Colloidal Synthesis and Characterization of Nanowires of Triclinic Cu$_3$SnS$_4$

Maya Mathew $^1$, KC Preetha $^2$

$^1$ Payyannur College, Payyannur, PIN 670327
$^2$ Sree Narayana College, Kannur PIN 670007
E-mail: mayamathew02@gmail.com

Abstract. In this paper we report the colloidal synthesis and characterization of triclinic nanowires of Cu$_3$SnS$_4$. The XRD pattern of the as-prepared sample matches well with JCPDS No. 33-0501. Triclinic crystals of average crystallite size of about 3.7 nm were formed. The absorption spectrum consists of two SPR peaks which are characteristic of nanowires, corresponding to the axial and longitudinal vibrations of electrons on its surface. The bandgap of Cu$_3$SnS$_4$ nanowire is found to be 1.66 eV and so it can find application in the absorber layer of solar cells.

1. Introduction
The current research is to explore new and efficient materials for increasing the efficiency of solar cells above the Shockley Queisser limit [1-6]. Nanostructures are widely studied as they pose promising applications due to their unusual properties [7]. Materials exhibiting surface plasmon resonance are very important for solar cells due to the presence of free electrons which enhance light absorption at the desired wavelength [8]. Cost effective materials are on demand now for lowering the production cost of solar cells. One among such materials is Copper tin sulphide (CTS). Several forms of CTS have been studied and reported. It is a p-type semiconductor having a high absorption coefficient of 10$^4$ cm$^{-1}$ and a band gap lying in the near IR range, which makes it an ideal material for IR photodetection and in photovoltaics. Bulk crystals, microspheres, nanowires and quantum dots of CTS have been synthesized. Solvothermal synthesis, hydrothermal synthesis, microwave irradiation etc. were the techniques used for the synthesis of these nanostructures [9].

In this paper we describe a very cost effective and simple technique for the synthesis of nanowires of copper tin sulphide. The so prepared nanowires have been found to possess novel properties which can be adopted in solar cell absorber layer to increase its efficiency.

2. Experimental
2.1. Materials and Methods
The precursors used were copper chloride (CuCl$_2$.2H$_2$O), Tin chloride (SnCl$_2$.2H$_2$O) and Sodium sulphide (Na$_2$S). Trisodium citrate (TSC) was used as the capping agent. Millimolar solutions of Copper chloride (CuCl$_2$.2H$_2$O), Tin chloride (SnCl$_2$.2H$_2$O) and Sodium sulphide (Na$_2$S) in
the ratio of 3:1:4 were taken using water as the solvent. 1.6M solution of sodium citrate was used as the capping agent.

2.2. Characterization
For characterization, X-ray diffractometer (Bruker AXS-8 advance) with Cu Kα radiation of wavelength 1.5406 Å as the source, Scanning Electron Microscope (JEOL Model JSM6490) equipped with an EDAX analyzer to investigate qualitatively the sample stoichiometry, a Hitachi-U-3410 UV-Vis-NIR spectrophotometer and FTIR (ATR) were used.

3. Results and Discussions
3.1. Structural studies
Figure 1 shows the XRD pattern of CTS nanowires. The peaks characteristic of triclinic Cu₃SnS₄ has been labelled according to JCPDS No. 33-0501. The d-spacing and other information regarding the crystallites have been tabulated below (Table.1). The crystallite size and lattice parameters have been calculated from the most intense peak corresponding to (116) (Table 2).

![Figure 1. XRD pattern of nanowires of Cu₃SnS₄](image)

| 2-theta | h  | k  | l  | d-spacing |
|---------|----|----|----|-----------|
| 22.9    | 1  | 1  | 6  | 3.88      |
| 28.5    | 0  | 0  | 12 | 3.13      |
| 29.4    | 2  | 1  | 0  | 3.04      |
| 32.1    | 1  | 1  | 11 | 2.79      |
| 48.3    | 0  | 0  | 20 | 1.88      |

**Table 1.** Particulars of crystallites of triclinic Cu₃SnS₄.

| hkl    | FWHM (m°) | Crystallite size(nm) | a  | b  | c  |
|--------|-----------|----------------------|----|----|----|
| (116)  | 2.3209    | 3.766                | 6.525 | 7.523 | 37.66 |

**Table 2.** Crystallite size of Cu₃SnS₄.
3.2. Morphological studies

Figure 2 shows the SEM images of Cu₃SnS₄ taken at magnifications of 180X and 250X. The nanowires of Cu₃SnS₄ are clearly visible. Figure 3 gives the EDS spectrum, showing the presence of copper, tin and sulphur.

![SEM images of Cu₃SnS₄ nanowires](image)

**Figure 2.** SEM images of Cu₃SnS₄ nanowires (a) 180X (b) 250X.

![EDS spectrum of Cu₃SnS₄](image)

**Figure 3.** EDS spectrum of Cu₃SnS₄.

3.3. Surface Studies

FTIR of the as prepared sample were taken and studied for a better understanding of surface bonding and its properties. Figure 4 shows the FTIR spectrum of CTS nanowires. The list of bonds causing the vibrational energies is tabulated in Table 3.
Figure 4. FTIR spectrum of $Cu_3SnS_4$ nanowires.

| Wavenumber (in cm$^{-1}$) | Nature of bond  |
|---------------------------|-----------------|
| 1050                      | Ethane          |
| 1382                      | Butane          |
| 1563                      | Ethene          |
| 3323                      | Methyl alcohol  |

Table 3. Vibrational energies of CTS nanowires.

3.4. Optical Studies
Figure 5(a) shows the absorption spectrum of CTS nanowires. There are two Surface Plasmon Resonance (SPR) peaks in the NIR range of 800-900 nm corresponding to the electron oscillations along the axial and longitudinal directions. Plasmon resonance band observed in the absorption spectrum of $Cu_3SnS_4$ nanowires is depicted in figure 5(b). The band gap of CTS nanowires found from Tauc plot as shown in Figure 6 comes at 1.66 eV, favourable bandgap for a material used in the absorber layer of solar cells.

4. Conclusion
Through this work, we have achieved in synthesizing nanowires of copper tin sulphide using a cost effective colloidal synthesis technique. The crystals formed are that of $Cu_3SnS_4$, the XRD pattern matching with JCPDS 33-0501. The FTIR spectrum shows the presence of a citrate coating. SEM images confirm the formation of nanowires and EDS shows the presence of Cu, Sn and S. The bandgap of CTS nanowires is 1.66 eV which is apt for a material to be used as an absorber layer in solar cells.
Figure 5. (a) Absorption spectrum of Cu$_3$SnS$_4$ nanowires. (b) Plasmon resonance band observed in the absorption spectrum of Cu$_3$SnS$_4$ nanowires.

Figure 6. Bandgap of Cu$_3$SnS$_4$ nanowires at 1.66eV.

Acknowledgments
The authors would like to sincerely thank STIC, Cochin and NCESS, Trivandrum for rendering us the necessary characterization facilities.

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