



CARACTERIZAÇÃO ESTRUTURAL DO NOVO SEMICONDUTOR DE DIAMANTE CuNbGaSe_3



STRUCTURAL CHARACTERIZATION OF THE NEW DIAMOND-LIKE SEMICONDUCTOR CuNbGaSe_3

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RESUMO

O composto de calcogeneto CuNbGaSe_3 , pertencente ao sistema I-II-III-VI₃, foi analisado por meio de difração de raios-X sobre pó e sua estrutura cristalina foi refinada pelo método Rietveld. Este é um tipo de material semiconductor, que melhora as propriedades de semicondutores simples como o CuGaSe_2 porque ele acrescenta aplicações spintrônicas devido ao seu comportamento magnético. O padrão de pó foi composto de 94,2% da fase principal CuNbGaSe_3 e 5,8% da fase secundária $\text{Cu}_{0.667}\text{NbSe}_2$. Este material cristaliza com uma estrutura de tipo CuFeInSe_3 no grupo espacial tetragonal $P\bar{4}2c$ (Nº 112), os parâmetros da célula unitária $a = 5,6199(4)$ Å, $c = 11,0275(2)$ Å, $V = 348,28(4)$ Å³, com um estrutura de adamantane normal em que ocorre uma degradação de simetria da estrutura de calcopirita $I\bar{4}2d$ para uma estrutura relacionada $P\bar{4}2c$.

Palavras-chave: Calcogenetos, semicondutores, síntese química, difração de raios X, estrutura cristalina.

ABSTRACT

The chalcogenide compound CuNbGaSe_3 , belonging to the system I-II-III-VI₃, has been investigated by means of X-ray powder diffraction and its crystal structure has been refined by the Rietveld method. This is a material of the semiconductor type, which improves the properties of a simple semiconductor like CuGaSe_2 because it adds spintronic applications due to its magnetic behavior. The powder pattern was composed by 94.2% of the principal phase CuNbGaSe_3 and 5.8% of the secondary phase $\text{Cu}_{0.667}\text{NbSe}_2$. This material crystallizes with a CuFeInSe_3 -type structure in the tetragonal space group $P\bar{4}2c$ (Nº 112), unit cell parameters $a = 5.6199(4)$ Å, $c = 11.0275(2)$ Å, $V = 348.28(4)$ Å³, with a normal adamantane-structure where occurs a degradation of symmetry from the chalcopyrite structure $I\bar{4}2d$ to a related structure $P\bar{4}2c$.

Keywords: Chalcogenides, semiconductors, chemical synthesis, X-ray diffraction, crystal structure.

INTRODUCTION

The chalcopyrite family of compounds I-III-VI₂ (I = Cu, Ag, III = Al, Ga, In, VI = S, Se, Te) form a wide group of chalcogenide 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^o122), and the addition of a II-VI (II = Zn, Cd, Mn, Fe) binary compound produces alloys of the type (I-III-VI₂)_{1-x}(II-VI)_x (Parthé, 1995). Due to the great variety of possible compositions, these materials can be useful for applications such as tunable semiconductors (Ford *et al.*, 2011), photovoltaics (Guo *et al.*, 2010), spintronics (Chambers and Yoo, 2003), non-linear optics (Li *et al.*, 2011) and thermoelectrics (Sevik and Ca, 2010).

The formation of some quaternary with compositions Cu-II-III-Se₃ ($x = \frac{1}{2}$), Cu-II₂-III-Se₄ ($x = \frac{2}{3}$) and Cu₂-II-III-Se₅ ($x = \frac{1}{3}$) have been reported (Grima-Gallardo *et al.*, 2001a; 2001b, 2007a, 2007b, 2015), and the first crystal structure characterization of one I-II-III-VI₃ semiconductor member, indicated a degradation of symmetry from the chalcopyrite structure I $\bar{4}$ 2d to a related tetragonal structure P $\bar{4}$ 2c (Mora *et al.*, 2007).

In recent years, it has been of interest to carry out a systematic study of the crystal structure of chalcogenide diamond-like families (Delgado *et al.*, 2008; 2009; 2010; 2014; 2015), including compounds with niobium in their structure (Delgado *et al.*, 2009; Salas *et al.*, 2014; Grima-Gallardo *et al.*, 2016). Hence, here we report herein the structural characterization of a new quaternary compound, CuNbGaSe₃, using the Rietveld method from X-ray powder diffraction data.

MATERIALS AND METHODS

Synthesis

Starting materials (Cu, Nb, Ga, Se) with a nominal purity of (at least) 99.99 weight% were mixed together in the stoichiometric ratio in an evacuated and sealed quartz tube with the inner walls previously carbonized in order to prevent chemical reaction of the elements with the quartz. Polycrystalline ingots of about 1 g were prepared by the usual melt and anneal technique. The ampoule was heating slowly until 450 °C keeping

this temperature for 48 h; then the temperature was raised again, at a low rate until 1150 °C during 24 h. Mechanical shaking of the ampoule was used throughout the entire heating process. Then, the ampoule was cooled to room temperature at a very low rate during one week. Finally, the ampoule was placed in a furnace at 650 °C, keeping this temperature for one month. Figure 1 shows a picture of the furnace device used.



Figure 1. Picture of the furnace device used in the synthesis of the CuNbGaSe₃ compound

X-ray powder diffraction

For the X-ray analysis, a small quantity of the sample was ground mechanically in an agate mortar and pestle. The resulting fine powders were mounted on a flat zero-background holder covered with a thin layer of petroleum jelly. 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 (CuK α radiation: $\lambda = 1.54056$ Å; 40kV, 30mA). The specimen was scanned from 10°-100° 2 θ , with a step size of 0.02° and counting time of 40s. Quartz was used as an external standard.

RESULTS AND DISCUSSION:

Figure 2 shows the resulting X-ray powder diffractogram for the CuNbGaSe₃ compound. An automatic search in the PDF-ICDD database (ICDD, 2013), using the software available with the diffractometer, indicated that the powder pattern contained small amounts of Cu_{0.67}NbSe₂ (PDF N^o 74-0049), Bragg positions of the diffraction lines from this compound are also indicated in Figure 2. The 20 first peak positions of the main phase (CuNbGaSe₃) were indexed using the program Dicvol04 (Boultif and Louër, 2004), which gave a unique solution in a tetragonal cell with $a = 5.621(2)$ Å and $c =$

11.030(5) Å. These values are similar in magnitude to the parent chalcopyrite structure of CuGaSe_2 ($a = 5.614(1)$ Å, $c = 11.022(1)$ Å) (Mandel *et al.*, 1973). 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_3 -type compound, which crystallize in the tetragonal space group $P\bar{4}2c(N^\circ 112)$ (Mora *et al.*, 2007).

The Rietveld refinement (Rietveld, 1969) was carried out using the Fullprof program (Rodríguez-Carvajal, 1993). The atomic coordinates of CuFeInSe_3 (Mora *et al.*, 2007) were used as starting model for the quaternary CuNbGaSe_3 . Atomic positions of the $\text{Cu}_{0.67}\text{NbSe}_2$ binary (Voorhoeve-van den Berg, 1972) 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 2 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: CuNbGaSe_3 (94.2%) and $\text{Cu}_{0.67}\text{NbSe}_2$ (5.8%) (Hill and Howard, 1987).

CuNbGaSe_3 is a normal adamantane-structure compound (Parthé, 1995), where occurs a degradation of symmetry from the chalcopyrite structure $I\bar{4}2d$ to a related structure $P\bar{4}2c$. This condition can be seen in Figure 3 where a comparison is made between the chalcopyrite CuGaSe_2 $I\bar{4}2d$ structure and the $P\bar{4}2c$ structure of CuNbGaSe_3 . Therefore, in this quaternary structure, the introduction of an additional cation (Nb) produces an effect of "dilution" of this cation in the chalcopyrite structure leaving the cell volume almost unchanged (Mora *et al.*, 2007).

In this structure 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 4 shows a polyhedral view of the crystal structure with the four types of atoms-centered tetrahedra CuSe_4 , NbSe_4 , GaSe_4 and MSe_4 where all polyhedra are oriented in the same direction and are connected by the corners.

The bond distances Cu-Se [2.425(8) Å], Nb-Se [2.445(8) Å] and Ga-Se [2.438(8) Å] are in good agreement with those observed in the parent chalcopyrite structure CuGaSe_2 (Mandel *et al.*, 1973) and other adamantane compounds such as $\text{CuFe}(\text{Al},\text{Ga},\text{In})\text{Se}_3$ (Mora *et al.*, 2007; Delgado *et al.*, 2009), $\text{CuFe}_2(\text{Al},\text{Ga},\text{In})\text{Se}_4$ (Delgado *et al.*, 2008; Delgado *et al.*, 2015), $\text{CuNi}(\text{Ga},\text{In})\text{Se}_3$ (Delgado *et al.*, 2010), TlGaSe_2 (Delgado *et al.*, 2007) and Cu_3NbSe_4 (Lu and Ibers, 1993).

CuNbGaSe_3 is a material of the semiconductor type, which improves the properties of a simple semiconductor like CuGaSe_2 because it ads spintronic applications due to its magnetic behavior.

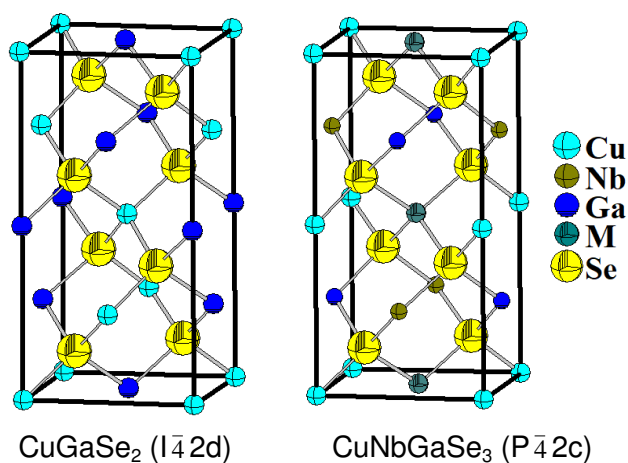


Figure 3. Unit cell diagram for the chalcopyrite CuGaSe_2 compared to the CuNbGaSe_3 compound

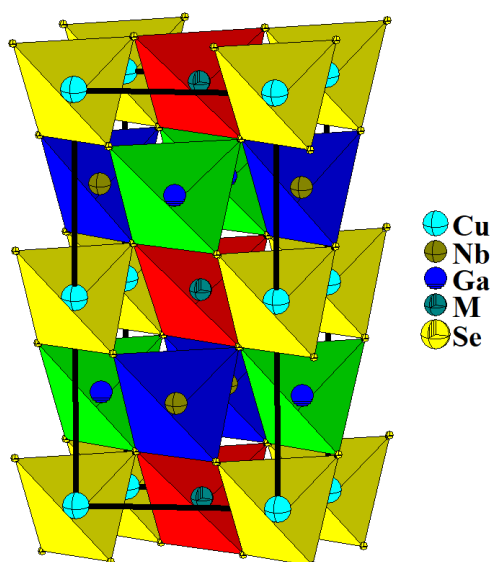


Figure 4. Polyhedral view of the CuNbGaSe_3 structure showing tetrahedral units

CONCLUSIONS:

The crystal structure of the new quaternary compound CuNbGaSe_3 was determined using X-ray powder diffraction data. This material crystallizes in the tetragonal space group $P\bar{4}2c$, with a CuFeInSe_3 -type structure. This is a new compound of the I-II-III-VI₃ family of semiconductors, with a normal adamantine-structure, where occurs a degradation of symmetry from the chalcopyrite structure $I\bar{4}2d$ to a related structure $P\bar{4}2c$.

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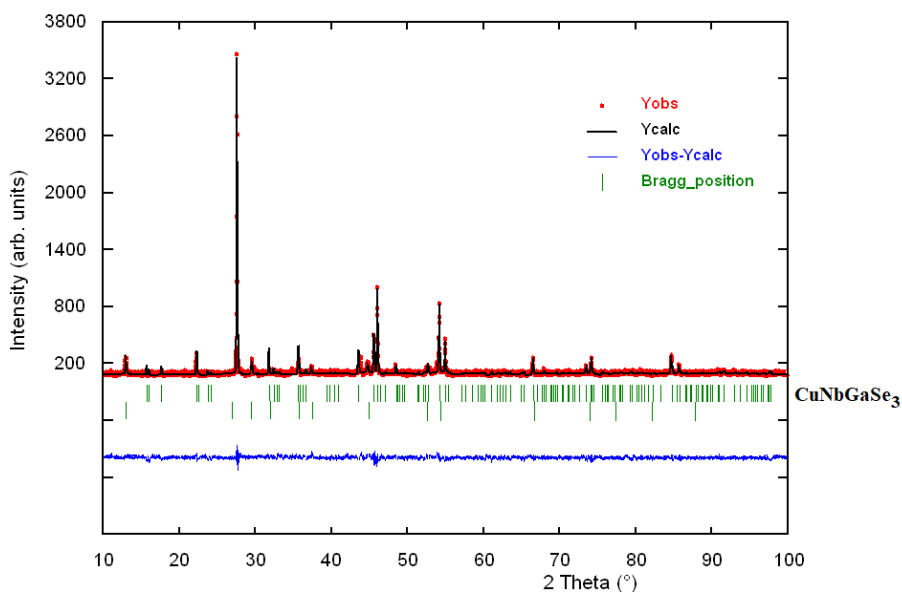


Figure 2. Rietveld final plot of CuNbGaSe_3 . The lower trace is the difference curve between observed and calculated patterns. The Bragg reflections are indicated by vertical bars

Table 1. Rietveld refinement results for CuNbGaSe_3 and $\text{Cu}_{0.667}\text{NbSe}_2$

Molecular formula	CuNbGaSe_3	$\text{Cu}_{0.667}\text{NbSe}_2$	
Molecular weight (g/mol)	1234.7	239.2	
a (Å)	5.6199(4)	5.490(4)	
c (Å)	11.0275(2)	13.630(5)	
V (Å ³)	348.28(4)	143.6(5)	
System	tetragonal	hexagonal	
Space group	$P4_2c$ (112)	$P6_3/mmc$ (194)	
Z	2.667 (8/3)	2	R_p (%) = 8.6
D_{calc} (g/cm ⁻³)	5.83	6.78	R_{wp} (%) = 8.9
Weightfraction (%)	94.2	5.8	R_{exp} (%) = 6.7
R_B (%)	8.8	9.0	$S = 1.3$

$$R_p = 100 \frac{\sum |y_{\text{obs}} - y_{\text{calc}}|}{\sum y_{\text{obs}}} \quad R_B = 100 \frac{\sum_k |l_k - |c_k||}{\sum_k |l_k|} \quad N-P+C = \text{degrees of freedom}$$

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

Table 2. Atomic coordinates, isotropic temperature factors and bond distances (Å) for CuNbGaSe_3 , derived from the Rietveld refinement. $M = (\text{Cu}1+\text{Nb}1+\text{Ga}1)$

Atom	Ox.	Site	x	y	z	foc	B (Å ²)			
Cu	+1	2e	0	0	0	1	0.5(4)			
Nb	+2	2d	0	1/2	1/4	1	0.5(4)			
Ga	+3	2b	1/2	0	1/4	1	0.5(4)			
		2f	1/2	1/2	0	1/3	0.5(4)			
M		2f	1/2	1/2	0	1/3	0.5(4)			
		2f	1/2	1/2	0	1/3	0.5(4)			
Se	-2	8n	0.255(1)	0.257(1)	0.123(1)	1	0.5(4)			
Cu-Se		2.425(8)	Nb-Se		2.445(8)	Ga-Se		2.438(8)	M-Se	2.367(8)