Structural refinement of the ternary chalcogenide compound Cu₂GeTe₃ by X-ray powder diffraction

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The Cu₂GeTe₃ compound crystallizes in the Imm2 (N° 44) space group, Z = 2, with a = 12.641(1) Å, b = 4.2115(2) Å, c = 5.9261(2) Å, V = 315.49(3) Å³. Its structure was refined from X-ray powder diffraction data using the Rietveld method. The refinement of 23 instrumental and structural variables led to R_p = 8.2%, R_wp = 11.6%, R_exp = 6.8%, R_B = 11.2% and S = 1.7, for 5501 step intensities and 253 independent reflections. This compound is isomorphous with Cu₂GeSe₃, and consists of a three-dimensional arrangement of slightly distorted CuTe₄ and GeTe₄ tetrahedra connected by common corners.

1 Introduction

Ternary compounds belonging to the family Cu₂–Ge–VI₃ (VI = S, Se, Te) have interesting semiconducting and optoelectronic properties, mainly in applications as photovoltaic and acoustic-optic devices in the near infrared [1]. These materials have low melting points [2], which diminish with increments of the atomic number of the anions.

Cu₂GeS₃ melts at 850 °C and its structure was investigated by single-crystal X-ray diffraction [3]. The structure is monoclinic, space group Cc, with unit cell parameters a = 6.449(2) Å, b = 11.319(3) Å, c = 6.428(2) Å and β = 108.37(2)°. Cu₂GeSe₃ melts in the range 760–788 °C [4–8] and its structure, also investigated by single-crystal X-ray diffraction [9], is orthorhombic Imm2, with unit cell parameters a = 11.869(3) Å, b = 3.960(1) Å, c = 5.485(1) Å. Cu₂GeTe₃ melts at 504 °C [8]. However, its crystal structure has not been fully characterized in the literature. Rivet [10] reported a tetragonal cell, with unit cell parameters a = 5.957(8) Å and c = 5.928(10) Å, using Debye-Scherrer powder photographic data. In a preliminary work [8], we had reported a powder diffraction pattern in which an orthorhombic Imm2 cell was observed, however, mixed with an unidentified secondary phase present in the pattern in minor quantities. In the present work, we confirmed the orthorhombic Imm2 cell, this time present in the pattern as a single phase, and the description of the structure is accomplished.

2 Experimental

The sample was synthesized by using the direct fusion technique. Stoichiometric quantities of Cu, Ge and Te elements were charged in an evacuated and sealed quartz ampoule, which was previously subject

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to pyrolysis in order to avoid reaction of the starting materials with quartz. The fusion process was carried out into a furnace (vertical position) heated up to 900 °C at a rate of 60 °C/h. The ampoule was kept at this temperature for a period of 12 days. Finally, the sample was cooled to room temperature at a rate of 6 °C/h during 2 days.

Chemical analysis of the sample was carried out with a Hitachi S-2500 scanning electron microscope (SEM) equipped with a Kevex EDX accessory. Three different regions of the ingot were scanned and the average atomic percentages, Cu (33.0%), Ge (22.4%) and Te (44.6%), gave an atomic ratio close to the ideal value 2:1:3.

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 $\theta/\theta$ reflection mode using a Siemens D5005 diffractometer equipped with an X-ray tube (CuK$_\alpha$ radiation: $\lambda = 1.5418$ Å; 30 kV, 15 mA) and a diffracted beam graphite monochromator. A fixed aperture and divergence slit of 1 mm, a 1 mm monochromator slit, and 0.6 mm detector slit were used. The specimen was scanned from 10–110° $2\theta$ with a step size of 0.02° and counting time of 45 s. Quartz was used as an external standard. For the pattern indexed, the instrument analytical software was used to establish the positions of the peaks from the $\alpha_1$ component and to strip mathematically the $\alpha_2$ component from each reflection. For the Rietveld refinement, the whole diffraction data was used.

### Table 1  X-ray powder diffraction data of Cu$_2$GeTe$_3$.

| $2\theta_{\text{obs}}$ (°) | $d_{\text{obs}}$ (Å) | $(I/I_0)_{\text{obs}}$ | $h$ | $k$ | $l$ | $2\theta_{\text{cal}}$ (°) | $d_{\text{cal}}$ (Å) | $\Delta 2\theta$ (°) |
|--------------------------|----------------------|------------------------|-----|-----|-----|--------------------------|----------------------|-------------------|
| 16.510                   | 5.3646               | 3.3                    | 1   | 0   | 1   | 16.504                  | 5.3666               | -0.006            |
| 25.937                   | 3.4323               | 100.0                  | 0   | 1   | 1   | 25.919                  | 3.4345               |                  |
| 29.986                   | 3.0166               | 3.6                    | 2   | 1   | 1   | 29.988                  | 3.0168               | -0.001            |
| 43.027                   | 2.1004               | 42.1                   | 3   | 1   | 2   | 43.019                  | 2.1007               | -0.008            |
| 50.843                   | 1.7943               | 19.7                   | 3   | 2   | 1   | 50.812                  | 1.7953               |                  |
| 53.344                   | 1.7159               | 3.3                    | 6   | 0   | 2   | 53.353                  | 1.7156               | 0.009             |
| 62.325                   | 1.4885               | 5.3                    | 6   | 2   | 0   | 62.320                  | 1.4886               | -0.005            |
| 68.973                   | 1.3635               | 8.9                    | 3   | 2   | 3   | 68.786                  | 1.3636               | -0.007            |
| 70.728                   | 1.3308               | 2.7                    | 9   | 1   | 0   | 70.737                  | 1.3307               | 0.009             |
| 78.671                   | 1.2152               | 7.8                    | 9   | 2   | 2   | 78.672                  | 1.2152               | 0.001             |
| 78.901                   | 1.2122               | 7.3                    | 7   | 3   | 3   | 78.895                  | 1.2123               | -0.006            |
| 84.561                   | 1.1449               | 4.3                    | 6   | 0   | 4   | 84.512                  | 1.1455               |                  |
| 84.869                   | 1.1415               | 3.5                    | 0   | 3   | 3   | 84.874                  | 1.1415               | 0.005             |
| 93.984                   | 1.0533               | 2.7                    | 3   | 0   | 5   | 84.885                  | 1.1414               |                  |
| 94.322                   | 1.0504               | 3.2                    | 9   | 1   | 1   | 93.980                  | 1.0534               | -0.004            |
| 99.990                   | 1.0056               | 3.8                    | 6   | 3   | 3   | 99.987                  | 1.0056               | -0.003            |
Table 2  Unit cell, atomic coordinates, isotropic temperature factors, bond distances (Å) and angles (°) for Cu₂GeTe₃, derived from the Rietveld refinement.

| atom    | ox. | site | x     | y   | z     | foc | B (Å²)   |
|---------|-----|------|-------|-----|-------|-----|----------|
| Cu      | +1  | 4c   | 0.174(2) | 0   | 0.247(2) | 1   | 0.8(3)   |
| Ge      | +4  | 2b   | 0      | 1/2 | 0.773(3) | 1   | 0.8(3)   |
| Te₁     | -2  | 4c   | 0.345(2) | 0   | 0.003(2) | 1   | 0.8(3)   |
| Te₂     | -2  | 2a   | 0      | 0   | 0     | 1   | 0.8(3)   |
| Cu–Te₁  | 2.60(3) | Cu–Te₁(i) | 2.61(1) | Cu–Te₁(ii) | 2.61(1) | Cu–Te₂ | 2.64(2) |
| Ge–Te₁  | 2.53(2) | Ge–Te₁(iii) | 2.53(2) | Ge–Te₂(iv) | 2.50(1) | Ge–Te₂(v) | 2.50(1) |
| Te₁–Cu–Te₁(i) | 113.6(9) | Te₁–Cu–Te₁(i) | 113.6(8) | Te₁–Cu–Te₂ | 112.6(9) |
| Te₁–Ge–Te₂(iv) | 109.9(9) | Te₁–Ge–Te₂(iv) | 109.9(8) | Te₁–Ge–Te₃(iii) | 101.5(9) |
| Te₂(v)–Ge–Te₂(vi) | 114.9(9) | Te₂(v)–Ge–Te₁(iii) | 109.9(8) | Te₂(v)–Ge–Te₁(iii) | 109.9(9) |

Symmetry codes: (i) 0.5 – x, 0.5 – y, 0.5 + z; (ii) 0.5 – x, –0.5 – y, 0.5 + z; (iii) –0.5 + x, 0.5 + y, 0.5 + z; (iv) x, 1 + y, 1 + z; (v) x, y, 1 + z.

3 Results and discussion

The X-ray diffractogram of Cu₂GeTe₃ shows a single phase. The 19 measured reflections were completely indexed in an orthorhombic cell by using the program DICVOL91 [11]. Systematic absences (hkl: h + k + l = 2n) indicate a body-centered lattice. A detailed pattern examination established that this material is isomorphic with the Cu₃GeSe₃ compound [9], which crystallizes in an orthorhombic cell, space group Imm2 (N° 44). This cell is related with the pseudo-tetragonal cell reported by Rivet [10] in the following way:

\[ a_{\text{ort}} = \frac{3\sqrt{2}}{2} a_{\text{tet}}, \quad b_{\text{ort}} = \frac{\sqrt{2}}{2} a_{\text{tet}}, \quad c_{\text{ort}} = c_{\text{tet}}, \quad V_{\text{ort}} = \frac{2}{3} V_{\text{tet}}. \]

The entire powder diffraction dataset of Cu₂GeTe₃ was reviewed by means of the NBS*AIDS program [12] with the following results: unit cell parameters: \( a = 12.623(2) \, \text{Å}, \quad b = 4.2134(2) \, \text{Å}, \quad c = 5.9290(4) \, \text{Å} \), and figures of merit \( M_{19} = 65.7 \) [13] and \( F_{19} = 30.4 \) (0.0056, 112) [14]. X-ray powder diffraction data of Cu₂GeTe₃ are given in Table 1.

The Rietveld refinement [15] of the Cu₂GeTe₃ structure was carried out using the FULLPROF program [16] available in the software package WINPLOTR [17]. Initial positional parameters were taken...
from those of Cu₂GeSe₃ [2] and unit cell parameters were those obtained from the NBS*AIDS refinement. The \( z \) coordinate of Te₂ atom was fixed to define the origin (see Table 2). The angular dependence of the peak full width at half maximum (FWHM) was described by the Caglioti’s formula [18]. Peak shapes were described by the parameterized Thompson–Cox–Hastings pseudo-Voigt profile function [19]. The background variation was described by a polynomial with six coefficients. With the diffraction data available it was only possible to described the thermal motion of the atoms by one overall isotropic temperature factor.

The final figures of merit for 23 instrumental and structural variables were: \( R_p = 8.2\% \), \( R_wp = 11.6\% \), \( R_{exp} = 6.8\% \), \( R_B = 11.2\% \) and \( S = 1.7 \), for 5501 step intensities and 253 independent reflections. The final Rietveld plot is shown in Fig. 1. Unit cell parameters, atomic coordinates, isotropic temperature factor, bond distances and angles are shown in Table 2.

The compound Cu₂GeTe₃ have a sphalerite derivative structure whose prototype is the Cu₂GeSe₃-type. The structure consists of a three-dimensional arrangement of distorted CuTe₄ and GeTe₄ tetrahedra connected by common corners. Each ion is tetrahedrally coordinated, which is characteristic of the so-called adamantane structure compounds [20]. Fig. 2a) shows the unit cell diagram of Cu₂GeTe₃ and Fig. 2b) shows the stacking of the tetrahedra that are formed by the telluride anions and centered by the cations, along the 100 direction. Both figures were prepared with the DIAMOND software [21].

The interatomic distances are shorter than the sum of the respective ionic radii for structures tetrahedrally bonded [22]. The Cu–Te [mean value 2.62(2) Å] bond distances are in good agreement with those found in related compounds such as CuInTe₂ (2.59 Å) [23] and CuGaTe₂ (2.62 Å) [24]. The Ge–Te bond distances [mean value 2.52(2) Å] are also close to similar bonds found in the compounds Ag₄GeTe₆ (2.54 Å) [25] and K₂GeTe₄ (2.51–2.54 Å) [26]. The tetrahedra containing the Cu cations [mean value Te–Te distance 4.26(2) Å] are slightly larger than those containing Ge cations [mean value Te–Te distance 4.10(2) Å].

4 Conclusion

The Cu₂GeTe₃ was obtained as a single phase, and its structure was refined by the Rietveld method using X-ray powder diffraction data. This compound is isostructural with Cu₂GeSe₃, and consists of a three-dimensional arrangement of slightly distorted CuTe₄ and GeTe₄ tetrahedra connected by common corners.

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