

## **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 ( $\alpha$ ), and the dimensional misfits ( $\Delta$ ) 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  $\text{cm}^{-1}$  and from 2671 to 2620  $\text{cm}^{-1}$ , respectively. For the Ge-series samples, the OH and OD stretching bands shift downward from 3610 to 3523  $\text{cm}^{-1}$  and from 2667 to 2611  $\text{cm}^{-1}$ , 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  $\text{cm}^{-1}$  of full-width at half height (FWHH)] I bands ( $\text{M1M2M2} = \text{MgMgAl}^{3+}/\text{MgMgGa}^{3+}$ ) and a narrow (FWHH = 23–33  $\text{cm}^{-1}$ ) 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  $\text{cm}^{-1}$ , 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  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  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