

Synthesis and crystal structure of three new quaternary compounds in the system $(\text{Cu-III-Se}_2)_{1-x}\text{ZnSe}_x$ (III = Al, Ga, In), formed by Zn incorporation in Cu-III-Se₂ chalcopyrites

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The crystal structure of the chalcogenide alloys CuZnAlSe_3 , CuZnGaSe_3 and CuZnInSe_3 , new members of the system I-II-III-VI₃, were characterized using X-ray powder diffraction data. All materials crystallize in the tetragonal space group $P_4 2c$ ($N^\circ 112$) with a CuFeInSe_3 -type structure.

Keywords: Chalcogenides; semiconductors; chemical synthesis; X-ray diffraction; crystal structure.

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1. Introduction

The compounds with ternary structures of the chalcopyrite family Cu-III-Se_2 (III = Al, Ga, In) form an wide group of semiconductor materials with diverse optical and electrical properties [1]. They crystallize with tetragonal symmetry in the space group $I_4 2d$ ($N^\circ 122$), and the addition of a Fe-Se binary compound produces alloys of the type $(\text{Cu-III-Se}_2)_{1-x}(\text{Fe-Se})_x$ [2]. Recently, the formation of some member with compositions Cu-Fe-III-S_3 ($x = 1/2$), $\text{Cu-Fe}_2\text{-III-Se}_4$ ($x = 2/3$) and $\text{Cu}_2\text{-Fe-III-Se}_5$ ($x = 1/3$) have been reported [3-20]. 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 [21].

The first crystal structure characterization of one I-II-III-VI₃ semiconductor member, CuFeInSe_3 , indicated a degradation of symmetry from the chalcopyrite structure $I_4 2d$ to a related structure $P_4 2c$ [8].

In this work, we report a detailed structural analysis of three new members of the Cu-II-III-Se_3 family, CuZnAlSe_3 , CuZnGaSe_3 and CuZnInSe_3 which was performed using X-ray powder diffraction by means of the Rietveld method.

2. Experimental

Starting materials (Cu, Zn, Al, Ga, 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 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.

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 106 μ , 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 ($\text{CuK}\alpha$ radiation: $\lambda = 1.54056 \text{ \AA}$; 40 kV, 30 mA) 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 40 s. Quartz was used as an external standard.

3. Results and discussion

The X-ray diffractograms of three alloys CuZn-III-Se_3 (III = Al, Ga, In) showed single phases. The powder patterns were indexed using the program Dicvol04 [22], and tetragonal cells with similar magnitudes to the parent chalcopyrite structures, CuAlSe_2 [23], CuGaSe_2 [24], CuInSe_2 [25] were found. Systematic absences are consistent with a P 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 [8]; the first structural characterization of a I-II-III-VI₃ semiconductor member, which crystallizes in the space group $P_4 2c$ with unit cell parameters similar to the parent CuInSe_2 [25].

The Rietveld refinements [26] of the structures were carried out using the Fullprof program [27]. The atomic coordinates of CuFeInSe_3 [8] were used as starting model for each

TABLE I. Rietveld refinement results for the alloys CuZnAlSe₃, CuZnGaSe₃ and CuZnInSe₃.

molecular formula	CuZnAlSe ₃	CuZnGaSe ₃	CuZnInSe ₃
molecular weight (g/mol)	1047.36	1161.30	1281.53
<i>a</i> (Å)	5.6083(2)	5.6165(3)	5.7922(4)
<i>c</i> (Å)	10.992(1)	11.075(1)	11.658(1)
<i>c/a</i>	1.96	1.97	1.97
<i>V</i> (Å ³)	345.73(4)	351.49(4)	391.12(8)
<i>Z</i>	1	1	1
space group	P ₄ 2c (N° 112)	P ₄ 2c (N° 112)	P ₄ c (N° 112)
<i>d</i> _{calc} (g/cm ⁻³)	4.95	5.49	5.44
Temperature (K)	298(1)	298(1)	298(1)
wavelength (CuKα)	1.54056 Å	1.54056 Å	1.54056 Å
step intensities	4501	4501	4501
independent reflections	134	134	134
<i>R_p</i> (%)	8.1	8.7	8.8
<i>R_{wp}</i> (%)	9.1	9.4	9.4
<i>R_{exp}</i> (%)	6.5	6.7	6.7
<i>R_B</i> (%)	9.5	9.6	9.6
χ^2	1.4	1.4	1.44

$$R_p = 100 \sum |y_{\text{obs}} - y_{\text{calc}}| / \sum |y_{\text{obs}}| \quad R_{wp} = 100 [\sum_w |y_{\text{obs}} - y_{\text{calc}}|^2 / \sum_w |y_{\text{obs}}|^2]^{1/2} \quad R_B = 100 \sum_k |I_k - I_{c_k}| / \sum_k |I_k|$$

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

TABLE II. Atomic coordinates, isotropic temperature factors, bond distances (Å) and angles (°) for CuZnAlSe₃, derived from the Rietveld refinement.

Atom	Ox.	Site	x	y	z	Foc	B (Å ²)
Cu	+1	2c	0	1/2	1/4	1	0.6(5)
Zn	+2	2e	0	0	0	1	0.6(5)
Al	+3	2b	1/2	0	1/4	1	0.6(5)
Cu1	+1	2f	1/2	1/2	1/2	1/3	0.6(5)
Zn1	+2	2f	1/2	1/2	1/2	1/3	0.6(5)
Al1	+3	2f	1/2	1/2	1/2	1/3	0.6(5)
Se	-2	8n	0.258(1)	0.252(1)	0.126(1)	1	0.6(5)
Cu-Se	2.426(8)	Zn-Se	2.451(8)	Al-Se ⁱ	2.387(8)	2f-Se ⁱⁱ	2.386(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} -Zn-Se ^{vii}	108.0(2) x2	Se ^{vii} -Zn-Se	112.6(2) x2	Se-Zn-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.

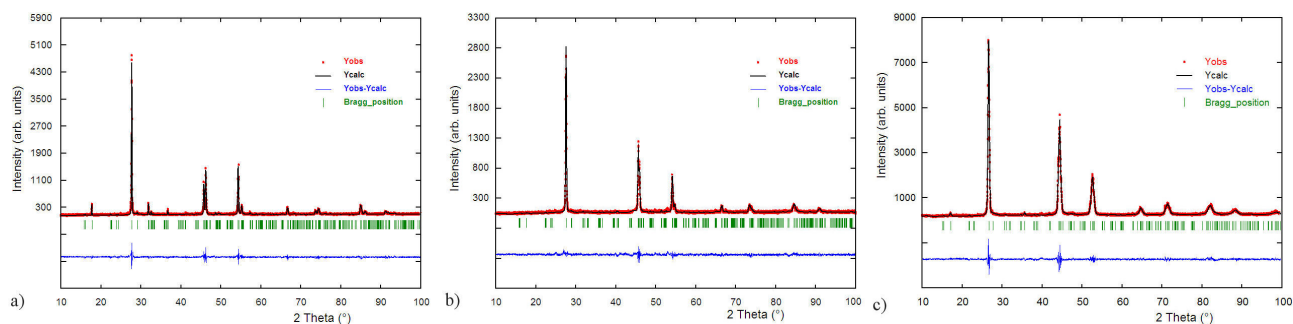


FIGURE 1. Rietveld final plots of a) CuZnAlSe_3 , b) CuZnGaSe_3 and c) CuZnInSe_3 . The lower trace is the difference curve between observed and calculated patterns. The Bragg reflections are indicated by vertical bars.

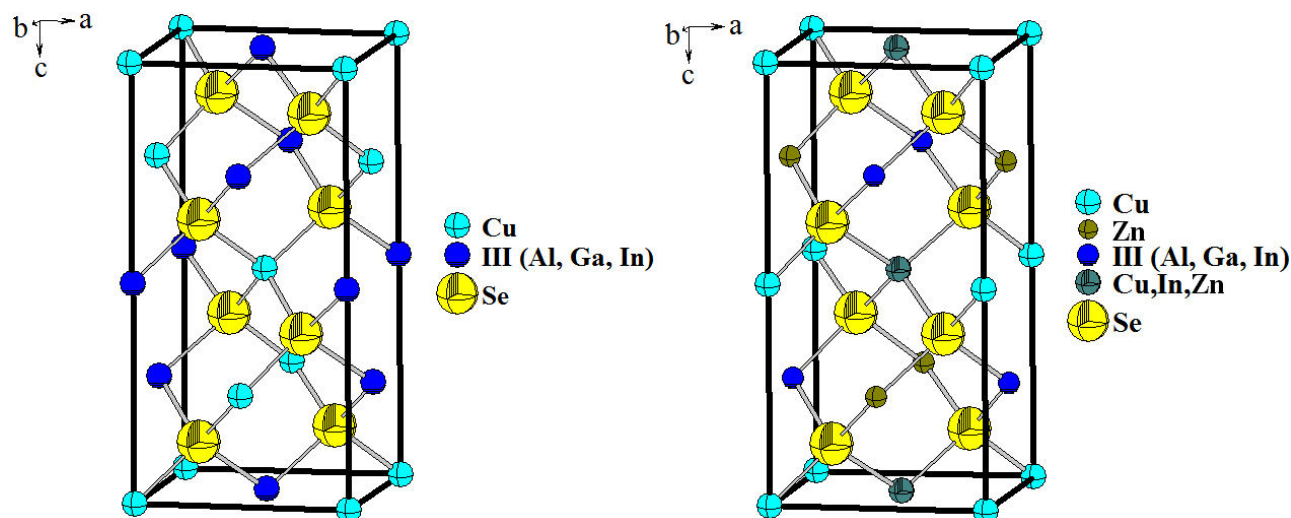


FIGURE 2. Unit cell diagram for the chalcopyrite Cu-III-Se_2 compared to the Cu-Zn-III-Se_3 compounds.

refinement. The angular dependence of the peak full width at half maximum (FWHM) was described by the Caglioti's formula [28]. Peak shapes were described by the parameterized Thompson-Cox-Hastings pseudo-Voigt profile function [29]. 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 summarized in Table I. Figure 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 II, III and IV.

CuZnAlSe_3 , CuZnGaSe_3 and CuZnInSe_3 are normal adamantane-structure compounds [2] related to the CuAlSe_2 , CuGaSe_2 and CuInSe_2 chalcopyrite parent structures, where the Zn cation are "diluted" leaving the cell volume almost unchanged. Figure 2 show the unit cell diagram for the Cu-Zn-III-Se_3 compounds compared to the chalcopyrite Cu-III-Se_2 parents, and Table V show a comparison between the unit

cell parameters and the bond distances for the three phases of both families of compounds.

In CuZnAlSe_3 , the tetrahedra containing the Cu atoms [mean Se...Se distance 3.97(1) Å] are slightly smaller than those containing the M (Cu1 or Zn1 or Al1) atoms [mean Se...Se distance 4.20(1) Å], Al atoms [mean Se...Se distance 3.97(1) Å], and Zn atoms [mean Se...Se distance 4.00(1) Å], respectively. In CuZnGaSe_3 , the tetrahedra around the cations, in mean Se...Se distance, are: M (Cu1, Zn1, Ga1) 3.90(1) Å, Cu 3.96(1) Å, Ga 3.90(1) Å, and Zn 4.00(1) Å, respectively. In CuZnInSe_3 , the tetrahedra around the cations, in mean Se...Se distance, are: M (Cu1, Zn1, In1) 3.94(1) Å, Cu 3.97(1) Å, In 3.91(1) Å, and Zn 4.10(1) Å, respectively.

The Cu-Se, Zn-Se and III (Al,Ga,In)-Se bond distances in all compounds (Table II, III and IV) are in good agreement with those observed in the parent chalcopyrite structures (Table V) and other quaternary adamantane structure compounds such as $\text{CuFe(Al,Ga,In)Se}_3$ [8,17], $\text{CuFe}_2(\text{Al,Ga,In)Se}_4$ [14,19], $\text{Cu}_2\text{FeSnSe}_4$ [30], $\text{Cu}_2\text{ZnGeSe}_4$ [31] and $\text{Cu}_2\text{ZnSnSe}_4$ [32].

TABLE III. Atomic coordinates, isotropic temperature factors, bond distances (Å) and angles (°) for CuZnGaSe₃, derived from the Rietveld refinement.

Atom	Ox.	Site	<i>x</i>	<i>y</i>	<i>z</i>	Foc	B (Å ²)
Cu	+1	2c	0	1/2	1/4	1	0.6(4)
Zn	+2	2e	0	0	0	1	0.6(4)
Ga	+3	2b	1/2	0	1/4	1	0.6(4)
Cu1	+1	2f	1/2	1/2	1/2	1/3	0.6(4)
Zn1	+2	2f	1/2	1/2	1/2	1/3	0.6(4)
Ga1	+3	2f	1/2	1/2	1/2	1/3	0.6(4)
Se	-2	8n	0.254(1)	0.256(1)	0.124(1)	1	0.6(4)
Cu-Se	2.426(8)	Zn-Se	2.452(8)	Ga-Se ⁱ	2.439(8)	2f-Se ⁱⁱ	2.387(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} -Zn-Se ^{vii}	108.4(2) x2	Se ^{vii} -Zn-Se	111.7(2) x2	Se-Zn-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.

TABLE IV. Atomic coordinates, isotropic temperature factors, bond distances (Å) and angles (°) for CuZnInSe₃, derived from the Rietveld refinement.

Atom	Ox.	Site	<i>x</i>	<i>y</i>	<i>z</i>	Foc	B (Å ²)
Cu	+1	2c	0	1/2	1/4	1	0.6(4)
Zn	+2	2e	0	0	0	1	0.6(4)
In	+3	2b	1/2	0	1/4	1	0.6(4)
Cu1	+1	2f	1/2	1/2	1/2	1/3	0.6(4)
Zn1	+2	2f	1/2	1/2	1/2	1/3	0.6(4)
In1	+3	2f	1/2	1/2	1/2	1/3	0.6(4)
Se	-2	8n	0.227(1)	0.255(1)	0.124(1)	1	0.6(4)
Cu-Se	2.429(8)	Zn-Se	2.450(8)	In-Se ⁱ	2.615(8)	2f-Se ⁱⁱ	2.670(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} -Zn-Se ^{vii}	110.4(2) x2	Se ^{vii} -Zn-Se	107.7(2) x2	Se-Zn-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 V. Comparative table of unit cell parameters and bond distances for the Cu-III-Se₂ chalcopyrite compounds and the related Cu-Zn-III-Se₃ alloys (III= Al Ga, In). ([*] = this work).

Compound	SG	a (Å)	c (Å)	c/a	V (Å ³)	Cu-Se (Å)	Zn-Se (Å)	III-Se (Å)	Ref.
CuAlSe ₂	I ₄ 2d	5.606(5)	10.90(1)	1.94	342.6(5)	2.438(1)	-	2.373(1)	[23]
CuGaSe ₂	I ₄ 2d	5.614(1)	11.022(1)	1.96	347.4(1)	2.446(9)	-	2.387(9)	[24]
CuInSe ₂	I ₄ 2d	5.781(1)	11.642(3)	2.01	389.1(2)	2.432(1)	-	2.591(1)	[25]
CuZnAlSe ₃	P ₄ 2c	5.6083(2)	10.992(1)	1.96	345.73(3)	2.426(8)	2.451(8)	2.387(8)	[*]
CuZnGaSe ₃	P ₄ 2c	5.6255(3)	11.107(1)	1.97	351.49(4)	2.426(8)	2.452(8)	2.439(8)	[*]
CuZnInSe ₃	P ₄ 2c	5.7922(4)	11.658(1)	1.97	391.12(8)	2.429(8)	2.450(8)	2.615(8)	[*]

4. Conclusion

The crystal structure of the semiconductor compounds CuZnAlSe₃, CuZnGaSe₃ and CuZnInSe₃ were determined using X-ray powder diffraction data. All compounds crystallize in the tetragonal space group P₄ 2c, with a sphalerite derivative structure, and are isomorphous with CuFeInSe₃.

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