

Transmission electron microscopy investigation of Ag-free lillianite and heyrovskýite from Vulcano, Aeolian Islands, Italy

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ABSTRACT

We present a transmission electron microscopy (TEM) investigation of lillianite ($\text{Pb}_3\text{Bi}_2\text{S}_6$) and heyrovskýite ($\text{Pb}_6\text{Bi}_2\text{S}_9$), from Vulcano, Aeolian Islands, Italy. The minerals investigated represent the only naturally occurring Ag- and Cu-free sulfosalts in the lillianite homologous series (LHS). Three methods (crushing, ion-milling, and ultramicrotomy) were used to prepare TEM specimens. Selected area electron diffraction (SAED) patterns and high-resolution TEM (HRTEM) images indicate well-ordered crystals with only minor stacking faults and, more rarely, nanoscale intergrowths of lillianite and heyrovskýite. The latter were sometimes found to form an incommensurate structural modulation with an angle of $\sim 29^\circ$ relative to \mathbf{b}^* in the $(hk0)$ plane and a wavelength of $\sim 75 \text{ \AA}$. This represents the first observation of such incommensurate modulations in heyrovskýite. Although considerable evidence points toward an artifact induced by the sample preparation technique (i.e., ion-milling), the possibility that the incommensurate modulation could be a primary feature of heyrovskýite itself cannot be completely ruled out. The modulation could derive from an ordering process of Pb and Bi cations over Me4 and Me5 sites within the PbS-like layer or from ordering of vacancies, naturally present or induced by Bi_2S_3 sublimation during ion-milling.

Keywords: Lillianite, heyrovskýite, Vulcano, incommensurate modulation, TEM