

Evidence of a new ordered vacancy crystal structure in the compound $\text{Cu}_3\text{In}_7\text{Te}_{12}$

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ABSTRACT

The crystal structure of the ordered vacancy compound (OVC) $\text{Cu}_3\text{In}_7\text{Te}_{12}$ is analyzed using powder X-ray diffraction data. It is found that this OVC crystallizes with a chalcopyrite-related structure, in the tetragonal space group $P\bar{4}2c$ (N° 112), with unit cell parameters and volume $a = 6.1720(2)$ Å, $c = 12.3597(8)$ Å, and $V = 470.83(4)$ Å³. The Rietveld refinement of 28 instrumental and structural parameters led to $R_p = 9.27$ %, $R_{wp} = 10.30$ %, $R_{exp} = 6.95$ % and $S = 1.48$, for 4501 step intensities and 130 independent reflections, respectively. This compound is isostructural with $\text{Cu}_3\text{In}_7\text{Se}_{12}$, and has a defect adamantane structure.

Keywords: semiconductors, ordered vacancy compounds, crystal structure, X-ray diffraction, Rietveld.

1. INTRODUCTION

The ternary compound CuInTe_2 , belonging to the I-III-VI₂ family of chalcopyrite semiconductors, crystallize in the tetragonal space group $I\bar{4}2d$ with unit cell parameters $a = 6.1944(20)$ and $c = 12.4157(40)$ Å [1]. This material has been found to be a suitable material for thermoelectric (TE) applications [2-5]. Hence, it is also expected that ordered vacancy compounds (OVC's) of the Cu-In-Te system [6], which can be described as normal tetrahedral structures with a certain fixed number of unoccupied structure sites [7] and can be generated through the formula $\text{Cu}_{n-3}\text{In}_{n+1}\text{Te}_{2n}$, such as CuIn_5Te_8 ($n = 4$), CuIn_3Te_5 ($n = 5$), $\text{Cu}_3\text{In}_7\text{Te}_{12}$ ($n = 6$), $\text{Cu}_5\text{In}_9\text{Te}_{16}$ ($n = 8$), and $\text{Cu}_3\text{In}_5\text{Te}_9$ ($n = 9$) [8], could also be employed for TE applications [9]. This is because most of them have low carrier concentrations [10], a tetragonal distortion parameter η ($\eta = c/2a$) close to unity [6], and also an energy gap less than about 1.2 eV [11], which are some of the conditions required to achieve promising materials for TE applications [2]. As regard to the crystal structure of these Cu-In-Te OVC's, although it has been suggested that most of them crystallize in tetragonal chalcopyrite-related structures [4,10,12-14], their actual crystal structures and corresponding space groups have not yet been established, as evidenced by a search in the Inorganic Crystal Structure Database (ICSD) [15].

Hence, in the present work, the crystal structure of $\text{Cu}_3\text{In}_7\text{Te}_{12}$ (or $\text{Cu}_3\text{In}_7[\]_2\text{Te}_{12}$, where $[]$ represents the cationic vacancy) is established from the Rietveld refinement analysis of powder X-ray diffraction data.

2. MATERIALS AND METHODS

Polycrystalline samples of $\text{Cu}_3\text{In}_7\text{Te}_{12}$ used in this study were prepared from the melt by the vertical Bridgman-Stockbarger technique in a multiple zone furnace. Stoichiometric mixture of highly pure components of Cu, In and Te (99.999 %) were introduced in a quartz ampoule sealed under vacuum ($\sim 10^{-3}$ Pa). Initially, the ampoule was heated from room temperature to 1170 K at a rate of 20 K/h. The molten mixture was then heated to 1370 K at 10 K/h and kept at this temperature for 12 h. To assure a homogeneous mixing of the melt, the ampoule was carefully agitated periodically. It was later cooled at 10 K/h to 1090 K, and at 5 K/h to 800 K. In order to guarantee the equilibrium condition of the synthesized material, the ingot was annealed at

this temperature for 120 h. The furnace was then turned off and the ingot cooled down to the room temperature.

For the X-ray diffraction analysis, a small quantity of the sample, cut from the ingot, was ground mechanically in an agate mortar and pestle. The resulting fine powder was mounted on a flat zero-background holder covered with a thin layer of petroleum jelly. The powder X-ray diffraction data was collected at 293(1) K, in θ/θ reflection mode using a Siemens D5005 diffractometer equipped with an X-ray tube (CuK α radiation: $\lambda = 1.5418$ Å; 40kV, 30mA). A fixed aperture and divergence slit of 1 mm, a 1 mm monochromator slit, and a 0.1 mm detector slit, were used. The specimen was scanned from 10° - 100° 2θ , with a step size of 0.02° and counting time of 10s. Quartz was used as an external standard. The Bruker AXS analytical software was used to establish the positions of the peaks.

3. RESULTS AND DISCUSSION

Figure 1 shows the resulting powder X-ray diffractogram for $\text{Cu}_3\text{In}_7\text{Te}_{12}$. The 20 first peak positions were indexed using the program Dicvol04 [16], which gave a unique solution in a tetragonal cell. Lack of systematic absences (hkl : $h+k+l$), indicates a primitive type lattice. In addition, the condition hhl : $l = 2n+1$ suggests the extension symbol $P\bar{4}2c$. A revision of the diffraction lines, taking into account the sample composition, unit cell parameters, and lattice-type, suggests that this material is isostructural with $\text{Cu}_3\text{In}_7\text{Se}_{12}$. This is the first compound with the $\text{I}_3\text{-III}_7\text{-[]}_2\text{-VI}_{12}$ formula which has been reported to crystallize in a tetragonal structure with space group $P\bar{4}2c$ (N° 112) [17]. The resulting X-ray powder diffraction data for $\text{Cu}_3\text{In}_7\text{Te}_{12}$ will be submitted to the Powder Diffraction File of the International Centre for Diffraction Data (ICDD) [18].

The Rietveld refinement [19] of the whole diffraction pattern was carried out using the Fullprof program [20, 21], with the unit cell parameters found in the indexing. For the refinement of $\text{Cu}_3\text{In}_7\text{Te}_{12}$, the atomic coordinates of the compound $\text{Cu}_3\text{In}_7\text{Se}_{12}$ [17], were used as initial model, with the cation distribution shown in Table III. The angular dependence of the peak full width at half maximum (FWHM), was described by the Cagliotti's formula [22]. Peak shapes were described by the parameterized Thompson-Cox-Hastings pseudo-Voigt profile function [23]. 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 1 shows the observed, calculated, and difference profile for the final cycle of refinement. Atomic coordinates, isotropic temperature factor, bond distances, and angles are shown in Table 2. This Table also shows the Bond Valence Sum (BVS) [24,25] results for $\text{Cu}_3\text{In}_7\text{Te}_{12}$, indicating that the oxidation state for each ion is in good agreement with the expected formal oxidation state of Cu^{1+} , In^{3+} and Te^{2-} ions.

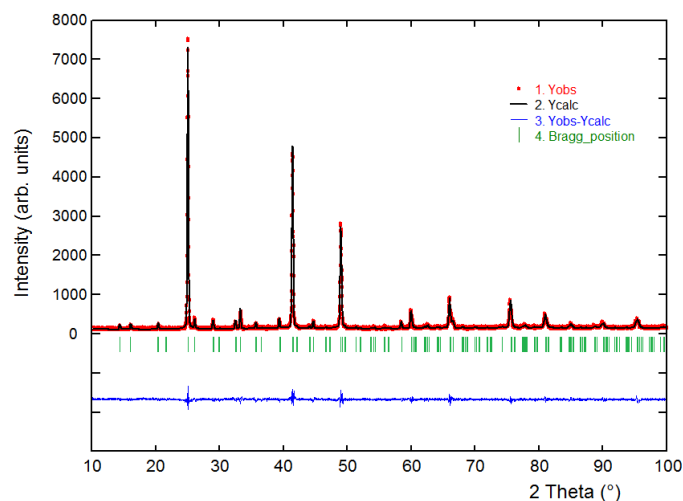


Figure 1: Rietveld refinement plot for $\text{Cu}_3\text{In}_7\text{Te}_{12}$. The lower trace is the difference curve between observed and calculated patterns. The Bragg reflections are indicated by vertical bars.

From refinement by the Rietveld method by using powder X-ray diffraction data, it has been found that this material crystallizes in the tetragonal space group $P\bar{4}2c$, with a chalcopyrite-related structure. This

consists of a three-dimensional arrangement of distorted CuTe_4 and InTe_4 tetrahedra connected by common faces. In this structure, each Te atom is coordinated by four cations (one Cu and three In) located at the corners of a slightly distorted tetrahedron. In the same way, each cation is tetrahedrally bonded to four anions. This array is expected for adamantane compounds [7].

The Cu-Te and In-Te bond distances for $\text{Cu}_3\text{In}_7\text{Te}_{12}$ here obtained, are in good agreement with those reported in the ICSD database [15] for other adamantane structure compounds such as CuInTe_2 [26], AgIn_5Te_8 [27], $\text{CuTa}_2\text{InTe}_4$ [28], Cu_3NbTe_4 [29], AgInTe_2 [1] and $\text{CuCo}_2\text{InTe}_4$ and $\text{CuNi}_2\text{InTe}_4$ [30].

Table 1: Rietveld refinement results for $\text{Cu}_3\text{In}_7\text{Te}_{12}$.

molecular formula	$\text{Cu}_3\text{In}_7\text{Te}_{12}$	wavelength (CuK_α)	1.5418 Å
molecular weight (g/mol)	1683.7	data range 2θ (°)	10-100
a (Å)	6.1720(2)	step size 2θ (°)	0.02
c (Å)	12.3597(8)	counting time (s)	10
c/a	2.00	step intensities	4501
V (Å ³)	470.83(4)	independent reflections	130
Z	0.667	R_p (%)	9.27
crystal system	tetragonal	R_{wp} (%)	10.30
space group	$P\bar{4}2c$ (N° 112)	R_{exp} (%)	6.95
d_{calc} (g/cm ⁻³)	5.99	R_B (%)	6.10
temperature (K)	298(1)	S	1.48

$$R_{exp} = 100 [(N-P+C) / \sum_w (y_{obs}^2)]^{1/2}$$

$$R_p = 100 \sum |y_{obs} - y_{calc}| / \sum |y_{obs}|$$

$$R_{wp} = 100 [\sum_w |y_{obs} - y_{calc}|^2 / \sum_w |y_{obs}|^2]^{1/2}$$

$$R_B = 100 \sum_k |I_k - Ic_k| / \sum_k |I_k|$$

$$S = [R_{wp} / R_{exp}]$$

$N-P+C$ is the number of degrees of freedom

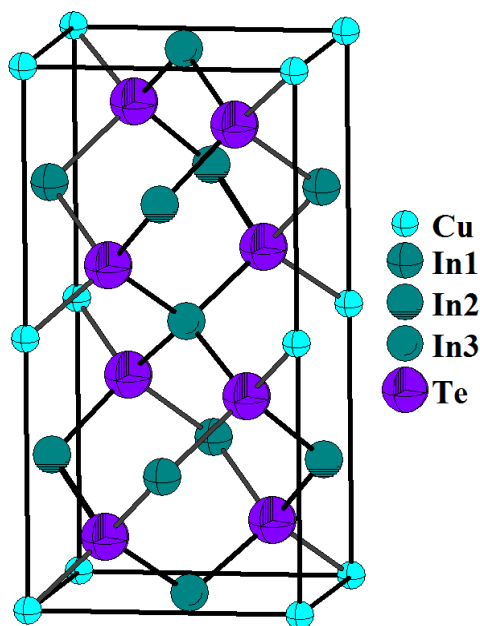


Figure 2: Unit cell diagram for the ordered vacancy compound $\text{Cu}_3\text{In}_7\text{Te}_{12}$.

Table 2: Atomic coordinates, isotropic temperature factors, bond distances (Å) and angles (°) for $\text{Cu}_3\text{In}_7\text{Te}_{12}$, derived from the Rietveld refinement. Bond valence sum (BVS) are also showed.

Atom	Ox.	BVS	Site	x	y	z	foc	B (Å ²)
Cu	+1	1.3	2e	0	0	0	1	0.4(3)
[]			2a	0	0	¼	1	
In1			2b	½	0	¼	1	0.4(3)
In2	+3	3.3	2d	0	½	¼	1	0.4(3)
In3			2f	½	½	0	⅓	0.4(3)
Te	-2	2.4	8n	0.223(1)	0.261(1)	0.118(1)	1	0.4(3)
Cu-Se ⁱ	2.572(9)		In1-Te ⁱⁱⁱ	2.860(9)	In2-Te ⁱⁱ	2.595(9)	In3-Te ^{iv}	2.688(9)

 Symmetry codes: ⁽ⁱ⁾ y, -x, -z; ⁽ⁱⁱ⁾ 1-x, 1-y, z; ⁽ⁱⁱⁱ⁾ x, -y, 0.5-z; ^(iv) -x, y, 0.5-z.

 Bond valence sum (BVS): $V_i = \sum_j \exp [(R_o - R_{ij}) / b]$, $b = 0.37 \text{ \AA}$, $r_o(\text{Cu-Te}) = 2.27 \text{ \AA}$, $(\text{In-Te}) = 2.69 \text{ \AA}$

4. CONCLUSIONS

In conclusion, it is established that the ordered vacancy compound $\text{Cu}_3\text{In}_7\text{Te}_{12}$ (or $\text{Cu}_3\text{In}_{72}\text{Te}_{12}$) crystallizes with a chalcopyrite-related structure in the tetragonal space group $P\bar{4}2c$, and represents a new semiconductor with formula $\text{I}_3\text{-III}_7\text{-}[\]_2\text{-VI}_{12}$.

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