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Preparation of $CuAlTe_2$ Thin Films by Auto-Combustion

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Abstract

$CuAlTe_2$ films have been fabricated using a novel technique called auto combustion or self-propagating high-temperature synthesis (SHS) through thermal evaporation. This process involved depositing the films onto a mixture of Cu, Al, and Te powder that was cold-pressed. The as-grown films exhibited a chalcopyrite structure with a preferred orientation along the (112) direction, and their lattice constants were determined to be: a=6.058 Å and c=11.98 Å. SEM analysis revealed that the resulting thin films had a nano-structured morphology. Additionally, a direct band-gap value of 2.08 eV was observed.

Keywords: *$CuAlTe_2$, SHS, Thin Films, Structural Properties, Optical Properties, Band Gap.*

1. INTRODUCTION

The auto-combustion method, also known as self-propagating high-temperature synthesis (SHS), is a well-known technique for making different high-temperature ceramics [1-5]. This method is great for producing borides, carbides, nitrides, and oxides [4 ,6, 7, 8]. Unlike other methods that need lots of knowledge, high-temperature furnaces, and take a long time, SHS has many benefits. It helps make materials very pure, needs less energy, and keeps the process simple [9-13]. The heat created during the SHS reaction is used to keep the chemical reaction going. When the SHS reaction starts at a specific ignition temperature (T_i), it spreads through the reactants at a certain speed, forming the final product. The heat released by the reaction is the main energy source in this process. The success of making a particular molecule or composite this way, and keeping the reaction going, depends on how much heat is created by the reaction and how much is lost to the surroundings [14]. The adiabatic temperature (T_{ad}) is important because it shows the highest potential temperature increase of the system only from the reaction's heat when the system is isolated. Experimental data suggests that Tad needs to be over 1800 K for the process to sustain itself [15,16]. Assuming all reactants turn into products, Tad can be calculated. Since most reactions start at temperatures (T_i) higher than room temperature, it's assumed that all the heat made by the reaction goes into raising the product's temperature without any heat lost. The total change in enthalpy, ΔH_{Ti}, at any given temperature (T_i), can be found using this equation.

$$\Delta H_T = \int_{T_i}^{T_{ad}} \sum_i \Delta Cp_i \, dT \qquad (1)$$

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Where, ΔH_T represents the change in enthalpy associated with the exothermic reaction, and ΔC_{pi} refers to the difference in specific heats between the products (represented by i) and the reactants at a constant pressure. Equation 1 does not take into account various phase transformations of the reactants and products for the sake of simplicity. It is widely known that various high-temperature materials can be synthesized using Self-Propagating High-Temperature Synthesis (SHS) techniques. Unlike other methods, SHS does not require high temperatures for melting and is particularly suitable for producing semiconductors. In fact, we have successfully employed SHS to manufacture semiconductors, such as $CuAlTe_2$ compound. $CuAlTe_2$ belongs to the group of I-III-VI_2 ternary semiconductor compounds, where I can be Cu or Ag, III can be Al, Ga, or in, and VI can be S, Se, or Te. These compounds crystallize in the chalcopyrite structure and possess physical properties that make them suitable for a wide range of applications, including solar cells, light-emitting devices, and optical filters [17-19].

In order to develop technology for such devices, it is essential to investigate fundamental optical properties like absorption. The properties of $CuAlTe_2$ have not received sufficient attention and exhibit significant variations. For instance, at room temperature, the optical band gap energy (Eg) ranges from 1.2 to 2.45 eV [20-22].

The paper discussed in this context centers on the investigation of the structural, morphological, and optical properties of $CuAlTe_2$. It particularly examines a $CuAlTe_2$ ingot fabricated using the novel self-propagating high-temperature synthesis (SHS) method. Additionally, the paper explores $CuAlTe_2$ thin films generated through thermal evaporation employing the $CuAlTe_2$ ingot obtained from the SHS technique. The study endeavors to offer in-depth insights into the characteristics and attributes of both the $CuAlTe_2$ ingot and the resultant thin films, aiming to explore their potential applications across diverse fields.

2. STRUCTURE OF CRYSTAL $CuAlTe_2$

In our current study, we investigate the chalcopyrite crystal structure of $CuAlTe_2$, which is depicted in **Figure 1**.

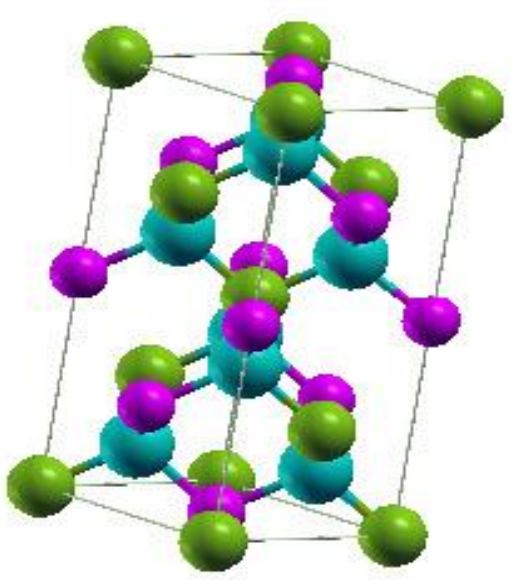

Fig 1: The unit cell of $CuAlTe_2$ in a body-centered tetragonal (BCT) structure

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In this structure, each tellurium ion (represented by the light blue color) is coordinated with two aluminum ions (violet) and two copper ions (green). Additionally, each copper ion and each aluminum ion are coordinated with four tellurium ions. This information is mentioned in the article titled $CuAlTe_2$ under High Temperature: an ab initio Approach" and is likely discussing the crystal structure of $CuAlTe_2$ at elevated temperatures using an ab initio computational approach.

3. METHODS OF FABRICATION OF $CuAlTe_2$

3.1. Preparation of crystal by SHS technical

The experimental setup and parameters for synthesizing the $CuAlTe_2$ sample using the SHS method are meticulously outlined in the text. Firstly, the stoichiometry of the compound, comprising 25% Cu, 25% Al, and 50% Te, is established. Precise weighing procedures are ensured using an OHAUS electronic balance from Germany, boasting a precision of 0.0001 g, with the total compound weight set at 4 grams. The compacting process involves axial compression of precursors using a NOSHOK press from Germany, applying a pressure of 12 tons. Utilizing a cylindrical die with a counter punch and stainless steel punch ensures uniformity. The resulting sample dimensions, meticulously measured using a caliper with an accuracy of 0.01 mm under 900 psi pressure, manifest as 26 mm in height and 4 mm in diameter. Synthesis of the $CuAlTe_2$ sample takes place under a primary vacuum of 21 psi for a duration of 30 minutes. The specific experimental parameters, regrouped in **Table 1**, encompass critical variables such as temperature, heating rate, and additional pertinent details. These comprehensive insights into the experimental setup and conditions employed significantly enhance understanding and reproducibility in the synthesis of $CuAlTe_2$ using the SHS method.

Table 1: Parameters of the SHS reaction

The distance between the graphite and the sample (mm)	Ignition time (s)	Ignition Intensity (A)	Reaction time (s)
2	Very fast	40	Immediate

The synthesis of $CuAlTe_2$ involves the use of a graphite plate to initiate and drive the reaction. The graphite plate, measuring $7\times5\times0.5$ mm³ as depicted in **Figure 2**, serves as the catalyst for the reaction. Positioned parallel to one side of the graphite plate, the sample maintains a maximum distance of approximately 2 mm from it. Radiation emitted by the graphite plate primarily heats the sample, ensuring precise and reproducible temperature control linked directly to the electrical power supplied to the system. Within the reaction chamber, the graphite plate connects to two copper electrodes, electrically isolated from each other. A high-intensity current of around 40 amps is applied to these copper electrodes to induce heating in the graphite plate. The rapid diffusion of heat throughout the material, including the $CuAlTe_2$ sample, occurs within seconds after the reaction initiation. These details underscore the importance of the graphite plate for radiation-based heating and the meticulously controlled electrical heating process in the synthesis of $CuAlTe_2$.

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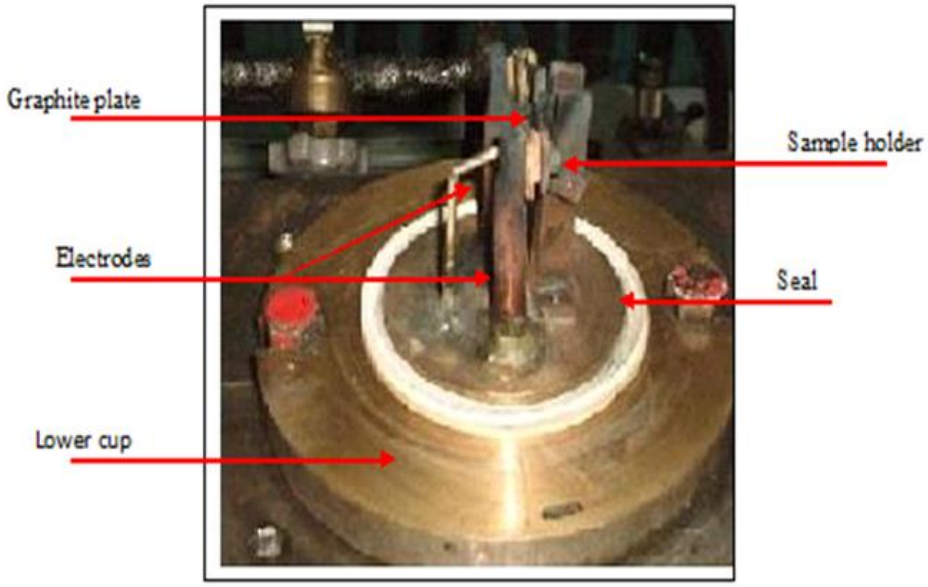

Fig 2: Priming system of SHS process

3.2. Prepared the thin film from SHS process

Thin films of $CuAlTe_2$ were prepared using the self-combustion method (SHS). Prior to the fabrication process, the $CuAlTe_2$ ingot underwent a brief dramping treatment to break and activate it. This step was essential as the thermal evaporation method cannot be achieved solely from elements in powder form. The thin films were grown thermally on glass substrates within a vacuum environment of 10^{-6} Torr, using a BALZERS coating unit. A tungsten boat heated by Joule effect was employed to evaporate the $CuAlTe_2$ material obtained via the SHS method. Throughout the deposition process, the substrate temperature was maintained at 350°C (refer to Figure 3).

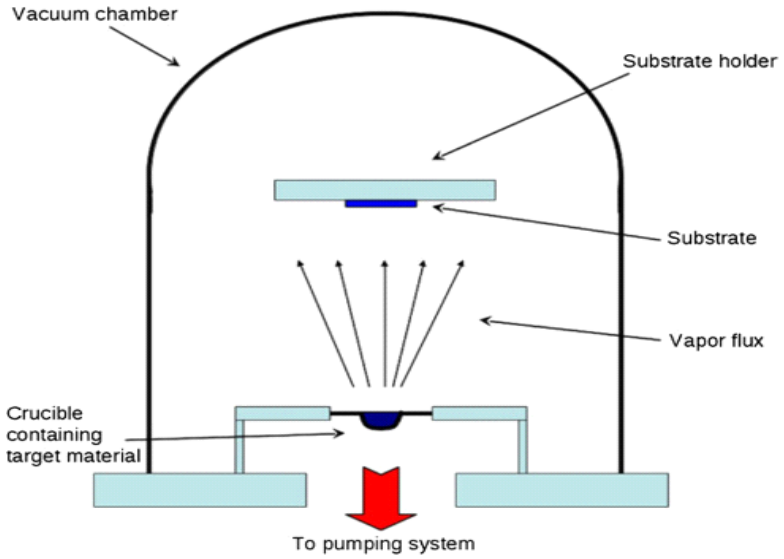

Fig 3: Principle of thermal evaporation

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The techniques and instruments used for structural and morphological analysis, as well as optical characterization of the $CuAlTe_2$ ingot and thin films, are detailed. Structural analysis was conducted using a PANalytical X'Pert Pro Diffractometer with monochromatic Cu Kα radiation (λ = 1.5406 Å) in the 10°-100° range, with a step size of 0.02. The diffractometer operated at 40 kV and 30 mA, and experimental data was fitted using ASTM values. Morphological analysis utilized a scanning electron microscope (SEM) model JEOL JSM-6400 F, while optical characterization was performed on $CuAlTe_2$ thin films at room temperature using a Shimadzu UV-3101PC spectrophotometer, covering a wavelength range of 200-2500 nm. These techniques and instruments offer valuable insights into the structural, morphological, and optical properties of the materials, facilitating a comprehensive characterization.

4. RESULTS AND DISCUSSION

4. 1. Results of XRD

4. 1. 1. X-ray of $CuInSe_2$ ingot obtained by SHS process

The product obtained by self-combustion (SHS) is generally porous, with a porosity rate. Porosity can be attributed to the following factors: change in molar volume that accompanies the formation of products, existing porosity in the raw sample, gases and moisture absorbed during the reaction.

Figure 4 shows the x-ray diffraction peaks of $CuAlTe_2$ bulk compound synthesized by SHS process. The characteristic peaks of the chalcopyrite type structure such as (101), (112), (103), (211), are clearly visible, the intensity of the peak (112) is small, possible tuo to the insufficient orientation of the grains private to DRX device.

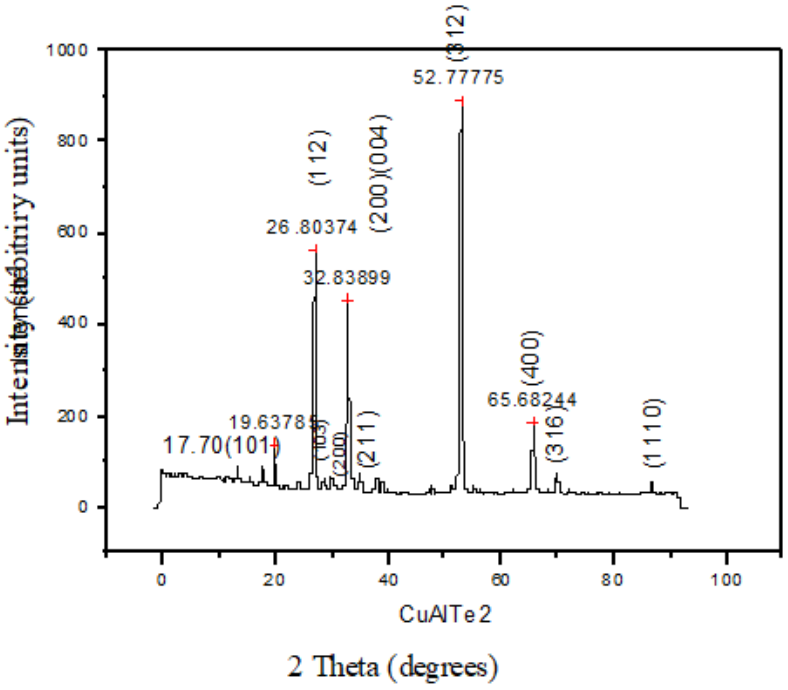

Fig 4: The X-ray diffraction peaks of $CuAlTe_2$ bulk compound synthesized by SHS process

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In the analysis (figure 4), the estimation of $CuAlTe_2$ crystallite size and lattice parameters derived from the SHS bulk compound is explored. Using Scherrer's formula:

$$S = \frac{0.9\lambda}{\beta \cos\theta} \qquad (2)$$

The crystallite size (S) is calculated, taking into account the X-ray radiation wavelength (λ = 0.15406 nm), full width at half maximum (FWHM) of the diffraction peak (B), and diffraction angle (2θ). The calculated S values, determined from the (1 1 2) reflection of the tetragonal $CuAlTe_2$ phase, approximate 80 nm. Additionally, lattice parameters of the $CuAlTe_2$ phase, specifically a = 6.075 Å and c = 11.91 Å, with a c/a ratio of 1.96, are derived. These findings provide valuable insights into the structural characteristics of $CuAlTe_2$. The analysis further emphasizes the efficacy of SHS in $CuAlTe_2$ synthesis, highlighting its speed and sustainability during the combustion propagation reaction, where the amount of heat is pivotal in achieving the necessary adiabatic temperature (987 °C). Previous successful demonstrations of $CuAlTe_2$ synthesis using SHS are noted [23].

4.1.2. X-ray of $CuAlTe_2$ thin films deposited from SHS bulk compound

The X-ray diffraction of $CuAlTe_2$ thin films obtained by thermal evaporation as depicted in (**figure. 5**), show the prominent and characteristic peaks of the chalcopyrite like structure suitable for photovoltaic conversion. It is noted that the chalcopyrite structure of $CuAlTe_2$ did not change and remained the same, meaning that all peaks properties of this material appear alike ingot or thin film, this explains that the technique auto-combustion or SHS is effective for making semiconductors, and it was possible to achieve good quality thin films prepared from SHS $CuAlTe_2$ and bulk compound. Hence, the SHS process is very advantageous to synthesize rapidly and with a low cost our product. The lattice parameters are a=6.058 Å and c= 11.98 Å, c/a ratio is 1.98 and grain size of thin film is 12 nm.

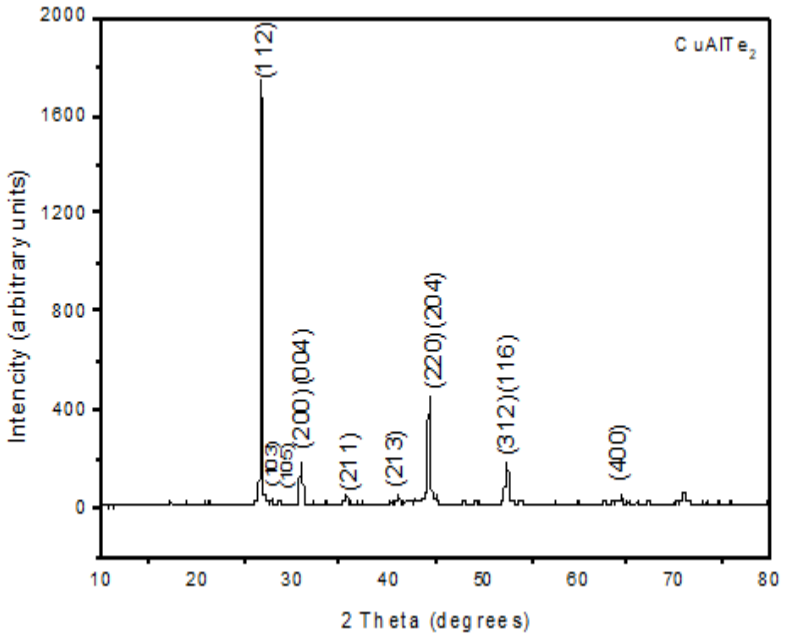

Fig 5: The X-ray diffraction of $CuAlTe_2$ thin films obtained by thermal evaporation

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Based on the X-ray diffraction (XRD) results presented in Figure 5, the findings from the analysis of $CuAlTe_2$ prepared by SHS ingot and thermally deposited thin films align with previous references [24, 25]. These results imply that the properties of the materials obtained are highly conducive to solar cell fabrication.

4. 2. Surface morphology

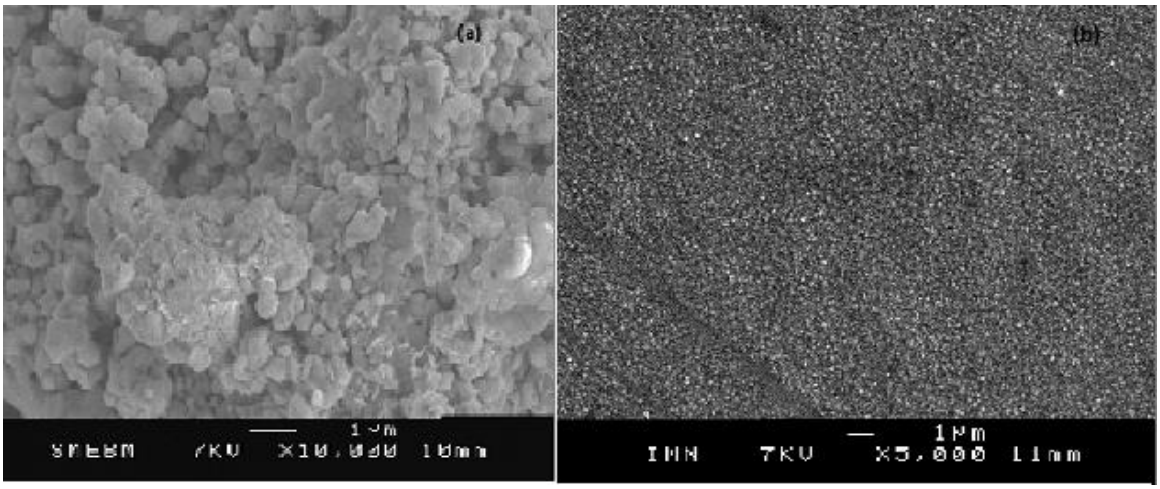

Fig 6: SEM of: (a) $CuAlTe_2$ prepared by SHS method, (b) thermally evaporated $CuAlTe_2$ thin films surface

Figure 6 (a): illustrates the microstructure of the $CuAlTe_2$ bulk compound synthesized using the SHS method, revealing the presence of unfilled spaces and voids attributed to the rapid and exothermic nature of the self-propagating combustion mode during the SHS process. In **Figure 6 (b)**, SEM images of the surface of thermally evaporated $CuAlTe_2$ thin films display a relatively compact and dense surface morphology characterized by nano-sized particles. However, despite this appearance, the average crystallite sizes determined from the XRD data are 10 nm and 14 nm. Thus, it is conceivable that each grain observed in the SEM profile contains numerous individual crystallites, approximately of equal size.

4. 3. Optical properties

The optical absorption is calculated using the equation:

$$\alpha h\nu = A\,(h\nu - Eg)^{n} \qquad (3)$$

Where Eg is the band gap, α is the absorption coefficient, and ν is the frequency. A is a constant, and n can take values of 1/2, 3/2, 2 and 3 depending on the mode of inert- band transition: direct-allowed, direct-forbidden, indirect-allowed and indirect-forbidden transition, respectively. For $CuAlTe_2$ thin films, a value of n=1/2 provides the best fit for the optical absorption data. The graph illustrating the variation of the absorption coefficient with wavelength is shown in **figure 7**.

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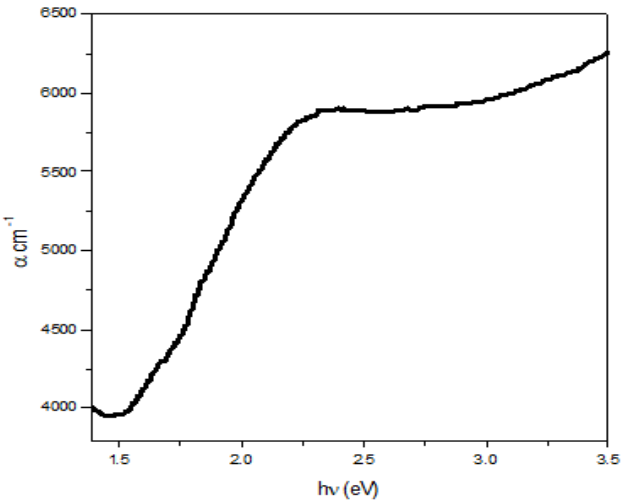

Fig 7: Dependence of the absorption coefficient *α* for $CuAlTe_2$ at 350 K

The graph presented in **Figure 8** illustrates the dependence of the optical coefficient α on photon energy (hν). With α exceeding 10^4 cm^{-1}, the films exhibit high quality, rendering them suitable for solar cell fabrication. By plotting $(\alpha h\nu)^2$ against hν, optical band gaps can be ascertained. This method enables the analysis of the correlation between the square of the product of α and hν, and photon energy, offering insights into the energy necessary for electronic transitions within the material and facilitating the determination of optical band gaps.

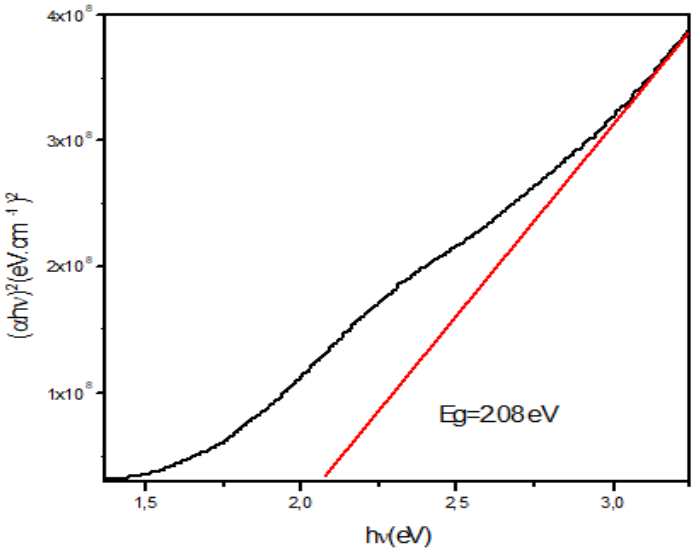

Fig 8: Plot of $(\alpha h\nu)^2$ vs. hν for $CuAlTe_2$ thin films

The band gap of $CuAlTe_2$ thin films, fabricated via thermal evaporation at 350 K using the SHS method, is determined to be 2.08 eV. This finding aligns excellently with values reported in the literature [26, 27]. Additionally, further investigation reveals that annealed $CuAlTe_2$ films exhibit direct optical band gap energies ranging from 2.3 to 2.05 eV [28]. Furthermore, for $CuAlTe_2$ thin films subjected to heat treatment at 300°C following fabrication by RF sputtering, the direct band gap value at room temperature was found to be (2.45±0.02) eV [20]

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5. CONCLUSION

In conclusion, the utilization of the SHS process proved highly successful in fabricating high-quality polycrystalline $CuAlTe_2$. Through precise control of parameters such as reaction temperature, reactant ratios, and heating rates, the synthesis process ensured the formation of well-defined crystalline structures. Additionally, thin films derived from this material were effectively deposited onto substrates using techniques such as thermal evaporation. SEM analysis provided insights into the surface morphology, confirming the chalcopyrite nature of the samples. Of particular significance is the exceptional quality exhibited by the thin films, characterized by appropriate band gaps and absorption coefficients surpassing 10^4 cm^{-1}. These results underscore the importance of the SHS method in fabricating $CuAlTe_2$ crystals, offering promising avenues for applications in various fields.

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