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Crystal structure of a synthetic tin-selenium representative of the cylindrite structure type

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Abstract

The synthetic tin-selenium member of the cylindrite structural family, with the empirical formula $Sn_{31.52}Sb_{6.23}Fe_{3.12}S_{59.12}$ based on electron-microprobe data, has a triclinic crystal structure composed of two alternating layer types, both with a pronounced one-dimensional modulation, and with a non-commensurate layer match in two dimensions. The pseudotetragonal (Q) layer is a *Me*Se layer two-atomic planes thick with lattice parameters a = 5.969(2) Å, b = 6.004(1) Å, and the layer-stacking vector c = 12.238(1) Å, α = 87.98(4)°, β = 83.14(3)°, and γ = 90.01(4)°. The pseudohexagonal (H) layer is a single-octahedral *Me*Se_2 layer with a = 3.831(1) Å, b = 6.580(3) Å, c = 12.151(5) Å, α = 87.79(4)°, β = 90.59(3)°, and γ = 89.99(3)°; the $\boldsymbol{a}$ and $\boldsymbol{b}$ vectors of the two subsystems are parallel, the $\boldsymbol{c}$ vectors diverge. The transversal wave-like modulation has the wave-normal parallel to $\boldsymbol{b}$, so that the modulation vector $\boldsymbol{q}$ is $0.0001(3)\,\boldsymbol{a}^* + 0.1921(4)\,\boldsymbol{b}^* - 0.0119(3)\,\boldsymbol{c}^*$ in terms of the pseudohexagonal subsystem. Superspace structure refinement in the superspace group $X\bar{1}$ where X stands for non-primitive centering vectors (½,½,0,0,0), (0,0,0,0,½), (½,½,0,0,½) in five-dimensional superspace, and based on 2128 observed reflections, resulted in R_1 = 0.038 for all reflections. Composition of the H layer has been modeled as $Sn^{4+}_{240}Fe^{2+}_{54}Se_{588}$, that of the Q layer as $Sn^{2+}_{306}Sb^{3+}_{108}Se_{414}$. The cation-anion distances in the Q layer vary between 2.63 and 3.30 Å, indicating that the cations present are primarily Sn^{2+} (and Sb^{3+}), whereas distances in the H layer lie between 2.665 and 2.721 Å and correspond to Sn^{4+} with admixture of Fe^{2+}. The shortest cation-anion distance across the interlayer space is 3.24 Å. Relations between layer match and the modulation vector, divergence of layer stackings of the two components, and reasons for the modulation and for the pronounced disorder of the Q component, as well as the differences and similarities with levyclaudite, franckeite, and synthetic layer-misfit compounds are discussed in detail. In its structural principles, although not in numerical values, the Sn-Se cylindrite corresponds fully to the natural Pb-Sn-S cylindrite previously described.

Keywords: Cylindrite, tin-antimony-iron selenide, non-commensurate layer structure, layer-misfit structure, interlayer match