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Mathesiusite, $K_5(UO_2)_4(SO_4)_4(VO_5)(H_2O)_4$, a new uranyl vanadate-sulfate from Jáchymov, Czech Republic

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Abstract

Mathesiusite, $K_5(UO_2)_4(SO_4)_4(VO_5)(H_2O)_4$, a new uranyl vanadate-sulfate mineral from Jáchymov, Western Bohemia, Czech Republic, occurs on fractures of gangue associated with adolfpateraite, schoepite, čejkaite, zippeite, gypsum, and a new unnamed K-UO_2-SO_4 mineral. It is a secondary mineral formed during post-mining processes. Mathesiusite is tetragonal, space group $P4/n$, with the unit-cell dimensions a = 14.9704(10), c = 6.8170(5) Å, V = 1527.78(18) Å^3, and Z = 2. Acicular aggregates of mathesiusite consist of prismatic crystals up to ~200 μm long and several micrometers thick. It is yellowish green with a greenish white streak and vitreous luster. The Mohs hardness is ~2. Mathesiusite is brittle with an uneven fracture and perfect cleavage on {110} and weaker on {001}. The calculated density based on the empirical formula is 4.02 g/cm^3. Mathesiusite is colorless in fragments, uniaxial (–), with ω = 1.634(3) and ε = 1.597(3). Electron microprobe analyses (average of 7) provided: K_2O 12.42, SO_3 18.04, V_2O_5 4.30, UO_3 61.46, H_2O 3.90 (structure), total 100.12 (all in wt%). The empirical formula (based on 33 O atoms pfu) is: $K_{4.87}(U_{0.99}O_2)_4(S_{1.04}O_4)_4(V_{0.87}O_5)(H_2O)_4$. The eight strongest powder X-ray diffraction lines are [d_{obs} in Å (hkl) I_{rel}]: 10.64 (110) 76, 7.486 (200) 9, 6.856 (001) 100, 6.237 (101) 85, 4.742 (310) 37, 3.749 (400) 27, 3.296 (401) 9, and 2.9409 (510) 17. The crystal structure of mathesiusite was solved from single-crystal X-ray diffraction data and refined to R_1 = 0.0520 for 795 reflections with $I > 3\sigma(I)$. It contains topologically unique heteropolyhedral sheets based on $[(UO_2)_4(SO_4)_4(VO_5)]^{5-}$ clusters. These clusters arise from linkages between corner-sharing quartets of uranyl pentagonal bipyramids, which define a square-shaped void at the center that is occupied by V^{5+} cations. Each pair of uranyl pentagonal bipyramids shares two vertices of SO_4 tetrahedra. Each SO_4 shares a third vertex with another cluster to form the sheets. The K^+ cations are located between the sheets, together with a single H_2O group. The corrugated sheets are stacked perpendicular to **c**. These heteropolyhedral sheets are similar to those in the structures of synthetic uranyl chromates. Raman spectral data are presented confirming the presence of UO_2^{2+}, SO_4, and molecular H_2O.

Keywords: Mathesiusite, new mineral, uranyl sulfate, vanadate, crystal structure, Raman spectroscopy, oxidation zone, Jáchymov