Elucidating the natural–synthetic mismatch of Pb$^{2+}$Te$^{4+}$O$_3$: The redefinition of fairbankite to Pb$_{12}$((Te$^{4+}$O$_3$)$_{11}$(SO$_4$)$_2$)

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ABSTRACT

For four decades fairbankite was reported to have the formula Pb$^2+$(Te$^{4+}$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 Pb$_{12}$((Te$^{4+}$O$_3$)$_{11}$(SO$_4$)$_2$. 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, $c = 14.4916(5)$ Å, $\alpha = 75.161(5)^\circ$, $\beta = 81.571(4)^\circ$, $\gamma = 83.744(4)^\circ$, $V = 1036.35(9)$ Å$^3$, and $Z = 1$] is the first atomic arrangement known to contain a Te$^{4+}$O$_3$ non-cyclic, finite building unit. Fairbankite has an average structure, formed from a 3D framework of Pb$^2+$, Te$^{4+}$ polyhedra, Te$^{4+}$O$_3$ 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$_7$ disphenoids. The disphenoids allow for the creation of two dimeric Te$_4$O$_7$ units in addition to the Te$_4$O$_7$ 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.

INTRODUCTION

A detailed description of synthetic compounds with the apparently simple formula Pb$^{2+}$Te$^{4+}$O$_3$ (monoclinic $\alpha$-Pb$^{2+}$Te$^{4+}$O$_3$, tetragonal $\beta$-Pb$^{2+}$Te$^{4+}$O$_3$, and triclinic $\gamma$-Pb$^{2+}$Te$^{4+}$O$_3$) is given by Weil et al. (2018). A synthetic cubic form of Pb$^{2+}$Te$^{4+}$O$_3$ has also been reported (Gaitán et al. 1987), but no crystal structure is known and its identity is therefore dubious (Weil et al. 2018). Neither of the two minerals with the reported formula Pb$^{2+}$Te$_4$O$_3$ (plum-oughite and fairbankite) showed unit-cell data matching the two minerals with the reported formula Pb$_{12}$((Te$^{4+}$O$_3$)$_{11}$(SO$_4$)$_2$. 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, $c = 14.4916(5)$ Å, $\alpha = 75.161(5)^\circ$, $\beta = 81.571(4)^\circ$, $\gamma = 83.744(4)^\circ$, $V = 1036.35(9)$ Å$^3$, and $Z = 1$] is the first atomic arrangement known to contain a Te$^{4+}$O$_3$ non-cyclic, finite building unit. Fairbankite has an average structure, formed from a 3D framework of Pb$^{2+}$, Te$^{4+}$ polyhedra, Te$^{4+}$O$_3$ 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$_7$ disphenoids. The disphenoids allow for the creation of two dimeric Te$_4$O$_7$ units in addition to the Te$_4$O$_7$ 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.

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