

SYNTHESIS AND CHARACTERIZATION OF THE TERNARY CHALCOGENIDE COMPOUND Cu_3NbTe_4

G. E. DELGADO*, A. J. MORA, P. GRIMA-GALLARDO^a, S. DURÁN^a,
M. MUÑOZ^a, M. QUINTERO^a

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

*^aCentro de Estudios de Semiconductores, Departamento de Física, Facultad de Ciencias,
Universidad de Los Andes, Mérida 5101, Venezuela.*

The ternary chalcogenide compound Cu_3NbTe_4 crystallizes in the cubic $P\bar{4}3m$ space group (N° 215), $Z = 1$, with $a = 5.9217(1) \text{ \AA}$, $V = 207.65(1) \text{ \AA}^3$. Its structure was refined from X-ray powder diffraction data using the Rietveld method. This compound is characterized for a three-dimensional arrangement of CuTe_4 and NbTe_4 tetrahedra connected by common edges, and is a new telluride of the $\text{I}_3\text{-V-VI}_4$ family that crystallizes with sulvanite-type structure.

(Received July 30, 2009; accepted 6 August, 2009)

Keywords: Chalcogenide, Synthesis, X-ray powder diffraction, Rietveld refinement

1. Introduction

Ternary chalcogenide compounds of the type $\text{Cu}_3\text{-M-VI}_4$ (M= V, Nb, Ta, VI= S, Se, Te) are interesting materials due principally to their potential applications as electronic devices, especially as light-modulators [1,2]. Several authors have reported the preparation of this type of materials and have associated their structures with that of the mineral sulvanite, Cu_3VS_4 , which crystallizes with cubic symmetry $P\bar{4}3m$ [3,4]. The crystal structures of Cu_3VSe_4 [5], Cu_3NbS_4 [6], Cu_3NbSe_4 [7], Cu_3TaS_4 [8], Cu_3TaSe_4 [9] and Cu_3TaTe_4 [10], has been previously established by means of X-ray diffractometry. In contrast, the telluride derivative Cu_3NbTe_4 has not been characterized so far. In this work, we report the synthesis and structural characterization of this ternary chalcogenide compound from X-ray powder diffraction data using the Rietveld method.

2. Experimental

The sample was synthesized using the melt and annealing technique as described elsewhere [9]. Stoichiometric quantities of Cu, Nb and Te elements with purity of 99.9%, were charged in an evacuated quartz ampoule, which was previously subject to pyrolysis in order to avoid reaction of the starting materials with quartz. Then, the ampoule was sealed under vacuum and the fusion process was carried out inside a furnace (vertical position) heated up to 1500 °C at a rate of 20 °C/hour, with a stop of 48 hours at 450 °C (melting temperature of Te). The ampoule was shaking using a mechanical system during all the heating process in order to guarantee the complete mixing of all the elements, especially Ta, which has a very high melting point (2996 °C). Then, the temperature was gradually raised at the same rate up to 850°C. The ampoule was kept at this temperature for a period of 30 days. Finally, the sample was cooled to room temperature at a rate of 10 °C/hour.

* Corresponding author: gerzon@ula.ve

For the X-ray analysis, a small quantity of the sample was ground mechanically in an agate mortar and pestle. The resulting fine powder was mounted on a zero-background holder covered with a thin layer of petroleum jelly. The X-ray powder diffraction data were collected at 298(1) K, in a Philips PW-1250 diffractometer equipped with an X-ray tube (CuK α radiation: $\lambda = 1.5418$ Å; 40kV, 25mA), a diffracted beam graphite monochromator and a scintillation detector. The specimen was scanned from 10-100° (2 θ), in steps of 0.02° and counting time of 15s/step. Silicon was used as an external standard.

3. Results and discussion

The X-ray diffractogram of Cu₃NbTe₄ shows a single phase. Some peaks with very low intensities cannot be indexed, which could be some impurities or oxides. The measured reflections were completely indexed in a cubic cell by using the program Dicvol04 [11] with the unit cell parameter $a = 5.912(2)$ Å, and figures of merit $M_{18} = 42.6$ [12] and $F_{18} = 25.2$ (0.0143, 50) [13]. As expected, this material is isostructural with the mineral sulvanite Cu₃VS₄, which crystallize in the space group P $\bar{4}$ 3m (N° 215). The Rietveld refinement [14] of the Cu₃NbTe₄ structure was carried out using the Fullprof program [15]. Initial positional parameters were taken from those of Cu₃TaSe₄ [9] and unit cell parameters were those obtained above. The angular dependence of the peak full width at half maximum (FWHM) was described by Caglioti's formula. Peak shapes were described by the 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. The final figures of merit for 14 instrumental and structural variables were: $R_p = 5.4$ %, $R_{wp} = 6.9$ %, $R_{exp} = 5.8$ %, $S = 1.2$ and $\chi^2 = 1.4$ for 4501 step intensities and 33 independent reflections. The final Rietveld plot is shown in Figure 1. Figure 2 shows the unit cell diagram of Cu₃NbTe₄. Unit cell parameters, atomic coordinates, isotropic temperature factor, bond distances are shown in Table 1.

This ternary compound crystallizes in a sulvanite-type structure, which consists of a three-dimensional arrangement of CuTe₄ and NbTe₄ tetrahedra connected by common edges. Figure 2 shows how the tetrahedral leave a channel at the centre, with a shortest Te...Te distances in this cavity of 4.075(5) Å. The tetrahedra containing the Cu cations [mean value Te-Te distances 4.226(5) Å] is lightly shorter than those containing the Nb atoms [mean value Te-Te distances 4.299(5) Å].

Table (1) Unit cell, atomic coordinates and isotropic temperature factors for Cu₃NbTe₄.

Space group P $\bar{4}$ 3m (N° 215), Z = 1, $a = 5.9217(1)$ Å, V = 207.65(1) Å ³							
Atom	Ox.	Site	x	y	z	foc	B (Å ²)
Cu	+1	3d	½	0	0	1	1.0(6)
Nb	+5	1a	0	0	0	1	1.0(6)
Te	-2	4d	0.2567(6)	0.2567(6)	0.2567(6)	1	1.0(6)

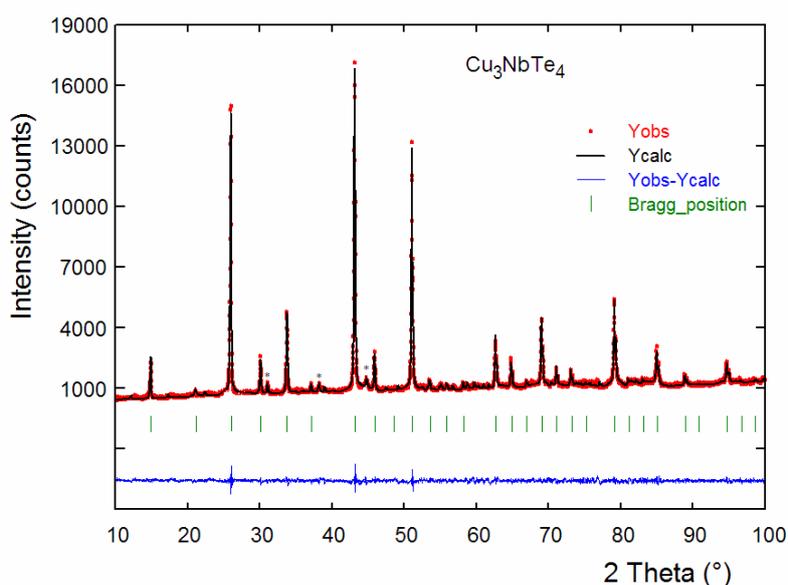


Fig. (1) Final Rietveld plot showing the observed, calculated and difference patterns of Cu_3NbTe_4 . Unindexed peaks are denoted by asterisks (*)

The interatomic distances in the Cu_3NbTe_4 structure, Cu-Te: 2.588(4) Å and Nb-Te: 2.633(4) Å, are shorter than the sum of their respective ionic radii [16]. Both bond distances compare well with the same in some chalcogenide compounds such as: CuNbTe_2 [17], CuInTe_2 [18], CuGaTe_2 [19], Cu_3TaTe_4 [10], Cu_2SnTe_3 [20], Cu_2GeTe_3 [21] and $\text{CuTa}_2\text{InTe}_4$ [22]. Table 4 show a comparison between the unit cell parameters and bond distances for the three phases of the family $\text{Cu}_3\text{-Nb-VI}_4$ with VI = S, Se, Te.

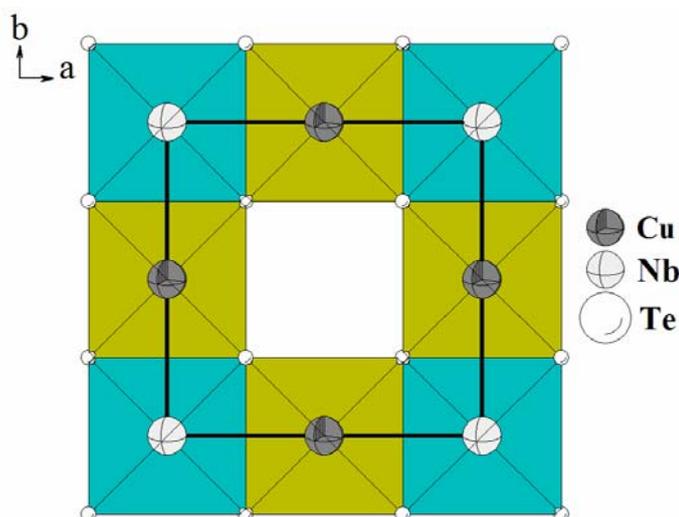


Fig. (2) .Unit cell diagram of Cu_3NbTe_4 with the stacking of the CuTe_4 and NbTe_4 tetrahedra

Table (2) Comparative table of the $\text{Cu}_3\text{-Nb-VI}_4$ chalcogenide compounds ([*] = this work)

	a (Å)	V (Å ³)	Cu-VI (Å)	Nb-VI (Å)	Ref.
Cu_3NbS_4	5.001(6)	166.38(3)	2.359(1)	2.311(1)	[6]
Cu_3NbSe_4	5.638(1)	179.22(6)	2.442(1)	2.443(1)	[7]
Cu_3NbTe_4	5.9217(1)	205.65(1)	2.588(4)	2.633(4)	[*]

4. Conclusions

The crystal structure of the ternary Cu_3NbTe_4 was refined by the Rietveld method using X-ray powder diffraction data. This compound is isostructural with the mineral sylvanite, and consists of a three-dimensional arrangement of CuTe_4 and NbTe_4 tetrahedra connected by common edges.

Acknowledgements

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

References

- [1] M.L. Doublet, S. Remy, F. Lemoigno. *J. Chem. Phys.* **113**, 5879 (2000).
- [2] N. Shannon, R. Joynt. *Sol. State Comm.* **115**, 411 (2000).
- [3] L. Pauling, R. Hultgren. *Z. Kristallogr.* **84**, 204 (1932).
- [4] C. Mujica, G. Carvajal, J. Llanos, O. Wittke. *Z. Kristallogr. NCS* **213**, 12 (1998).
- [5] K.O. Klepp, D. Gurtner. *Z. Kristallogr. NCS* **215**, 4 (2004).
- [6] M. Kars, A. Rebbah, H. Rebbah. *Acta Cryst. E* **61**, I180 (2005).
- [7] Y-J. Lu, J.A. Ibers. *J. Solid State Chem.* **107**, 58 (1993).
- [8] G.E. Delgado, A.J. Mora, S. Durán, M. Muñoz, P. Grima-Gallardo. *Interciencia*. In press.
- [9] G.E. Delgado, A.J. Mora, S. Durán, M. Muñoz, P. Grima-Gallardo. *J. Alloys Comp.* **439**, 346 (2007).
- [10] J. Li, H.-Y. Guo, D.M. Proserpio, A. Sironi. *J. Solid State Chem.* **117**, 247 (1995).
- [11] A. Boultif, D. Louër. *J. Appl. Cryst.* **37**, 724 (2004).
- [12] G.S. Smith, R.L. Snyder. *J. Appl. Cryst.* **12**, 60 (1979).
- [13] P.M. de Wolff. *J. Appl. Cryst.* **1**, 108 (1968).
- [14] H.M. Rietveld. *J. Appl. Cryst.* **2**, 65 (1969).
- [15] J. Rodriguez-Carvajal, Fullprof, version 5.0, LLB, CEA-CNRS, France (2009).
- [16] S.D. Shannon. *Acta Cryst. A* **32**, 751 (1976).
- [17] T. Soergel, M. Jansen. *Sol. Stat. Sci.* **6**, 1259 (2004).
- [18] K.S. Knight. *Mater. Res. Bull.* **27**, 161 (1992).
- [19] M. León, J.M. Merino, J.L. de Vidales, *J. Mater. Sci.* **27**, 4495 (1992).
- [20] G.E. Delgado, A.J. Mora, G. Marcano, C. Rincón, *Cryst. Res. Technol.* **43**, 433 (2008).
- [21] G.E. Delgado, A.J. Mora, M. Pirela, A. Velázquez, M. Villarroel, B.J. Fernández, *Phys. Stat. Sol. (a)* **201**, 2900 (2004).
- [22] G.E. Delgado, A.J. Mora, P. Grima-Gallardo, M. Muñoz, S. Durán, M. Quintero. *Physica B* **403**, 3228 (2008).