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The new mineral tomiolloite, $Al_{12}(Te^{4+}O_3)_5[(SO_3)_{0.5}(SO_4)_{0.5}](OH)_{24}$: A unique microporous tellurite structure

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Abstract

Tomiolloite (IMA2021-019) is a new aluminum tellurite sulfite-sulfate mineral discovered at the Bambolla mine, Moctezuma, Sonora, Mexico, a well-known tellurium (Te) mineral locality. Tomiolloite forms roughly spherical clusters of crystals comprised of very thin, needle-like crystals (1 μm diameter, ~40 μm length) around a core of small, stubbier, broken crystals. Tomiolloite is generally found growing on tellurite or quartz. The strongest powder X-ray diffraction lines are [d_{obs} Å (I_{obs}) (*hkl*)]: 11.667 (89) (100), 8.240 (38) (101), 4.107 (29) (202,211,121), 3.223 (100) (203,302,130), and 2.905 (37) (213,123,222,400). The empirical formula of tomiolloite, as determined by electron microprobe analysis, is $(Al_{10.64}Te^{6+}_{1.01}Fe^{3+}_{0.31}Zn_{0.04})_{\Sigma 12}(Te^{4+}_{5.00}Pb_{0.02})_{\Sigma 5.02}(S^{4+}_{0.49}S^{6+}_{0.49}Si_{0.02})_{\Sigma 1.00}O_{21.53}[(OH)_{20.86}Cl_{0.11}]_{\Sigma 20.97}$, which is simplified to the ideal formula $Al_{12}(Te^{4+}O_3)_5[(SO_3)_{0.5}(SO_4)_{0.5}](OH)_{24}$. Significant Te^{6+} substitution for Al^{3+} is observed in tomiolloite, verified by X-ray photoelectron spectroscopy and crystal-structure analysis. The structure of tomiolloite was determined using synchrotron single-crystal X-ray diffraction, showing that tomiolloite is hexagonal and crystallizes in the space-group $P6_3/m$, with the unit-cell parameters $a = 13.3360(19)$ Å, $c = 11.604(2)$ Å, $V = 1787.3(6)$ Å^3, and $Z = 2$. Tomiolloite has a unique microporous framework structure, which bears a slight similarity to that of zemannite, but it has a much larger cavity diameter (8.85 Å). The framework is built from edge-sharing $M\varphi_6$ octahedra (M = Al^{3+} and Te^{6+}), $Te^{4+}O_3$ trigonal pyramids, and $Te^{4+}O_4$ disphenoids. $M\varphi_6$ octahedra edge-share to form crankshaft-shaped chains along c, with $Te^{4+}O_n$ polyhedra filling notches in the crankshafts and providing linkages between adjacent chains. The framework has an overall positive charge, which is balanced by the presence of both sulfite (SO_3^{2-}) trigonal pyramids and sulfate (SO_4^{2-}) tetrahedra in the channels.

Keywords: New mineral, crystal structure, tellurium oxysalt, microporous, synchrotron radiation, X-ray diffraction, Moctezuma, Sonora, Mexico; Microporous materials: crystal-chemistry, properties, and utilizations