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Periodic and non-periodic stacking in molybdenite (MoS_2) revealed by STEM

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Abstract

Polytypism is a typical feature of layered minerals with differences only in stacking sequences. There is no obvious "phase" boundary among different polytypes, although the frequency of polytypes occurrence is related to its crystallization environment. In the past decades, X-ray studies of molybdenite specimens from a variety of geological environments have revealed that most molybdenite crystals contain both $2H_1$ (hexagonal) and $3R$ (rhombohedral) polytypes. However, the stacking sequences of these molybdenite polytypic intergrowths and their formation mechanism are not well understood. Here, we report stacking faults and domains of long-period polytypes identified by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) in a molybdenite sample from a carbonatite vein in the Huanglongpu Mo-Pb ore deposit in Qinling orogenic belt, Northern China. Several layers of disordered domains intergrown with ordered $2H_1$ domain were recognized based on the contrast in HAADF image with one-dimensional lattice fringes. In addition, a 30-layer long-period polytype was unambiguously identified by a STEM image. The stacking sequences of 4-, 6-, and 8-layer disordered domains and the 30-layer long-period polytype were further examined using HRSTEM images at the atomic resolution. A $2H_3$ polytype with three repetitions was also discovered in the sample. We propose that non-equilibrium conditions related to the fluctuation of fluid composition during crystallization resulted in the oscillation of $2H_1$ and $3R$ polytypes and intergrowth of various disordered domains. More broadly, our study demonstrates that HAADF-STEM imaging method may be applicable for studying other disordered layered crystals and twinned minerals.

Keywords: Molybdenite (MoS_2), polytype, non-equilibrium crystallization, HAADF-STEM, layered minerals, stacking fault; Applications of Fluid, Mineral, and Melt Inclusions