shows the presence of Cu₂SnS₃ in cubic phase with compositional ratio Cu:Sn:S of 2:1:3 confirmed by EPMA. The average crystallite size calculated from Scherrer relation is 4.5 nm. Optical study disclosed an absorption coefficient of 10⁴ cm⁻¹ and a direct band gap of 1.11 eV. The morphology studied with the aid of scanning electron microscopy reveals the formation of compact and homogenous films with spherical particles with size ranging from 200-300 nm. Temperature variation of conductivity in the temperature range from RT to liquid nitrogen temperature i.e. 77 K divulged presence of two separate electrical transport mechanism: from 77 K – 238 K, variable range hopping and from 238-300 K thermally activated transport with activation energy of 25 meV.

Chino et al. [15] from the group of Prof. Katagiri deposited Cu₂SnS₃ films by sulfurization of Cu/Sn films deposited by e-beam evaporation. The sulfurization of films was carried out under high pressure of N₂ to suppress the re-evaporation of SnS. The films annealed at or below 823 K, showed presence of mainly tetragonal Cu₂SnS₃ whereas above 823 K, XRD indicates cubic and monoclinic structure. X-ray Fluoroscence (XRF) confirms the presence of Cu and Sn with Cu/Sn ratio ranging from 1.85 – 2.05 for temperatures 723 – 853 K. SEM divulged increase in grain size with increasing the annealing temperature. Band gap of the films lies between 0.95 – 1.0 eV with absorption coefficient >10⁴ cm⁻¹. Heterojunction solar cell of device structure: glass/Mo/CTS/CdS (CBD)/ZnO:Al (RF sputtering)/Al were fabricated. The best performing cell delivered a photo-conversion efficiency of 2.54 % with Jₜ, Vₜ and FF of 28.0 mA/cm², 211 mV and
0.43, respectively. It was found that the shunt resistance ($R_{SH}$) increases with increasing annealing temperature, thus causing the increase in the grain size and device structure.

2.2.4 Inferences:

1. The number of reports on deposition of CTS is very less to draw any general conclusion about the suitability of the method.
2. The preparation routes included multiple steps for deposition of metal film and/or binary sulfides and finally heating with or without sulphur atmosphere to yield CTS.
3. Not much work is there on direct liquid coating technique based deposition of Cu$_2$SnS$_3$ thin films. Mostly deposition routes employed physical deposition routes, atleast partially.
4. In most of the routes the other undesired products such as binary copper or tin sulfides also formed.
5. Cu$_2$SnS$_3$ exists in number of crystal structures such as cubic, tetragonal, monoclinic and triclinic depending upon conditions during and after deposition.
6. There is no agreement upon the optical properties such as band gap. Partially this may be due to presence of impurities.
7. There is no detailed study on the electrical and photoelectrical properties of Cu$_2$SnS$_3$ thin films especially transport properties.
8. There were no reports on heterojunctions (or any type rectifying contact, except the first in 1987) based on Cu$_2$SnS$_3$ before the period of this dissertation. Three heterojunction thin film solar cells reported are during the period of this work.
9. There is no report on modeling of rectifying junctions based on Cu$_2$SnS$_3$

2.3 CTS in monocrystalline, polycrystalline and nanocrystalline solid forms

As in case of thin films, reports on CTS in monocrystalline, polycrystalline and nanocrystalline solid forms are scanty and it is difficult to classify the work according to any category. Therefore a chronological treatment while discussion of reports is followed. The time line show shift in focus from monocrystalline in early days to polycrystalline and nanocrystalline forms in later period.
Khanafer et al. [2] describes the synthesis of Cu₂SnS₃ crystals in both monoclinic and cubic structure by reaction of Cu, Sn, S at > 1023 K using Bridgeman technique. The lattice parameters determined for the two form are: (i) cubic: a = 0.5445 nm and (ii) monoclinic: a = 2.310 nm, b = c = 0.625 nm and α = 101°. The resistivity of Cu₂SnS₃ single crystal in both forms is of order 10⁻² Ohm-cm in the temperature range of 77 K to room temperature. The Hall measurement carried out only on monoclinic form and suggest it to have n-type conduction with majority carrier concentration of 10²⁰ cm⁻³ and electron mobility 0.5 cm²V⁻¹s⁻¹.

Chen et al. [16] prepared single crystals of Cu₂SnS₃ by the direct reaction of stoichiometric amounts of elements: Cu, Sn, S at 1323 K for two days. The reaction mixture was then cooled to 973 K at rate of 5 K/hr. and finally quenched in air. This resulted in prismatic shaped crystals of Cu₂SnS₃. The electron probe micro analysis (EPMA) of the single crystals indicated a stoichiometry of 2:1:3 for the Cu:Sn:S. The single crystal X-ray diffraction data has been studied extensively. The full profile structural refinement of XRD data suggests the crystals to have tetragonal symmetry with I-42m space group. The structure is analogous to stannite structure and consists of composite metal sites i.e. Cu and Sn occupy the same site. The structure contains nearly regular tetrahedron around each metal site surrounded by chalcogen ions and no two metal sites are linked directly. The lattice parameters of the refined unit cell are a = 0.54126 nm and c = 1.0823 nm.

Onoda et al. [17] reports the synthesis of single crystal of Cu₂SnS₃ by direct reaction of Cu₂S and SnS₂ at 1123 K for two days, followed by cooling and maintaining at 873 K and finally quenching in water. The resultant crystals were needle shaped. EPMA disclosed the approximate composition of Cu:Sn:S as 1.98:1.05:3. The single crystal X-ray diffraction data suggested monoclinic unit cell with lattice parameters a = 1.9958 nm, b = 1.11537 nm and c = 0.6665 nm with β = 109.39°. The authors point out that both monoclinic and tetragonal phases are slight distortion of cubic phase only. The tetragonal structure is intermediate structure between the high temperature form and monoclinic form. The monoclinic structure as said in the beginning is the superstructure of sphalerite structure. As in the tetragonal structure, in monoclinic structure as well all the metal sites are tetrahedrally coordinated. However there are two different tetrahedron environment for Cu atoms located as single atom or at composite site.

Fiechter et al. [18] studied the phase diagram of Cu-Sn-S ternary system using differential thermal analysis and X-ray diffraction. Cu₂SnS₃ forms at midpoint of Cu₂S
and SnS$_2$ line and melts at 1129 K. The X-ray diffraction of Cu$_2$SnS$_3$ indicates cubic zinc blende crystal structure. Based on this, ingots of Cu$_2$SnS$_3$ were prepared by reacting Cu$_2$S and SnS$_2$ in 1:1 ratio. By ellipsometric measurements a direct band gap of 0.93 eV was determined for Cu$_2$SnS$_3$ ingots.

Li et al. [19] synthesized nanocrystalline Cu$_2$SnS$_3$ using solvothermal technique. Ethylenediamine (boiling point = 389 K) was used as the solvent. Cu$_2$SnS$_3$ was prepared by reaction of stoichiometric amounts of CuCl$_2$, Sn powder and S powder in supercritical ethylenediamine at 453 K in teflon lined autoclave for 15 hrs. Use of ethylenediamine offers two prong advantages due to its suitable boiling point and its capability to form chelate with metal ions. X-ray diffraction indicated the formation of Cu$_2$SnS$_3$ in monoclinic phase. Both TEM and XRD (broadening of peak) suggested formation of nanocrystalline product with median sizes around 10 nm. The composition of the product from X-ray photoelectron spectroscopy indicated presence of Cu, Sn, S with relative ratio of 1.986: 1.0: 3.035, respectively. From the absorption data a band gap of 1.88 eV was determined. The temperature variation of conductivity in temperature range of 18 to 300 K showed a linear behaviour. However no specific activation energy for the transport was derived.

Bloeb and Jansen [20] synthesized microcrystalline Cu$_2$SnS$_3$ by wet chemical route. First suspensions of CuCl$_2$, SnCl$_4$ and excess thiourea were made in diethylene glycol. The mixture was then heated at 448 K. To avoid the formation of CuS, an excess of SnCl$_4$ than the stoichiometric metal ratio was added. Finally in order to remove the surface bound diethylene glycol, the solids were washed with ethanol and centrifuged. The final product was dried at room temperature in vacuum. XRD indicated the formation of cubic Cu$_2$SnS$_3$ with average crystallite size of 4 nm. The scanning electron micrographs show presence of spherical particles, with sizes ranging from 750 – 850 nm.

Wu et al. [21] synthesized Cu$_2$SnS$_3$ in hexagonal structure using solvothermal technique. The reaction was carried out at 453 K for 12 hrs. The composition of the product was analyzed with EDAX and ICP-OES, latter gave the relative elemental ratio of 2.202: 1.116: 2.996. XPS confirmed the presence of Cu, Sn, S respectively in +1, +4 and -2 states only. TEM depicted presence of spherical particles with size ~ 60 nm and High Resolution – TEM again indicated the presence of hexagonal CTS. The experimental XRD for the product matches with the simulated XRD calculated from $\alpha$-CuSe structure. The electronic structure calculations were done, which predicts hexagonal CTS to be conducting as finite density of states were calculated at Fermi level. A current-
Voltage (I-V) characteristic of the product was linear and gave conductivity value of 3.43 s/cm. No actual measurements were performed to find carrier concentration and mobility. The material was proposed to be a potential candidate for Li-ion battery application owing to its good conductivity and large interplanar distance, however, no electrochemical cell was tested.

Liu et al. [22] prepared nanocrystalline alloys of CTS with ZnS and CuInS₂ by a wet chemical technique. Use of two different capping agents during the synthesis resulted in Zinc Blende or wurtzite structure. Both compositions i.e. \((\text{ZnS})_x (\text{Cu}_2\text{SnS}_3)_{1-x}\) and \((\text{CuInS}_2)_x(\text{Cu}_2\text{SnS}_3)_{1-x}\) were found to follow Vegard’s law over entire composition range. From the optical studies it was found that band gap of \((\text{ZnS})_x (\text{Cu}_2\text{SnS}_3)_{1-x}\) varies from 3.63 to 0.94 eV and for \((\text{CuInS}_2)_x(\text{Cu}_2\text{SnS}_3)_{1-x}\) varies from 1.35 to 0.94 eV for \(x\) changing from 1 to 0. XPS confirmed presence of Cu, Sn, S in +1, +4, -2 states, respectively and EDS spectrum indicated the composition to be nearly stoichiometric. TEM divulged presence of spherical particles with sizes varying in narrow range of 10-12 nm.

Qu et al. [23] synthesized mesoporous Cu₂SnS₃ using solvothermal route. The reaction mixture consisted of stoichiometric amounts of CuCl, SnCl₄ and thiourea dissolved in ethanol as Cu, Sn and S sources respectively. Along with this PEG-1000 was added as capping agent. The reaction was carried out at 453 K for 20 hrs. The final product was washed with ethanol and dried in vacuum for 4 hrs. The X-ray diffraction of the final product indicated the formation of cubic CTS. SEM revealed the presence of spherical aggregates of sizes around 200 nm with porous morphology. Also, TEM showed presence voids within aggregates. The products were found to consist of Cu₂SnS₃ with Cu rich composition as analyzed by EDS. The surface area and pore size distribution was studied by Braunauer-Emmet-Teller (BET) method based on N₂ adsorption – desorption. As synthesized CTS exhibited a surface area of 17.9 m²/g and pore distribution within range of 2 – 15 nm with a pore volume of 0.091 cm³/g. Charge – discharge cycles of actual electrochemical cells consisting of CTS as anode were also investigated. It was found that discharge capacity of cell reduced from initial cycle value of 936 mAh⁻¹ to 436 mAh⁻¹ after 50th cycle with a cut off voltage of 1.3 V. The analysis of anode after initial cycles suggested decomposition of CTS to Cu and Sn nanoparticles.

Liang et al. [24] synthesized nanostructured Cu₂SnS₃ using solvothermal technique. The reaction was carried out using ethylene glycol as the medium with metal salts (CuCl₂ and SnCl₂) and thiourea as sulphur source, respectively. The reaction mixture
was heated at 453 K for 16 hrs. The final product was washed with ethanol and dried under vacuum at 333 K for 6 hrs. XRD suggested formation of cubic structure and EDS showed the presence of Cu, Sn, S with relative ratio of 21.75, 12.15, 35.35, respectively. XPS also indicated the presence of only Cu, Sn, S +1, +4, -2 states, respectively. SEM depicted spherical aggregates surrounded by flake shaped structures. From the absorption in UV-Vis spectrum, a band gap of 1.26 eV was deduced. The reaction was carried using other solvents such as 1,4 butanediol, glycol, ethanediamine. Changing the solvent resulted in Cu2SnS3 in different structural phases including wurtzite and cubic phase.

Chen and Ma [25] prepared nanostructured Cu2SnS3 from solvothermal route. The metal salts and thioacetamide as S source were dissolved in water-ethanol mixture and heated in an autoclave in temperature range 453-493 K for various duration 5.5 – 12.5 hrs. XRD indicated Cu2SnS3 with a transition in structural phase from cubic to hexagonal by changing the concentration of ethanol in solvent mixture. The formation of tetragonal CTS in 50 % ethanol concentration was confirmed by Raman spectroscopy. UV-Vis spectroscopy revealed a band gap of 1.42 eV.

Chen and Waclawik [26] prepared Cu2SnS3 by wet chemical route. The synthesis included overnight reaction of CuI, SnCl2 and dodacanethiol as the sulphur source at 493 K. The final product varied from wurtzite to cubic (zinc blende), depending upon, whether octadecence or oleylamine was used as solvent. TEM showed CTS-Zinc Blende (ZB) to be nanocrystalline with trigonal pyramidal shape with size around 150 nm. Wurtzite CTS synthesized octadecene as solvent was also confirmed by selective area electron diffraction.

2.3.1 Inferences:

1. As seen from the studies on monocrystalline CTS, it exists in number of structural phases i.e. cubic, tetragonal, monoclinic. These forms are super structures of zinc blende structure and are homomorphic. Thus have similar diffraction pattern to other zinc blende kind of structures such as ZnS and CZTS.

2. Most of the methods of synthesis of polycrystalline and nanocrystalline CTS include either solvothermal or wet chemical route, which in general are tedious, time consuming, require special conditions and capping agents and often the yields are low.

3. Characterization of these products does not focus on CTS as a photovoltaic material.
4. No report is there using these forms for deposition of solar cells via a direct liquid coating.

2.4 Photovoltaic properties

Investigations on photovoltaic properties of CTS are sparse. As mentioned earlier, Kuku and Faklujo [3] in 1987 was first to fabricate CTS Schottky barrier solar cell with modest photoconversion efficiency of 0.11 %. After 25 years, in 2012 studies have yielded solar cells with efficiencies of nearly 3 %. Table 2.2 presents properties of CTS thin film solar cells reported so far.

<table>
<thead>
<tr>
<th>Author</th>
<th>Method of preparation</th>
<th>Solar Cell architecture</th>
<th>Efficiency (%)</th>
<th>V_oc (mV)</th>
<th>J_sc (mA/cm)</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kuku &amp; Faklujo (1987) [3]</td>
<td>Vacuum Evaporation</td>
<td>SLG/Al/CTS/In/Ag Schottky</td>
<td>0.11</td>
<td>170</td>
<td>0.3</td>
<td>0.41</td>
</tr>
<tr>
<td>Berg et al. (2012) [8]</td>
<td>ED Cu/Sn + heat S &amp; SnS</td>
<td>SLG/Mo/CTS/CdS/i-ZnO/ZnO:Al/Ni-Al</td>
<td>0.54</td>
<td>104</td>
<td>17.1</td>
<td>0.30</td>
</tr>
<tr>
<td>Koike et al. (2012) [9]</td>
<td>ED Cu/Sn + heat S</td>
<td>SLG/Mo/CTS/CdS/i-ZnO/ZnO:Al/Al</td>
<td>2.84</td>
<td>249</td>
<td>29.3</td>
<td>0.39</td>
</tr>
<tr>
<td>Chino et al. (2012) [15]</td>
<td>Cu/Sn EB evap.+ heat S &amp; N2</td>
<td>SLG/Mo/CTS/CdS/i-ZnO/ZnO:Al/Al</td>
<td>2.54</td>
<td>211</td>
<td>28.0</td>
<td>0.43</td>
</tr>
</tbody>
</table>

Table 2.2 reveals that for best solar cells, V_{oc} is about 250 mV which is lower than that expected. Further, Fill Factor is about 0.4 which is also low. Presently, fabrication of solar cell involve multiple steps including sulfurization of sequentially deposited layers of metals. Secondly, heterojunction developed so far use Mo as back contact and no alternative back contact have been tried. As been observed for in case of CZTS solar cells, the presence of MoS_{2} interfacial layer which leads to an additional barrier causing deteriorating effect on device performance [27]. V_{oc} of the cells is much lower than expected theoretical barrier height. This indicates probably non-uniformity and leakage at the junction which lowers the shunt resistance and thus V_{oc}.

The above literature review on CTS is summarized and presented in Table 2.3 and 2.4.
**Table 2.3: Summary of reports on Cu₂SnS₃ thin films**

<table>
<thead>
<tr>
<th>Authors &amp; year</th>
<th>Synthesis</th>
<th>Structure &amp; composition</th>
<th>Morphology</th>
<th>Optical properties</th>
<th>Electrical, Photovoltaic Properties &amp; Misc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Kuku &amp; Faklujo (1987)</td>
<td>v. evap. CTS ingots A. without Cu atm B. with Cu atm @ 1100 °C</td>
<td>A. CuₓₙSnS₁₋ₓ B. Cuₓ₂SnS₂₋ₓ</td>
<td>A. Eₕ: 1.065 (ID), 1.658 (D) eV B. Eₕ: 1.510(ID), 1.770 (D) eV</td>
<td>A. p-type, p: 1.7 Ohm.cm SLG/Al/CTS/Au Schottky solar cell PCE: 0.11 %, Vₘₚ: 170 mV, Jₘₚ: 0.3 mA cm⁻², FF: 0.41</td>
<td></td>
</tr>
<tr>
<td>2 Bouaziz et al (2009)</td>
<td>CuₓS (SP) + SnS₂ (SP) + heat (550 °C, S atm)</td>
<td>cubic CTS + CuₓS</td>
<td>rough, with blobs structures due to micro droplets, rms roughness: 118 nm</td>
<td>Eₕ: 1.15 eV (D) α: &gt;10⁶ cm⁻¹ η: 2.2-2.8 (400-1800 nm)</td>
<td></td>
</tr>
<tr>
<td>3 Amlouk et al. (2010)</td>
<td>SnS₂ (SP) + Cu (v. evap.) + heat (550 °C, S atm) Cu/Sn: 0.53</td>
<td>cubic CTS + CuₓS + SnS₂</td>
<td>perturbed surface with round aggregates</td>
<td>Eₕ: 1.75 eV (D) Microharness: 950 Hv (mean)</td>
<td></td>
</tr>
<tr>
<td>4 Fernandes et al. (2010)</td>
<td>Cu/Sn (dc magn. Sputt.) + heat (S atm; 350, 400, 450 °C) KCN etch</td>
<td>350 °C: tetr. CTS, (Raman:303, 355 cm⁻¹; 400 °C: cubic CTS (Raman:336, 351 cm⁻¹) + CuₓS Cu rich comp. (ICP-OES)</td>
<td>Rough films voids &amp; cracks</td>
<td>Eₕ: 0.96 eV (D) cubic; 1.35 eV (D) tetr. α: &gt;10⁴ cm⁻¹</td>
<td></td>
</tr>
<tr>
<td>5 Avallenda et al. (2010)</td>
<td>SnS (CBD) + CuS (CBD) + heat (vacuum, 350 °C)</td>
<td>triclinic CTS + CuₓS</td>
<td>Eₕ: 0.95 eV (D) α: &gt;10⁴ cm⁻¹</td>
<td>p-type; p: 10¹⁵ cm⁻³; μ: 80 cm²V⁻¹s⁻¹ Carrier transport: 10 – RT (TA) with Eₚ: 0.45 eV</td>
<td></td>
</tr>
<tr>
<td>6 Bouaziz et al. (2011)</td>
<td>Cu/Sn (v. evap.) + heat (S atm, 530 °C) Cu/Sn: 2:1:3</td>
<td>compact, homogenous films ranging 200-300 nm</td>
<td>Eₕ: 1.15 eV (D) α: &gt;10⁴ cm⁻¹</td>
<td>p-type; Carrier transport: 77-238 K (VRH) &amp; 77-238 K (TA) with Eₚ: 0.025 eV</td>
<td></td>
</tr>
<tr>
<td>Table 2.3: Summary of reports on Cu₂SnS₃ thin films (Contd.)</td>
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<tr>
<td>7</td>
<td>Berg et al. (2012)</td>
<td>Cu/Sn on Mo subs. (ED) + heat (S &amp; SnS atm, 550 °C)</td>
<td>monoclinic CTS + Cu₂S; Cu:Sn::1:9:1</td>
<td>rough, patchy with pinholes</td>
<td>E₀: 0.95 eV (D)</td>
</tr>
<tr>
<td>8</td>
<td>Adelfard et al. (2012)</td>
<td>SP of Aq. P. Sol. [Cu (OAc)₂ + SnCl₂+Tu] + KCN etch</td>
<td>monoclinic CTS + Cu₂S, Cu rich</td>
<td>Rough, patchy, inhomogenous, cracks &amp; voids</td>
<td>E₀: 1.68 eV (D)</td>
</tr>
<tr>
<td>9</td>
<td>Koike et al. (2012)</td>
<td>Cu/Sn on Mo subs. (ED) + heat (S atm, 580 °C)</td>
<td>tetr. CTS</td>
<td>presence of voids</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Chino et al. (2012)</td>
<td>Cu/Sn EB evap.+ heat (S &amp; N₂ atm, 450-550 °C)</td>
<td>&lt;550 °C tetr., &gt;550 °C cubic &amp; monoclinic</td>
<td>Increase in grain size with temperature</td>
<td>0.95-1.0 eV (D)</td>
</tr>
<tr>
<td>11</td>
<td>Mathews et al. (2013)</td>
<td>SnS/Cu on SnO₂:F (ED) + Heat (S atm' 350 °C)</td>
<td>Monoclinic CTS + Cu₂S; Cu:Sn::1:9:1:2.85</td>
<td>Platelet like structures</td>
<td>E₀: 1.05 eV (D)</td>
</tr>
<tr>
<td>12</td>
<td>Guan et al. (2013)</td>
<td>SILAR from SnCl₂, CuCl₂, Na₂S aq. Sol. + heat (380, 400 °C)</td>
<td>380 °C: tetr. CTS 400 °C: cubic CTS</td>
<td>Rough with small grains</td>
<td>E₀: 1.05 eV (D)</td>
</tr>
</tbody>
</table>
### Table 2.4: Summary of reports on Cu$_2$SnS$_3$ in Mono-, poly- & nano-crystalline forms

<table>
<thead>
<tr>
<th>Authors &amp; year</th>
<th>Form &amp; Synthesis</th>
<th>Structure &amp; composition</th>
<th>Shape &amp; size</th>
<th>Optical properties</th>
<th>Electrical properties &amp; Misc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Khanafer et al. (1974)</td>
<td>Monocrystalline CTS Cu, Sn, S + heat 750 °C Bridgeman technique</td>
<td>cubic: a: 0.5445 nm monoclinic: a: 2.310 nm, b=c: 0.625 nm; α: 101°</td>
<td></td>
<td></td>
<td>ρ: 10$^8$ Ohm cm (cubic &amp; monoclinic; 77 K-RT) monoclinic: n-type; n: 10$^{20}$ cm$^{-3}$; μ: 0.5 cm$^2$V$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>2 Chen et al. (1998)</td>
<td>Monocrystalline CTS Cu, Sn, S + heat 1050 °C 2 days Cooled to 750 °C @ 5°C/hr. &amp; quenched in air</td>
<td>tetragonal CTS (I-42m) Rietveld analysis A: 0.54126 nm, c: 1.0823 nm Cu:Sn:S::2:1:3 (EPMA)</td>
<td>prismatic shape crystals</td>
<td></td>
<td>Extensive XRD studies</td>
</tr>
<tr>
<td>3 Onoda et al. (2000)</td>
<td>Monocrystalline CTS Cu$_2$S$^+$ Sn$_i$S$_3$ + heat 850 °C 2 days, Cooled to 600 °C. &amp; quenched in water</td>
<td>monoclinic CTS a: 1.9558 nm, b: 1.11537 nm, c: 0.6665 nm; α: 109.39° Cu:Sn:S::1.98:1.05:3 (EPMA)</td>
<td>needle shape crystals</td>
<td></td>
<td>Extensive XRD studies</td>
</tr>
<tr>
<td>4 Flechter et al. (2003)</td>
<td>CTS ingots Cu$_2$S$^+$Sn$_i$S$_3$ +heat</td>
<td>cubic CTS</td>
<td></td>
<td></td>
<td>Ellipsometric measurements E$_p$: 0.95 eV (D) α: &gt;10$^4$ cm$^{-1}$ Cu-Sn-S phase diagram studies melting point of CTS: 856 °C</td>
</tr>
<tr>
<td>5 Li et al. (2000)</td>
<td>Nanocrystalline CTS Solvothermal: CuCl$_2$SnCl$_3$, S in ethylene diamine @ 180 °C</td>
<td>monoclinic CTS Cu:Sn:S::1.986:1.0:3.035</td>
<td>Spherical particles with median size ~10 nm</td>
<td>E$_p$: 1.88 eV</td>
<td>σ vs 1/T (10-300 K): linear behaviour</td>
</tr>
<tr>
<td>6 Bloeb &amp; Jansen (2003)</td>
<td>Microcrystalline CTS Wet chemical route: CuCl$_2$SnCl$_3$, excess TU in diethylene glycol @ 175 °C</td>
<td>cubic CTS</td>
<td>Spherical particles with median sizes: 750-850 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Table 2.4: Summary of reports on Cu$_2$SnS$_3$ in Mono-, poly- &amp; nano- crystalline forms (contd.)</td>
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<tr>
<td>7</td>
<td>Wu et al. (2007)</td>
<td>nanocrystalline CTS</td>
<td>hexagonal CTS</td>
<td>Cu:Sn:S::2.202:1.116:2.996</td>
<td>( \sigma: 3.43 \text{ S/cm} )</td>
</tr>
<tr>
<td>8</td>
<td>Qu et al. (2011)</td>
<td>mesoporous CTS</td>
<td>cubic CTS</td>
<td>Spherical particles with median size ( \sim 60 \text{ nm} )</td>
<td>BET: surface area 17.9 m$^2$/g, pore distribution 2-15 nm, Studied electrochemical cell using CTS as anode</td>
</tr>
<tr>
<td>9</td>
<td>Liu et al. (2010)</td>
<td>Nanocrystalline CTS (ZnS)$_x$ (Cu$_x$SnS$<em>3$)$</em>{1-x}$, and (CulnS)$_x$,(Cu$_x$SnS$<em>3$)$</em>{1-x}$</td>
<td>ZB and wurtzite CTS follow Vegard's law for all ( x ) nearly stoic. (EDS)</td>
<td>Spherical particles with median sizes: 10-12 nm</td>
<td>( E_g: 0.94-3.35 \text{ eV} ) (ZnS)$_x$ (Cu$_x$SnS$<em>3$)$</em>{1-x}$, ( ; 0.94-1.35 \text{ eV} ) (CulnS)$_x$,(Cu$_x$SnS$<em>3$)$</em>{1-x}$</td>
</tr>
<tr>
<td>10</td>
<td>Liang et al. (2013)</td>
<td>nanocrystalline CTS</td>
<td>cubic CTS</td>
<td>Spherical aggregates with flake like structure around</td>
<td>( E_g: 1.26 \text{ eV} )</td>
</tr>
<tr>
<td>11</td>
<td>Chen &amp; Ma (2013)</td>
<td>nanocrystalline CTS</td>
<td>cubic to hexagonal with ethanol concentration</td>
<td>Tetragonal CTS for 50% ethanol (Raman)</td>
<td>( E_g: 1.42 \text{ eV} ) (tetragonal)</td>
</tr>
<tr>
<td>12</td>
<td>Chen &amp; Waclawik (2013)</td>
<td>nanocrystalline CTS</td>
<td>cubic to hexagonal with ethanol concentration</td>
<td>Tetragonal CTS for 50% ethanol (Raman)</td>
<td>( E_g: 1.42 \text{ eV} ) (tetragonal)</td>
</tr>
</tbody>
</table>

**Source:** Table 2.4 from the given document.
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http://dx.doi.org/10.1016/j.tsf.2012.05.085.


[22] 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$_2$SnS$_3$)$_{1-x}$ nanocrystals with arbitrary composition and broad tunable band gaps, Chemical Communications 47 (2011) 964-966

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