High-pressure structural behavior of hydrogrossular, katoite $Ca_3Al_2(O_4H_4)_3$

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Nominally anhydrous minerals (NAMs) in the Earth's mantle are important because they may potentially introduce a large amount of water in the Earth mantle thus significantly modifying its elastic properties. Calcium aluminum garnet, grossular $Ca_3Al_2(SiO_4)_3$, with the largest divalent cation Ca^{2+} and the smallest trivalent cation Al^{3+} exhibits a complete solid solution with katoite, $Ca_3Al_2(O_4H_4)_3$, which is the Si-free end member of the hydrogrossular. Katoite is known as a typical model for the hydrogarnet substitution ($Si^{4+}\leftrightarrow 4H^{+}$) in garnets and other silicates. The replacement Si^{4+} by $4H^{+}$ results in profound changes in the physical properties and thermodynamic stability of garnet structure. We carried out high-pressure Raman spectroscopy, high-pressure single-crystal synchrotron X-ray diffraction study, and high-pressure neutron diffraction study to clarify the physical and structural properties of katoite at the mantle condition. Raman spectra collected at ambient conditions clearly showed the OH stretching vibration at 3652 cm^{-1}. Translational OH motion and mixed translational/librational motions of O_4H_4 were observed at 537 cm^{-1} and 332 cm^{-1}, respectively. It is noteworthy that with increasing pressure the OH stretching vibration mode exhibited a negative pressure shifts above 5 GPa, which is responsible for the hydrogen bonding formation in the O_4H_4 cluster. In addition, the pressure dependence of the full width half maximum (FWHM) of the OH stretching mode was also changed at the pressure, which is interpretable as a result of peak-splitting derived from cubic-tetragonal transformation. The results of high-pressure single-crystal X-ray diffraction and high-pressure neutron diffraction studies exhibited a discontinuous volume change occurs between 5 and 6 GPa, which supports the cubic (space group *Ia*-3*d*) to tetragonal (space group *I*-43*d*) phase transformation.

Keywords: hydrogrossular, katoite, high-pressure Raman spectroscopy, high-pressure single-crystal synchrotron X-ray diffraction, high-pressure neutron diffraction, structural phase transformation

