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X-RAY POWDER DIFFRACTION DATA AND RIETVELD REFINEMENT OF THE TERNARY SEMICONDUCTOR CHALCOGENIDES $AgInSe_2$ AND $AgInTe_2$

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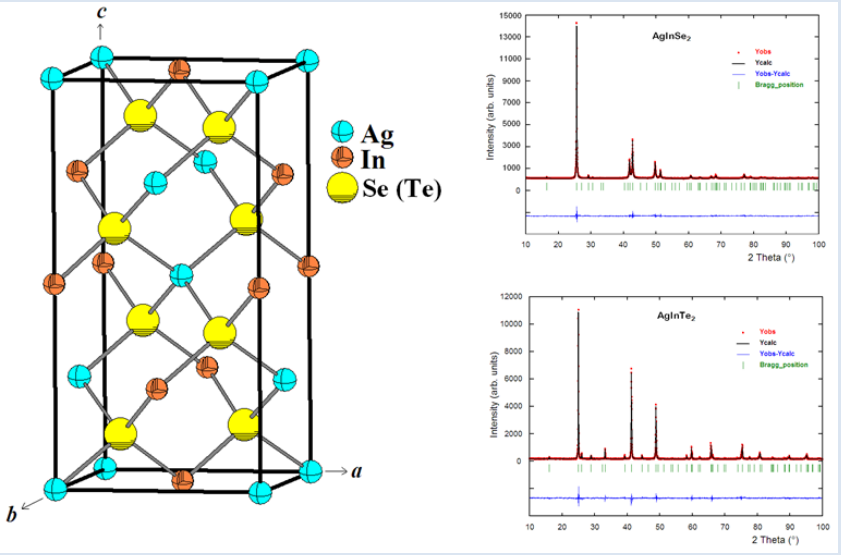

ABSTRACT

The ternary chalcogenides $AgInSe_2$ and $AgInTe_2$ were studied by X-ray powder diffraction structure refinement using the Rietveld method. Both compounds crystallizes with a chalcopyrite structure in the space group $I\bar{4}2d$ (N° 122), Z = 4, and unit cell parameters ***a*** = 6.0988(2) Å, ***c*** = 11.7086(6) Å, V = 435.51(3) Å^3 for $AgInSe_2$ and ***a*** = 6.4431(4) Å, ***c*** = 12.6362(9) Å, V = 524.57(6) Å^3 for $AgInTe_2$. Improved X-ray powder diffraction data are reported with figures of merit M_{19} = 84.0, F_{19} = 40.7 (0.0071, 66) for $AgInSe_2$, and M_{20} = 80.8, F_{23} = 39.0 (0.0075, 79) for $AgInTe_2$.

Keywords: Semiconductors, Chalcogenides, Rietveld refinement, X-ray powder diffraction data.

DATOS DE DIFRACCIÓN DE RAYOS-X Y REFINAMIENTO RIETVELD DE LOS SEMICONDUCTORES CALCOGENUROS TERNARIOS $AgInSe_2$ Y $AgInTe_2$

RESUMEN

Los calcogenuros ternarios $AgInSe_2$ y $AgInTe_2$ se estudiaron mediante refinamiento Rietveld utilizando datos de difracción de rayos-X en muestras policristalinas. Ambos compuestos cristalizan con una estructura tipo calcopirita en el grupo espacial $I\bar{4}2d$, (N° 122), Z = 4, y parámetros de celda unidad ***a*** = 6.0988(2) Å, ***c*** = 11.7086(6) Å, V = 435.51(3) Å^3 para $AgInSe_2$ y ***a*** = 6.4431(4) Å, ***c*** = 12.6362(9) Å, V = 524.57(6) Å^3 para $AgInTe_2$. Se reportan mejores datos de difracción de polvo con figuras de mérito M_{19} = 84.0, F_{19} = 40.7 (0.0071, 66) para $AgInSe_2$, y M_{20} = 80.8, F_{23} = 39.0 (0.0075, 79) para $AgInTe_2$.

Palabras Claves: Semiconductores, Calcogenuros, Refinamiento Rietveld, Datos de difracción de polvo.

1. INTRODUCTION

Chalcogenide semiconductors of the type Ag-In-VI (VI = S, Se, Te) have been studied because of their possible technological applications as photo-voltaic detectors, solar cells, light emitting diodes, modulators, filters and their use in nonlinear optics [1-2]. Following the rules of formation of semiconductor compounds [3], in the system Ag-In-VI, stoichiometric compounds with three compositions can be form: $AgInVI_2$, $AgIn_3VI_5$ and $AgIn_5VI_8$. These materials belong to the normal structure compounds (I-III-VI_2) and the defect structure compounds (I-III_3-□-VI_5, I-III_5-□$_2$-VI_8), respectively [4].

From the crystallographic point of view, in the Ag-In-S system, the $AgInS_2$ ternary compound crystallizes in two polymorphs: a tetragonal chalcopyrite-type phase (space group $I\bar{4}2d$) and an orthorhombic wurtzite-like phase (space group $Pna2_1$). These phases were simultaneously characterized from a unique X-ray powder diffraction pattern [5]. In the Ag-In-Se and Ag-In-Te systems, the ternaries $AgInSe_2$ [6] and $AgInTe_2$ [7] were reported, at room temperature, in undistorted chalcopyrite-type structures. Both materials have been studied under high pressure and temperature and have been reported to have a first-order structural phase transition from chalcopyrite structure to a cation-disorder NaCl-like structure [8]. In particular, for these ternaries chalcopyrite phases appear reported only poor quality X-ray powder diffraction data in the Powder Diffraction File PDF-ICDD [9], as shown in Table 1.

Table 1. X-ray powder diffraction data reported for the ternaries $AgInSe_2$ and $AgInTe_2$ in the Powder Diffraction File PDF-ICDD [9].

Phase	*PDF code*	*Unit cell (Å) parameters*	*Figures of merit*	*Quality mark*
$AgInSe_2$	35-1099	***a***= 6.104 ***c***= 11.714	F_{30}= 11	"i"
	39-0952	***a***= 6.077 ***c***= 11.55	F_{22}= 7	"i"
	75-0118	***a***= 6.090 ***c***= 11.670	-	"c"
$AgInTe_2$	49-1301	***a***= 6.324 ***c***= 12.86	F_6= 2	"i"
	75-0119	***a***= 6.406 ***c***= 11.560	-	"c"

"i" intensities, "c" calculated, "*" high quality

Therefore, in this work, we present the detailed structural characterization of the $AgInSe_2$ and $AgInTe_2$ compounds using Rietveld refinement and reported better X-ray powder diffraction data.

2. EXPERIMENTAL PART

The samples were synthesized by the melt and annealing technique. Stoichiometric quantities of Ag, In and Se (Te) powders with a nominal purity of 99.99 wt% (Fisher Scientific), were evacuated in sealed quartz ampoules and deposited into an one zone furnace, and then submitted to direct fusion. The mixture, en each case, was slowly heated up to 250°C at a rate of 5°C/hour. The ampoules were kept at this temperature for a period of 6 hours. Then, the temperature was gradually raised at the same rate up to 590°C. It was kept at this condition for 24 hours. Subsequently, it was heated at 800°C at 10°C/hour and remained at this temperature for 3 hours. Then, the reacted mixtures were heated up to 1050°C at the same rate. Finally, the furnace was turned off and the ingots were cooled to room temperature in about a day.

Chemical analysis of the resultant ingots were carried out with a Hitachi S-2500 SEM equipped with a Kevex EDX accessory. Three different regions of each ingot were scanned. The error standardless analysis was around 5%.

Small quantities of each sample were ground mechanically in an agate mortar and pestle. The resulting fine powders were mounted on a flat zero-background holder (a plate of single crystalline silicon cut parallel to the 510 lattice planes) covered with a thin layer of petroleum jelly. The X-ray powder diffraction data were collected at room temperature, in θ/θ reflection mode using a Siemens D5005 diffractometer (Bragg-Brentano geometry) equipped with an X-ray tube (CuKα radiation: λ= 1.54059 Å; 40kV, 30mA) and a diffracted beam graphite monochromator. Fix 1 mm aperture slit, 1 mm divergence slit and a 0.1 mm monochromator slit and a 0.6 mm detector slit were used. The specimens were scanned in the 2θ range of 10-100°, the scan step was 0.02°, and the time of counting in every step was 35s. Quartz was used as an external standard.

3. RESULTS AND DISCUSSION

3.1 Chemical analysis

The following average atomic percentages were obtained from the EDX study: Ag (24.4%), In (26.7%), Se (48.9%) for $AgInSe_2$, and Ag (23.5%), In (26.3%), Te (51.2%) for $AgInTe_2$. These results are in good quality agreement with the ideal composition 1:1:2 for each compound.

3.2 X-ray powder diffraction

The 19 ($AgInSe_2$) and 23 ($AgInTe_2$) peak positions measured from the patterns were input to the auto-indexing program Dicvol04 [10]. Unique solutions were readily obtained in a tetragonal system. A comparison of the powder patterns taking into account the chemical composition, crystal system and cell parameters, showed that these materials are isostructural with the $AgInS_2$ chalcopyrite phase, which crystallize in the tetragonal space group $I\bar{4}2d$ (Nº 122) [5]. The complete powder diffraction dataset of both compounds were reviewed and the unit cell refined with the NBS*AIDS program [11] in the space group $I\bar{4}2d$. From these analyses, the refined unit cell parameters given in the Tables 2 and 3 were obtained. These tables contain the observed and calculated X-ray powder diffraction data for $AgInSe_2$ and $AgInTe_2$, with the M_N [12] and F_N [13] figures of merit.

These powder data are improved that the three pattern with low quality (PDF 35-1099, PDF 38-0952, PDF 75-0118) reported for $AgInSe_2$ and the two (PDF 49-1301, PDF 75-0119) reported for $AgInTe_2$ in the ICDD Powder Diffraction Files [9].

The crystal structure refinement was performed by means of Rietveld method [14], using the Fullprof program [15]. The starting parameters were taken from the $AgInSe_2$ and $AgInTe_2$ undistorted chalcopyrite-type structures

[6,7] with the unit cell given in Tables 2 and 3. The structural refinement was carried out following the same procedure employed elsewhere [5, 16]. Details of the Rietveld refinement results for each compound are given in Tables 4 and 5. These tables contain the atomic coordinates, isotropic temperature factors and bond distances for each compound. Figures 1 and 2 shows the observed, calculated and difference profile for the final Rietveld refinements of $AgInSe_2$ and $AgInTe_2$. Figure 3 shows the unit cell diagram of the semiconducting compounds prepared with the program Diamond [17].

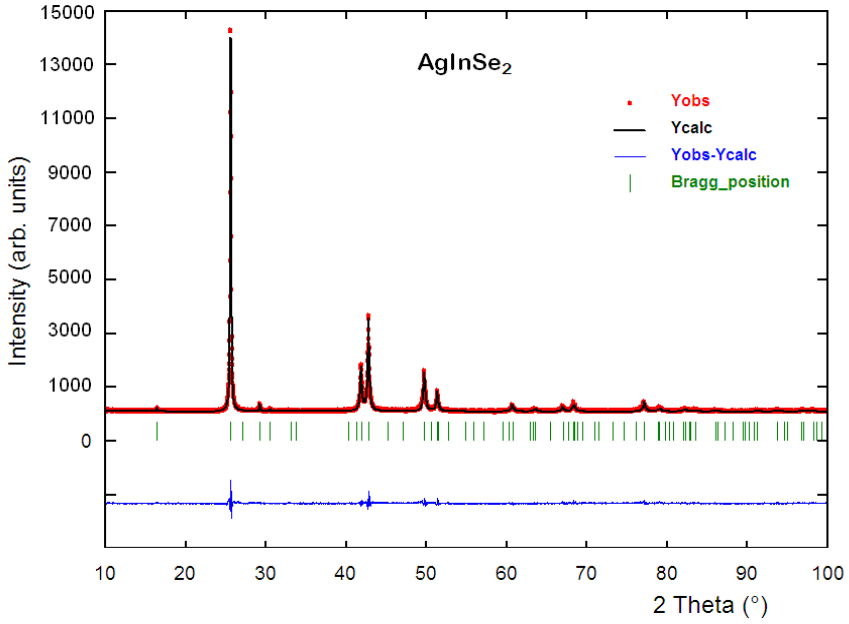

Figure 1. Final Rietveld refinement plot for $AgInSe_2$. The lower trace is the difference curve between observed and calculated patterns. The Bragg reflections are indicated by vertical bars.

Table 2. X-ray powder diffraction data for $AgInSe_2$.

Space group $I\bar{4}2d$ (N° 122), Z = 2, ***a*** = 6.0988(2) Å, ***c*** = 11.7086(6) Å, V = 435.51(3) $Å^3$
M_{19} = 84.0 [13]; F_{19} = 40.7 (0.0071, 66) [14]

$2\theta_{obs}$ (°)	d_{obs} (Å)	$(I/I_o)_{obs}$	*H*	*k*	*l*	$2\theta_{cal}$ (°)	d_{cal} (Å)	$\Delta 2\theta$ (°)
16.367	5.4112	1.1	1	0	1	16.374	5.4090	0.007
25.635	3.4720	100.0	1	1	2	25.634	3.4722	-0.001
29.262	3.0494	2.7	2	0	0	29.262	3.0494	0.000
30.522	2.9263	1.4	0	0	4	30.513	2.9272	-0.009
41.870	2.1557	12.8	2	2	0	41.859	2.1563	-0.011
42.796	2.1112	25.7	2	0	4	42.785	2.1117	-0.011
49.740	1.8315	11.2	3	1	2	49.731	1.8318	-0.009
			1	1	6	51.347	1.7779	
51.373	1.7770	5.8						
			2	1	5	51.383	1.7767	0.010
60.681	1.5248	2.4	4	0	0	60.687	1.5247	0.006
63.504	1.4637	1.4	0	0	8	63.509	1.4636	0.005
66.977	1.3960	2.0	3	3	2	66.973	1.3960	-0.004
			3	1	6	68.321	1.3717	0.010
68.311	1.3719	3.1						
			3	2	5	68.352	1.3712	
77.078	1.2363	3.3	4	2	4	77.085	1.2362	0.007
78.997	1.2110	1.7	2	2	8	78.997	1.2110	0.000
82.201	1.1717	1.4	5	1	2	82.186	1.1719	-0.015
83.439	1.1574	1.1	3	3	6	83.443	1.1574	0.004
85.954	1.1299	1.2	1	1	0	85.948	1.1300	-0.006
93.680	1.0559	1.1	4	0	8	93.690	1.0559	0.010
96.840	1.0297	1.2	5	3	2	96.849	1.0296	0.009

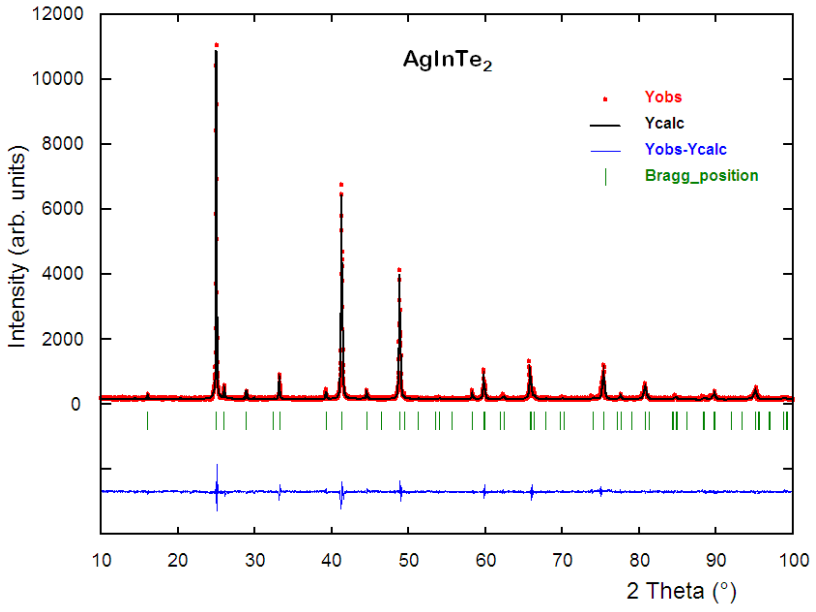

Figure 2. Final Rietveld refinement plot for $AgInTe_2$. The lower trace is the difference curve between observed and calculated patterns. The Bragg reflections are indicated by vertical bars.

Table 3. X-ray powder diffraction data for $AgInTe_2$.

Space group $I\bar{4}2d$ (N° 122), Z = 2, ***a*** = 6.4524(3) Å, ***c*** = 12.6330(8) Å, V = 525.96(5) $Å^3$
M_{20} = 80.8 [13]; F_{23} = 39.0 (0.0075, 79) [14]

$2\theta_{obs}$ (°)	d_{obs} (Å)	$(I/I_o)_{obs}$	*H*	*k*	*l*	$2\theta_{cal}$ (°)	d_{cal} (Å)	$\Delta 2\theta$ (°)
15.416	5.7428		1	0	1	5.7463	15.407	-0.009
24.045	3.6979		1	1	2	3.6986	24.040	-0.005
25.226	3.5274		1	0	3	3.5264	25.233	0.007
28.213	3.1603		0	0	4	3.1582	28.232	0.019
31.810	2.8107		2	1	1	2.8132	31.781	-0.029
39.931	2.2558		2	0	4	2.2569	39.911	-0.020
42.611	2.1199		3	0	1	2.1203	42.603	-0.008
46.753	1.9413		3	1	2	1.9416	46.744	-0.009
49.220	1.8496		2	2	4	1.8493	49.229	0.009
57.042	1.6132		4	0	0	1.6131	57.044	0.002
58.392	1.5790		0	0	8	1.5791	58.388	-0.004
62.788	1.4786		3	3	2	1.4786	62.790	0.002
63.407	1.4657		3	1	6	1.4653	63.427	0.020
64.837	1.4368		4	0	4	1.4366	64.847	0.010
71.877	1.3124		4	2	4	1.3123	71.878	0.001
72.774	1.2984		2	2	8	1.2984	72.773	-0.001
76.745	1.2408		5	1	2	1.2408	76.747	0.002
77.329	1.2329		3	3	6	1.2329	77.330	0.001
78.494	1.2175		1	1	10	1.2175	78.493	-0.001
81.812	1.1763		2	0	10	1.1763	81.808	-0.004
86.092	1.1284		4	0	8	1.1284	86.092	0.000
89.925	1.0900		5	3	2	1.0900	89.928	0.003
94.982	1.0449		4	1	9	1.0449	94.976	-0.006

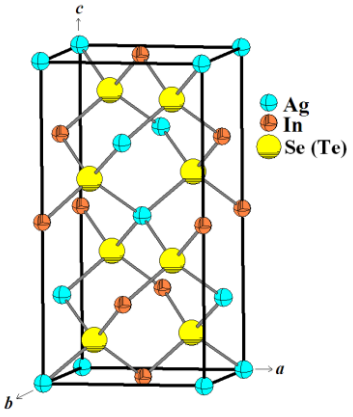

Figure 3. Unit cell diagram for the ternary chalcogenides $AgInSe_2$ and $AgInTe_2$.

Table 4. Rietveld refinement results for $AgInSe_2$.

Compound			*$AgInSe_2$ [This work]*	*$AgInSe_2$ [Ref. 6]*
crystal system			tetragonal	
space group			$I\bar{4}2d$	
a (Å)			6.0988(2)	6.104(2)
c (Å)			11.7086(6)	11.712(5)
c/a			1.92	
V (Å^3)			435.51(3)	
mol. w. (g/mol)			380.61	
d_{calc} (g/cm^3)			5.80	
Atomic coordinates		site		
Ag		4(*a*)	0, 0, 0	
In		4(*b*)	0, 0, ½	
Se		8(*d*)	*x*, ¼, ⅛	*x* = 0.2539(5)	*x* = 0.25
Isotropic temp. factor				
B_{iso} (Å^2)			0.6(3)	
Bond distances				
Ag-Se			2.621(2)	2.61
In-Se			2.593(2)	2.61
Rietveld R factors				
R_p (%)			8.3	
R_{wp} (%)			10.3	
R_B (%)			10.1	
R_{exp} (%)			7.2	
S			1.4	

$R_p = 100\ \Sigma|y_{obs} - y_{calc}| / \Sigma|y_{obs}|$ $R_{wp} = 100\ [\Sigma_w|y_{obs} - y_{calc}|^2 / \Sigma_w|y_{obs}|^2]^{1/2}$ $R_B = 100\ \Sigma_k|I_k - Ic_k| / \Sigma_k |I_k|$

S (goodness of fit) = R_{wp}/R_{exp} $R_{exp} = 100\ [(N\text{-}P+C) / \Sigma_w(y_{obs}^2)]^{1/2}$ N-P+C= degrees of freedom

The ternary chalcogenides $AgInSe_2$ and $AgInTe_2$ are chalcopyrite-like compounds and can be described as derivatives of the sphalerite structure. In this type of materials, each cation is surrounded by four anions (Se or Te), and each anion is surrounded by two Ag and two In atoms. This array is expected for adamantane compounds [3]. The bond distances Ag-Se (Te) and In-Se (Te) are in good agreement with similar distances in other adamantane-type compounds found in the ICSD database [18], and agrees with the bond strength reported from *ab initio* calculations [19].

Table 5. Rietveld refinement results for $AgInTe_2$.

Compound			*$AgInTe_2$ [This work]*	*$AgInTe_2$ [Ref. 7]*
crystal system			tetragonal	
space group			$I\bar{4}2d$	
a (Å)			6.4431(4)	6.104(2)
c (Å)			12.6362(9)	11.712(5)
c/a			1.96	
V (Å^3)			524.57(6)	
mol. w. (g/mol)			477.89	
d_{calc} (g/cm^3)			6.05	
Atomic coordinates		site		
Ag		4(*a*)	0, 0, 0	
In		4(*b*)	0, 0, ½	
Te		8(*d*)	*x*, ¼, ⅛	*x* = 0.2602(5)	*x* = 0.25
Isotropic temp. factor				
B_{iso} (Å^2)			0.7(5)	
Bond distances				
Ag-Te			2.811(2)	2.76
In-Te			2.734(2)	2.76
Rietveld R factors				
R_p (%)			7.9	
R_{wp} (%)			10.5	
R_B (%)			10.0	
R_{exp} (%)			7.1	
S			1.5	

$R_p = 100\ \Sigma|y_{obs} - y_{calc}| / \Sigma|y_{obs}|$ $\quad R_{wp} = 100\ [\Sigma_w|y_{obs} - y_{calc}|^2 / \Sigma_w|y_{obs}|^2]^{1/2}$ $\quad R_B = 100\ \Sigma_k|I_k - Ic_k| / \Sigma_k |I_k|$

S (goodness of fit) = R_{wp}/R_{exp} $\quad R_{exp} = 100\ [(N-P+C) / \Sigma_w(y_{obs}^2)]^{1/2}$ $\quad$ N-P+C= degrees of freedom

4. CONCLUSIONS

The crystal structure of the ternary semiconductor chalcogenides $AgInSe_2$ and $AgInTe_2$ were Rietveld refined using X-ray powder diffraction data. These compounds crystallize in the chalcopyrite-type structure and are reported improved X-ray powder diffraction data.

5. ACKNOWLEDGEMENTS

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