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Structural Characterization of Two New Quaternary Chalcogenides: $CuCo_2InTe_4$ and $CuNi_2InTe_4$

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The crystal structure of the chalcogenide compounds $CuCo_2InTe_4$ and $CuNi_2InTe_4$, two new members of the I-II_2-III-VI_4 family, were characterized by Rietveld refinement using X-ray powder diffraction data. Both materials crystallize in the tetragonal space group $I_{\bar{4}}2m$ (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 lattice[1]. The DMS materials more frequently studied are alloys obtained from the tetrahedrally coordinated derivatives of the II-VI semiconductor family[2]. 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 cations[3], and fulfil the rules of adamantane compound formation[2,3]. 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 maintained[2].

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 semiconductors[4], photovoltaics[5], spintronics[6], non-linear optics[7] and thermoelectrics[8]. 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_2[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 $I_{\bar{4}}2m$ (No. 121)[11], or in a wurtzite derivative structure (wurtzite-stannite) with orthorhombic space group $Pmn2_1$ (No. 31)[12]. This last structure can be considered as a superstructure to wurtzite, where $a \sim 2a_w$, $b \sim \sqrt{3}b_w$, and $c \sim c_w$[12].

The quaternaries $CuFe_2(Al,Ga,In)Se_4$[13,14], $CuTa_2InTe_4$[15], $AgFe_2GaTe_4$[16] and the stable forms at higher temperatures of $CuZn_2(Al,Ga,In)S_4$[17], crystalizes in stannite-type structure while $AgCd_2GaS_4$[18], $AgCd_2GaSe_4$[19], $Ag_{1-X}Cu_XCd_2GaS_4$[20], $AgCd_2Ga_{1-X}In_XS_4$[21] and $AgCd_{2-X}Mn_XGaS_4$[22] have been reported with a wurtz-stannite structure.

In recent years, it has been of interest to carry out a systematic study of the crystal structure of quaternary diamond-like families[13-16, 23-26]. Hence, in this work we report the X-ray powder diffraction analysis and crystal structure of the quaternary compounds $CuCo_2InTe_4$ and $CuNi_2InTe_4$, 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 $CuCo_2InTe_4$ and $CuNi_2InTe_4$ 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

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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 CuK_{α} 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 ¼° divergent slit, 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 $CuCo_2InTe_4$ and $CuNi_2InTe_4$. An automatic search in the PDF-ICDD database[27], 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 Figure 2. The 20 first peak positions of the main phase, en each case, was indexed using the program Dicvol04[28], which gave a unique solution in tetragonal cells with a = 6.195(2) Å, c = 12.400(4) Å for $CuCo_2InTe_4$, and a = 6.160(2) Å, c = 12.365(4) Å for $CuCo_2InTe_4$.

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 $CuFe_2InSe_4$[13] and $AgFe_2GaTe_4$[16]; the firsts of the I-II_2-III-VI_4 family with a stannite structure[11], which crystallize in the tetragonal space group $I\bar{4}2m$ (No. 121). It should be mentioned that Rietveld refinement were performed in the $I\bar{4}$ (No. 82) space group but did not produce a chemically sound structure, ruled out a kesterite structure.

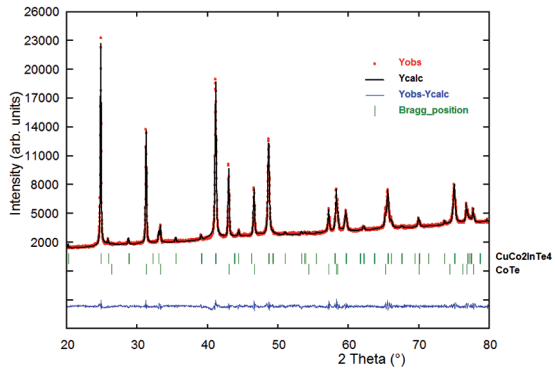

Figure 1: Final Rietveld plot showing the observed, calculated and difference pattern for the $CuCo_2InTe_4$ compound. The Bragg reflections for both phases are indicated by vertical bars.

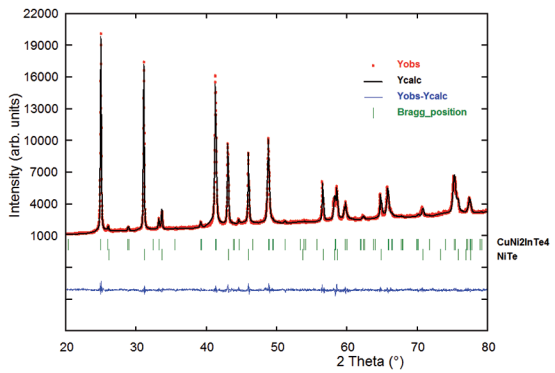

Figure 2: Final Rietveld plot showing the observed, calculated and difference pattern for the $CuNi_2InTe_4$ compound. The Bragg reflections for both phases are indicated by vertical bars.

The Rietveld refinement[29] of the whole diffraction patterns was carried out using the Fullprof program[30], with the unit cell parameters mentioned above. The atomic coordinates of the compound $CuFe_2InSe_4$[13] were used as initial model. Atomic positions of the CoTe[31] and NiTe[32] binaries were included as secondary phases in the refinements of $CuCo_2InTe_4$ and $CuNi_2InTe_4$, respectively.

The angular dependence of the peak full width at half maximum (FWHM) was described by the Caglioti's formula[33]. Peak shapes were described by the parameterized Thompson-Cox-Hastings pseudo-Voigt profile function[34]. 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 percentages[35] shows in Tables 1 and 2. Figure 3 shows the unit cell diagram for the $CuCo_2InTe_4$ and $CuNi_2InTe_4$ phases.

Table 1: Rietveld refinement results for $CuCo_2InTe_4$ and CoTe.

Molecular formula	$CuCo_2InTe_4$	CoTe	
Molecular weight (g/mol)	806.63	186.53	
a (Å)	6.1997(1)	3.8939(1)	
c (Å)	12.380(1)	5.3728(2)	
V (Å^3)	475.84(4)	70.55(1)	
System	tetragonal	hexagonal	
Space group	*I-42m* (No. 121)	*P6$_3$/mmm* (No. 194)	
Z	2	2	R_{exp} (%) = 6.7
D_{calc} (g/cm^{-3})	5.63		R_p (%) = 7.2
Weight fraction (%)	65.2	34.6	R_{wp} (%) = 9.5
R_B (%)	8.5	7.9	S = 1.4

$R_{exp} = 100\ [(N-P+C) / \Sigma_w(y_{obs}^2)]^{1/2}$ N-P+C is the number of degrees of freedom

$R_{wp} = 100\ [\Sigma_w|y_{obs} - y_{calc}|^2 / \Sigma_w|y_{obs}|^2]^{1/2}$ $R_p = 100\ \Sigma|y_{obs} - y_{calc}| / \Sigma|y_{obs}|$

$R_B = 100\ \Sigma_k|I_k - Ic_k| / \Sigma_k |I_k|$ $S = [R_{wp} / R_{exp}]$

Table 2: Rietveld refinement results for $CuNi_2InTe_4$ and NiTe.

Molecular formula	$CuNi_2InTe_4$	NiTe	
Molecular weight (g/mol)	806.15	186.29	
a (Å)	6.1669(1)	3.9411(2)	
c (Å)	12.370(1)	5.3177(3)	
V (Å^3)	470.44(4)	71.53(1)	
System	tetragonal	hexagonal	
Space group	*I-42m* (No. 121)	*P6$_3$/mmm* (No. 194)	
Z	2	2	R_{exp} (%) = 6.5
D_{calc} (g/cm^{-3})	5.69		R_p (%) = 7.2
Weight fraction (%)	58.3	41.7	R_{wp} (%) = 9.6
R_B (%)	8.7	8.0	S = 1.5

$R_{exp} = 100\ [(N-P+C) / \Sigma_w(y_{obs}^2)]^{1/2}$ N-P+C is the number of degrees of freedom

$R_{wp} = 100\ [\Sigma_w|y_{obs} - y_{calc}|^2 / \Sigma_w|y_{obs}|^2]^{1/2}$ $R_p = 100\ \Sigma|y_{obs} - y_{calc}| / \Sigma|y_{obs}|$

$R_B = 100\ \Sigma_k|I_k - Ic_k| / \Sigma_k |I_k|$ $S = [R_{wp} / R_{exp}]$

Table 3: Atomic coordinates, isotropic temperature factor, bond distances (Å) and angles (°) for $CuCo_2InTe_4$.

Atom	Ox.	Wyck.	*x*	*y*	*z*	Foc	B (Å^2)
Cu	+1	2*a*	0	0	0	1	0.31(5)
Co	+2	4*d*	0	½	¼	1	0.31(5)
In	+3	2*b*	0	0	½	1	0.31(5)
Te	-2	8*i*	0.264(1)	0.264(1)	0.124(1)	1	0.31(5)
Cu - Te^{i}	2.576(9)		Co - Te	2.693(9)		In - Te	2.777(9)
Te - Cu - Te^{ii}	106.9(2)	x4	Te - Co - Te^{iv}	109.6(2)	x4	Te^{i} - In - Te^{iv}	107.8(2) x4
Te - Cu - Te^{iii}	110.6(2)	x2	Te - Co - Te^{v}	109.2(2)	x2	Te^{iv} - In - Te^{vi}	112.7(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.

Quaternary $CuCo_2InTe_4$ and $CuNi_2InTe_4$ are normal adamantane-structure compound and can be described as derivative of the sphalerite with a stannite-type structure[2]. 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[36]. 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[37]; such as $CuTa_2InTe_4$[15], $CuInTe_2$[38], $AgIn_5Te_8$[39], Cu_3NbTe_4[40] and $AgInTe_2$[41].

Table 4: Atomic coordinates, isotropic temperature factor, bond distances (Å) and angles (°) for $CuNi_2InTe_4$.

Atom	Ox.	Wyck.	*x*	*Y*	*z*	Foc	B (Å^2)
Cu	+1	2*a*	0	0	0	1	0.23(5)
Ni	+2	4*d*	0	½	¼	1	0.23(5)
In	+3	2*b*	0	0	½	1	0.23(5)
Te	-2	8*i*	0.264(1)	0.264(1)	0.125(1)	1	0.23(5)
Cu - Te^{i}	2.574(9)		Ni - Te	2.676(9)		In - Te	2.773(9)
Te - Cu - Te^{ii}	106.2(2) x4		Te - Ni - Te^{iv}	109.5(2) x4		Te^{i} - In - Te^{iv}	108.1(2) x4
Te - Cu - Te^{iii}	111.2(2) x2		Te - Ni - Te^{v}	109.4(2) x2		Te^{iv} - In - Te^{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.

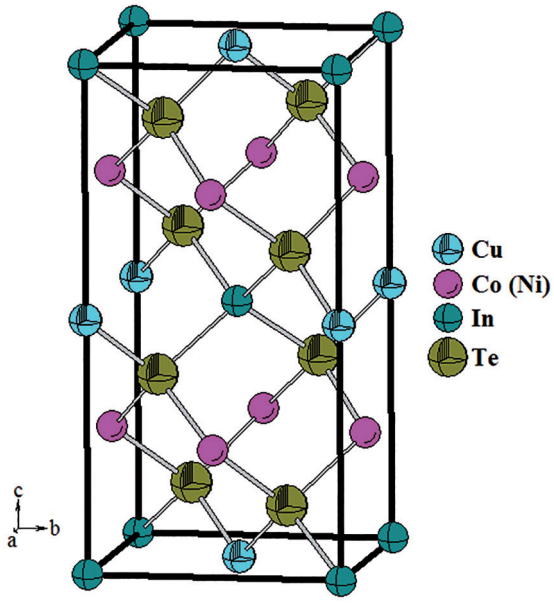

Figure 3: Unit cell diagram for the $CuCo_2InTe_4$ and $CuNi_2InTe_4$ phases.

4. Conclusions

The crystal structure of the quaternary compounds $CuCo_2InTe_4$ and $CuNi_2InTe_4$ was determined using X-ray powder diffraction. $CuCo_2InTe_4$ and $CuNi_2InTe_4$ crystallize in the tetragonal space group $I\bar{4}2m$ with a stannite-type structure.

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