Synthesis and Crystal Structure of Three New Quaternary Compounds in the system Cu-Mn-III-Se₃ (III = Al, Ga, In)

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Received: October 03, 2016; Revised: November 27, 2017; Accepted: December 28, 2017

Chalcogenide alloys CuMnAlSe₃, CuMnGaSe₃, and CuMnInSe₃, new members of the semiconductor system I-II-III-VI₃, were synthetized and structurally characterized by the Rietveld method using X-ray powder diffraction data. All compounds crystallize in the tetragonal space group P4 2c ( Nº 112) with a CuFeInSe₃-type structure.

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

1. Introduction

The Cu-III-Se₂ (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 properties¹. These materials crystallize with tetragonal symmetry in the space group I4 2d (Nº122), and the addition of a Fe-Se binary compound produces alloys of the type (Cu-III-Se₂)₁₋ₓ (FeSe)ₓ. Some previous results on the formation, structural characterization, thermal and magnetic properties on these alloys with compositions Cu-Fe-III-Se₃ (x = ½), Cu-Fe₂-III-Se₄ (x = ⅔) and Cu₂-Fe-III-Se₅ (x = ⅓) have been reported³–15. All these phases fulfill the rules of formation of adamantane compounds² and belong to the normal semiconductor compound families of the third, fourth and fifth-order derivatives of the II-VI binary semiconductors, respectively⁶. 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-VI₁ semiconductor member, CuFeInSe₃, indicated a degradation of symmetry from the chalcopyrite structure I4 2d to a related structure P4 2c. In this work, we report a detailed synthesis and structural analysis of three new members of this family; CuMnAlSe₃, CuMnGaSe₃ and CuMnInSe₃, 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-Se₃ (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
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-Se₃ (III= Al, Ga, In) showed single phases. The powder patterns were indexed using the program Dicvol04, and tetragonal cells with similar magnitudes to the parent chalcopyrite structures, CuAlSe₂, CuGaSe₂, CuInSe₂ 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 CuFeInSe₆ which crystallizes in the space group P42c.

The Rietveld refinements of the structures were carried out using the Fullprof program. The atomic coordinates of CuFeInSe₆ 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. Peak shapes were described by the parameterized Thompson-Cox-Hastings pseudo-Voigt profile function. 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 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.

| Table 1. Rietveld refinement results for the alloys CuMnAlSe₃, CuMnGaSe₃, and CuMnInSe₃. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| molecular formula | CuMnAlSe₃ | CuMnGaSe₃ | CuMnInSe₃ |
| 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/2a | 0.98 | 0.98 | 1.00 |
| V (Å³) | 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/cm³) | 4.91 | 5.40 | 5.33 |
| Temperature (K) | 298(1) | 298(1) | 298(1) |
| wavelength (CuKα) | 1.54056 Å | 1.54056 Å | 1.54056 Å |
| data range 2θ (°) | 10-100 | 10-100 | 10-100 |
| step size 2θ (°) | 0.02 | 0.02 | 0.02 |
| counting time (s) | 40 | 40 | 40 |
| step intensities | 4501 | 4501 | 4501 |
| independent reflections | 134 | 134 | 134 |
| R exp (%) | 9.2 | 9.6 | 9.6 |
| R p (%) | 6.7 | 6.9 | 6.9 |
| χ² | 1.4 | 1.4 | 1.4 |
| R p (%) | 8.2 | 8.9 | 8.9 |
| R exp (%) | 9.5 | 9.6 | 9.6 |

R exp = 100 Σ|yobs - ycalc| / Σ|yobs| R p = 100 [Σ|yobs - ycalc| / Σ|yobs|]¹/² χ² = [R exp / R p]² R p = 100 Σ|l_k - I_k| / Σ|I_k| R exp = 100 [(N-P+C) / Σ(|yobs|²)]¹/² N-P+C = degrees of freedom
Synthesis and Crystal Structure of Three New Quaternary Compounds in the system Cu-Mn-III-Se (III = Al, Ga, In)

**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 (°) for CuMnAlSe$_3$, derived from the Rietveld refinement.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Ox.</th>
<th>Site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>foc</th>
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<td>2e</td>
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<td>½</td>
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<tr>
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<td>Mn-Se</td>
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<td>Al-Se</td>
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<td>Mn-Se</td>
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<tr>
<td>Al-Se</td>
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<tr>
<td>Se</td>
<td>109.5(2)</td>
<td></td>
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<td>Cu-Se</td>
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<td>Cu-Se</td>
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<tr>
<td>Mn-Se</td>
<td>107.2(2)</td>
<td></td>
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**Table 3.** Atomic coordinates, isotropic temperature factors, bond distances (Å) and angles (°) for CuMnGaSe$_3$, derived from the Rietveld refinement.

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<th>Ox.</th>
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<th>$y$</th>
<th>$z$</th>
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<td>0</td>
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<td>1</td>
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<td>0</td>
<td>¼</td>
<td>1</td>
<td>0.6(4)</td>
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<tr>
<td>Cu1</td>
<td>+1</td>
<td>2f</td>
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<td>½</td>
<td>½</td>
<td>½</td>
<td>0.6(4)</td>
</tr>
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<td>Mn1</td>
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<td>½</td>
<td>½</td>
<td>½</td>
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<td>½</td>
<td>½</td>
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<td>0.6(4)</td>
</tr>
<tr>
<td>Se</td>
<td>-2</td>
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<td>0.255(1)</td>
<td>0.257(1)</td>
<td>0.124(1)</td>
<td>1</td>
<td>0.6(4)</td>
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<table>
<thead>
<tr>
<th>Bond Distance</th>
<th>Angle</th>
<th>Symmetry Codes</th>
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<tr>
<td>Cu-Se</td>
<td>2.419(8)</td>
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<td>Mn-Se</td>
<td>2.452(8)</td>
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<tr>
<td>Ga-Se</td>
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<td>Mn-Se</td>
<td>2.452(8)</td>
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<tr>
<td>Ga-Se</td>
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<tr>
<td>Se</td>
<td>109.5(2)</td>
<td></td>
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<td>Cu-Se</td>
<td>110.0(2)</td>
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**Table 5.** Comparison of the unit cell parameters and bond distances for Cu-Mn-III-Se$_3$ and Cu-Mn-Se$_2$. 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.

**Table 6.** Comparison of the unit cell parameters and bond distances for Cu-Mn-III-Se$_3$ and Cu-Mn-Se$_2$. 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. The comparison between the unit cell parameters and bond distances for the three phases of both families of compounds.
Table 4. Atomic coordinates, isotropic temperature factors, bond distances (Å) and angles (°) for CuMnInS$_3$, derived from the Rietveld refinement.

<table>
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<th>Atom</th>
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<th>y</th>
<th>z</th>
<th>foc</th>
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<td>¼</td>
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<tr>
<td>Mn</td>
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<td>2e</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.6(4)</td>
</tr>
<tr>
<td>In</td>
<td>+3</td>
<td>2b</td>
<td>½</td>
<td>0</td>
<td>¼</td>
<td>1</td>
<td>0.6(4)</td>
</tr>
<tr>
<td>Cu1</td>
<td>+1</td>
<td>2f</td>
<td>½</td>
<td>½</td>
<td>½</td>
<td>½</td>
<td>0.6(4)</td>
</tr>
<tr>
<td>Mn1</td>
<td>+2</td>
<td>2f</td>
<td>½</td>
<td>½</td>
<td>½</td>
<td>½</td>
<td>0.6(4)</td>
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<tr>
<td>In1</td>
<td>+3</td>
<td>2f</td>
<td>½</td>
<td>½</td>
<td>½</td>
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<td>0.6(4)</td>
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<tr>
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<td>0.255(1)</td>
<td>0.124(1)</td>
<td>1</td>
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Cu-Se: 2.428(8)  Mn-Se: 2.448(8)  In-Se: 2.569(8)

Se$^{iii}$-Cu-Se$^{ii}$: 114.5(2)  (x2)
Se$^{iii}$-Mn-Se$^{ii}$: 108.6(2)  (x2)
Se$^{iii}$-In-Se$^{ii}$: 110.4(2)  (x2)
Se$^{ii}$-M-Se$^{ii}$: 108.5(2)  (x4)

Table 5. Comparative table of unit cell parameters and bond distances for the Cu-III-Se$_2$ chalcopyrite compounds and the related Cu-Mn-III-Se$_3$ alloys (III= Al, Ga, In). ([*] = this work).

<table>
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<tr>
<th>Compound</th>
<th>SG</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>η</th>
<th>V (Å$^3$)</th>
<th>Cu-Se (Å)</th>
<th>Mn-Se (Å)</th>
<th>III-Se (Å)</th>
<th>Ref.</th>
</tr>
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<td>CuAlSe$_2$</td>
<td>$Iar{4}2d$</td>
<td>5.606(5)</td>
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<td>2.438(1)</td>
<td>-</td>
<td>2.373(1)</td>
<td>[18]</td>
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<tr>
<td>CuGaSe$_2$</td>
<td>$Iar{4}2d$</td>
<td>5.614(1)</td>
<td>11.022(1)</td>
<td>0.98</td>
<td>347.4(1)</td>
<td>2.446(9)</td>
<td>-</td>
<td>2.387(9)</td>
<td>[19]</td>
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<tr>
<td>CuInSe$_2$</td>
<td>$Iar{4}2d$</td>
<td>5.781(1)</td>
<td>11.642(3)</td>
<td>1.01</td>
<td>389.1(2)</td>
<td>2.432(1)</td>
<td>-</td>
<td>2.591(1)</td>
<td>[20]</td>
</tr>
<tr>
<td>CuMnAlSe$_3$</td>
<td>P4$_2$1c</td>
<td>5.6034(6)</td>
<td>10.977(1)</td>
<td>0.98</td>
<td>344.66(6)</td>
<td>2.423(8)</td>
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<td>CuMnGaSe$_3$</td>
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<td>348.68(4)</td>
<td>2.419(8)</td>
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<tr>
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<td>390.58(8)</td>
<td>2.428(8)</td>
<td>2.448(8)</td>
<td>2.614(8)</td>
<td>[*]</td>
</tr>
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</table>

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. 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$_4$, III$_4$, 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. The Table 5 contains the $a$, $c$, and $\eta$ values for the Cu-Mn-III-Se$_3$ compounds. One can see that $\eta$ is close to unity for all compositions, which is indicative of small lattice distortions in the samples synthesized.
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\(_4\), CuNi(Al,Ga)In Se\(_3\), CuFe(Al,Ga,In)Se\(_2\), CuFeSnSe\(_4\), CuZnGeSe\(_4\), CuZnSnSe\(_4\), Cu(Cd,Mn)GeSe\(_4\) and CuGaMnSe\(_3\).

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\(\overline{4}\)2c, with a sphalerite derivative structure, and are isomorphous with CuFeInSe\(_3\).

5. Acknowledgements

This work was supported by CDCHT-ULA (Grant C-1740-11-05-AA and C-1885-14-05-B) and FONACIT (Grants LAB-97000821, PEII-1697 and project Nº 2011001341).

6. References

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(III = Al, Ga, In)


