LETTER

Te-rich raspite, Pb(W_{0.56}Te_{0.44})O₄, from Tombstone, Arizona, U.S.A.: The first natural example of Te⁶⁺ substitution for W⁶⁺

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ABSTRACT

Te-rich raspite, Pb(W_{0.56}Te_{0.44})O₄, 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 Te⁶⁺ substitution for W⁶⁺. It displays monoclinic symmetry with space group $P2_1/a$ and unit-cell parameters a = 13.621(3), b = 5.019(1), c = 5.586(1)Å, $\beta = 107.979(5)^\circ$, and V = 363.2(2) Å³. 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 Pb₁₀₀W₁₀₀O₄, $P2_1/a$ symmetry, and unit-cell parameters a = 13.5773(8), b = 4.9806(3), c = 5.5670(3) Å, $\beta = 107.658(3)^{\circ}$, and V = 358.72(4) Å³ is presented. Compared with regular raspite (PbWO₄), the partial substitution of the small radius Te^{6+} for larger W⁶⁺ 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 (PbWO₄), 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, PbWO₄-III, can be synthesized by quenching from high-

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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 Pb²⁺ and W⁶⁺. 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})O₄, and a regular raspite of ideal composition PbWO₄, from single-crystal X-ray diffraction experiments along with Raman spectra measured before and after heat-treatments, revealing that the substitution of Te⁶⁺ for W⁶⁺ 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, emmonsite, 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), WO₃ 30.93(1.55), TeO₃ 18.26(1.75), and Al₂O₃ 0.12(4) for Te-rich raspite, and PbO 48.85(28) and WO₃ 50.93(32) for

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regular raspite. The resultant empirical formulas are $Pb_{0.96}(W_{0.57}Te_{0.44}Al_{0.01})_{1.02}O_4$ and $Pb_{1.00}W_{1.00}O_4$ 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 MoKa 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 suggest 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 Te-raspite structure refinements, the Pb site was assumed to be fully occupied by Pb and the M (= W + Te) site by (0.56 W + 0.44 Te). The Pb site occupancy was also varied during the refinement, which produced a refined occupancy of 1.01. A full Pb occupancy model was thus adopted. For the regular raspite, the structure refinement indicated the ideal formula PbWO4. Final atomic coordinates and displacement parameters are listed in Table 2, and selected bond lengths and angles in Table 3. (CIF1 available.)

The Raman spectra of Te-rich and regular raspite were recorded on randomly oriented crystals on a Thermo-Almega microRaman system, using a solid-state laser with a frequency of 532 nm and a thermoelectrically cooled CCD detector.

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The laser is partially polarized with 4 cm-1 resolution and a spot size of 1 µm.

To better understand the effect of the Te⁶⁺ substitution for W⁶⁺ on the raspiteto-stolzite transformation, we also carried out high-temperature annealing experiments on both Te-rich and regular raspite. The two samples were heated at a series of increasing temperatures from 390 to 600 °C in air in 10 or 20 °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 1.
 Crystallographic data and refinement results for Te-rich and regular raspites

TABLE 3.	Selected bond distances and angles for Te-rich and regular
	raspites

regular raspites			Pb(W _{0.56} Te _{0.44})O ₄ PbWO ₄			
	Te-rich raspite	Regular raspite	W-01	1.929(5)	1.886(5)	
Chemical formula	$Pb(W_{0.56}Te_{0.44})O_4$	PbWO ₄	W-01'	2.118(5)	2.192(5)	
Crystal size (mm)	stal size (mm) 0.05 × 0.04 × 0.04 0.05 ×		W-O2	1.941(5)	1.930(5)	
Space group	<i>P</i> 2 ₁ / <i>a</i> (No. 14)	P2 ₁ /a (No. 14)	W-O2'	2.080(5)	2.116(5)	
a (Å)	13.621(3)	13.5773(8)	W-O3	1.800(5)	1.767(6)	
b (Å)	5.0187(12)	4.9806(3)	W-04	1.807(5)	1.800(5)	
c (Å)	5.5858(14)	5.5670(3)	Average	1.946	1.9450	
β (°)	107.979(5)	107.658(3)				
V (ų)	363.19(15)	358.72(4)	OV	9.472	9.426	
Ζ	4	4	OQE	1.029	1.038	
ρ _{cal} (g/cm³)	7.869	8.426	OAV	85.4	104.2	
λ (Å)	0.71073	0.71073				
µ (mm⁻¹)	67.40	78.76	Pb-O1	2.665(5)	2.663(5)	
2θ range for data collection ≤65.34		≤65.15	Pb-O1'	2.958(5)	2.773(6)	
No. of reflections colle	ected 5113	8180	Pb-O2	2.412(4)	2.323(5)	
Index ranges	–20 ≤ <i>h</i> ≤ 15,	–20 ≤ <i>h</i> ≤ 19,	Pb-O3	2.571(5)	2.545(6)	
	$-7 \le k \le 7, -8 \le l \le 8$	$0 \le k \le 7, 0 \le l \le 8$	Pb-O3'	2.823(6)	2.946(6)	
No. of independent reflections 1336 1315			Pb-O4	2.495(5)	2.529(6)	
No. of reflections with	$1 > 2\sigma(l)$ 1211	1156	Pb-O4'	2.495(5)	2.486(5)	
No. of parameters refined 57		56	Average	2.635	2.610	
R _{int}	0.033	0.048	Del la del al antes	24.205	22.022	
Final <i>R</i> factors $[l > 2\sigma(l)] R_1 = 0.026, wR_2 = 0.052$ $R_1 = 0.025, wR_2 = 0.053$			Polynedral volume	24.295	23.923	
Final <i>R</i> factors (all data) $R_1 = 0.031$, $wR_2 = 0.054$ $R_1 = 0.032$, $wR_2 = 0.055$			Note: OV = octahedral volume, OQE = octahedral quadratic elongation, OAV =			
Goodness-of-fit	1.13	1.06	octahedral angle variance (Robinson et al. 1971).			

TABLE 2. Coordinates and dis	placement parameters o	f atoms in Te-rich ras	pite and regular rasi	oite

Atom	Х	У	Ζ	U_{iso}	U_{11}	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
				Te-	rich raspite (R1	30514)				
Pb	0.15739(2)	0.19923(6)	0.16068(6)	0.02070(9)	0.0182(1)	0.0245(2)	0.0206(2)	-0.0067(1)	0.0078(1)	-0.0008(1)
М	0.07414(2)	0.75045(6)	0.59996(6)	0.01008(9)	0.0106(1)	0.0080(1)	0.0108(1)	0.0013(1)	0.0020(1)	0.0000(1)
01	0.0195(4)	0.0548(10)	0.7274(9)	0.0131(9)	0.0136(22)	0.0147(21)	0.0087(21)	-0.0042(17)	0.0001(17)	0.0031(17)
02	0.0614(4)	0.4347(9)	0.3918(9)	0.0111(9)	0.0121(21)	0.0082(19)	0.0162(23)	0.0000(16)	0.0091(18)	0.0002(16)
O3	0.1472(4)	0.6318(11)	0.9075(9)	0.0182(10)	0.0198(25)	0.0213(25)	0.0093(22)	0.0069(19)	-0.0017(19)	-0.0034(20)
04	0.1847(4)	0.8853(10)	0.5273(10)	0.0150(9)	0.0103(22)	0.0186(23)	0.0162(23)	0.0083(19)	0.0043(19)	0.0007(18)
				Reg	ular raspite (R)50567)				
Pb	0.14961(2)	0.19458(6)	0.16665(5)	0.01241(9)	0.01146(14)	0.01554(15)	0.01123(14)	-0.00060(9)	0.00496(10)	0.00496(10)
W	0.07711(2)	0.74936(5)	0.61164(5)	0.00792(8)	0.00726(14)	0.00834(14)	0.00809(14)	0.00048(9)	0.00222(10)	0.00222(10)
01	0.0172(4)	0.0442(11)	0.7282(10)	0.0117(10)	0.011(2)	0.014(3)	0.009(3)	-0.0001(19)	0.002(2)	0.002(2)
02	0.0627(4)	0.4416(11)	0.3930(10)	0.0112(10)	0.008(2)	0.012(2)	0.017(3)	-0.003(2)	0.009(2)	0.009(2)
03	0.1468(4)	0.6191(12)	0.9101(10)	0.0155(11)	0.014(3)	0.017(3)	0.015(3)	0.002(2)	0.003(2)	0.003(2)
04	0.1865(4)	0.8922(11)	0.5388(10)	0.0135(11)	0.010(3)	0.016(3)	0.016(3)	0.004(2)	0.005(2)	0.005(2)
Note: M	= 0.56 W + 0.44 T	e.								

so-called second-order Jahn-Teller (SOJT) effect of W^{6+} , 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 *M*O₆ 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). Similar results have been observed for the LaNi_{0.8}M_{0.2}O₃ solid solution ($M = Mo^{6+}$, Te⁶⁺, W⁶⁺), in which the unit-cell volume of the Te-bearing phase is larger than that of the W-bearing phase (Alvarez et al. 1995, 1997).

From the crystal-chemical point of view, because six-coordinated W^{6+} , Mo^{6+} , and Te^{6+} 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 $LaNi_{0.8}M_{0.2}O_3$ ($M = Mo^{6+}$, Te^{6+} , W^{6+}) (Alvarez et al. 1995, 1997), Pb₂Mg($W_{1-x}Te_x$)O₆ (Rivezzi and Sciau 1998), LiY($W_{1-x}Te_x$)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⁺



FIGURE 1. Crystal structure of Te-rich raspite. The octahedra and spheres represent the MO_6 (M = W + Te) groups and Pb atoms, respectively. (Color online.)

in minerals, despite the common substitution between W^{6+} and Mo^{6+} , 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 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.

► 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.)



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 Te⁶⁺ substitution for W⁶⁺.

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 Te6+-O bond compared to the weaker W⁶⁺-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 Te6+ for W6+.

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