Abstract

Hydrous minerals play an important role in transportation of water from the Earth's surface to its interior were water is carried within the crystallographic structure of H-bearing minerals in the form of hydroxyl group (O-H), molecular water (H_2O), or simply H. The works presented here investigate the high-pressure behaviour of selected important geological materials: δ-AlOOH, lawsonite ($CaAl_2Si_2O_7(OH)_2.H_2O$), brucite ($Mg(OH)_2$) and brucite like structures, a common structural unit of the majority of the layered hydrous mineral. δ-AlOOH and brucite has been debated for their hydrogens' position within the lattice under pressure, whereas in the case of lawsonite, the stability limit of its high-pressure monoclinic phase remained unknown.

The high-pressure study on δ-AlOOH were carried out using density functional theory (DFT) based first principles calculations. The study captured the $P21nm$-$Pnnm$ transition of δ-AlOOH at 8 GPa and further resolved the existing discrepancy on determining the hydrogen bond symmetrization pressure of δ-AlOOH, where in the later case, a better agreement was obtained with the experimentally estimated values of 6-15 GPa. The hydrogen bond symmetrization causes anomaly in sound velocity profile of δ-AlOOH which have important geophysical implications. The asymmetric to symmetric phase change and the $P21nm$ to $Pnnm$ phase transition in δ-AlOOH were characterised by the disappearance of mode corresponding to O-H stretching vibration and appearance of new A_{1g} Raman mode at 500 cm^{-1} respectively.

Brucite ($Mg(OH)_2$) has been investigated for its ground state crystal structure at ambient condition owing to the existing discrepancy on determining the preferred atomic site for hydrogen in the lattice. In this work, the symmetry for brucite lattice at ambient condition was confirmed to be P-3m1 from its structural, mechanical and vibrational properties. The pressure response of hydrogen sublattice in $M(OH)_2$(M=Mg, Co amd Ni) were probed using combined DFT and synchrotron X-ray powder diffraction (XRPD) measurements which showed that these layered hydroxides undergoes pressure induced hydrogen ordered (P-3m1) - disordered (P-3) transition. Careful analysis of synchrotron XRPD data of brucite at low temperatures, β-$Co(OH)_2$ and β-$Ni(OH)_2$ at high pressures showed that, even though X-ray diffraction is known for its limitations on locating hydrogen atoms, the collective effect of disordering in hydrogen sublattice is reflected in the behaviour of certain Bragg peaks corresponding to hydrogen sublattice.

Lawsonite was studied in its high-pressure monoclinic phase for determining its stability regime under pressure. The monoclinic phase exhibits lattice dynamical instability above 25 GPa driven by softening of phonon modes. Prior to reaching its stability limit, a regime of structural anomaly exists at 20 GPa due to formation of new hydrogen bonds and increase in repulsion between hydrogen atoms of hydroxyl-water pairs as well as hydroxyl-hydroxyl pairs. The high-pressure behaviour of monoclinic lawsonite is characterised by the softening of O-H stretching vibrations mode in Raman spectra which confirms the role of increasing strength of hydrogen bonds under pressure.