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A new ordered vacancy compound; preparation and crystal structure of $Ag_3In_5\square Te_9$

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The new ordered vacancy compound $Ag_3In_5\square Te_9$ was synthesized by the melt and annealing technique and its structure was refined from X-ray powder diffraction pattern using the Rietveld method. The title compound crystallizes in the tetragonal space group P$\bar{4}$2c (N° 112), with $a = 6.3453(2)$ Å, $c = 12.5754(7)$ Å, $V = 506.32(4)$ Å^3. The refinement of 23 instrumental and structural parameters led to $R_p = 5.4$%, $R_{wp} = 5.8$%, $R_{exp} = 5.1$%, $S = 1.1$. This ternary compound is isostructural with $Cu_3In_5\square Te_9$ and have a defect adamantane structure.

Keywords: Ordered vacancy compound; crystal structure; X-ray powder diffraction; Rietveld refinement; $AgInTe_2$

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1. Introduction

The compounds with ternary chalcogenide structures of the chalcopyrite family I-III-VI_2 (where I = Cu or Ag; III = Al, Ga or In; and VI = S, Se or Te), form a wide group of semiconductor materials with diverse optical and electrical properties [1]. They crystallize with tetragonal symmetry in the space group I$\bar{4}$2d (N°122) being isostructural with the $CuFeS_2$ mineral (chalcopyrite) from which they take their name [2]. This family of compounds fulfill the rules of formation of adamantane compounds and belongs to the normal semiconductor compound families [3].

In particular, the ternary chalcopyrite semiconductor $CuInSe_2$ has emerged as a leading material for the preparation of photovoltaic devices due to their potential applications in solar cell technology [4]. In studying the defect physics of $CuInSe_2$, Zhang *et. al*. [5] have suggested that the presence of the donor-acceptor defect pair ($2V^1$-Cu + In^{2+}Cu) could be used to explain the existence, according $Cu_{n-3}In_{n+1}Se_{2n}$, of $CuIn_5Se_8$ ($n = 4$), $CuIn_3Se_5$ ($n = 5$), $Cu_3In_7Se_{12}$ ($n = 6$), $Cu_2In_4Se_7$ ($n = 7$), $Cu_5In_9Se_{16}$ ($n = 8$), $Cu_3In_5Se_9$ ($n = 9$) as due to the repeat of a single unit of this defect pair for each $n = 4$, 5, 6, 7, 8 and 9 units, respectively, of $CuInSe_2$. These new materials, which have a deficiency of cations over the anions, belongs to the defect semiconductor families [3], and are known as ordered vacancy compounds (OVC's) [6].

Similarly we can define Ag-content derivatives, from the chalcopyrite $AgInTe_2$, and the existence of several of these compositions has been shown from the phase diagrams analysis of the AgTe-In_2Te_3 pseudo-binary system [7,8], such as $AgIn_5Te_8$ ($n = 4$), $AgIn_3Te_5$ ($n = 5$) and $Ag_3In_5Te_9$ ($n = 9$), which can be written as $AgIn_5\square_2Te_8$, $AgIn_3\square Te_5$ and $Ag_3In_5\square Te_9$, where □ represents the cation vacancy. The semiconducting behavior of these OVC's has been explained, based on the four electrons-per-site rule, by assigning to this vacancy a zero valent atom [5].

While Cu-content OVC's are of great interest for thermoelectric applications [9], the Ag-content compounds are potential candidates for several applications as photoabsorbers in solar cells, opto-electronics devices and photoelectrochemical cells [10], Concerning the crystal structures in the Ag-In-Te system, the ternary compositions $AgInTe_2$ [11], $AgIn_5\square_2Te_8$ [12] and $AgIn_3\square Te_5$ [13] crystalize in tetragonal structures with space groups I$\bar{4}$2d (N° 122), P$\bar{4}$2m (N° 111) and P$\bar{4}$2c (N° 112), respectively. For $Ag_3In_5Te_9$ only a report in the literature shown a tetragonal unit cell with parameters $a = 8.738$ and $c = 7.147$, without space group assigned [14].

Therefore, in this work, we report a detailed structural analysis of the new ternary compound $Ag_3In_5\square Te_9$, which crystallize with a P-chalcopyrite structure [15]. From this study, unit cell parameters, atomic coordinates, isotropic temperature factors and other relevant geometric data could be determined using X-ray powder diffraction data.

2. Experimental

The sample was synthesized by direct fusion of stoichiometric quantities of Ag, In and Te (99.99%) in a sealed, evacuated quartz ampoule and subsequent quenching in water. The mixture was slowly heated up to 523 K at a rate of 4 K/min. The ampoule was kept at this temperature for a period of 6 hours in order to allow the exothermic reaction between In and Te. Then, the temperature was gradually raised at the same rate up to 773 K. It was kept at this condition for 24 hours. Subsequently, it was heated up to 1323 K, which is higher than the melting points of the constituent elements, and kept at this temperature for 7 days. The charge in the ampoule was allowed to react in this molten state for 60 h with intermittent shaking in order to improve the homogeneity. Finally, the ampoule with the charge in the molten state was quenched in water. The chemical composition of $Ag_3In_5Te_9$ crystals was determined by energy dispersive spectroscopic (EDS) analysis using a JSM-6400 electron microscope. The atomic compositions of the studied sample are: Ag (17.0%), In (29.9%) and Te (53.1%), from three different regions of the ingot. These percentages are in good quality agreement with the ideal composition 3: 5: 9. For the X-ray analysis, a small quantity of the sample, cut from the ingot, was ground mechanically in an agate mortar and pestle. The resulting fine powder was mounted on a flat holder covered with a thin layer of petroleum jelly. The X-ray powder diffraction data was collected at 293(1) K, in $\theta/2\theta$ reflection mode with Bragg-Brentano geometry, using a Panalytical X'pert diffractometer equipped with an X-ray tube (CuKα radiation: $\lambda = 1.5418$ Å; 40kV, 30 mA). The specimen was scanned from 10-100° 2θ, with a step size of 0.02° and counting time of 20 s. Silicon (SRM-640) was used as an external standard. The Panaytical X'pert Pro analytical software was used to establish the positions of the peaks.

3. Results and discussion

The X-ray diffractogram of $Ag_3In_5\square Te_9$ shows a single phase. The peak positions were extracted by means of single-peak profile-fittings carried out with the *WinPLOTR* software [16]. The first 20 peak positions measured from the pattern were input to the auto-indexing program DICVOL04 [17].

A unique solution was obtained in a tetragonal system with unit cell parameters $a = 6.186(1)$ Å, $c = 12.365(2)$ Å. The lack of systematic absence condition $h + k + l$ in the general reflections of the type hkl indicating a P-type cell and rule out the I-type cell of the chalcopyrite structure. In addition, the conditions hhl: $l = 2n$ and $00l$: $l = 2n$ suggests the extension symbol P$\bar{4}$2c. A comparison of the pattern taking into account the chemical composition, crystal system and cell parameters, showed that this material is isostructural with the $Cu_3In_5\square_2Te_9$ compound, the first crystal structure reported for a I_3-III_5-$\square_2$-VI_9 member, which crystallize in the tetragonal space group P$\bar{4}$2c (N° 112) [18] with a P-chalcopyrite structure [15].

For the Rietveld refinement [19], the whole diffraction data was used. This was carried out using the Fullprof program [20] available in the software package *WinPLOTR* [15]. The atomic coordinates of the $Cu_3In_5\square_2Te_9$ compound [17], were used as starting parameters and the unit cell parameters were those obtained from indexing. The angular dependence of the peak full width at half maximum (FWHM) was described by the usual constrain imposed by the Caglioti's formula [21]. Peak shapes were described by the parameterized Thompson-Cox-Hastings pseudo-Voigt profile function [22]. The background was described by the automatic interpolation of 67 points throughout the whole pattern. With the diffraction data available it was only possible to described the thermal motion of the atoms by one overall isotropic temperature factor.

The final figures of merit for 23 instrumental and structural variables were: $R_p = 5.4\%$, $R_{wp} = 5.8\%$, $R_{exp} = 5.1\%$, for 4501 step intensities and 152 independent reflections. The final Rietveld plot is shown in Fig. 1. Unit cell parameters, atomic coordinates, isotropic temperature factor, bond distances and angles are listed in Table I.

The structure of the ternary phase $Ag_3In_5\square Te_9$ is a P-chalcopyrite-like compound [18], and can be described as a derivative of the sphalerite structure. In this structure the anions (Te) form a close-packed arrangement with the tetrahedral sites occupied by the cations (Ag, In) and vacancies ($\square$) in a partially ordered fashion. This array is expected for adamantane compounds [3] and can be observed in the unit cell diagram of this ternary chalcogenide compound (Fig. 2).

TABLE I. Rietveld refinement details for $Ag_3In_5\square Te_9$.

Molecular formula	$Ag_3In_5\square Te_9$	wavelength (CuKα)	1.5418 Å
Molecular weight (g/mol)	1973.44	data range 2θ(°)	10-100
a (Å)	6.3453(2)	step size 2θ (°)	0.02
c (Å)	12.5754(7)	counting time (s)	20
c/a	1.98	step intensities	4501
V (Å^3)	506.32(4)	independent reflections	152
Z	0.889 (8/9)	R_p (%)	5.4
Crystal system	tetragonal	R_{wp} (%)	5.8
Space group	P$\bar{4}$2c (N° 112)	R_{exp} (%)	5.1
dcalc (g/cm^{-3})	6.47	R_B (%)	4.7
Temperature (K)	298(1)	S	1.1

$R_{exp} = 100[(\text{N-P+C})/\sum_w (y_{obs}^2)]^{1/2}$, $R_p = 100\sum |y_{obs} - y_{calc}|/\square|y_{obs}|$ $R_{wp} = 100[\sum_w |y_{obs} - y_{calc}|^2/\sum_w |y_{obs}|^2]^{1/2}$,
$S = [R_{wp}/R_{exp}]$ $R_B = 100\sum_k |I_k - I_{c_k}|/\sum_k |I_k|$, N-P+C is the number of degrees of freedom

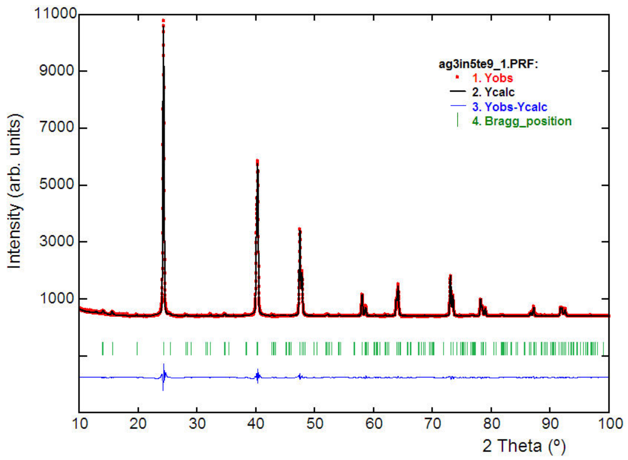

FIGURE 1. Final Rietveld refinement plot showing the observed, calculated and difference pattern for $Ag_3In_5□Te_9$. The Bragg reflections are indicated by vertical bars.

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 behavior was also found in some materials with compositions I-II-III-VI$_3$, I-III$_3$-□-VI$_5$, I$_3$-III$_7$-□$_2$-VI$_{12}$ and I$_3$-III$_5$-□-VI$_9$, trying to derive structural models that describe their crystalline structures from X-ray powder diffraction data. These are the cases of the seminal reports of the compounds with structure-types $CuFeInSe_3$ [23], $AgIn_3□Te_5$ [13], $Cu_3In_7□_2Se_{12}$ [24] and $Cu_3In_5□Te_9$ [17], respectively.

The tetrahedra containing the Ag atoms [mean Te...Te distance 4.584(7) Å] are lightly smaller than those containing the In2 atoms [mean Te ... Te distance 4.532(7) Å], M [mean Te ... Te distance 4.498(7) Å] and In1 atoms [mean Te ... Te distance 4.288(7) Å], respectively.

The Ag-Te [2.897(5) Å] and In-Te [2.701(5) Å] bond distances compare quite well with those observed in other adamantane structure compounds such as $AgInTe_2$ [11], $AgIn_5□_2Te_8$ [12], $AgIn_3□Te_5$ [13], $CuInTe_2$ [25], $CuTa_2InTe_4$ [26], $Ag_2FeGaTe_4$ [27], $CuCo_2InTe_4$ and $CuNi_2InTe_4$ [28], Ag_2SnTe_3 [29] and $Cu_3In_7□_2Te_{12}$ [30]. Table III shown the unit cell and bond lengths comparison between the four compounds of the Ag-In-Te system reported so far.

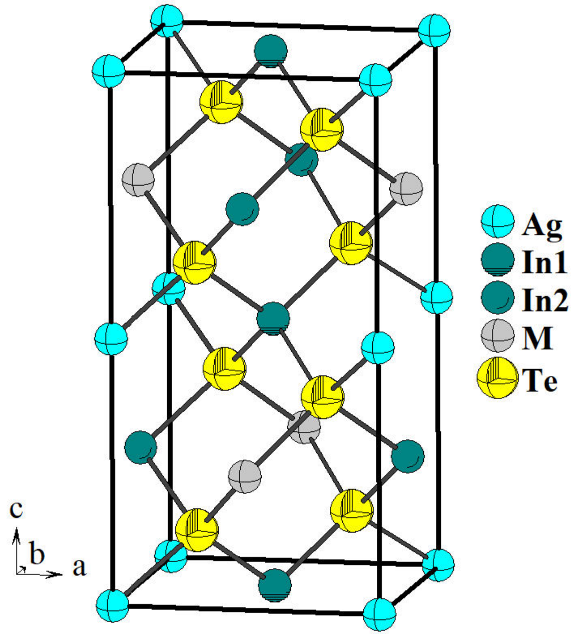

FIGURE 2. Unit cell diagram for the new P-chalcopyrite compound $Ag_3In_5□Te_9$ ($P\bar{4}2c$). M (Wyckoff site 2b) = Ag2 (0.333), In3 (0.222), □ (0.445).

TABLE II. Atomic coordinates, occupancy factors, isotropic temperature factors, bond lengths (Å) and angles (°) for $Ag_3In_5□Te_9$, derived from the Rietveld refinement.

Atom	Ox.	Wyck.	x	y	z	foc	B (Å^2)
Ag1	+1	2e	0	0	0	1	0.4(2)
In1	+3	2f	1/2	1/2	0	1	0.4(2)
In2	+3	2d	0	1/2	1/4	1	0.4(2)
Ag2		2b				0.333	0.4(2)
In3		2b	1/2	0	1/4	0.222	0.4(2)
□	-	2b				0.445	-
Te	-2	8n	0.2637(7)	0.2608(7)	0.1217(5)	1	0.4(2)
Ag1-Te	2.897(5)		In1-Te	2.626(5)		In2-Te	2.776(5)
Te^{i}-Ag1-Te	107.3(1)		Te^{ii}-Ag1-Te^{iv}	113.9(1)		Te^{iii}-Ag1-Te^{iv}	107.3(1)
Te^{ii}-Ag1-Te^{iii}	107.3(1)		Te^{iii}-Ag1-Te	113.9(1)		Te-Ag1-Te^{iv}	107.3(1)
Te^{viii}-In1-Te	108.7(1)		Te^{viii}-In1-Te^{x}	109.9(2)		Te-In1-Te^{x}	108.7(1)
Te^{viii}-In1-Te^{ix}	108.7(1)		Te-In1-Te^{ix}	109.9(2)		Te^{ix}-In1-Te^{x}	108.7(1)
Te-In2-Te^{v}	x2 105.9(2)		Te-In2-Te^{vi}	x2 113.7(2)		Te-In2-Te^{vii}	x2 108.9(1)

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

TABLE III. Comparative table of space group, unit cell parameters and bond distances for the ternary compounds of the Ag-In-Te system reported so far ([*] = this work).

	Space group	Unit cell (Å)	c/a	V (Å^3)	Ag-Te (Å)	In-Te (Å)	Ref.
$AgInTe_2$	I$\bar{4}$2d (122)	6.4431(4) 12.6362(9)	1.96	524.57(6)	2.811(2)	2.734(2)	[11]
$AgIn_5\Box_2Te_8$	P$\bar{4}$2m (111)	6.1952(2) 12.419(4)	2.00	476.7(2)	2.890(6)	2.764(6)	[12]
$AgIn_3\Box Te_5$	P$\bar{4}$2c (112)	6.2443(8) 12.5058(4)	2.00	487.62(9)	2.7243(4)	2.7052(4)	[13]
$Ag_3In_5\Box Te_9$	P$\bar{4}$2c (112)	6.3453(2) 12.5754(7)	1.98	506.32(4)	2.897(5)	2.701(5)	[*]

4. Conclusions

The new ordered vacancy compound $Ag_3In_5\Box Te_9$ was obtained as a single phase and its structure was refined by the Rietveld method using X-ray powder diffraction data. This compound is isostructural with $Cu_3In_5\Box Te_9$, and crystallizes in the tetragonal space group P$\bar{4}2c$ with a P-chalcopyrite structure. This is the first silver compound of the I_3-III_5-$\Box$-VI_9 family which is structurally characterized in detail.

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