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The vibrational spectrum of synthetic hydrogrossular (katoite) $Ca_3Al_2(O_4H_4)_3$: A low-temperature IR and Raman spectroscopic study

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ABSTRACT

The powder IR spectra of synthetic hydrogrossular, $Ca_3Al_2(O_4H_4)_3$, were recorded at temperatures between 298 and 10 K and the polarized single-crystal Raman spectra at 298 and 4 K. The results were interpreted using factor group analysis which predicts the number and symmetry of the different IR- and Raman-active modes. A first attempt was made to assign the observed bands in the IR and Raman spectra to various atomic or polyhedral motions and to make a first-order lattice dynamic analysis. The mode assignments for grossular, $Ca_3Al_2(SiO_4)_3$, and hydrogrossular were compared. The measured spectra are considerably different in the high-wavenumber region, where O-H stretching modes occur, between 298 and 10/4 K. In the Raman spectra two different symmetry O-H bands are observed at 3648 cm^{-1} ($A_{1g} + E_g$) and 3653 cm^{-1} (F_{2g}) at room temperature, while at 4 K several O-H bands are present. At room temperature an IR-active O-H band located around 3662 cm^{-1} narrows and shifts to higher wavenumbers and also develops structure below about 80 K. Concomitantly, several weak intensity O-H bands located around 3600 cm^{-1} begin to appear and they become sharper and increase in intensity with further decreases in temperature down to 10 K. The spectra indicate that the vibrational behavior of individual OH groups and their collective interactions measurably affect the lattice dynamic (i.e., thermodynamic) behavior of hydrogrossular. The (O_4H_4) group in garnet is best described as a “chemical component” that can substitute for SiO_4 tetrahedra and not as a “structural or polyhedral unit”. The line widths of the IR and Raman O-H bands at low and room temperature were interpreted qualitatively based on the time scales associated with the Raman and IR experiment, which are different in magnitude. The results of this study demonstrate the need for making spectroscopic measurements at low temperatures when studying the vibrational behavior of O-H modes in minerals.