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STUDY THE EFFECT OF THE SINTERING TEMPERATURE ON THE MICROSTRUCTURE AND OPTICAL REFLECTANCE OF THE COMPACTED BULK $CUALS_2$ FABRICATED BY POWDER METALLURGY TECHNIQUE (P/M)

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ABSTRACT: *In this work, the effect of the sintering temperature of the bulk compacted powder sample on the microstructure and reflectance of the bulk $CuAlS_2$, which fabricated by powder metallurgy [P/M] technique, has been studied. The bulk was produced by [P/M] at compacting pressure of 350 MPa, sintering time 2 hr and different sintering temperature (100, 150, 200, 250 and 300°C). X-ray diffraction [XRD], scanning electron microscopy [SEM], energy dispersive analysis [EDS], and optical reflectance measurements were used for characterization of the prepared samples. The analysis of X-ray diffraction [XRD] indicated a formation of $CuAlS_2$ phase with preferring orientations of [1 1 2], [2 0 0], [2 2 0] and [0 0 8]. The intensity of $CuAlS_2$ phase continuously increases with increasing the sintering temperature. It has been observed that the crystallite size increases with increasing of the sintering temperature from 24.25 nm at 100°C to 31.33 nm at 300°C, giving an indication of enhancement in the crystallinity. The analysis of [SEM] indicated the treated surface morphology of the bulk $CuAlS_2$. An increase in crystallization and formation of the $CuAlS_2$ phase was observed with increasing the sintering temperature. The cluster size shows remarkable rise with the increase of sintering temperature which confirms improvement in grain growth. The optical data shows, that with increasing the sintering temperature the reflectance decreased to 15% at 200°C in the near of infrared region [NIR] and 10% at 200°C and 250°C in the visible region [VIS].*
KEYWORDS: $CuAlS_2$, powder metallurgy, sintering temperature, optical reflectance

INTRODUCTION

The solar energy harvesting industry attracts attention and is considered the main way to overcome the limited supply of fossil energy and the problems of the environment. It is a field of new renewable energy and generates power by employing solar cell technology to convert the limitless solar energy into electrical energy. Solar cell technology is mainly focusing on the development of solar cells, which contain greater efficiency of energy conversion for solar energy that is coming towards earth. Currently, different types of solar cells are being updated and used in changing circumstances [1]. Si-based solar cells need the anti-reflection coating layer, to minimize light reflection, in order to maximize conversion efficiency [2]. The I–III–

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VI_2 chalcopyrite semiconductor compounds as $CuAlS_2$, $CuGaS_2$, $CuAlSe_2$, and $CuInS_2$ have been attracted much interest [3]. This is due to their potential applications such as solar cells [4], and photovoltaic optical detectors [5,6]. It is also found that the chalcopyrite $CuAlS_2$ is a heartening material for applications of solar cells [7]. This is due to the broad optical energy gap which up to [3.60eV] at room temperature. As well in solar cells, for its excellent structural and visual properties, and also the wide optical energy gap of $CuAlS_2$ crystalline thin films could be expected as a new alternative to a cadmium-free layer. The chalcopyrite semiconductor, $CuAlS_2$ can also be used as a selective window coating material because of its high absorption coefficient in [NIR] region, and [UV] region of the electromagnetic spectrum [5]. A number of methods have been performed to produce $CuAlS_2$ films including metal decomposition, iodine transport, single source thermal evaporation, spray pyrolysis [7], vacuum co-evaporation technique [8], chemical vapor transport method, electrophoretic deposition [EPD] [9], RF magnetron sputtering system [10], horizontal Bridgman method [11], chemical spray pyrolysis [CSP], chemical bath deposition [CBD] [12], and spark plasma sintering [13]. For the first time, $CuAlS_2$ has been fabricated by P/M technique in this study. Powder metallurgy process have many advantages such as; high rates of production, production of complex shapes, and cost in producing accurate shapes is low compared with other manufacturing processes.

EXPERIMENTAL

Materials and methods

Elemental Cu [purity 99.99%], Al [purity 99.99%], and S [purity 99.99%] powders with particle size of 200 μm, have been produced from the company of Dop Organic Kimya San.ve Tic. ltd. Sti [Ostim-ANKARA.TORKIYE]. Mixtures of $CuAlS_2$ have been prepared by mixing a triple composition of $Cu_{63.546}$, $Al_{26.981}$ and $S_{64.118}$ with 1:1:2 atomic weight, At% (Cu=41.1, Al=17.45, S=41.45). The mixing process was carried out in a mixer for two hours. The mixture was then placed inside a circular cross-section die made of k100 steel of internal diameter 20.1 mm. Then the compression process was performed using by a cold pressing technique under 350 MPa. For this purpose, a digital compression of testing machine 2000 kn capacity model CO55D has been used. The green samples were then ejected from the die with a diameter of 20.1 mm and a thickness of 5 mm. The samples have been prepared for the present mixtures at the different sintering temperature of 100, 150, 200, 250, and 300°C for 2 hr. The samples are left to be cooled in the oven until reach room temperature. The sintering process was carried out using a vacuum tube furnace, with using argon as sintering atmosphere.

Structural Analysis

The microstructure of the bulk was investigated using X-ray diffractometer [Philips model PW1710, Holland] of Cu-kα [λ =1.541838 ˚A] by varying the diffraction angle 2θ from 20◦ to 100◦ with a step width of 0.04, to evaluate the crystalline phase and orientation. Energy dispersive analysis of X-ray [EDS], and surface morphology of the bulk was analyzed by scanning electron microscopy of model Quanta 250 FEG [Field Emission Gun], and unit energy dispersive EDS, with accelerating voltage 30 kV, magnification Starts from 14x to 1000000.000x and high resolution.

Optical reflectance
The wavelength of the reflection spectra ranges 200-2500 nm at the normal range was employed by means of a Jasco V-570 UV - Visible - NIR spectrophotometer with a photometric accuracy of transmittance ± 0.3 % and absorbance ± 0.002-0.004.

RESULTS AND DISCUSSION

Microstructure analysis
X-ray diffraction analysis
Fig. 1 shows the XRD patterns of bulk $CuAlS_2$ which was prepared at different sintering temperatures of 100, 150, 200, 250, and 300°C. Some diffraction peaks of $CuAlS_2$ phases of the orientation [1 1 2], [2 0 0], [2 1 1], [2 2 0], [3 1 0], [3 1 4], [3 0 5], [0 0 8], [2 1 7], [3 1 6], [4 2 2], [4 2 4], and [1 1 10] appeared at 2θ of 29.789° , 33.361°, 38.986°, 48.44°, 54.26°, 65.54°, 69.44°, 72.02°, 74.44°, 78.62°, 82.7°, 90.16° and 99.38° respectively to be belonging to $CuAlS_2$ chalcopyrite structure [JCDPS Card No. 04-013-0170] [3, 4]. The intensity of $CuAlS_2$ phases at [1 1 2], [2 0 0], [2 2 0] and [0 0 8] continuously increases with increasing sintering temperature. Whilst, the intensity of $CuAlS_2$ phases at [2 1 1], [3 1 0], [3 1 4], [2 1 7], [3 1 6], [4 2 2], [4 2 4] and [1 1 10] continuously increases with increasing sintering temperature up to 200°C, then it decreases thereafter as the temperature increases. The crystallite size of the bulk $CuAlS_2$ at different sintering temperatures is presented in Fig. 2. It has been observed that the crystallite size increases with increasing of the sintering temperature from 24.25 nm at 100°C to 31.33 nm at 300°C, giving an indication of enhancement in the crystallinity. The reason may be attributed to that the sufficient amount of energy acquired by the atoms for diffusion in the crystal lattice [14]. Through searching and matching the JCPDS standard cards, many phases have been found such as Al_2S_3, CuAl, CuS, and S. These results regarding to the presence of multiphase structure, which reported by other authors for different chalcopyrite compounds using different deposition methods [15, 16].

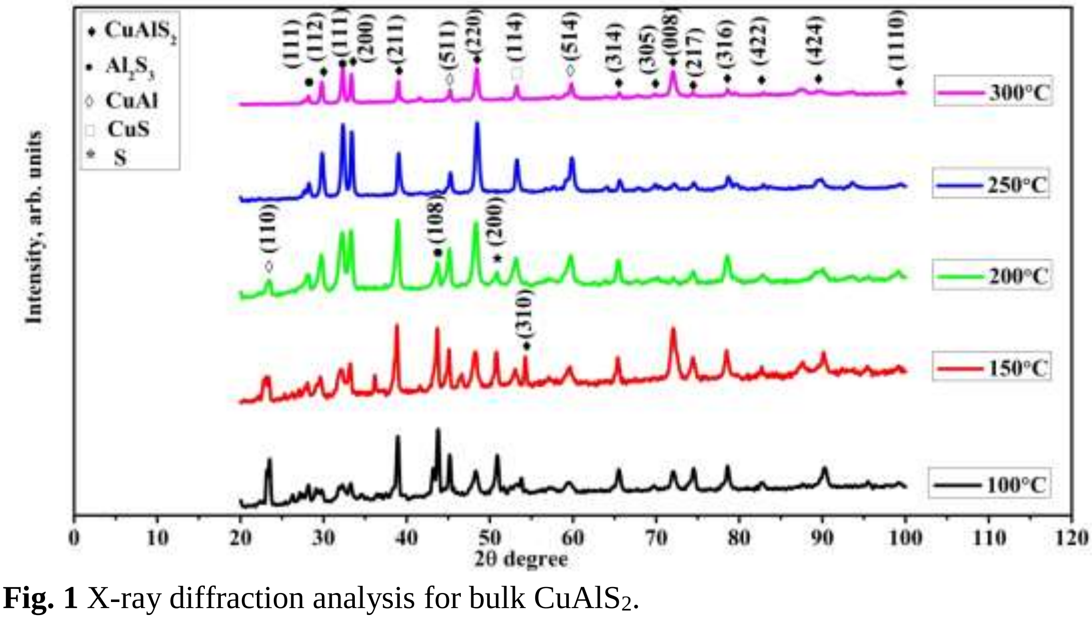

Fig. 1 X-ray diffraction analysis for bulk $CuAlS_2$.

The crystalline sizes have been determined by the Debye Scherrer relation [7].

$$D = \frac{K\lambda}{FWHM\ Cos\ \theta}$$

where D (nm) is the size of crystalline, $k \approx 0.90$ is a dimensionless shape factor, λ (nm) is the incident radiation wavelength, θ (rad) is the reflectance angle of Bragg and *FWHM* is the full width at half maximum.

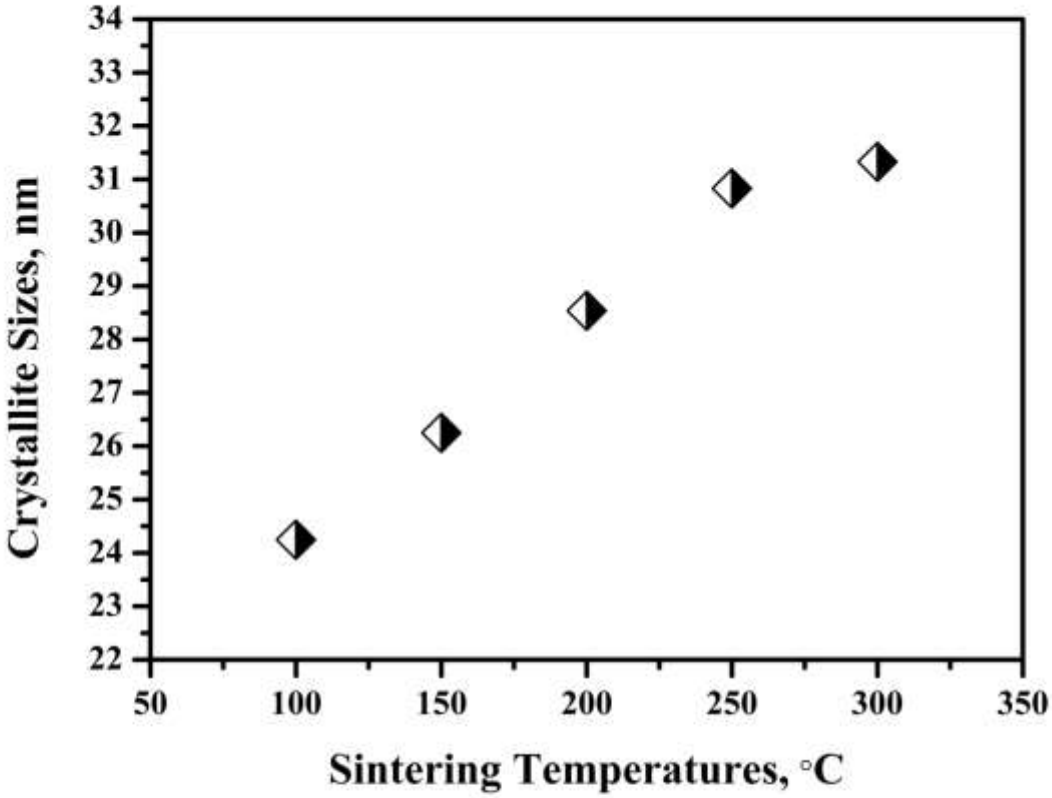

Fig. 2 Crystalline size of bulk $CuAlS_2$ at different sintering temperatures.

SEM analysis

Fig. 3 shows the treated surface morphology of bulk $CuAlS_2$ at (a) 100, (b) 250 and, (c) 300°C respectively. An increase in crystallization and formation of the $CuAlS_2$ phase was observed with increasing the sintering temperature. It can be noted that there are no pore between the granules. The cluster size shows remarkable rise with the sintering temperature which confirms improvement in crystal growth [17]. The relation between grain sizes and sulfur content at different temperatures could be attributed to the crystal structural modifications as seen in XRD analysis. The grain sizes that are calculated by both XRD and SEM measurements are found to be different. The reason returns to that the grain sizes appeared in SEM images are the grains that appeared only at the surface of bulk, while grain size calculated from the XRD is the average value of the grain sizes distributed throughout the thickness of the bulk. A similar observation was obtained by other researchers [18].

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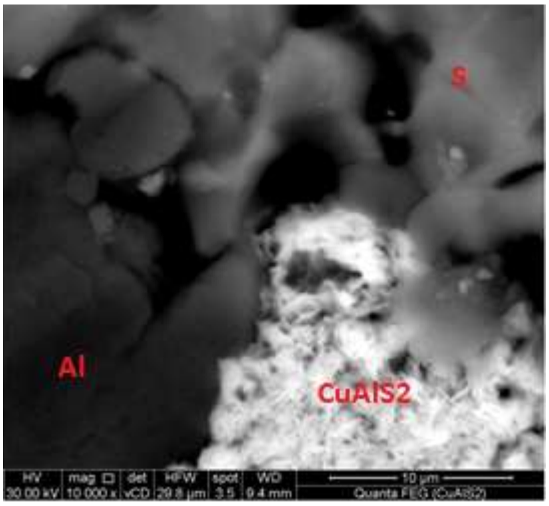
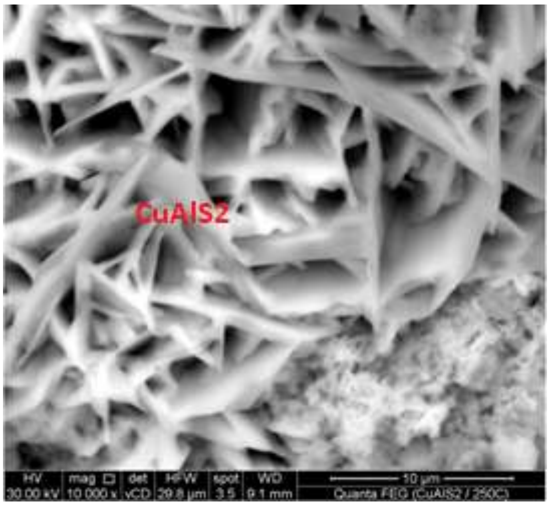


(a)



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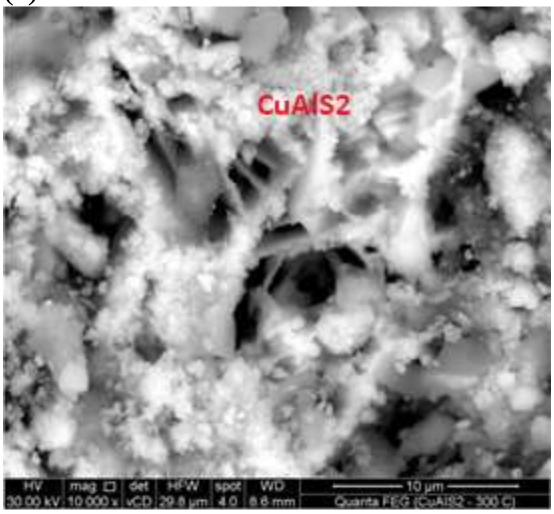
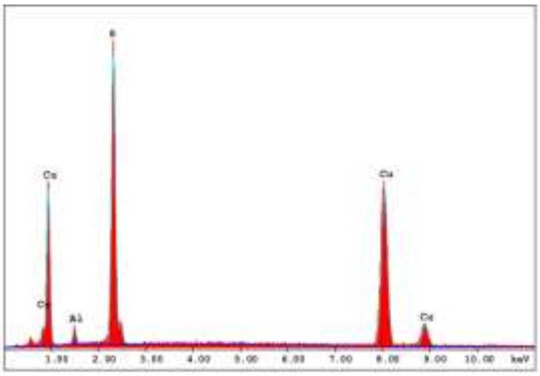


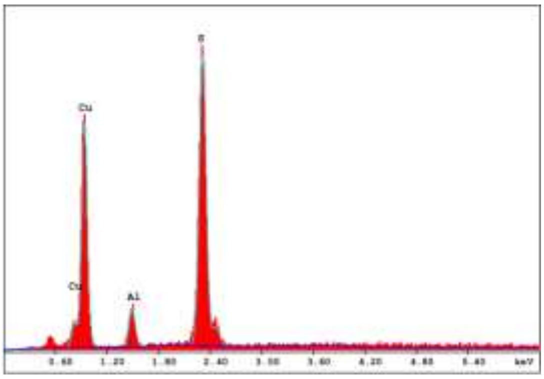
(c)

Fig. 3 SEM analysis for bulk $CuAlS_2$ at different temperatures, **(a)** 100°C, **(b)** 250°C, and **(c)** 300°C at 10000X.

EDS analysis

Energy dispersive [EDS] analysis as apparent in Fig. 4 shows that there are three elements is Cu, Al, and S in the bulk. The proportion of Cu, Al, and S is presented in Table 1. It has been observed that the stoichiometry ratios of the obtained materials and the starting materials were changed as the sintering temperature increases up to 300°C. This is due to the evaporation a certain amount of the sulfur during the sintering process. The results also showed that there is no trace of impurities.


(a)


(b)

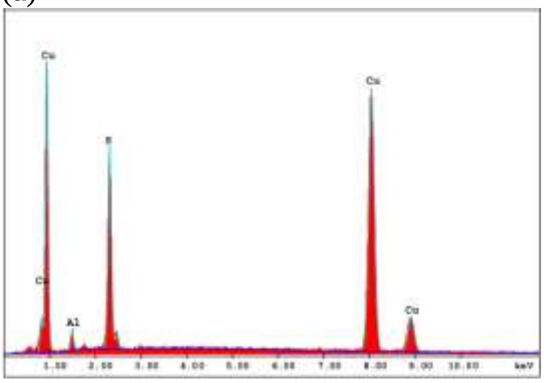

(c)

Fig. 4 EDS analysis for bulk $CuAlS_2$ at **(a)** 100°C, **(b)** 250°C, and **(c)** 300°C.

Table 1 EDS data for bulk $CuAlS_2$

Element	At %	At %	At %
	100°C	250°C	300°C
Cu	41.20	40.98	42.31
Al	17.32	18.09	17.52
S_2	41.48	40.93	40.17
Total	100.00	100.00	100.00

Optical reflectance measurements

The opposite behavior was also observed for the optical reflectance of the bulk $CuAlS_2$ as shown in Fig. 5. With increasing the sintering temperatures the reflectance decreases gradually. Where the values of the reflectance were decreased from 19% at 100°C to 15% at 200°C in the near infrared region [NIR] and from 23% at 100°C to 10% at 200°C and, 250°C in the visible [VIS] region at a wavelength starting from 200 to 2500 nm. The reflectance behavior of bulk $CuAlS_2$ can be interpreted as due to the high transparency in the visible [VIS] and infrared [NIR] regions, which is a consequence with the wide bandgap of the bulk [6]. This data indicates that the prepared $CuAlS_2$ by P/M method is a promising for working in the solar cells application.

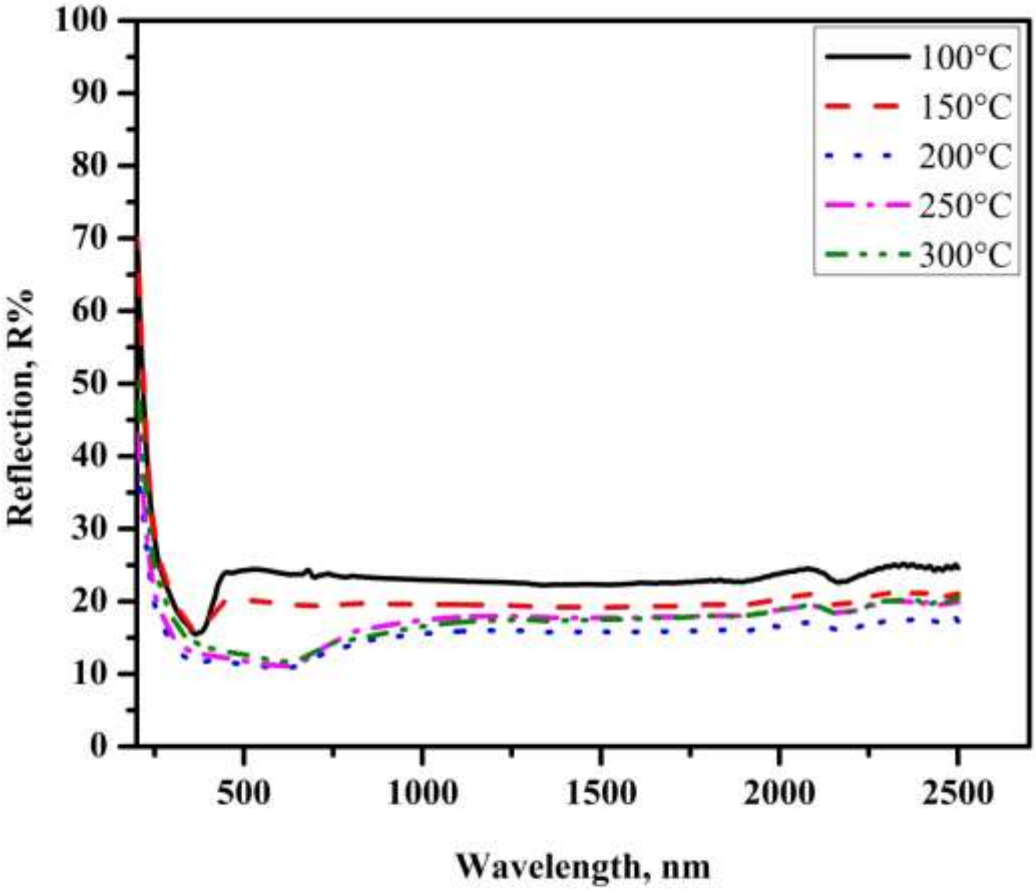


Fig. 5 Reflectance of bulk $CuAlS_2$ at different sintering temperatures.

CONCLUSION

The effect of sintering temperature on the microstructure and optical reflectance of bulk $CuAlS_2$ which was fabricated by powder metallurgy technique [P/M] has been studied. It has been found that sintering process technique is succeeded in improving the microstructure and hence the optical reflectance of bulk $CuAlS_2$. The properties of bulk $CuAlS_2$ have been evaluated by different characterization and testing techniques including, X-ray diffraction, SEM, EDS, and reflectance measurements. The results can be concluded as follows:

1. The bulk $CuAlS_2$ was successfully prepared by pressing and sintering into the vacuum tube furnace under argon as sintering atmosphere at different sintering temperatures of 100, 150, 200, 250 and 300°C.
2. XRD analysis reveals that the formation of $CuAlS_2$ with chalcopyrite structure as a dominant phase with preferred orientations of [1 1 2], [2 0 0], [2 2 0] and [0 0 8].
3. The analysis of SEM indicated that the crystallinity of the treated surface morphology of the bulk has been enhanced by increasing the sintering temperature. Also, the cluster size shows remarkable rise with the increase in the sintering temperature.

4. It has been observed that the stoichiometry ratios of the obtained materials and the starting materials were changed as the sintering temperature increases up to 300°C. This is due to the evaporation a certain amount of the sulfur during the sintering process.
5. With increasing the sintering temperature, the optical performance of the bulk $CuAlS_2$ has been improved and has a significant decrease in the reflectance [up to 10 %] at 250°C.

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