

Elucidating the natural–synthetic mismatch of $\text{Pb}^{2+}\text{Te}^{4+}\text{O}_3$: The redefinition of fairbankite to $\text{Pb}_{12}^{2+}(\text{Te}^{4+}\text{O}_3)_{11}(\text{SO}_4)$

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ABSTRACT

For four decades fairbankite was reported to have the formula $\text{Pb}^{2+}(\text{Te}^{4+}\text{O}_3)$, but repeated attempts to isolate fairbankite crystals for structural determination found only the visually similar cerussite and, more rarely, anglesite. The crystal-structure determination of fairbankite using single-crystal X-ray diffraction, supported by electron microprobe analysis and X-ray powder diffraction on the type specimen, has shown that fairbankite contains essential S, along with Pb, Te, and O. The chemical formula of fairbankite has been revised to $\text{Pb}_{12}^{2+}(\text{Te}^{4+}\text{O}_3)_{11}(\text{SO}_4)$. This change has been accepted by the IMA–CNMNC, Proposal 19-I. The crystal structure of fairbankite [space group $P1$ (no. 1); revised cell: $a = 7.0205(3)$ Å, $b = 10.6828(6)$ Å, $c = 14.4916(8)$ Å, $\alpha = 75.161(5)^\circ$, $\beta = 81.571(4)^\circ$, $\gamma = 83.744(4)^\circ$, $V = 1036.35(9)$ Å³, and $Z = 1$] is the first atomic arrangement known to contain a $\text{Te}_3^{4+}\text{O}_6^{2-}$ non-cyclic, finite building unit. Fairbankite has an average structure, formed from a 3D framework of Pb^{2+}O_n polyhedra, Te^{4+}O_n polyhedra, and SO_4 tetrahedra in a 12:11:1 ratio. The stereoactive lone pairs of the Pb^{2+} and Te^{4+} cations are oriented into void space within the structure. Fairbankite contains two mixed sites statistically occupied by Te^{4+} and S^{6+} in approximately 4:1 and 1:4 ratios. These two sites possess Te^{4+} in trigonal-pyramidal environment and S^{6+} in tetrahedral environment (with an additional O site to create tetrahedral SO_4 shape for the S-dominant site). Six of the 10 fully occupied Te^{4+} sites have Te^{4+} in trigonal-pyramidal environment, while four have Te^{4+} at the center of highly distorted Te^{4+}O_4 disphenoids. The disphenoids allow for the creation of two dimeric $\text{Te}_2^{4+}\text{O}_8^{2-}$ units in addition to the $\text{Te}_3^{4+}\text{O}_6^{2-}$ trimeric unit, which contains two disphenoids. All linkage between disphenoids and trigonal pyramids is via corner-linking. Secondary connectivity is via long Te–O and Pb–O bonds.

Keywords: Lead tellurite, fairbankite, redefinition, crystal structure, tellurium oxysalt, average structure; Tombstone, Arizona, U.S.A.