

THE CRYSTAL STRUCTURE OF DUGGANITE, $\text{Pb}_3\text{Zn}_3\text{Te}^{6+}\text{As}_2\text{O}_{14}$

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ABSTRACT

The crystal structure of dugganite, ideally $\text{Pb}_3\text{Zn}_3\text{Te}^{6+}\text{As}_2\text{O}_{14}$, a 8.460(2), c 5.206(2) Å, V 322.6(2) Å³, space group $P321$, $Z = 1$, has been solved by direct methods and Patterson techniques, and refined to an R index of 2.7% based on 636 unique reflections measured using $\text{MoK}\alpha$ radiation on an automated four-circle diffractometer. The structure consists of heteropolyhedral sheets of edge-sharing TeO_6 octahedra and PbO_8 snub disphenoids, oriented parallel to (001). The sheets are cross-linked by AsO_4 and ZnO_4 tetrahedra, which share corners to form an interlinked, two- and three-connected two-dimensional net parallel to (001). Chermnykhite and kuksite are considered to be isostructural with dugganite, but with V and P respectively dominant at the As site.

Keywords: dugganite, crystal structure, tellurate, arsenate, lead.

SOMMAIRE

Nous avons affiné la structure cristalline de la dugganite, de formule idéale $\text{Pb}_3\text{Zn}_3\text{Te}^{6+}\text{As}_2\text{O}_{14}$, a 8.460(2), c 5.206(2) Å, V 322.6(2) Å³, groupe spatial $P321$, $Z = 1$, par méthodes directes et par techniques de Patterson, jusqu'à un résidu R de 2.7%; cet affinement a utilisé 636 réflexions uniques mesurées avec rayonnement $\text{MoK}\alpha$ et un diffractomètre automatisé à quatre cercles. La structure contient des feuillets de hétéropolyèdres, plus précisément des octaèdres TeO_6 à arêtes partagées et des disphénoïdes aplatis PbO_8 , orientés parallèles à (001). Ces feuillets sont interliés par des tétraèdres AsO_4 et ZnO_4 partageant des coins, pour former un réseau à deux et trois noeuds en deux dimensions parallèle à (001). Nous considérons la chermnykhite et la kuksite des minéraux isostructuraux, avec V et P, respectivement, comme occupants du site As.

(Traduit par la Rédaction)

Keywords: dugganite, structure cristalline, tellurate, arsenate, plomb.

INTRODUCTION

Dugganite was first described by Williams (1978) from three mine dumps in the Tombstone District, Cochise County, Arizona. The type material was discovered at the Emerald mine dump, occurring as "spherules of water-green hexagonal prisms abundant in a sugary, vuggy quartz matrix". Numerous crystals of dugganite were discovered at this locality, associated with parakhinite and other Te-oxysalt minerals. At the Old Guard mine dump, crystals of khinite are replaced on the outside by a druse of minute crystals of dugganite. Other minerals found at this site include chlorargyrite, chrysocolla, quetzalcoatlite, and tenorite. At both the Emerald and Old Guard mine dumps, crystals of dugganite were found associated with bromargyrite, chlorargyrite, and numerous unidentified

Te-oxysalt minerals in quartz or manganese oxide gangue material. At the dump of the Joe Shaft mine, dugganite was found with other Te-oxysalt minerals, cerussite, emmonsite, and rodalquilarite.

Using Weissenberg and rotation photographs, Williams (1978) showed that dugganite is hexagonal, "perhaps" $P6/mmm$. Cell dimensions were refined from powder data: a 8.472(5), c 5.208(5) Å. The average chemical composition (obtained using spectroscopic techniques) was found to be PbO 55.3, CuO 1.2, ZnO 17.6, As_2O_5 10.4, TeO_3 14.0, H_2O (by the Penfield method) 1.5, total 100.0 wt.%. Trace amounts of CO_2 , Mo, Ag, and Cd also were detected. Additional (partial) analyses showed some substitution of Te for As. The chemical formula suggested by Williams (1978) was $\text{Pb}_3\text{Zn}_3(\text{TeO}_6)_x(\text{AsO}_4)_{2-x}(\text{OH})_{6-3x}$, with x in the range 0.94 to 1.33.

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A mineral resembling dugganite was also described by Kim *et al.* (1988) as a product of supergene oxidation in the Kuranakh deposit (central Aldan, Yakutia, Russia), where it is associated with calcite, cinnabar, gold, orpiment, altaite, clausthalite, descloizite, kuranakhite, naumannite, tiemannite, and yafsoanite. Single-crystal X-ray studies showed that the mineral is orthorhombic, with space group *Cmmm*, *C222*, *C2mm*, *Cm2m* or *Cmm2*. Cell dimensions were refined from powder data: *a* 8.57(3), *b* 14.84(5), *c* 5.21(3) Å. The authors noted that X-ray data for "normal" dugganite can also be indexed on this cell. The average chemical composition (based on seven electron-microprobe analyses) was found to be (in wt.%) PbO 51.47, ZnO 18.82, SiO₂ 0.96, P₂O₅ 0.70, V₂O₅ 3.61, As₂O₅ 12.16, Sb₂O₅ 0.07, TeO₃ 12.61, total 100.40. Note that this is *not* the average composition abstracted in *Am. Mineral.* (76, 1440, 1991); that one was based on results of earlier analyses obtained using different standards and a non-standard data-reduction routine. Recalculation on the basis of six Pb plus Zn atoms gave the formula Pb₂Zn₃Te(As,V,Si)₂(O,OH)₁₄. Other analogues of this mineral that contain V + Si >> As, or with significant substitution of P for As, were reported but not studied in detail by Kim *et al.* (1988).

Kim *et al.* (1990) described cheremnykhite and kuksite, two new minerals associated with dugganite in the Kuranakh deposit. The formulae, determined from results of electron-microprobe analyses, were Pb₂Zn₃TeO₆(VO₄)₂ for cheremnykhite and Pb₂Zn₃TeO₆(PO₄)₂ for kuksite. X-ray-diffraction studies showed that both minerals are orthorhombic (*Cmmm*, *C222*, *C2mm*, *Cm2m* or *Cmm2*), with cell dimensions similar to those previously determined for dugganite from the same deposit (Kim *et al.* 1988). Their conclusion was that cheremnykhite, kuksite and dugganite are isostructural.

Dugganite has also been described from the Centennial Eureka mine dump in Juab County, Tintic district, Utah, where it occurs with other secondary Cu-, Te-oxysalt minerals (Marty *et al.* 1993).

The structure of dugganite was solved as part of a long-term project on the crystal chemistry of the Te-oxysalt minerals.

EXPERIMENTAL

Electron-microprobe analyses were obtained using a JEOL 733 electron microprobe with Tracor Northern 5500 and 5600 automation. The wavelength-dispersion mode was used. The operating conditions were as follows: voltage 15 kV, beam current 20 nA, and beam diameter 5 µm. Data for Si, P, Ca, As, and Te were collected for 25 s; data for all other elements were collected for 50 s. The following standards were used: almandine (AlKα), zircon (SiKα), Pb₂Ti(PO₄)₆ (PKα), CaTa₄O₁₁ (CaKα), VP₂O₇ (VKα), cuprite (CuKα), willemitite (ZnKα), mimetite (AsLα), TeO₂ (TeLα), and

crocoite (PbMα). Mg, Fe, Co, and Ni were sought, but not detected. Data were reduced using a PAP routine (program XMAQNT by C. Davidson, CSIRO). The analytical results are given in Table 1, together with those of Williams (1978) and Kim *et al.* (1988).

TABLE 1. CHEMICAL COMPOSITION OF DUGGANITE

	Williams (1978)*	Kim et al. (1988)†	This study‡
CaO wt. %	negligible	—	0.24
PbO	55.3	51.47	53.13
CuO	1.2	0.00	1.06
ZnO	17.6	18.82	17.25
Al ₂ O ₃	—	—	0.07
SiO ₂	—	0.96	1.08
P ₂ O ₅	—	0.70	4.90
V ₂ O ₅	—	3.61	0.03
As ₂ O ₅	10.4	12.16	8.28
Sb ₂ O ₅	—	0.07	—
TeO ₃	14.0	12.61	13.48
H ₂ O	1.5	—	—
TOTAL	100.0	100.40	99.50
Ca ²⁺	negligible	—	0.06
Pb ²⁺	3.43	2.94	3.04
Cu ²⁺	0.21	0.00	0.17
Zn ²⁺	3.00	2.95	2.71
Al ³⁺	—	—	0.02
Si ⁴⁺	—	0.20	0.23
P ⁵⁺	—	0.13	0.88
V ⁵⁺	—	0.51	0.00
As ⁵⁺	1.25	1.35	0.92
Sb ⁵⁺	—	0.01	—
Te ⁶⁺	1.11	0.92	0.98
H ⁺	2.31	—	—
O ²⁻	14.25	14.02	13.90

Note: Oxides are in weight percent; analyses are normalized on nine cations per formula unit. *Average of four AAS analyses for Pb, Cu, Zn, and three visible spectroscopy analyses for Te. As (two analyses) by UV spectroscopy. Trace Cd, Ag, Mo, CO₂. Water by the Penfield method. †Average of seven electron microprobe analyses. ‡Average of six electron microprobe analyses.

The crystal used in this study is from the 400-foot level of the Empire mine, near Tombstone, Arizona. It was examined with a petrographic microscope

TABLE 2. MISCELLANEOUS INFORMATION: DUGGANITE

a (Å)	8.480(2)	Rad/mono	MoK α /graphite
c	5.208(2)	Total reflections	3746
V (Å ³)	322.8(2)	Unique reflections	638
Space group	F321	R _{int} (%)	9.8
Z	1	[I \geq 3 σ (I)]	558
Crystal size (mm)	0.1 \times 0.08 \times 0.05	R (%)	2.7
μ (MoK α ; mm ⁻¹)	49.89	wR (%)	2.9
$R = \sum F_o - F_c / \sum F_o$			
$wR = \left[\sum (w \cdot F_o - F_c)^2 / \sum w \cdot F_o^2 \right]^{1/2}$, $w = 1$			

for evidence of twinning; none was seen. The crystal was mounted on a Siemens P3 automated four-circle diffractometer equipped with a molybdenum-target X-ray tube (operating at 55 kV, 35 mA) and a precisely oriented graphite-crystal monochromator mounted with equatorial geometry. Fifty reflections in the range 7.83 to 45.69° 2 θ were centered using an automated search routine, and the correct unit-cell was selected from an array of real-space vectors corresponding to potential unit-cell axes. Least-squares refinement of these reflections produced the cell dimensions given in

TABLE 3. ATOMIC PARAMETERS FOR DUGGANITE

Site	x	y	z	U ₁₁ *	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃	U _{eq}
Te	0	0	0	305(6)	305(6)	158(7)	153(3)	0	0	256(5)
As	1/3	2/3	0.5294(6)	237(11)	237(11)	369(18)	119(5)	0	0	281(9)
Pb	0.59472(9)	0	0	359(3)	380(4)	303(3)	190(2)	10(1)	20(3)	345(2)
Zn	0.2466(2)	0	1/2	343(8)	286(9)	248(9)	143(5)	-7(4)	-14(8)	299(7)
O(1)	0.122(1)	0.212(1)	0.217(2)	325(43)	363(48)	247(35)	109(38)	43(32)	-50(31)	339(35)
O(2)	0.467(2)	0.200(2)	0.339(2)	502(64)	671(77)	398(59)	48(62)	178(49)	-77(53)	632(56)
O(3)	1/3	2/3	0.239(4)	407(59)	407(59)	668(123)	203(30)	0	0	494(57)

*U_{ij} and U values are listed $\times 10^4$

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR DUGGANITE

Te-O(1)	$\times 6$	1.925(8)	O(1)b-Pb-O(1)i	$\times 2$	65.9(3)
<Te-O>		1.925	O(1)b-Pb-O(2)b	$\times 2$	72.8(4)
			O(1)b-Pb-O(2)j	$\times 2$	133.0(4)
As-O(2)a	$\times 3$	1.64(1)	O(1)b-Pb-O(2)i	$\times 2$	85.4(3)
-O(3)		1.51(2)	O(1)b-Pb-O(3)c	$\times 2$	78.2(2)
<As-O>		1.61	O(1)b-Pb-O(3)f	$\times 2$	132.5(2)
			O(1)-Pb-O(2)	$\times 2$	113.4(3)
Pb-O(1)b	$\times 2$	2.40(1)	O(2)-Pb-O(2)b	$\times 2$	53.5(5)
-O(2)	$\times 2$	3.00(1)	O(2)-Pb-O(2)j		100.0(5)
-O(2)b	$\times 2$	2.70(1)	O(2)-Pb-O(3)c	$\times 2$	89.0(4)
-O(3)c	$\times 2$	2.88(1)	O(2)-Pb-O(3)f	$\times 2$	70.0(4)
<Pb-O>		2.74	O(2)b-Pb-O(3)c	$\times 2$	113.4(5)
			O(2)b-Pb-O(3)f	$\times 2$	74.3(5)
Zn-O(1)d	$\times 2$	1.91(1)	<O-Pb-O>		91.5
-O(2)	$\times 2$	1.97(1)			
<Zn-O>		1.94	O(1)d-Zn-O(1)a		129.8(4)
			O(1)d-Zn-O(2)	$\times 2$	103.8(5)
O(1)-Te-O(1)e	$\times 6$	89.2(3)	O(1)d-Zn-O(2)k	$\times 2$	101.5(4)
O(1)-Te-O(1)f	$\times 3$	85.5(5)	O(2)-Zn-O(2)k		117.8(9)
O(1)-Te-O(1)g	$\times 3$	86.8(5)	<O-Zn-O>		109.7
<O-Te-O>		90.2			
O(2)a-As-O(3)	$\times 3$	114.7(4)			
O(2)a-As-O(2)h	$\times 3$	103.8(5)			
<O-As-O>		109.3			

Note: <M-L> denotes the mean metal-ligand distance (Å). Equivalent positions: a = y, x, z-1; b = $\bar{y}+1, x-y, z$; c = x, y-1, z; d = $\bar{x}+y, \bar{x}, z$; e = $\bar{y}, x-y, z$; f = y, x, z; g = $\bar{x}, \bar{x}+y, z$; h = x-y, $\bar{y}+1, z+1$; i = $\bar{x}+1, \bar{x}+y, z$; j = x-y, \bar{y}, z ; k = x-y, $\bar{y}, z+1$.

TABLE 5. BOND-VALENCE* ARRANGEMENT IN DUGGANITE

	Te	As [†]	Pb	Zn	Total
O(1)	0.88(2) $\times 6 \downarrow$		0.46(1) $\times 2 \downarrow$	0.58(2) $\times 2 \downarrow$	2.02(3)
O(2)		1.18(3) $\times 3 \downarrow$	0.092(5) $\times 2 \downarrow \times 1 \rightarrow$	0.48(3) $\times 2 \downarrow$	1.95(4)
			0.202(6) $\times 2 \downarrow \times 1 \rightarrow$		
O(3)		1.67(9)	0.134(4) $\times 2 \downarrow \times 3 \rightarrow$		2.07(9)
Total	5.88(5)	5.2(1)	1.78(2)	2.12(5)	

*Calculated from the curves of Bressé & O'Keeffe (1991). † Calculated assuming 54% As and 46% P.

Table 2, together with the orientation matrix relating the crystal axes to the diffractometer axes. Intensity data were collected in the θ -2 θ scan mode, using 96 steps with a scan range from [2 θ (MoK α_1) - 1.1]° to [2 θ (MoK α_2) + 1.1]° and a variable scan-rate between 0.5 and 29.3°/min depending on the intensity of an initial one-second count at the center of the scan range. Backgrounds were measured for half the scan time at the beginning and end of each scan. The stability of the crystal alignment was monitored by collecting two standard reflections every 25 measurements. One sphere of reflections (3746 measurements, exclusive of standards) was collected from 3 to 60° 2 θ . Eighteen of the reflections were rejected because of asymmetric backgrounds. Fourteen strong reflections uniformly distributed with regard to 2 θ were measured at 5° intervals of ψ (the azimuthal angle corresponding to

rotation of the crystal about its diffraction vector) from 0 to 355°, after the method of North *et al.* (1968). These data (994 measurements) were used to calculate an absorption correction. The merging *R* index for the ψ -scan data set decreased from 8.5% before the absorption correction to 3.2% after the absorption correction. This correction was then applied to the entire data-set; minimum and maximum transmissions were 0.030 and 0.068, respectively. The data were also corrected for Lorentz, polarization and background effects, averaged and reduced to structure factors. Of the 636 unique reflection, 558 were classed as observed [$I \geq 3\sigma(I)$].

STRUCTURE SOLUTION AND REFINEMENT

The Siemens SHELXTL PC system of programs was used throughout this study. Scattering curves for neutral atoms together with anomalous dispersion coefficients were taken from Cromer & Mann (1968) and Cromer & Liberman (1970). Miscellaneous information concerning the collection and refinement of the data are given in Table 2.

The mean value of $[E^2 - 1]$ was found to be 0.65, which implies a non-centrosymmetric space group. Both direct methods and Patterson techniques were used to solve the structure. The structure was refined in *P321* to an *R* index of 4.7% for an isotropic displacement model. Conversion to anisotropic displacement factors for all of the atoms in the structure resulted in convergence at *R* and *wR* indices of 2.7 and 2.9%, respectively (3.9 and 10.4% for all 636 data). Addition of an isotropic extinction correction did not improve the results. Positional coordinates and anisotropic and equivalent isotropic displacement factors are given in Table 3. Interatomic distances and angles are given in Table 4, and a bond-valence analysis in Table 5. Structure factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

DESCRIPTION OF THE STRUCTURE

There are four distinct cation sites in the structure of dugganite. The atom at the *Te* site, at special position *1a* (0,0,0), is coordinated by six O atoms forming a slightly distorted octahedron. The Te–O distances are 1.925 Å, and the O–Te–O angles range from 85.5 to 96.8° (mean 90.2°). The Te–O distances are similar to those previously described for leisingite (1.922 Å; Margison *et al.* 1997), jensenite (1.936 Å; Grice *et al.* 1996), frankhawthorneite (1.939 Å; Grice & Roberts 1995), parakhinite (1.92 Å; Burns *et al.* 1995), yafsoanite (1.929 Å; Jarosch & Zemann 1989), and carlfriesite (1.933 Å; Effenberger *et al.* 1978). The bond-angle distortion parameter (σ^2 ; Hawthorne *et al.* 1989) is 16.9. The variance in the octahedron angle is 18.45, the mean quadratic elongation of the octahedron (Robinson *et al.* 1971) is 1.0053, and the polyhedral

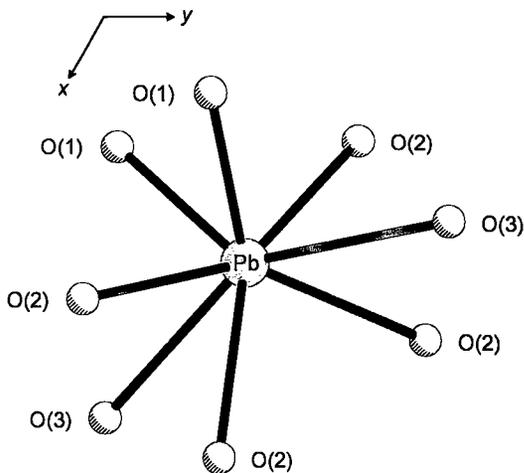


FIG. 1. Coordination of the Pb atom in dugganite.

volume is 9.43 Å³. The electron-microprobe data, refined site-occupancy, and bond-valence analysis confirm that the site is completely occupied by Te⁶⁺.

The atom at the *As* site, special position *2d* ($\frac{1}{2}, \frac{2}{3}, z$), is coordinated by four O atoms forming a distorted tetrahedron. The As–O distances are 1.64 Å ($\times 3$) and 1.51 Å (mean 1.61 Å), and the O–As–O angles are 103.8° and 114.7° (mean 109.3°). The bond-length (Δ ; Hawthorne *et al.* 1989) and bond-angle distortion parameters are 0.0049 and 29.73, respectively. The variance in the tetrahedron angle is 35.93, the mean quadratic elongation of the tetrahedron is 1.0080, and the polyhedron volume is 2.11 Å³. The average electron-microprobe-derived composition indicates that the *As* site is occupied by As⁵⁺ (45%), P⁵⁺ (43%), Si⁴⁺ (11%) and Al³⁺ (1%). Refinement of the site occupancy for As and P shows 54(2)% As, 46(2)% P. The mean bond-valence (Brese & O'Keeffe 1991) obtained using these proportions is 5.2 valence units (*vu*). The bond valence obtained using proportions derived from the average electron-microprobe data is 5.0 *vu*, and the values for the coordinating O(2) and O(3) atoms are 1.91 and 2.02 *vu*, respectively.

The atom at the *Pb* site, at special position *3e* ($x, 0, 0$) is coordinated by eight O atoms, forming a distorted snub disphenoid (Johnson 1965) (Fig. 1). The Pb–O distances range from 2.40 to 3.00 Å (mean 2.74 Å), and the O–Pb–O angles vary from 65.9° to 133.0° (mean 91.5°). The polyhedral volume is 34.40 Å³. The Pb site is almost completely occupied by Pb²⁺, although the electron-microprobe results suggest a small amount of substitution (2%) by Ca²⁺. Pb²⁺ is commonly lone-pair stereoactive, which typically results in a very asymmetrical (one-sided) coordination, with the lone pair

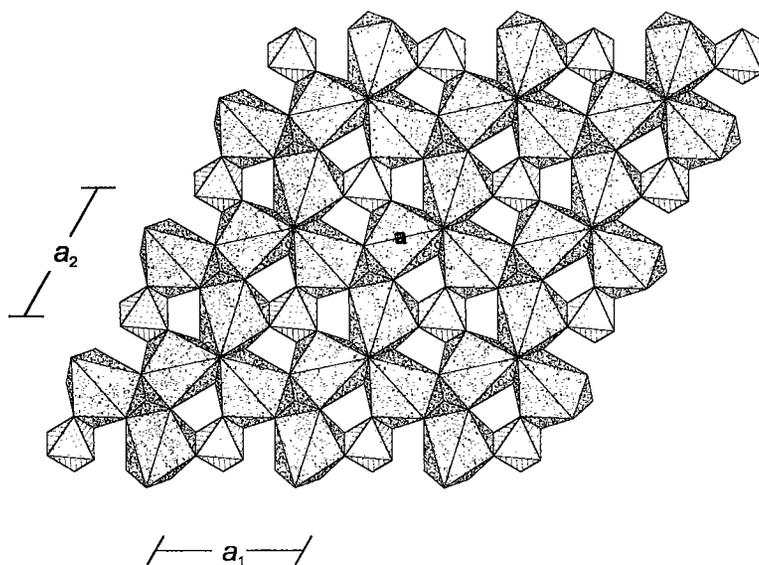


FIG. 2a. The heteropolyhedral sheet in the dugganite structure, projected onto (001). The TeO_6 octahedra are indicated by a regular dot pattern, and the PbO_8 polyhedra, by a random dot pattern. Polyhedron "a" is in the same orientation as in Figure 1.

of electrons positioned on the opposite side of the atom to the coordinating anions. However, the coordination of Pb^{2+} in dugganite is relatively symmetrical, and difference-Fourier maps show no evidence of a lone pair of electrons.

The atom at the Zn site, special position $3f(x, 0, \frac{1}{2})$, is coordinated by four O atoms forming a distorted tetrahedron. The Zn–O distances range from 1.91 to 1.97 Å (mean 1.94 Å); these are similar to the ^{64}Zn –O length (1.97 Å) calculated using ionic radii from Shannon (1976). The O–Zn–O angles range from 101.5 to 129.8° (mean 109.7°). There are two additional O(1) atoms at distances of 2.90 Å; it is unlikely that they form bonds with the atom at the Zn position. The bond-length and bond-angle distortion parameters are 0.00096 and 112.38, respectively. The tetrahedron angle variance is 135.30, the mean quadratic elongation of the tetrahedron is 1.0363, and the polyhedral volume is 3.55 Å³. The Zn site is almost completely occupied by Zn^{2+} . The average electron-microprobe results suggest a minor amount (6%) of substitution by Cu^{2+} , although Cu^{2+} does not commonly occur in tetrahedral coordination (Eby & Hawthorne 1993).

The TeO_6 octahedra and PbO_8 polyhedra share edges to form a sheet of heteropolyhedra parallel to (001) (Fig. 2a). Each TeO_6 octahedron shares three

edges, each with a different PbO_8 polyhedron; the length of the shared edges is 2.61 Å. As expected, this is shorter than the unshared edges of the octahedron (2.70 Å × 6 and 2.88 Å × 3). Each PbO_8 polyhedron shares one edge with a TeO_6 octahedron, one edge with an AsO_4 tetrahedron (length 2.58 Å), and four edges with four other PbO_8 polyhedra. The length of the latter edges is 3.36 Å, which is shorter than the mean (3.87 Å) of the 12 unshared edges (3.04, 3.34, 3.47, 4.10, 4.59, and 4.65 Å, all × 2).

The AsO_4 and ZnO_4 tetrahedra share corners to form an interlinked, two- and three-connected two-dimensional net parallel to (001) (Fig. 2b). The two AsO_4 tetrahedra in each unit cell point in opposite directions, with apical O(3) atoms oriented $\pm z$. The three basal O(2) atoms are shared with different ZnO_4 tetrahedra. Each ZnO_4 tetrahedron shares two corners with AsO_4 tetrahedra. The rather complex Schläfli symbol (O'Keeffe & Hyde 1980) for the resulting net is $(12^2.12^3)_6$. It is interesting to note that if the TeO_6 octahedra are considered as part of the net, the resultant Schläfli symbol is the much more conventional 6^3 .

The sheets of heteropolyhedra are linked by AsO_4 and ZnO_4 tetrahedra (Fig. 3). Each AsO_4 tetrahedron shares an apical O(3) atom with three PbO_8 polyhedra,

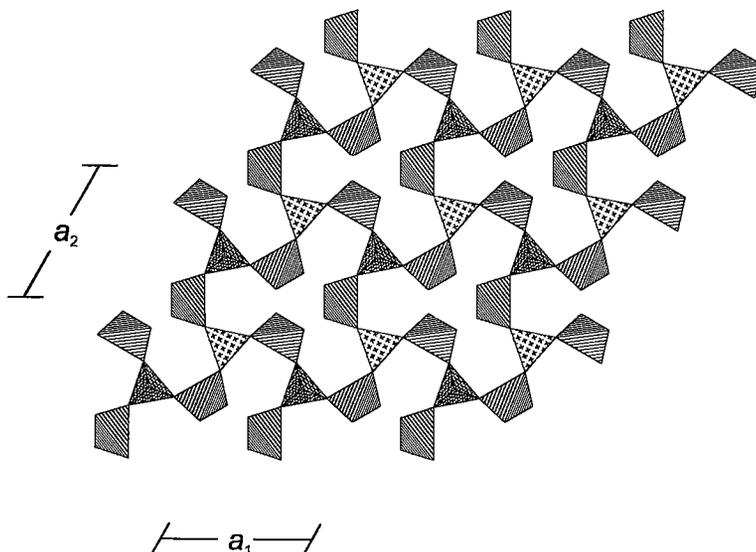


FIG. 2b. The layer of tetrahedra in the dugganite structure, projected onto (001). The AsO_4 tetrahedra are shaded with crosses, and the ZnO_4 tetrahedra are ruled.

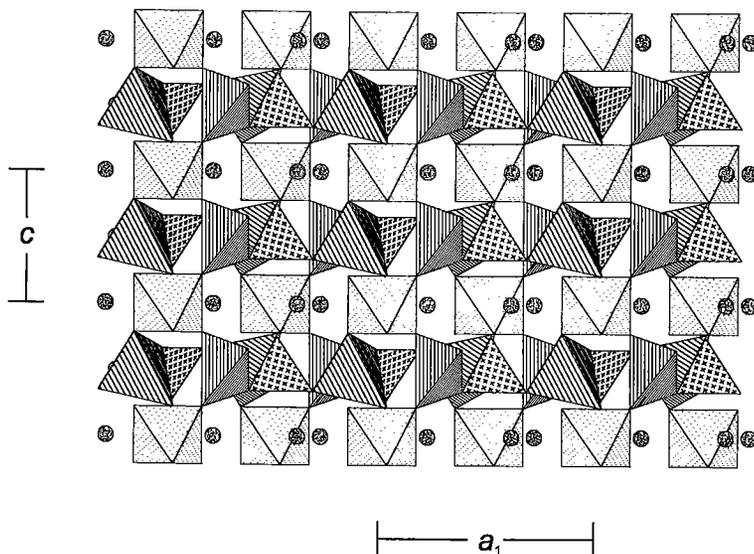


FIG. 3. The dugganite structure projected onto (100). The shading is the same as in Figure 2 (with Pb atoms as spheres).

and three basal As–O(2) edges (2.58 Å) with three PbO_8 polyhedra in a different sheet. The AsO_4 and TeO_6 polyhedra have no anions in common and thus are not directly joined. Each ZnO_4 tetrahedron shares two

corners with two TeO_6 octahedra in different sheets, and four corners with six different PbO_8 polyhedra. The sheets of heteropolyhedra and layers of tetrahedra alternate along c to form the three-dimensional structure.

DISCUSSION

The ideal formula of dugganite is $\text{Pb}_3\text{Zn}_3\text{TeAs}_2\text{O}_{14}$. The electron microprobe and bond-valence analyses imply that there is little to no OH or H_2O in the structure. The empirical formula, based on the average results of the electron-microprobe analyses, and calculated on the basis of nine cations per formula unit, is $(\text{Pb}_{3.04}\text{Ca}_{0.06})_{\Sigma 3.10}(\text{Zn}_{2.71}\text{Cu}_{0.17})_{\Sigma 2.88}\text{Te}_{0.98}(\text{As}_{0.92}\text{P}_{0.88}\text{Si}_{0.23}\text{Al}_{0.02})_{\Sigma 2.05}\text{O}_{13.90}$. This is similar to the formula based on the structure analysis, which is $\text{Pb}_3\text{Zn}_3\text{Te}(\text{As}_{1.08}\text{P}_{0.92})_{\Sigma 2.00}\text{O}_{14}$. The empirical formulae calculated from the analyses in Williams (1978) and Kim *et al.* (1988) (on the basis of nine cations per formula unit) are $\text{Pb}_{3.44}(\text{Zn}_{3.00}\text{Cu}_{0.21})_{\Sigma 3.21}\text{Te}_{1.11}\text{As}_{1.25}\text{O}_{11.94}\text{OH}_{2.31}$ and $\text{Pb}_{2.94}\text{Zn}_{2.95}\text{Te}_{0.92}(\text{As}_{1.35}\text{V}_{0.51}\text{Si}_{0.20}\text{P}_{0.13}\text{Sb}_{0.01})_{\Sigma 2.20}\text{O}_{14.02}$, respectively. Note that in each study, As is the dominant cation in the As position. As noted above, minerals with V (cheremnykhite) and P (kuksite) dominant at the As site have been described by Kim *et al.* (1990), and are presumed to be isostructural with dugganite.

Kim *et al.* (1988, 1990) chose an orthorhombic unit-cell ($a \sim 8.6$, $b \sim 14.8$, $c \sim 5.2$ Å) for all three minerals, and suggested $Cmmm$, $C222$, $C2mm$, $Cm2m$ or $Cmm2$ as possible space-groups. The orthorhombic cell can be derived from a hexagonal unit-cell by using the formula $b_{\text{orth}} \approx 2a_{\text{hex}} \cdot \cos 30^\circ$. However, it would only be necessary to use this cell if there were ordering, *e.g.*, of As between pseudo-equivalent As positions, and there is no evidence for this. In addition, the space groups proposed by Kim *et al.* (1988, 1990) are neither subgroups or supergroups of $P321$. Without studying the samples described by Kim *et al.* (1988, 1990), we suggest that dugganite, cheremnykhite and kuksite are isostructural, and crystallize in the hexagonal system with space group $P321$.

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REFERENCES

BRESE, N.E. & O'KEEFFE, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr.* **B47**, 192-197.

BURNS, P.C., COOPER, M.A. & HAWTHORNE, F.C. (1995): Parakhinite, $\text{Cu}^{2+}_3\text{PbTe}^{6+}\text{O}_6(\text{OH})_2$: crystal structure and revision of chemical formula. *Can. Mineral.* **33**, 33-40.

CROMER, D.T. & LIBERMAN, D. (1970): Relativistic calculation of anomalous scattering factors for X rays. *J. Chem. Phys.* **53**, 1891-1898.

_____ & MANN, J.B. (1968): X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Crystallogr.* **A24**, 321-324.

EBY, R.K. & HAWTHORNE, F.C. (1993): Structural relations in copper oxysalt minerals. I. Structural hierarchy. *Acta Crystallogr.* **B49**, 28-56.

EFFENBERGER, H., ZEMANN, J. & MAYER, H. (1978): Carlfriesite: crystal structure, revision of chemical formula, and synthesis. *Am. Mineral.* **63**, 847-852.

GRICE, J.D., GROAT, L.A. & ROBERTS, A.C. (1996): Jensenite, a cupric tellurate framework structure with two coordinations of copper. *Can. Mineral.* **34**, 55-59.

_____ & ROBERTS, A.C. (1995): Frankhawthorneite, a unique HCP framework structure of a cupric tellurate. *Can. Mineral.* **33**, 649-653.

HAWTHORNE, F.C., GROAT, L.A. & EBY, R.K. (1989): Antlerite, $\text{Cu}_3\text{SO}_4(\text{OH})_4$, a heteropolyhedral wallpaper structure. *Can. Mineral.* **27**, 205-209.

JAROSCH, D. & ZEMANN, J. (1989): Yafsoanite: a garnet type calcium - tellurium (VI) - zinc oxide. *Mineral. Petrol.* **40**, 111-116.

JOHNSON, N.W. (1965): Convex polyhedra with regular faces. *Can. J. Math.* **18**, 169-200.

KIM, A.A., ZAYAKINA, N.V., LAVRENT'EV, YU.G. & MAKHOTKO, V.F. (1988): Vanadian silician variety of dugganite - the first find in the USSR. *Mineral. Zh.* **6**, 85-89 (in Russ.).

_____, _____ & MAKHOTKO, V.F. (1990): Kuksite $\text{Pb}_3\text{Zn}_3\text{TeO}_6(\text{PO}_4)_2$ and cheremnykhite $\text{Pb}_3\text{Zn}_3\text{TeO}_6(\text{VO}_4)_2$ - new tellurates from the Kuranakh gold deposit (central Aldan, southern Yakutia). *Zap. Vses. Mineral. Obshchest.* **119**, 50-57 (in Russ.).

MARGISON, S.M., GRICE, J.D. & GROAT, L.A. (1997): The crystal structure of leisingite, $(\text{Cu}^{2+}, \text{Mg}, \text{Zn})_2(\text{Mg}, \text{Fe})\text{Te}^{6+}\text{O}_6 \cdot 6\text{H}_2\text{O}$. *Can. Mineral.* **35**, 759-763.

MARTY, J., JENSEN, M.C. & ROBERTS, A.C. (1993): Minerals of the Centennial Eureka mine, Tintic District, Eureka, Utah. *Rocks & Minerals* **68**, 406-416.

NORTH, A.C.T., PHILLIPS, D.C. & MATHEWS, F.S. (1968): A semi-empirical method of absorption correction. *Acta Crystallogr.* **A24**, 351-359.

O'KEEFFE, M.O. & HYDE, B.G. (1980): Plane nets in crystal chemistry. *Phil. Trans. R. Soc. London* **295A**, 553-618.

ROBINSON, K., GIBBS, G.V. & RIBBE, P.H. (1971): Quadratic elongation: a quantitative measure of distortion in coordination polyhedra. *Science* **172**, 567-570.

SHANNON, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **A32**, 751-767.

WILLIAMS, S.A. (1978): Khinite, parakhinite, and dugganite, three new tellurates from Tombstone, Arizona. *Am. Mineral.* **63**, 1016-1019.

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