The crystal structure of franckeite, \( \text{Pb}_{21.7}\text{Sn}_{9.3}\text{Fe}_{4.0}\text{Sb}_{8.1}\text{S}_{56.9} \)

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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, \( \text{Pb}_{21.7}\text{Sn}_{9.3}\text{Fe}_{4.0}\text{Sb}_{8.1}\text{S}_{56.9} \), is an MS layer (\( \text{M} = \text{Pb}^{2+}, \text{Sn}^{2+}, \text{Sb}^{3+} \)) four atomic planes thick, with \( a = 5.805(8) \), \( b = 5.856(16) \AA \), and the layer-stacking vector \( c = 17.338(5) \AA \). The lattice angles are \( \alpha = 94.97(2)^{\circ} \), \( \beta = 88.45(2)^{\circ} \), \( \gamma = 89.94(2)^{\circ} \); the modulation vector \( \mathbf{q} = -0.00129(8) \mathbf{a}^{*} + 0.128436(10) \mathbf{b}^{*} - 0.0299(3) \mathbf{c}^{*} \). The H layer is a single-octahedron \( \text{MS}_2 \) layer (\( \text{M} = \text{Sn}^{4+}, \text{Fe}^{2+} \)) with \( a = 3.665(8) \), \( b = 6.2575(16) \), \( c = 17.419(5) \AA \), \( \alpha = 95.25(2)^{\circ} \), \( \beta = 95.45(2)^{\circ} \), \( \gamma = 89.97(2)^{\circ} \); the modulation vector is \( \mathbf{q} = -0.00087(8) \mathbf{a}^{*} + 0.13725(16) \mathbf{b}^{*} - 0.0314(4) \mathbf{c}^{*} \). The \( \mathbf{a} \) and \( \mathbf{b} \) vectors of both subsystems are parallel; the \( \mathbf{c} \) vectors diverge. (3+2)D superspace refinement was performed in the superspace group \( \Gamma \), using 7397 observed reflections. It resulted in the overall \( R(\text{obs}) \) 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 \( \text{Pb}_{21.7}(\text{Sn}, \text{Sb})_{36} \), whereas that of cations, which are adjacent to the interspace with lone electron pairs, with a configuration analogous to that observed in orthorhombic \( \text{SnS} \), corresponds to \( (\text{Sn}, \text{Sb})_{0.73}\text{Pb}_{0.27} \). Iron is dispersed over the octahedral \( \text{Sn}^{2+} \) sites in the H layer. Transversal modulation of the Q slab is achieved by local variations in the \( \text{Pb}(\text{Sn}, \text{Sb}) \) ratios at its surface and interior. Its purpose is to re-establish a one-dimensional commensurate layer 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 (\( \text{Pb}^{2+}, \text{Sn}^{2+} \)) and \( \text{Sn}^{4+} \). Their replacement by a \( \text{Pb}^{2+}:\text{Bi}^{3+} \) 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

INTRODUCTION AND HISTORY OF INVESTIGATION

Franckeite is a complex sulfide of \( \text{Pb}, \text{Sn}^{2+}, \text{Sn}^{4+}, \text{Sb}, \) and \( \text{Fe} \), described first by Stelzner (1893) from Bolivia. Until the 1970s it aroused little attention, mostly of field mineralogists (Bonshtedt-Kupletskaya and Chukrov 1960), but after the interesting results of studies on related cylindrite (Makovicky 1970, 1974; Mozgova et al. 1975) became known, attention was directed to franckeite as well. X-ray crystallography of Sn-rich franckeite was described by Makovicky (1976), whereas that of Pb-rich franckeite by Wolf et al. (1981). They were described under the names incaite and potosite, respectively. Li (1990) quotes additional crystallographic studies by Wang (1989); these data are summarized by Makovicky and Hyde (1992). Organova et al. (1980) published a Patterson function of franckeite but the work apparently did not proceed any further. Extensive HRTEM and electron diffraction study of franckeite was performed by Williams and Hyde (1988) and Williams (1989). Models of the crystal structure of franckeite in a projection along the non-modulated direction of a layer were constructed using the HRTEM data by these authors and by Wang (1989) and Wang and Kuo (1991). A STM study of a cleavage surface of franckeite was performed by Ma et al. (1997), whereas Henriksen et al. (2002) made a detailed study by STM and AFM. The classical chemical analyses of franckeite were summarized by Bonshtedt-Kupletskaya and Chukrov (1960). Further contributions to the chemistry of franckeite were made by Makovicky (1974), Wolf et al. (1981), Williams (1989), and especially by Mozgova et al. (1975) and Bernhardt (1984), using electron microprobe. Synthetic studies performed by Li (1984) confirmed the idea, derived from chemical analyses, that

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