A NEW STRUCTURAL MODIFICATION OF STANNITE

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ABSTRACT

The crystal structure of the phase α-SnCu$_2$FeS$_4$, has been examined by EDX and electron and X-ray difraction techniques. This compound crystallizes in the tetragonal space group P4 (No. 81) with a=c= 541.4 (4) pm, Z=1, and it is a derivative structure of the basic sphalerite structure. The refinement of the structure converged to the final agreement index R(F)=0.060.

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RESUMEN

La estructura cristalina de la fase a-SnCu$_2$FeS$_4$ ha sido analizada por técnicas de difracción de rayos-X, electrones y Energía Dispersiva de Rayos-X. Este compuesto cristaliza en el sistema tetragonal, grupo espacial P4 (No. 81) with a=c=541,4(4) pm, Z=1 y puede ser descrita como una estructura derivada de la esfalerita. El refinamiento final de la estructura convergió a R(F)=0,060.

Palabras Claves: calcogenuros, difracción de electrones, microscopía electrónica, difracción de rayos-X.

INTRODUCTION

Ternary and quaternary chalcogenides have attracted growing interest in recent years due to their physical and chemical properties, which are very promising in important technologies such as nonlinear optics, solar energy conversion, cathodes in electrochemical cells ([1]-[4]).

In previous papers, we have reported on the solid state chemistry of alkali or alkali earth metals copper-iron-chalcogenides ([5]-[8]). As a result of an attempt to prepare substitutional solid solutions in the Sn-Cu-Fe-S system we have found a new structural modification of the stannite SnCu$_2$FeS$_4$ ([9]).

EXPERIMENTAL

Crystal of a-SnCu$_2$FeS$_4$ were obtained by solid state reaction of SnS, Aldrich, (0.37 g) and CuFeS2 (0.92 g). The mixture was heated in a tightly sealed graphite crucible at 1323K in a vertical furnace for 24 h under an Ar atmosphere. The sample was then allowed to cool over a period of 50 h at room temperature. The components of the sample were determined by qualitative XEDS analysis and the crystal structure determination by both electron and X-ray diffraction.

Chalcopyrite was synthesized by sulfurization of a stoichiometric mixture of copper oxide (Baker Reagents) and iron (Merck) with CS$_2$ as sulfiding agents carried by Ar. The mixture was pressed into a pellet and heated at 775 K by 12 h.

Electron diffraction patterns and chemical analyses were obtained using a JEOL JEM 1210 microscope operating at 120kV equipped with a side-entry 60º/30º double tilt GATHAN 646 analytical specimen holder and a link QX2000 EDX element analysis system. The specimen for electron microscopy were prepared by grinding the powder sample, dispersing it in n-butanol and depositing a droplet of this suspension on a carbon coated film supported on an alumina grid.

The data for the crystal structure determination of α-SnCu$_2$FeS$_4$ were obtained with the four circles diffractometer Enraf-Nonius CAD4 using graphite monochromated Mo Kα (λ =71.069 pm) radiation.

The EDX measurements confirm the presence of the four elements, Sn, Cu, Fe, and S in the α-SnCu$_2$FeS$_4$ single crystal. Figure 1 shows and EDX curve for α-SnCu$_2$FeS$_4$ single crystal.
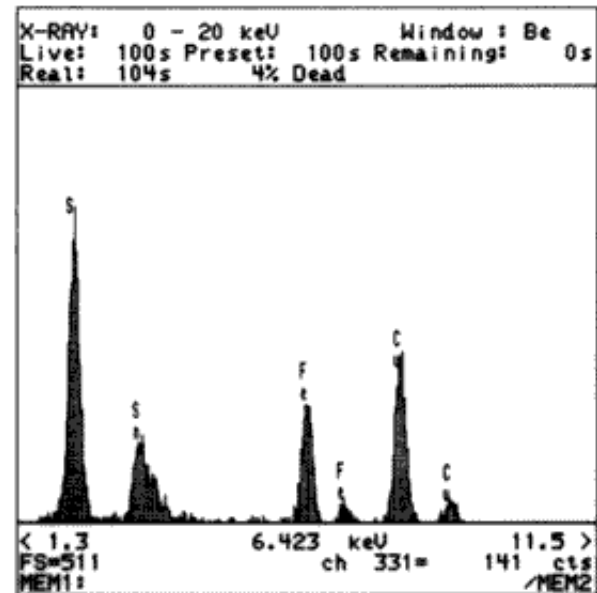
Fig.1. EDX curve for α-SnCu$_2$FeS$_4$ single crystal

Electron diffraction studies of this sample and the subsequent reconstruction of the reciprocal lattice indicates that there not any systematic absences, thus corresponding to an extinction symbol P_ . Figure 2 shows the electron diffraction pattern for α-SnCu$_2$FeS$_4$ single crystal.
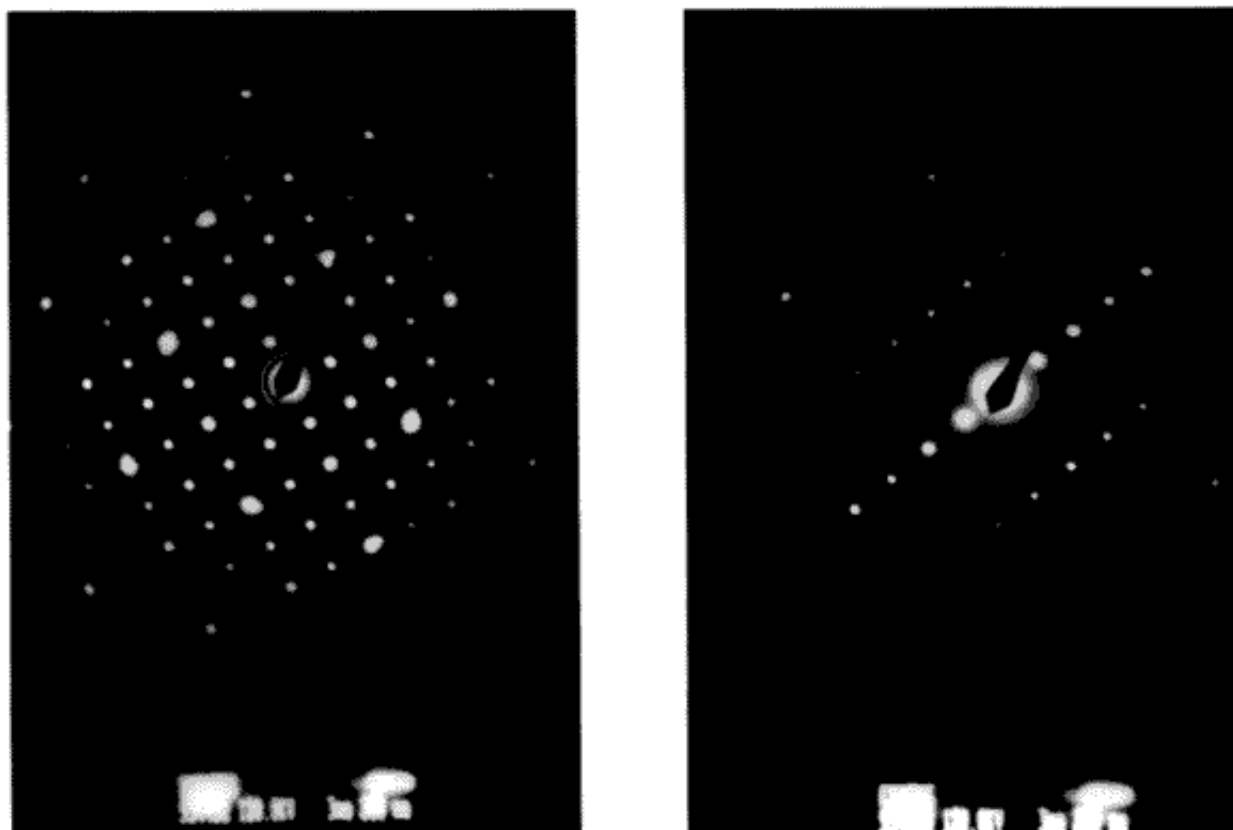
Fig.2. Electron diffraction pattern for a crystal of α-SnCu2FeS4

On the other hand, a crystal of α-SnCu$_2$FeS$_4$ was selected and mounted into a glass capillary for X-ray analysis with a four circles diffractometer. Cell parameters were refined from 25 centered reflections. Intensities were measured in the ω-2θ scan mode and the absorption correction was done empirically by y-scanning.

The structure was solved by the direct method in the space group $\overline{P4}$ and subsequently refined by the full least-squares method using the SHELXL-97 program system (10). The anisotropic refinement converged to R=0.060.

The crystallographic data as well as details of the structure analysis of $\alpha-$ SnCu$_2$FeS$_4$ are given in Table 1.

Table I. Crystallographic Data and Details of the Structure Analysis for α-SnCu$_2$FeS$_4$

Formula	SnCu$_2$FeS$_4$
Crystal system	Tetragonal
Space group	P4 (No. 81)
a (pm)	541.4 (3)
c (pm)	541.4 (3)
Z	1
Volume (10^6 pm^3)	158.61 (5)
μ MoKα (mm^{-1})	22.44
ρ (g cm^3)	5.416
Diffractometer	Enraf Nonius CAD 4
Radiation, monochromator	Mo Kα, highly oriented graphite crystal
Temperature of measurement (K)	298
θ max. (^{o})	full hemisphere
Index range	$-7 \leq h \leq 7$, $-7 \leq k \leq 7$, $-7 \leq l \leq 7$
Measured reflections	1932
Unique reflections	487
Number of refined parameters	20
S= goodness of fit	1.09
Final R[a]	0.060

[a]$R = \Sigma(|Fo| - |Fc|) / \Sigma|Fo|$

RESULT AND DISCUSSION

The refined atomic coordinates, equivalent displacement factors and site occupation are given in Table 2. Selected interatomic distances and angles are given in Table 3. The crystal structure, plotted using the program *CrystalMaker 4.0* (11), is shown in Fig. 3.

Table II. Fractional Atomic Coordinates, and Equivalent Displacement Parameters (in pm2).

Atom	Position	x	y	z	S.O.F.	U_{eq}[a]
Sn	1a	0	0	0	1	26(6)
Cu	2g	0	1/2	0.5003(8)	1	180(7)
Fe	1c	1/2	1/2	0	1	105(7)
S	4h	0.2552(3)	0.2551(3)	0.2554(4)	1	70(8)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Table III. Selected Interatomic Distances (pm) and Angles (°) with Standard Deviation in Parentheses.

Interatomic distances		Bond angles	
Cu-S	232.9 (3) x 2	S-Cu-S	110.6 (3) x 2
	232.7 (3) x 2		107.2 (3) x 2
Fe-S	232.9 (4) x 4	S-Fe-S	110.6 (3) x 2
			107.2 (3) x 2
Sn-S	239.3 (3) x 4	S-Sn-Cu	109.4 (2) x 4

The structure of α-SnCu$_2$FeS$_4$, is a normal tetrahedral compound which may be regarded as a derivative of the basic sphalerite structure. As it is expected for this type of structure, each S atom is surrounded by four cations (two Cu, one Fe and one Sn), and each cation is coordinated by four sulfur atoms. The tetrahedra surrounding the Sn atoms are the most regular.
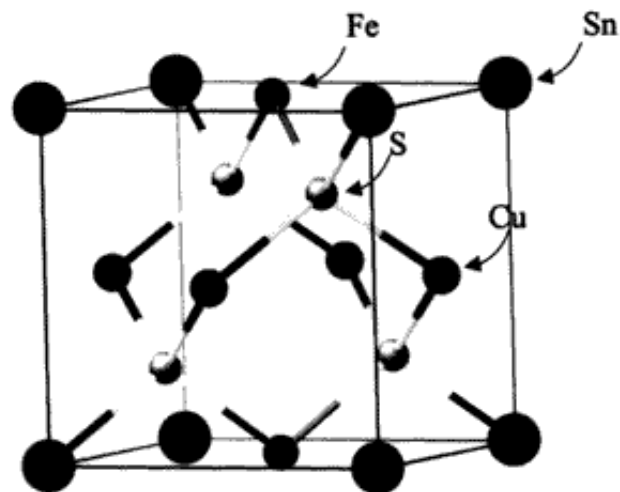
Fig.3. Unit cell of of α-SnCu$_2$FeS$_4$

Taking into account the metric of the unit cell of α-SnCu$_2$FeS$_4$ (a=b=c=541.3 pm) , the structure was first intended to solve in the following space groups: Pm3$^-$ (No. 221), P43$^-$m(No. 215), P432 (No. 207), Pm 3$^-$ (No. 200), and P23 (No. 195). All results shown either six-fold coordination for the copper, iron, tin, and sulfur atoms or very high residual factors.

Finally, is known that the symmorphic space group for the sphalerite structure is $T_d{}^2$ (F4 3m), a study of the subgroups of the crystallographic Td (4 3m) point group indicated that the lower possible symmetry was 4. Due to the electron diffraction results verify that there not any systematic absences, the structure was solved in the space group P4$^-$.

ACKNOWLEDMENTS

REFERENCES

1. R.L. Glitzendanner, and F.L Di Salvo, Inorg. Chem. 35, 2623 (1996)   [Links]

2. R.A. Smith, Semiconductors, Cambridge University Press,Cambridge, 1978, p. 438   [Links]

3. M. Oledzka, K.V. Ramanujachary, and M. Greenblatt, Mater. Res. Bull. 33, 855 (1998)

4. P. Wu, M.A. Pell, J.A. Cody, and J.A Ibers, J. Alloys and Compounds, 224, 199 (1995)   [Links]

5. C. Mujica, J. Páez, and J. Llanos, Mater Res. Bull., 29, 263 (1994).   [Links]

6. J. Llanos, P. Valenzuela, C. Mujica, A. Buljan, and R. Ramírez, J. Solid State Chem., 122, 31 (1996).   [Links]

7. J. Llanos, C. Mujica, O. Wittke, P. Gómez-Romero, and R: Ramírez, J. Solid State Chem.,128, 62 (1997)   [Links]

8. R.Ramírez, A. Bulján, J.C. Noya , and J. Llanos. Chem. Phys.,189, 585 (1994).   [Links]

9. G.M. Sheldrick, SHELXS-97, SHELXL-97, University of Göttingen, 1997   [Links]

10. S.R. Hall, J.T. Szymanski, and J. M. Stewart, Can. Mineral. 16, 147 (1978)   [Links]

11. D.C. Palmer, CrystalMaker 4.0. An interactive crystallography program for Macintosh, 1999   [Links]