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# Synthesis and crystal structure of $Cu_4TiS_4$: a novel chalcogenide with tetrahedrally coordinated titanium

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**Abstract**

Dark red single crystals of $Cu_4TiS_4$ were prepared by reacting an intimate mixture of $Cu_2S$, Ti and S at 500°C. $Cu_4TiS_4$ is tetragonal, space group $I\bar{4}2m$ with $a = 5.448(1)$ Å, $c = 10.565(2)$ Å, $Z = 2$. The crystal structure is of a new type. It was determined from diffractometer data and refined to a conventional $R$ of 0.024 for 132 $F_o$s and 17 variables. The crystal structure is based on a cubic close packing of chalcogen with Cu and Ti in tetrahedral interstices. This results in a three-dimensional framework of vertex sharing $CuS_4$ tetrahedra which are connected with the almost regular $TiS_4$ tetrahedra through common edges. The bond lengths are $d(\text{Ti–S}) = 2.278$ Å and $d(\text{Cu–S}) = 2.333$ to 2.351 Å.

*Keywords:* Preparation; Crystal structure; Sulphides; Copper thiotitanate

## 1. Introduction

Structural information on intermediate phases in the ternary system Cu–Ti–S is scarce, the only compounds known so far being the thiospinel $CuTi_2S_4$ [1] and its defect variant $Cu_xTi_2S_4$ [2]. $CuTi_2S_4$ has been shown to undergo a phase transition to an NiAs-type structure at pressures above 50 kbar [3].

Recent investigations of the quaternary systems Tl(I)–Cu(I)–T(IV)–Q (T = Zr, Hf; Q = S, Se) have revealed the existence of a number of intermediate phases which, in a partial ionic description, are characterized by the formation of layered complex anions, formed by $T^{IV}$ centred octahedra and Cu centred tetrahedra [4,5] with $Tl^+$ as counter ions separating the layers. Interestingly the structural chemistry revealed in these phases finds no correspondence in the homologous titanium quaternaries. The reason for this is the unexpected preference for tetrahedral coordination of the tetravalent titanium observed in the intermediate phases of these systems [6]. This preference has already become manifest in the new ternary compound $Cu_4TiS_4$, which will be presented below as a first result of our investigations in this field.

## 2. Experimental

### 2.1. Synthesis

Starting materials: Ti powder 99.9%, Cu powder 99.99%, S 99.99%, Tl 99.9% (all supplied by Alfa Ventron). The following master alloys were prepared: $Cu_2S$ was synthesized by reacting a stoichiometric mixture of the elements, followed by annealing at 300°C; $Tl_2S$ was prepared from a melt with stoichiometric composition by slow cooling. For their preparation all samples were sealed into silica tubes under a vacuum of $10^{-2}$ Pa.

Single crystals of $Cu_4TiS_4$ were originally obtained by slow cooling of a melt of nominal composition $TlCu_3TiS_4$ from 870°C to ambient temperature. The major part of the crushed sample consisted of coarse plate-like crystals which displayed metallic lustre in the reflected and a deep red colour in the transmitted light. This and the absence of metallic conductivity indicated that this new phase was a valence compound. In the course of the crystal structure analysis it turned out that this compound was actually a ternary phase. The proposed composition $Cu_4TiS_4$ was finally

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corroborated by a semi-quantitative energy dispersive X-ray microprobe analysis (Tracor TN2000) operated on a Jeol 2400 scanning electron microscope. This resulted in a Cu/Ti/S ratio of 3.8:1:4.2, which is close to the stoichiometry expected from the structure determination. In addition, the analysis also confirmed the absence of any traces of thallium.

The preparation of bulk single phase samples of $Cu_4TiS_4$, however, turned out to be rather difficult because the compound undergoes decomposition at temperatures above 645°C through a presumably peritectoid reaction. Prolonged heating of powdered mixtures of $Cu_2S$, Ti and S above this temperature led to a practically irreversible segregation of agglomerations of elemental Cu which, because of sluggish diffusion, could not be brought back into equilibrium at lower temperatures. The powder diagrams of samples which had been annealed at 700°C and then cooled slowly did not show any diffraction lines due to $Cu_4TiS_4$.

The synthesis of single phase material was finally accomplished by annealing 3 g of a cold pressed stoichiometric mixture of Cu, Ti and S for two months at 500°C, crushing and reannealing for another two weeks. The Guinier diagram (Cu $K\alpha_1$ radiation, $\lambda = 1.54056$ Å) of this sample was in excellent agreement with the theoretical powder diffraction pattern of $Cu_4TiS_4$ calculated and refined by the `finax` program [7]. Attempts to synthesize homologous compounds in the Cu–Ti–Se and Cu–Ti–Te systems were without positive results.

### 2.2. Structure determination

Preliminary roentgenographical investigations by Weissenberg techniques revealed a body centred tetragonal unit cell, Laue group $4/mmm$. Apart from Bravais centring no other systematic extinctions occurred which led to $I422$, $I4mm$, $I\bar{4}m2$, $I\bar{4}2m$ and $I4/mmm$ as possible space groups.

For the collection of intensity data a prismatic crystal with dimensions 0.075 × 0.050 × 0.040 $mm^3$ was mounted on a Kappa-diffractometer (Enraf–Nonius CAD4). The data collection was performed at ambient temperature (21°C) with conventional background–peak–background scans ($\omega$–$2\theta$ scan mode, scan width $0.80° + 0.35° \tan\theta$, maximum scan time 120 s) over the angular range $2° \leq 2\theta \leq 56°$. Final cell parameters were determined from a least squares refinement of the setting angles ($36° \leq 2\theta \leq 44°$) of 24 reflections carefully centred at four different diffractometer settings. Crystal data and details of the structure refinement are given in Table 1.

Table 1
Crystallographic data for $Cu_4TiS_4$

| | |
|---|---|
| Pearson symbol | $tI18$ |
| $a$ (Å) | 5.448(1) |
| $c$ (Å) | 10.565(2) |
| Space group | $I\bar{4}2m$ (No. 121) |
| $Z$ | 2 |
| $V$ ($Å^3$) | 313.6 |
| $d_x$ (g $cm^{-3}$) | 4.56 |
| $M_r$ | 430.32 |
| $\mu$ (Mo $K\alpha$) ($cm^{-1}$) | 157.67 |
| $F(000)$ | 404 |
| *Structural refinement* | |
| Unique reflections | 138 |
| Observed reflections | $132 \geq 3.0\sigma(F_o)^2$ |
| Variables | 17 |
| $R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$ | 0.024 |
| $R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$ | 0.023 |
| $w = [\sigma(F_o^2)^2 + (0.005F_o^2)^2]^{-1/2}$ | |
| Residual electron density (e $Å^{-3}$) | 0.75 |

The crystal structure was solved by direct methods in the space group $I\bar{4}2m$ (`multan` 82) [8]. While the statistics of the normalized structure factors failed to give an unambiguous indication for the presence of a symmetry centre, attempts to solve and refine the crystal structure in the centrosymmetric space group $I4/mmm$ were unsuccessful. A (from a crystal chemical viewpoint) reasonable model with an ordered occupation of the metal sites could only be refined in the acentric space group $I\bar{4}2m$, leading to the formula $Cu_4TiS_4$. In the final refinements an isotropic correction for secondary extinction was included. The final shift over error ratio was less than 0.005. A difference Fourier map calculated at this stage of refinement revealed no physically significant peaks.

All calculations were performed on a DEC Microvax 3520 computer using programs of the MolEN crystallographic software package [9]. Atomic scattering factors for the neutral atoms and coefficients for anomalous dispersion effects were taken from the *International Tables for X-Ray Crystallography* [10,11]. Absorption effects were neglected ($\mu R < 0.8$). The final positional parameters and anisotropic thermal parameters are listed in Tables 2 and 3 respectively. Structure factor tables have been deposited with the Fachinformationszentrum Karlsruhe, Eggenstein-Leopoldshafen 2, D-76344 Karlsruhe, Germany under CSD No. 59077.

Table 2
Positional and equivalent isotropic thermal parameters for $Cu_4TiS_4$

| Atom | W.P. | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|---|
| Cu(1) | 4e | 0.500 | 0.500 | 0.2396(1) | 1.30(1) |
| Cu(2) | 4c | 0.500 | 0.000 | 0.500 | 1.24(2) |
| Ti | 2a | 0.500 | 0.500 | 0.500 | 0.43(2) |
| S | 8i | 0.2415(3) | 0.2415(3) | 0.1245(1) | 0.83(2) |

$B_{eq} = (B_{11} + B_{22} + B_{33})/3$.

Table 3
Anisotropic thermal parameters ($Å^2$) for $Cu_4TiS_4$

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Cu(1) | 0.0218(3) | 0.0218(3) | 0.0155(4) | −0.004(1) | 0 | 0 |
| Cu(2) | 0.0178(5) | 0.0058(5) | 0.0234(4) | 0 | 0 | 0 |
| Ti | 0.0047(6) | 0.0047(6) | 0.0089(8) | 0 | 0 | 0 |
| S | 0.0098(5) | 0.0098(5) | 0.0153(7) | 0.0010(6) | 0.0009(6) | 0.0009(6) |

The form of the anisotropic displacement parameter is: $\exp[-2\pi^2\{h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2kha^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23}\}]$ where $a^*b^*$ and $c^*$ are reciprocal lattice constants.

## 3. Discussion

$Cu_4TiS_4$ crystallizes with a new structure, characterized by a three-dimensional framework, which is based on a cubic close packing of chalcogen atoms. Copper and titanium atoms occupy the centres of the 5/8 of tetrahedral interstices in an ordered fashion. The $TiS_4$ tetrahedron showing almost regular $T_d$ symmetry has, similar to the $VS_4$ tetrahedron in the $Cu_3VS_4$ (sulvanite) [12,13] structure, all edges in common with the $CuS_4$ tetrahedra. In contrast to $Cu_3VS_4$, two crystallographically different sites Cu(1) and Cu(2) can be distinguished. Their sulphur coordinations show pronounced deviations from regular tetrahedral symmetry (Table 4). As can be seen from Fig. 1, the $CuS_4$ tetrahedra are connected to the $TiS_4$ tetrahedra in different ways. The $Cu(2)S_4$ tetrahedra share two opposite edges along the *a*-direction, yielding slabs which correspond to the layers of $Cu_2WS_4$ [14], while the $Cu(1)S_4$ tetrahedra have only one edge in common with $TiS_4$ (in the *c*-direction). With each other the $CuS_4$ tetrahedra exclusively share corners, which results in a sphalerite-like Cu–S partial structure.

The Ti–S bond length calculates as 2.278(1) Å, a value which is in good agreement with the average bond lengths in $Tl_4TiS_4$ [15] ($\bar{d} = 2.263$ Å) and $Na_4TiS_4$ [16] ($\bar{d} = 2.258$ Å), the only other thiotitanates so far known to contain Ti in a tetrahedral sulphur coordination. The Cu–S bond lengths lie within a narrow range of 2.333(1) to 2.351(2) Å. These values are intermediate compared with those in structurally related compounds like $Cu_3VS_4$ ($d$(Cu–S) = 2.298 Å) [13] or $Cu_2WS_4$ ($d$(Cu–S) = 2.357 Å) [14]. Both bond lengths and coordination of the metal atoms are hence consistent with an electrovalent description of this compound as $Cu(I)_4Ti(IV)S_4$.

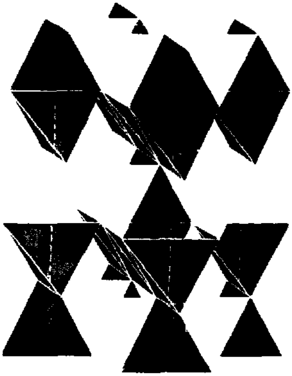

Fig. 1. Perspective view of the crystal structure of $Cu_4TiS_4$ in polyhedral representation. The $TiS_4$ tetrahedra are drawn as full tetrahedra, heavily and lightly shaded tetrahedra are occupied by Cu(1) and Cu(2) respectively.

Table 4
Interatomic distance (Å) and bond angles (deg) for $Cu_4TiS_4$

| | | | |
|---|---|---|---|
| Cu(1) | S | 2.334(2) 2× | |
| Cu(1) | S | 2.351(2) 2× | |
| Cu(1) | Ti | 2.751(2) | |
| S | Cu(1) | S | 104.67(9) |
| S | Cu(1) | S | 108.57(7) 4× |
| S | Cu(1) | S | 117.2(1) |
| Cu(2) | S | 2.333(1) 4× | |
| Cu(2) | Ti | 2.724(1) | |
| S | Cu(2) | S | 105.74(7) 2× |
| S | Cu(2) | S | 111.34(7) 2× |
| S | Cu(2) | S | 111.39(8) 2× |
| Ti | S | 2.278(1) 4× | |
| S | Ti | S | 109.45(4) 4× |
| S | Ti | S | 109.51(7) 2× |
| Cu(2) | S | Ti | 72.40(5) 2× |
| Cu(1) | S | Ti | 72.91(5) |
| Cu(1) | S | Cu(2) | 105.65(5) 2× |
| Cu(1) | S | Cu(1) | 110.92(6) |
| Cu(2) | S | Cu(2) | 111.30(6) |
| Cu(1) | S | Cu(2) | 111.50(5) |
| Cu(1) | S | Ti | 176.17(8) |

The only other chalcogenides of copper having so far been reported with the formula type $A_4MX_4$ are $Cu_4SiS_4$ [17] and $Cu_4SnS_4$ [18]. Of these only the latter has been structurally characterized. As in the present compound all metal atoms are here in tetrahedral sulphur coordination. Being based on a hexagonal close packing of chalcogen atoms the crystal structure of $Cu_4SnS_4$ shows a markedly different linkage of the tetrahedra compared with the title compound. The $SnS_4$ tetrahedra share only vertices with the $CuS_4$ tetrahedra, while edge sharing occurs between the $CuS_4$ tetrahedra. This difference may be attributed to a size effect, since cation–cation repulsion between Cu and Sn should become more effective because of the larger radius of the $Sn^{4+}$ ion, making edge sharing less favourable compared with $Cu_4TiS_4$. It may, however, be doubted whether this is the reason for this difference, since even in cases where the cation sizes [19] are inversed, for instance in the tetrahedral structures of $Cu_3PSe_4$ [20] and $Cu_3NbSe_4$ [21], edge sharing to $CuS_4$ tetrahedra is exclusively found in the transition metal compound.

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