

THE CRYSTAL STRUCTURE OF WINSTANLEYITE, TiTe_3O_8 , FROM THE GRAND CENTRAL MINE, TOMBSTONE, ARIZONA

LUCA BINDI[§] AND CURZIO CIPRIANI

*Museo di Storia Naturale – sez. di Mineralogia e Litologia – Università degli Studi di Firenze,
via La Pira 4, I-50121 Firenze, Italy*

ABSTRACT

We have refined the crystal structure of winstanleyite from the type locality, the Grand Central mine, Tombstone, Arizona, in space group $I2_1/a\bar{3}$ to a final R index of 2.03%. Unit-cell parameters of the crystal examined are: a 10.965(1) Å, V 1318.3(2) Å³, Z = 8. The structure previously reported for the synthetic analogue was confirmed, although a higher precision of refinement was achieved. The crystal-chemical environment of both Ti and Te cations is considered in relation with that in other tellurite structures.

Keywords: winstanleyite, walfordite, crystal-structure refinement, Tombstone, Arizona.

SOMMAIRE

Nous avons affiné la structure cristalline de la winstanleyite provenant de la localité type, la mine Grand Central, à Tombstone, en Arizona, dans le groupe spatial $I2_1/a\bar{3}$ jusqu'à un résidu final R de 2.03%. Les paramètres réticulaire du cristal choisi sont: a 10.965(1) Å, V 1318.3(2) Å³, Z = 8. Nous confirmons la structure décrite antérieurement pour l'analogue synthétique, avec une précision améliorée. Nous évaluons l'environnement cristalochimique des cations Ti et Te en relation de celui d'autres structures de tellurites.

(Traduit par la Rédaction)

Mots-clés: winstanleyite, walfordite, affinement de la structure, Tombstone, Arizona.

INTRODUCTION

The compound TiTe_3O_8 was first synthesized by Meunier & Galy (1971), who solved the crystal structure in the space group $I2_1/a\bar{3}$, using three-dimensional photographic X-ray data (R = 5.4% for 238 observed reflections). Some years later, Williams (1979) found the natural analogue of the synthetic TiTe_3O_8 at the Grand Central mine, Tombstone, Arizona. The mineral, named winstanleyite, was recovered in fragments of a granodiorite dike, associated with jarosite, chlorargyrite and rodalquilarite. By means of a powder X-ray investigation, Williams (1979) showed winstanleyite to be cubic, a 10.963 Å, with space group $I2_1/a\bar{3}$. More recently, Back *et al.* (1999) described the new species walfordite, $(\text{Fe}^{3+}, \text{Te}^{6+})\text{Te}_3\text{O}_8$, from the El Indio – Tambo mining property, Chile. By means of a detailed structural study, these authors have pointed the similarities between the crystal structure of walfordite and that

of the synthetic phase $M^{4+}\text{Te}^{4+}_3\text{O}_8$ (Meunier & Galy 1971), and classified the mineral as the Fe^{3+} analogue of winstanleyite.

Owing to the scarcity of suitable crystals for a full structural study and to the presence of complex intergrowths with opal, Williams (1979) was not able to proceed to a crystal-structure refinement of the natural material. In this paper, we report the refinement of the crystal structure of natural winstanleyite from the type locality.

EXPERIMENTAL METHODS AND STRUCTURE REFINEMENT

Several crystals of winstanleyite (Fig. 1), taken from a micromount preserved at the Museo di Storia Naturale, Università degli Studi di Firenze, catalogue number 44757/G, were checked by Weissenberg and precession film techniques. An analysis of extinction

[§] E-mail address: lbindi@steno.geo.unifi.it

conditions on X-ray precession photographs indicated winstanleyite to be cubic, with space group $I2_1/a\bar{3}$ (space group #206). This finding is in agreement with that previously determined by Meunier & Galy (1971) for the synthetic TiTe_3O_8 .

A single crystal of winstanleyite of high diffraction-quality was selected for the structural study. We determined the unit-cell dimension a to be $10.965(1)$ Å by least-squares refinement of the setting angles of 25 reflections ($18^\circ < \theta_{\text{MoK}\alpha} < 25^\circ$).

The data collection was performed with a Nonius Mach-3 single-crystal diffractometer with $\text{MoK}\alpha$ radiation monochromatized by a flat graphite crystal. The intensities of 786 reflections were reduced for Lorentz and polarization effects and subsequently corrected for absorption following the semi-empirical method of North *et al.* (1968). The structure refinement was performed in the space group $I2_1/a\bar{3}$, starting from the atom coordinates of the synthetic TiTe_3O_8 (Meunier & Galy 1971), using the program SHELXL-93 (Sheldrick 1993). Neutral-atom scattering curves for Ti and Te were taken from *The International Tables of X-ray Crystallography*, volume IV (Ibers & Hamilton 1974). Convergence was rapidly obtained for an anisotropic model

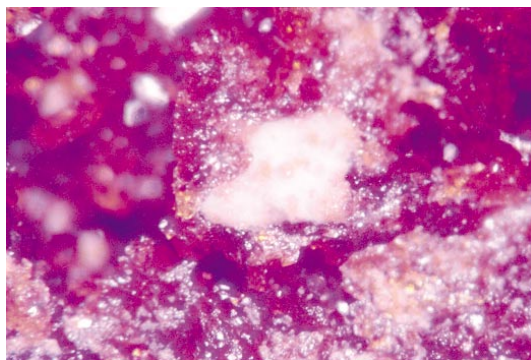


FIG. 1. Crystals of winstanleyite, the small yellow grains, on a matrix of jarosite (dark red) and feldspar (white). Magnification: 80 \times .

of the structure. Using a weighting scheme $w = k/\sigma^2(F_o)$, the structure refinement converged to a final $R = 2.03\%$ for 370 reflections with $F_o > 4\sigma(F_o)$, and $R = 2.05\%$ for all 388 independent reflections. Inspection of the difference-Fourier map revealed maximum positive and negative peaks of $0.93 e^{-\text{\AA}^3}$ and $-0.79 e^{-\text{\AA}^3}$, respectively. Experimental details of the data collection are reported in Table 1. Fractional coordinates and anisotropic displacement parameters of the atoms are given in Table 2. A list of the observed and calculated structure-factors is available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

CHEMICAL COMPOSITION

Owing to the brittleness of the mineral, it was not possible to obtain polished surfaces for crystals embedded in resin; in addition, the small amount of material available precluded standard electron-microprobe analyses. Therefore, semiquantitative analyses were carried out by means of an EDAX energy-dispersion system.

The same crystal used for the structural study was analyzed by means of a Philips SEM515 at 25 kV accelerating voltage and with a spot size of 100 nm. The crystal was found to be homogeneous within analytical error. The average chemical composition (eight analyses on different spots), together with ranges of wt. % of oxides, is reported in Table 3. On the basis of eight atoms of oxygen, the formula of the winstanleyite studied here is $(\text{Ti}_{0.96}\text{Fe}^{3+}_{0.04})\text{Te}_{3.00}\text{O}_8$. It shows a low iron con-

TABLE 1. DATA AND EXPERIMENTAL DETAILS FOR THE CRYSTAL OF WINSTANLEYITE SELECTED FOR STUDY

space group	$I2_1/a\bar{3}$ (#206)	cell parameter a	10.965(1) Å
		V	1318.3(2) Å ³
crystal size	30 \times 50 \times 55 μm		
radiation	$\text{MoK}\alpha$, 50 kV, 28 mA	theta range	1–32°
scan mode	ω	scan width	2.50°
scan speed	1.65°/min		
independent refl.	388	refl. with $F_o > 4\sigma(F_o)$	370
μ (mm ⁻¹)	14.32	$ E^2 - 1 $	0.707
R_{merge} before/after	12.34 / 5.71%		
R_{obs}	2.03%	R_{all}	2.05%

TABLE 2. FRACTIONAL COORDINATES AND ANISOTROPIC DISPLACEMENT PARAMETERS OF ATOMS IN WINSTANLEYITE

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
Ti	0	0	0	0.0244(2)	0.0244(2)	0.0244(2)	-0.0001(2)	-0.0001(2)	-0.0001(2)	0.0244(2)
Te	0.20907(2)	0	$1/4$	0.0275(1)	0.0274(1)	0.0274(1)	0	0	0.0001(1)	0.0274(1)
O1	0.4386(1)	0.1333(1)	0.3987(1)	0.0228(4)	0.0228(4)	0.0227(5)	-0.0002(4)	-0.0003(4)	-0.0002(4)	0.0224(2)
O2	0.1729(1)	0.1729(1)	0.1729(1)	0.0225(3)	0.0225(3)	0.0225(3)	0.0005(4)	0.0005(4)	0.0005(4)	0.0225(3)

tent with respect to those compositions reported by Williams (1979) for two small samples from type locality: $(\text{Ti}_{0.80}\text{Fe}^{3+}_{0.23})\text{Te}_{3.02}\text{O}_8$ and $(\text{Ti}_{0.75}\text{Fe}^{3+}_{0.23})\text{Te}_{3.07}\text{O}_8$.

RESULTS

In addition to a much higher precision of the refinement, this structural study showed winstanleyite to have a structure topologically identical to that of the synthetic compound TiTe_3O_8 (Meunier & Galy 1971). This result is not surprising, since the chemical composition of the sample studied here approaches closely that of the synthetic end-member.

TABLE 3. COMPOSITION OF WINSTANLEYITE, WITH RANGE OF VALUES ENCOUNTERED

TiO_2 wt%	13.75	13.25 – 13.91
TeO_2	85.60	85.54 – 86.22
Fe_2O_3	0.65	0.55 – 0.71

As outlined by Meunier & Galy (1971), the structure of winstanleyite can be described as of the fluorite type, with a face-centered cubic array of cations in the subcell (Fig. 2). Both Ti and Te cations show a six-fold coordination, but major differences in the distribution of the oxygen atoms forming the polyhedra can be noted. The $[\text{TiO}_6]$ octahedron is quite regular, whereas the $[\text{TeO}_6]$ polyhedron shows four shorter Te–O bonds of average length 1.990 Å, and two long bonds of 2.915 Å on the opposite side (Fig. 3). This one-sided coordination is characteristic of Te^{4+} with a stereoactive non-bonding lone pair of electrons (Andersson *et al.* 1973, Brown 1974) and consequently is a common feature of several tellurite structures [walfordite (Back *et al.* 1999), denningite (Walitzki 1965), mackayite (Pertlik & Gieren 1977), sonoraite (Donnay *et al.* 1970), spiroffite (Cooper & Hawthorne 1996), and teineite (Effenberger 1977)].

In Table 4, we report the bond distances and angles in the structure of winstanleyite. The Ti–O bond distances (1.955 Å) is identical to the value observed by Meunier & Galy (1971) for synthetic TiTe_3O_8 [1.96(6)], and it is slightly shorter than that observed for

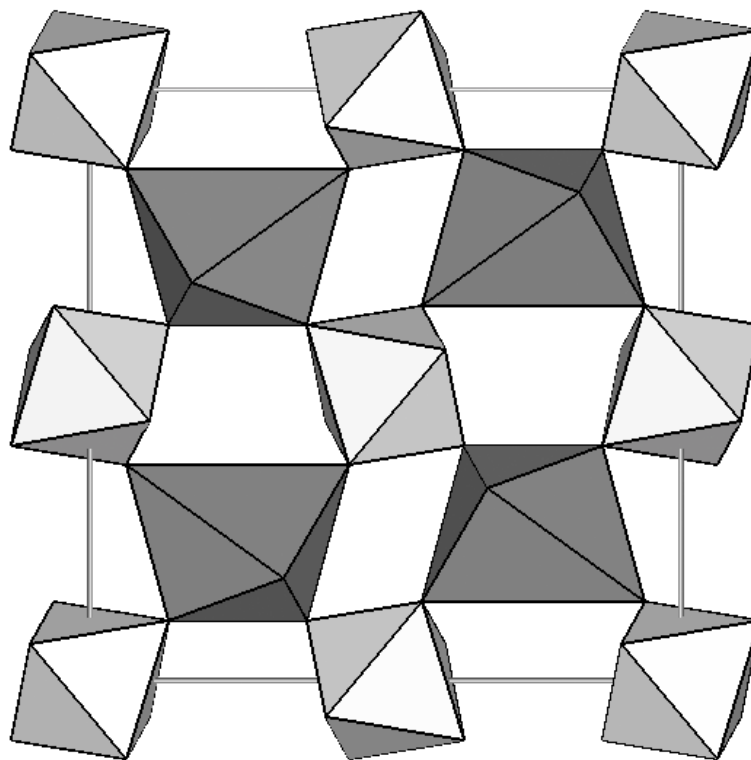


FIG. 2. Crystal structure of winstanleyite projected onto (100). The unit cell is outlined. The light and dark grey polyhedra refer to Ti–O and Te–O, respectively.

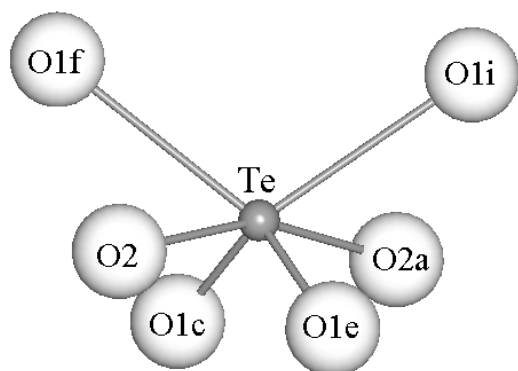


FIG. 3. The distribution of oxygen atoms forming the Te polyhedron.

TABLE 4. WINSTANLEYITE: SELECTED BOND DISTANCES (Å) AND INTERATOMIC ANGLES (°)

Ti–O1 (× 6)	1.955(1)	O1–Ti–O1	180.00(9)
		O1–Ti–O1	91.62(5)
		O1–Ti–O1	88.38(5)
Te–O2, a (× 2)	2.113(1)	O2–Te–O1c	80.32(4)
Te–O1 c,e (× 2)	1.867(1)	O2–Te–O1e	86.02(6)
Te–O1 f,i (× 2)	2.915(1)	O2–Te–O1f	59.05(5)
mean	2.298	O2–Te–O1i	137.47(6)
		O2–Te–O2a	158.37(7)
		O1c–Te–O1e	101.48(8)
		O1c–Te–O1f	136.38(6)
		O1c–Te–O1f	91.52(7)
		O1c–Te–O2a	86.02(6)
		O1e–Te–O1f	91.52(7)
		O1e–Te–O1i	136.38(6)
		O1e–Te–O2a	80.32(4)
		O1f–Te–O1i	107.27(6)
		O1f–Te–O2a	137.47(6)
		O1i–Te–O2a	59.05(5)

walfordite, the Fe³⁺ analogue of winstanleyite [1.991(7) Å; Back *et al.* (1999)]. The Te–O bond distances (1.867–2.915 Å) are within the range observed in other tellurite structures [1.85–2.92 Å in synthetic TiTe₃O₈, 1.86–2.92 Å in synthetic SnTe₃O₈, 1.89–2.99 Å in synthetic HfTe₃O₈, 1.95–2.96 Å in synthetic ZrTe₃O₈; Meunier & Galy (1971), 1.78–2.82 Å in synthetic UTe₃O₈; Galy & Meunier (1971), 1.91–2.89 Å in synthetic TeO₂; Leciejewicz (1961), and 1.880–2.904 Å in walfordite; Back *et al.* (1999)].

The bond-valence sums for the various atomic sites based on the constants of Brese & O'Keeffe (1991) are reported in Table 5.

In Table 6, we compare the X-ray powder pattern originally observed for the type material (Williams 1979) with that calculated using the structural parameters obtained in this study. Calculated and observed

TABLE 5. BOND-VALENCE (*v_{ij}*) ARRANGEMENT FOR WINSTANLEYITE

	Ti	Te	Σ O
O1	0.685 ⁶ 1	1.346 ² 1 0.079 ² 1	2.110
O2		0.692 ² 1 ³ –	2.076
	4.110	4.234	

Note: calculated from the bond-valence curves of Brese & O'Keeffe (1991).

TABLE 6. X-RAY POWDER-DIFFRACTION PATTERNS FOR WINSTANLEYITE AND SYNTHETIC TiTe₃O₈

<i>hkl</i>	<i>d_{calc}</i> (Å)	¹ <i>I_{I_{calc}}</i>	<i>d_{obs}</i> (Å)	² <i>I_{I_o}</i>
200	5.483	5	5.482	20
211	4.476	33	4.474	60
220	3.877	7	3.877	20
222	3.165	100	3.165	100
321	2.931	13	2.930	40
400	2.741	31	2.741	70
411	2.585	18	2.583	40
420	2.452	11	2.452	30
431	2.150	3	2.151	30
521	2.002	4	2.001	20
440	1.938	27	1.938	80
433	1.881	8	1.881	30
600	-	-	1.825	5
611	1.779	5	1.778	30
620	1.734	7	1.734	20
541	1.692	5	1.692	30
622	1.653	22	1.653	80
631	1.617	4	1.617	30
444	1.583	5	1.582	20
543	1.551	4	1.551	20
721	1.492	3	1.493	20
642	1.465	3	1.466	10
651	1.393	3	1.392	40
800	-	-	1.371	10
741	1.350	3	1.350	40
820	1.330	3	1.330	20
653	1.311	2	1.311	20
822	-	-	1.293	5
831	-	-	1.275	40
662	-	-	1.258	30
840	-	-	1.226	30
833	-	-	1.211	10
842	1.196	3	1.197	30
761	-	-	1.183	30
			1.157	20

1: *d* values calculated on the basis of *a* = 10.965(1) Å.

Intensities calculated using XPOW software version 2.0 (Downs *et al.* 1993). Only reflections with *I_{I_{calc}}* > 2 are listed.

2: observed powder pattern and indexing originally reported by Williams (1979).

data are in good agreement, although several intense lines at high 2θ (Williams 1979) do not correspond with those calculated in this study. This feature is probably due to the slight differences in chemical composition between the two samples.

ACKNOWLEDGEMENTS

We greatly benefitted from the reviews provided by Joel D. Grice, Patrick Rozier and Associate Editor Mati Raudsepp. We are also grateful to Robert F. Martin for his suggestions on improving the manuscript. Financial support was provided by M.I.U.R., cofinanziamento 2003, project "Crystal chemistry of metalliferous minerals" and by the University grant (60%) issued to Curzio Cipriani.

REFERENCES

- ANDERSSON, S., ÅSTRÖM, A., GALY, J. & MEUNIER, G. (1973): Simple calculations of bond lengths and bond angles in certain oxides, fluorides or oxide fluorides of Sb^{3+} , Te^{4+} and Pb^{2+} . *J. Solid State Chem.* **6**, 187-190.
- BACK, M.E., GRICE, J.D., GAULT, R.A., CRIDDLE, A.J. & MANDARINO, J.A. (1999): Walfordite, a new tellurite species from the Wendy open pit, El Indio – Tambo mining property, Chile. *Can. Mineral.* **37**, 1261-1268.
- BRESE, N.E. & O'KEEFFE, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr.* **B47**, 192-197.
- BROWN, I.D. (1974): Bond valences as an aid to understanding the stereochemistry of O and F complexes of Sn(II), Sb(III), Te(IV), I(V) and Xe(VI). *J. Solid State Chem.* **11**, 214-233.
- COOPER, M.A. & HAWTHORNE, F.C. (1996): The crystal structure of spiroffite. *Can. Mineral.* **34**, 821-826.
- DONNAY, G., STEWART, J.M. & PRESTON, H. (1970): The crystal structure of sonoraite, $\text{Fe}^{3+}\text{Te}^{4+}\text{O}_3(\text{OH})\cdot\text{H}_2\text{O}$. *Tschermaks Mineral. Petrogr. Mitt.* **14**, 27-44.
- DOWNS, R.T., BARTELMERHS, K.L., GIBBS, G.V. & BOISEN, M.B., JR. (1993): Interactive software for calculating and displaying X-ray or neutron powder diffractometer patterns of crystalline materials. *Am. Mineral.* **78**, 1104-1107.
- EFFENBERGER, H. (1977): Verfeinerung der Kristallstruktur von synthetischem Teineit $\text{CuTeO}_3\cdot 2\text{H}_2\text{O}$. *Tschermaks Mineral. Petrogr. Mitt.* **24**, 287-298.
- GALY, J. & MEUNIER, G. (1971): A propos de la cliffordite UTe_3O_8 . Le système $\text{UO}_3\text{-TeO}_2$ à 700°C. Structure cristalline de UTe_3O_9 . *Acta Crystallogr.* **B27**, 608-616.
- IBERS, J.A. & HAMILTON, W.C., eds. (1974): *International Tables for X-ray Crystallography*, vol. IV. The Kynoch Press, Dordrecht, The Netherlands.
- LECIEJEWICZ, J. (1961): The crystal structure of tellurium dioxide. A redetermination by neutron diffraction. *Z. Kristallogr.* **116**, 345-353.
- MEUNIER, G. & GALY, J. (1971): Sur une déformation inédite du réseau de type fluorine. Structure cristalline des phases MTe_3O_8 ($M = \text{Ti, Sn, Hf, Zr}$). *Acta Crystallogr.* **B27**, 602-607.
- NORTH, A.C.T., PHILLIPS, D.C. & MATHEWS, F.S. (1968): A semiempirical method of absorption correction. *Acta Crystallogr.* **A24**, 351-359.
- PERTLIK, F. & GIEREN, A. (1977): Verfeinerung der Kristallstruktur von Mackayite, $\text{Fe}(\text{OH})[\text{Te}_2\text{O}_5]$. *Neues Jahrb. Mineral., Monatsh.*, 145-154.
- SHELDRIK, G.M. (1993): *SHELXL-93: a New Structure Refinement Program*. University of Göttingen, Göttingen, Germany.
- WALITZI, E.M. (1965): Die Kristallstruktur von Denningit, $(\text{Mn,Ca,Zn})\text{Te}_2\text{O}_5$. Ein Beispiel für die Koordination um vierwertiges Tellur. *Tschermaks Mineral. Petrogr. Mitt.* **10**, 241-255.
- WILLIAMS, S.A. (1979): Girdite, oboyerite, fairbankite, and winstanleyite, four new tellurium minerals from Tombstone, Arizona. *Mineral. Mag.* **43**, 453-457.

Received September 7, 2003, revised manuscript accepted November 27, 2003.