Uranotungstite, the only natural uranyl tungstate: Crystal structure revealed from 3D electron diffraction

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ABSTRACT

Uranotungstite is an uranyl-tungstate mineral that was until recently only partially characterized with a formula originally given as (Fe2+,Ba,Pb)(UO2)2(WO4)(OH)4.12H2O and an unknown crystal structure. This mineral has been reinvestigated by electron microprobe analysis coupled with three-dimensional electron diffraction. According to the electron microprobe data, the holotype material from the Menzenschwand uranium deposit (Black Forest, Germany) has the empirical formula (Ba0.33,Pb0.27)(U0.99,Fe0.76,Mn0.73)O4·(OH)2·(H2O)4·(H2O)1.67·12H2O (average of 8 points calculated on the basis of 2U apfu; H2O content derived from the structure). According to the precession-assisted 3D ED data, holotype uranotungstite from Menzenschwand is monoclinic, P21/m, with a = 6.318(5) Å, b = 7.388(9) Å, c = 13.71(4) Å, β = 99.04(13)°, and V = 632(2) Å3 (Z = 2). The structure refinement of the 3D ED data using the dynamical approach (Rd = 0.0846 for 3287 independent observed reflections) provided a structure model composed of heteropolyhedral sheets. A β-UO4-type sheet of idealized composition [(UO2)2(WO4)2·(OH)2·(H2O)4]0.75·(H2O)0.25·(H2O)1.67·12H2O is composed of UO4 polyhedra linked by (W,Fe)O6 polyhedra in which the W:Fe ratio is variable as well as the bulk occupancy of this site; the W site may also host a minor proportion of Cu, Mg, or V. In uranotungstite, the interlayer spaces between adjacent U-W-O sheets host water on one side and, on the other side, a partially occupied cation site mostly occupied by Ba and, to a lesser extent, Pb, as well as a partially occupied H2O site. This work is the first structural description of a natural uranyl-tungstate mineral and confirms the great structural and chemical flexibility of β-UO4-type sheets.

Keywords: Uranotungstite, uranyl tungstate, crystal structure, crystal chemistry, Menzenschwand, 3D electron diffraction

INTRODUCTION

Uranotungstite is the only uranyl tungstate known in nature and is a rare alteration product of oxidation-hydration weathering of uraninite. Its rarity mostly arises from a rather unusual association of uranium and tungsten in the most common types of uranium deposits worldwide. It was described for the first time by Walenta (1985) from the Menzenschwand deposit (also referred to as Krunkelbach) uranium deposit in the Black Forest, Baden-Württemberg, Germany. The type material forms spherulitic aggregates of 0.3 mm in diameter and is associated with meta-uranocircite, metaheinrichite, and other secondary uranium minerals. Apart from the commonly observed yellow, brown-yellow to orange colors, the mineral may also be olive-green, greenish, or blackish. Electron microprobe analysis (EMPA) of the type material led to the reported empirical formula (Fe0.38,Ba0.3,Pb0.3)4.11,U1.83W0.93H3.9O12, where Fe was considered divalent. This formula was then idealized to (Fe,Ba,Pb)(UO2)2(WO4)(OH)4.12H2O by Walenta (1985). Later on, more uranotungstite was found by Walenta (1985) from the Clara barite-fluorite mine in the Black Forest, Germany, but in the Clara mine material, only traces of Ba and no Pb were semi-quantitatively detected.

Based on the morphology of the lath-like crystals of the type material, the mineral was first assumed to be orthorhombic, and unit-cell parameters a = 9.22, b = 13.81, c = 7.17 Å (Z = 2) were proposed on the basis of a tentatively indexed X-ray powder diffraction pattern. The lath-like crystals show (010) as a flattening plane, and they exhibit perfect cleavage. Unlike the type material from Menzenschwand, the Clara mine samples rather show thin platy, subparallel crystals with diamond-shaped outlines. Nevertheless, the crystal structure of the type material could not be determined by X-ray diffraction (powder or single crystal) due to the very small size and subparallel intergrowth of the crystals. More generally, except for its original description, the mineral has remained poorly