

Mid- and far-infrared spectra of synthetic $\text{CaMg}_2(\text{Al}_{4-x}\text{Ga}_x)(\text{Si}_{1-y}\text{Ge}_y)\text{O}_{10}(\text{OH},\text{OD})_2$ -clintonite: Characterization and assignment of the $\text{Ca-O}_{\text{inner}}$ and $\text{Ca-O}_{\text{outer}}$ stretching bands

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ABSTRACT

X-ray diffraction Rietveld structure refinement and mid- and far-infrared spectral studies have been done on Ga-for-Al and Ge-for-Si substituted synthetic clintonites (Cln), $\text{CaMg}_2(\text{Al}_{4-x}\text{Ga}_x)(\text{Si}_{1-y}\text{Ge}_y)\text{O}_{10}(\text{OH},\text{OD})_2$ ($x = 0.0\text{--}4.0$, $y = 0.0\text{--}1.0$). Rietveld analyses indicate that there is complete solid-solution in both the $(\text{Al}_{4-x}\text{Ga}_x)\text{Si}$ -, $(\text{Al}_{4-x}\text{Ga}_x)\text{Ge}$ -clintonite series. With increasing Ga-for-Al, the mean tetrahedral bond-length, $\langle\text{T-O}\rangle$, and mean tetrahedral basal oxygen separation, $\langle{}^{[4]}\text{O}_{\text{bas}}\text{-O}_{\text{bas}}\rangle$ increase, whereas the octahedral and interlayer parameters, the tetrahedral rotation angles (α), and the dimensional misfits (Δ) vary little. With increasing Ga-for-Al substitution in the Si-series the broad OH and OD stretching bands shift downward from 3607 to 3529 cm^{-1} and from 2671 to 2620 cm^{-1} , respectively. For the Ge-series samples, the OH and OD stretching bands shift downward from 3610 to 3523 cm^{-1} and from 2667 to 2611 cm^{-1} , respectively. According to the data of the curve fitting analysis, both the OH- and OD-stretching bands are modeled by at least three broad [wider than 37 cm^{-1} of full-width at half height (FWHH)] I bands ($\text{M1M2M2} = \text{MgMgAl}^{3+}/\text{MgMgGa}^{3+}$) and a narrow (FWHH = 23–33 cm^{-1}) and weak N band ($\text{M1M2M2} = \text{MgMgMg}$) on the highest frequency side. In some samples, a very weak and broad V (one vacant M site) band at the lowest frequency region is observed. Tetrahedral Si-O, Al-O, and Ga-O stretching bands lie in fairly discrete regions, which are at 1030–830, 880–760, and 790–640 cm^{-1} , respectively. However, the band regions for both the tetrahedral Al-O and Ge-O stretching as well as the Ge-O and Ga-O stretching bands closely overlap each other. In the 720–500 cm^{-1} region, Si-O-Al, Al-O-Al, Si-O-Ga, Al-O-Ge, Al-O-Ga, Ge-O-Ga, and Ga-O-Ga deformational bands (tetrahedral-chain bending and “breathing” modes) are observed to overlap strongly. Around 300 and 200 cm^{-1} one observes the $\text{Ca-O}_{\text{inner}}$ and $\text{Ca-O}_{\text{outer}}$ stretching bands, respectively, which show a slight downward frequency shift ($\sim 7 \text{ cm}^{-1}$ per Ga apfu) with Ga-for-Al substitution.

Keywords: Rietveld refinement, far infrared spectra, synthetic clintonite, $\text{Ca-O}_{\text{inner}}$ stretching band, $\text{Ca-O}_{\text{outer}}$ stretching band