Far-infrared spectra of synthetic $[(Al_{2-x}Ga_x)(Si_{2-y}Ge_y)](OH,OD,F)_2$-kinoshitalite: Characterization and assignment of interlayer Ba-O$_{inner}$ and Ba-O$_{outer}$ stretching bands

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ABSTRACT

Far-infrared spectroscopy and X-ray diffraction Rietveld structure-refinement of synthetic kinoshitalite (Kn) solid solutions, BaMg$_x$[(Al$_{2-x}$Ga$_x$)(Si$_{2-y}$Ge$_y$)]O$_{10}$(OH,OD,F)$_2$: ($x = 0.0–2.0$, $y = 0.0–2.0$), show that there is complete solid solution for all compositions in each (OH/OD)- and F-series: $[(Al_xGa_{2-x})(Si_{2-y}Ge_y)]$, $[(Al_{2-x}Ga_x)Si_{2-y}]$, $[(Ga_{2-x}Si_x)Ge_y]$, $[(Al_{2-x}Ga_x)Ge_y]$-Kn, and in OH/OD-for-F substituted $[(Al_xSi_{2-x})]$-, $[(Ga_{2-x}Si_x)Si_{2-y}]$-, $[(Ga_{2-x}Si_x)Ge_y]$-Kn end-member compositions. In the far-infrared region, 170–40 cm$^{-1}$, three kind of bands are observed; an in-plane tetrahedral torsional mode, an interlayer Ba-O$_{inner}$ stretching vibration and a Ba-O$_{outer}$ stretching vibration. With increasing tetrahedral Al-for-Ga and Si-for-Ge substitution, the frequencies and intensities of the tetrahedral in-plane torsional modes decrease in both the (OH/OD)- and F-bearing phases, but in the (Ga$_{2-x}Si_x$)-, (Ga$_{2-x}Si_x$)-, (Ga$_{2-x}Si_x$)-Ge$_y$-Kn end-member compositions, the frequencies are unaffected by (OH/OD)-for-F substitution. The frequencies of both the Ba-O$_{inner}$ and Ba-O$_{outer}$ stretching bands increase with increasing Al-for-Ga and Si-for-Ge substitution, but the frequencies of the Ba-O$_{outer}$ stretching bands decrease with increasing (OH/OD)-for-F substitution in the (Ga$_{2-x}Si_x$)-, (Ga$_{2-x}Si_x$)-, (Ga$_{2-x}Si_x$)-, (Ga$_{2-x}Si_x$)-, (Ga$_{2-x}Si_x$)-Kn end-member compositions. The frequency difference between the Ba-O$_{inner}$ and Ba-O$_{outer}$ stretching bands is linearly related to the tetrahedral rotation angles ($\alpha$), and these differences are about 10 cm$^{-1}$ larger in the (OH/OD)-bearing phases than in the corresponding F-bearing phases. The ranges of absorption frequencies and their corresponding deformation modes are as follows: (1) in-plane tetrahedral torsional mode, 105–150 cm$^{-1}$; (2) Ba-O$_{outer}$ stretching vibration, 105–140 cm$^{-1}$; and (3) Ba-O$_{outer}$ stretching vibration, 75–90 cm$^{-1}$.

Keywords: Far-infrared spectra, synthetic kinoshitalite, in-plane torsional mode, Ba-O$_{inner}$ stretching band, Ba-O$_{outer}$ stretching band

INTRODUCTION

The development of Fourier transform infrared (FTIR) spectroscopy has made possible the routine measurement of absorption spectra in the far-infrared (FIR) frequency range of 300–30 cm$^{-1}$. This is a region where calculations of normal modes for vibrational spectra of 2:1 phyllosilicates predict four fundamental, infrared-active, interlayer vibrational modes (Ishii et al. 1967). Tateyama et al. (1977) were the first to assign the strong band near 100 cm$^{-1}$ in the spectra of K-bearing micas to K-O$_{inner}$ stretching. Farmer (1974), Prost and Laperche (1990), Laperche and Prost (1991), and Diaz et al. (2000) identified two in-plane modes at 107 and 110 cm$^{-1}$ and one out-of-plane mode at 143 cm$^{-1}$ involving K and two double trigonal rings in muscovite, with the maximum absorption directions near $b$, $c$, and $c^*$-axis, respectively. Loh (1973), Velde (1978), Roth (1978), Velde and Couty (1985), Schroeder (1990), and Boukili et al. (2001) also reported FIR spectra of micas, and Beran (2002) and Fleet (2003) reviewed FTIR work on micas, including that in the mid-IR (MIR) and FIR regions. However, no consistent relations have yet been found for FIR bands assignment. The purpose of this paper is to characterize and assign the three FIR bands, which appear in the 170–40 cm$^{-1}$ region in synthetic kinoshitalite, BaMg$_x$[(Al$_{2-x}Ga_x$)(Si$_{2-y}Ge_y$)]O$_{10}$(OH,OD,F)$_2$: ($x = 0.0–2.0$, $y = 0.0–2.0$), particularly the (Ga$_{2-x}Si_x$)-, (Ga$_{2-x}Si_x$)-, (Ga$_{2-x}Si_x$)-, (Ga$_{2-x}Si_x$)-, (Ga$_{2-x}Si_x$)-kinoshitalite (Kn) series with (OH/OD) ↔ F substitution. The interlayer cation in kinoshitalite is Ba$^{2+}$, the ionic radius of which is slightly smaller than that of K$^+$, and thus stronger force constants for I-O$_{inner}$ and I-O$_{outer}$ bonds are expected in Ba-bearing micas than in K-bearing micas.

EXPERIMENTAL AND ANALYTICAL METHODS

Synthesis

Hydrothermal experiments at 660–735 °C, 85–212 MPa, and durations of 160–1463 h were done in cold-sealed Tuttle-type vessels. The starting materials were made from mixtures of reagent-grade oxides (MgO, Al$_2$O$_3$, Ga$_2$O$_3$, SiO$_2$, GeO$_2$) and carbonates (BaCO$_3$) with an excess of 5 wt% SiO$_2$ and GeO$_2$. The starting materials were mixed together and decarbonated by roasting for about 30 min at approximately 900 °C in air, and then sealed in 5.0 mm outer-diameter × 4.7 mm