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Atomic Scale Structure and Chemistry Study of Franckeite - A Natural van-der-Waals Heterostructure - Using Scanning Transmission Electron Microscopy and Atom Probe Tomography

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Franckeite (~$Pb_{22}Sn_9Fe_4Sb_8S_{57}$) is a sulfosalt mineral from Bolivia that was firstly described by Stelzner [1]. This structure is composed by a stacking of incommensurate 2D layers, labelled H-layer and Q-layer, which are connected by van der Waals interactions. This natural occurring van der Waals heterostructure received attention recently due to its remarkable semiconducting properties and the possibility for exfoliation of layer stacks and their incorporation into devices [2,3]. The knowledge on its structure and chemistry at atomic level is crucial for an understanding of its properties and the potential to design similar heterostructures. An extensive and recent review on preceding characterization results is given in the work of Makovicky et al. [4] in which a refinement of the previously reported structure and chemistry based on X-ray data was presented. In particular, a detailed description of the atomic site modulation caused by the incommensurate structure was proposed. Such modulations in Franckeite, and its related mineral Cylindrite, have been already imaged before using transmission electron microscopy (TEM) [5,6] or with imaging modes more directly interpretable in high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) [7]. HAADF imaging enabled the visualization of the nature of the two-layer types in Franckeite, and the way in which they are stacked, by choosing viewing directions contained with the strong natural cleavage planes (van der Waals gap). The pseudo hexagonal H-layer was reported as a single-octahedron MS2 layer (M = Sn^{4+}, Fe^{2+}). The pseudo tetragonal Q-layer was described as a 4-atomic-planes thick (2 bilayers) MS layer (M = Pb^{2+}, Sn^{2+}, Sb^{3+}). However, spatial resolution of HAADF STEM was not sufficient at the time of the cited work to resolve single projected atom columns. Recent works on Franckeite [2,3] have demonstrated the possibility of such a study.

We focus here on the characterization of Franckeite using STEM (Figure 1) and atom probe tomography (APT) (Figure 2) extracted from a bulk specimen. STEM imaging in various low-index zone axes, within the van der Waals gap plane, gives new insights into the atomic structure of the layers and their stacking (e.g. see Figure 1). Complementary 3D reconstruction of the chemistry at atomic scale, using APT, allows us to probe the chemical homogeneity of the material and systematic chemical ordering according to the known modulation within the layers. Our work therefore presents results of crystallographic structure and chemical ordering at the atomic scale in Franckeite that can be used as a basis for comparisons to future artificially implemented modifications in this naturally occurring van der Waals heterostructure.

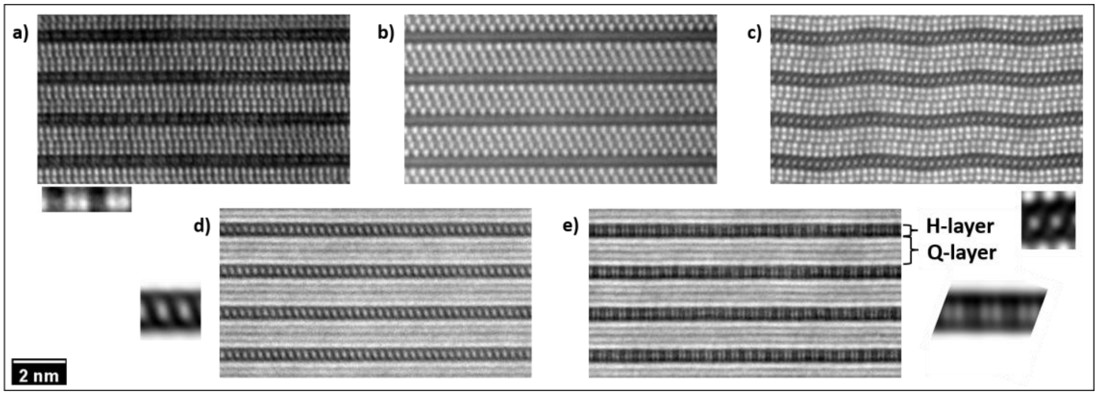

Figure 1. HAADF STEM images of viewing directions contained with the van der Waals gap plane. a) Along and c) perpendicular to modulation direction allowing to resolve projected atom columns in both H-layer and Q-layer. b) Resolving atom columns only in the four atomic layer thick Q-layer. d) and e) Resolving atom columns only in the SnS2-like H-layer. Scale bar the same for all images (bottom left). Additional insets show template averaged images of the projected H-layer (scale bar does not apply).

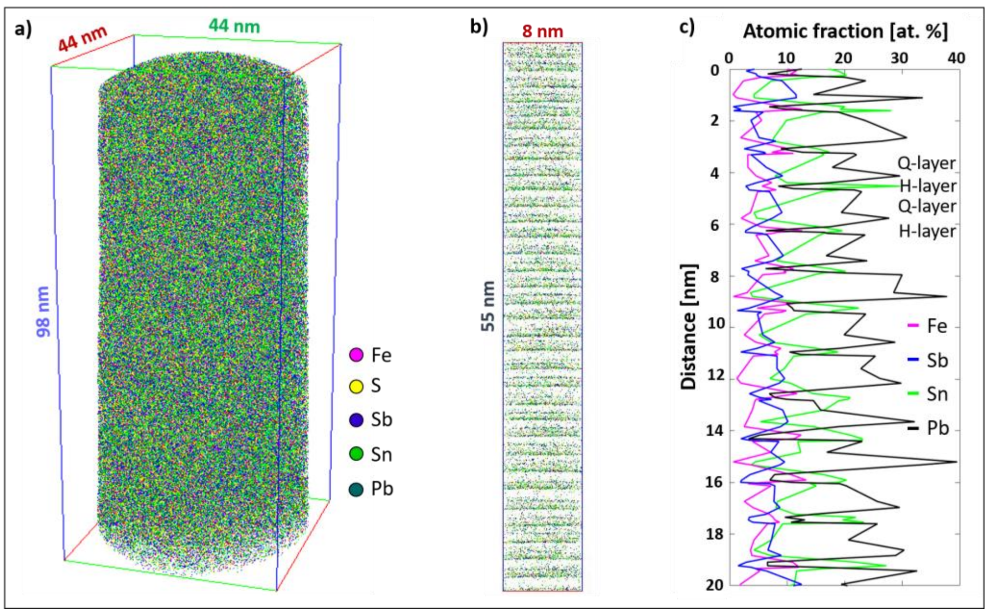

Figure 2. APT analysis of Franckeite. a) Reconstructed acquired volume. Besides the single atoms in the legend, several molecules have been identified in the mass-over-charge spectrum. b) Extracted cylinder volume from the pole region in a) that can be identified as the pole perpendicular to the H- and Q-layers which are resolved in the projection shown. c) 1D concentration plot along the pole direction reveals the alternating Sb and Pb rich planes in Q-layers and alternating Fe and Sn rich planes in H-layers.

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