

Crystal structure of the quaternary compounds $\text{CuFe}_2\text{AlSe}_4$ and $\text{CuFe}_2\text{GaSe}_4$ from X-ray powder diffraction

G E DELGADO^{1,*}, A J MORA¹, P GRIMA-GALLARDO², M MUÑOZ², S DURÁN²,
M QUINTERO² and J M BRICEÑO³

¹Laboratorio de Cristalografía, Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, Mérida 5101, Venezuela

²Centro de Estudios de Semiconductores, Departamento de Física, Facultad de Ciencias, Universidad de Los Andes, Mérida 5101, Venezuela

³Laboratorio de Análisis Químico y Estructural, Departamento de Física, Facultad de Ciencias, Universidad de Los Andes, Mérida 5101, Venezuela

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Abstract. The crystal structure of the quaternary compounds $\text{CuFe}_2\text{AlSe}_4$ and $\text{CuFe}_2\text{GaSe}_4$, belonging to the system I-II₂-III-VI₄, were characterized using X-ray powder diffraction data. Both compounds crystallize in the tetragonal space group I_42m (No. 121), $Z = 2$, with unit cell parameters $a = 5.609(1)$ Å, $c = 10.963(2)$ Å for $\text{CuFe}_2\text{AlSe}_4$ and $a = 5.6165(3)$ Å, $c = 11.075(1)$ Å for $\text{CuFe}_2\text{GaSe}_4$. These compounds are isostructural with $\text{CuFe}_2\text{InSe}_4$, and have a normal adamantane stannite structure.

Keywords. Semiconductors; chalcogenides; chemical synthesis; X-ray powder diffraction; crystal structure.

1. Introduction

The compounds with ternary structures of the chalcopyrite family I-III-VI₂ (I = Cu, Ag; III = Al, Ga, In, VI = S, Se, Te) form an extensive group of semiconductor materials with diverse optical and electrical properties,¹ and used as absorbent layer in thin films for solar cells.^{2,3} From the structural point of view they crystallize with tetragonal symmetry in the space group I_42d (No. 122) being isostructural with the CuFeS_2 mineral (chalcopyrite) from which they take their name.⁴ The addition of a II-VI binary compound to ternary chalcopyrite structures (I-III-VI₂) produces alloys of composition (I-III-VI₂)_{1-x}(II-VI)_x.⁵ The formation of some member with compositions I-II-III-VI₃ ($x = 1/2$), I-II₂-III-VI₄ ($x = 2/3$) and I₂-II-III-VI₅ ($x = 1/3$) have been reported.^{6,7} All these phases fulfil the rules of the formation of adamantane compounds⁵ and belong to the normal semiconductor compound families of the third-, fourth- and fifth-order derivatives of the II-VI binary semiconductors, respectively. In particular, the family of compounds I-II₂-III-VI₄ belongs to the two possible normal compound families of fourth derivatives of the II-VI binary semiconductors with three types of cations, the other family being I₂-II-IV-VI₄.⁸ Due to the great variety of possible compositions, these quaternary diamond-like materials can be useful for applications such as tunable semiconductors,⁹ photovoltaics,^{10,11} spintronics,¹¹ non-linear optics¹² and thermoelectrics.¹³

The crystal structure study of the quaternary $\text{CuFe}_2\text{InSe}_4$ indicated that this material crystallizes in the tetragonal stannite structure, space group I_42m , and constituted the first compound of the I-II₂-III-VI₄ family that crystallizes in a sphalerite derivative structure.¹⁴ In contrast, all the phases reported of the type $\text{AgCd}_2\text{GaS}_4$,¹⁵ $\text{AgCd}_2\text{GaSe}_4$,¹⁶ $\text{Ag}_{1-x}\text{Cu}_x\text{Cd}_2\text{GaS}_4$,¹⁷ $\text{AgCd}_2\text{Ga}_{1-x}\text{In}_x\text{S}_4$ ¹⁸ and $\text{AgCd}_{2-x}\text{Mn}_x\text{GaS}_4$ ¹⁹ crystallize in the orthorhombic space group $\text{Pmn}2_1$ with structures related to the wurtzite.

In recent years, it has been of interest to carry out a systematic study of the crystal structure of quaternary diamond-like families.^{14,20–25} Hence, here a report of the structural characterization of two new quaternary compounds, $\text{CuFe}_2\text{AlSe}_4$ and $\text{CuFe}_2\text{GaSe}_4$, using the Rietveld method from X-ray powder diffraction data, has been made.

2. Experimental

The samples were synthesized using the melt and annealing technique. Starting materials (Cu, Fe, Al or Ga and Se) with a nominal purity of 99.99 wt% in the stoichiometric ratio were mixed together in evacuated and sealed quartz tube ($\sim 10^{-4}$ Torr) which inner walls were previously subjected to pyrolysis in order to avoid reaction of the starting materials with quartz. The fusion process was carried out inside a furnace (vertical position) heated up to 1500°C at a rate of 20 deg h⁻¹, with a stop of 48 h at 220°C (melting temperature of Se) in order to maximize the formation of binary species at low temperature and minimize the presence of unreacted Se at high temperatures. The ampoule was shaken using a

* Author for correspondence (gerzon@ula.ve)

mechanical system during all the heating process in order to help the complete mixing of all the elements. The maximum temperature (1500°C) was keeping for other 48 h with the mechanical shaken system on. Then, the mechanical shaken system was turning off and the temperature was gradually down, at the same rate of 20 deg h⁻¹, until 600°C. The ampoule was kept at this temperature for a period of 30 days. Finally, the sample was cooled to room temperature at a rate of 10 deg h⁻¹.

The stoichiometric relation of the samples was investigated by the scanning electron microscopy (SEM) technique, using a Hitachi S2500 microscope equipped with a Kedex EDX accessory. The average chemical composition of different regions of each sample gave the atomic percentages: Cu (13.4%), Fe (22.9%), Al (12.5%), Se (51.2%) for CuFe₂AlSe₄ and Cu (13.2%), Fe (23.1%), Ga (12.5%), Se (51.2% for CuFe₂GaSe₄. These values are in good agreement with the ideal composition 1 : 2 : 1 : 4.

Thermal studies show the formations of each phase were published elsewhere.^{6,7}

For the X-ray analysis, a small quantity of the samples, cut from the ingot, were ground mechanically in an agate mortar and pestle. The resulting fine powders, sieved to 106 μm, 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 (CuK α radiation: $\lambda = 1.54059 \text{ \AA}$; 40 kV, 30 mA) and a Ge(111) primary 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° to 100° 2 θ , with a step size of 0.02° and counting time of 40 s. Quartz was used as an external standard. The Bruker AXS analytical software was used to establish the positions of the peaks.

3. Results and discussion

The X-ray diffractograms of CuFe₂AlSe₄ and CuFe₂GaSe₄ showed single phases. The powder patterns were indexed using the program Dicvol04,²⁶ and tetragonal cells with similar magnitudes to the parent chalcopyrite structures, CuAlSe₂²⁷ and CuGaSe₂,²⁸ were found. Systematic absences indicate I-type lattices. A detailed pattern examination taking into account the sample composition, cell parameters and lattice-type, suggested that both compounds are isostructural with the quaternary CuFe₂InSe₄¹⁴ which crystallizes in the space group I₄2m with unit cell parameters similar to the

Table 1. Rietveld refinement results for CuFe₂AlSe₄ and CuFe₂GaSe₄.

Molecular formula	CuFe ₂ AlSe ₄	CuFe ₂ GaSe ₄
Molecular weight (g mol ⁻¹)	518.06	560.80
<i>a</i> (Å)	5.6045(3)	5.6107(2)
<i>c</i> (Å)	10.965(1)	11.076(1)
<i>cla</i>	1.96	1.97
<i>V</i> (Å ³)	344.42(4)	348.67(4)
<i>Z</i>	2	2
Crystal system	Tetragonal	Tetragonal
Space group	I ₄ 2m (No. 121)	I ₄ 2m (No. 121)
<i>d</i> _{calc} (g cm ⁻³)	4.995	5.341
Temperature (K)	298(1)	298(1)
Wavelength (Cu K α)	1.5418 (Å)	1.5418 (Å)
Data range 2 θ (deg)	10–100	10–100
Step size 2 θ (deg)	0.02	0.02
Counting time (s)	40	40
Step intensities	4501	4501
<i>R</i> _p (%)	11.2	7.9
<i>R</i> _{wp} (%)	12.2	8.6
<i>R</i> _{exp} (%)	9.9	6.5
<i>R</i> _B (%)	9.5	8.6
<i>S</i>	1.2	1.3

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

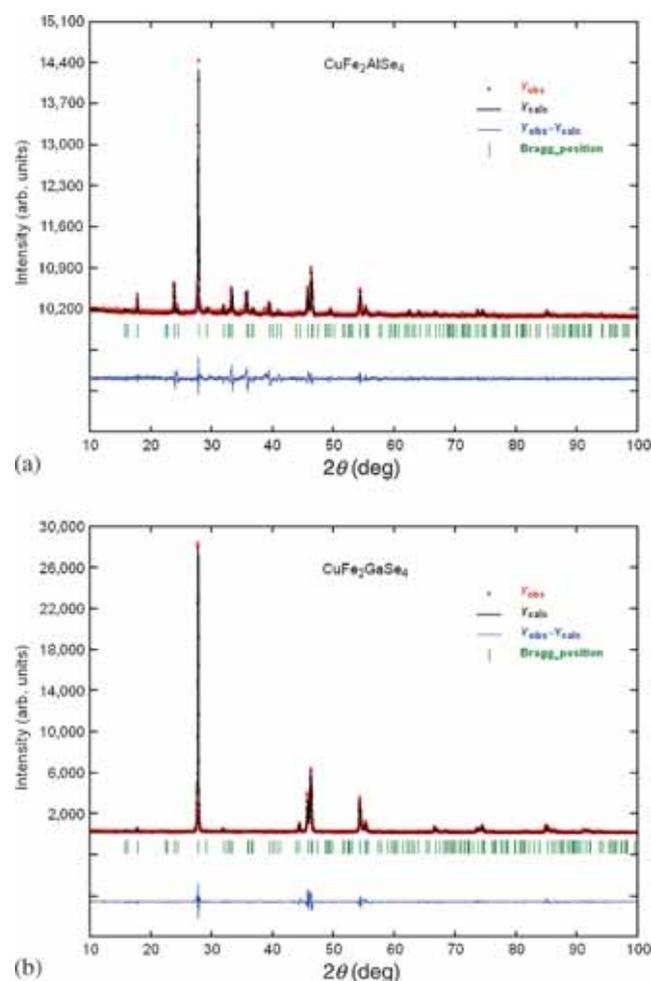


Figure 1. Rietveld final plots of (a) CuFe₂AlSe₄ and (b) CuFe₂GaSe₄. The lower trace is the difference curve between observed and calculated patterns. The Bragg reflections are indicated by vertical bars.

Table 2. Unit cell, atomic coordinates, isotropic temperature factor and selected geometric parameters (\AA , deg) for $\text{CuFe}_2\text{AlSe}_4$.

Atom	Ox.	Wyck.	x	y	z	F_{oc}	B (\AA^2)
Cu	+1	2a	0	0	0	1	0.46(5)
Fe	+2	4d	0	1/2	1/4	1	0.46(5)
Al	+3	2b	0	0	1/2	1	0.46(5)
Se	-2	8i	0.2538(7)	0.2459(7)	0.1207(6)	1	0.46(5)
Cu–Se ⁱ		2.410(5)	Fe–Se	2.437(5)	Al–Se ⁱ		2.360(5)
Se–Cu–Se ⁱⁱ		$107.6(2) \times 4$	Se–Fe–Se ^{iv}	$109.7(2) \times 4$	Se ⁱ –Al–Se ^{iv}		$108.4(2) \times 4$
Se–Cu–Se ⁱⁱⁱ		$113.2(1) \times 2$	Se–Fe–Se ^v	$109.0(1) \times 2$	Se ^{iv} –Al–Se ^{vi}		$111.6(1) \times 2$

Symmetry codes:

(i) $-0.5 + x, -0.5 + y, 0.5 + z$; (ii) $-y, x, -z$; (iii) $-x, -y, z$; (iv) $-0.5 + y, 0.5 - x, 0.5 - z$; (v) $-x, 1 - y, z$; (vi) $0.5 - y, -0.5 + x, 0.5 - z$.**Table 3.** Unit cell, atomic coordinates, isotropic temperature factor and selected geometric parameters (\AA , deg) for $\text{CuFe}_2\text{GaSe}_4$.

Atom	Ox.	Wyck.	x	Y	z	F_{oc}	B (\AA^2)
Cu	+1	2a	0	0	0	1	0.53(5)
Fe	+2	4d	0	1/2	1/4	1	0.53(5)
Ga	+3	2b	0	0	1/2	1	0.53(5)
Se	-2	8i	0.2505(6)	0.2505(6)	0.1231(5)	1	0.53(5)
Cu–Se ⁱ		2.410(4)	Fe–Se	2.431(4)	Ga–Se		2.404(4)
Se–Cu–Se ⁱⁱ		$108.7(1) \times 4$	Se–Fe–Se ^{iv}	$109.5(2) \times 4$	Se ⁱ –Ga–Se ^{iv}		$108.8(1) \times 4$
Se–Cu–Se ⁱⁱⁱ		$111.1(1) \times 2$	Se–Fe–Se ^v	$109.4(1) \times 2$	Se ^{iv} –Ga–Se ^{vi}		$110.9(1) \times 2$

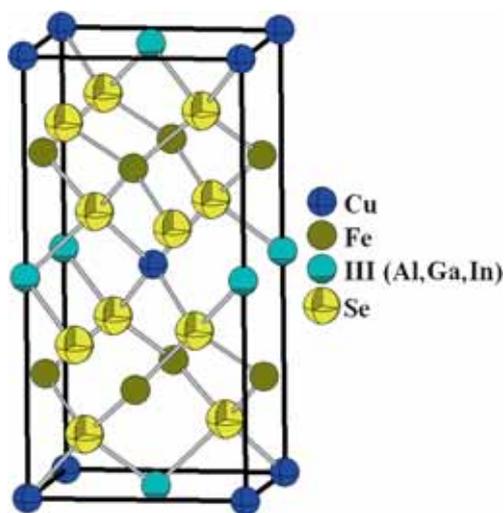
Symmetry codes:

(i) $-0.5 + x, -0.5 + y, 0.5 + z$; (ii) $-y, x, -z$; (iii) $-x, -y, z$; (iv) $-0.5 + y, 0.5 - x, 0.5 - z$; (v) $-x, 1 - y, z$; (vi) $0.5 - y, -0.5 + x, 0.5 - z$.

parent CuInSe_2 .²⁹ It should be mentioned that a Rietveld refinement was performed in the I_4 (No. 82) space group but did not produce a chemically sound structure, discarding a kesterite structure.

On the other hand, it is worth noting that these powder patterns of $\text{CuFe}_2\text{AlSe}_4$ and $\text{CuFe}_2\text{GaSe}_4$ are close with those previously reported for the quaternary phases CuFeAlSe_3 and CuFeGaSe_3 ²³ which crystallize in the P_42c space group, however the systematic absences analyses indicate I-type and P-type lattices, respectively. Rietveld refinements were performed also in the P_42c space group but neither produces a chemically sound structure.

The Rietveld refinements³⁰ of the structures were carried out using the Fullprof program.³¹ The atomic coordinates of $\text{CuFe}_2\text{InSe}_4$ ¹⁴ were used as starting model for the refinements. The angular dependence of the peak full-width at half-maximum (FWHM) was described by Caglioti's formula.³² Peak shapes were described by the parameterized Thompson–Cox–Hastings pseudo-Voigt profile function.³³ 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 both compounds are summarized in table 1. Figure 1 shows the observed,

**Figure 2.** Unit cell diagram for the $\text{Cu-Fe}_2\text{-III-Se}_4$ compounds.

calculated and difference profile for the final cycle of Rietveld refinements for $\text{CuFe}_2\text{AlSe}_4$ and $\text{CuFe}_2\text{GaSe}_4$. Atomic coordinates, isotropic temperature factor, bond distances and angles for each compound are shown in tables 2 and 3.

Table 4. Comparative table of unit cell parameters and bond distances for the Cu–III–Se₂ chalcopyrite compounds and the related Cu–Fe₂–III–Se₄ quaternary compounds.

Compound	SG	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	Cu–Se (Å)	Fe–Se (Å)	III–Se (Å)	Ref.
CuFe ₂ AlSe ₄	I ₄ 2m	5.6045(3)	10.965(1)	344.428(4)	2.410(5)	2.437(5)	2.360(5)	This work
CuFe ₂ GaSe ₄	I ₄ 2m	5.6107(2)	11.076(1)	348.67(4)	2.410(4)	2.431(4)	2.404(4)	This work
CuFe ₂ InSe ₄	I ₄ 2m	5.7694(3)	11.495(1)	382.62(4)	2.432(5)	2.438(5)	2.576(8)	[14]
CuAlSe ₂	I ₄ 2d	5.606(5)	10.90(1)	342.6(5)	2.438(1)	—	2.373(1)	[27]
CuGaSe ₂	I ₄ 2d	5.614(1)	11.022(1)	347.4(1)	2.446(9)	—	2.387(9)	[28]
CuInSe ₂	I ₄ 2d	5.781(1)	11.642(3)	389.1(2)	2.432(1)	—	2.591(1)	[29]

These compounds are normal adamantane-structure materials and can be described as derivative of the sphalerite structure.⁵ Figure 2 shows the unit cell diagram for both Cu–Fe₂–III–Se₄ compounds, and table 4 shows a comparison between the unit cell parameters and the bond distances for the three phases of both families of compounds Cu–III–Se₂ and Cu–Fe₂–III–Se₄. The Cu–Se, Fe–Se and III–Se distances are in good agreement with those observed in other adamantane structure compounds found in the ICSD database.³⁴ In particular, for the CuFe₂GaSe₄ compound, the structure agrees with the DFT calculations reported in recent times.³⁵

4. Conclusions

The crystal structure of the semiconductor compounds CuFe₂AlSe₄ and CuFe₂GaSe₄ were determined using X-ray powder diffraction. Both compounds crystallize in the tetragonal space group I₄2m, with a sphalerite derivative structure, and are isomorphic with CuFe₂InSe₄.

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