

Atomistic simulations to resolve the structure complexity of hexagonal phyllomanganates

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Hexagonal phyllomanganates are a major manganese oxide phase in marine sediment. The mineral structures appear simple but are not fully understood yet because they generally occur as small and poorly crystalline particles and exhibit a large variation in the chemical and structure compositions in terms of Mn(III) content, Mn(IV) vacancy defects and interlayer water content. In this study, we attempted to isolate the effects of the vacancy and interlayer water content on the mineral structure by using classical molecular dynamics (MD) simulations. We present the MD simulation results performed for chalcophanite ($\text{ZnMn}_3\text{O}_7 \cdot 3\text{H}_2\text{O}$), jianshuiite ($\text{MgMn}_3\text{O}_7 \cdot 3\text{H}_2\text{O}$), and ernienickelite ($\text{NiMn}_3\text{O}_7 \cdot 3\text{H}_2\text{O}$), which have 14.3% ratio of Mn(IV) vacancies. The calculated lattice parameters as a function of water content reproduced the real-time XRD data collected in a previous dehydration experiment. Distribution of calculated dipole moments of water molecules in the interlayer revealed that not only water content but also water structure greatly impact the interlayer spacing of the phyllomanganates. We examined ranciéite or takanelite $[(\text{Ca}^{2+}, \text{Mn}^{2+})_{2x}(\text{Mn}^{4+}_{1-x}\text{X}_x)\text{O}_2 \cdot n\text{H}_2\text{O}]$, whose structure is similar to chalcophanite but contains less amount of Mn(IV) vacancies (10%) which are randomly distributed. By comparison of Ca- and Mn-analogues of chalcophanite, we discuss relations between vacancy content/ordering and the mineral lattice parameters. Our MD simulations provide atomistic insights into phyllomanganate structures that cannot be obtained by spectroscopy alone.

Keywords: Hexagonal phyllomanganates, molecular dynamics simulations, structural parameters