


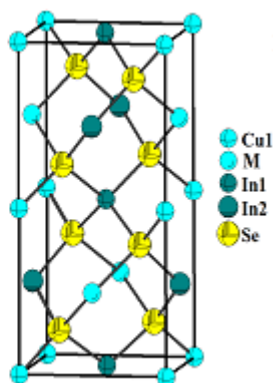
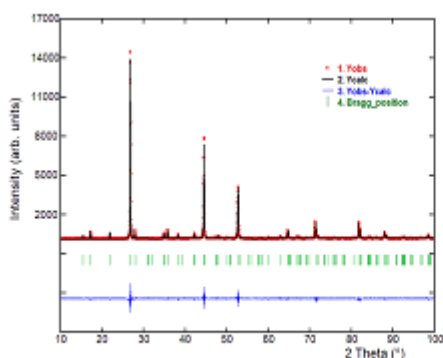
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Synthesis and Crystal Structure of the Ordered Vacancy Compound $\text{Cu}_3\text{In}_5\text{□Se}_9$

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This work focuses on the preparation and structural characterization of the semiconductor $\text{Cu}_3\text{In}_5\text{□Se}_9$, an important member of ordered vacancy compounds family, belonging to the semiconductor system $\text{I}_3\text{-III}_5\text{-□-VI}_9$, where □ denotes the cation vacancy which is included in the formula to maintain the same number of cations and anions sites. This material was synthesized by the Bridgman-Stockbarger technique, and its structure was refined from powder X-ray diffraction data using the Rietveld method. $\text{Cu}_3\text{In}_5\text{□Se}_9$ crystallizes with tetragonal symmetry in the space group $P\bar{4}2c$ (N° 112), with $a = 5.7657(1) \text{ \AA}$, $c = 11.5353(4) \text{ \AA}$, $V = 383.47(2) \text{ \AA}^3$. This ternary compound consists of a three-dimensional arrangement of distorted CuSe_4 and InSe_4 tetrahedral connected by common faces. In this structure, each Se atom is coordinated by four cations located at the corners of a slightly distorted tetrahedron, and each cation is tetrahedrally bonded to four anions. $\text{Cu}_3\text{In}_5\text{□Se}_9$ is related to the p-type CuInSe_2 and n-type CuIn_3Se_5 semiconductor compounds, which are being used in the preparation of high-efficiency solar cells.

Graphical abstract



Keywords

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1. Introduction

Chalcopyrite compounds of the Cu-III-Se_2 family (III= Al, Ga, In) form a broad group of semiconductor materials with different optical and electrical properties [1]. They crystallize with tetragonal symmetry in the space group $I\bar{4}2d$ (N°122).

In recent years considerable attention has been focused

on the detailed study of the ordered vacancy compounds (OVCs) related to the chalcopyrite compounds, particularly CuInSe_2 which has emerged as a leading material for the preparation of photovoltaic devices due to their potential applications in solar cell technology [2, 3].

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In studying the defect physics of CuInSe_2 , Zhang *et al.* [4] have suggested that the presence of the donor-acceptor defect pair ($2\text{V}^{1-}\text{Cu}+\text{In}^{2+}\text{Cu}$) in this material explains the existence of the CuIn_5Se_8 ($n=4$), $\text{Cu}_2\text{In}_6\text{Se}_{10}$ (CuIn_3Se_5) ($n=5$), $\text{Cu}_3\text{In}_7\text{Se}_{12}$ ($n=6$), $\text{Cu}_2\text{In}_4\text{Se}_7$ ($n=7$), $\text{Cu}_5\text{In}_9\text{Se}_{16}$ ($n=8$) and $\text{Cu}_3\text{In}_5\text{Se}_9$ ($n=9$) OVCs, according to the $\text{Cu}_{n-3}\text{In}_{n+1}\text{Se}_{2n}$ formula. All these ternary phases fulfill the rules of formation of adamantane compounds and belong to the defect or vacancy semiconductor compound families [5].

The materials of the Cu-In-Se system are of considerable technological interest due to their use in the preparation of solar cells with efficiency higher than 23% [6-8]. Also, Cu-based chalcogenides, have received increasing attention as promising thermoelectric materials due to their high efficiency, tunable transport properties, high elemental abundance, and low toxicity [9].

From the structural point of view, several authors have reported that most of these OVCs crystallize in chalcopyrite-related structures [10-14]. In particular, the ternary compound $\text{Cu}_3\text{In}_5\text{Se}_9$ ($n=6$), or more precisely $\text{Cu}_3\text{In}_5\Box\text{Se}_9$, where \Box denotes the cation vacancy which is included in the formula to maintain the same number of cations and anions sites, belongs to the family of $\text{I}_3\text{-III}_5\text{-VI}_9$ OVCs. Concerning its crystal structure, scarce information has been reported in the literature. According to Parlak *et al.* [15], this compound crystallizes in the orthorhombic $Pmm2$ space group with unit cell parameters $a=9.767(2)$ Å, $b=9.225(5)$ Å, $c=5.257(2)$ Å as shown in the PDF-051-0803 file found in the Powder Diffraction File database (ICDD, 2017). Meanwhile, Rincón *et al.* [3] reported a tetragonal $P\bar{4}2c$ cell with parameters $a=5.7630(4)$ Å, $c=11.5370(8)$ Å. In any case, the crystal structure of this material was not determined.

For this reason, in the present work, the structural characterization of the ordered vacancy compound $\text{Cu}_3\text{In}_5\Box\text{Se}_9$ from powder X-ray powder diffraction data, using the Rietveld method, is reported. From the study, to establish its crystal structure unequivocally; unit cell parameters, atomic coordinates, isotropic temperature factors, and other relevant geometric data, are determined.

2. Results and Discussion

The precise determination of peak positions was carried out employing the Winplotr analytical software [18]. The indexing of the powder X-ray diffraction data was performed using the computer program Dicvol04 [19]. The twenty-first peak positions measured from the powder pattern were used as input data. A unique solution was readily obtained in a tetragonal system. The analysis of the systematically absent reflections showed the space group to be $P\bar{4}2c$. The Rietveld refinement [20] was carried out using the program Fullprof program [21]. The initial model of $\text{Cu}_3\text{In}_5\Box\text{Se}_9$ was obtained from the isostructural compound $\text{Cu}_3\text{In}_5\Box\text{Te}_9$ [22]. The results of the Rietveld refinement are summarized in Table 1. Figure 1 shows the room temperature Rietveld refined powder X-ray diffraction data, which confirms the single-phase nature and the tetragonal crystal structure of $\text{Cu}_3\text{In}_5\Box\text{Se}_9$. Table 2 shows the atomic coordinates, isotropic temperature factor, and bond distances.

$\text{Cu}_3\text{In}_5\Box\text{Se}_9$, an ordered vacancy compound of the $\text{I}_3\text{-III}_5\text{-VI}_9$ family of semiconductors, has a defective adamantane structure [5] and crystallizes in a P -chalcopyrite cell [12]. However, in this compound, a degradation of symmetry from

the chalcopyrite structure $I\bar{4}2d$ to a related $P\bar{4}2c$ structure occurs. This lowering of symmetry arises from the statistical occupancy of the Wyckoff positions $2b$ ($\frac{1}{2}, 0, \frac{1}{4}$) by either of two cations: Cu2, In3, and vacancies being these positions the ones associated with the centering of the cell. In the P -chalcopyrite structure, the introduction of additional cations in the crystal lattice of the chalcopyrite parent produces a degradation of symmetry from the space group $I\bar{4}2d$ to the related $P\bar{4}2c$, which leaves the cell volume almost unchanged [23]. This condition can be seen in Figure 2, where it makes a comparison between the chalcopyrite $I\bar{4}2d$ structure of CuInSe_2 and the P -chalcopyrite $P\bar{4}2c$ structure of $\text{Cu}_3\text{In}_5\Box\text{Se}_9$ is made. In this structure, each Se atom is coordinated by four cations: one Cu1, one In1, one In2, and one M [with (M = Cu2 (0.333), In3 (0.222), \Box (0.445))], located at the corners of a tetrahedron slightly distorted. Similarly, each cation is tetrahedrally bonded to four anions.

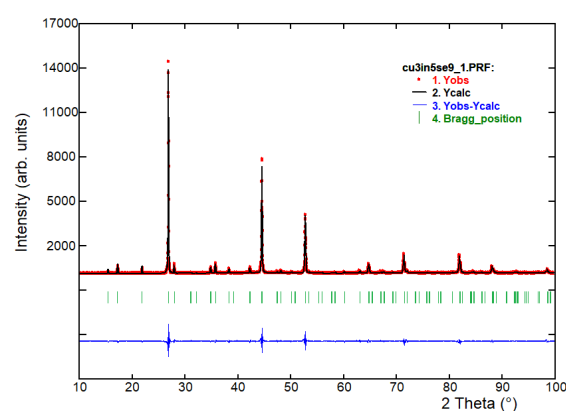


Fig. 1. Rietveld final plot of $\text{Cu}_3\text{In}_5\Box\text{Se}_9$. The lower trace is the difference curve between observed and calculated patterns. The Bragg reflections are indicated by vertical bars.

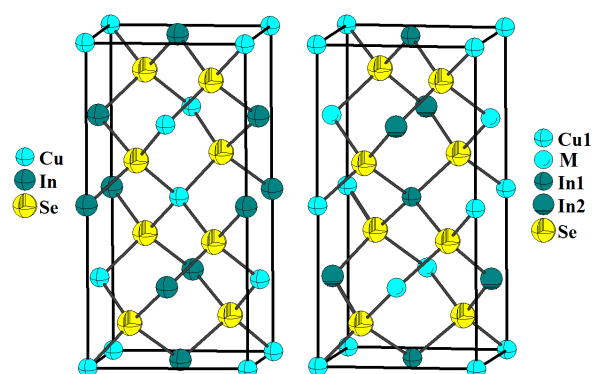


Fig. 2. Unit cell diagram for the chalcopyrite CuInSe_2 ($I\bar{4}2d$) vs P -chalcopyrite $\text{Cu}_3\text{In}_5\Box\text{Se}_9$ ($P\bar{4}2c$). (M = Cu2 (0.333), In3 (0.222), \Box (0.445)).

In the $\text{Cu}_3\text{In}_5\Box\text{Se}_9$ crystal structure, the tetrahedra containing the Cu atoms [mean Se-Se distance 3.954(8) Å] are lightly smaller than those containing the In2 [mean Se-Se distance 4.161(8) Å], M atoms [mean Se-Se distance 4.224(8) Å] and In1 atoms [mean Se-Se distance 4.235(9) Å], respectively. The interatomic distances are shorter than the sum of the specific ionic radii for tetrahedrally bonded structures [24]. The Cu-Se [2.414(6) Å] and In-Se [2.496(6) Å]

average] bond distances compare well to those observed in other adamantane structure compounds such as CuInSe_2 (2.432 Å - 2.591 Å) [25], Cu_2SnSe_3 (2.415 Å) [26], CuFeInSe_3

(2.421 Å - 2.520 Å) [23], $\text{CuFe}_2\text{InSe}_4$ (2.417 Å - 2.50 Å) [27], $\text{CuMn}_2\text{InSe}_4$ (2.447 Å - 2.594 Å) [28] and $\text{Cu}_3\text{In}_7\text{Se}_{12}$ (2.419 Å - 2.523 Å) [29].

Table 1. Rietveld refinement results for $\text{Cu}_3\text{In}_5\text{Se}_9$.

Molecular formula	$\text{Cu}_3\text{In}_5\text{Se}_9$	wavelength (CuK α)	1.54056 Å
Molecular weight (g/mol)	1311.35	data range 2 θ (°)	10-100
a (Å)	5.7657(1)	step size 2 θ (°)	0.02
c (Å)	11.5353(4)	counting time (s)	30
c/a	2.00	step intensities	4501
V (Å ³)	383.47(2)	independent reflections	160
Z	0.889 (8/9)	R _p (%)	7.5
Crystal system	tetragonal	R _{wp} (%)	9.2
Space group	$P\bar{4}2c$ (N° 112)	R _{exp} (%)	6.4
d _{calc} (g/cm ³)	5.72	R _B (%)	7.8
Temperature (K)	298(1)	S	1.4

$R_p = 100 \sum |y_{\text{obs}} - y_{\text{calc}}| / \sum y_{\text{obs}}$. $R_B = 100 \sum_k |l_k - |c_k|| / \sum_k |l_k|$. $S = [R_{wp}/R_{exp}]$. $R_{wp} = 100 [\sum_w |y_{\text{obs}} - y_{\text{calc}}|^2 / \sum_w |y_{\text{obs}}|^2]^{1/2}$. $R_{exp} = 100 [(N+C) / \sum_w (y_{\text{obs}}^2)]^{1/2}$. $N+C$ = degrees of freedom

Table 2. Atomic coordinates, occupancy factors, isotropic temperature factors, bond lengths (Å), and angles (°) for $\text{Cu}_3\text{In}_5\text{Se}_9$, derived from the Rietveld refinement.

Atom	Ox.	Wyck.	x	y	z	foc	B (Å ²)	
Cu1	+1	2e	0	0	0	1	0.5(2)	
In1	+3	2f	½	½	0	1	0.5(2)	
In2	+3	2d	0	½	¼	1	0.5(2)	
Cu2	+1	2b				0.333	0.5(2)	
In3	+3	2b	½	0	¼	0.222	0.5(2)	
□	-	2b				0.445	-	
Te	-2	8n	0.2299(8)	0.2511(8)	0.1218(7)	1	0.5(2)	
Cu1-Se	2.414(6)	In1-Se	2.541(6)	In2-Se	2.450(6)			
Se ⁱ -Cu1-Se ⁱⁱ	x2	108.4(2)	Se ⁱ -Cu1-Se	x4	110.0(2)	Se ⁱⁱⁱ -In1-Se	x2	108.0(2)
Se ⁱⁱⁱ -In1-Se ^{iv}	x4	112.5(2)	Se ^v -In2-Se	x2	108.3(2)	Se-In2-Se ^{vi}	x2	105.7(2)
Se-In2-Se ^{vii}	x2	114.5(2)	Se ^{iv} -M-Se ^v	x4	109.9(2)	Se ^{iv} -M-Se ^{viii}	x2	105.7(2)

Symmetry codes: (i) -y, x, -z; (ii) -x, -y, z; (iii) y, 1-x, -z; (iv) 1-x, 1-y, z; (v) -x, y, 0.5-z; (vi) -x, 1-y, z; (vii) x, 1-y, 0.5-z; (viii) 1-x, y, 0.5-z

3. Material and Methods

3.1. Synthesis

Ingots of $\text{Cu}_3\text{In}_5\text{Se}_9$ were prepared by the vertical Bridgman-Stockbarger technique. They were obtained by heating the stoichiometric mixture of Cu, In, and Se sealed in evacuated quartz ampoules, previously subject to pyrolysis to avoid the reaction of the starting materials with quartz. The ampoules were placed in a multiple-zone vertical furnace. They were initially heated from room temperature to 1150 °C at a rate of 10 °C/h with a dwell time of 12 h at 300 °C. The molten mixture was kept at this temperature for 24 h. To assure a homogeneous mixing, the ampoule was agitated periodically. It was later cooled at a rate of 10 °C/h up to 900 °C, then at 1 °C/h to 700 °C. The cooling rate from 700 to 530 °C was 5 °C/h. The ingots were annealed at this temperature for 120 h. The furnace was then turned off, and the ingot cooled down to room temperature at 40 °C/h. Figure 3 shows an image of the oven used.



Fig. 3. Picture of the vertical furnace for growth by Bridgman-Stockbarger technique of the $\text{Cu}_3\text{In}_5\text{Se}_9$ compound.

3.2. Chemical Analysis

The chemical composition of the ingots was determined at several points by energy-dispersive X-ray spectroscopic (EDS) using a KeveX model Delta-3 system connected to a Hitachi model S-2500 scanning electron microscope (SEM). The error in the standardless analysis was around 5%. Samples obtained from the central part of relatively homogeneous ingots gave representative compositions of Cu:In:Se as 17.69:29.27:53.04 atomic percentage, respectively, very close to the ideal value 3:5:9. Figure 4 shows the EDS plot results used to determine the chemical composition of the crystal.

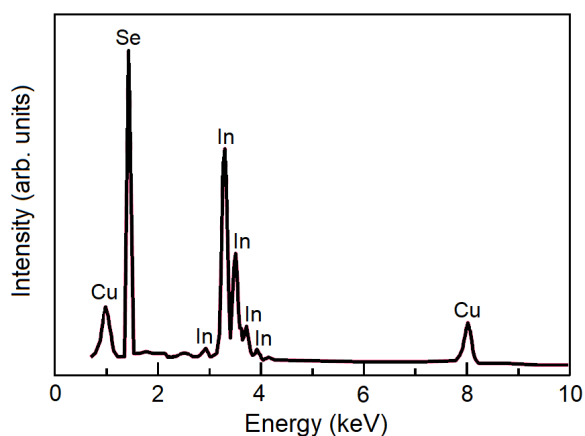


Fig. 4. Energy-dispersive X-ray spectroscopic (EDS) plot for $\text{Cu}_3\text{In}_5\text{Se}_9$.

3.3. Powder X-Ray Diffraction

A small quantity of the sample was ground in an agate mortar and pestle. The resulting powder was mounted on a flat zero-background holder. X-ray diffraction data were measured, in θ/θ reflection mode, using a Siemens D5005 diffractometer equipped with an X-ray tube (CuK α radiation: $\lambda = 1.54059 \text{ \AA}$; 40kV, 30 mA) and a diffracted beam graphite monochromator. Data were collected at room temperature. The specimen was scanned in the 2θ range of $10\text{--}110^\circ$, the scan step was 0.02° , and the time of counting in every step was 30 s. Quartz was used as an external standard.

4. Conclusions

The ternary semiconductor $\text{Cu}_3\text{In}_5\text{Se}_9$, belonging to the ordered vacancy compounds of the Cu-In-Se semiconductor system, was synthesized by the Bridgman-Stockbarger technique and its crystal structure was characterized by X-ray diffraction analysis. Rietveld refinement from the powder X-ray data allowed us to determine the crystal structure of this compound. This OVC crystallizes in the tetragonal space group $P\bar{4}2c$, with a $\text{Cu}_3\text{In}_5\text{Te}_9$ -type structure. This is a new structural characterization of one member of the $\text{I}_3\text{-III}_5\text{-VI}_9$ family of semiconductors with a defective adamantine structure. $\text{Cu}_3\text{In}_5\text{Se}_9$ is related to the p -type CuInSe_2 and n -type CuIn_3Se_5 semiconductor compounds, which are being used in the preparation of highly efficient solar cells.

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Author Contributions

Gerzon E. Delgado: Conceptualization, Writing – review & editing, Supervision. Giovanni Marin: Methodology. Syed Wasim: Methodology. Carlos Rincón: Conceptualization, Writing – review & editing. Dinesh P. Singh: Methodology

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