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

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ABSTRACT

The crystal structure of dugganite, ideally Pb$_3$Zn$_3$Te$_{6+}$As$_2$O$_{14}$, $a$ 8.460(2), $c$ 5.206(2) Å, $V$ 322.6(2) Å$^3$, 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 MoKα radiation on an automated four-circle diffractometer. The structure consists of heteropolyhedral sheets of edge-sharing TeO$_6$ octahedra and PbO$_6$ 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). Cheremnykhite 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.

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$_2$O$_3$ 10.4, TeO$_3$ 14.0, H$_2$O (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 Pb$_3$Zn$_3$(TeO$_3$)$_x$(AsO$_4$)$_{2-x}$(OH)$_{6-2x}$, with $x$ in the range 0.94 to 1.33.
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, descloisezite, kuranakhite, naumannite, tiemannite, and yafsoanite. Single-crystal X-ray studies showed that the mineral is orthorhombic, with space group Cmmm, C222, C22m, Cm2m or Cmmm. Cell dimensions were refined from powder data: \( a = 8.57(3) \) Å, \( b = 14.84(5) \) Å, \( c = 5.21(3) \) 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 55.3, ZnO 18.82, SiO\(_2\) 0.96, P\(_2\)O\(_5\) 0.70, V\(_2\)O\(_5\) 3.61, As\(_2\)O\(_3\) 12.16, Sb\(_2\)O\(_3\) 0.07, TeO\(_2\) 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 \( \text{Pb}_3\text{Zn}_3\text{Te}(\text{As},\text{V},\text{Si})_2(\text{O},\text{OH})_{14} \). Other analogues of this mineral that contain \( \text{V} + \text{Si} \gg \text{As} \), 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 kukuikite, two new minerals associated with dugganite in the Kuranakh deposit. The formulae, determined from results of electron-microprobe analyses, were \( \text{Pb}_2\text{Zn}_2\text{Te}_2(\text{V},\text{Si})_2(\text{O},\text{OH})_{14} \) for cheremnykhite and \( \text{Pb}_2\text{Zn}_2\text{Te}_2(\text{P})_2(\text{O})_6 \) for kukuikite. X-ray-diffraction studies showed that both minerals are orthorhombic (Cmmm, C222, C2mm, Cm2m or Cmmm), with cell dimensions similar to those previously determined for dugganite from the same deposit (Kim et al. 1988). Their conclusion was that cheremnykhite, kukuikite 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 (AlK\(_2\)O), zircon (SiK\(_2\)O), Pb\(_2\)Ti(PO\(_4\))\(_6\) (PK\(_2\)O), CaT\(_2\)O\(_{11}\) (CaK\(_2\)O), VP\(_2\)O\(_5\) (VK\(_2\)O), cuprite (CuK\(_2\)O), willemite (ZnK\(_2\)O), mimetite (AsLa), TeO\(_2\) (TeLa), and crocoite (PbMg). 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>
<thead>
<tr>
<th>Element</th>
<th>Williams (1978)*</th>
<th>Kim et al. (1988)+</th>
<th>This study‡</th>
</tr>
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<tr>
<td>CaO wt.%</td>
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<td>51.47</td>
<td>53.13</td>
</tr>
<tr>
<td>PbO</td>
<td>55.3</td>
<td>51.47</td>
<td>53.13</td>
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<td>CuO</td>
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<td>1.06</td>
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<td>Al(_2)O(_3)</td>
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<td>0.96</td>
<td>0.98</td>
<td>1.08</td>
</tr>
<tr>
<td>P(_2)O(_5)</td>
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<td>0.70</td>
<td>4.90</td>
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<td>10.4</td>
<td>12.16</td>
<td>8.28</td>
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<td>Sb(_2)O(_3)</td>
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<td>–</td>
</tr>
<tr>
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<td>12.61</td>
<td>13.48</td>
</tr>
<tr>
<td>H(_2)O</td>
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</tr>
<tr>
<td>TOTAL</td>
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<td>100.40</td>
<td>99.50</td>
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</table>

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, CO\(_2\). 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...
The crystal structure of Dugganite was investigated using 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° 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.

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° 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.

Table 2, together with the orientation matrix relating the crystal axes to the diffractometer axes. Intensity data were collected in the 0–20 scan mode, using 96 steps with a scan range from 20 (MoKα1) – 1.1° to 20 (MoKα2) + 1.1° and a variable scan-rate between 0.5 and 2°/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" 20. Eighteen of the reflections were rejected because of asymmetric backgrounds. Fourteen strong reflections uniformly distributed with regard to 20 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 ≥ 3σ(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 [I/σ² - 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 after 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 (σ²; Hawthorne et al. 1989) is 16.9. The variance in the octahedron angle is 18.4°, the mean quadratic elongation of the octahedron (Robinson et al. 1971) is 1.0053, and the polyhedral 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 (½,½, z), is coordinated by four O atoms forming a distorted tetrahedron. The As–O distances are 1.64 Å (x 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 polyhedral 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...
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 $3f(x,0,1/2)$, 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 $^{42}$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 Å$^3$. 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$_6$ 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$_6$ 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$_6$ 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$_6$ 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 Schlafli 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 Schlafli 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$_6$ polyhedra,
Fig. 2b. The layer of tetrahedra in the dugganite structure, projected onto (001). The AsO₄ tetrahedra are shaded with crosses, and the ZnO₄ 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 PbO₆ polyhedra in a different sheet. The AsO₄ and TeO₆ polyhedra have no anions in common and thus are not directly joined. Each ZnO₄ tetrahedron shares two corners with two TeO₆ octahedra in different sheets, and four corners with six different PbO₆ polyhedra. The sheets of heteropolyhedra and layers of tetrahedra alternate along c to form the three-dimensional structure.
The ideal formula of dugganite is $\text{Pb}_3\text{Zn}_3\text{Te}\text{As}_8\text{O}_{14}$.

The electron microprobe and bond-valence analyses imply that there is little to no OH or H$_2$O 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 $(\text{Pb}_{3.04}\text{Ca}_{0.06})_{\delta}\text{Te}_{0.98}(\text{As}_{0.92}\text{P}_{0.88}\text{Si}_{0.23}\text{Al}_{0.00})_{\delta}\text{O}_{13.90}$. This is similar to the formula based on the structure analysis, which is $\text{Pb}_3\text{Zn}_3\text{Te}\text{As}_{1.08}\text{P}_{0.92}\text{O}_{14}$. 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 $\text{Pb}_{3.04}(\text{Zn}_{3.06}\text{Cu}_{0.21})_{\delta}\text{Te}_{1.10}\text{As}_{1.33}\text{V}_{0.51}\text{Si}_{0.20}\text{P}_{0.10}\text{Sb}_{0.01}\text{O}_{12.02}$, and $\text{Pb}_2\text{Zn}_{2.95}\text{Te}_{0.99}(\text{As}_{1.35}\text{V}_{0.51}\text{Si}_{0.20}\text{P}_{0.10}\text{Sb}_{0.01})_{\delta}\text{O}_{12.02}$, 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 ($a \approx 8.6$, $b \approx 14.8$, $c \approx 5.2$ Å) for all three minerals, and suggested C$\text{mmm}$, C$\text{222}$, C$\text{2mm}$, C$\text{m2m}$ or C$\text{mm2}$ as possible space-groups. The orthorhombic cell can be derived from a hexagonal unit-cell by using the formula $b_{\text{hex}} = 2a_{\text{hex}} \cos 30^\circ$. 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 P$\text{3}2\text{1}$. 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 P$\text{3}2\text{1}$.

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