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Dimorphism of Hydrothermal Synthesized Copper Tellurite, $CuTeO_3$: The Structure of a Monoclinic Representative

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The crystal structure of monoclinic $CuTeO_3$ ($CuTeO_3$-II) was determined by direct methods and Fourier summations from single-crystal X-ray data (a = 5.214(1) Å, b = 9.108(2) Å, c = 5.965(1) Å, β = 95.06(1)°; space group $P2_1/n - C^5_{2h}$; $Z = 4$; $R = 0.035$). The Cu atom is [4 + 1] coordinated and the Te atom [3 + 2] coordinated to oxygen atoms. Each two CuO_4 "square" is combined via a common O–O edge to formal Cu_2O_6 groups, which are moreover combined by the fifth Cu–O bond to formal CuO_3 sheets parallel to (010). The connection of the coordination polyhedra around the Cu and Te atoms results in a framework. $CuTeO_3$-II was synthesized under hydrothermal conditions at 500(5) K. A comparison with $CuTeO_3$-I (orthorhombic) based on crystal chemistry is given.

Introduction

The investigation of the crystal chemistry of tellurium(IV)–oxygen compounds is one of the working topics at the Institut für Mineralogie und Kristallographie der Universität Wien (*1–4*). Recent studies concerning the syntheses of copper-bearing tellurites under hydrothermal conditions yielded a new compound which was identified to be a monoclinic modification of $CuTeO_3$. Single crystals were quite suitable for a structure determination.

Recently Lindqvist (*5*) published the crystal structure of an orthorhombic modification of $CuTeO_3$, which was synthesized by Moret *et al.* (*6*) under hydrothermal conditions at 623 K. Later on Spiridonov (*7*) reported about the natural occurrence of this compound (mineral name: balyakinite). For distinction in the present paper this orthorhombic compound is denoted as $CuTeO_3$-I, whereas the monoclinic one is denoted as $CuTeO_3$-II. For comparison of the two modifications the data for $CuTeO_3$-I given by Lindqvist (*5*) were used.

Experimental

The compound $CuTeO_3$-II was synthesized by a hydrothermal treatment of 1 g of an equimolar mixture of elementary Te (powder) and $Cu(NO_3)_2 \cdot 3H_2O$ in a Teflon-lined reactor. The volume of the reactor (6 cm^3) was filled up to about 80% with an aqueous solution of $Na_2S \cdot 9H_2O$ (approximately 1 *M*). A temperature of 500(5) K was maintained for 100 days. After cooling to room temperature during 10 hr, the following solid reaction products were obtained: $CuTe_2O_5$ (*8, 9*), bluish green short prismatic crystals of $Cu_7(OH)_6(TeO_3)_2$

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TABLE I

SUMMARY OF CRYSTAL DATA, DATA OF INTENSITY MEASUREMENTS AND CRYSTAL STRUCTURE REFINEMENT FOR $CuTeO_3$-II

$a = 5.214(1)$ Å	Graphite monochromatized Mo$K\alpha$ radiation
$b = 9.108(2)$ Å	Crystal dimension: $0.06 \times 0.15 \times 0.09$ mm^3
$c = 5.965(1)$ Å	$2\theta/\omega$ scan mode with a step width of 0.03°
$\beta = 95.06(1)°$	Steps/reflection: 40 + (α_1, α_2) splitting
$V = 282.2$ Å^3	Time/step: 0.5 to 1.5 sec
$Z = 4\{CuTeO_3\}$	Range of data: $2° < 2\theta < 70°$
Space group: $P2_1/n$-C_{2h}^5	Total No. of measured reflections: 2630
$\rho_{calc} \approx 5.63$ g · cm^{-3}	No. of independent reflections: 1250
μ(Mo$K\alpha$) ~ 177 cm^{-1}	Internal, R_{int}: 0.058
No. of variables: 47	Reflections with $F_0 > 3\sigma_{F_0}$: 1143
R: 0.035	3 standard reflections
R_W: 0.031; $W = 1/[\sigma(F_0)]^2$	Secondary extinction (*17*): $2.2(1) \times 10^{-5}$

Note. Stoe four-circle diffractometer; program system STRUCSY (Stoe & Cie, Darmstadt, FRG) on an Eclipse S 140 at room temperature.

$(SO_4)_2$, and green prismatic crystals of $CuTeO_3$-II, elongated parallel to [010]. $CuTe_2O_5$ was identified by an X-ray powder pattern. The chemical formulas of the last two compounds were determined by a combination of quantitative X-ray spectrometer analysis and structure determination.

The accurate 2ϑ values for the lattice parameter determination (39 reflections) as well as the X-ray intensity data of $CuTeO_3$-II were collected with a Stoe AED-2 four-circle diffractometer (Table I). The intensities were corrected for absorption (empirical ψ scans of three reflections, min and max absorption correction coefficients: 0.10 and 0.32) as well as for Lorentz and polarization effects. The crystal structure was derived by a direct method and Fourier summations. Atomic coordinates and thermal parameters of all atoms were fit by least-squares techniques. The results are listed in Table II. Complex scattering functions for neutral atoms, used in all calculations, were taken from (*10*). Some selected interatomic distances and bond valences (*11*) are given in Table III.

Discussion

In $CuTeO_3$-II the Cu atom has four nearest O atom neighbors (Cu–O < 2.0 Å) arranged in a distorted CuO_4 "square." Two such squares are connected via a center of symmetry by a common O–O edge (atoms O(1), resp., O(1′)) to formal Cu_2O_6 groups. The angle O(1)–Cu–O(1′) with 81.2° and the edge O(1)–O(1′) with 2.57 Å represent the smallest values found in the Cu coordination polyhedron. It should be mentioned that one of the two O–Cu–O angles between opposite O atoms within the CuO_4 square is only 156.2°, whereas the other one measures 176.9°. In addition the Cu atom has a fifth O atom neighbor (Cu–O = 2.43 Å), which completes the Cu polyhedron to a tetragonal pyramid. The further connection of these $Cu^{[4+1]}O_5$ coordination polyhedra over common oxygen atoms results in formal CuO_3 sheets parallel to (010).

The coordination figure of the Te atom by O atoms is obviously caused by the lone-pair electrons as characteristic for the oxi-

TABLE II

THE FINAL POSITIONAL AND THERMAL PARAMETERS FOR $CuTeO_3$-II

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	0.7425(1)	0.5187(1)	0.3695(1)	0.0085(3)	0.0111(2)	0.0098(2)	−0.0012(2)	0.0005(2)	0.0023(2)
Te	0.7576(1)	0.2025(1)	0.5995(1)	0.0077(1)	0.0088(1)	0.0069(1)	−0.0006(1)	0.0010(1)	0.0003(1)
O(1)	0.9099(7)	0.3929(4)	0.6096(6)	0.0104(13)	0.0102(13)	0.0140(14)	0.0008(13)	−0.0015(10)	0.0007(12)
O(2)	0.9360(7)	0.1370(4)	0.3609(6)	0.0099(14)	0.0192(15)	0.0091(13)	−0.0012(14)	0.0055(9)	−0.0033(12)
O(3)	−0.0092(7)	0.1396(4)	0.8482(6)	0.0123(14)	0.0127(13)	0.0084(13)	0.0048(12)	−0.0018(10)	−0.0008(11)

Note. All atoms at general positions of space group $P2_1/n$. The anisotropic temperature factors are given in the form $\exp(-2\pi^2\sum_{i=1}^3\sum_{j=1}^3 U_{ij}h_ih_ja_i^*a_j^*)$.

TABLE III

SELECTED CATION-OXYGEN DISTANCES UP TO 3.0 Å IN $CuTeO_3$-II

Cu–O(1) = 1.977(3)	0.43	Te–O(1) = 1.905(4)	1.07
–O(1′) = 1.977(4)	0.43	–O(2) = 1.865(4)	1.18
–O(2) = 1.921(4)	0.51	–O(3) = 1.921(3)	1.03
–O(3) = 1.946(4)	0.47	–O(3′) = 2.425(3)	0.37
–O(3′) = 2.427(4)	0.13	–O(2′) = 2.800(4)	0.19
$\Sigma(s)$ = 1.97		$\Sigma(s)$ = 3.84	
$\Sigma(s)$ O(1) = 1.93			
$\Sigma(s)$ O(2) = 1.88			
$\Sigma(s)$ O(3) = 2.00			

Note. The bond valences (s) are calculated according to Brown and Wu (*11*).

dation state IV. Three O atoms (average Te–O = 1.897 Å) form the base and the Te atom the apex of the trigonal pyramidal TeO_3 group. Including the fourth and the fifth O atom neighbors within the coordination sphere (Te–O = 2.43 and 2.80 Å), the polyhedron may be described as a distorted octahedron, with one corner vacant. Next neighbors have Te–O > 3.0 Å and are excluded from discussion.

The Cu_2O_6 and TeO_3 groups are connected by common O atom corners to a framework structure. A projection of this structure is given in Fig. 1. For both cations, Cu(II) and Te(IV), the coordination polyhedra are in agreement with crystal chemical experience (cf. for Cu (*12–14*) and for Te (*3*)).

The coordination polyhedra for $CuTeO_3$-II are quite similar to those determined for the compound $CuTeO_3$-I. For comparison the calculated coordination numbers of all atoms (*15, 16*) and the volumes of the space-filling polyhedra together with their

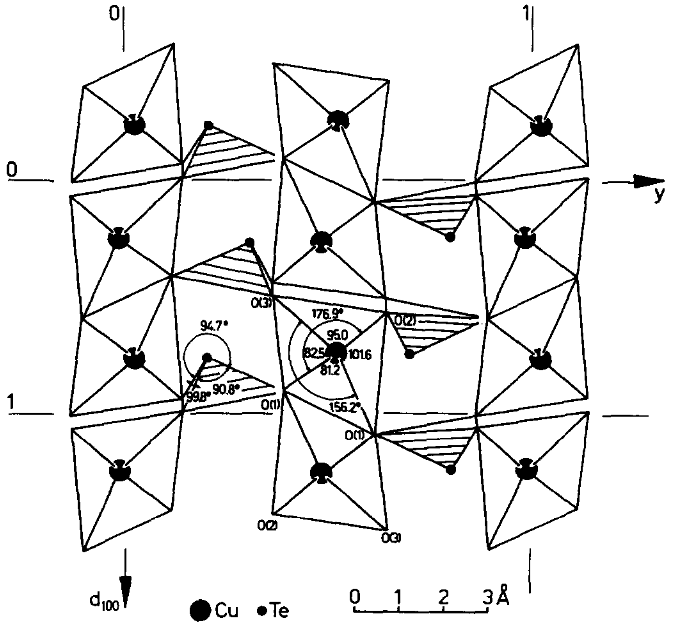

FIG. 1. The crystal structure of $CuTeO_3$-II in a projection parallel to z. For clearness the Cu–O and Te–O distances of the second sphere are not drawn. The angles within the two different coordination polyhedra are given in degrees.

TABLE IV

DATA FOR COORDINATION AND SPACE-FILLING POLYHEDRA (BASED ON $r_{Cu} : r_{Te} : r_o = 1 : 1 : 1$)

	CuTeO$_3$-I							CuTeO$_3$-II					
Atom	a	b	c	d	e	f	Atom	a	b	c	d	e	f
Cu	4.45	4.56	9	7	6	12.44	Cu	4.83	4.63	14	9	7	11.81
Te(1)	6.50	4.98	12	10	10	13.13	Te	5.52	4.64	15	13	9	14.24
Te(2)	6.16	4.83	15	13	10	15.18	O(1)	5.10	4.83	16	14	12	14.12
O(1)	5.05	4.95	14	14	11	13.38	O(2)	5.72	4.63	19	18	14	16.56
O(2)	5.18	4.56	17	16	15	17.39	O(3)	5.65	4.80	14	13	12	13.81
O(3)	5.33	5.20	12	12	12	12.06							
O(4)	6.01	5.08	19	17	13	14.18							

Note. These calculations were performed with the program system "Kristallchemie" (*18*).

Coordination number refers to Hoppe (*15*) (a) and O'Keeffe (16) (b). Total number of faces (n.o.f.) in the space-filling polyhedra (c); n.o.f. > 1% of greatest face (d); n.o.f. > 10% of greatest face (e). Volume of the single polyhedron in Å^3 (f).

number of faces are given for both compounds (Table IV). For comparable magnitudes these values are within the same range and show only minor differences. Reasons for these minor differences are the irregularities of the coordination polyhedra, caused by the Jahn–Teller effect for Cu and by the lone-pair electrons for Te.

TABLE V

X-RAY POWDER DIFFRACTION DATA OF CuTeO$_3$-II

$h\ k\ l$	d_{hkl}	I_{calc}	I_{obs}	$h\ k\ l$	d_{hkl}	I_{calc}	I_{obs}
0 1 1	4.68	13	10	0 4 1	2.13	16	20
0 2 0	4.55	9	10	0 3 2	2.12	5	
1 1 0	4.51	3	5	1 4 0	2.09	13	
1 0 1	3.75	6		2 1 −2	2.00	24	30
1 1 −1	3.73	100	100	0 1 3	1.94	3	
0 2 1	3.61	3		2 3 −1	1.91	20	20
1 1 1	3.47	53	40	1 0 −3	1.91	4	
1 2 0	3.42	48	40	2 1 2	1.84	20	20
1 2 −1	3.04	54	60	2 3 1	1.84	17	
1 2 1	2.90	53	50	1 2 −3	1.76	18	10
0 1 2	2.82	45	50	0 5 1	1.74	5	
0 3 1	2.70	50	40	2 4 0	1.71	15	10
2 0 0	2.60	39	70	3 1 $\bar{1}$	1.67	5	
1 1 −2	2.57	30		1 2 3	1.67	14	15
0 2 2	2.49	3		2 4 −1	1.67	4	
1 3 −1	2.44	11	5	0 3 3	1.66	4	
1 1 2	2.40	18	10	2 4 1	1.62	7	10
1 3 1	2.36	14	5	3 2 0	1.62	5	
0 4 0	2.28	4		3 1 1	1.60	4	
1 2 2	2.18	6		3 2 −1	1.60	6	5

Note. Debye–Scherrer geometry. Cu*Kα* radiation (*19*). The calculated intensities are listed for $I_{calc} \geq 3$ and $d_{hkl} > 1.60$ Å.

The connection of the coordination polyhedra is quite different in these two compounds. In both cases two CuO$_4$ "squares" are connected via a common O–O edge to Cu$_2$O$_6$ groups. In CuTeO$_3$-I these groups are combined to chains parallel to [100] (over common O atom corners; Cu–O < 2.0 Å), whereas in CuTeO$_3$-II no further connection of the Cu$_2$O$_6$ groups by Cu–O < 2.0 Å is given. Although the two copper tellurites show different connections of the coordination polyhedra, it seems important to mention that the two compounds have the same specific gravity within limits of error, i.e., 5.637 for CuTeO$_3$-I and 5.629 g · cm^{-3} for CuTeO$_3$-II.

To help with identification, Table V lists the observed and calculated X-ray powder patterns for CuTeO$_3$-II.

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