Te-rich raspite, Pb(W_{0.56}Te_{0.44})O_4, from Tombstone, Arizona, U.S.A.: The first natural example of Te\textsuperscript{6+} substitution for W\textsuperscript{6+}

MARCELO B. ANDRADE\textsuperscript{1,*}, HEXIONG YANG\textsuperscript{1}, ROBERT T. DOWNS\textsuperscript{1}, ROBERT A. JENKINS\textsuperscript{1} AND ISABEL FAY\textsuperscript{1}

\textsuperscript{1}Department of Geosciences, University of Arizona, Tucson, Arizona 85721-0077, U.S.A.

**Abstract**

Te-rich raspite, Pb(W_{0.56}Te_{0.44})O_4, from the Grand Central mine, Tombstone, Arizona, U.S.A., was studied with single-crystal X-ray diffraction, Raman spectroscopy, and electron microprobe analysis. The mineral represents the first natural example of Te\textsuperscript{6+} substitution for W\textsuperscript{6+}. It displays monoclinic symmetry with space group $P2_1/a$ and unit-cell parameters $a = 13.621(3)$ Å, $b = 5.019(1)$ Å, $c = 5.586(1)$ Å, $\beta = 107.979(5)^\circ$, and $V = 363.2(2)$ Å$^3$. Its structure consists of distorted MO$_6$ ($M = W + Te$) octahedra sharing edges to form zigzag chains running parallel to [010]. These octahedral chains are linked together by seven-coordinated Pb$^{2+}$ cations. In addition, a refinement of the regular raspite structure with measured chemistry Pb$_{10}$W$_{10}$O$_{40}$, $P2_1/a$ symmetry, and unit-cell parameters $a = 13.5773(8)$ Å, $b = 4.9806(3)$ Å, $c = 5.5670(3)$ Å, $\beta = 107.658(3)^\circ$, and $V = 358.72(4)$ Å$^3$ is presented. Compared with regular raspite (PbWO$_4$), the partial substitution of the small radius Te\textsuperscript{6+} for larger W\textsuperscript{6+} results in a decrease in the MO$_6$ octahedral distortion, with a concomitant increase in the MO$_6$ octahedral volume and the average Pb-O bond length. In addition, as should be expected for mixed occupancy compounds, most Raman bands for the mixed Te-rich raspite are broader than the corresponding ones for the end-member regular raspite. High-temperature annealing experiments reveal that Te-rich raspite transforms irreversibly to the stolzite structure at 590(10) °C, which is considerably higher than the reported transformation temperature of 395(5) °C for regular raspite.

**Keywords:** Te-rich raspite, lead tungstate, stolzite, crystal structure, X-ray diffraction, Raman spectra, phase transformation

**Introduction**

Naturally occurring lead tungstate (PbWO$_4$), has been reported to crystallize in the high-temperature tetragonal $I4_1/a$ stolzite structure (Plakhov et al. 1970) or the low-temperature monoclinic $P2_1/a$ raspite structure (Fujita et al. 1977). These phases are useful as compounds in scintillators that possess many unique physical properties, such as high density, short radiation length, short decay constant, and high radiation hardness (e.g., Arora and Chudasama 2007; Yeom and Lim 2012). They have been used as laser host materials (Chen et al. 2001), scintillators in high-energy physics detectors (Kobayashi et al. 1998; Annenkov et al. 2002), and an oxide ion conductor (Takai et al. 1999). Furthermore, considerable efforts have been devoted to synthesize nanobelt or bamboo-leaf-like raspite to understand its luminescence properties (George et al. 2008; Zheng et al. 2010).

Relative to the tetragonal stolzite, the low-temperature monoclinic raspite is rare in nature and transforms irreversibly to stolzite between 400 and 450 °C (Shaw and Claringbull 1955; Bastians et al. 2004). In addition, a third monoclinic ($P2_1/n$) phase, PbWO$_4$-III, can be synthesized by quenching from high-pressure and high-temperature conditions (Richter et al. 1976). Raspite was originally described by Hlawatsch (1897) from Broken Hill, New South Wales, Australia. Shaw and Claringbull (1955) conducted the first X-ray structural analysis on this mineral, but only located the positions of Pb\textsuperscript{2+} and W\textsuperscript{6+}. A detailed structural model of raspite was reported by Fujita et al. (1977) without anisotropic displacement parameters for O atoms ($R = 0.080$). This paper reports the structure determinations of a Te-rich raspite, Pb(W_{0.56}Te_{0.44})O_4, and a regular raspite of ideal composition PbWO$_4$, from single-crystal X-ray diffraction experiments along with Raman spectra measured before and after heat-treatments, revealing that the substitution of Te\textsuperscript{6+} for W\textsuperscript{6+} can appreciably expand the phase stability field of raspite as a function of temperature.

**Experimental Procedures**

The Te-rich raspite specimen used in this study is from the Grand Central mine, Tombstone, Arizona, U.S.A., and is in the collection of the RRUFF Project (http://rruff.info/R130514). The crystals are pale yellow-to-colorless, elongated, and prismatic-to-tabular. They are associated with chlorargyrite, enargite, ottoite, quartz, and jarosite. The regular raspite specimen is from Broken Hill, New South Wales, Australia (http://rruff.info/R050567) and the crystals display similar morphology to the Te-rich raspite. The chemical compositions of the two samples were analyzed using a Cameca SX100 electron microprobe at 20 kV and 20 nA with a beam size of <1 mm. The following standards were used: NBS K458 glass (Pb), scheelite (W), zinc telluride (Te), and anorthite (Al). The average compositions (wt%) (9 analysis points for both samples) are PbO 50.79(51), WO$_3$ 30.93(1.55), TeO$_2$ 18.26(1.75), and Al$_2$O$_3$ 0.12(4) for Te-rich raspite, and PbO 48.85(28) and WO$_3$ 50.93(32) for...
regular raspite. The resultant empirical formulas are Pb\(_{0.56}\)(Te\(_{0.44}\)Al\(_{2}\))\(_2\)O\(_4\) and Pb\(_{0.56}\)Te\(_{0.44}\)O\(_4\) for Te-rich and regular raspite, respectively.

Single-crystal X-ray diffraction data for Te-rich and regular raspite were collected from nearly equi-dimensional crystals on a Bruker X8 APEX2 CCD X-ray diffractometer equipped with graphite-monochromatized MoK\(\alpha\) radiation. Reflections with \(I > 2\sigma(I)\) were indexed based on a monoclinic unit cell (Table 1). No satellite or super-lattice reflections were observed. The intensity data were corrected for X-ray absorption using the Bruker program SADABS. The systematic absence of reflections suggests the unique space group \(P2_1/a\). The crystal structure was solved and refined using SHELX97 (Sheldrick 2008). The positions of all atoms were refined with anisotropic displacement parameters. For simplicity, during the structure refinements, the Pb site was assumed to be fully occupied by W\(^{6+}\). The full Pb occupancy model was thus adopted. For the regular raspite, the structure refinement indicated the ideal formula PbWO\(_4\). Final atomic coordinates and displacement parameters are listed in Table 2, and selected bond lengths and angles in Table 3.

The Raman spectra of Te-rich and regular raspite were recorded on a Thermo-Almna microRaman system in the temperature range of 350 to 650 \(^\circ\)C in air in 10 or 20 \(^\circ\)C steps for 24 h duration at each temperature. Both samples were examined by Raman spectroscopy at each step after cooling to bracket the temperature ranges for the phase transformation.

### Results and Discussion

#### Crystal Structure

The crystal structure of Te-rich raspite is characterized by distorted MO\(_6\) (\(M = W + Te\)) octahedra sharing edges to form zigzag chains parallel to [010]. These octahedral chains are interlinked by Pb atoms coordinated to seven O atoms (Fig. 1, Table 3). Compared with the MO\(_6\) octahedron in regular raspite, that in Te-rich raspite is noticeably less distorted, as measured by the octahedral angle variance (OAV) and quadratic elongation (OQE) indices (Robinson et al. 1971), 85 and 1.029, respectively, for the MO\(_6\) octahedron in Te-rich raspite and 104 and 1.038 for that in regular raspite (Table 3). The greater distortion of the MO\(_6\) octahedron in regular raspite stems primarily from the

<table>
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<tr>
<th>Atom</th>
<th>(x)</th>
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<th>(z)</th>
<th>(U_{iso})</th>
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<td>Pb</td>
<td>0.15739(2)</td>
<td>0.19923(6)</td>
<td>0.16068(6)</td>
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<td>0.0182(1)</td>
<td>0.0245(2)</td>
<td>0.0206(2)</td>
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<td>0.0195(4)</td>
<td>0.0548(10)</td>
<td>0.727(9)</td>
<td>0.013(1)</td>
<td>0.0136(22)</td>
<td>0.0147(21)</td>
<td>0.0087(21)</td>
<td>0.0042(17)</td>
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<tr>
<td>O2</td>
<td>0.0614(4)</td>
<td>0.4347(9)</td>
<td>0.3918(9)</td>
<td>0.011(1)</td>
<td>0.0121(21)</td>
<td>0.0082(19)</td>
<td>0.0162(23)</td>
<td>0.0000(16)</td>
<td>0.0009(18)</td>
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<tr>
<td>O3</td>
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<td>0.6318(11)</td>
<td>0.9075(9)</td>
<td>0.0182(10)</td>
<td>0.0198(25)</td>
<td>0.0213(25)</td>
<td>0.0093(22)</td>
<td>0.0069(19)</td>
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<tr>
<td>O4</td>
<td>0.1847(4)</td>
<td>0.8853(10)</td>
<td>0.5273(10)</td>
<td>0.0150(9)</td>
<td>0.0103(22)</td>
<td>0.0186(23)</td>
<td>0.0262(19)</td>
<td>0.0083(19)</td>
<td>0.0043(19)</td>
</tr>
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Note: \(M = 0.56 \ W + 0.44 \ Te\).
so-called second-order Jahn-Teller (SOJT) effect of W⁶⁺, owing to its empty d-shell (e.g., Ra et al. 2003; Lufaso and Woodward 2004). In contrast, Te⁶⁺ has a full d-shell, which suppresses part of the SOJT distortions.

The partial substitution of smaller Te⁶⁺ (r = 0.56 Å) for larger W⁶⁺ (r = 0.60 Å) (Shannon 1976) results in little change in the average M-O bond distance, but a significant increase in the average Pb-O bond length from 2.610 Å in regular raspite to 2.635 Å in Te-rich raspite (Table 3). Nevertheless, due to less distortion, the volume of the MO₆ octahedron in Te-rich raspite (9.472 Å³) is larger than that in regular raspite (9.426 Å³) (Table 3). Thus, it appears that the Te⁶⁺ substitution for W⁶⁺ in raspite reduces its structural packing efficiency, making the unit-cell parameters of Te-rich raspite greater than those of regular raspite (Table 1).

From the crystal-chemical point of view, because six-coordinated W⁶⁺, Mo⁶⁺, and Te⁶⁺ have similar ionic radii, 0.60, 0.59, and 0.56 Å (Shannon 1976), respectively, one may expect extensive solid solutions among them. This is indeed the case for some synthetic compounds, such as LaNi₀.₈M₀.₂O₃ (M = Mo⁶⁺, Te⁶⁺, W⁶⁺) (Alvarez et al. 1995, 1997), Li₇(Y₄,Te₃)O₈ (Wang et al. 2010), and various Mo-Te mixed oxides used as catalysts in the gas phase selective oxidation of hydrocarbons (e.g., López Nieto et al. 2003; Holmberg et al. 2007; Botella et al. 2009). However, there has been no report thus far for the significant substitution of Te⁶⁺ for W⁶⁺ or Mo⁶⁺ in minerals, despite the common substitution between W⁶⁺ and Mo⁶⁺, as in the scheelite group of minerals (Tyson et al. 1988; Zhang et al. 1998) and in stolzite from France (Chiappero et al. 2011). Therefore, our Te-rich raspite represents the first natural example of Te⁶⁺ substituting for W⁶⁺.

Raman spectra

Both raspite and stolzite have been previously investigated with Raman spectroscopy (Frost et al. 2004; Bastians et al. 2004; Yang and Huang 2012). Detailed assignments of major Raman bands for raspite have been proposed by Bastians et al. (2004). Figure 2 shows the Raman spectra of Te-rich and regular raspite. Evidently, the two spectra are analogous, but some differences between them are discernible. Specifically, as a consequence of the partial Te⁶⁺ substitution for W⁶⁺ (Te-W disordering) in the octahedral site, most Raman bands for Te-rich raspite are considerably broader than the corresponding ones for regular raspite. In particular, between 840 and 920 cm⁻¹, there is only one strong, sharp band at 870 cm⁻¹ for regular raspite, which is ascribable to the W-O symmetrical stretching vibrations within the WO₆ octahedron (Bastians et al. 2004; Yang and Huang 2012). In contrast, there are two strong overlapped bands in the

**Figure 1.** Crystal structure of Te-rich raspite. The octahedra and spheres represent the MO₆ (M = W + Te) groups and Pb atoms, respectively. (Color online.)

**Figure 2.** Raman spectra of Te-rich and regular raspites at room temperature. The spectra are shown with vertical offset for more clarity. (Color online.)

**Figure 3.** Raman spectra of regular and Te-rich raspites annealed at different temperatures. The Raman spectrum of stolzite was taken from the RRUFF Project (http://rruff.info/R050568) for comparison. The spectra are shown with vertical offset for more clarity. Annealing temperatures are indicated on the left.
same region for Te-rich raspite, the major one at 881 cm$^{-1}$ and the shoulder at 871 cm$^{-1}$ (Fig. 2), which may be assigned to the Te-O and W-O symmetrical stretching vibrations within the MO$_6$ octahedron, respectively, as the Te-O bond is shorter and stronger with more covalent nature than the W-O bond (Wang et al. 2010). The bands between 620 and 750 cm$^{-1}$ for the two minerals have been assigned to the M-O anti-symmetrical vibrations (Bastians et al. 2004; Yang and Huang 2012). Similarly, these bands are broader and more complex for Te-rich raspite than for regular raspite due to the partial Te$^{6+}$ substitution for W$^{6+}$.

The irreversible transformation from the raspite to stolzite structure has been the subject of several investigations because it puts operational constraints on high-tech applications (Shaw and Claringbull 1955; Bastians et al. 2004; Wang et al. 2010; Yang and Huang 2012). Te/W are tetrahedrally coordinated in stolzite, in contrast to six coordinated in raspite. Since the raspite to stolzite transformation is not reversible, our Raman spectra measured from the annealed samples indicate the temperatures at which the phase transformation occurred, which is 395(5) °C for regular raspite and 590(10) °C for Te-rich raspite (Fig. 3). The higher phase transition temperature for Te-rich raspite is a consequence of the stronger Te$^{6+}$-O bond compared to the weaker W$^{6+}$-O bond (Wang et al. 2010), thus requiring more energy to break. In other words, our data indicate that the phase stability field of raspite as a function of temperature can be markedly increased through the substitution of Te$^{6+}$ for W$^{6+}$.

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