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Synthesis and characterization of a new copper iron telluride

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Abstract

$(CuFe)_{2.2}Te_2$ (tetragonal, space group *P4/nmm* (No. 129), $a = 398.9$ (1), $c = 609.4(3)$ pm, $Z = 1$) crystallizes in a defect structure of the Cu_2Sb type. Tellurium atoms form a tetragonally deformed fcc-like lattice in which one-half of the tetrahedral sites are statistically occupied by copper and iron atoms in the ratio 1:1. The remaining iron atoms are randomly distributed in the square pyramidal or pseudo-octahedral sites. XPS analysis reveals the presence of one valence state for copper, Cu(I), whereas iron exists as Fe(II) and Fe(III). The synthesis of $(CuFe)_{2.2}Te_2$ was performed from the elements at a final temperature of 973 K.

Keywords: Copper iron telluride; Synthesis

1. Introduction

The I–III–VI_2 ternary semiconductors have attracted a lot of interest in recent years because of their optical, electrical and magnetic properties [1–3]. In particular, the copper compounds have emerged as useful materials for use as detectors, photovoltaic cells and photoelectrochemical devices.

Our investigations have been centering on the chemistry of copper–iron sulfide and selenide for use as cathodic materials in secondary batteries. We have been successful in synthesizing new phases where Li, Na and K are inserted in the above-mentioned chalcogenides [4–7]. Recently, we extended our work into the tellurides, and several attempts have been made to obtain phases such as $Li_xCuFeTe_2$.

However, $CuFeS_2$ and $CuFeSe_2$ crystallize in the zinc-blende-related chalcopyrite structure and sulvanite-derivative structure, respectively [8]. Since no detailed structural and stoichiometric study of copper–iron tellurides has been reported as yet, the synthesis and crystal structure determination of $(CuFe)_{2.2}Te_2$ was undertaken in the present paper.

2. Experimental

Mixtures of 1.91 g (0.03 mol) of Cu, 1.71 g (0.03 mol) of Fe and 7.66 g (0.06 mol) of Te were heated at 623 K in vacuum-sealed glass tubes, over a period of 24 h. The reaction mixture was then finely ground and heated at 973 K for 48 h in vacuum-sealed silica tubes. The sample was then allowed to cool down to room temperature over a period of three days. The reaction product (EDAX: Cu, Fe, Te) consisted of golden thin platelets. Quantitative elemental analysis gave a composition of $(CuFe)_{2.2}Te_2$ (Cu, 17.87%; Fe, 16.24%; Te, 65.24%). The nature of this material was established by a single-crystal X-ray diffraction study.

3. Structural analysis

Intensity data for the crystal structure were collected on a Syntex P3 diffractometer (Mo Kα, graphite monochromator). Cell parameters have been refined from 22 centered reflections. Intensities were measured in the ω–2θ scan mode and the absorption correction was done empirically by Ψ scanning. Details of the structure analysis appear in Table 1. The program systems SHELXS and SHELX were used for all calculations [9–10]. Bond distances and angles were calculated using the program ORFFE [11].

Final atomic coordinates, anisotropic displacement parameters and site occupation factors are listed in Table 2. Selected interatomic distances and bond angles are given in Table 3.

4. X-Ray photoelectron spectral analysis

The X-ray photoelectron spectral (XPS) studies were carried out to examine the oxidation states of the

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Table 1
Crystallographic data and details of the structure analysis for $(CuFe)_{2.2}Te_2$

Crystal system	Tetragonal
Space group	*P4/nmm* (No. 129)
a (pm)	398.9(1)
c (pm)	609.4(3)
Z	1
Volume (10^6 pm^3)	96.97(3)
μ (Mo Kα cm^{-1})	312.3
Diffractometer	Syntex P3
Radiation, monochromator	Mo Kα (71.073 pm), graphite
Scan mode	ω 2θ
2θ max.	45
Measured intensities	274
Unique reflections	89
Number of refined parameters	13
Final R, $R(w)$	0.049, 0.048

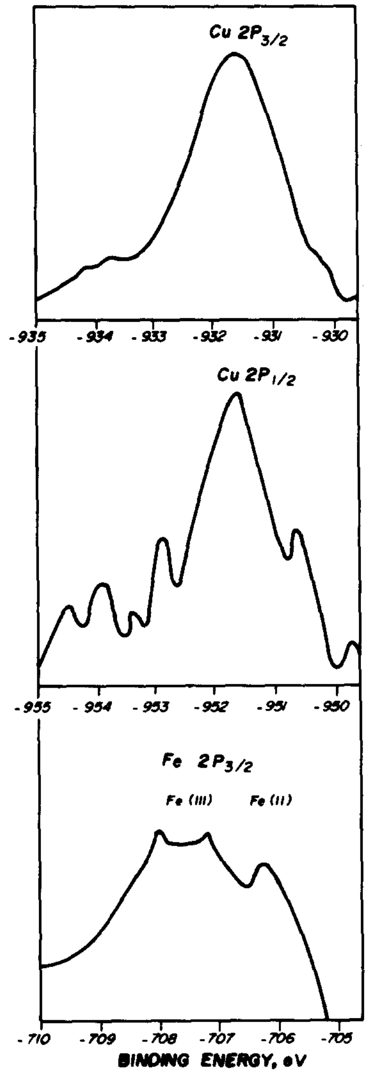

Fig. 1. XPS spectra of Cu(2p) and Fe(2p) peaks of $(CuFe)_{2.2}Te_2$.

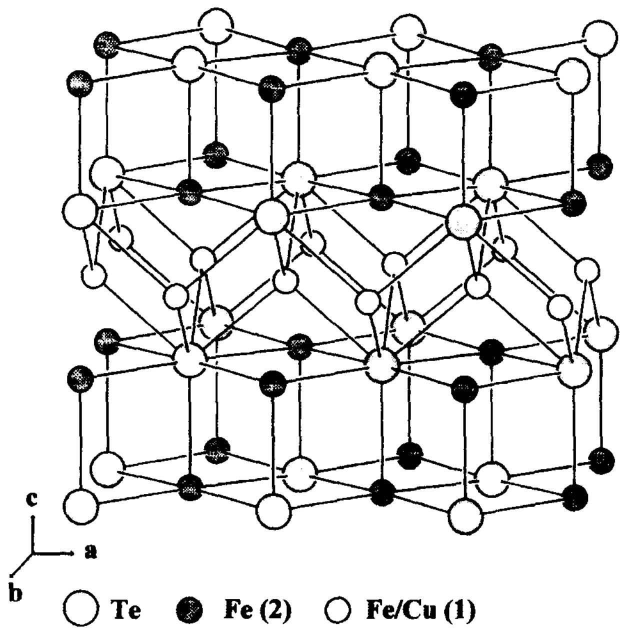

Fig. 2. Projection of the $(CuFe)_{2.2}Te_2$ structure along the c axis.

transition metals in $(CuFe)_{2.2}Te_2$. The XPS spectra of the copper–iron telluride for Cu(2p) and Fe(2p) are shown in Fig. 1. The observed value of the binding energies for Cu($2p_{3/2}$) and Fe($2p_{3/2}$) are 931.7, 707.7 and 706.2 eV respectively. The full width at half maximum calculated for Cu($2p_{3/2}$) is 1.8 eV. This value is in good agreement with the reported value [12], indicating presence of Cu(I). The photoelectron spectroscopic spectrum for Fe(2p), however, indicates that the iron is in both the 2^+ and 3^+ states.

5. Discussion

The structure of $(CuFe)_{2.2}Te_2$ is closed related to the defective Cu_2Sb or the filled PbO structure, based on a tetragonally deformed fcc-like lattice in which half of the tetrahedral interstices are equally and randomly occupied by copper and iron, forming a single layer per unit cell. The refined occupancy (1.06(3)) for an iron atom in the position 2a is consistent with a 50% occupancy for both copper and iron. The remaining iron atoms occupy, partially and ramdomly, two layers of the square-pyramidal or pseudo-octahedral sites, a fact which is consistent with iron in oxidation state III. Fig. 2 shows a projection of $(CuFe)_{2.2}Te_2$ along the c axis.

The geometry around the Cu/Fe atoms is distorted tetrahedral, with equivalent bond lengths from the transition metal atom to all four tellurium atoms. The distances are 261.2(2) pm, which are in the normal range of Cu/Fe–Te distances and the angles are 114.9(4) and 99.09(8)°.

Table 2
Final atomic coordinates, equivalent and anisotropic displacement parameters (pm^2). Standard deviation given in parentheses. $U_{12} = U_{13} = U_{23} = 0$

Atom	Positions	x	y	z	S.O.F.	U_{eq}	U_{11}	U_{22}	U_{33}
Fe1 [a]	2a	0	0	0	1.06(3)	329(12)	379(19)	U_{11}	229(24)
Fe2 [a]	2c	0	$\frac{1}{2}$	0.289(4)	0.22(4)	374(59)	430(97)	U_{11}	262(112)
Te	2c	0	$\frac{1}{2}$	0.7209(3)	1	319(5)	370(9)	U_{11}	215(10)

[a] These positions were calculated using scattering factor for iron.

Table 3
Selected interatomic distances (pm) and selected angles (°) with standard deviation given in parentheses

Interatomic distance		Bond angles	
Fe1–Te	262.1(2)×4	Te–Fe1–Te	114.90(4)×4
Fe2–Te	282.1(7)×4		99.09(8)×2
	263.0(2)	Te–Fe2–Te	91.2(5)×4
			88.8(5)×4

The remaining iron atoms have a square-pyramidal geometry where the apex of the pyramid is located slightly off-center. Fe2–Te distances range from 263.0(2) to 282.1(7) pm. Short Cu/Fe–Cu/Fe contacts are also observed in this compound, ranging from 282.1(5) pm for Cu/Fe1–Cu/Fe1 to 266.0(2) pm for Cu/Fe1–Fe2.

More work is in progress in order to prepare phases such as $M_xCu_yFe_zTe_2$, where M = Li, Na or K.

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