STRUCTURAL ANALYSIS OF THE TERNARY Cu_3TaS_4

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

SUMMARY

The ternary Cu_3TaS_4 compound crystallizes in the cubic $P\bar{4}3m$ space group (Nº 215), Z = 1, with ***a*** = 5.5145(1) Å, V = 167.70 (1) $Å^3$. Its structure was refined from X-ray powder diffraction data using the Rietveld method. This compound is isostructural with the sulvanite mineral, Cu_3VS_4, and is characterized for a three-dimensional arrangement of CuS_4 and TaS_4 tetrahedra connected by common edges.

RESUMEN

El compuesto ternario Cu_3TaS_4 cristaliza en el grupo especial cúbico $P\bar{4}3m$ (Nº 215), Z = 1, con ***a*** = 5.5145(1) Å, V = 167.70 (1) $Å^3$. Su estructura se refinó por el método Rietveld utilizando difracción de rayos-X en muestra policiristalinas. Este compuesto es isoestructural con el mineral sulvanita, Cu_3VS_4, y se caracteriza por un arreglo tridimensional de tetraedros CuS_4 y TaS_4 conectados por ejes comunes.

Keywords: Inorganic materials; Semiconductors; Crystal structure; X-ray diffraction.

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.

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

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

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

Introduction

Ternary compounds belonging to the family Cu_3-III-VI_4 (III= V, Nb, Ta, VI= S, Se) are interesting materials due principally to their potential applications as electronic devices, especially as light-modulators (Doublet *et al.*, 2000; Shannon and Joynt, 2000). 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 $P\bar{4}3m$ (Pauling and Hultgren, 1932; Mujica *et al.*, 2005). The crystal structures of Cu_3VSe_4 (Klepp and Gurtner, 2000), Cu_3NbSe_4 (Lu and Ibers, 1993), Cu_3TaSe_4 (Delgado *et al.*, 2007) and Cu_3NbS_4 (Kars *et al.*, 2005) has been previously established by means of X-ray diffractometry. In contrast, for Cu_3TaS_4 only a work was reported without a detailed crystal structure characterization (van Arkel and Crevecoeur, 1963). Thus, in this work, we report the structural analysis of the ternary compound Cu_3TaS_4 from X-ray powder diffraction data using the Rietveld method.

Experimental

The sample was synthesized using the melt and annealing technique as described elsewhere (Delgado *et al.*, 2007). For the X-ray analysis, a small quantity of the sample was ground mechanically in an agate mortar and pestle, and then sieved to 106 μm to get a homogeneous grain size. 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: λ= 1.5418 Å; 40kV, 25mA), a diffracted beam graphite monochromator and a scintillation detector. The specimen was scanned from 10-100° (2θ), in steps of 0.02° and counting time of 150s/step. Silicon was used as an external standard.

Results and discussion

The X-ray diffractogram of Cu_3TaS_4 shows a single phase. The measured reflections were completely indexed in a cubic cell by using the program Dicvol04 (Boultif and Louër, 2004). As expected, this material is isostructural with the mineral sulvanite Cu_3VS_4, which crystallize in the space group $P\bar{4}3m$ (Nº 215). The entire powder diffraction dataset of Cu_3TaS_4 was reviewed by means of the NBS*AIDS program (Mighell *et al*., 1981) with the following results: $\boldsymbol{a}$ = 5.5149(1) Å, V = 167.73(1) Å^3, and figures of merit M_{20} = 394.1 (de Wolff, 1968)] and F_{21} = 172.5 (0.0049, 25) (Smith and Snyder, 1979).

The Rietveld refinement (Rietveld *et al*., 1969) of the Cu_3TaS_4 structure was carried out using the Fullprof program (Rodriguez-Carvajal, 2007). Initial positional parameters were taken from those of Cu_3TaSe_4 (Delgado *et al*., 2007) 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 = 4.4 %, R_{wp} = 6.8 %, R_{exp} = 5.5 %, S = 1.2 and χ^2 = 1.5 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 Cu_3TaS_4. Unit cell parameters, atomic coordinates, isotropic temperature factor, bond distances are shown in Table I.

This ternary compound crystallizes in a sulvanite-type structure, which consists of a three-dimensional arrangement of CuS_4 and TaS_4 tetrahedra connected by common edges. Figure 2 shows how the tetrahedral leave a channel at the centre, with a shortest S…S distances in this cavity of 3.900(4) Å.

The tetrahedra containing the Cu cations [mean value S-S distances 3.900(4) Å] is lightly larger than those containing the Ta atoms [mean value S-S distances 3.860(4) Å].

TABLE I
UNIT CELL, ATOMIC COORDINATES, ISOTROPIC TEMPERATURE FACTORS AND BOND DISTANCES (Å) FOR Cu_3TaS_4.

Space group $P\bar{4}3m$ (Nº 215), Z = 1, *a* = 5.5145(1) Å, V = 167.70(1) $Å^3$							
Atom	Ox.	Site	*x*	*y*	*z*	foc	B ($Å^2$)
Cu	+1	3*d*	½	0	0	1	1.2(5)
Ta	+5	1*a*	0	0	0	1	1.2(5)
S	-2	4*d*	0.2475(5)	0.2475(5)	0.2475(5)	1	1.2(5)
Cu-S: 2.380(3) Å				Ta-S: 2.364(3) Å			

The interatomic distances in the Cu_3TaS_4 structure are shorter than the sum of their respective ionic radii (Shannon, 1976). The Cu-S, 2.380(3) Å, bond distance is lightly larger than the same distance in related Cu_3-III-S_4 compounds Cu_3NbS_4 (2,359 Å) (Kars *et al.*, 2005) and Cu_3VS_4 (2.299 Å) (Mujica *et al.*, 1998). In these compounds, the III-S distance decreases with the ionic radii of the M^{+5} atom (Shannon, 1976), Ta-S 2.364(3) Å, Nb-S 2.311 Å and V-S 2.219 Å.

Conclusions

The crystal structure of the ternary Cu_3TaS_4 was refined by the Rietveld method using X-ray powder diffraction data. This compound is isostructural with the mineral sulvanite, and consists of a three-dimensional arrangement of CuS_4 and TaS_4 tetrahedra connected by common edges.

Acknowledgements

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

REFERENCES

Arkel van AE, Crevecoeur C (1963) Quelques sulfures et seleniures complexes. *J. Less-Comm. Metals 6*: 177-180.

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

Delgado GE, Mora AJ, Durán S, Muñoz M, Grima-Gallardo P (2007) Structural characterization of the ternary compound Cu_3TaSe_4. *J. Alloys Comp. 439*, 346-349.

Doublet ML, Remy S, Lemoigno F (2000) Density functional theory analysis of the local chemical bonds in the periodic tantalum chalcogenides TaX_2 (X = S, Se, Te). *J. Chem. Phys. 113*: 5879-5889.

Kars M, Rebbah A, Rebbah H (2005) Cu_3NbS_4. *Acta Cryst. E61*, I180-I181.

Klepp KO, Gurtner D (2004) Crystal structure of tricopper tetraselenidovanadate (V), Cu_2VSe_4. *Z. Krystallogr. NCS 215*, 4-4.

Lu Y-J, Ibers JA (1993) Synthesis and characterization of Cu_3NbSe_4 and KCu_2TaSe_4. *J. Solid State Chem. 107*, 58-62.

Mighell AD, Hubbard CR, Stalick JK (1981) National Bureau of Standars, Tech. Note 1141.

Mujica C, Carvajal, G, Llanos J, Wittke O. (1998) Redetermination of the crystal structure of copper(I) tetrathiovanadate (sulvanite), Cu_3VS_4. *Z. Kristallogr. NCS* 213, 12-12.

Pauling L, Hultgren R (1932) The crystal structure of sulvanite Cu_3VS_4. *Z. Kristallogr. 84*: 204-212.

PDF-ICDD (2007) Powder Diffraction File (Set 1-57), International Centre for Diffraction Data, 12 Campus Boulevard, Newtown Square, PA, USA.

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.

Shannon N, Joynt R (2000) Interpretation of photoemission spectra of $(TaSe_4)_2I$ as evidence of charge-density-wave fluctuations. *Sol. State Comm. 115*: 411-415.

Shannon SD (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst. A32*: 751-767.

Smith GS, Snyder RL (1979) F_N: A criterion for rating powder diffraction patterns and evaluating the reability of powder pattern indexing. *J. Appl. Cryst. 12*: 60-65.

Wolff de PM (1968) A simplified criterion for the reliability of a powder pattern indexing. *J. Appl. Cryst. 1*: 108-113.

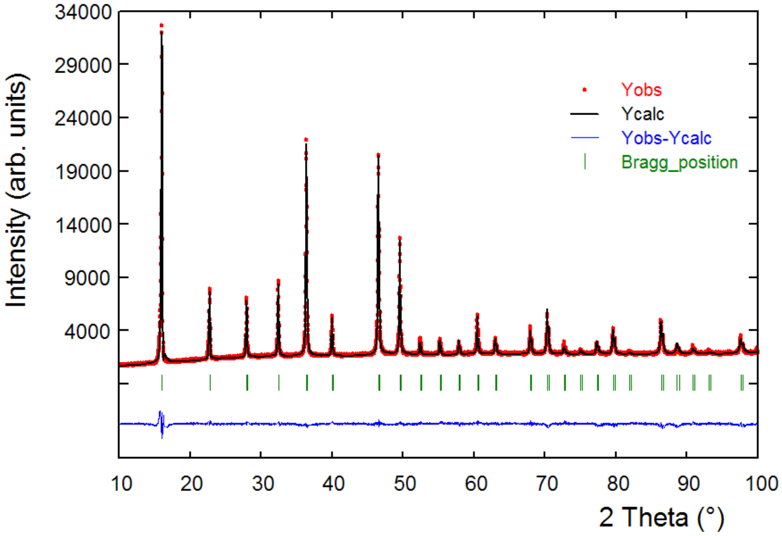

Figure 1. Final Rietveld plot showing the observed, calculated and difference patterns of Cu_3TaS_4.

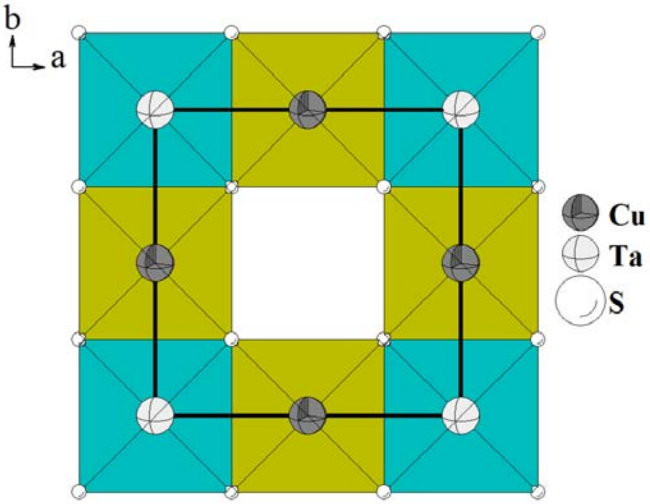

Figure 2. Unit cell diagram of Cu_3TaS_4 show the stacking of the CuS_4 and TaS_4 tetrahedra.