Structural Characterization of Two New Quaternary Chalcogenides: CuCo$_2$InTe$_4$ and CuNi$_2$InTe$_4$

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The crystal structure of the chalcogenide compounds CuCo$_2$InTe$_4$ and CuNi$_2$InTe$_4$, two new members of the I-II, III-IV-VI$_4$ family, were characterized by Rietveld refinement using X-ray powder diffraction data. Both materials crystallize in the tetragonal space group $I-2m$ (No. 121), $Z=2$, with a stannite-type structure, with the binaries CoTe and NiTe as secondary phases.

Keywords: alloys, semiconductors, chemical synthesis, structural characterization, X-ray powder diffraction

1. Introduction

Diluted magnetic semiconductors (DMS) are of great interest because of their peculiar magnetic and magnetooptical properties arising from the presence of magnetic ions in the lattice1. The DMS materials more frequently studied are alloys obtained from the tetrahedrally coordinated derivatives of the II-VI semiconductor family2. One of these derivative families are the quaternary semiconductors with formula I-II$_2$-III-VI$_4$ and I$_2$-II-IV-VI$_4$, which belong to the normal compound of fourth derivatives of the II-VI binary semiconductors with three types of cations3, and fulfill the rules of adamantane compound formation2,3. According to these rules, the cation substitution is performed in such a way that an average number of four valence electrons per atomic site and a value eight for the ratio valence electrons to anions is maintained4.

Due to the great variety of possible compositions (I= Cu, Ag, II= Zn, Cd, Mn, Fe, III= Al, Ga, In, IV= Si, Ge, Sn, VI= S, Se, Te), these quaternary diamond-like materials can be useful for applications such as tunable semiconductors5, photovoltaics6, spintronics5, non-linear optics2 and thermoelectrics8. In general, the quaternary compounds I-II$_2$-III-VI$_4$ can be formed by the addition of a II-VI binary compound to ternary chalcopyrite structures I-III-VI$_4$.9,10. Structural studies carried out on some members of this family indicate that they crystallize in a sphalerite derivative structure (stannite) with tetragonal space group $I-2m$ (No. 121)9,11, or in a wurtzite derivative structure (wurtzite-stannite) with orthorhombic space group $Pmn2_1$ (No. 31)2,12. This last structure can be considered as a superstructure to wurtzite, where $a=2a_w$, $b=\sqrt{3}b_w$, and $c=c_w$.12

The quaternaries CuFe$_x$(Al,Ga,In)Se$_4$, CuCo$_2$InTe$_4$, AgFe$_x$Ga$_{1-x}$Te$_4$, and the stable forms at higher temperatures of CuZn$_x$(Al,Ga,In)S$_4$,17, crystallizes in stannite-type structure while AgCd$_x$Ga$_{1-x}$S$_4$, AgCd$_x$Ga$_{1-x}$Se$_4$, Ag$_{1-x}$Cu$_x$Cd$_4$Ga$_{16}$S$_{21}$, AgCd$_x$Ga$_{1-x}$S$_4$,20 and AgCd$_x$In$_x$S$_4$,21 and AgCd$_x$Mn$_{1-x}$Ga$_2$S$_4$,22 have been reported with a wurzt-stannite structure.

In recent years, it has been of interest to carry out a systematic study of the crystal structure of quaternary diamond-like families13-16,23-26. Hence, in this work we report the X-ray powder diffraction analysis and crystal structure of the quaternary compounds CuCo$_2$InTe$_4$ and CuNi$_2$InTe$_4$, two new members of the I-II$_2$-III-VI$_4$ family, which crystallize with a stannite structure.

2. Experimental procedures

2.1. Synthesis

Nominally CuCo$_2$InTe$_4$ and CuNi$_2$InTe$_4$ samples were synthesized using the melt-anneal method. Stoichiometric quantities of Cu, Co, Ni, In, Te elements with purity of at least 99.99% (GoodFellow) were charged in an evacuated synthetic silica glass ampoule, which was previously subjected to pyrolysis in order to avoid reaction of the starting materials with silica glass. Then, the ampoule was sealed under vacuum (~10$^{-4}$Torr) and the fusion process was carried out inside a furnace (vertical
position) heated up to 1500 K at a rate of 20 K/h, with a stop of 48 h at 722.5 K (melting temperature of Te) in order to 
maximize the formation of binary species at low temperature 
and minimize the presence of unreacted Te at high temperatures. 
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 (1500 K) 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 873 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. The obtained 
ingots were bright gray in color and homogeneous to the eye.

2.2. X-ray powder diffraction

X-ray powder diffraction patterns were recorded using a PANalytical X’Pert Pro MPD powder X-ray diffractometer 
operating in Bragg-Brentano geometry using CuKα radiation with 
an average wavelength of 1.5418 Å. A tube power of 45 kV and 
40 mA was employed. A nickel filter was used in the diffracted 
beam optics and the data were collected with the X’Celerator 
one-dimensional silicon strip detector. A ½° antiscatter slit, and a 0.02 rad soller slit were set at both the 
incident and diffracted beams. The scan range was from 5 to 
145° 2θ with a step size of 0.008° and a scan speed of 0.0106°/s.

3. Results and Discussion

Figure 1 and 2 shows the resulting X-ray powder 
diffractogram for the quaternary compounds CuCo₄InTe₄ and 
CuNi₄InTe₄. An automatic search in the PDF-ICDD database²⁷, 
using the software available with the diffractometer, indicated 
that the powder patterns contained important amounts of 
the binaries CoTe (PDF N° 70-2887) and NiTe (PDF N° 
89-2019), respectively.

Bragg positions of the diffraction lines from these 
binaries are also indicated in Figure 1 and 2. The 20 
first peak positions of the main phase, en each case, 
was indexed using the program Dicvol04²⁸, which gave 
a unique solution in tetragonal cells with a = 6.195(2) Å, 
c = 12.400(4) Å for CuCo₄InTe₄, and a = 6.160(2) Å, c = 
12.365(4) Å for CuCo₄InTe₄.

The systematic absences study (hkl: h + k + l = 2n) indicated 
an I-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 body center cell suggested that this 
material is isostructural with CuFe₂InSe₄ and AgFe₂GaTe₄; 
the firsts of the I-II,-III-VI₁ family with a stannite structure¹¹, 
which crystallize in the tetragonal space group I₄₁2m (No. 
121). It should be mentioned that Rietveld refinement 
were performed in the I₂ (No. 82) space group but did not produce 
a chemically sound structure, ruled out a kesterite structure.

Figure 1: Final Rietveld plot showing the observed, calculated 
and difference pattern for the CuCo₄InTe₄ compound. The Bragg 
reflections for both phases are indicated by vertical bars.

Figure 2: Final Rietveld plot showing the observed, calculated 
and difference pattern for the CuNi₄InTe₄ compound. The Bragg 
reflections for both phases are indicated by vertical bars.

The Rietveld refinement²⁹ of the whole diffraction patterns 
was carried out using the Fullprof program³⁰, with the unit cell 
parameters mentioned above. The atomic coordinates of the 
compound CuFe₂InSe₄ were used as initial model. Atomic 
positions of the CuFe₂ and NiTe²⁵ binaries were included 
as secondary phases in the refinements of CuCo₄InTe₄ and 
CuNi₄InTe₄, respectively.

The angular dependence of the peak full width at 
half maximum (FWHM) was described by the Caglioti’s 
formula³¹. Peak shapes were described by the parameterized 
Thompson-Cox-Hastings pseudo-Voigt profile function³². 
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 summarized in Tables 
1 and 2. Figures 1 and 2 shows the observed calculated and 
difference profile for the final cycle of Rietveld refinement 
in both materials. Atomic coordinates, isotropic temperature 
factor, bond distances and angles are shown in Tables 3 
and 4. The final Rietveld refinement converged to the 
weight fraction percentages³³ shows in Tables 1 and 2. 
Figure 3 shows the unit cell diagram for the CuCo₄InTe₄ 
and CuNi₄InTe₄ phases.
Structural Characterization of Two New Quaternary Chalcogenides: CuCo$_2$InTe$_4$ and CuNi$_2$InTe$_4$

Table 1: Rietveld refinement results for CuCo$_2$InTe$_4$ and CoTe.

<table>
<thead>
<tr>
<th>Molecular formula</th>
<th>CuCo$_2$InTe$_4$</th>
<th>CoTe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight (g/mol)</td>
<td>806.63</td>
<td>186.53</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>6.1997(1)</td>
<td>3.8939(1)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>12.380(1)</td>
<td>5.3728(2)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>475.84(4)</td>
<td>70.55(1)</td>
</tr>
<tr>
<td>System</td>
<td>tetragonal</td>
<td>hexagonal</td>
</tr>
<tr>
<td>Space group</td>
<td>$I-4/m$ (No. 121)</td>
<td>$P6_3/mmm$ (No. 194)</td>
</tr>
<tr>
<td>$Z$</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$\Delta$ calc (g/cm$^3$)</td>
<td>5.63</td>
<td>7.9</td>
</tr>
<tr>
<td>Weight fraction (%)</td>
<td>65.2</td>
<td>34.6</td>
</tr>
<tr>
<td>$R_{wp}$ (%)</td>
<td>9.5</td>
<td>9.5</td>
</tr>
<tr>
<td>$R_B$ (%)</td>
<td>8.5</td>
<td>7.9</td>
</tr>
<tr>
<td>$S$ = $[R_{wp}/R_{exp}]$</td>
<td>1.4</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table 2: Rietveld refinement results for CuNi$_2$InTe$_4$ and NiTe.

<table>
<thead>
<tr>
<th>Molecular formula</th>
<th>CuNi$_2$InTe$_4$</th>
<th>NiTe</th>
</tr>
</thead>
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<tr>
<td>Molecular weight (g/mol)</td>
<td>806.15</td>
<td>186.29</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>6.1669(1)</td>
<td>3.9411(2)</td>
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<tr>
<td>$c$ (Å)</td>
<td>12.370(1)</td>
<td>5.3177(3)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>470.44(4)</td>
<td>71.53(1)</td>
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<tr>
<td>System</td>
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<td>hexagonal</td>
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<tr>
<td>Space group</td>
<td>$I-42m$ (No. 121)</td>
<td>$P6_3/mmm$ (No. 194)</td>
</tr>
<tr>
<td>$Z$</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$\Delta$ calc (g/cm$^3$)</td>
<td>5.69</td>
<td>7.9</td>
</tr>
<tr>
<td>Weight fraction (%)</td>
<td>58.3</td>
<td>41.7</td>
</tr>
<tr>
<td>$R_{wp}$ (%)</td>
<td>9.6</td>
<td>9.6</td>
</tr>
<tr>
<td>$R_B$ (%)</td>
<td>8.7</td>
<td>8.0</td>
</tr>
<tr>
<td>$S$ = $[R_{wp}/R_{exp}]$</td>
<td>1.5</td>
<td>1.4</td>
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Table 3: Atomic coordinates, isotropic temperature factor, bond distances (Å) and angles (°) for CuCo$_2$InTe$_4$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Ox.</th>
<th>Wyck.</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>Foc</th>
<th>B (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>+1</td>
<td>2$a$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.31(5)</td>
</tr>
<tr>
<td>Co</td>
<td>+2</td>
<td>4$d$</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>1</td>
<td>0.31(5)</td>
</tr>
<tr>
<td>In</td>
<td>+3</td>
<td>2$b$</td>
<td>0</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>1</td>
<td>0.31(5)</td>
</tr>
<tr>
<td>Te</td>
<td>-2</td>
<td>8$i$</td>
<td>0.264(1)</td>
<td>0.264(1)</td>
<td>0.124(1)</td>
<td>1</td>
<td>0.31(5)</td>
</tr>
<tr>
<td>Cu - Te</td>
<td>Co - Te</td>
<td>2.576(9)</td>
<td>2.693(9)</td>
<td>In - Te</td>
<td>2.777(9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Te - Cu - Te$^{ii}$</td>
<td>x4</td>
<td>Te - Co - Te$^{iv}$</td>
<td>109.6(2)</td>
<td>x4</td>
<td>Te$^{e}$ - In - Te$^{iv}$</td>
<td>107.8(2) x4</td>
<td></td>
</tr>
<tr>
<td>Te - Cu - Te$^{ii}$</td>
<td>x2</td>
<td>Te - Co - Te$^{iv}$</td>
<td>109.2(2)</td>
<td>x2</td>
<td>Te$^{e}$ - In - Te$^{iv}$</td>
<td>112.7(2) x2</td>
<td></td>
</tr>
</tbody>
</table>

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.

Quaternary CuCo$_2$InTe$_4$ and CuNi$_2$InTe$_4$ are normal adamantane-structure compound and can be described as derivative of the sphalerite with a stannite-type structure. As expected for adamantane structure compounds, each anion is coordinated by four cations (two Co or Ni, one Cu and one In) located at the corners of a slightly distorted tetrahedron. Cu, Co (Ni) and In cations are similarly coordinated by four anions. The interatomic distances are shorter than the sum of the respective ionic radii for structures tetrahedrally bonded. The Cu-Te, Co-Te, Ni-Te and In–Te bond distances are in good agreement with those observed in other adamantane structure compounds found in the ICSD database; such as CuTa$_2$InTe$_4$, CuInTe$_2$, AgIn$_2$Te$_8$, Cu$_3$NbTe$_4$ and AgInTe$_2$. 
Table 4: Atomic coordinates, isotropic temperature factor, bond distances (Å) and angles (°) for CuNi\textsubscript{2}InTe\textsubscript{4}.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Ox.</th>
<th>Wyck.</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Foc</th>
<th>B (Å\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>+1</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.23(5)</td>
</tr>
<tr>
<td>Ni</td>
<td>+2</td>
<td>4d</td>
<td>0</td>
<td>1/2</td>
<td>1/2</td>
<td>1</td>
<td>0.23(5)</td>
</tr>
<tr>
<td>In</td>
<td>+3</td>
<td>2b</td>
<td>0</td>
<td>0</td>
<td>1/2</td>
<td>1</td>
<td>0.23(5)</td>
</tr>
<tr>
<td>Te</td>
<td>-2</td>
<td>8i</td>
<td>0.264(1)</td>
<td>0.264(1)</td>
<td>0.125(1)</td>
<td>1</td>
<td>0.23(5)</td>
</tr>
</tbody>
</table>

Cu - Te\textsuperscript{i} 2.574(9)
Ni - Te\textsuperscript{i} 2.676(9)
In - Te\textsuperscript{i} 2.773(9)
Te - Cu - Te\textsuperscript{ii} 106.2(2) x4
Te - Ni - Te\textsuperscript{iv} 109.5(2) x4
Te - In - Te\textsuperscript{iv} 108.1(2) x4
Te - Cu - Te\textsuperscript{iii} 111.2(2) x2
Te - Ni - Te\textsuperscript{v} 109.4(2) x2
Te - In - Te\textsuperscript{vi} 112.2(2) x2

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.

4. Conclusions

The crystal structure of the quaternary compounds CuCo\textsubscript{2}InTe\textsubscript{4} and CuNi\textsubscript{2}InTe\textsubscript{4} was determined using X-ray powder diffraction. CuCo\textsubscript{2}InTe\textsubscript{4} and CuNi\textsubscript{2}InTe\textsubscript{4} crystallize in the tetragonal space group I\textsubscript{4}2\textsubscript{m} with a stannite-type structure.

5. Acknowledgments

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6. References


