Preparation and crystal structure characterization of CuNiGaSe_3 and CuNiInSe_3 quaternary compounds

G E DELGADO*, A J MORA, P GRIMA-GALLARDO†, S DURÁN†, M MUÑOZ† and M QUINTERO†

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

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

MS received 15 May 2009; revised 18 September 2009

Abstract. Samples of the quaternary chalcogenide compounds, CuNiGaSe_3 and CuNiInSe_3 , prepared by direct fusion and annealing method, were characterized by X-ray powder diffraction. In each case, the crystal structure was refined using the Rietveld method. Both compounds were found to crystallize in the tetragonal system, space group $P4_2c$ ($N^\circ 112$), with unit cell parameter values $a = 5.6213(1) \text{ \AA}$, $c = 11.0282(3) \text{ \AA}$, $V = 348.48(1) \text{ \AA}^3$ and $a = 5.7857(2) \text{ \AA}$, $c = 11.6287(5) \text{ \AA}$, $V = 389.26(3) \text{ \AA}^3$ for CuNiGaSe_3 and CuNiInSe_3 , respectively. These compounds have a normal adamantane structures and are isostructural with CuFeInSe_3 .

Keywords. Chalcogenides; synthesis; X-ray powder diffraction; crystal structure.

1. Introduction

The addition of a II–VI binary to chalcopyrite I–III–VI₂ structures, produces alloys with composition $(\text{I–III–VI}_2)_{1-x}(\text{II–VI})_x$. All the possible phases fulfill the rules for the formation of adamantane compounds (Parthé 1995) giving materials with semiconductor behaviour, which belong to the compound families derivatives of the II–VI binary (Delgado 1998). Recently, it has been shown that when $x = 1/2$, the formation of alloys with composition I–II–III–VI₃ are obtained (Grima-Gallardo and Ruiz 1999; Grima-Gallardo *et al* 2001a, b; Mora *et al* 2007). In a recent work carried out on the CuFeInSe_3 material (Mora *et al* 2007), it was found that this compound crystallizes in a primitive tetragonal structure with space group $P4_2c$. This result is in contrast with the space group $I4_2d$ of the related I–III–VI₂ chalcopyrite structure, indicating a degradation of symmetry but maintaining the volume almost unchanged.

From the point of view of technological purposes, these compounds could be interesting for magnetic devices and other applications in spintronics. Transition–Metal (TM) doping of semiconductors has attracted increasing interest since the discovery of ferromagnetism persisting up to relative high temperatures in the prototype Mn-doped GaAs (Dietl *et al* 2000, 2001). Recently, attention has been focused on chalcopyrite alloys (Medvedkin *et al* 2000; Cho *et al* 2002; Freeman and Zhao

2003; Demin *et al* 2004, 2005; Sarkisov and Picozzi 2007) due to their presumed ferromagnetism persisting up to room temperature. Although precise calculations demonstrate that: (a) the magnetic moments may be tuned with impurities and (b) the Curie temperature is proportional to hole concentration, the origin of the ferromagnetism in these magnetic semiconductors is still under intense discussion.

In the present work, we report a detailed crystallographic characterization of the two new chalcogenide quaternary compounds, CuNiGaSe_3 and CuNiInSe_3 , which belong to the system $(\text{Cu–III–Se}_2)_{1-x}(\text{NiSe})_x$, where III = Al, Ga and $x = 1/2$. The structural study was carried out by Rietveld refinement using X-ray powder diffraction data.

2. Experimental

2.1 Synthesis

Polycrystalline ingots of CuNiGaSe_3 and CuNiInSe_3 were prepared by the melt and annealing technique. Starting materials (Cu, Ni, Ga or In, and Se) with a nominal purity of $< 99.99 \text{ wt\%}$ in the stoichiometric ratio were mixed together in an evacuated and sealed quartz tube with the inner walls having been carbonized. Each sample, about 1 g, was prepared, lowering the temperature from 1500 K 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.

*Author for correspondence (gerzon@ula.ve)

2.2 Chemical analysis

The stoichiometric relation of the samples was investigated by SEM technique, using a Hitachi S2500 microscope equipped with a Kedex EDS accessory. The average chemical composition of three different regions of each ingot gave the atomic percentages: Cu (15.5%), Ni (16.7%), Ga (16.3%), Se (51.5%) for CuNiGaSe₃, and Cu (17.8%), Ni (15.0%), In (17.7%), Se (49.5%) for CuNiInSe₃. These values are 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 and mounted on a flat zero-background holder covered with a thin layer of grease. The X-ray powder diffraction data were collected, at room temperature, in θ/θ reflection mode using a Siemens D5005 diffractometer equipped with an X-ray tube (CuK α radiation: $\lambda = 1.5418$ Å; 40 kV, 30 mA). 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° 2 θ , 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 powder X-ray diffractograms of CuNiGaSe₃ and CuNiInSe₃ were found, in each case, to be typical of a

tetragonal structure, and no extra diffraction lines, due to the presence of secondary phases, were observed in these diffraction patterns indicating that the investigated samples were single phases. The diffraction peaks in the XRD patterns for both compounds were indexed using the program Dicvol04 (Boultif and Ler 2004), and, as was indicated above, tetragonal cells with similar magnitudes to the parent chalcopyrite structures, CuGaSe₂ (Mandel *et al* 1977) and CuInSe₂ (Knight 1992), were found. Systematic absence indicates *P*-type lattices, suggesting that both compounds are isostructural with the recently reported CuFeInSe₃ (Mora *et al* 2007), which crystallizes in the space group *P*42*c* with unit cell parameters similar to the parent CuInSe₂ (Knight 1992).

The Rietveld refinements (Rietveld 1969) of the whole diffraction patterns were carried out using the FullProf program (Roisnel and Rodriguez-Carvajal 2001; Rodriguez-Carvajal 2008). The atomic coordinates of CuFeInSe₃ (Mora *et al* 2007) were used as starting model for the refinements. The angular dependence of the peak full

Figure 1. Rietveld final plots of CuNiGaSe₃ and CuNiInSe₃. The lower trace is the difference curve between observed and calculated patterns. The Bragg reflections are indicated by vertical bars.

Table 1. Rietveld refinement results for CuNiGaSe₃ and CuNiInSe₃.

Molecular formula	CuNiGaSe ₃	CuNiInSe ₃
Molecular weight (g/mol)	1143.43	1263.67
<i>a</i> (Å)	5.6213(1)	5.7857(2)
<i>c</i> (Å)	11.0282(3)	11.6287(5)
<i>c/a</i>	1.6	2.0
<i>V</i> (Å ³)	348.48(1)	389.26(3)
<i>Z</i>	8/3	8/3
Crystal system	Tetragonal	Tetragonal
Space group	<i>P</i> 42 <i>c</i> (N°112)	<i>P</i> 42 <i>c</i> (N° 112)
<i>d</i> _{calc} (g/cm ^{−3})	5.45	5.39
Temperature (K)	298(1)	298(1)
Step intensities	4501	4501
Independent reflections	134	134
<i>R</i> _p (%)	8.5	8.7
<i>R</i> _{wp} (%)	8.9	9.1
<i>R</i> _{exp} (%)	6.5	6.6
<i>S</i>	1.4	1.4
χ^2	1.9	1.9

$R_p = 100 \sum |y_{obs} - y_{calc}| / \sum y_{obs}$, $R_{wp} = 100 [\sum w(y_{obs} - y_{calc})^2 / \sum w y_{obs}^2]^{1/2}$, $S = R_{wp} / R_{exp}$ (goodness of fit), $\chi^2 = [R_{wp} / R_{exp}]$, $R_{exp} = 100 [(N - P + C) / \sum w(y_{obs}^2)]^{1/2}$, $N - P + C = \text{degrees of freedom}$

Table 2. Atomic coordinates and isotropic temperature factors for CuNiGaSe_3 and CuNiInSe_3 .

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>f</i> _{oc}	<i>B</i> (Å ²)
CuNiGaSe_3						
Cu	2 <i>c</i>	0	1/2	1/4	1	0.5(4)
Ni	2 <i>e</i>	0	0	0	1	0.5(4)
Ga	2 <i>b</i>	1/2	0	1/4	1	0.5(4)
M*	2 <i>f</i>	1/2	1/2	1/4	1	0.5(4)
Se	8 <i>n</i>	0.257(1)	0.259(1)	0.124(1)	1	0.5(4)
CuNiInSe_3						
Cu	2 <i>c</i>	0	1/2	1/4	1	0.6(3)
Ni	2 <i>e</i>	0	0	0	1	0.6(3)
In	2 <i>b</i>	1/2	0	1/4	1	0.6(3)
M [#]	2 <i>f</i>	1/2	1/2	1/2	1	0.6(3)
Se	8 <i>n</i>	0.229(1)	0.258(1)	0.124(1)	1	0.6(3)

$$M^* = 1/3\text{Cu} + 1/3\text{Ni} + 1/3\text{Ga}; M^\# = 1/3\text{Cu} + 1/3\text{Ni} + 1/3\text{In}$$

Table 3. Bond distances (Å) for CuNiGaSe_3 and CuNiInSe_3 , derived from the Rietveld refinements.

	Cu–Se	Ni–Se	Ga–Se ⁽ⁱ⁾	In–Se ⁽ⁱ⁾	2f–Se ⁽ⁱⁱ⁾
CuNiGaSe_3	2.419(8)	2.465(8)	2.432(8)		2.360(8)
CuNiInSe_3	2.421(8)	2.462(8)		2.614(8)	2.549(8)

Symmetry codes: (i) $1 - x, y, 0.5 - z$; (ii) $1 - x, 1 - y, z$

Figure 2. Unit cell diagram for the quaternary compounds, Cu-Ni-III-Se_3 (III = Ga, In).

width at half maximum (FWHM) was described by the Cagliotti's formula (Cagliotti *et al* 1958). Peak shapes were described by the parametrized Thompson–Cox–Hastings pseudo-Voigt profile function (Thompson *et al* 1987). 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, calculated and difference profile for the final cycle of Rietveld refinements for CuNiGaSe_3 and CuNiInSe_3 . Atomic coordinates and isotropic temperature factors are listed in table 2. Bond distances for each compound are given in table 3.

CuNiGaSe_3 and CuNiInSe_3 are normal adamantane-structure compounds (Parthé 1995) related to the CuGaSe_2 and CuInSe_2 chalcopyrite parent structures. It is observed that the dilution of the Ni cation in the chalcopyrite I–III–VI₂ leaves the cell volume almost unchanged. Figure 2 shows the unit cell diagram for both Cu-Ni-III-Se_3 compounds.

In CuNiGaSe_3 , the tetrahedra containing M (Cu1 or Ni1 or Ga1) atoms (Se...Se distance, 3.86(1) Å) are slightly smaller than those containing the Cu atoms (Se...Se distance, 3.95(1) Å), Ga atoms (Se...Se distance, 3.97(1) Å), and Ni atoms (Se...Se distance, 4.03(1) Å), respectively. In contrast, for CuNiInSe_3 , the tetrahedra containing the Cu atoms (Se...Se distance, 3.95(1) Å) are slightly smaller than those containing the Ni atoms (Se...Se distance 4.02(1) Å), M (Cu1, Ni1, In1) atoms (Se...Se distance 4.16(1) Å), and In atoms (Se...Se distance 4.27(1) Å), respectively.

The inter-atomic distances in both compounds (table 3) are in good agreement with those observed in other ada-

mantane structure compounds, in particular, with the ternary related compounds I–III–VI₂, CuAlSe₂ (Hahn *et al* 1953), CuGaSe₂ (Mandel *et al* 1977) and CuInSe₂ (Knight 1992), and with the other I–II–III–VI₃ compounds CuFeInSe₃ (Mora *et al* 2007), CuFeAlSe₃ and CuFeGaSe₃ (Delgado *et al* 2009) reported so far.

4. Conclusions

The crystal structure of the new quaternary chalcogenide compounds CuNiGaSe₃ and CuNiInSe₃ were determined using X-ray powder diffraction data. Both compounds are isostructural with CuFeInSe₃ and crystallize in the tetragonal space group *P*4₂*c*.

Acknowledgements

This work was supported by CDCHT-ULA and FONACIT (Grant LAB-97000821).

References

- Boulton A and Löuer D 2004 *J. Appl. Cryst.* **37** 724
 Cagliotti G, Paoletti A and Ricci F P 1958 *Nucl. Instrum.* **3** 223
 Cho S *et al* 2002 *Phys. Rev. Letts* **88** 2572031
 Delgado G E, Mora A J, Contreras J E, Grima-Gallardo P, Durán S, Muñoz M and Quintero M 2009 *Cryst. Res. Technol.* **44** 548
 Delgado J M 1998 *Inst. Phys. Conf. Series* **152** 45
 Demin R, Koroleva L, Marenkin S, Mikhailov S, Szymczak R and Barn M 2004 *Phys. Status Solidi* **C1** 3225
 Demin R, Koroleva L, Marenkin S, Mikhailov S, Aminov T, Szymczak H, Szymczak R and Barn M 2005 *J. Magn. Magn. Mater.* **290** 1379
 Dielt T, Ohno H, Matsukura F, Cibert J and Ferrand D 2000 *Science* **287** 1019
 Dielt T, Ohno H and Matsukura F 2001 *Phys. Rev.* **B63** 19520
 Freeman A J and Zhao Y-J 2003 *J. Phys. Chem. Solids* **64** 1453
 Grima-Gallardo P and Ruiz J 1999 *Phys. Status Solidi (a)* **173** 283
 Grima-Gallardo P, Cárdenas K, Quintero M, Ruiz J and Delgado G E 2001a *Mater. Res. Bull.* **36** 861
 Grima-Gallardo P, Cárdenas K, Molina L, Quintero M, Ruiz J, Delgado G E and Briceño J M 2001b *Phys. Status Solidi (a)* **187** 395
 Hahn H, Frank G, Klingler W, Meyer A D and Stoerger G 1953 *Z. Anorg. Allg. Chem.* **271** 153
 Knight K S 1992 *Mater. Res. Bull.* **27** 161
 Mandel L, Tomlinson R D and Hampshire M J 1977 *J. Appl. Cryst.* **10** 130
 Medvedkin G A, Ishibashi T, Nishi T, Hayata K, Hasegawa Y and Sato K 2000 *Jap. J. Appl. Phys.* **39** L949
 Mora A J, Delgado G E, Grima-Gallardo P and Quintero M 2007 *Phys. Status Solidi (a)* **204** 547
 Parthé E 1995 in *Intermetallic compounds, principles and applications* (eds) J H Westbrook and R L Fleischer (Chichester, UK: John Wiley & Sons) **Vol. 1**.
 Rietveld H M 1969 *J. Appl. Cryst.* **2** 65
 Rodriguez-Carvajal J 2008 Fullprof, version 4.4, LLB, CEA-CNRS, France
 Roisnel T and Rodriguez-Carvajal J 2001 *Mater. Sci. Forum* **378–381** 118
 Sarkisov S Y and Picozzi S 2007 *J. Phys. Condens. Matter* **19** 016210
 Thompson P, Cox D E and Hastings J B 1987 *J. Appl. Cryst.* **20** 79