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Preparation and structural characterization of the new diamond-like semiconductor $CuMnInSe_3$

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Abstract

The chalcogenide compound $CuMnInSe_3$, belonging to the system I-II-III-VI_3, has been investigated by means of X-ray powder diffraction and its crystal structure has been refined by the Rietveld method. The powder pattern was composed by 85.3% of the principal phase $CuMnInSe_3$ and 14.7% of the secondary phase MnSe. This material crystallizes with a $CuFeInSe_3$-type structure in the tetragonal space group $P\bar{4}2c$ (Nº 112), with unit cell parameters a = 5.7907(5) Å, c = 11.648(1) Å, V = 390.58(8) Å^3.

Keywords: Chalcogenides; Semiconductors; Chemical synthesis; X-ray diffraction; Crystal structure.

Preparación y caracterización estructural del nuevo semiconductor tipo-diamante $CuMnInSe_3$

Resumen

El compuesto calcogenuro $CuMnInSe_3$, perteneciente al sistema I-II-III-VI_3, ha sido investigado mediante difracción de rayos-X en muestras policristalinas y su estructura cristalina ha sido refinada utilizando el método Rietveld. El patrón de polvo se compone de 85,3 % de la fase principal $CuMnInSe_3$ y 14,7 % de la fase secundaria MnSe. Este material cristaliza con una estructura tipo $CuFeInSe_3$ en el grupo espacial $P\bar{4}2c$, (N° 112), con parámetros de celda unidad a = 5,7907(5) Å, c = 11,648(1) Å, V = 390,58(8) Å^3.

Palabras clave: Calcogenuros; Semiconductores; Síntesis química; Datos de difracción de polvo; Estructura cristalina.

Introduction

The chalcopyrite family of compounds I-III-VI_2 (I = Cu, Ag, III = Al, Ga, In, VI = S, Se, Te) form a wide group of chalcogenide semiconductor materials with diverse optical and electrical properties [1]. They crystallize with tetragonal symmetry in the space group $I\bar{4}2d$ (N°122), and the addition of a II-VI (II = Zn, Cd, Mn, Fe) binary compound produces alloys of the type $(I\text{-}III\text{-}VI_2)_{1-X}(II\text{-}VI)_X$ [2]. Due to the great variety of possible compositions, these materials can be useful for applications such as tunable semiconductors [3], photovoltaics [4], spintronics [5], non-linear optics [6] and thermoelectrics [7].

The formation of some quaternary with compositions Cu-II-III-Se_3 (x = ½), Cu-II_2-III-Se_4 (x =⅔) and Cu_2-II-III-Se_5 (x = ⅓) have been reported [8-11], and the first crystal structure characterization of one I-II-III-VI_3 semiconductor member, indicated a degradation of symmetry from the chalcopyrite structure I$\bar{4}$2d to a related tetragonal structure P$\bar{4}$2c [12].

In recent years, it has been of interest to carry out a systematic study of the crystal structure of quaternary diamond-like families [13-17]. Hence, here we report herein the structural characterization of a new quaternary compound, $CuMnInSe_3$, using the Rietveld method from X-ray powder diffraction data.

Experimental

Starting materials (Cu, Mn, In and Se) with a nominal purity of (at least) 99.99 wt% in the stoichiometric ratio were mixed together in an evacuated and sealed quartz tube, which was previously subjected to pyrolysis in order to avoid reaction of the starting materials with silica glass. The ampoule was shaken using a mechanical system during the entire heating process in order to aid the complete mixing of all the elements. The maximum temperature (1500K) was held for an additional 48 hours with the mechanical shaking system on. Then, the mechanical shaking system was turning off and the temperature was gradually lowered, at the same rate of 20 K/h, until 850 K. The ampoule was held at this temperature for a period of 30 days. Finally, the sample was cooled 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 [8-11].

For the X-ray analysis, a small quantity of the sample was ground mechanically in an agate mortar and pestle. The resulting fine powders, sieved to 46μ, 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 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.

Results and discussion

Figure 1 shows the resulting X-ray powder diffractogram for the $CuMnInSe_3$ compound. An automatic search in the PDF-ICDD database [18], using the software available with the diffractometer, indicated that the powder pattern contained small amounts of MnSe (PDF N° 11-683), Bragg positions of the diffraction lines from this compound are also indicated in Figure 1. The 20 first peak positions of the main phase ($CuMnInSe_3$) were indexed using the program Dicvol04 [19], which gave a unique solution in a tetragonal cell with a = 5.789(2) Å and c = 11.647(4) Å. These values are similar in magnitude to the parent chalcopyrite structure of $CuInSe_2$ (a = 5.781(1) Å, c = 11.642(3) Å) [20]. The lack of systematic absence condition $h+k+l$ in the general reflections of the type hkl indicated a P-type cell. A revision of the diffraction lines of the main phase taking into account the sample composition, unit cell parameters as well as the primitive cell suggested that this material is isostructural with the $CuFeInSe_3$-type compound, which crystallize in the tetragonal space group P$\bar{4}$2c (Nº 112) [12].

The Rietveld refinement [21] was carried out using the Fullprof program [22]. The atomic coordinates of $CuFeInSe_3$ [12] were used as starting model for the quaternary $CuMnInSe_3$. Atomic positions of the MnSe binary [23] were included as secondary phase in the refinement. The angular dependence of the peak full width at half maximum (FWHM) was described by the Caglioti's formula [24]. Peak shapes were described by the parameterized Thompson-Cox-Hastings pseudo-Voigt profile function [25]. 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 are summarizes in Table 1. Figure 1 show the observed, calculated and difference profile for the final cycle of Rietveld refinement. Atomic coordinates, isotropic temperature factor, bond distances and angles are shown in Table 2. The final Rietveld refinement converged to the following weight fraction percentages: $CuMnInSe_3$ (85.3%) and MnSe (14.7%) [26].

An important structural characteristic 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 [27]. The value of η show in Table 1, close to unity, is indicative of small lattice distortions in the sample synthesized.

Table 1
Rietveld refinement results for CuMnInSe3 and MnSe.

Molecular formula	CuMnInSe3	MnSe	
Molecular weight (g/mol)	1253.7	133.9	
a (Å)	5.7907(5)	5.462(3)	
c (Å)	11.648(1)	-	
η=c/2a (Å)	1.01	-	
V (Å^3)	390.58(8)	162.95(9)	
System	tetragonal	cubic	
Space group	$P\bar{4}2c$ (N° 112)	$Fm\bar{3}m$ (Nº 225)	
Z	2.667 (8/3)	4	Rp (%) = 8.8
Dcalc (g/cm^{-3})	5.33	5.46	Rwp (%) = 9.4
Weight fraction (%)	85.3	14.7	Rexp (%) = 6.7
RB (%)	9.6	9.1	S = 1.4

$R_p = 100\ \text{å}|y_{obs} - y_{calc}| / \text{å}|y_{obs}|$ $R_B = 100\ \text{å}_k|I_k - Ic_k| / \text{å}_k |I_k|$

$R_{wp} = 100\ [\text{å}_w|y_{obs} - y_{calc}|^2 / \text{å}_w|y_{obs}|^2]^{1/2}$ $S = [R_{wp} / R_{exp}]$

$R_{exp} = 100\ [(N+C) / \text{å}_w(y_{obs}^2)]^{1/2}$ N-P+C= degrees of freedom

$CuMnInSe_3$ is a normal adamantane-structure compound [2], where occurs a degradation of symmetry from the chalcopyrite structure $I\bar{4}2d$ to a related structure $P\bar{4}2c$. This situation can be seen in Figure 2 where a comparison is made between the chalcopyrite $CuInSe_2$ $I\bar{4}2d$ structure and the $P\bar{4}2c$ structure of $CuMnInSe_3$. Therefore, in this quaternary structure, 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 [12].

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. Figure 3 shows a polyhedral view of the crystal structure with the four types of atoms-centered tetrahedra $CuSe_4$, $MnSe_4$, $InSe_4$ and MSe_4 where all polyhedra are oriented in the same direction and are connected by the corners.

The tetrahedrons containing the In atoms [mean Se…Se distance 3.90(1) Å] are slightly smaller than those containing the M (Cu1, Mn1, In1) 3.91(1) Å, Cu atoms [means Se…Se distance 3.96(1) Å] and Mn atoms [mean Se…Se distance 4.00(1) Å] respectively.

The bond distances Cu-Se [2.428(8) Å], Mn-Se [2.448(8) Å] and In-Se [2.614(8) Å] are in good agreement with those observed in the parent chalcopyrite structure $CuInSe_2$ [20] and other adamantane quaternary compounds such as $CuFe(Al,Ga,In)Se_3$ [12, 14], $CuFe_2(Al,Ga,In)Se_4$ [13, 17], $Cu_2FeSnSe_4$ [28] and $Cu_2MnSnSe_4$ [29].

Table 2

Atomic coordinates, isotropic temperature factors, bond distances (Å) and angles (°) for CuMnInSe3, derived from the Rietveld refinement. M = (Cu1+Mn1+In1)

Atom	Ox.	Site	*x*	*y*	*z*	foc	B (Å^2)
Cu	+1	*2e*	0	0	0	1	0.6(4)
Mn	+2	*2d*	0	½	¼	1	0.6(4)
In	+3	*2b*	½	0	¼	1	0.6(4)
		2f	½	½	0	⅓	0.6(4)
M		*2f*	½	½	0	⅓	0.6(4)
		2f	½	½	0	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-$\mathrm{Se^{i}}$	2.614(8)	M-$\mathrm{Se^{ii}}$	2.569(8)

$\mathrm{Se^{iii}}$-Cu-$\mathrm{Se^{iv}}$	114.5(2)	$\mathrm{Se^{iii}}$-Cu-$\mathrm{Se^{v}}$	108.6(2)	$\mathrm{Se^{iii}}$-Cu-Se	105.6(2)
$\mathrm{Se^{vi}}$-Mn-$\mathrm{Se^{vii}}$	110.4(2)	$\mathrm{Se^{vii}}$-Mn-Se	107.7(2)	Se-Mn-$\mathrm{Se^{viii}}$	110.4(2)
Se-In-$\mathrm{Se^{viii}}$	105.6(2)	Se-In-$\mathrm{Se^{i}}$	111.2(2)	Se-In-$\mathrm{Se^{ix}}$	111.7(2)
$\mathrm{Se^{vi}}$-M-Se	108.5(2)	Se-M-$\mathrm{Se^{ii}}$	111.5(2)		

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.

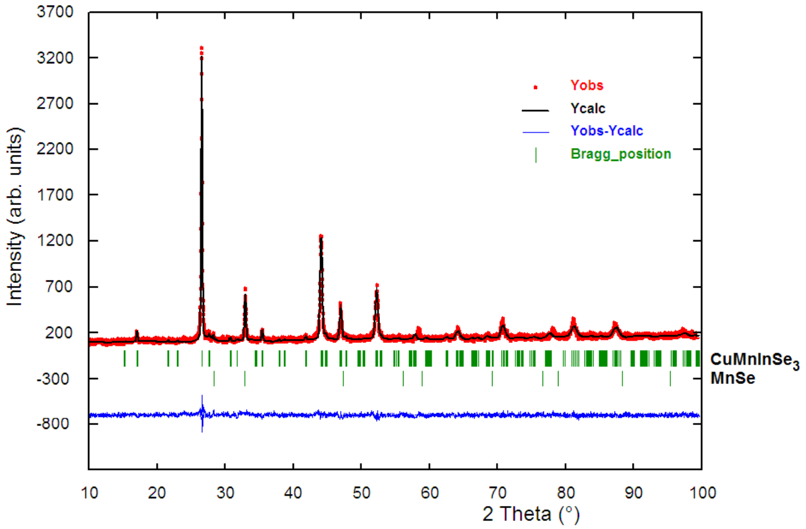
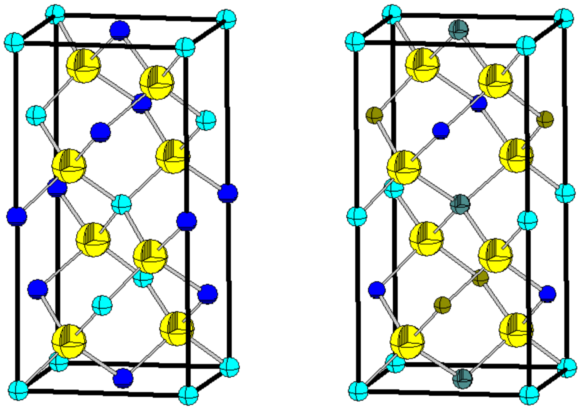


Figure 1. Rietveld final plot of CuMnInSe$_3$. The lower trace is the difference curve between observed and calculated patterns. The Bragg reflections are indicated by vertical bars.



$CuInSe_2$ ($I\bar{4}2d$) $CuMnInSe_3$ ($P\bar{4}2c$)

Figure 2. Unit cell diagram for the chalcopyrite $CuInSe_2$ compared to the $CuMnInSe_3$ compound.

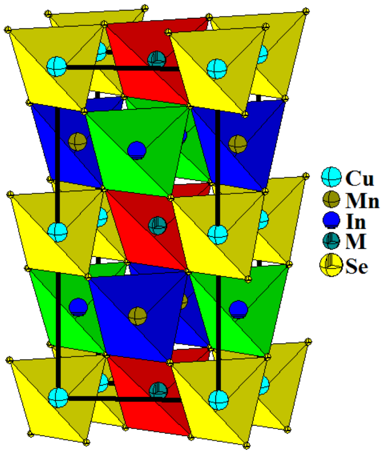


Figure 3. Polyhedral view of the $CuMnInSe_3$ structure showing tetrahedral units.

Conclusions

The crystal structure of the new quaternary compound $CuMnInSe_3$ was determined using X-ray powder diffraction data. This material crystallizes in the tetragonal space group $P\bar{4}2c$, with a $CuFeInSe_3$-type structure. This is a new compound of the I-II-III-VI_3 family of semiconductors.

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References

[1] Shay J.L., Wernik J.H.: “Ternary chalcopyrite semiconductors: Growth, electronic properties and applications”, Pergamon Press., Oxford, 1974.

[2] Parthé E.: Wurtzite and Sphalerite Structures. In: J.H. Westbrook, R.L. Fleischer (eds), Intermetallic Compounds, Principles and Applications, Vol. 1, John Wiley & Sons, Chichester, UK (1995).

[3] Ford G.M., Guo Q., Agrawal R., Hillhouse H.W., Hugh W.: “Earth abundant element $Cu_2Zn(Sn_{1-X}Ge_X)S_4$ nanocrystals for tunable band gap solar cells: 6.8% efficient device fabrication”, Chemistry of Materials, Vol. 23, No. 10 (2011) 2626-2629.

[4] Guo Q., Ford G.M., Yang W.C., Walker B.C., Stach E.A., Hillhouse H.W., Agrawal R.: “Fabrication of 7.2% efficient CZTSSe solar cells using CZTS nanocrystals”, Journal of American Chemical Society, Vol. 132, No. 49 (2010) 17384-17386.

[5] Chambers S.A., Yoo Y.K: “New materials for spintronics”, MRS Bulletin, Vol. 28 (2003) 706-710.

[6] Li Y., Fan W., Sun H., Cheng X., Li P., Zhao X.: “Electronic, optical and lattice dynamic properties of the novel diamond-like semiconductors Li_2CdGeS_4 and Li_2CdSnS_4”. Journal of Physics: Condensed Matter, Vol. 23, No. 22 (2011), 11.

[7] Sevik C., Ca T.: “Ab initio study of thermoelectric transport properties of pure and doped quaternary compounds”, Physical Review B, Vol. 82, No. 4 (2010), 7.

[8] Grima-Gallardo P., Cárdenas K., Quintero M., Ruiz J., Delgado G.E.: “X-ray diffraction studies on $(CuAlSe_2)_X(FeSe)_{1-X}$ alloys”, Materials Research Bulletin, Vol. 36, No. 6 (2001) 861-866.

[9] Grima-Gallardo P., Muñoz M., Delgado G.E., Briceño J.M., Ruiz J.: “The $(CuGaSe_2)_{1-X}(MgSe)_X$ alloy system (0 □ x □ 0.5): X-ray diffraction, energy dispersive spectrometry and differential thermal analysis”, physica status solidi (b), Vol. 241, No. 8 (2004) 1789-1794.

[10] Grima-Gallardo P., Muñoz M., Durán S., Delgado G.E., Quintero M., Ruiz J.: “Preparation and investigation of the quaternary alloy $CuTaInSe_3$”, Materials Research Bulletin, Vol. 42, No. 12 (2007) 2067-2071.

[11] Grima-Gallardo P., Torres S., Quintero M., Nieves L., Moreno E., Delgado G.E.: “Phase Diagram of $(CuInSe_2)_{1-x}(FeSe)_x$ alloys”, Journal of Alloys and Compounds, Vol. 630, No. 5 (2015) 146-150.

[12] Mora A.J., Delgado G.E., Grima-Gallardo P.: “Crystal structure of $CuFeInSe_3$ from X-ray powder diffraction data”, physica status solidi (a), Vol. 204, No. 2 (2007) 547-554.

[13] Delgado G.E., Mora A.J., Grima-Gallardo P., Quintero M.: “Crystal structure of $CuFe_2InSe_4$ from X-ray powder diffraction”, Journal of Alloys and Compounds, Vol. 454, No. 1 (2008) 306-309.

[14] Delgado G.E., Mora A.J., Contreras J.E., Grima-Gallardo P., Durán S., Muñoz M., Quintero M.: “Crystal structure characterization of the quaternary compounds $CuFeAlSe_3$ and $CuFeGaSe_3$”, Crystal Research and Technology, Vol. 44, No. 5 (2009) 548-552.

[15] Delgado G.E., Mora A.J., Grima-Gallardo P., Durán S., Muñoz M., Quintero M.: “Preparation and crystal structure analysis of $CuNiGaSe_3$ and $CuNiInSe_3$ quaternary compounds”, Bulletin of Materials Science, Vol. 33, No. (5) (2010) 637-640.

[16] Delgado G.E., Quintero E., Tovar R., Grima-Gallardo P., Quintero M.: “Synthesis and crystal structure of the quaternary compound $AgFe_2GaTe_4$”, Journal of Alloys and Compounds, Vol. 613, No. 1 (2014) 143-145.

[17] Delgado G.E., Mora A.J., Grima-Gallardo P., Muñoz M., Durán S., Quintero M,. Briceño J.M.: “Crystal structure of the quaternary compounds $CuFe_2AlSe_4$ and $CuFe_2GaSe_4$ from X-ray powder diffraction”, Bulletin of Materials Science, Vol. 38, No. 4 (2015) 1061-1064.

[18] International Centre for Diffraction Data (ICDD), Powder Diffraction File (Set 1-65). Newtown Square, PA, USA, 2013.

[19] Boultif A., Louër D.: “Powder pattern indexing with the dichotomy method”. Journal of Applied Crystallography, Vol. 37, No. 5 (2004) 724-731.

[20] Knight K.S. “The crystal structures of $CuInSe_2$ and $CuInTe_2$”, Materials Research Bulletin, Vol. 27, No. 2 (1992) 161-167.

[21] Rietveld H.M.: “A profile refinement method for nuclear and magnetic structures”, Journal of Applied Crystallography, Vol. 2, No. 2 (1969) 65-71.

[22] Rodriguez-Carvajal J.: “Recent advances in magnetic structure determination by neutron powder diffraction”, Physica B: Condensed Matter, Vol. 192, Nos. 1-2 (1993) 55-69.

[23] Johnston W.D., Heikes R.R.: “A Study of the System $Li_XMn_{(1-X)}Se$”, Journal of American Chemical Society, Vol. 80, No, 22 (1958) 5904-5907.

[24] Cagliotti G., Paoletti A., Ricci F.P.: “Choice of collimators for a crystal spectrometer for neutron diffraction”. Nuclear Instruments, Vol. 3, No. 4 (1958) 223-228.

[25] Thompson P., Cox D.E., Hastings J.B.: “Rietveld refinement of Debye-Scherrer synchrotron X-ray data from Al_2O_3”. Journal of Applied Crystallography, Vol. 20, No. 2 (1987) 79-83.

[26] Hill R.J., Howard J.C.: “Quantitative phase analysis from neutron powder diffraction data using the Rietveld method”, Journal of Applied Crystallography, Vol. 20, No. 6 (1987) 467-474.

[27] Rodulfo de Gil E.: “Ternary semiconducting compounds with chalcopyrite-type structure: I. Fundamental equation and its physically acceptable solutions”, physica status solidi (a), Vol. 70, No. 2 (1982) 519-523.

[28] Roque-Infante E., Delgado J.M., López-Rivera S.A.: “Synthesis and crystal structure of $Cu_2FeSnSe_4$, a I_2 III V VI_4 semiconductor”, Materials Letters, Vol. 33, No. 1-2 (1997) 67-70.

[29] Sachanyuk V.P., Olekseyuk I.D., Parasyuk O.V.: “X-ray powder diffraction study of the $Cu_2Cd_{1-X}Mn_XSnSe_4$ alloys”, physica status solidi (a), Vol. 203, No. 3 (2006) 459-465.

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