STRUCTURAL CHARACTERIZATION OF THE SYSTEM $CuFeIIISe_3$ (III= Al, Ga, In)

Gerzon E. Delgado, Asiloé J. Mora, Jines E. Contreras, Pedro Grima-Gallardo, Sonia Durán, Marcos Muñoz and Miguel Quintero

SUMMARY

In this work we report the structural characterization of the semiconductor system $CuFeIIISe_3$ (III= Al, Ga, In), using X-ray powder diffraction data. All compounds crystallize in the tetragonal space group $P\bar{4}2c$ (Nº 112), Z = 1, with unit cell parameters ***a*** = 5.609(1) Å, ***c*** = 10.963(2) Å for $CuFeAlSe_3$, ***a*** = 5.6165(3) Å, ***c*** = 11.075(1) Å for $CuFeGaSe_3$, and ***a*** = 5.7762(3) Å, ***c*** = 11.5982(7) Å for $CuFeInSe_3$.

RESUMEN

En este trabajo se reporta la caracterización estructural del sistema semiconductor $CuFeIIISe_3$ (III= Al, Ga, In), utilizando difracción de rayos-X en muestras policristalinas. La tres fases cristalizan en el grupo espacial tetragonal $P\bar{4}2c$, Z= 1, con parámetros de celda unidad ***a*** = 5.609(1)Å, ***c*** = 10.963(2)Å para $CuFeAlSe_3$, ***a*** = 5.6165(3)Å, ***c*** = 11.075(1)Å para $CuFeGaSe_3$ y ***a*** = 5.7762(3)Å, ***c*** = 11.5982(7)Å para $CuFeInSe_3$.

Keywords: Chalcogenides, Semiconductors, Chemical synthesis, X-ray diffraction, Crystal structure.

Gerzon E. Delgado. MSc. en Química, Universidad de Los Andes, Venezuela. Profesor Universidad de Los Andes. e-mail: gerzon@ula.ve

Asiloé J. Mora. PhD. en Química, Universidad de Keele, UK. Profesora Universidad de Los Andes.

Jines E. Contreras. MSc. en Química, Universidad de Los Andes, Venezuela. Profesor Universidad

Pedro Grima-Gallardo. PhD. en Ciencia de Materiales, Universidad Pierre et Marie Curie, Francia. Profesor Universidad de Los Andes.

Sonia Durán. Lic. en Física, Universidad de Los Andes, Venezuela.

Marcos Muñoz. Lic. en Física, Universidad de Los Andes, Venezuela.

Miguel Quintero. PhD. en Física, Universidad de Ottawa, Canadá. Profesor Universidad de Los Andes.

Introduction

The compounds with ternary structures of the chalcopyrite family $CuIIISe_2$ (III = Al, Ga, In) form an extensive group of semiconductor materials with diverse optical and electrical properties (Shay and Wernik, 1974). From the structural point of view they crystallize with tetragonal symmetry in the space group $I\bar{4}2d$ (N°122). The addition of a Fe-Se binary compound to chalcopyrite produces alloys of composition $(Cu\text{-}III\text{-}Se_2)_{1-x}$ $(Fe\text{-}Se)_x$. All these phases belong to the normal semiconductor compound families (Parthé, 1995; Delgado, 1998). Recently, the formation of some member with compositions $CuFeIIISe_3$ (x= ½), $CuFe_2IIISe_4$ (x= ⅔) and $Cu_2FeIIISe_5$ (x= ⅓) have been reported (Grima-Gallardo and Ruiz, 1999; Grima-Gallardo *et al*., 2001a; Grima-Gallardo *et al*., 2001b; Mora *et al*., 2007).

In a previous work, the crystal structure characterization of the first I-II-III-VI_3 semiconductor member, $CuFeInSe_3$, indicated a degradation of symmetry from the chalcopyrite structure $I\bar{4}2d$ to a related structure $P\bar{4}2c$ (Mora *et al*., 2007). In this work, we report a structural analysis for the three members of the $CuFeIIISe_3$ family (III= Al, Ga, In) using X-ray powder diffraction data.

Experimental

Ingots of $CuFeAlSe_3$, $CuFeGaSe_3$ and $CuFeInSe_3$ were prepared by the melt and annealing technique as described elsewhere (Grima-Gallardo *et al*., 2001). The stoichiometric relation of the sample was investigated by SEM technique, using a Hitachi S2500 microscope equipped with a Kedex EDX accessory. The average chemical composition of different regions of each sample gave atomic percentages in good agreement with the ideal composition 1:1:1:3.

For the X-ray analysis, small quantities of the samples were ground mechanically in an agate mortar and pestle. The resulting fine powders, were mounted on a flat zero-background holder. 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= 1.5418 Å; 40kV, 30mA) using a secondary beam graphite monochromator. 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.

Results and discussion

The three X-ray diffractograms showed single phases. The powder patterns were indexed using the program Dicvol04 (Boultif and Louër, 2004), and tetragonal cells with similar magnitudes to the parent chalcopyrite structures; $CuAlSe_2$ (Hahn *el at*., 1953), $CuGaSe_2$ (Mandel *et al*., 1973) and $CuInSe_2$ (Knight, 1992), were founds. Systematic absences indicate P-type lattices. The crystal structure determination was performed using several structural models derived from the structure of the selenium rich phase $CuInSe_{2.3}$ (Höenle *et al*., 1988) by permuting the cations in the available Wyckoff positions. Details of this determination were described elsewhere (Delgado *et al*., 2007).

The Rietveld refinements (Rietveld, 1969) of the structures were was carried out using the Fullprof program (Rodriguez-carvajal, 2007). The atomic coordinates of $CuFeInSe_3$ (Delgado *et al*., 2007) were used as starting model for the refinements. 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.

Figure 1 show the observed, calculated and difference profile for the final cycle of Rietveld refinements for $CuFeAlSe_3$, $CuFeGaSe_3$ and $CuFeInSe_3$. Figure 2 show the unit cell diagram of the chalcopyrite $CuIIISe_2$ structures compared to $CuFeIIISe_3$ compounds, and Table I show a comparison between the unit cell parameters for both families.

TABLE I

UNIT CELL PARAMETERS FOR THE $CuIIISe_2$ CHALCOPYRITES AND THE RELATED $CuFeIIISe_3$ COMPOUNDS

Compound	SG	***a*** (Å)	***c*** (Å)	***c***/a	V ($Å^3$)	Ref.
$CuAlSe_2$	$I\bar{4}2d$	5.606(5)	10.90(1)	2.12	342.6(5)	(Hahn *et al*., 1953)
$CuFeAlSe_3$	$P\bar{4}2c$	5.609(1)	10.963(2)	1.95	344.9(1)	
$CuGaSe_2$	$I\bar{4}2d$	5.614(1)	11.022(1)	1.79	347.4(1)	(Mandel *et al*., 1973)
$CuFeGaSe_3$	$P\bar{4}2c$	5.6165(3)	11.075(1)	1.97	349.36(4)	
$CuInSe_2$	$I\bar{4}2d$	5.781(1)	11.642(3)	2.01	389.1(2)	(Knight, 1992)
$CuFeInSe_3$	$P\bar{4}2c$	5.7762(3)	11.5982(7)	2.00	386.97(3)	

$CuFeIIISe_3$ (III= Al, Ga, In) are normal adamantane-structure compounds (Parthé, 1995) related to the $CuIIISe_2$ chalcopyrite parent structures, where the Fe cation is "diluted" leaving the cell volume almost unchanged. In these compounds occurs a degradation of symmetry from the chalcopyrite structure $I\bar{4}2d$ to a related structure $P\bar{4}2c$. In these new structures, each Se atom is coordinated by four cations [one Cu, one Fe, one III cation and one M cation (either Cu1, Fe1 or III1)] located at the corners of a lightly distorted tetrahedron. In the same way each cation is tetrahedrally bonded to four anions.

Conclusions

The $CuFeIIISe_3$ (III= Al, Ga, In) compounds crystallizes in a sphalerite derivative structure, in which the introduction of the additional cation Fe in the chalcopyrite $CuIIISe_2$ leaves the cell volume unchanged from the space groups $I\bar{4}2d$ to $P\bar{4}2c$.

Acknowledgements

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

REFERENCES

Boultif A, Louër D (2004) Powder pattern indexing with the dichotomy method. *J. Appl. Cryst. 37*: 724-731.

Delgado GE, Mora AJ, Grima-Gallardo P, Quintero M (2008) Crystal structure of $CuFe_2InSe_4$ from X-ray powder diffraction *J. Alloys Comp. 454*: 306-309.

Delgado JM (1998) Crystal chemistry of diamond-like and other derivative semiconducting compounds. *Inst. Phys. Conf. Series 152*: 45-50.

Grima-Gallardo P, Ruiz J (1999) X-rays and DTA of $CuFeGaSe_3$ and $CuFeInSe_3$ quaternary compounds. *Phys. Stat. Sol. (a) 173*: 283-288.

Grima-Gallardo P, Cárdenas K, Quintero M, Ruiz J, Delgado GE (2001) X-ray diffraction studies on $(CuAlSe_2)_X(FeSe)_{1-X}$ alloys *Mater. Res. Bull. 36*: 861-866.

Grima-Gallardo P, Cárdenas K, Molina L, Quintero M, Ruiz J, Delgado GE, Briceño JM (2001) A comparative study of $(Cu\text{-}III\text{-}Se_2)_X\text{-}(FeSe)_{1-X}$ alloys (III: Al, Ga, In) ($0 \leq x \leq 1$) by X-ray diffraction (XRD), Differencial thermal analysis (DTA) and Scanning electron microscopy (SEM)". *Phys. Stat. Sol. (a) 187*: 395-406.

Hahn H, Frank G, Klinger W, Meyer AD, Stöerger G (1953) Untersuchungen über ternäre Chalkogenide V. *Z. Anorg. Allg. Chem. 271*: 153-170.

Höenle W, Kühn G, Boehnke UC (1988) Crystal structures of two quenched Cu-In-Se phases. *Cryst. Res. Technol. 23*: 1347-1354.

Knight KS (1992) The crystal-structures of $CuInSe_2$ and $CuInTe_2$. *Mater. Res. Bull. 27*: 161-167.

Mandel L, Tomlinson RD, Hampshire MJ (1977) Crystal data for $CuGaSe_2$. *J. App. Cryst. 10*: 130-131.

Mora AJ, Delgado GE, Grima-Gallardo P, Quintero P (2007) Crystal structure of $CuFeInSe_3$ from X-ray powder diffraction data. *Phys. Stat. Sol. 204*: 547-554.

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

Rietveld HM (1969) A profile refinement method for nuclear and magnetic structures. *J. Appl. Cryst., 2*: 65-71.

Rodriguez-Carvajal J (2007) Fullprof, version 4.0, LLB, CEA-CNRS, France.

Shay JL, Wernik JH (1974) Ternary chalcopyrite semiconductors: Growth, electronic properties and applications, Pergamon Press. Oxford, UK.

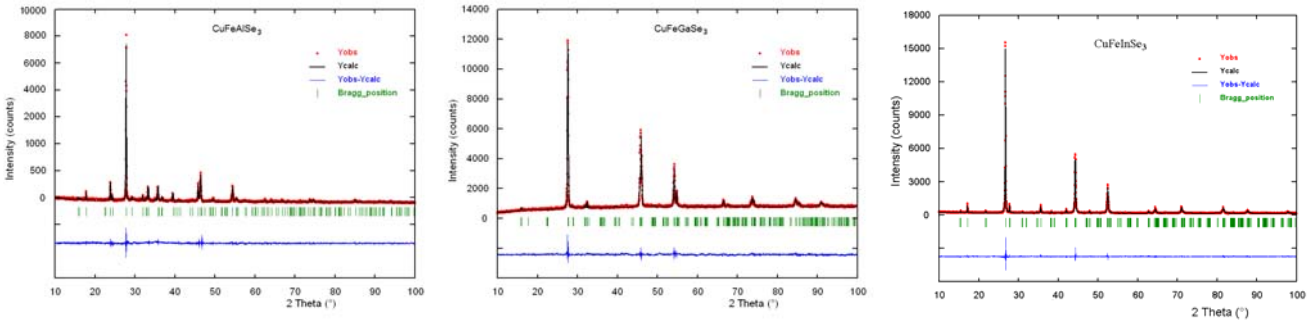

Figure 1. Rietveld final plots of $CuFeAlSe_3$, $CuFeGaSe_3$ and $CuFeInSe_3$.

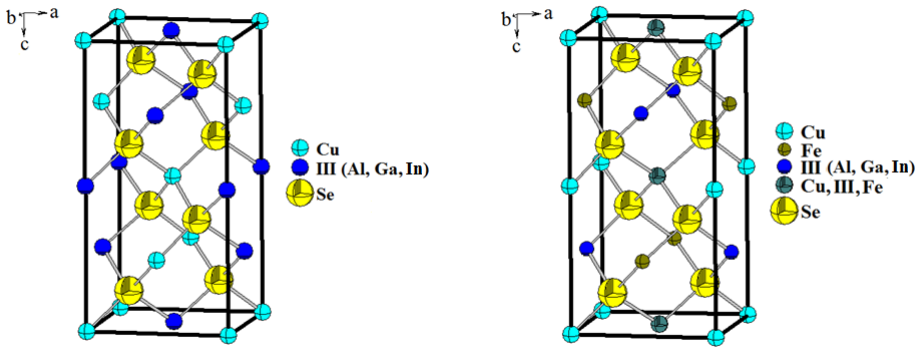

Figure 2. Unit cell diagram for the chalcopyrite $CuIIISe_2$ compared to the $CuFeIIISe_3$ compounds.