STRUCTURAL CHARACTERIZATION OF THE DILUTED MAGNETIC SEMICONDUCTOR CuGa$_{(1-X)}$Mn$_{(X)}$Se$_2$

G. E. DELGADO[*], J. L. VILLEGAS[a,b], P. SILVA[a], V. SAGREDO[C]
Laboratorio de Cristalografía, Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, Mérida 5101, Venezuela.
[a]*Laboratorio de Física de la Materia Condensada, Centro de Física, Instituto Venezolano de Investigaciones Científicas IVIC, Caracas 1020a, Venezuela.*
[b]*Universidad Nacional Experimental Politécnica UNEXPO, Vicerrectorado Barquisimeto 3001, Venezuela.*
[c]*Laboratorio de Magnetismo, Departamento de Física, Facultad de Ciencias, Universidad de los Andes, Mérida 5101, Venezuela.*

The crystal structure of the diluted magnetic compounds CuGa$_{(1-X)}$Mn$_{(X)}$Se$_2$, x = 0.1, 0.3, 0.5, were characterized using X-ray powder diffraction data. All compounds crystallize in the tetragonal space group I$\bar{4}$2d (Nº 122), with a chalcopyrite-type structure. In all alloys, Mn-substituted of I-III-VI$_2$ chalcopyrites, the Mn cation preferred the Ga site which supports its ferromagnetic properties. These results are consistent with the first-principles calculations reported so far.

1. Introduction

The compounds with ternary structures of the chalcogenide chalcopyrite family I–III–VI$_2$ (I = Cu, Ag; III = Al, Ga, In, VI = S, Se, Te) form an extensive group of semiconductor materials with diverse optical and electrical properties [1]. Ternary alloys with this composition are well known by their potential applications in the industry of solar cell devices [2]. From the structural point of view they crystallize with tetragonal symmetry in the space group I$\bar{4}$2d (N° 122) being isostructural with the CuFeS$_2$ mineral from which they take their name [3]. The addition of a magnetic cation to chalcopyrites produce interesting materials because they show both magnetic and semiconductor behavior [4]. Such materials are known as Diluted Magnetic Semiconductors DMS, and have attracted a new interest because of possible applications in magnetic-electronic ("spintronics") devices [5].

Recent studies have shown that doping of I-III-VI$_2$ chalcopyrite ternaries by doses of Mn leads to an appearance of ferromagnetism [6-10]. In the case of the ternary CuGaSe$_2$, it was shown theoretically that the substitution of Mn^{2+} on the Ga^{3-} site does produce the holes necessary for ferromagnetism (FM) [6, 7]. First-principles calculations, predicted them to be a new class of ferromagnetic semiconductors with Curie temperatures of 80-180 K [6, 8]. The same authors, have recently predicted the site preference of Mn in several I-III-VI$_2$ compounds, using first-principles total-energy calculations, and found that the preference of Mn on the III site is enhanced by Cu-rich growth conditions [9, 10].

With the purpose to confirm experimentally the theoretical structural model proposed by Zhao and Zunger [9, 10], in this work we present a detailed X-ray powder diffraction study of the diluted magnetic semiconductor CuGa$_{(1-X)}$Mn$_{(X)}$Se$_2$ (x = 0.1, 0.3, 0.5), where the diamagnetic Ga^{3+} cations are substituted by the magnetic Mn^{2+}.

*gerzon@ula.ve

2. Experimental

Samples of $CuGa_{(1-X)}Mn_{(X)}Se_2$ were grown by the chemical transport method. Starting materials for the crystal growth were polycrystalline compounds synthesized by direct fusion of stoichiometric quantities of the pure elements. The crystals were grown by chemical transport in sealed, evacuated quartz ampoule, which was previously subject to pyrolisis in order to avoid reaction of the charge with quartz. The transport process was done by using 4 mg/cm^3 of iodine as transport agent. The time of growth was ten days. The temperature gradient in the horizontal two zone furnace was about 50°C/cm with average temperature 925°C. The samples were then cooled to room temperature for the period of four days.

X-ray powder diffraction pattern was collected, at room temperature, in a Phillips PW-1250 goniometer using monocromatized CuKα radiation (λ= 1.5418 Å). A small quantity of the sample was ground mechanically in an agate mortar and pestle and mounted on a flat holder covered with a thin layer of grease. The specimens were scanned from 10-100° 2θ, with a step size of 0.02° and counting time of 15s. Silicon was used as an external standard.

3. Results and discussion

The X-ray diffractograms of $CuGa_{(1-X)}Mn_{(X)}Se_2$, x = 0.1, 0.3, 0.5, showed single phases, Fig. (1). The powder patterns were indexed using the program Dicvol04 [11], and tetragonal cells with similar magnitudes to the parent chalcopyrite structure, $CuGaSe_2$ [12], were founds. Systematic absences indicate I-type lattices. A detailed pattern examination taking into account the sample composition, cell parameters and lattice-type, suggested that all alloys crystallizes in the space group $I\bar{4}2d$. The substitution of Mn^{2+} by Ga^{3+} produced no structural changes.

The Rietveld refinements [13] of the structures were was carried out using the Fullprof program [14]. The atomic coordinates of $CuGaSe_2$ [12] were used as starting model for the refinements, with the cation distribution show in Table 1. The angular dependence of the peak full width at half maximum (FWHM) was described by the Caglioti's formula [15]. Peak shapes were described by the parameterized Thompson-Cox-Hastings pseudo-Voigt profile function [16]. 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 phases are summarizes in Table (1). This table contains the atomic coordinates, isotropic temperature factor and bond distances for each alloy. Figure (2) shows the observed, calculated and difference profile for the final cycle of Rietveld refinements for the tree alloys.
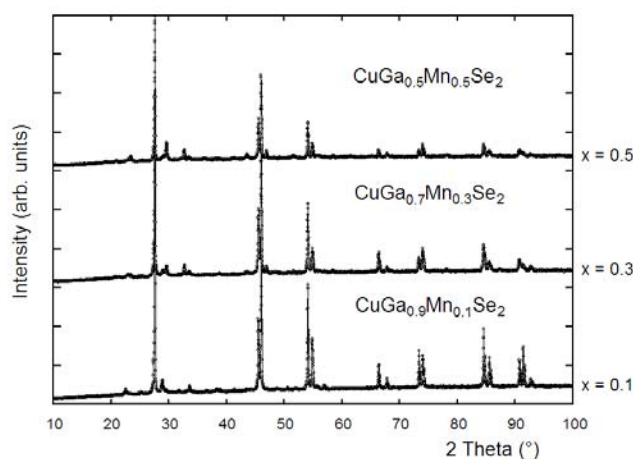

Fig. (1) Powder X-ray diffraction patterns for the diluted magnetic semiconductor system $CuGa_{(1-X)}Mn_{(X)}Se_2$.

As it is observed in Table 1, the occupancy factors for Ga^{3+} and Mn^{2+} cations are in good agreement with the nominal compositions. The occupancy factors indicate the molecular formulas: $CuGa_{0.89}Mn_{0.11}Se_2$, $CuGa_{0.68}Mn_{0.32}Se_2$ and $CuGa_{0.51}Mn_{0.49}Se_2$, for the phases with x = 0.1, 0.3 and 0.5, respectively.

All phases have a chalcopyrite structure and are normal adamantane-structure compounds [17], where the Ga cation is "diluted" with a magnetic Mn cation. Figure (3) shows the chalcopyrite unit cell diagram for all phases.

Table (1) Rietveld refinement results for $CuGa_{(1-X)}Mn_{(X)}Se_2$.

Composition (x)		0 Ref. [12]	0.1	0.3	0.5	1 Ref. [7]
mol. formula		$CuGaSe_2$	$CuGa_{0.9}Mn_{0.1}Se_2$	$CuGa_{0.7}Mn_{0.3}Se_2$	$CuGa_{0.5}Mn_{0.5}Se_2$	$CuMnSe_2$
crystal system		tetragonal	tetragonal	tetragonal	tetragonal	tetragonal
space group		$I\bar{4}2d$	$I\bar{4}2d$	$I\bar{4}2d$	$I\bar{4}2d$	$I\bar{4}2d$
a (Å)		5.5963(1)	5.6074(2)	5.6242(2)	5.6436(2)	5.69
c (Å)		11.0036(2)	11.0201(4)	11.0683(4)	11.1237(4)	11.24
c/a		1.97	1.97	1.97	1.97	1.98
V ($Å^3$)		344.62	346.50(2)	350.11(2)	354.29(2)	363.91
mol. w. (g/mol)		291.19	289.71	286.75	283.80	276.40
d_{calc} (g/cm^3)		5.61	5.55	5.44	5.32	-
	site	occupancy factors for cations				
Cu 4(a)	0, 0, 0	1	1	1	1	
Ga 4(b)	0, 0, ½	1	0.89(5)	0.68(5)	0.51(5)	
Mn		0	0.11(5)	0.32(5)	0.49(5)	
	site	atomic coordinate for anion x				
Se 32(e)	x, ¼, ⅛	0.2423(2)	0.2450(9)	0.2441(9)	0.2434(9)	
		isotropic temperature factors				
B_{iso} ($Å^2$)			0.5(4)	0.6(4)	0.5(4)	
		bond distances				
Cu-Se		2.385(1)	2.398(3)	2.403(3)	2.411(3)	
Ga(Mn)-Se		2.435(1)	2.430(3)	2.442(3)	2.454(3)	
		R factors				
R_{exp} (%)			7.1	7.4	7.5	
R_p (%)			6.7	6.9	7.2	
R_{wp} (%)			8.3	8.6	9.1	
S			1.2	1.2	1.2	
χ^2 (%)			1.4	1.4	1.5	

$R_p = 100 \sum|y_{obs} - y_{calc}| / \sum|y_{obs}|$ $R_{wp} = 100 [\sum_w|y_{obs} - y_{calc}|^2 / \sum_w|y_{obs}|^2]^{1/2}$ S (godnes of fit) $= R_{wp} / R_{exp}$

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

The Cu-Se bond distances in the three alloys (Table 1) are in good agreement with those observed in other chalcogenide structure compounds as Cu_2GeSe_3 (2.411 Å) [18] and (2.41) [19], Cu_3PSe_4 (2.418 Å average) [20], $CuInSe_2$ (2.432 Å) [21], Cu_2SnSe_3 (2.415 Å average) [22], $Cu_2Cd_{0.5}Mn_{0.5}GeSe_4$ (2.42 average) [23], Cu_3TaSe_4 (2.454 Å) [24], $CuFe_2InSe_4$ (2.456 Å) [25], $CuTaInSe_3$ (2.438 Å) [26], $CuFeAlSe_3$ (2.418 Å) and $CuFeGaSe_3$ (2.421 Å) [27], $CuFeInSe_3$ (2.423 Å) [28], $CuNiGaSe_3$ (2.419 Å) and $CuNiInSe_3$ (2.421 Å) [29]. The Ga-Se bond distances are also in good agreement with similar distances in the ternary compounds $CdGa_2Se_4$ (2.424 Å) [30], $ZnGa_2Se_4$ (2.43 Å average) [31], $MnGa_2Se_4$ (2.43 Å) [32], $AgGaSe_2$ (2.395 Å) [33], $LiGaSe_2$ (2.400 Å) [34] and $TlGaSe_2$ (2.41 Å average) [35].

Figure (4) shows the evolution of the unit cell volume for the $CuGa_{(1-X)}Mn_{(X)}Se_2$ system as function of Mn content (x). In this figure, the experimental value for x = 0 ($CuGaSe_2$) [12] and the theoretical value for x = 1 ($CuMnSe_2$) from first-principles calculation [7], were included.
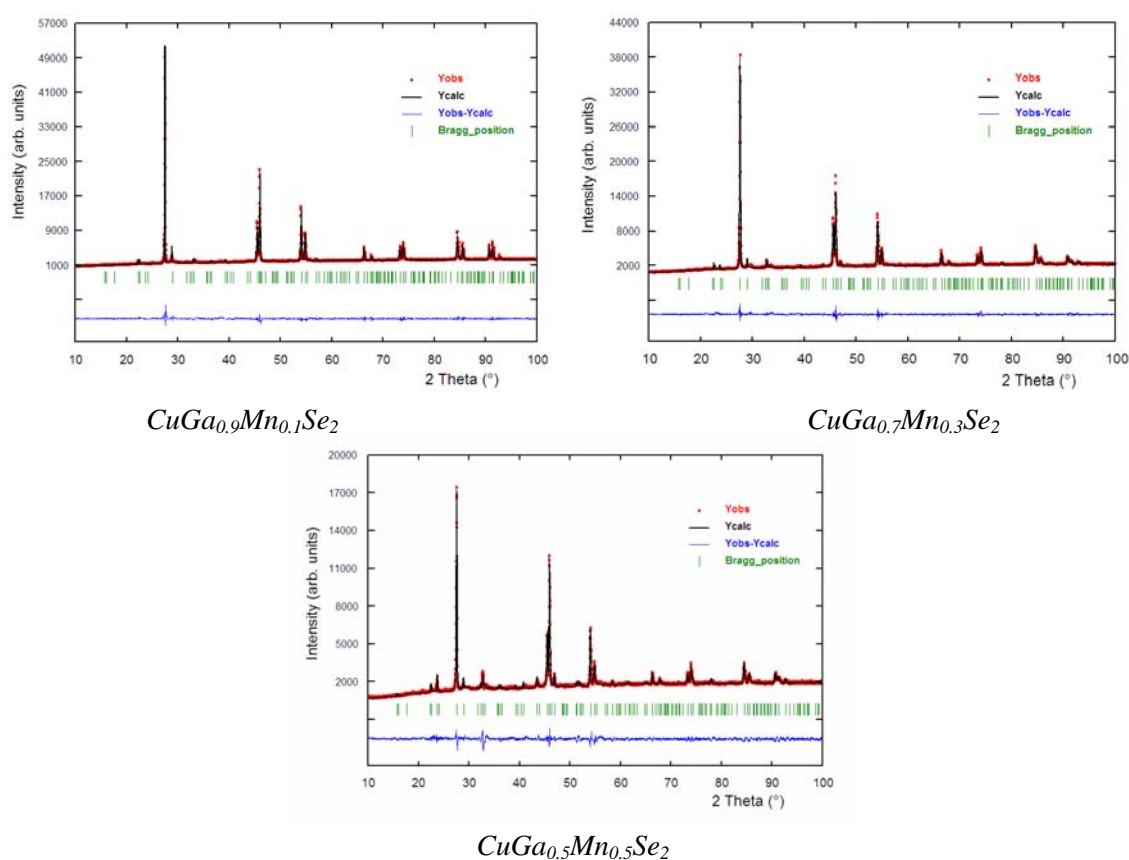

CuGa_{0.9}Mn_{0.1}Se_2   *CuGa_{0.7}Mn_{0.3}Se_2*

CuGa_{0.5}Mn_{0.5}Se_2

Fig. (2) Rietveld refinement plots for the diluted magnetic semiconductor system CuGa_{(1-X)}Mn_{(X)}Se_2

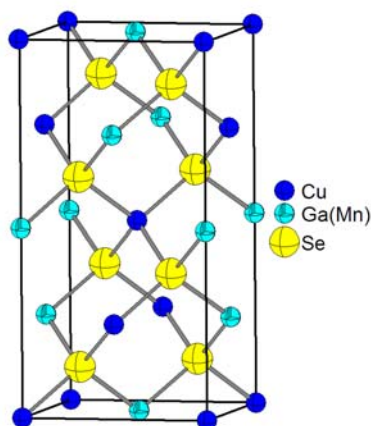*Fig. (3) Chalcopyrite unit cell diagram for the chalcogenide system CuGa$_{(1-X)}$Mn$_{(X)}$Se$_2$*

For the complete CuGa$_{(1-X)}$Mn$_{(X)}$Se$_2$ system, the unit cell volume increases linearly with increasing Mn^{2+} content and follows, within the limits of experimental error, Vegard's rule [36]. These incrases can be expected in view of the fact that the ionic radius of 0.61 Å for Ga^{3+} cations is smaller than that of 0.80 Å for Mn^{2+} cations [37]. Figure (4) show how the unit cell volume increases, which suggests for this system, a solid solution formation in all range of compositions.
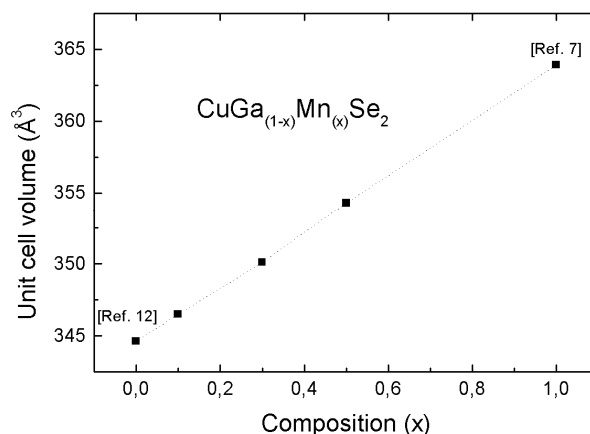

Fig. (4) Unit cell volume as function of the Mn content (x) in CuGa$_{(1-X)}$Mn$_{(X)}$Se$_2$. The dot lines represent linear regression.

4. Conclusions

The Rietveld refinement analysis of the CuGa$_{(1-X)}$Mn$_{(X)}$Se$_2$ (x = 0.1, 0.3, 0.5) system by X-ray powder diffraction confirms that these alloys crystallizes in a chalcopyrite structure. The structure implies a substitution of Mn in the Ga cation sites, whitout structural changes. The linear variation of the unit cell volume with x suggests complete solid solubility in this system.

Acknowledgements

References

[1] J. L. Shay, J. H. Wernik, Ternary chalcopyrite semiconductors: Growth, electronic properties and applications (Pergamon Press, Oxford, 1974).
[2] L. Pauling, L. O. Brockway, Z. Kristallogr. 82, 1988 (1932).
[3] A. Rockett, R.W. Birkmire. J. Appl. Phys. **70**, R81 (1991).
[4] J. Furdyna, J. Kossut, Diluted Magnetic Semiconductors, Semiconductors and Semimetals, vol. 25, Academic Press, Boston, 1986.
[5] H. Ohno, Science **281**, 951 (1998).
[6] S. Picozzi, Y.-J. Zhao, A.J. Freeman, B. Delley, Phys. Rev. B **66**, 205206 (2002).
[7] Y.-J. Zhao, A.J. Freeman, J. Magn. Magn. Mater. **246**, 145 (2002).
[8] A.J. Freeman, Y.J. Zhao. J. Phys. Chem. Sol. **64**, 1453 (2003).
[9] Y.-J. Zhao, A. Zunger, Phys. Rev. B **69**, 075208 (2004).
[10] Y.-J. Zhao, A. Zunger, Phys. Rev. B **69**, 104422 (2004).
[11] A. Boultif, D. Louër, J. Appl. Cryst. **37**, 724 (2004).
[12] S.C. Abrahams, J.L. Bernstein. J. Chem. Phys. **59**, 5415 (1973).
[13] H.M. Rietveld, J. Appl. Cryst. **2**, 65 (1969).
[14] J. Rodriguez-Carvajal, Fullprof: (version 2009), Laboratoire Léon Brillouin (CEA-CNRS), France.

[15] G. Cagliotti, A. Paoletti, F.P. Ricci. Nucl. Instrum. **3**, 223 (1958).

[16] P. Thompson, D.E. Cox, J.B. Hastings, J. Appl. Cryst. **20**, 79 (1987).

[17] E. Parthé, in: J. H. Westbrook, R. L. Fleischer (Eds.), Intermetallic compounds, principles and applications, Vol. 1, John Wiley & Sons, Chichester, UK, Chap. 14 (1995).

[18] E. Parthé, J. Garín, Monatsh. Chem. **102**, 1197 (1971).

[19] G. Marcano, C. Rincón, G. Marín, G.E. Delgado, A.J. Mora, J.L. Herrera-Pérez, J.G. Mendoza-Alvarez, P. Rodríguez. Solid State Comm. **146**, 65 (2008).

[20] J. Garín, E. Parthé, Acta Cryst. B**28**, 3672 (1972).

[21] K. S. Knight, Mater. Res. Bull. **27**, 161 (1992).

[22] G.E. Delgado, A.J. Mora, G. Marcano, C. Rincón, Mat. Res. Bull. **38**, 1949 (2003).

[23] G.E. Delgado, E. Quintero, R. Tovar, M. Quintero. Cryst. Res. Technol. **39**, 807 (2004).

[24] G.E. Delgado, A.J. Mora, S. Durán, M. Muñoz, P. Grima-Gallardo, J. Alloys Comp. **439**, 346 (2007).

[25] G.E. Delgado, A.J. Mora, P. Grima-Gallardo, M. Quintero. J. Alloys Comp. **454**, 306 (2008).

[26] G.E. Delgado, A.J. Mora, P. Grima-Gallardo, S. Durán, M. Muñoz, M. Quintero. Cryst. Res. Technol. **43**, 783 (2008).

[27] G.E. Delgado, A.J. Mora, J.E. Contreras, P. Grima-Gallardo, S. Durán, M. Muñoz, M. Quintero. Cryst. Res.Technol. **44**, 548 (2009).

[28] A.J. Mora, G.E. Delgado, P. Grima-Gallardo, M. Quintero, Phys. Stat. Sol. **204**, 547 (2007).

[29] G.E. Delgado, A.J. Mora, P. Grima-Gallardo, S. Durán, M. Muñoz, M. Quintero. Submitted to publication.

[30] L. Gastaldi, M.G. Simeone, S. Viticoli. Solid State Comm. **55**, 605 (1985).

[31] T. Hanada, F. Izumi, Y. Nakamura, O. Nittono, Q. Huang, A. Santoro. Physica B **241**, 373 (1998).

[32] M. Cannas, L. Garbato, A. Geddo Lehmann, N. Lampis, F. Ledda. Cryst. Res. Technol. **33**, 417 (1998).

[33] A. Chahed, O. Benhelal, H. Rozale, S. Laksari, N. Abbouni. phys. stat. sol. B **244**, 629 (2007).

[34] L. Isaenko, A. Yelisseyev, S. Lobanov, A. Titov, V. Petrov, J.J. Zondy, P. Krinitsin, A. Merkulov, V. Vedenyapin, J. Smirnova. Cryst. Res. Technol. **38**, 379 (2003).

[35] G.E. Delgado, A.J. Mora, F.V. Perez, J. Gonzalez. Cryst. Res. Technol. **42**, 663 (2007).

[36] L.Vegard. Z. Phys. **39**, 275 (1921).

[37] S.D. Shannon, Acta Cryst. A **32**, 751 (1976).