American Mineralogist, Volume 96, pages 1686–1702, 2011

The crystal structure of franckeite, $Pb_{21.7}Sn_{9.3}Fe_{4.0}Sb_{8.1}S_{56.9}$

E. Makovicky,[1,*] V. Petříček,[2] M. Dušek,[2] and D. Topa[3]

[1]Department of Geography and Geology, University of Copenhagen, Østervoldgade 10, DK1350 Copenhagen, Denmark
[2]Institute of Physics, Czech Academy of Sciences, Na Slovance 2, CZ-18040 Prague 8, Czech Republic
[3]Department of Material Research and Physics, University of Salzburg, Hellbrunnerstrasse 34, A-5020 Salzburg, Austria

Abstract

The layer-like crystal structure of franckeite from the mine of San José, Bolivia, exhibits a pronounced one-dimensional transversal wave-like modulation and a non-commensurate layer match in two dimensions. It consists of alternating pseudohexagonal (H) layers and pseudotetragonal (Q) slabs and forms a homologous pair with cylindrite, which has thinner Q slabs. The Q slabs in franckeite are four atomic layers thick. The two components have their own lattices and a common modulation. The Q slab of the refined franckeite structure, $Pb_{21.74}Sn_{9.34}Fe_{3.95}Sb_{8.08}S_{56.87}$, is an MS layer (M = Pb^{2+}, Sn^{2+}, Sb^{3+}) four atomic planes thick, with a = 5.805(8), b = 5.856(16) Å, and the layer-stacking vector c = 17.338(5) Å. The lattice angles are $\alpha = 94.97(2)°$, $\beta = 88.45(2)°$, $\gamma = 89.94(2)°$; the modulation vector $q = –0.00129(8)\ \mathbf{a}^* + 0.128436(10)\ \mathbf{b}^* – 0.0299(3)\ \mathbf{c}^*$. The H layer is a single-octahedron MS_2 layer (M = Sn^{4+}, Fe^{2+}) with a = 3.665(8), b = 6.2575(16), c = 17.419(5) Å, $\alpha = 95.25(2)°$, $\beta = 95.45(2)°$, $\gamma = 89.97(2)°$; the modulation vector is $q = –0.00087(8)\ \mathbf{a}^* + 0.13725(16)\ \mathbf{b}^* – 0.0314(4)\ \mathbf{c}^*$. The **a** and **b** vectors of both subsystems are parallel; the **c** vectors diverge. (3+2)D superspace refinement was performed in the superspace group $C\bar{1}$, using 7397 observed reflections. It resulted in the overall R(obs) value equal to 0.094. The Q slabs are composed of two tightly bonded double-layers, separated by an interspace hosting non-bonding electron pairs. Average composition of cations on the outer surface was refined as $Pb_{0.74}(Sn,Sb)_{0.26}$, whereas that of cations, which are adjacent to the interspace with lone electron pairs, with a configuration analogous to that observed in orthorhombic SnS, corresponds to $(Sn,Sb)_{0.73}Pb_{0.27}$. Iron is dispersed over the octahedral Sn^{4+} sites in the H layer. Transversal modulation of the Q slab is achieved by local variations in the Pb:(Sn,Sb) ratios at its surface and interior. Its purpose is to re-establish a one-dimensional commensurate contact along [010] between the curved Q and H surfaces to the greatest extent possible. Layer-stacking disorder and divergence of the Q and H stacking directions, and the divergence between modulation wave-front and these stacking directions are typical for the composite structures of franckeite and cylindrite. Because of the increased rigidity of the Q component, franckeite usually forms masses of curved crystals rather than cylindrical aggregates. The existence of this family depends critically on the radius ratios of the cations involved, especially those involving (Pb^{2+}, Sn^{2+}) and Sn^{4+}. Their replacement by a Pb^{2+}:Bi^{3+} combination leads to misfit layer structures of a very different type, typified by cannizzarite.

Keywords: Franckeite, Pb-Sn-Sb-Fe sulfide, modulated layer-misfit crystal structure, 2D–non-commensurate layer structure, San José, Bolivia