Chapter 6

Summary

In summary, 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 which is a common structural unit of the majority of the layered hydrous mineral such as clay, talc and serpentine has been studied. δ-AlOOH and brucite have been debated for their hydrogen position under pressure whereas in case of lawsonite, the stability limit of its high-pressure monoclinic phase remained unexplored. These issues have been addressed and a consistent picture between theoretical results and the experimental observations is provided. The work presented in the thesis is divided into three major parts (1) hydrogen bond symmetrization and its effect on physical properties of δ-AlOOH, (2) pressure induced crystal structure changes in brucite like structures and (3) stability limit of high-pressure phase of lawsonite ($CaAl2Si_2O_7(OH)2$. H_2O). Theoretical studies were performed on these compounds using first principles calculations based on density functional theory (DFT), and experiments were conducted on $M(OH)_2$ compounds using diamond anvil cell in conjunction with synchrotron based X-ray powder diffraction (XRPD).

The indication of hydrogen bond symmetrization in hydrous minerals at Earth's lower mantle condition is well documented in theoretical calculations [38–43, 83, 86, 195]. Hence, studying the effect of hydrogen bond symmetrization in physical properties of minerals is of utmost important. One of the important hydrous mineral which has been a topic of debate between experimental and theoretical studies is δ-AlOOH where the theoretically predicted hydrogen bond symmetrization pressure of 30 GPa [41] couldn't address the experimentally observed jump in measured sound velocity of δ-AlOOH at 15 GPa [44]. In this work, DFT based calculation determined the pressure at which hydrogen bond symmetrization occurs as 15 GPa. Prior to the symmetrization of hydrogen bond, δ-AlOOH undergoes $P21nm$ to $Pnnm$ structural phase transition consistent with reported experimental observations [84]. Further, the effect of hydrogen bond symmetrization on the vibrational properties and elastic properties was studied. The hydrogen bond symmetrization significantly affects the elastic constants and hence the sound velocity in δ-AlOOH. The sound velocity shows anomalous increase across the symmetrization pressure. This is consistent with the velocity jump recorded by Mashino et al. [44] in δ-AlOOH at 15 GPa. Compressibility study shows that hydrogen bond lying parallel to b-c plane undergoes larger compression as compared to the AlO_6 octahedra lying along the a direction. The compressibility along b-c plane decreases due to strengthening of hydrogen bond and hence as a result, a axis becomes more compressible above hydrogen bond symmetrization pressure. Further, the pressure dependence of axial ratio confirms the $P21nm$-$Pnnm$ phase transition at 8 GPa corroborating with the findings of Kuribayashi et al. [80] from the XRD measurement. Raman spectroscopic investigation showed that both $P21nm$ to $Pnnm$ phase transition and asymmetric to symmetric phase change in δ-AlOOH can be characterised by the appearance of Raman perk at 500 cm^{-1} and disappearance of Raman peak corresponding to O-H stretching vibration respectively. The findings of this work have geophysical implications where it can be related to the anomalous behaviour of seismic velocity beneath the Deccan Volcanic Provinces of India and the Java subduction zone.

Brucite has been undergone ample of theoretical end experimental investigations particularly focussing on the pressure induced hydrogen order-disorder transition [108, 111, 123, 124, 130, 135–138], however, discrepancy existed in determining the ground state structure of brucite where three competing models : P-3m1 [137], P-3 [136] and $C2/m$ [138] where proposed. Though neutron diffraction (ND) studies are preferred over X-ray diffraction for refining hydrogen positions, the reported ND studies failed to provide consistent picture of ground state symmetry of brucite [108, 124]. The literature survey addressing these discrepancies are presented in Section (4.3). We resolved this discrepancy by investigating the crystal structure using density functional theory from geometrical relaxation employing non-empirical vdW functional. The lattice dynamical and mechanical stability of brucite in P-3m1 symmetry were confirmed using phonon dispersion curves and elastic constant calculations. The transition from P-3m1 to P-3 symmetry was predicted to occur at small volume perturbation. Despite having known limitations by XRD techniques in probing the individual atomic sites for hydrogen atom in a crystal structure, we showed that the collective effect of disordering in hydrogen sublattice can be captured from the analysis of synchrotron-based XRD data. The hydrogen order-disorder transition in brucite predicted by DFT based calculations under compressive volume perturbation corresponds to the anomalous behaviour of (003) and (013) Bragg peak under volume compression on thermal contraction, where the anomalous behaviour of the peaks results from the charge density variation along the hydrogen containing (003) and (013) lattice planes. The disordering is driven by the increase in repulsion between the hydrogen atoms of the closest hydroxyl group lying on opposite layers of MgO_6 octahedra. Hence, the transition to hydrogen disordered state is expected to be a general characteristic of brucite like structures. Therefore, the materials isostructural to the brucite such as β-$Co(OH)_2$ and β-$Ni(OH)_2$ were studied using the combined DFT and synchrotron XRPD techniques. high-pressure DFT calculations showed that the β-$Co(OH)_2$ and β-$Ni(OH)_2$ undergo hydrogen ordered (P-3m1) to hydrogen disordered (P-3) transition above 5 GPa. The effect of hydrogen order-disorder transition was observed in high-pressure XRD data where the (003) and (013) Bragg peak exhibited anomalous behaviour across 2.5 and 5 GPa for β-$Co(OH)_2$ and β-$Ni(OH)_2$ respectively. This further makes one-to one correspondence to the reported anomalous behaviour in full width at half maximum (FWHM) of $A_{1g}(2)$ mode of β-$Co(OH)_2$ and β-$Ni(OH)_2$ across 2.5 and 5 GPa respectively [154]. Thus, we showed that the effect of this transition in brucite like structure can be probed using combined DFT and synchrotron XRD measurements.

Lawsonite was studied for its structural behaviour in its high-pressure monoclinic phase which has been reported at 8∼11 GPa as a result of phase transition from its low-pressure orthorhombic structure. The monoclinic phase of lawsonite was shown to be dynamically stable up to 25 GPa, beyond which the structure is unstable and is likely to undergo structural phase transition. The dynamical instability is characterised by softening of phonon modes along **A-E** direction and **Y** symmetry point of the Brillouin zone. Bond length analysis with pressure showed that the predicted instability is due to the increase in coordination number of calcium atom above 25 GPa. Structural analysis further showed that the monoclinic phase goes through geometrical frustration due to increase in repulsion between hydrogen atoms of hydroxyl-water pairs (H_O--H_W) as well as hydroxyl-hydroxyl pairs (H_O--H_O). The observed structural anomaly occurs above 20 GPa and is a precursor to the structural transformation above 25 GPa. At pressure above 20 GPa, the compressibility of b-axis becomes lower than a-axis. The H_O--H_O separation which initially increases in order to minimize the repulsion, decreases above 20 GPa and H_O--H_W repulsion dominates H_O--H_O repulsion thereby causing an increase in both repulsive forces. The high-pressure behaviour of monoclinic lawsonite is characterised by the softening of O-H stretching vibrations mode in Raman spectra which confirms the increase in hydrogen bond strength. Further, under compression, the separation between water molecule and neighbouring oxygen atoms decreases which results in formation of new hydrogen bonds of water. The increasing hydrogen bond and formation of new hydrogen bonds of water molecule cause the water molecule to displace from its initial position. Above 20 GPa, the change in position of water molecule with pressure decreases and the displacement tends to cease as pressure reaches 25 GPa. Thus, the origin of additional weak hydrogen bonds and increasing H--H repulsion causes the crystal structure to exhibit anomalous behaviour at $\sim$20 GPa as precursor to the possible phase transition above 25 GPa. Further, above 20 GPa, the decreasing Ca-O bond lengths cause an increase in coordination number of calcium, therefore, the post monoclinic structure is likely to have increased coordination number of calcium.

6.1 Future scope

It is noteworthy that since the theoretical studies conducted do not include the effect of temperature, one should consider the effect of temperature while applying the results to condition in the Earth's mantle. For example, temperature can affect the hydrogen bond symmetrization in two contradictory ways: Increase in temperature will expand the crystal lattice thereby increasing the O--O distance. This results in an increase in symmetrization pressure. However, on the contrary, the thermal vibration decreases the symmetrization pressure. The overall effect is governed by the dominant factors. Similar shift in symmetrization pressure was observed in the case of phase D where the pressure at which change in relative compressibility of the lattice occurs shift by +3 GPa with temperature reaching to 1300 K [196]. Hence the symmetrization pressure for δ-AlOOH should shift by several GPa at condition in the Earth's mantle condition. The same requirement holds for studying the stability limit of lawsonite. The temperature affects the transition pressure of monoclinic lawsonite. Our study also demonstrates the efficient use of combing first principles calculation with the synchrotron XRPD for investigating the behaviour of hydrogen sublattice in the system. The high-pressure study on brucite shows that the hydrogen order-disorder transition occurs under small volume compression in brucite whereas the pressure limit is below 5 GPa for β-$Co(OH)_2$ and β-$Ni(OH)_2$. Hence, future high-pressure theoretical studies on brucite and brucite type hydroxides should incorporate hydrogen disorderness in studying their structural studies or any related properties at high-pressure as the physical properties of a materials are strongly dependent on the atomic configuration. Further, the combination of experimental diffraction and DFT calculations on studying the hydrogen order-disorder transition showed that, even though X-ray diffraction is known for its limitations in determining the atomic sites for hydrogen atom in a crystal structure, the collective effect of disordering in hydrogen sublattice affects the behaviour of certain Bragg reflections corresponding to hydrogen sublattice and can be captured from a careful analysis of a systematic high quality X-ray diffraction data.