Structural refinement of the ternary chalcogenide compound Cu_2GeTe_3 by X-ray powder diffraction

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The Cu_2GeTe_3 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, $V = 315.49(3)$ Å^3. 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 isostructural with Cu_2GeSe_3, and consists of a three-dimensional arrangement of slightly distorted $CuTe_4$ and $GeTe_4$ tetrahedra connected by common corners.

1 Introduction

Ternary compounds belonging to the family $Cu_2–Ge–VI_3$ (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.

Cu_2GeS_3 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 $\beta = 108.37(2)°$. Cu_2GeSe_3 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. Cu_2GeTe_3 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 θ/θ 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° 2θ, 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 α_1 component and to strip mathematically the α_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$_3$.

$2\theta_{obs}$ (°)	d_{obs} (Å)	$(I/I_0)_{obs}$	h	k	l	$2\theta_{cal}$ (°)	d_{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	
			3	0	1	25.944	3.4313	0.007
29.587	3.0166	3.6	2	1	1	29.586	3.0168	–0.001
29.986	2.9774	7.5	3	1	0	29.988	2.9772	0.002
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	
			6	1	1	50.854	1.7939	0.011
53.344	1.7159	3.3	6	0	2	53.353	1.7156	0.009
			7	1	0	55.373	1.6578	
62.325	1.4885	5.3	6	2	0	62.320	1.4886	–0.005
62.623	1.4821	4.3	0	0	4	62.616	1.4823	–0.007
68.610	1.3667	5.7	0	3	1	68.610	1.3667	0.000
68.793	1.3635	8.9	3	2	3	68.786	1.3636	–0.007
			6	1	3	68.822	1.3630	
70.728	1.3308	2.7	9	1	0	70.737	1.3307	0.009
			6	2	2	70.760	1.3303	
78.671	1.2152	7.8	3	3	2	78.672	1.2152	0.001
78.901	1.2122	7.3	0	2	4	78.895	1.2123	–0.006
			6	0	4	78.940	1.2117	
84.561	1.1449	4.3	9	2	1	84.512	1.1455	
			0	3	3	84.567	1.1448	0.006
84.869	1.1415	3.5	0	1	5	84.874	1.1415	0.005
			3	0	5	84.885	1.1414	
93.984	1.0533	2.7	0	4	0	93.980	1.0534	–0.004
94.322	1.0504	3.2	6	2	4	94.331	1.0504	0.009
99.990	1.0056	3.8	12	1	1	99.965	1.0058	
			6	3	3	99.987	1.0056	–0.003

Table 2 Unit cell, atomic coordinates, isotropic temperature factors, bond distances (Å) and angles (°) for Cu_2GeTe_3, derived from the Rietveld refinement.

Space group Imm2 (N° 44), Z = 2
$a = 12.641(1)$ Å, $b = 4.2115(2)$ Å, $c = 5.9261(2)$ Å, V = 315.49(3) Å^3

atom	ox.	site	x	y	z		foc	B (Å^2)
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$^{(i)}$	2.53(2)	Ge–Te1$^{(iii)}$	2.53(2)	Ge–Te2$^{(iv)}$	2.50(1)	Ge–Te2$^{(v)}$	2.50(1)

Te1–Cu–Te1$^{(ii)}$	113.6(9)	Te1–Cu–Te1$^{(i)}$	113.6(8)	Te1–Cu–Te2	112.6(9)
Te1$^{(ii)}$–Cu–Te1$^{(i)}$	107.8(9)	Te1$^{(ii)}$–Cu–Te2	104.2(8)	Te1$^{(i)}$–Cu–Te2	104.2(9)
Te1$^{(i)}$–Ge–Te2$^{(v)}$	109.9(9)	Te1$^{(i)}$–Ge–Te2$^{(iv)}$	109.9(8)	Te1$^{(i)}$–Ge–Te1$^{(iii)}$	101.5(9)
Te2$^{(v)}$–Ge–Te2$^{(vi)}$	114.9(9)	Te2$^{(v)}$–Ge–Te1$^{(iii)}$	109.9(8)	Te2$^{(iv)}$–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 Cu_2GeTe_3 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 Cu_3GeSe_3 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: $a_{ort} = 3\sqrt{2}/2\ a_{tet}$, $b_{ort} = \sqrt{2}/2\ a_{tet}$, $c_{ort} = c_{tet}$, $V_{ort} = 2/3 V_{tet}$. The entire powder diffraction dataset of Cu_2GeTe_3 was reviewed by means of the NBS*AIDS program [12] with the following results: unit cell parameters: $a = 12.623(2)$ Å, $b = 4.2134(2)$ Å, $c = 5.9290(4)$ 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 Cu_2GeTe_3 are given in Table 1.

The Rietveld refinement [15] of the Cu_2GeTe_3 structure was carried out using the FULLPROF program [16] available in the software package WINPLOTR [17]. Initial positional parameters were taken
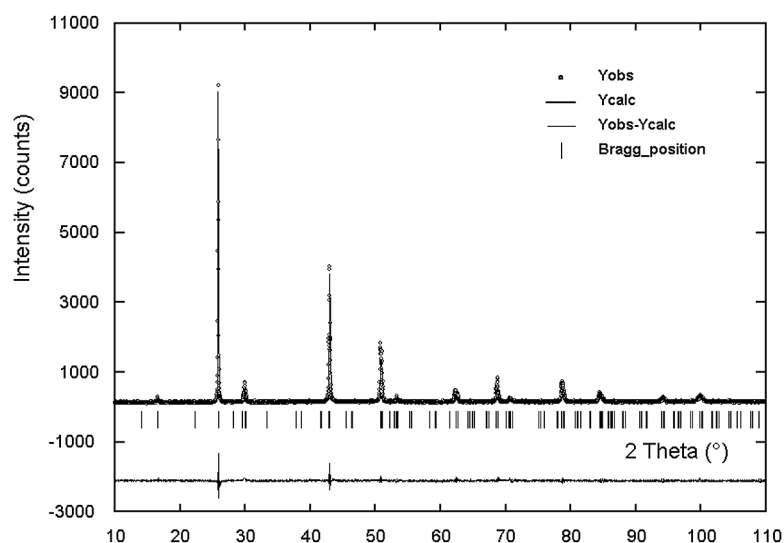
Fig. 1 Final Rietveld plot showing the observed, calculated and difference patterns of Cu_2GeTe_3.
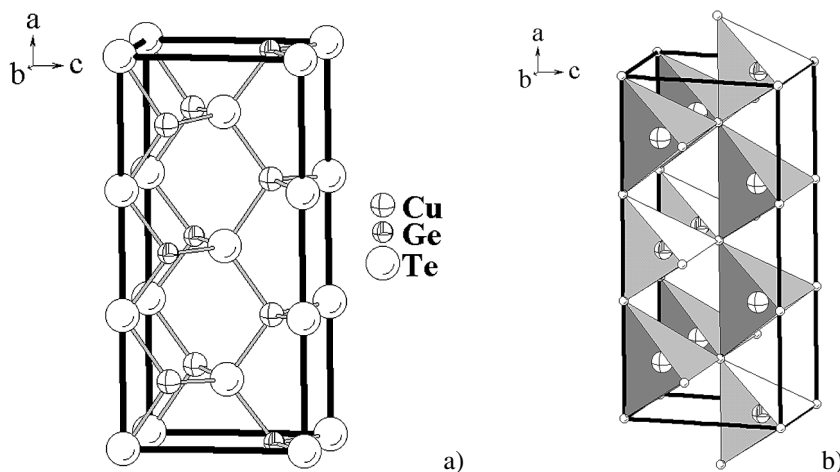
Fig. 2 a) Unit cell diagram of Cu_2GeTe_3 b) Unit cell showing the tetrahedral coordination around the cations and the stacking of tetrahedra along 100 direction.

from those of Cu_2GeSe_3 [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 Cu_2GeTe_3 have a sphalerite derivative structure whose prototype is the Cu_2GeSe_3-type. The structure consists of a three-dimensional arrangement of distorted $CuTe_4$ and $GeTe_4$ 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 Cu_2GeTe_3 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 $CuInTe_2$ (2.59 Å) [23] and $CuGaTe_2$ (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 Ag_8GeTe_6 (2.54 Å) [25] and K_2GeTe_4 (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 Cu_2GeTe_3 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 Cu_2GeSe_3, and consists of a three-dimensional arrangement of slightly distorted $CuTe_4$ and $GeTe_4$ tetrahedra connected by common corners.

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