Chapter 4
Wet Chemical Synthesis and Characterization of CuAlS$_2$ Nanoparticles
4.1. INTRODUCTION

The I–III–VI$_2$ chalcopyrite compounds (I = Cu, Ag; III = Al, Ga, In; and VI = S, Se, Te) have generated much interest as semiconductors [1, 2] due to their use in photovoltaic optical detectors, solar cells, and light emitting diodes or in nonlinear optical devices. Among chalcopyrite semiconductors, CuAlS$_2$ has the widest optical bandgap of 3.49 eV and the doped CuAlS$_2$ are the candidates for full color optical material [3-5]. In addition, the exciton binding energy of this material (70 meV) [6] is larger than other ultraviolet emitting materials such as ZnO (60 meV), ZnS (39 meV) and GaN (21 meV) [7]. In other words, excitons in CuAlS$_2$ can exist stably at room temperature (the thermal energy of room temperature is 24 meV) [6]. Therefore, CuAlS$_2$ is expected to be a material for an ultraviolet emitter with high emission efficiency at room temperature. This compound can be considered as a prospective material for green-to-blue light emitting diode (LED) application [8].

In recent time the CuAlS$_2$ in nano form has been synthesized by different techniques, such as nanoparticles by facile heat arrested method [9], nanocrystals by colloidal route [10], nanocrystals by ball milling [11], nanowires by the direct polyol method [12], nanorods by wet chemical method [13], etc. Among these synthesis methods, the wet chemical method was found to be more convenient, less expensive and easy to tailor the chemistry of the nanostructures.

In this paper the wet chemical method was used to synthesise CuAlS$_2$ nanoparticles. The synthesized nanoparticles comparative study of the average crystallite size from the powder X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements were carried out. The stress, strain and crystallite size values were estimated using different means of Hall-Williamson relation such as, uniform deformation model (UDM), uniform stress deformation model (USDM), uniform deformation energy-density model (UDED) and also by size-strain plot method (SSP).
4.2. EXPERIMENTAL

Cupric chloride (CuCl₂·2H₂O) [S D Fine-Chem. Ltd., Mumbai, India], triethanolamine (TEA) (C₆H₁₅NO₃) [Sisco Chem. Pvt. Ltd., Mumbai, India], aluminium chloride (AlCl₃·6H₂O) [Oxford Laboratory, Mumbai, India], ammonia liquid (NH₃) [Chiti-Chem Corporation, Vadodara, India], sodium hydroxide pellets (NaOH) [Loba Chemie, Mumbai, India] and thiourea (NH₂CSNH₂) [Chiti-Chem Corporation, Vadodara, India] were used for the synthesis of CuAlS₂ nanoparticles.

In the synthesis of CuAlS₂ nanoparticles by wet chemical method, initially 10 ml of 0.5M copper (II) chloride (CuCl₂·2H₂O) solution was mixed with 5 ml of 3.7M TEA solution in a 100ml clean glass beaker under continuous stirring for 5 minute. The CuCl₂·2H₂O acts as precursor for Cu and TEA acted as capping agent to slow down the release of the metal ions resulting in slow precipitation of the compound by ion-ion reaction and to prevent the agglomeration of the desired metal ions. Then in the above solution, 16 ml of 7.6M NH₃ solution was added and stirred for 5 minute. In continuous stirring, 10 ml of 0.5M aluminium chloride (AlCl₃·6H₂O) solution was added and stirred for 5 minutes. Then 10 ml of 2.5M NaOH solution was mixed under continuous stirring. The stirring was continued for another 5 minute. Finally under continuous stirring, 10 ml of 1.0M thiourea solution was mixed and stirred for 5 minute. At last, 38 ml of deionised water was added to make the final solution 100 ml. The final solution of 100 ml immediately turned greenish-black in colour, the precipitates generated get settled at the bottom of the beaker. After 4 hrs the final solution was filtered out to get nanoparticles yield. The obtained nanoparticles were washed with distilled water and methanol for several times. After multiple wash, they were dried in oven at 50°C for 24 hrs to obtained nanoparticles yield, Figure 1. The reaction mechanism of CuAlS₂ nanoparticles synthesis is as below;

\[
\begin{align*}
\text{CuCl}_2\cdot2\text{H}_2\text{O} + 2\text{NaOH} + \text{TEA} & \rightarrow [\text{Cu (TEA)}]^+ + 2\text{NaCl} + 2\text{OH}^- + 2\text{H}_2\text{O} \\
\text{AlCl}_3\cdot6\text{H}_2\text{O} + 3\text{NaOH} + 3\text{NH}_3 & \rightarrow [\text{Al (NH}_3)_3]^{+3} + 3\text{NaCl} + 6\text{H}_2\text{O} + 3\text{OH}^- \\
2(\text{NH}_2)_2\text{CS} + 2\text{OH}^- & \rightarrow 2\text{C}_2\text{H}_2\text{N}_2 + 2\text{H}_2\text{O} + 2\text{HS}^- \\
2\text{HS}^- + 2\text{OH}^- & \rightarrow 2\text{S}^{2-} + 2\text{H}_2\text{O} \\
[\text{Cu (TEA)}]^+ + [\text{Al (NH}_3)_3]^{+3} + 2\text{S}^{2-} + 3\text{H}_2\text{O} & \rightarrow \text{CuAlS}_2 \downarrow + \text{TEA} + 3\text{NH}_4\text{OH}
\end{align*}
\]
4.3. RESULTS AND DISCUSSION

4.3.1 ENERGY DISPERSIVE ANALYSIS OF X-RAY (EDAX) ANALYSIS

The chemical compositions of the synthesized CuAlS$_2$ nanoparticles were determined by energy dispersive analysis of X-rays (EDAX). The EDAX spectrum is shown in Figure 2, the observed weight % of the elements with standard values are tabulated as inset of the Figure 2.

The values clearly states that the synthesized CuAlS$_2$ nanoparticles are sulfur rich. No extra peaks were observed in the EDAX spectrum stating that the synthesized CuAlS$_2$ nanoparticles are free from impurities or contaminants.
Figure 2: EDAX spectrums along with inset table of chemical composition of CuAlS₂ nanoparticles.

4.3.2. X-RAY DIFFRACTION (XRD) ANALYSIS

The XRD pattern of the CuAlS₂ nanoparticles is shown in Figure 3. The peaks intensity are sharp at top and broad at half maxima, confirming that the sample is of high quality having good polycrystallinity with fine grain size.

The X-ray diffractograms of CuAlS₂ nanoparticles was analyzed by Powder-X software to determined crystal structure, lattice parameters, 2θ angle, miller indices and inter planer spacing (d). The obtained values are tabulated in Table 1 which was found to match with the JCPDS File No. 25-0014.
Figure 3: Powder X-ray diffractograms of CuAlS$_2$ nanoparticles.

Table 1: The observed lattice parameters with standard data, 2θ angle, miller indices, interplaner spacing (d), %d error with standard data.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Lattice parameters Observed / JCPDS 25-0014</th>
<th>Standard</th>
<th>Observed</th>
<th>%d Error (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a = b (Å)  c (Å)</td>
<td>2θ degree (h k l)</td>
<td>(h k l)</td>
<td>2θ degree</td>
</tr>
<tr>
<td>CuAlS$_2$ nanoparticles</td>
<td>5.325 / 10.32 / 5.325 / 10.39</td>
<td>29.35   (1 1 2)</td>
<td>(1 1 2)</td>
<td>29.157</td>
</tr>
<tr>
<td></td>
<td></td>
<td>33.93   (2 0 0)</td>
<td>(2 0 0)</td>
<td>33.348</td>
</tr>
<tr>
<td></td>
<td></td>
<td>48.35   (2 2 0)</td>
<td>(2 2 0)</td>
<td>48.032</td>
</tr>
<tr>
<td>Tetragonal (I)</td>
<td>58.64 (1 1 6)</td>
<td>58.917</td>
<td></td>
<td>1.57</td>
</tr>
</tbody>
</table>
The percentage d errors were calculated from the obtained XRD d values and standard inter planer spacing. The %d error is below 1% stating the material to be of single CuAlS$_2$ phase. With the help of obtained lattice parameters, the X-ray density ‘$\rho$’ of the synthesized nanoparticles of CuAlS$_2$ was calculated by equation (1),

$$\rho = \frac{\sum A}{VN}$$  \hspace{1cm} (1)

Where $\sum A$ is the total weight of the atoms in the unit cell = $MZ$

$M$ is the molecular weight and $Z$ is the number of molecules/unit cell,

$N$ is the Avogadro number and

$V$ is the volume of the unit cell

The calculated X-ray density value came out to be 3.52 gm/cm$^3$. The calculated value of density of CuAlS$_2$ nanoparticles is slightly more than the reported value 3.43 gm/cm$^3$[14]. This is due to the reduction observed in lattice parameter c. The average number of unit cell per nanoparticles was calculated by taking ratio of volume of nanoparticles to the volume of unit cell of CuAlS$_2$ molecule. The average value came out to be ~1300. With the help of lattice parameters and miller indices, the angle $\theta$ between each planes were calculated in degree by equation (2)[15] for tetragonal system. The obtained values are tabulated in Table 2;

$$\cos \theta = \frac{h_1h_2+k_1k_2+l_1l_2}{\sqrt{(h_1^2+k_1^2+l_1^2)(a^2)(a^2+c^2)}}$$  \hspace{1cm} (2)

<table>
<thead>
<tr>
<th>(h k l)</th>
<th>(1 1 2)</th>
<th>(2 0 0)</th>
<th>(2 2 0)</th>
<th>(1 1 6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1 1 2)</td>
<td>0.00</td>
<td>55.06</td>
<td>35.87</td>
<td>29.40</td>
</tr>
<tr>
<td>(2 0 0)</td>
<td>55.06</td>
<td>0.00</td>
<td>45.02</td>
<td>72.81</td>
</tr>
<tr>
<td>(2 2 0)</td>
<td>35.87</td>
<td>45.02</td>
<td>0.00</td>
<td>65.27</td>
</tr>
<tr>
<td>(1 1 6)</td>
<td>29.40</td>
<td>72.81</td>
<td>65.27</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 2: Inter-planar angles in degree.
4.3.2.1. SCHERRER'S METHOD

The peak broadening in XRD pattern occurs due to decrease in crystallite size and lattice strain due to dislocation [16]. The particles size of the as-synthesized CuAlS$_2$ nanoparticles was determined from the XRD peak broadening employing Scherrer’s equation (3):

$$\frac{\cos \theta}{\lambda} = \frac{K}{D} \left( \frac{1}{\beta_{hkl}} \right)$$  \hspace{1cm} (3)

where $D$ is the crystallite size in nanometers,

$\lambda$ is the wavelength of the X-ray (0.154056 nm for CuK$\alpha$ radiation),

$K$ is a constant equal to 1,

$\beta_{hkl}$ is the peak width at half-maximum intensity and

$\theta$ is the peak position.

The value of crystallite size $D$ was evaluated from the slope of the plot of $\frac{\cos \theta}{\lambda}$ versus $\frac{1}{\beta_{hkl}}$ for as-synthesized CuAlS$_2$, Figure 4. The graphical and analytically determined crystallite sizes are tabulated in Table 3.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Results</th>
<th>D (nm)</th>
<th>$\varepsilon \times 10^{-3}$</th>
<th>$\sigma$ (MPa)</th>
<th>$u$ (kJm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scherrer’s method</td>
<td>Graphical</td>
<td>9.80</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Analytical</td>
<td>7.64</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hall-Williamson relation</td>
<td>UDM</td>
<td>8.28</td>
<td>1.09</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>USDM</td>
<td>8.08</td>
<td>0.72</td>
<td>73.28</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>UDEDMS</td>
<td>8.20</td>
<td>0.94</td>
<td>96.30</td>
<td>45.40</td>
</tr>
<tr>
<td>Size-Strain Plot method</td>
<td>Graphical</td>
<td>7.06</td>
<td>0.65</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TEM</td>
<td>Image</td>
<td>8.15</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 4: Scherrer’s plot of the as-synthesized CuAlS$_2$ nanoparticles.

4.3.2.2. HALL-WILLIAMSON RELATIONS

The strain in nanoparticles is due to crystalline imperfections and distortion. They are related by Stokes – Wilson [17] formula $\varepsilon = \frac{\beta_{hkl}}{4\tan\theta}$. Thus the full width at half maxima due to strain varies as $\tan\theta$. While the full width at half maxima due to grain size varies as $1/\cos\theta$. The dependence of full width at half maxima on strain and grain size is related by the Hall – Williamson relation. The Hall - Williamson (H-W) equation (4) is simply the addition of the Scherrer’s equation and Stokes - Wilson formula.

$$\beta_{hkl} = \left(\frac{k\lambda}{D \cos\theta}\right) + \left(4 \varepsilon \tan\theta\right) \quad (4)$$

Rearranging equation (4) gives:

$$\frac{\beta_{hkl}\cos\theta}{\lambda} = \left(\frac{K}{D}\right) + \varepsilon \left(\frac{4\sin\theta}{\lambda}\right) \quad (5)$$
Equations (4) and (5) represent the Uniform Deformation Model (UDM), where all the material properties are independent of the direction because the strain was assumed to be uniform in all crystallographic directions. The graph of \( \frac{4\sin\theta}{\lambda} \) versus \( \frac{\beta_{hkl}\cos\theta}{\lambda} \) was plotted for the prominent XRD peaks of CuAlS\(_2\) nanoparticles, Figure 5. The slope and ordinate intercept of the fitted line gave the strain and crystallite size respectively. The slope showed a positive strain for the CuAlS\(_2\) nanoparticles. The positive value is due to the minor lattice shrinkage seen in the value of the XRD determined lattice parameters. The results of the UDM analysis for the CuAlS\(_2\) nanoparticles are tabulated in Table 3.

![Figure 5](image.png)

**Figure 5:** The modified form of Hall-Williamson analysis assuming UDM for CuAlS\(_2\) nanoparticles.

The Hooke’s law relates the linear proportionality between the stress and strain;

\[
\sigma = Y\varepsilon \quad (6)
\]
Where \( \sigma \) is the stress, \( \varepsilon \) is strain and \( Y \) is the modulus of elasticity or Young’s modulus. This equation (6) is valid for a significantly small strain. Assuming a small strain to be present in the CuAlS\(_2\) nanoparticles, Hooke’s law can be used here. With a further increase in strain, the crystallite size deviates in linear proportion. Applying the Hooke’s law approximation to equation (5) yields:

\[
\frac{\beta_{hkl} \cos \theta}{\lambda} = \left( \frac{K}{D} \right) + \sigma \left( \frac{4 \sin \theta}{\lambda Y_{hkl}} \right)
\]

(7)

This relation is known as the Uniform Stress Deformation Model (USDM). For a tetragonal crystal, Young’s modulus is given by the following equation (8) [18].

\[
Y_{hkl} = \frac{(h^2+k^2+L^2)^2}{s_{11}(h^4+k^4)+(2s_{12}+s_{66})h^2k^2+(2s_{13}+s_{44})(h^2+k^2)L^2+s_{33}L^4}
\]

(8)

Where \( L = aI/c \)

Here \( a \) and \( c \) are the lattice parameters of nanoparticles; \( h, k \) and \( l \) are miller indices taken from Table 1.

\[
\begin{align*}
C_1 &= [C_{33}(C_{11}+C_{12})-2C_{13}^2] \\
S_{11} &= [(C_{11}C_{33}-C_{13}^2)/(C_{11}-C_{12})] C_1 \\
S_{12} &= -[(C_{12}C_{33}-C_{13}^2)/(C_{11}-C_{12})] C_1 \\
S_{13} &= -[C_{13}/C_1] \\
S_{33} &= [(C_{11}+C_{12})]/C_1 \\
S_{44} &= 1/C_{44} \\
S_{66} &= 1/C_{66}
\end{align*}
\]

(9)

Here elastic compliance constants \( S_{ij} \) (m\(^2\)N\(^{-1}\)) were calculated by using above relations (9) [19]. In this calculation, the elastic stiffness constants \( C_{ij} \) (Nm\(^{-2}\)) of CuAlS\(_2\) were taken from the reported values [20]. The evaluated values of \( S_{ij} \) with taken values of \( C_{ij} \) are tabulated in Table 4.
Table 4: Elastic constant of CuAlS\textsubscript{2} nanoparticles.

<table>
<thead>
<tr>
<th>C\textsubscript{11} (Nm\textsuperscript{-2})</th>
<th>C\textsubscript{12} (Nm\textsuperscript{-2})</th>
<th>C\textsubscript{13} (Nm\textsuperscript{-2})</th>
<th>C\textsubscript{33} (Nm\textsuperscript{-2})</th>
<th>C\textsubscript{44} (Nm\textsuperscript{-2})</th>
<th>C\textsubscript{66} (Nm\textsuperscript{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>133.001</td>
<td>80.762</td>
<td>84.552</td>
<td>135.064</td>
<td>56.543</td>
<td>53.762</td>
</tr>
<tr>
<td>S\textsubscript{11} (m\textsuperscript{2}N\textsuperscript{-1})</td>
<td>S\textsubscript{12} (m\textsuperscript{2}N\textsuperscript{-1})</td>
<td>S\textsubscript{13} (m\textsuperscript{2}N\textsuperscript{-1})</td>
<td>S\textsubscript{33} (m\textsuperscript{2}N\textsuperscript{-1})</td>
<td>S\textsubscript{44} (m\textsuperscript{2}N\textsuperscript{-1})</td>
<td>S\textsubscript{66} (m\textsuperscript{2}N\textsuperscript{-1})</td>
</tr>
<tr>
<td>1.421 × 10\textsuperscript{-11}</td>
<td>-4.938 × 10\textsuperscript{-12}</td>
<td>-5.802 × 10\textsuperscript{-12}</td>
<td>1.467 × 10\textsuperscript{-11}</td>
<td>1.769 × 10\textsuperscript{-11}</td>
<td>1.860 × 10\textsuperscript{-11}</td>
</tr>
</tbody>
</table>

The determined value of the Young’s modulus, Y\textsubscript{hkl}, for tetragonal CuAlS\textsubscript{2} nanoparticles came out to be 102.13 GPa, which is nearly equal to the reported value 106.91 GPa [20]. The USDM plot of \( \frac{\beta\textsubscript{hkl}\cos\theta}{\lambda} \) versus \( \frac{4\sin\theta}{\lambda Y\textsubscript{hkl}} \) for the CuAlS\textsubscript{2} nanoparticles are shown in Figure 6. The parameters like, stress calculated from the slope of the fitted line, the strain calculated using equation (6) and crystallite size determined from intercept are tabulated in Table 3. They are in good agreement with the values obtained from UDM.

**Figure 6:** The modified form of Hall-Williamson analysis using USDM for CuAlS\textsubscript{2} nanoparticles.
There is another model called the Uniform Deformation Energy Density Model (UDEDM) to determine the crystallite size, strain and stress. The energy density can also be determined by the model. For an elastic system that follows Hooke’s law, the energy density \( u \) can be given as,

\[
  u = (\varepsilon^2 Y_{hkl})/2.
\]  

(10)

Then equation (5) can be rewritten using equation (10);

\[
  \frac{\beta_{hkl} \cos\theta}{\lambda} = \left( \frac{K}{D} \right) + \sqrt{u} \left( \frac{4\sin\theta}{\lambda} \right) \sqrt{\frac{2}{Y_{hkl}}}.
\]  

(11)

Plot of \( \frac{\beta_{hkl} \cos\theta}{\lambda} \) versus \( \left( \frac{4\sin\theta}{\lambda} \right) \sqrt{\frac{2}{Y_{hkl}}} \) is shown in Figure 7.

**Figure 7:** The modified form of Hall-Williamson analysis using UDEDM for CuAlS$_2$ nanoparticles.
The square of the slope of fitted line gave the energy density $u$ and the reciprocal of the $y$-intercept provided the crystallite size $D$. While stress and strain were calculated by using equations (6) and (10) respectively. All the values are tabulated in Table 3. The value of the crystallite size determined is in good agreement with other models.

### 4.3.2.3. SIZE-STRAIN PLOT METHOD

The grain size and strain can be evaluated using Size-Strain Plot (SSP) method. In this estimation, it is assumed that the crystallite size profile is illustrated by a Lorentzian function and the strain profile by a Gaussian function [21]. Hence we have,

$$
(d_{hkl} \beta_{hkl} \cos \theta)^2 = \frac{K}{D} (d_{hkl}^2 \beta_{hkl} \cos \theta) + \left(\frac{\varepsilon}{2}\right)^2
$$

(12)

Where $K$ is a constant that depends on the shape of the particle; for spherical particles it is taken as 1.

![Figure 8: The SSP plot of CuAlS$_2$ nanoparticles.](image-url)
In Figure 8, the graph of \((d_hk_l\beta_{hk_l}\cos\theta)^2\) versus \((d_hk_l\beta_{hk_l}\cos\theta)\) was plotted for the prominent XRD peaks of CuAlS\(_2\) nanoparticles. In this case, the crystallite size was determined from the slope of the line and square root of y-intercept gave the strain. The obtained values are tabulated in Table 3.

4.3.3. TRANSMISSION ELECTRON MICROSCOPY (TEM) ANALYSIS

The crystallite size and crystallinity of the as synthesized CuAlS\(_2\) nanoparticles were determined by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) pattern respectively. The TEM image and SAED pattern of as synthesized CuAlS\(_2\) nanoparticles were recorded using Philips, Tecnai 20 transmission electron microscope. The obtained image and SAED pattern is shown in Figure 9 (a) and (b).

![Figure 9: (a) TEM image of CuAlS\(_2\) nanoparticles.](image)
The Figure 9 (a) clearly shows particles to be spherical in shape. The average particles size determined from the TEM image comes out to be ~ 8 nm which is in good agreement with the crystallite size obtained from the XRD analysis. The selected area electron diffraction (SAED) pattern for CuAlS$_2$ nanoparticles (Figure 9(b)) shows ring pattern, confirming the synthesized nanoparticles are polycrystalline in nature. The rings were indexed as (112), (200), (220) and (116) indices associated with tetragonal crystal structure. The indexed planes are in agreement with the XRD planes.

4.3.4. OPTICAL ANALYSIS

The optical absorption spectrum obtained for the CuAlS$_2$ nanoparticles synthesized by wet chemical method is shown in Figure 10. The clear colloid obtained after 30 min sonication of CuAlS$_2$ nanoparticles dispersed in pure methanol was used as sample and only methanol
was used as reference. The obtained spectra clearly states that the synthesized CuAlS$_2$ nanoparticles have high absorption in the ultra violet range with absorption edge lying at 319 nm corresponding to energy 3.89 eV. Straight falling of absorbance in obtained spectra clearly states that the sizes of the particles are uniform in nature which is in good agreement with the crystallite size obtained from the XRD analysis and TEM image.

![Absorbance spectra of CuAlS$_2$ nanoparticles dispersed in methanol.](image)

**Figure 10:** Absorbance spectra of CuAlS$_2$ nanoparticles dispersed in methanol.

The energy bandgap $E_g$ was determined from the optical absorption data using the near-band edge absorption relation [22],

$$(\alpha h\nu)^n = A (h\nu - E_g)$$

Where, n characterizes the transition. For direct allowed and forbidden transitions, $n = 2$ and $2/3$ respectively, and $n = 1/2$ and $1/3$ for indirect allowed and forbidden transitions, respectively. The absorption coefficient ‘$\alpha$’ was calculated employing the relation [22].
\[ \alpha = \frac{A\rho}{Mc} \]  \hspace{1cm} (14)

Where \( A \) is the absorbance of the light through sample, \( \rho \) is the density of CuAlS\(_2\), \( c \) is the sample concentration dispersed in methanol, \( M \) is the molecular weight of CuAlS\(_2\) and \( l \) is the path length of light.

\[ R = 0.9869 \]

\[ Eg = 3.83 \text{ eV} \]

**Figure 11:** The plot of \((\alpha h\nu)^2\) against \(h\nu\) for CuAlS\(_2\) nanoparticles.

The analysis of equation (13) showed that, \( n = 2 \) fitted for the as-synthesized CuAlS\(_2\) samples confirming direct allowed transition. Figure 11 shows the plot of \((\alpha h\nu)^2\) against \(h\nu\) for CuAlS\(_2\) nanoparticles. The intercept of the straight line on the photon energy axis gives the bandgap value \( E_g \) of 3.83 eV. This bandgap value is more than reported value (3.49 eV) for bulk CuAlS\(_2\) chalcopyrite [5] which confirmed the blue shift occurred due to particles size decrease.

The sizes of CuAlS\(_2\) nanoparticles were determined using Brus equation [23, 24],
\[ E_{\text{Absorption}} = E_{\text{bulk}} + \left( \frac{h^2}{8R^2} \right) \left[ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right] \] (15)

Where \( E_{\text{Absorption}} \) is energy band gap of CuAlS\(_2\) nanoparticles, \( E_{\text{bulk}} \) is the energy band gap of the bulk CuAlS\(_2\), the ratio between the effective masses of the electron to hole \( s = \frac{m_e^*}{m_h^*} = 0.165 \) [25] and \( R \) is radius of particles size.

The average particles size of the CuAlS\(_2\) nanoparticles determined from the Brus equation comes out to be \(~7\) nm which is in good agreement with the crystallite size obtained from the XRD analysis and TEM image.

4.4. CONCLUSIONS

The CuAlS\(_2\) nanoparticles were successfully synthesized by wet chemical methods at room temperature. The EDAX analysis confirmed that the synthesized CuAlS\(_2\) nanoparticles were perfectly stoichiometric and do not contain any other impurity. The X-ray diffraction showed that the synthesized CuAlS\(_2\) nanoparticles have tetragonal structure. The determined lattice parameters, density, numbers of unit cell per nanoparticles and inter planer angles are in good agreement with the reported data. The crystallite size determined from XRD data employing Scherrer’s formula, Hall-Williamson modified forms like; uniform deformation model (UDM), uniform stress deformation model (USDM), uniform deformation energy-density model (UDEDM) and the size-strain plot method (SSP) were in good agreement with each other. The TEM image showed spherical nanoparticles having size \(~8\) nm. The selected area electron diffraction pattern of the nanoparticles showed ring pattern stating polycrystallinity and corresponding miller indices planes matches with the XRD. The obtained optical bandgap value of CuAlS\(_2\) nanoparticles \( E_g \) is 3.83 eV, which is more than reported value of 3.49 eV for bulk CuAlS\(_2\) chalcopyrite which confirmed the blue shift occurred due to particles size decrease. The average particles size of the CuAlS\(_2\) nanoparticles determined using Brus equation is \(~7\) nm, which is in good agreement with the crystallite size obtained from the XRD analysis and TEM image.
REFERENCES:


