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$\overline{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$\overline{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$\overline{4}$2d (N°122), and the addition of a II-VI (II = Zn, Cd, Mn, Fe) binary compound produces alloys of the type (I-III-VI$_2$)$_{1-x}$(II-VI)$_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 η = $c/2a$ (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)	-	
$\eta=c/2a$ (Å)	1.01	-	
V (Å³)	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

CuMnInSe₃ 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 CuInSe₂ I $\bar{4}$ 2d structure and the P $\bar{4}$ 2c structure of CuMnInSe₃. 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 CuSe₄, MnSe₄, InSe₄ and MSe₄ 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 CuInSe₂ [20] and other adamantane quaternary compounds such as CuFe(Al,Ga,In)Se₃ [12, 14], CuFe₂(Al,Ga,In)Se₄ [13, 17], Cu₂FeSnSe₄ [28] and Cu₂MnSnSe₄ [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 (Å²)
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-Se^i	2.614(8)	M-Se^{ii}	2.569(8)
Se^{iii}-Cu-Se^{iv}	114.5(2)	Se^{iii}-Cu-Se^{v}	108.6(2)	Se^{iii}-Cu-Se	105.6(2)
Se^{vi}-Mn-Se^{vii}	110.4(2)	Se^{vii}-Mn-Se	107.7(2)	Se-Mn-Se^{viii}	110.4(2)
Se-In-Se^{viii}	105.6(2)	Se-In-Se^{i}	111.2(2)	Se-In-Se^{ix}	111.7(2)
Se^{vi}-M-Se	108.5(2)	Se-M-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.
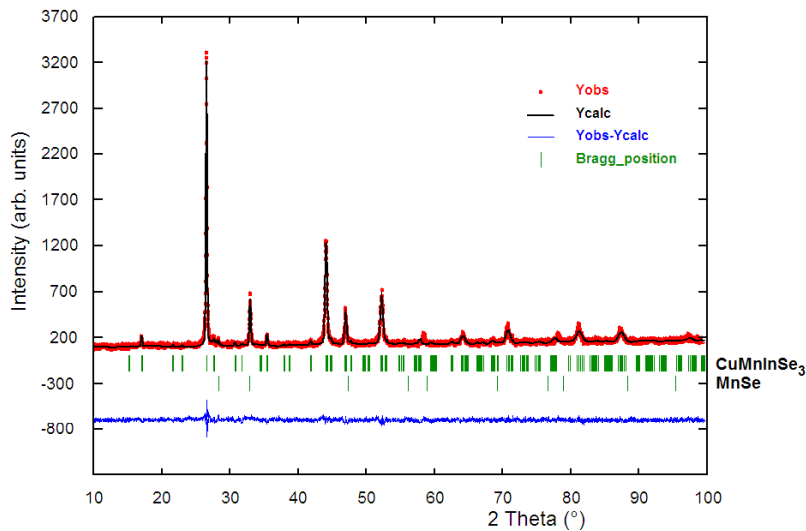

Figure 1. Rietveld final plot of CuMnInSe$_3$. The lower trace is the difference curve between observed and calculated patterns. The Bragg reflections are indicated by vertical bars.
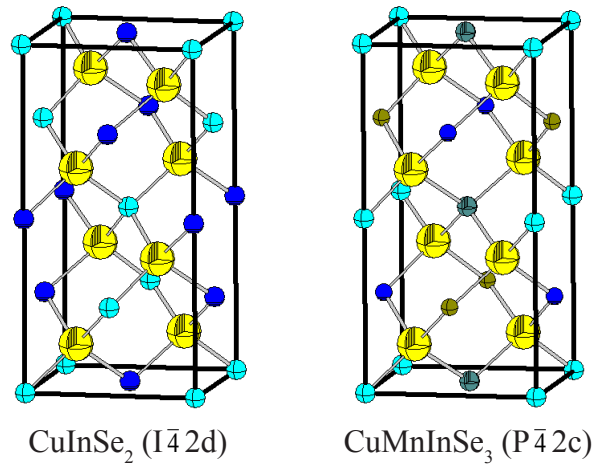
Figure 2. Unit cell diagram for the chalcopyrite CuInSe$_2$ compared to the CuMnInSe$_3$ compound.
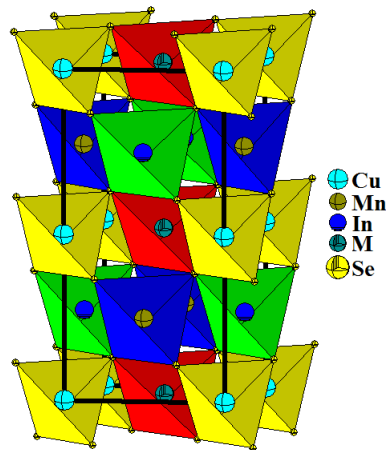

Figure 3. Polyhedral view of the CuMnInSe$_3$ structure showing tetrahedral units.

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.

Acknowledgements

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