X-ray diffraction reveals two structural transitions in szomolnokite

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ABSTRACT

Hydrated sulfates have been identified and studied in a wide variety of environments on Earth, Mars, and the icy satellites of the solar system. The subsurface presence of hydrous sulfur-bearing phases to any extent necessitates a better understanding of their thermodynamic and elastic properties at pressure. End-member experimental and computational data are lacking and are needed to accurately model hydrous, sulfur-bearing planetary interiors. In this work, high-pressure X-ray diffraction (XRD) and synchrotron Fourier-transform infrared (FTIR) measurements were conducted on szomolnokite (FeSO₄·H₂O) up to ~83 and 24 GPa, respectively. This study finds a monoclinic-triclinic (C₂/c to P̅T) structural phase transition occurring in szomolnokite between 5.0(1) and 6.6(1) GPa and a previously unknown triclinic-monoclinic (P̅T to P₂₁) structural transition occurring between 12.7(3) and 16.8(3) GPa. The high-pressure transition was identified by the appearance of distinct reflections in the XRD patterns that cannot be attributed to a second phase related to the dissociation of the P̅T phase, and it is further characterized by increased H₂O bonding within the structure. We fit third-order Birch-Murnaghan equations of state for each of the three phases identified in our data and refit published data to compare the elastic parameters of szomolnokite, kieserite (MgSO₄·H₂O), and blödite (Na₂Mg(SO₄)₂·4H₂O).

At ambient pressure, szomolnokite is less compressible than blödite and more than kieserite, but by 7 GPa both szomolnokite and kieserite have approximately the same bulk modulus, while blödite’s remains lower than both phases up to 20 GPa. These results indicate the stability of szomolnokite’s high-pressure monoclinic phase and the retention of water within the structure up to pressures found in planetary deep interiors.

Keywords: Szomolnokite, hydrated sulfates, high pressure, X-ray diffraction, infrared spectroscopy, equation of state

INTRODUCTION

Szomolnokite (FeSO₄·H₂O) is a hydrous, ferrous iron-sulfate belonging to the kieserite group of minerals which is composed of monoclinic hydrated metal sulfates. On Earth, szomolnokite and other metal sulfates naturally occur as weathering products of pyrite or pyrrhotite and have been studied in relation to evaporation deposits, hydrothermal systems, and mine waste (Chou et al. 2013; Dyar et al. 2013; Machado de Oliveira et al. 2019). Because ferrous iron-sulfates can host numerous other divalent metals, such as Cu and Mn, they are capable of releasing significant amounts of other trace metals into the surrounding environment. Szomolnokite has been detected on Mars using absorption spectroscopy (Bishop et al. 2009; King and McLennan 2010; Chou et al. 2013). This has led to hydrated sulfates’ importance as potential hosts for water at depth, their use in determining past hydrological activity on the surface of Mars, and their role in volatile and sulfur cycling (Lichtenberg et al. 2010; Wendt et al. 2011; McCanta et al. 2014; Franz et al. 2019). On Venus, sulfates are hypothesized to exist at the surface and crust (Barsukov et al. 1982). Additionally, hydrous metal sulfates have been proposed to exist on the surface of icy moons in our solar system owing to their spectral similarity between laboratory measurements and remote observations (Dalton and Pitman 2012; Ligier et al. 2019; Trumbo et al. 2020).

Hydrated sulfates have been characterized under a range of pressures and temperatures. Szomolnokite has a monoclinic crystal structure (space group C2/c) at ambient conditions as determined by early X-ray diffraction (XRD) measurements on powdered szomolnokite (Pistorius 1960), and ambient-pressure, single-crystal XRD measurements (Wildner and Giester 1991; Giester et al. 1994) (see Table 1). At ambient conditions, szomolnokite belongs to the kieserite group, which consists of monoclinic, hydrous metal sulfates (M₅O₄·H₂O). The kieserite