

ESTRUTURA CRISTALINA DO COMPOSTO CUATERNÁRIO SEMICONDUTOR  
CuFeCrSe<sub>3</sub>CRYSTAL STRUCTURE OF THE QUATERNARY SEMICONDUCTOR COMPOUND  
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Received 14 April 2019; received in revised form 14 July 2019; accepted form 19 July 2019

## RESUMO

Os compostos com estruturas ternárias da família da calcopirita Cu-III-Se<sub>2</sub> (III = Al, Ga, In, Cr) formam um amplo grupo de materiais semicondutores com diversas propriedades ópticas e elétricas, e a adição do composto binário FeSe produz ligas do tipo (Cu-III-Se<sub>2</sub>)<sub>1-x</sub>(Fe-Se)<sub>x</sub>. Esses tipos de materiais têm recebido atenção crescente como promissores materiais termoelétricos devido à sua alta eficiência, propriedades de transporte sintonizáveis, alta abundância elementar e baixa toxicidade. Este trabalho buscou sintetizar e caracterizar estruturalmente um novo material pertencente a este sistema semicondutor com  $x = \frac{1}{2}$ , o composto quaternário CuFeCrSe<sub>3</sub>. Este material foi preparado pela técnica de fusão e recozimento e sua estrutura foi refinada a partir do padrão de difração de raios-X usando o método de Rietveld. O padrão de raios X em pó foi composto principalmente de CuFeCrSe<sub>3</sub> (79,1%) com CuCr<sub>2</sub>Se<sub>4</sub> (20,9%) aparecendo como fase secundária. A fase principal cristaliza com a simetria tetragonal no grupo espacial  $P\bar{4}2c$  (Nº 112),  $Z = 1$ , com  $a = 5.5082(2) \text{ \AA}$ ,  $c = 10.943(1) \text{ \AA}$ ,  $V = 332.01(1) \text{ \AA}^3$ . O refinamento de 18 parâmetros instrumentais e estruturais levou a  $R_p = 8,8\%$ ,  $R_{wp} = 9,1\%$ ,  $R_{exp} = 7,8\%$  e  $S = 1,2$ . Este material, pertencente ao sistema semicondutor I-II-III-VI<sub>3</sub>, cristaliza com uma estrutura do tipo CuFeInSe<sub>3</sub> numa estrutura normal de adamantano. O CuFeCrSe<sub>3</sub> é um novo composto semicondutor relacionado à fase superiônica CuCrSe<sub>2</sub>, e pode ser considerado como potencial candidato a aplicações termoelétricas de média temperatura.

**Palavras-chave:** Difração de raios X, estrutura cristalina, calcogenetos, semicondutores, síntese química.

## ABSTRACT

The compounds with ternary structures of the chalcopyrite family Cu-III-Se<sub>2</sub> (III = Al, Ga, In, Cr) form a wide group of semiconductor materials with diverse optical and electrical properties, and the addition of FeSe binary compound produces alloys of the type (Cu-III-Se<sub>2</sub>)<sub>1-x</sub>(Fe-Se)<sub>x</sub>. These types of materials have received increasing attention as promising thermoelectric materials due to their high efficiency, tunable transport properties, high elemental abundance and low toxicity. This work aims to synthesize and characterize structurally a new material belonging to this semiconductor system with  $x = \frac{1}{2}$ , the quaternary compound CuFeCrSe<sub>3</sub>. This material was prepared by the melt and anneal technique and its structure was refined from X-ray powder diffraction pattern using the Rietveld method. The X-ray powder pattern was mainly composed of CuFeCrSe<sub>3</sub> (79.1%) with CuCr<sub>2</sub>Se<sub>4</sub> (20.9%) appearing as secondary phase. The principal phase crystallizes with tetragonal symmetry in the space group  $P\bar{4}2c$  (Nº 112),  $Z = 1$ , with  $a = 5.5082(2) \text{ \AA}$ ,  $c = 10.943(1) \text{ \AA}$ ,  $V = 332.01(1) \text{ \AA}^3$ . The refinement of 18 instrumental and structural parameters led to  $R_p = 8.8 \%$ ,  $R_{wp} = 9.1 \%$ ,  $R_{exp} = 7.8 \%$  and  $S = 1.2$ . This material, belonging to the semiconductor system I-II-III-VI<sub>3</sub>, crystallizes with a CuFeInSe<sub>3</sub>-type structure in a normal adamantane-structure. CuFeCrSe<sub>3</sub> is a new semiconductor compound, related to the superionic phase CuCrSe<sub>2</sub>, and can be considered as a potential candidate for medium-temperature thermoelectric applications.

## 1. INTRODUCTION

The compounds with ternary structures of the chalcopyrite family Cu-III-Se<sub>2</sub> (III = Al, Ga, In, Cr) form a wide group of semiconductor materials with diverse optical and electrical properties (Shay and Wernik, 1974). They crystallize with tetragonal symmetry in the space group I $\bar{4}$ 2d (N°122), and the addition of a FeSe binary compound produces alloys of the type (I-III-Se<sub>2</sub>)<sub>1-x</sub>(Fe-Se)<sub>x</sub> (Parthé, 1995). The synthesis and crystal structure characterization of some member with compositions Cu-Fe-III-S<sub>3</sub> ( $x = \frac{1}{2}$ ), Cu-Fe<sub>2</sub>-III-Se<sub>4</sub> ( $x = \frac{2}{3}$ ) and Cu<sub>2</sub>-Fe-III-Se<sub>5</sub> ( $x = \frac{1}{3}$ ) have been reported (Delgado *et al.*, 2008; 2009; 2010; 2014; 2015; Grima-Gallardo *et al.*, 2000; 2001a; 2001b, 2007a, 2007b, 2015; Mora *et al.*, 2007; Flores-Cruz *et al.*, 2018). All these phases fulfill the rules of formation of adamantane compounds and belong to the normal semiconductor compound families (Parthé, 1995). These types of materials, Cu-based chalcogenides, have received increasing attention as promising thermoelectric materials due to their high efficiency, tunable transport properties, high elemental abundance and low toxicity (Wei *et al.*, 2019). In particular, the ternary CuCrSe<sub>2</sub> is considered a superionic crystal because exhibit ionic mobilities comparable to liquids while maintaining a periodic crystalline lattice (Niedziela *et al.*, 2018), and is a potential candidate for medium-temperature thermoelectric applications (Cheng *et al.*, 2015).

In this work, we report a detailed structural analysis of the quaternary semiconductor CuFeCrSe<sub>3</sub>, a new member of the Cu-II-III-Se<sub>3</sub> family, which is a related compound of the superionic crystal CuCrSe<sub>2</sub>.

## 2. MATERIALS AND METHODS

### 2.1. Preparation

Starting materials (Cu, Fe, Cr, Se) with nominal purity of 99.99 % in the stoichiometric ratio were mixed together in an evacuated and sealed quartz tube with the inner walls previously carbonized in order to avoid reactions of the starting materials with the quartz ampoule. Polycrystalline ingots of about 1 g were prepared by the melt and anneal technique as previously

described (Grima-Gallardo *et al.*, 2000; Flores-Cruz *et al.*, 2018).

### 2.2. X-ray powder diffraction

A small quantity of the sample was ground mechanically in an agate mortar and pestle. The resulting fine powder was mounted on a flat zero-background holder covered with a thin layer of petroleum jelly. The X-ray powder diffraction data was collected at room temperature, in  $\theta/\theta$  reflection mode using a Siemens D5005 diffractometer equipped with an X-ray tube (CuK $\alpha$  radiation:  $\lambda = 1.54059$  Å; 40kV, 30 mA) and a diffracted beam graphite monochromator. The specimen was scanned from 10-100° 2 $\theta$ , with a step size of 0.02° and counting time of 20 s. Quartz was used as an external standard. For the Rietveld refinement, the whole diffraction data was used.

## 3. RESULTS AND DISCUSSION:

A search in the ICDD-PDF database (ICDD, 2013) using the software available with the diffractometer was performed, and one known +phases present in small quantities was readily identified: CuCr<sub>2</sub>Se<sub>4</sub> (PDF N° 81-1986). The peak positions of each phase were extracted by means of single-peak profile-fittings carried out with the DIFFRACplus software. The remaining intense peaks corresponding to the phase of interest, CuFeCrSe<sub>3</sub>, were readily indexed in a tetragonal cell with:  $a = 5.51(2)$  Å and  $c = 10.94(5)$  Å, using the program Dicvol04 (Boultif and Louër, 2004). A revision of the diffraction lines of the main phase taking into account the sample composition, unit cell parameters as well as the primitive cell suggested that this material is isostructural with the CuFeInSe<sub>3</sub>-type compound, which crystallize in the tetragonal space group P $\bar{4}$ 2c (N° 112) (Mora *et al.*, 2007).

The Rietveld refinement (Rietveld, 1969) was carried out using the Fullprof program (Rodríguez-Carvajal, 1993). The atomic coordinates of CuFeInSe<sub>3</sub> (Mora *et al.*, 2007) were used as starting model for the quaternary CuFeCrSe<sub>3</sub>. Atomic positions of the ternary CuCr<sub>2</sub>Se<sub>4</sub> (Okonska-Kozłowska *et al.*, 1993) were included as secondary phase in the refinement. The angular dependence of the peak full width at half maximum (FWHM) was described by the Caglioti's formula (Caglioti *et al.*, 1958). Peak

shapes were described by the parameterized 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 are summarized in Table 1. Figure 1 shows the observed, calculated and difference profile for the final cycle of Rietveld refinement. Atomic coordinates, isotropic temperature factor and bond distances are shown in Table 2. The final Rietveld refinement converged to the following weight fraction percentages: CuFeCrSe<sub>3</sub> (79.1%) and CuCr<sub>2</sub>Se<sub>4</sub> (20.9%).

CuFeCrSe<sub>3</sub> is a normal adamantane-structure compound (Parthé, 1995). The Se atoms form a close-packed arrangement where each anion is coordinated by four cations located at the corners of a slightly distorted tetrahedron. All cations are similarly coordinated by four anions. Figure 2 shows a polyhedral view of the crystal structure with the four types of atoms-centered tetrahedra CuSe<sub>4</sub>, FeSe<sub>4</sub>, CrSe<sub>4</sub> and MSe<sub>4</sub> where all polyhedra are oriented in the same direction and are connected by the corners.

The interatomic distances are shorter than the sum of the respective ionic radii for structures tetrahedrally bonded (Shannon, 1976). The bond distances Cu-Se [2.42(4) Å], Fe-Se [2.43(4) Å] and Cr-Se [2.36(4) Å] are in good agreement with those observed in other chalcogenide compounds such as CuCrSe<sub>2</sub> (Hahn and de Lorent, 1957), CuInSe<sub>2</sub> (Knight, 1992), Fe<sub>2</sub>CrSe<sub>4</sub>, (Delgado and Sagredo, 2004), CuFe(Al,Ga,In)Se<sub>3</sub> (Mora *et al.*, 2007; Delgado *et al.*, 2009), CuFe<sub>2</sub>(Al,Ga,In)Se<sub>4</sub> (Delgado *et al.*, 2008; Delgado *et al.*, 2015), CuNi(Ga,In)Se<sub>3</sub> (Delgado *et al.*, 2010), Cu<sub>3</sub>NbSe<sub>4</sub> (Lu and Ibers, 1993) and Cu<sub>3</sub>VSe<sub>4</sub> (Klepp and Gurtner, 2004).

CuFeCrSe<sub>3</sub> is a semiconductor compound with *n*-type conductivity (Grima-Gallardo *et al.*, 2000), related to the superionic phase CuCrSe<sub>2</sub>, which can be used as thermoelectric material.

#### 4. CONCLUSIONS:

The new quaternary semiconductor compound CuFeCrSe<sub>3</sub> was synthesized by the melt and anneal technique and its crystal structure was characterized by X-ray diffraction analysis. Rietveld refinement from the X-ray powder data allowed to determine the crystal structure of this compound. The X-ray powder

pattern was mainly composed of CuFeCrSe<sub>3</sub> (79.1%) with CuCr<sub>2</sub>Se<sub>4</sub> (20.9%) as secondary phase.

The new semiconductor compound CuFeCrSe<sub>3</sub>, belonging to the semiconductor system Cu-II-III-Se<sub>3</sub>, crystallizes in the tetragonal space group P4̄2c, with a CuFeInSe<sub>3</sub>-type structure. This is a new compound of the I-II-III-VI<sub>3</sub> family of semiconductors, with a normal adamantane-structure.

This quaternary material, related to the superionic phase CuCrSe<sub>2</sub>, can be considered as a potential candidate for medium-temperature thermoelectric applications.

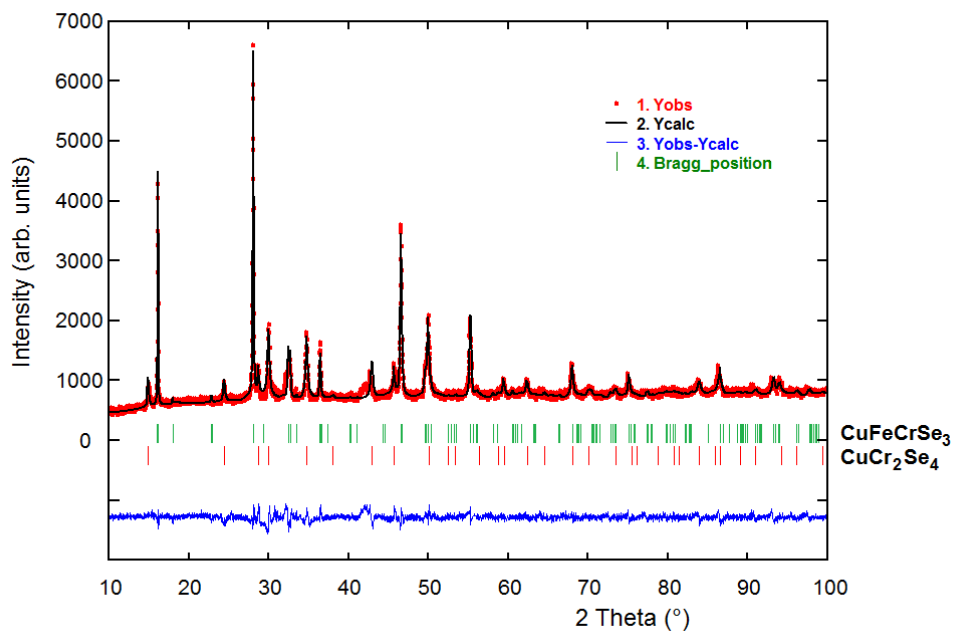
#### 5. ACKNOWLEDGMENTS:

This work was supported by CDCHT-UCLA (Grant C-1885-14-05-B) and FONACIT (Grants LAB-97000821, PEII-1697 and 2011001341).

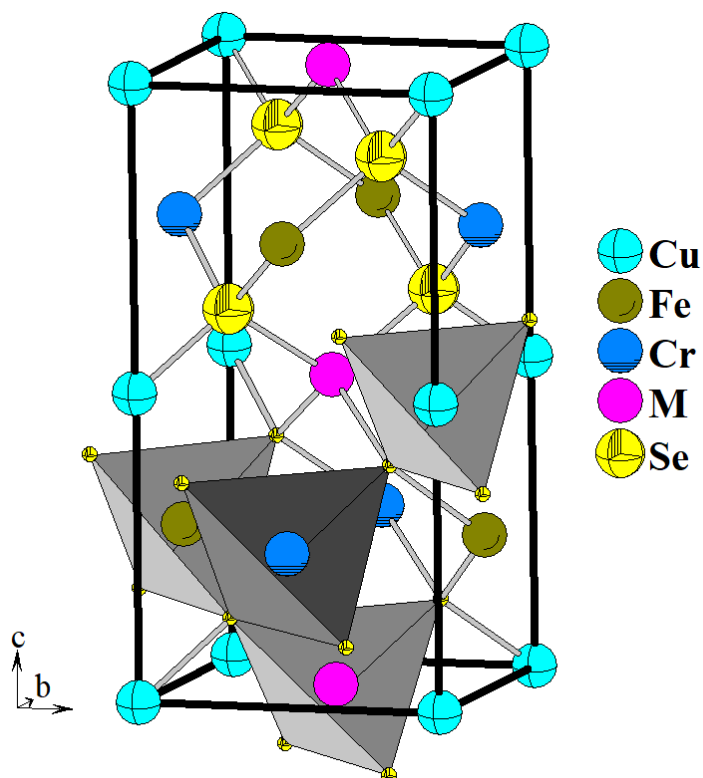
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**Figure 1.** Rietveld final plot of  $\text{CuFeCrSe}_3$ . The lower trace is the difference curve between observed and calculated patterns. The Bragg reflections are indicated by vertical bars



**Figure 2.** Unit cell diagram for the compound  $\text{CuFeCrSe}_3$  showing the tetrahedral around the cations

**Table 1.** Rietveld refinement results for  $\text{CuFeCrSe}_3$ 

Molecular formula	$\text{CuFeCrSe}_3$	Molecular weight (g/mol)	1088.6
$a$ (Å)	5.5082(2)	System	tetragonal
$c$ (Å)	10.943(1)	Space group	$P\bar{4}2c$ (112)
$V$ (Å <sup>3</sup> )	332.01(3)	$D_{\text{calc}}$ (g/cm <sup>-3</sup> )	5.44
Z	1	Weight fraction (%)	79.1
$R_p$ (%)	8.8	$R_B$ (%)	8.5
$R_{\text{wp}}$ (%)	9.1	$R_{\text{exp}}$ (%) = 7.8	S = 1.2

$$R_p = 100 \frac{\sum |y_{\text{obs}} - y_{\text{calc}}|}{\sum |y_{\text{obs}}|} \quad R_B = 100 \frac{\sum_k |I_k - I_{c,k}|}{\sum_k I_k} \quad S = [R_{\text{wp}} / R_{\text{exp}}]$$

$$R_{\text{wp}} = 100 \left[ \frac{\sum_w |y_{\text{obs}} - y_{\text{calc}}|^2}{\sum_w |y_{\text{obs}}|^2} \right]^{1/2} \quad R_{\text{exp}} = 100 \left[ \frac{(N+C)}{\sum_w (y_{\text{obs}}^2)} \right]^{1/2} \quad N-P+C = \text{degrees of freedom}$$

**Table 2.** Atomic coordinates, isotropic temperature factors and bond distances (Å) for  $\text{CuFeCrSe}_3$ , derived from the Rietveld refinement.  $M = (\text{Cu}1+\text{Fe}1+\text{Cr}1)$ 

Atom	Ox.	Site	$x$	$y$	$z$	foc	B (Å <sup>2</sup> )			
Cu	+1	2e	0	0	0	1	0.6(4)			
Fe	+2	2d	0	½	¼	1	0.6(4)			
Cr	+3	2b	½	0	¼	1	0.6(4)			
		2f	½	½	0	⅓	0.6(4)			
M		2f	½	½	0	⅓	0.6(4)			
		2f	½	½	0	⅓	0.6(4)			
Se	-2	8n	0.263(1)	0.251(1)	0.123(1)	1	0.6(4)			
Cu-Se		2.42(4)	Fe-Se		2.43(4)	Cr-Se		2.36(4)	M-Se	2.32(4)