

Research Article

Structural Investigation of Photocatalyst Solid $\text{Ag}_{1-x}\text{Cu}_x\text{InS}_2$ Quaternary Alloys Sprayed Thin Films Optimized within the Lattice Compatibility Theory (LCT) Scope

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$\text{Cu}_x\text{Ag}_{1-x}\text{InS}_2$ solid thin films were fabricated through a low-cost process. Particular process-related enhanced properties lead to reaching a minimum of lattice mismatch between absorber and buffer layers within particular solar cell devices. First, copper-less samples X-ray diffraction analysis depicts the presence of AgInS_2 ternary compound in chalcopyrite tetragonal phase with privileged (112) peak ($d_{112} = 1.70 \text{ \AA}$) according to JCPDS 75-0118 card. Second, when x content increases, we note a shift of the same preferential orientation (112) and its value reaches 1.63 \AA corresponding to CuInS_2 chalcopyrite tetragonal material according to JCPDS 89-6095 file. Finally, the formation and stability of these quaternaries have been discussed in terms of the lattice compatibility in relation with silver-copper duality within indium disulfide lattice structure. Plausible explanations for the extent and dynamics of copper incorporation inside AgInS_2 elaborated ternary matrices have been proposed.

1. Introduction

AgInS_2 and CuInS_2 , which are both chalcopyrite ternary solids belonging to I-III-VI₂ compounds, are attractive materials of photovoltaic cells and optoelectronic devices because of their good stability under solar radiation, their large absorption coefficient, and their band gap energy lying in 1.5–2.1 eV domain. Theoretical calculation regarding solar conversion efficiencies of 27–32% has been made with I-III-VI₂ ternaries as absorbers. Even thin film solar cells of 12% efficiency have been successfully reached [1, 2]. However, these ternaries solar cells are typically fabricated by means of high-cost techniques, so that low-cost methods demand is noticeably increasing.

Indeed, the spray pyrolysis technique has not been widely used for preparing a large scale of such ternary materials for energy conversion purpose. In the same line, the mixture of both Ag and Cu as precursors of ternary materials in the started spraying solutions could lead to some various alloys having interesting physical characterisations.

Ciszek has proposed a method to fabricate the quaternary $\text{Cu}_x\text{Ag}_{1-x}\text{InS}_2$ [3]. It is noted that CuInS_2 material solidifies in chalcopyrite structures [4] whereas AgInS_2 can solidify in two forms: chalcopyrite and orthorhombic [5, 6]. Moreover, the latest ternary compound could be obtained as n-type or p-type semiconductor using appropriate experimental chemical conditions [7–14].

In this work, we report for the first time the preparation on glass substrates at 420°C of quaternaries $\text{Cu}_x\text{Ag}_{1-x}\text{InS}_2$ thin films using the spray pyrolysis technique from aqueous solutions. Each ternary has been achieved in our laboratory using appropriate conditions [6–8]. On the other hand, the structures of these films were studied by means of X-ray diffraction apparatus (Panalytical X Pert PROMPD, $\lambda = 1.54056 \text{ \AA}$) within the lattice compatibility theory. The optical properties were obtained from the analysis of the experimental recorded transmission and reflectance spectral data over the wavelength range 300–1800 nm using unpolarized light by means of a spectrophotometer (Shimadzu UV 3100S) [15].

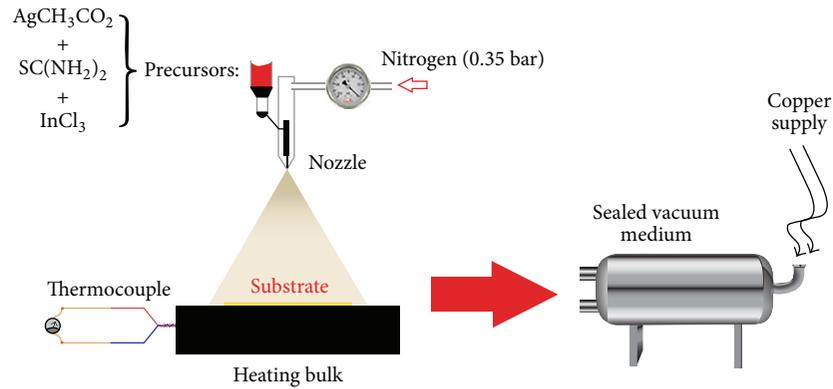


FIGURE 1: Global synthesis protocol scheme.

2. Results and Discussion

2.1. Experimental Details. Before copper processing, AgInS_2 thin films were first prepared at a glass substrate temperature of 420°C using an aqueous solution which contains silver acetate (AgCH_3CO_2), thiourea ($\text{SC}(\text{NH}_2)_2$), and indium chloride (InCl_3) as precursors. The precursor's concentrations are $[\text{Ag}^+]/[\text{In}^{3+}] = 1.3$ and $[\text{S}^{2-}]/[\text{In}^{3+}] = 5$. Molar ratios were prepared by mixing appropriate volumes of silver acetate 10^{-2} M , indium chloride 1.310^{-2} M , and thiourea 510^{-2} M . This protocol is considered as an optimal condition for preparing such a p-type compound [6–8]. The carrier gas was nitrogen (pressure $\approx 0.35\text{ bar}$) through a 0.5 mm diameter nozzle. The nozzle-to-substrate plane distance was fixed at the optimal value of 27 cm as demonstrated earlier, for the same disposal, by Boubaker et al. [16]. During the whole deposition process, precursor mixture flow rate was approximately 4 mL/min . In a second step, AgInS_2 sprayed thin films were annealed in a copper-rich sealed vacuum medium with different values of $x = [\text{Cu}^{2+}]/([\text{Ag}^+] + [\text{Cu}^{2+}])$. The values of x have been calculated using molar concentration data which were obtained via absorbance measurements. The whole protocol is summarized in Figure 1.

2.2. Analyses and Structural Patterns. The XRD spectra of the obtained compounds show in addition to the principle peak (112) the presence of (204), (312), and (116) additional peaks corresponding to the tetragonal structure of AgInS_2 with the presence of minor intensity peaks corresponding to AgInS_2 orthorhombic phase (Figure 1). These results have been obtained in other works [5–12].

XRD analysis corresponding to $\text{Cu}_x\text{Ag}_{1-x}\text{InS}_2$ alloys (Figure 2) exhibits a noticeable shift of (112) principle peak from 2θ position (27.08°), which is assigned to AgInS_2 material, to the angle (28.09°) corresponding to CuInS_2 solid compound. This proves the incorporation of copper in the AgInS_2 tetragonal matrix by taking the silver place.

2.3. Additional Conjoint Analyses. To reinforce and explain this interesting trend of Cu ions behavior, some lattice

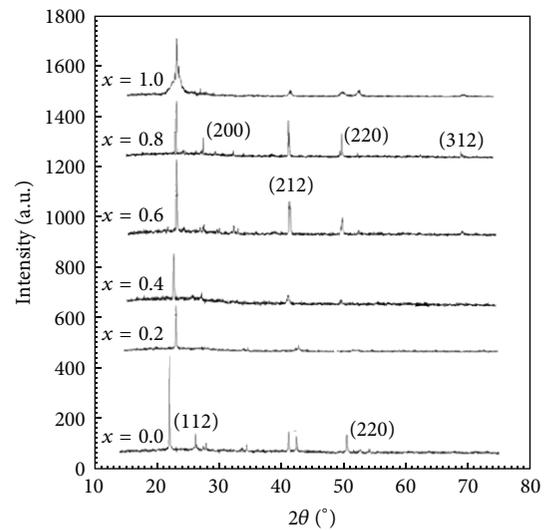


FIGURE 2: The XRD diagrams of $\text{Cu}_x\text{Ag}_{1-x}\text{InS}_2$ at various x ratio ($x = 0.0, 0.2, 0.4, 0.6, 0.8,$ and 1.0).

calculations were carried out. First, average crystallite size D values are obtained (Figure 1) from the Scherrer formula,

$$D = \frac{K\lambda}{\beta \cos\theta}, \quad (1)$$

where k is a constant $k = 0.9$. λ the length of wave $\lambda = 1.5418\text{ \AA}$. β is the full width at half maximum and θ is the angle of the strongest peak. Figure 2 gathers the variations of crystallite size along with those of energy band gap of $\text{Cu}_x\text{Ag}_{1-x}\text{InS}_2$ compounds with x ratio. The phenomenon of the decrease in the crystallite size ($D < 100\text{ nm}$) for films having $0.2 < x < 0.4$ can be explained by the low crystallization which is affected by the penetration of copper in the structure of AgInS_2 compound to form the quaternaries $\text{Cu}_x\text{Ag}_{1-x}\text{InS}_2$. The main event occurs when x is equal to unity and the CuInS_2 is definitely implemented while crystallization is highly improved ($D = 196.95\text{ nm}$). The parabolic fittings of both E_g and D versus x may explain the degradation of the structure when $0.2 < x < 0.6$

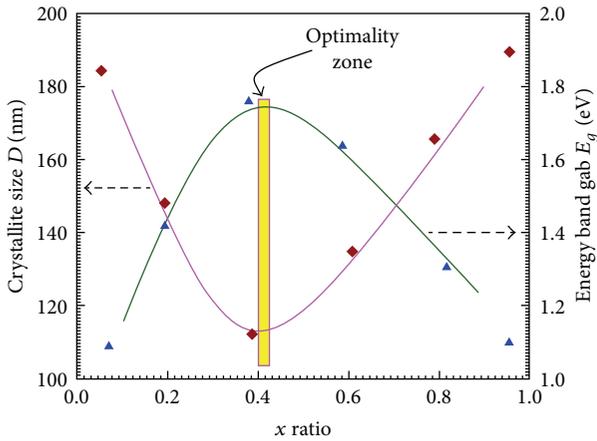


FIGURE 3: Conjoint variation of crystallite size D (nm) and energy band gap E_g of $\text{Cu}_x\text{Ag}_{1-x}\text{InS}_2$ with x ratio.

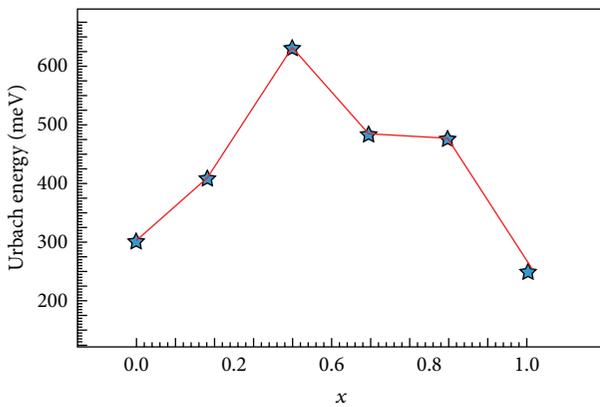


FIGURE 4: Variations of Urbach energy E_u of $\text{Cu}_x\text{Ag}_{1-x}\text{InS}_2$ with the x ratio.

and its enhancement for $0.6 < x < 1.0$. If criteria of stability are reported to a high bandgap along with reduced crystallite sizes [17–19], an optimality zone can be identified (shaded zone in Figure 3) thanks to the established second order fittings. This zone ($[0.40; 0.43]$) is in good concordance with several recently published values but seems to be more accurate.

2.4. Optical Study and Urbach Energy Analyses. The optical properties of the $\text{Cu}_x\text{Ag}_{1-x}\text{InS}_2$ thin films were determined from transmission and reflexion spectra in the range of 300–1800 nm wavelength range. Measurements were guides for evaluating Urbach energy E_u for each sample. In order to understand Urbach tailing alteration following copper ions insertion in the host AgInS_2 structures, Urbach energy E_u has been determined. This energy has been adopted as a reliable measure of the inhomogeneous disorder and atomic scale dispersion inside structures as it indicates the width of the band tails of the localized states in presence of defects. Figure 4 shows the low values of E_u corresponding to AgInS_2 and CuInS_2 compounds, which may be, among others (interstitials, antisites, vacancies, etc.), due to a minimum of

distortion of the band gap energy. Yet when $0.4 < x < 0.5$, the Urbach energy presented a maximum of distortion of the gap due to structure degradation and spin insatiability in the compound. These values are in good agreement with those reported in precedent sections concerning structural properties. They also confirm the nonlinearity of composition dependencies, as recorded, for similar compounds by Korzoun et al. [20].

3. Lattice Compatibility Theory (LCT) Analysis

3.1. Theoretical Fundamentals. According to the Lattice Compatibility Theory [21–28] and the generalized Simha-Somcynsky theory [28–31], any host lattice can be considered as a succession of elementary molecules and holes. Each cell in the occupied fraction is either empty or contains the molecule van-der-Waals volume as well as an inherent free volume. The behavior of any doping or introduced element is based on its interaction with existing host edifices. Preludes to this theory have been established by Boubaker et al. [25, 26] in the context of analysing Urbach tailing controversial behaviour in some nanocompounds as well as I-III-O₂ ternary oxides instability at low temperatures. It was also confirmed by Boubaker et al. [23, 24] on the bases of investigation on some copper-doped compounds. An original formulation of the Lattice Compatibility Theory [25, 26] has been established as follows:

“The stability of doping agents inside host structures is favored by geometrical compatibility, expressed in terms of matching patterns between doping agent intrinsic lattice and those of the host.”

3.2. Evidence of Optimality Occurrence. In the actually discussed case ($\text{Cu}_x\text{Ag}_{1-x}\text{InS}_2$ lattice), the nature of the highest occupied bands and the location of holes in both elemental copper and silver ions as well as CuInS_2 and AgInS_2 chalcopyrite lattice structures have been demonstrated to be determinant. In this context, fundamental geometrical observations concerning the structure of CuInS_2 and AgInS_2 ternary solid compounds (Figure 5) along with the host matrix were interpreted in terms of conventional lattice-linked parameters.

In this context, main lattice parameters of both CuInS_2 and AgInS_2 have been gathered in Figure 6, as extreme schemes ($x = 0$ and $x = 1$, resp.) for the x -dependent $\text{Cu}_x\text{Ag}_{1-x}\text{InS}_2$. Stoichiometry-related evolution of copper element incorporation inside the host matrix is equivalent to a gradual reduction of the first lattice parameter (a) along with a more amplified magnification of the third one (c). Under the presumption of a first-order linear x -dependent evolution, in concordance with Vegard’s law (in reference to difference in ionic radii between Ag and Cu, which prevents formation of solid solutions in the $\text{Cu}_x\text{Ag}_{1-x}\text{InS}_2$ system), a critical point could be detected at approximately $x = 0.42$ (Figure 6). This value is strongly supported by precedent analyses and studies about copper/silver substitution kinetics and extents [23, 24, 27–35] ternary chalcopyrite structures.

The Lattice Compatibility Theory (LCT) may give hence an explanation to the limit of incorporation of copper ions in

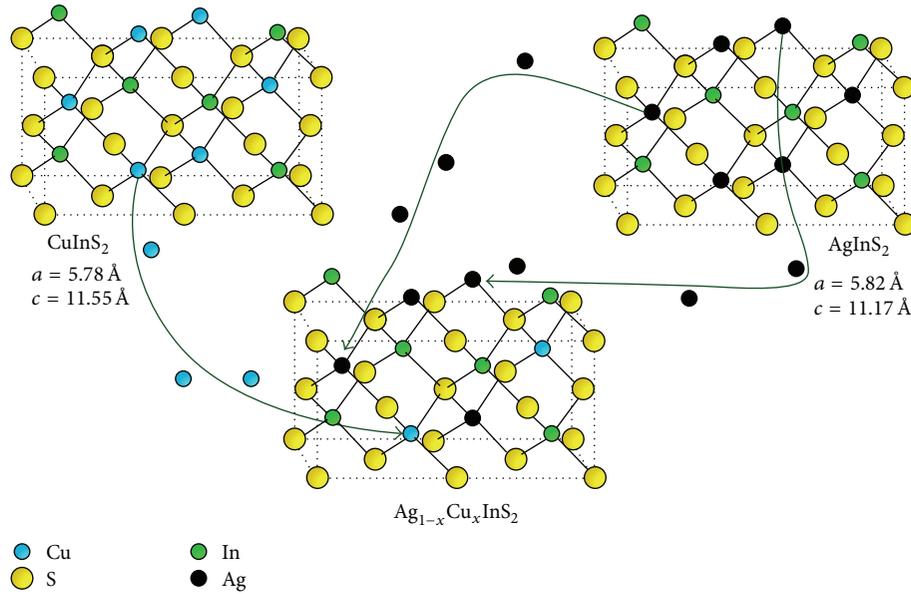


FIGURE 5: CuInS_2 , AgInS_2 , and $\text{Cu}_x\text{Ag}_{1-x}\text{InS}_2$ lattices elementary configuration.

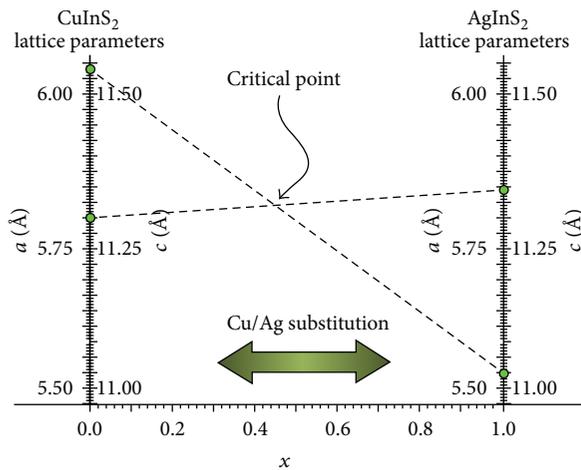


FIGURE 6: CuInS_2 , AgInS_2 , and $\text{Cu}_x\text{Ag}_{1-x}\text{InS}_2$ main lattice parameters x -dependent evolution scheme.

the AgInS_2 host matrix by taking silver's place, as confirmed earlier by the recorded XRD peak shift (Section 2.2).

4. Conclusion

The structural properties of $\text{Cu}_x\text{Ag}_{1-x}\text{InS}_2$ thin solid films, deposited on glass substrates by the spray pyrolysis technique from aqueous solutions using various ratios $x = [\text{Cu}]/([\text{Ag}]+[\text{Cu}])$ at 420°C as the substrate temperature, have been investigated. X-ray diffraction analysis confirms that all obtained solid films consist essentially of $\text{Cu}_x\text{Ag}_{1-x}\text{InS}_2$ quaternary tetragonal chalcopyrite compounds with (112) strong peak. On the other hand, it was recorded that the physical properties have been influenced by the penetration of the copper in the structure that showed clearly a band gap

energy E_g shift from 1.7 eV of AgInS_2 to 1.51 eV of CuInS_2 . A confirmed and experimentally supported extent of the cooper-to-silver ratio has been established through structure alteration in the framework of the Lattice Compatibility Theory (LCT) along with Simha-Somcynsky principles.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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