American Mineralogist, Volume 99, pages 1507–1510, 2014

LETTER

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

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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^{6+} substitution for W^{6+}. 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, β = 107.979(5)°, 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 $Pb_{1.00}W_{1.00}O_4$, $P2_1/a$ symmetry, and unit-cell parameters a = 13.5773(8), b = 4.9806(3), c = 5.5670(3) Å, β = 107.658(3)°, and V = 358.72(4) Å^3 is presented. Compared with regular raspite ($PbWO_4$), the partial substitution of the small radius Te^{6+} for larger W^{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