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 2$H_1$ (hexagonal) and 3$R$ (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 2$H_1$ 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 2$H_1$ 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 2$H_1$ and 3$R$ 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

INTRODUCTION

Molybdenite (MoS$_2$) is a layered sulfide mineral that commonly occurs in hydrothermal ore deposits and, like other layered minerals, exhibits polytypism. However, although the first well-established crystal structure of hexagonal-molybdenite ($2H_1$, space group $P6_3/mmc$) was determined by Dickinson and Pauling as early as in 1923 (Wickman and Smith 1970), the polytypism of molybdenite was not disclosed until the first synthetic rhombohedral-MoS$_2$ (3$R$, space group $R3m$) crystal obtained from a potassium carbonate melt was described by Bell and Herfert (1957). The 3$R$ polytype of molybdenite was further confirmed in later investigations of natural samples from various rocks formed in different petrogenetic environments (Traill 1963; Frondel and Wickman 1970; Ayres 1974; Newberry 1979a, 1979b). Since then, the polytypism has been widely studied because the polytypic nature of molybdenite is not only related to properties of the mineral itself but also their geochemical processes, including enrichment of trace elements (Frondel and Wickman 1970; Ayres 1974; Newberry 1979a, 1979b; McCandless et al. 1993; Voudouris et al. 2009; Drábek and Rieder 2010; Ciobanu et al. 2013; McFall et al. 2019; Plotinskaya et al. 2019).

The polytypes of molybdenite are derived by stacking the double layers of S-Mo-S sheets in different sequences following the rules of close-packed structures (Wickman and Smith 1970). In a basic S-Mo-S layer, the arrangement of S atoms around Mo atoms is either trigonal prismatic (e.g., 1$H$) or octahedral (e.g., 3$R$) (Katzke et al. 2004). However, octahedral stacking is a metastable state, and has only been reported in synthetic systems (Wypych and Schöllhorn 1992; Lin et al. 2014). Figure 1a shows six possible stacking sequences, with a view along the [110] direction. The italic capital letter $A$, $B$, and $C$ and the lowercase letter $a$, $b$, and $c$ represent three possible ($x,y$)-positions of S sheets and Mo sheets, respectively. Table 1 lists the positions of S and Mo atoms and the abbreviated and full symbols of S-Mo-S layer stacking sequences. There is a sixfold multiplicity for the stacking of adjacent layers (Fig. 1a), which gives rise to many possible stacking sequences and thus polytypes. According to

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