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Raman investigation of H_2O molecule and hydroxyl groups in the channels of hemimorphite

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ABSTRACT

Single-crystal polarized Raman spectra (40 to 4000 cm^{-1} at $4 \le T \le 860$ K) were measured for hemimorphite, $Zn_4Si_2O_7(OH)_2 \cdot H_2O$, to determine the behavior of H_2O molecules and OH groups in the channels. All observed stretching modes of the O-H vibrations could be assigned. Low-temperature Raman spectra show the presence of two different spatially divided regions in the crystal where the H_2O molecules and hydroxyl groups have slightly different positions in the channel. Two structural phase transitions were observed at 20–30 and 80–100 K, respectively, which reflect temperature replacement and reorientation of the H_2O molecules in the cavity. At $T > 100$ K, H_2O molecules are rotationally disordered around the ***c*** axis. An analysis of combined modes consisting of external and internal H_2O vibrations permits the frequency of translational T(H_2O) modes at 30, 53, 71, 90, 118, and 148 cm^{-1} to be determined. The T(H_2O) modes also can be observed directly at low frequencies in the Raman spectra. The dehydration process of hemimorphite was investigated by Raman measurements at elevated temperatures of the crystal. One of two hydroxyl groups in the dehydrated crystal is hydrogen-bonded to neighbor oxygen and disordered statistically.

Keywords: Hemimorphite, H_2O molecules, microporous minerals, Raman spectroscopy