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Synthesis and Crystal Structure of Three New Quaternary Compounds in the system Cu-Mn-III-Se_3 (III = Al, Ga, In)

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Chalcogenide alloys $CuMnAlSe_3$, $CuMnGaSe_3$ and $CuMnInSe_3$, new members of the semiconductor system I-II-III-VI_3, were synthetized and structurally characterized by the Rietveld method using X-ray powder diffraction data. All compounds crystallize in the tetragonal space group $P\bar{4}$ 2c (Nº 112) with a $CuFeInSe_3$-type structure.

Keywords: *Chalcogenides, Semiconductors, Chemical synthesis, X-ray powder diffraction, Structural characterization.*

1. Introduction

The Cu-III-Se_2 (III= Al, Ga, In) ternary chalcopyrite family have been object of a great quantity of work in the last years, because they form an wide group of semiconductor materials with diverse optical and electrical properties[1]. These materials crystallize with tetragonal symmetry in the space group $I\bar{4}$ 2d (N°122), and the addition of a Fe-Se binary compound produces alloys of the type $(Cu\text{-}III\text{-}Se_2)_{1-x}$ $(FeSe)_x$[2]. Some previous results on the formation, structural characterization, thermal and magnetic properties on these alloys with compositions Cu-Fe-III-Se_3 (x = ½), Cu-Fe_2-III-Se_4 (x = ⅔) and Cu_2-Fe-III-Se_5 (x = ⅓) have been reported[3-15]. All these phases fulfill the rules of formation of adamantane compounds[2] and belong to the normal semiconductor compound families of the third, fourth and fifth-order derivatives of the II-VI binary semiconductors, respectively[16]. Adamantane compounds are binary, ternary or quaternary normal tetrahedral structure compounds which are closely related to either cubic or hexagonal diamond.

The first crystal structure characterization of one I-II-III-VI_3 semiconductor member, $CuFeInSe_3$, indicated a degradation of symmetry from the chalcopyrite structure $I\bar{4}2d$ to a related structure $P\bar{4}2c$[6]. In this work, we report a detailed synthesis and structural analysis of three new members of this family; $CuMnAlSe_3$, $CuMnGaSe_3$ and $CuMnInSe_3$, which was performed using X-ray powder diffraction by means of the Rietveld method.

2. Experimental Procedures

2.1 Synthesis

Ingots of Cu-Mn-III-Se_3 (III= Al, Ga, In) were prepared by the melt and annealing technique. Starting materials (Cu, Mn, Al, Ga, In and Se), with a nominal purity of at least 99.99 % (GoodFellow) in the stoichiometric ratio, were mixed together in an evacuated and sealed quartz tube with inner walls previously carbonized. Polycrystalline ingots of about 1 g were prepared by the usual melting and annealing technique, lowering the temperature from 1500 to 850 K at a rate of 20 K/h, keeping this temperature for 30 days, and finally, cooling to room temperature at a rate of 10 K/h. Previous experience indicates that this procedure usually gives samples showing conditions corresponding to equilibrium near room temperature.

2.2 Chemical analysis

Compositional analysis of the ingots was determined at several points by energy dispersive X-ray (EDX) analysis using a Kevex Model Delta-3 system connected to a Hitachi Model S-2500 scanning electron microscope (SEM). In each

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case, the average chemical composition of the central part of the ingot from which the crystals were cut, gave the atomic percentage in good agreement with the ideal composition 1:1:1:3 The error in standardless analysis was around 5 %.

2.3 X-ray powder diffraction

For the X-ray analysis, small quantities of the samples were ground mechanically in an agate mortar and pestle. The resulting fine powders, sieved to 106μ, were mounted on a flat zero-background holder covered with a thin layer of petroleum jelly. The X-ray powder diffraction data were collected at 293(1) K, in θ/θ reflection mode using a Siemens D5005 diffractometer equipped with an X-ray tube (CuKα radiation: λ= 1.54056 Å; 40kV, 30mA) using a secondary beam graphite monochromator. A fixed aperture and divergence slit of 1 mm, a 1 mm monochromator slit, and a 0.1 mm detector slit were used. The specimens were scanned from 10°-100° 2θ, with a step size of 0.02° and counting time of 40s. Quartz was used as an external standard.

3. Results and Discussion

The X-ray diffractograms of three alloys Cu-Mn-III-Se_3 (III= Al, Ga, In) showed single phases. The powder patterns were indexed using the program Dicvol04[17], and tetragonal cells with similar magnitudes to the parent chalcopyrite structures, $CuAlSe_2$[18], $CuGaSe_2$[19], $CuInSe_2$[20] were founds. Systematic absences are consistent with a P-type Bravais lattice. A detailed pattern examination taking in account the sample composition, cell parameters and lattice-type, suggested that all compounds are isostructural with previously reported $CuFeInSe_3$[6] which crystallizes in the space group $P\bar{4}2c$.

The Rietveld refinements[21] of the structures were carried out using the Fullprof program[22]. The atomic coordinates of $CuFeInSe_3$[6] were used as starting model for each refinement. The angular dependence of the peak full width at half maximum (FWHM) was described by the Caglioti's formula[23]. Peak shapes were described by the parameterized Thompson-Cox-Hastings pseudo-Voigt profile function[24]. The background variation was described by a polynomial with six coefficients. The thermal motion of the atoms was described by one overall isotropic temperature factor. The results of the Rietveld refinement for the three alloys are summarizes in Table 1. Fig. 1 shows the observed, calculated and difference profile for the final cycle of Rietveld refinements. Atomic coordinates, isotropic temperature factor, bond distances and angles for each compound are shown in Tables 2, 3 and 4.

$CuMnAlSe_3$, $CuMnGaSe_3$ and $CuMnInSe_3$ are normal adamantane-structure compounds[2], where occurs a degradation of symmetry from the chalcopyrite structure $I\bar{4}2d$ to a related

Table 1. Rietveld refinement results for the alloys $CuMnAlSe_3$, $CuMnGaSe_3$ and $CuMnInSe_3$.

molecular formula	$CuMnAlSe_3$	$CuMnGaSe_3$	$CuMnInSe_3$
molecular weight (g/mol)	1019.49	1133.43	1253.67
a(Å)	5.6034(6)	5.6230(4)	5.7907(5)
c(Å)	10.977(1)	11.028(1)	11.648(1)
c/*a*	1.96	1.96	2.01
η =*c*/2*a*	0.98	0.98	1.00
V (Å^3)	344.66(6)	348.68(5)	390.58(8)
Z	1	1	1
crystal system	tetragonal	tetragonal	tetragonal
space group	P-42c (Nº 112)	P-42c (Nº 112)	P-42c (Nº 112)
d_{calc}(g/cm^{-3})	4.91	5.40	5.33
Temperature (K)	298(1)	298(1)	298(1)
wavelength (CuK_a)	1.54056 Å	1.54056 Å	1.54056 Å
data range 2q (º)	10-100	10-100	10-100
step size 2q (º)	0.02	0.02	0.02
counting time (s)	40	40	40
step intensities	4501	4501	4501
independent reflections	134	134	134
R_{wp}(%)	9.2	9.6	9.6
R_{exp}(%)	6.7	6.9	6.9
χ^2	1.4	1.4	1.4
R_p(%)	8.2	8.9	8.9
R_B(%)	9.5	9.6	9.6

$R_p = 100\ \Sigma|_{yobs\ -\ ycalc}| / \Sigma|_{yobs}|$ $R_{wp} = 100\ [\Sigma_w|_{yobs\ -\ ycalc}|^2 / \Sigma_w|_{yobs}|^2]^{1/2}$ $\chi^2 = [R_{wp} / R_{exp}]$ $R_B = 100\ \Sigma_k|I_k - I_{c\,k}| / \Sigma_k |I_k|$ $R_{exp} = 100\ [(N\text{-}P+C) / \Sigma_w(_{yobs}{}^2)]^{1/2}$
N P+C= degrees of freedom

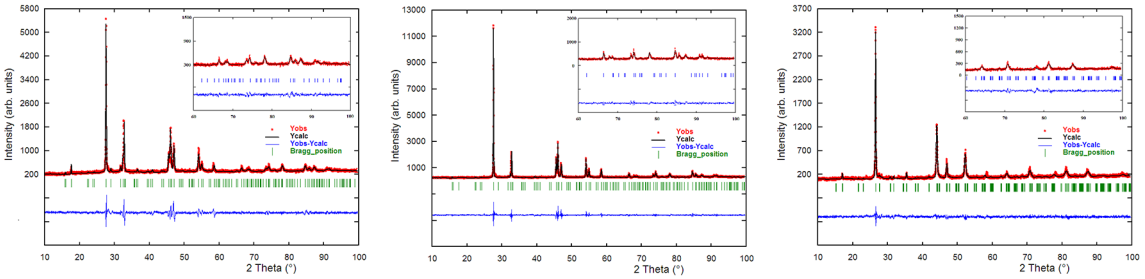

Figure 1. Rietveld final plots of a) $CuMnAlSe_3$, b) $CuMnGaSe_3$ and c) $CuMnInSe_3$. The lower curve represents the difference between observed and calculated patterns. The Bragg reflections are indicated by vertical bars.

Table 2. Atomic coordinates, isotropic temperature factors, bond distances (Å) and angles (º) for $CuMnAlS_{e3}$, derived from the Rietveld refinement.

Atom	Ox.	Site	*x*	*Y*	*z*	foc	B (Å^2)
Cu	+1	*2c*	0	½	¼	1	0.6(5)
Mn	+2	*2e*	0	0	0	1	0.6(5)
Al	+3	*2b*	½	0	¼	1	0.6(5)
Cu1	+1	*2f*	½	½	½	⅓	0.6(5)
Mn1	+2	*2f*	½	½	½	⅓	0.6(5)
Al1	+3	*2f*	½	½	½	⅓	0.6(5)
Se	-2	*8n*	0.257(1)	0.253(1)	0.125(1)	1	0.6(5)
Cu-Se	2.423(8)	Mn-Se	2.443(8)	Al-Se^{i}	2.397(8)	2f-Se^{ii}	2.377(8)
Se^{iii}-Cu-Se^{iv}	106.7(2) x2	Se^{iii}-Cu-Se^{v}		111.5(2) x2	Se^{iii}-Cu-Se		110.3(2) x2
Se^{vi}-Mn-Se^{vii}	108.0(2) x2	Se^{vii}-Mn-Se		112.6(2) x2	Se-Mn-Se^{viii}		108.0(2) x2
Se-Al-Se^{viii}	111.7(2) x2	Se-Al-Se^{i}		106.8(2) x2	Se-Al-Se^{ix}		110.1(2) x2
Se^{vi}-M-Se	109.5(2) x4	Se-M-Se^{ii}		109.4(2) x2			

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

Table 3. Atomic coordinates, isotropic temperature factors, bond distances (Å) and angles (º) for $CuMnGaS_{e3}$, derived from the Rietveld refinement.

Atom	Ox.	Site	*x*	*y*	*z*	foc	B (Å^2)
Cu	+1	*2c*	0	½	¼	1	0.6(4)
Mn	+2	*2e*	0	0	0	1	0.6(4)
Ga	+3	*2b*	½	0	¼	1	0.6(4)
Cu1	+1	*2f*	½	½	½	⅓	0.6(4)
Mn1	+2	*2f*	½	½	½	⅓	0.6(4)
Ga1	+3	*2f*	½	½	½	⅓	0.6(4)
Se	-2	*8n*	0.255(1)	0.257(1)	0.124(1)	1	0.6(4)
Cu-Se	2.419(8)	Mn-Se	2.452(8)	Ga-Se^{i}	2.432(8)	2f-Se^{ii}	2.374(8)
Se^{iii}-Cu-Se^{iv}	107.1(2) x2	Se^{iii}-Cu-Se^{v}		109.5(2) x2	Se^{iii}-Cu-Se		111.1(2) x2
Se^{vi}-Mn-Se^{vii}	108.4(2) x2	Se^{vii}-Mn-Se		111.7(2) x2	Se-Mn-Se^{viii}		108.4(2) x2
Se-Ga-Se^{viii}	110.9(2) x2	Se-Ga-Se^{i}		107.6(2) x2	Se-Ga-Se^{ix}		110.0(2) x2
Se^{vi}-M-Se	109.5(2) x4	Se-M-Se^{ii}		109.4(2) x2			

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

structure P$\bar{4}$2c. This situation can be clearly seen in Fig. 2 where a comparison is made between the chalcopyrite Cu-III-Se_2 I$\bar{4}$2d structure and the P$\bar{4}$2c structure of Cu-Mn-III-Se_3 (III= Al, Ga, In). Therefore, in the quaternary structures, the introduction of an additional cation (Mn) produces an effect of "dilution" of this cation in the chalcopyrite structure leaving the cell volume almost unchanged[6]. Table 5 show a comparison between the unit cell parameters and the bond distances for the three phases of both families of compounds.

Table 4. Atomic coordinates, isotropic temperature factors, bond distances (Å) and angles (º) for $CuMnInS_{e3}$, derived from the Rietveld refinement.

Atom	Ox.	Site	*x*	*y*	*z*	foc	B (Å^2)
Cu	+1	*2c*	0	½	¼	1	0.6(4)
Mn	+2	*2e*	0	0	0	1	0.6(4)
In	+3	*2b*	½	0	¼	1	0.6(4)
Cu1	+1	*2f*	½	½	½	⅓	0.6(4)
Mn1	+2	*2f*	½	½	½	⅓	0.6(4)
In1	+3	*2f*	½	½	½	⅓	0.6(4)
Se	-2	*8n*	0.227(1)	0.255(1)	0.124(1)	1	0.6(4)
Cu-Se	2.428(8)	Mn-Se	2.448(8)	In-Se^{i}	2.614(8)	2f-Se^{ii}	2.569(8)
Se^{iii}-Cu-Se^{iv}	114.5(2) x2	Se^{iii}-Cu-Se^{v}		108.6(2) x2	Se^{iii}-Cu-Se		105.6(2) x2
Se^{vi}-Mn-Se^{vii}	110.4(2) x2	Se^{vii}-Mn-Se		107.7(2) x2	Se-Mn-Se^{viii}		110.4(2) x2
Se-In-Se^{viii}	105.6(2) x2	Se-In-Se^{i}		111.2(2) x2	Se-In-Se^{ix}		111.7(2) x2
Se^{vi}-M-Se	108.5(2) x4	Se-M-Se^{ii}		111.5(2) x2			

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

Table 5. Comparative table of unit cell parameters and bond distances for the Cu-III-Se2 chalcopyrite compounds and the related Cu-Mn-III-Se3 alloys (III= Al Ga, In). ([*] = this work).

Compound	SG	***a*** (Å)	***c*** (Å)	η	V (Å^3)	Cu-Se (Å)	Mn-Se (Å)	III-Se (Å)	Ref.
$CuAlSe_2$	$I\bar{4}2d$	5.606(5)	10.90(1)	0.97	342.6(5)	2.438(1)	-	2.373(1)	[18]
$CuGaSe_2$	$I\bar{4}2d$	5.614(1)	11.022(1)	0.98	347.4(1)	2.446(9)	-	2.387(9)	[19]
$CuInSe_2$	$I\bar{4}2d$	5.781(1)	11.642(3)	1.01	389.1(2)	2.432(1)	-	2.591(1)	[20]
$CuMnAlSe_3$	$P\bar{4}2c$	5.6034(6)	10.977(1)	0.98	344.66(6)	2.423(8)	2.443(8)	2.397(8)	[*]
$CuMnGaSe_3$	$P\bar{4}2c$	5.6230(4)	11.028(1)	0.98	348.68(4)	2.419(8)	2.453(8)	2.432(8)	[*]
$CuMnInSe_3$	$P\bar{4}2c$	5.7907(5)	11.648(2)	1.00	390.58(8)	2.428(8)	2.448(8)	2.614(8)	[*]

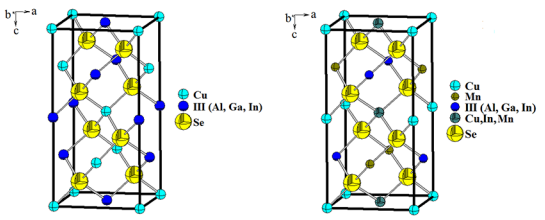

Figure 2. Unit cell diagram for the chalcopyrite Cu-III-Se_2 compared to the Cu-Mn-III-Se_3 compounds.

The structure of the tetragonal phases Cu-Mn-III-Se_3 can be described as derivative of the sphalerite structure[2]. In this structure the Se atoms form a close-packed arrangement where each anion is coordinated by four cations located at the corners of a slightly distorted tetrahedron. All cations are similarly coordinated by four anions. Fig. 3 shows a polyhedral view of the crystal structure with four types of atoms-centered tetrahedra MS_4 [CuS_4, MnS_4, $IIIS_4$ and $(CuInMn)S_4$] where all polyhedra are oriented in the same direction and are connected by the corners.

An important structural characteristic of the compounds under study is the parameter of tetragonal lattice distortion, which is determined as a deviation of the ratio $\eta = c/2a$ (*a* and *c* are unit-cell parameters) from unity[25]. The Table 5 contains the *a*, *c*, and η values for the Cu-Mn-III-Se_3 compounds. One can see that η is close to unity for all compositions, which is indicative of small lattice distortions in the samples synthesized.

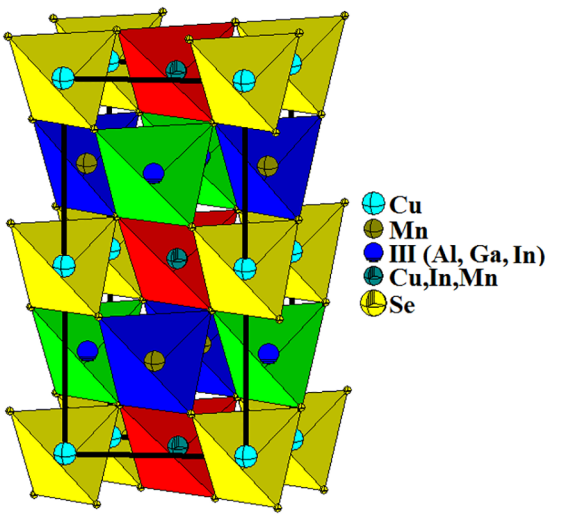

Figure 3. Polyhedral view of the Cu-Mn-III-Se_3 structures showing tetrahedral units.

The Cu-Se, Mn-Se and III (Al,Ga,In)-Se bond distances in all compounds (Tables 2, 3 and 4) are in good agreement with those observed in the parent chalcopyrite structures (Table 5) and other quaternary adamantane structure compounds such as CuFe(Al,Ga,In)Se_3[6,12], CuNi(Ga,In)Se_3[13], $CuFe_2$(Al,Ga,In)Se_4[9,14], $Cu_2FeSnSe_4$[26], $Cu_2ZnGeSe_4$[27], $Cu_2ZnSnSe_4$[28], Cu_2(Cd,Mn)$GeSe_4$[29] and $CuGaMnSe_2$[30].

4. Conclusions

The crystal structure of the semiconductor compounds $CuMnAlSe_3$, $CuMnGaSe_3$ and $CuMnInSe_3$ were determined using X-ray powder diffraction data. All compounds crystallize in the tetragonal space group $P\bar{4}2c$, with a sphalerite derivative structure, and are isomorphic with $CuFeInSe_3$.

5. Acknowledgements

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6. References

1. Shay JL, Wernik JH. *Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties and Applications*. Oxford: Pergamon Press; 1974.

2. Parthé E. Wurtzite and Zinc-Blende Structures. In: Westbrook JH, Fleischer RL, eds. *Intermetallic Compounds, Principles and Practices*. Volume 1. Chichester: John Wiley & Sons; 1995.

3. Grima-Gallardo P, Ruiz J. X-Rays and DTA of $CuFeGaSe_3$ and $CuFeInSe_3$ Quaternary Compounds. *Physica Status Solidi (a)*. 1999;173(2):283-288. DOI: 0.1002/(SICI)1521-396X(199906)173:2<283::AID-PSSA283>3.0.CO;2-I

4. Grima-Gallardo P, Cárdenas K, Quintero M, Ruiz J, Delgado GE. X-ray diffraction studies on $(CuAlSe_2)_X$ $(FeSe)_{1-X}$ alloys. *Materials Research Bulletin*. 2001;36(5-6):861-866. DOI: 10.1016/S0025-5408(01)00546-3

5. Grima-Gallardo P, Cárdenas K, Molina L, Quintero M, Ruiz J, Delgado GE, et al. A comparative Study of $(Cu\text{-}III\text{-}Se_2)_X$-$(FeSe)_{1-X}$ Alloys (III : Al, Ga, In) ($0 \leq x \leq 1$) by X-Ray Diffraction, Differencial Thermal Analysis and Scanning Electron Microscopy. *Physica Status Solidi (a)*. 2001;187(2):395-406. DOI: 10.1002/1521-396X(200110)187:2<395::AID-PSSA395>3.0.CO;2-2

6. Mora AJ, Delgado GE, Grima-Gallardo P. Crystal structure of $CuFeInSe_3$ from X-ray powder diffraction data. *Physica Status Solidi (a)*. 2007;204(2):547-554. DOI: 10.1002/pssa.200622395

7. Grima-Gallardo P, Muñoz-Pinto M, Durán-Piña S, Delgado GE, Quintero M, Briceño JM, et al. Preparation and investigation $(Cu\text{-}III\text{-}Se_2)_{1-X}(NbSe)_X$ alloys (III: Ga, In) with x = ½. *Physica Status Solidi (a)*. 2007;204(4):1093-1099. DOI: 10.1002/pssa.200622568

8. Grima-Gallardo P, Muñoz M, Durán S, Delgado GE, Quintero M, Ruiz J. Preparation and investigation of the quaternary alloy $CuTaInSe_3$. *Materials Research Bulletin*. 2007;42(12):2067-2071. DOI: 10.1016/j.materresbull.2007.02.003

9. Delgado GE, Mora AJ, Grima-Gallardo P, Quintero M. Crystal structure of CuFe2InSe4 from X-ray powder diffraction. *Journal of Alloys and Compounds*. 2008;454(1-2):306-309. DOI: 10.1016/j.jallcom.2006.12.057

10. Delgado GE, Mora AJ, Grima-Gallardo P, Muñoz M, Duran S, Quintero M. Crystal structure of the quaternary compound $CuTa_2InTe_4$ from X-ray powder diffraction. *Physica B: Condensed Matter*. 2008;403(18):3228-3230. DOI: 10.1016/j.physb.2008.04.022

11. Delgado GE, Mora AJ, Grima-Gallardo P, Durán S, Muñoz M, Quintero M. Crystal structure of the quaternary alloy $CuTaInSe_3$. *Crystal Research & Technology*. 2008;43(7):783-785. DOI: 10.1002/crat.200711154

12. Delgado GE, Mora AJ, Contreras JE, Grima-Gallardo P, Durán S, Muñoz M, et al. Crystal structure characterization of the quaternary compounds $CuFeAlSe_3$ and $CuFeGaSe_3$. *Crystal Research & Technology*. 2009;44(5):548-552. DOI: 10.1002/crat.200800596

13. Delgado GE, Mora AJ, Grima-Gallardo P, Durán S, Muñoz M, Quintero M. Preparation and crystal structure characterization of $CuNiGaSe_3$ and $CuNiInSe_3$ quaternary compounds. *Bulletin of Materials Science*. 2010;33(5):637-640. DOI: 10.1007/s12034-010-0097-6

14. Delgado GE, Mora AJ, Grima-Gallardo P, Muñoz M, Durán S, Quintero M, et al. Crystal structure of the quaternary compounds $CuFe_2AlSe_4$ and $CuFe_2GaSe_4$ from X-ray powder diffraction. *Bulletin of Materials Science*. 2015;38(4):1061-1064. DOI: 10.1007/s12034-015-0933-9

15. Grima-Gallardo P, Torres S, Quintero M, Nieves L, Moreno E, Delgado GE. Phase Diagram of $(CuInSe_2)_{1-X}(FeSe)_X$ alloys. *Journal of Alloys and Compounds*. 2015;630:146-150. DOI: 10.1016/j.jallcom.2015.01.015

16. Delgado JM. Crystal chemistry of diamond-like and other derivative semiconducting compounds. *Journal of Physics Conference Series*. 1998;152:45-50.

17. Boultif A, Louër D. Powder pattern indexing with the dichotomy method. *Journal of Applied Crystallography*. 2004;37:724-731. DOI: 10.1107/S00218898 04014876

18. Hahn H, Frank G, Klingler W, Meyer AD, Störger G. Untersuchungen über ternäre Chalkogenide. V. Über einige ternäre Chalkogenide mit Chalkopyritstruktur. *Zeitschrift für anorganische und allgemeine Chemie*. 1953;271(3-4):153-170. DOI: 10.1002/zaac.19532710307

19. Mandel L, Tomlinson RD, Hampshire MJ. Crystal data for $CuGaSe_2$. *Journal of Applied Crystallography*. 1977;10:130-131. DOI: 10.1107/S0021889877013065

20. Knight KS. The crystal structures of $CuInSe_2$ and $CuInTe_2$. *Materials Research Bulletin*. 1992;27(2):161-167. DOI: 10.1016/0025-5408(92)90209-I

21. Rietveld HM. A profile refinement method for nuclear and magnetic structures. *Journal of Applied Crystallography*. 1969;2:65-71. DOI : 10.1107/S0021889869006558

22. Rodríguez-Carvajal J. Recent advances in magnetic structure determination by neutron powder diffraction. *Physica B: Condensed Matter*. 1993;192(1-2):55-69. DOI: 10.1016/0921-4526(93)90108-I

23. Cagliotti G, Paoletti A, Ricci FP. Choice of collimators for a crystal spectrometer for neutron diffraction. *Nuclear Instruments*. 1958;3(4):223-228. DOI: 10.1016/0369-643X(58)90029-X

24. Thompson P, Cox DE, Hastings JB. Rietveld refinement of Debye-Scherrer synchrotron X-ray data from Al_2O_3. *Journal of Applied Crystallography*. 1987;20:79-83. DOI: 10.1107/S0021889887087090

25. Rodulfo de Gil E. Ternary semiconducting compounds with chalcopyrite-type structure: I. Fundamental equation and its physically acceptable solutions. *Physica Status Solidi (a)*. 1982;70(2):519-523. DOI: 10.1002/pssa.2210700220

26. Roque-Infante E, Delgado JM, López-Rivera SA. Synthesis and crystal structure of $Cu_2FeSnSe_4$, a I_2 II IV VI_4 semiconductor. *Materials Letters*. 1997;33(1-2):67-70. DOI: 10.1016/S0167-577X(97)00079-7

27. Parasyuk OV, Gulay LD, Romanyuk YE, Piskach LV. Phase diagram of the Cu2GeSe3-ZnSe system and crystal structure of the $Cu_2ZnGeSe_4$ compound. *Journal of Alloys and Compounds*. 2001;329(1-2):202-207. DOI: 10.1016/S0925-8388(01)01606-1

28. Olekseyuk ID, Gulay LD, Dydchak IV, Piskach LV, Parasyuk OV, Marchuk OV. Single crystal preparation and crystal structure of the $Cu_2Zn/Cd,Hg/SnSe_4$ compounds. *Journal of Alloys and Compounds*. 2002;340(1-2):141-145. DOI: 10.1016/S0925-8388(02)00006-3

29. Delgado GE, Quintero E, Tovar R, Quintero M. X-ray powder diffraction study of the semiconducting alloy $Cu_2Cd_{0.5}Mn_{0.5}GeSe_4$. *Crystal Research & Technology*. 2004;39(9):807-810. DOI: 10.1002/crat.200310257

30. Delgado GE, Villegas JL, Silva P, Sagredo V. Structural characterization of the diluted magnetic semiconductor $CuGa_{(1-x)}Mn_{(x)}Se_2$. *Chalcogenide Letters*. 2009;6(7):293-298.