Mid- and far-infrared spectra of synthetic $\text{CaMg}_x(\text{Al}_{4-x}\text{Ga}_x)(\text{Si}_{10-x}\text{Ge}_x)\text{O}_{10}(\text{OH})_2$-clintonite: Characterization and assignment of the Ca-O$_{inner}$ and Ca-O$_{outer}$ 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), CaMg$_x$(Al$_{4-x}$Ga$_x$)(Si$_{10-x}$Ge$_x$)O$_{10}$(OH$_2$)$_2$ ($x = 0.0–4.0, y = 0.0–1.0$). Rietveld analyses indicate that there is complete solid-solution in both the (Al$_{4-y}$Ga$_y$)Si$_y$(Al$_{4-y}$Ga$_y$)Ge-clintonite series. With increasing Ga-for-Al, the mean tetrahedral bond-length, $<T-O>$, and mean tetrahedral basal oxygen separation, $<\text{Si-O}_\text{bas}>$, 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 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 (M1M2M2$_x$ = MgMgAl$^{3+}$/MgMgGa$^{3+}$) and a narrow (FWHH $= 23–33$ cm$^{-1}$) and weak N band (M1M2M2$_x$ = MgMgMg) on the highest frequency side. In some samples, a very weak 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 Ca-O$_{inner}$ and Ca-O$_{outer}$ stretching bands, respectively, which show a slight downward frequency shift ($\sim 7$ cm$^{-1}$ per Ga apfu) with Ga-for-Al substitution.

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

INTRODUCTION

Clintonite, a trioctahedral brittle mica with the ideal composition $\text{Ca}$(Mg$_x$Al$_{4-x}$)(Al$_2$Si$_{10-x}$O$_{10}$)(OH,F)$_2$, has several interesting characteristic crystal-chemical features (Takéuchi and Sadanaga 1959; Takéuchi 1966; Joswig et al. 1986; MacKinney et al. 1988; Alieetti et al. 1997). First, its tetrahedral Al:$Si$ ratio is 3:1, and thus half of the T-O-T bonds violate the Al-avoidance principle or the “Lowenstein avoidance rule” by having Al$^{3+}$–Al$^{4+}$ bonds. Second, the tetrahedral cations are disordered and the tetrahedra are flattened as a consequence of the large Al content. Third, the large dimensional misfit of the tetrahedral and octahedral sheets is compensated by large tetrahedral rotation angles ($\alpha$). Research on the synthesis and stability of clintonite has been done by Olesch (1975) and Olesch and Seifert (1976). Both mid- and far-infrared (MIR and FIR) spectra for synthetic and natural clintonites have been reported by Farmer and Velde (1973). Jenkins (1989), in addition to investigating MIR band assignments for synthetic phlogopites, also investigated synthetic clintonite and its deuterium (D), Ni-, Ga-, and Ge chemical analogues. The purpose of this paper is to further assign and characterize some MIR and FIR bands based on the X-ray Rietveld refinement data for synthetic CaMg$_x$(Al$_{4-x}$Ga$_x$)Si$_{10}$(OH)$_2$- and CaMg$_x$(Al$_{4-x}$Ga$_x$)Ge$_{10}$(OH)$_2$-series clintonites, and their deuterated equivalents. In addition, two synthetic Ni-bearing Si-clintonites, Ni$_{2}$SiH-$\text{Cln}$, were also examined; substitutions were made in the various sites in the clintonite structure to observe the influence of different ions on the spectra.

EXPERIMENTAL AND ANALYTICAL METHODS

The experimental and analytical methods in this study are similar to those of Ishida and Hawthorne (2011). Synthesis

Experiments at 690–730 °C, 186–225 MPa, and durations of 231–434 h were done in cold-seal Tuttle-type vessels. The starting materials were made from mixtures of reagent-grade oxides (MgO, NiO, Al$_2$O$_3$, Ga$_2$O$_3$, SiO$_2$, and GeO$_2$) and carbonates (CaCO$_3$). The starting materials were mixed together and decarbonated by roasting for about 30 min at −900 °C in air, and then sealed in 5.0 mm outer-diameter × 4.7 mm inner-diameter × (~)35 mm long Au capsules with ~20 wt% distilled water. Bulk compositions investigated in this study are given in Table 1. Deuteration experiments were done at about 600 °C, 200 MPa for a duration of 1 day in the same vessels; similar amounts of materials were used for the OD-bearing samples, using D$_2$O (99.9% purity) with the solids sealed in Au capsules.

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