FTIR spectra for synthetic (Al/Ga,Si/Ge)-kinoshitalites: Detection of violation for the Loewenstein's rule

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X-ray diffraction Rietveld structure refinement and FTIR spectral study have been made for the tetrahedral Al-for-Ga and Si-for-Ge substituted synthetic kinoshitalites. Rietveld analyses indicate that there is a complete solid-solution in each tetrahedral series: with increasing nominal averaged tetrahedral ionic radius, the cell parameters a, b, and c increase linearly, and the beta-angles tend to decrease;the tetrahedral and interlayer sheet thicknesses increase, whereas the octahedral sheet thickness tends to decrease;the tetrahedral rotation angles and the dimensional misfits increase linearly. Frequencies for these OH/OD-stretching bands decrease with increasing nominal tetrahedral ionic radius, i.e., with increasing tetrahedral volume. Infrared OH/OD-stretching bands were analyzed more than two bands, N_A, N_{A1} and N_{A2}, accompanying with talc-like and excess water bands in some samples. Except in the (Al,Si)-Kn end member, two kinds of bending bands, T^{3+}-O-T^{3+} and T^{4+}-O-T^{4+} bendings,appear at either side of the T^{3+}-O-T^{4+} bending band showing violation of the Loewenstein rule (extended that here as T^{3+}-O-T^{3+} avoidance):in the (Al,Ge)-Kn series, Al-O-Al bend = 625 and Ge-O-Ge bend = 550 cm^{-1}; in the (Al,Ga)-Kn series, Si-O-Si bend = 640 and Ga-O-Ga bend = 550 cm^{-1}; in the (Ga,Ge)-Kn series, Ge-O-Ge bend = 580 and Ga-O-Ga bend = 530 cm^{-1}, respectively. A weak and broad OH-librational bands appear at range 750-520 cm^{-1}, which wavenumber are oppositely correlated to those of the OH/OD-stretching bands.