American Mineralogist, Volume 107, pages 2065–2074, 2022

Crystal structures and high-temperature and high-pressure vibrational spectra of synthetic fluorine-bearing brucites

Yunfan Miao[1], Xi Zhu[1], Yu Ye[1,*], Joseph R. Smyth[2], Dan Liu[1], Yancheng Hu[1], and Guangchen Chen[1]

[1]State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan, 430074, China
[2]Department of Geological Sciences, University of Colorado, Boulder, Colorado 80309, U.S.A.

Abstract

Brucite [$Mg(OH)_2$] has been extensively studied as a simple yet important analog for studying physical and chemical properties of hydrous minerals, and fluorine substitution ($OH^- = F^-$) is common in hydrous minerals since the radius of F^- is similar to that of O^{2-}. We synthesized two F-bearing brucite samples, $Mg(OH)_{1.78}F_{0.22}$ and $Mg(OH)_{1.16}F_{0.84}$, at 9.5 GPa and 1373 K. Single-crystal X-ray diffraction measurements indicate that both phases still crystallize in the space group of $P3m1$, and fluorine substitution significantly reduces the unit-cell volume, axial lengths, and averaged Mg-O(F) bond lengths. The averaged O···H distances get slightly shortened, and the H-O-H angles become smaller due to the fluorine effect. Additional IR-active OH-stretching bands are observed at 3660, 3644, and 3513 cm^{-1} for the F-bearing samples, besides the original one at 3695 cm^{-1}. In situ high-temperature and high-pressure Raman and Fourier transform infrared (FTIR) spectra were collected on the F-bearing brucite samples, and comparisons were made with the natural one with 0.7 mol% F^-. The temperature dependence $[(\partial v_i/\partial T)_P]$ of the OH-stretching modes is inversely correlated to the vibrational frequencies from 3500 to 3700 cm^{-1}, whereas $(\partial v_i/\partial P)_T$ is in positive correlation with v_i. In addition, the dehydration temperatures of the F-bearing brucites are 100–150 K higher than that for the F-free sample at ambient pressure. By creating new proton positions in lower energies, fluorine substitution stabilizes hydrous minerals (like brucite) to higher temperatures and significantly affects their thermodynamic properties, which has significant implications in mineral physical and geochemical studies.

Keywords: Brucite, fluorine substitution, crystal structure, high-temperature Raman spectra, high-pressure FTIR spectra, OH-stretching mode