

Crystal chemistry and high-temperature vibrational spectra of humite and norbergite: Fluorine and titanium in humite-group minerals

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ABSTRACT

The humite-group minerals along the brucite-olivine join may be important dense hydrous magnesium silicate (DHMS) phases in the subducting slab. Fluorine and titanium can be incorporated into their structures through the substitutions $(\text{OH})^- = \text{F}^-$ and $\text{Mg}^{2+} + 2(\text{OH})^- = \text{Ti}^{4+} + 2\text{O}^{2-}$. These substitutions have significant effects on the hydrogen bonding behavior in the structures. Structure refinements and in situ high-temperature Raman and Fourier transform infrared (FTIR) measurements were conducted on natural humite and norbergite crystals. Both minerals crystallize in space group *Pbnm*, and their isobaric Grüneisen parameters for the lattice and SiO_4 internal vibrations are compared with those of chondrodite, clinohumite, brucite, and forsterite. For the humite-group minerals, the OH-stretching modes above 3450 cm^{-1} are affected by local H-H repulsion, whereas the behavior of those below 3450 cm^{-1} can be explained by F^- and Ti^{4+} substitutions, either of which may relieve the H-H repulsion effect. The Raman-active OH bands below 3450 cm^{-1} are affected by Ti^{4+} substitution, while the IR-active bands can be affected by either F^- or Ti^{4+} substitutions. Based on an analysis of the high-*T* Raman and FTIR spectra, the OH vibrations above and below 3450 cm^{-1} behave differently as a function of temperature, and similar behavior has also been observed for other dense hydrous silicate phases in the hydrous peridotite system. Hence, the lengths of the oxygen-oxygen edges in MgO_6 octahedra where protonation can occur become similar to each other at elevated temperatures. This may provide an atomistic explanation for the electrical conductivity properties of DHMS phases at high temperatures.

Keywords: Humite-group minerals, Raman spectroscopy, FTIR spectroscopy, high temperature, OH-stretching mode, DHMS phases