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High-pressure Raman spectroscopic studies of hydrogarnet, katoite Ca3Al2(O4H4)3

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Because garnet is capable of incorporating small concentrations, a lot of attention has been devoted to the hydrogarnet known as nominally anhydrous minerals (NAMs). The calcium garnet exhibits the complete solid solution between grossular Ca3Al2(SiO4)3 and Si-free katoite, hydrogarnet Ca3Al2(O4H4)3. Lager et al. (2002) suggested that in the katoite a phase transition occurred from space group Ia3d to I-43d which is a non-centric subgroup of Ia3d with increasing inter-tetrahedral H H repulsion.

We report in situ Raman spectroscopic studies of katoite in a diamond-anvil cell under hydrostatic conditions up to 10 GPa at room temperature. The vibration modes observed in the study were analyzed theoretically by factor group analysis. Three bands near 332 and 537, 3652 cm-1 were observed clearly at 1.0 GPa. In the wavenumber region of lattice modes, the lower frequency peak was assigned to a mode of Eg + F2g symmetry and the higher frequency peak was assigned to a mode of A1g + F2g symmetry. In the OH stretching vibration region, the peak was assigned to A1g + 2Eg + 3F2g symmetry. The peak positions and shapes in the Raman spectra agree well with those measured under ambient conditions. The pressure dependences of the lattice modes and the OH stretching vibration mode show a positive and negative pressure shifts, respectively. A shorter (and so stronger) hydrogen bond is well known to have lower frequencies than a weaker hydrogen bond (Nakamoto et al., 1955), therefore the negative pressure shift observed in the study indicated that the hydrogen bonding strength in katoite was increased as a function of pressure. Peak shift of the OH stretching vibration mode showed defferent trends at pressure above 5 GPa. Increasing rate of full width half maximum (FWHM) for lattice mode was varied at 6 GPa.

When the phase transition in katoite occurs from space group Ia3d (point group Oh) to I-43d (Td) at about 5 GPa (Lager et al., 2002), the vibration modes are never splitted with the phase transition. On the other hand, when the symmetry changes from Oh (cubic) to D4h (tetragonal), the Eg and F2g modes split to A1g + B1g and B2g + Eg, respectively. Therefore the expansion of FWHM above 6 GPa is interpretable as the cubic-tetragonal transition. The results in the study indicate that in katoite structural phase transition occurs from cubic to tetragonal at about 6 GPa.

Keywords: katoite, high-pressure Raman spectroscory, phase transition