Chapter 5

Stability limit of high-pressure monoclinic phase of Lawsonite

5.1 Introduction

Subduction zones are major tectonic sites where sediments from oceanic crusts and lithospheric mantle descend into the Earth's interior. In this process, subducting plates carry a significant amount of water into Earth's interior in the form of hydrated minerals. This water influences the physicochemical properties of the mantle, such as elasticity, density, melting temperature and rheological properties [174–176]. Studying the role of hydrous minerals in the transfer, storage and cycling of water in the deep crust and mantle is an active field of research. Among them, lawsonite ($CaAl_2Si_2O_7(OH)_2{\cdot}H_2O$) is an important carrier of water in the subducted crust and deeper parts of the mantle [49–52] due to its large stability field and high water content ($\sim$11.5 wt%) [48]. Wickmann [177] determined the structure of the lawsonite for the first time and was later refined by Rumanova, and Skipetrova [178]. The structure consists of a cavity formed by a ring made up of two Si_2O_7 groups and two Al octahedra where one molecule of water and calcium occupies the cavity. Hydroxyl groups are attached to the edge-sharing Al-octahedra. Lawsonite undergoes several pressure-temperature induced structural phase transitions.

At ambient pressure and low temperatures, lawsonite undergoes two phase transitions: at 155(5) and 273(5) K: $Cmcm$ ($>$ 273 K) $\rightarrow$ $Pmcn$ ($<$ 273 K) $\rightarrow$ $P21cn$($<$ 155 K)

that involve changes in the hydrogen bonding of the hydroxyl group and water molecule [179–182]. In general, the transitions observed at low temperature and ambient pressure in lawsonite are likely to resemble its high-pressure behaviour. Holland et al. [183] studied the pressure dependence of lattice parameter of lawsonite at room temperature using energy-dispersive X-ray diffraction in a diamond-anvil cell. Infrared spectroscopic measurement of lawsonite up to 20 GPa at 300 K by Scott, and Williams [184] showed that the hydrogen bonding in lawsonite undergoes pressure induced changes within 8-9 GPa as they observed discontinuity in the shift of O-H stretching vibrational mode of hydroxyl units, whereas the bending and stretching vibrations of water molecule residing in the cavity were relatively unaffected which was attributed to rigid nature of the cavity. This structural change was later identified as pressure-induced reversible orthorhombic to monoclinic phase transition of lawsonite at 8.6 GPa by Daniel et al. [185] that was characterized by the splitting of diffraction lines, the appearance of new Raman bands and changes in the frequency shifts of the hydroxyl O–H stretching modes. Their high-pressure data were fitted using the space group $C1121/m$, conventionally represented as $P21/m$. They observed an increase in hydrogen bonding between the hydroxyl groups and the neighbouring oxygen atoms, however, the hydrogen bonds between the water molecule and the neighbouring anions were unaffected by this transition. They further showed that across the transition, the compressibility of lattice parameter b and c-axis decreases thereby decreasing the compressibility of cavities drastically, whereas the lattice parameter a, and therefore the Al-octahedra remains almost incompressible across the transition. These studies showed that the pressure induced transition is different from the low temperature phase transition sequence in lawsonite. A more detailed analysis of structural changes across $Cmcm$ to $P21/m$ transition in lawsonite was done by Pawley, and Allan [186] using angle dispersive synchrotron powder diffraction up to 16.5 GPa. They observed that the transition is of first order which exhibited a mixed phase region across the transition at 10-11 GPa. They further showed that the phase transition is driven by the shearing of the structure parallel to the chain of AlO_6 octahedral and an increase in coordination number of calcium. Another pressure induced phase in lawsonite was reported by Ballaran, and Angel [187] above 4 GPa where their single-crystal diffraction measurement showed that the lawsonite with $Cmcm$ symmetric orthorhombic structure transforms to orthorhombic

phase with primitive lattice above 4 GPa before it undergoes a transition to monoclinic phase at 9.5 GPa. The transition at 4 GPa was characterised by the presence of (017) reflection in the symmetry with primitive lattice, while it was absent in the *Cmcm* space group. Further, the orthorhombic-orthorhombic transition is accompanied by strains in each of the three lattice directions with negligible volume strain. The recent study on high-pressure structural phase transition in lawsonite was carried out by O'Bannon et al. [188]. They performed synchrotron single-crystal X-ray diffraction measurement on lawsonite at room temperature up to 10 GPa. They didn't observe orthorhombic *Cmcm* to primitive transition around 4 GPa, instead, it underwent isotropic compression in the orthorhombic phase with *Cmcm* symmetry up to 9.3 GPa, beyond which it undergoes a structural transition to monoclinic phase having $P21/m$ symmetry. According to their study, the orthorhombic to monoclinic structural transition in lawsonite is not driven by shearing of AlO_6 octahedra or increase in coordination number of calcium as reported by Pawley, and Allan [186] rather it is driven by two factors: (1) size mismatch of the Ca cation and (2) increase in compressional strain on bridging oxygen atom of Si_2O_7 group leading to its over-bonding nature. However, the refinement of single-crystal X-ray diffraction pattern by O'Bannon et al. [188] at high-pressures was done only for the metal atoms while the O-H bond lengths for the hydroxyls, water molecule as well as the H--H distance were kept fixed.

It is noteworthy that the high-pressure study of monoclinic lawsonite lacks theoretical investigation. Few studies which tackled lawsonite theoretically were carried out by Ackland [189] and Chantel et al. [190] where ambient *Cmcm* and the low temperature phases of lawsonite: $P21cn$ and *Cmcm* were considered. They showed structural instability of orthorhombic lawsonite around 8 GPa by the softening of elastic constants C_{22}, C_{13} around 8 GPa in orthorhombic symmetry. However, no explicit investigation was carried on the monoclinic phase in their study. In this work, we performed first principles calculations on lawsonite at high-pressure to investigate the structural evolution of lawsonite and determined the stability limit of lawsonite in the monoclinic phase. Our study shows that lawsonite exists in monoclinic phase up to 25 GPa beyond which the structure is unstable due to an increase in coordination number of calcium atoms that possibly drive the system to a structural phase transition. The pressure-induced increase in H--H repulsion and

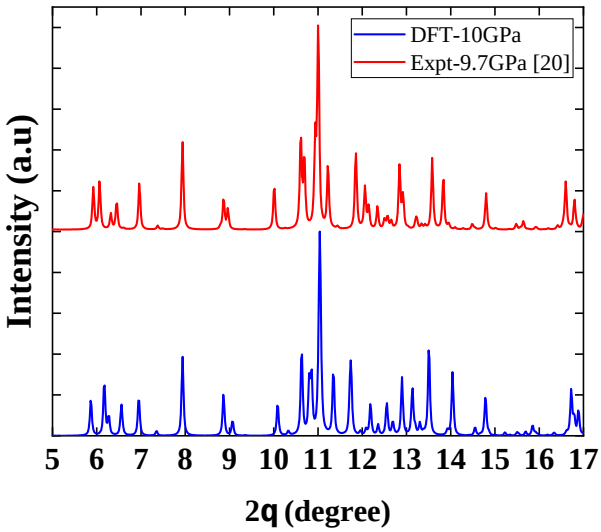
origin of additional weak hydrogen bonds of water causes the crystal structure to exhibit anomalous behaviour around 20 GPa as a precursor to the possible phase transition at 25 GPa. Till date, no high-pressure studies are reported exploring the stability limit of lawsonite above 20 GPa. Hence, this study will serve as a guideline to capture the phase transition in monoclinic lawsonite at higher pressures.

5.2 Methodology

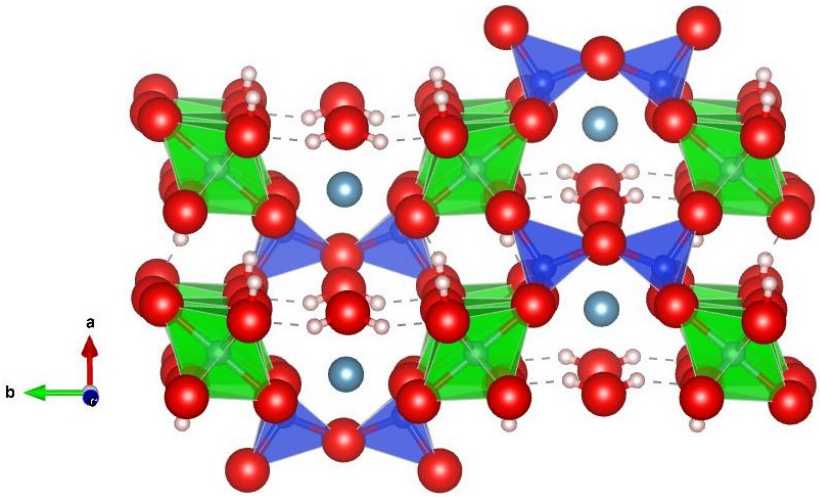
Total energy calculations were performed using Quantum Espresso [90, 91], which implements DFT to solve the Kohn-Sham equations. PBEsol [191] and local density approximations (LDA) [61] were used to treat the exchange-correlation functional for determining the structural and vibrational properties of monoclinic lawsonite respectively. The core and valence electrons were represented by Projector Augmented Wave (PAW) pseudopotentials [66] for evaluating structural properties and norm-conserving pseudopotentials under Martins-Troullier method [65] were used for evaluating vibrational frequencies since Raman intensity calculation is non-implemented using non-PBEsol functional in Quantum Espresso. To expand the one-electron orbital and electronic charge density, plane wave basis sets were used with kinetic energy cut-off set to 180 Ry. Brillouin zone integration was performed over 6×2×6 grid of **k**-point dimension generated under the Monkhorst-pack scheme [68]. To achieve the total energy convergence for the considered geometries, the forces on atoms were set to a threshold value of 10^{-4} Ry. The lattice dynamical properties were calculated using density functional perturbation theory (DFPT) [94]. Phonon frequencies were obtained by Fourier transform of dynamical matrix on a grid of 3×1×3 **q**-points. Raman activity of phonon modes was determined by implementing the second-order response method [192].

5.3 Results and Discussion

The phase transition of lawsonite from its low-pressure orthorhombic phase to its high-pressure monoclinic structure is shown to occur between 8-11 GPa [49, 185, 187], with the most recent study reporting a value of 9.7 GPa [188]. The initial structure for the



(a)



(b)

Figure 5.1: (a) Simulated XRD pattern of DFT optimised monoclinic structure of lawsonite at 10 GPa (upper panel) and form structural data of lawsonite at 9.7 GPa reported by O'Bannon et al. [188] (b) Optimised crystal structure of monoclinic lawsonite. Red, light blue and gren sphere represents oxygen, calcium and hydrogen atom respectively. SiO_4 and AlO_6 octahedra are shown in blue and green respectively.

optimization procedure at 10 GPa was adopted from the available XRD structural data of monoclinic lawsonite at 9.7 GPa [188]. The simulated XRD pattern for the optimized structure is compared to that generated for the experimentally reported monoclinic structure at 9.7 GPa in Fig. 5.1(a) which shows good agreement with each other. The optimized crystal structure of the monoclinic phase of lawsonite at 10 GPa is shown in Fig. 5.1(b). The labeling of oxygen atoms in the following discussion (and figures) was

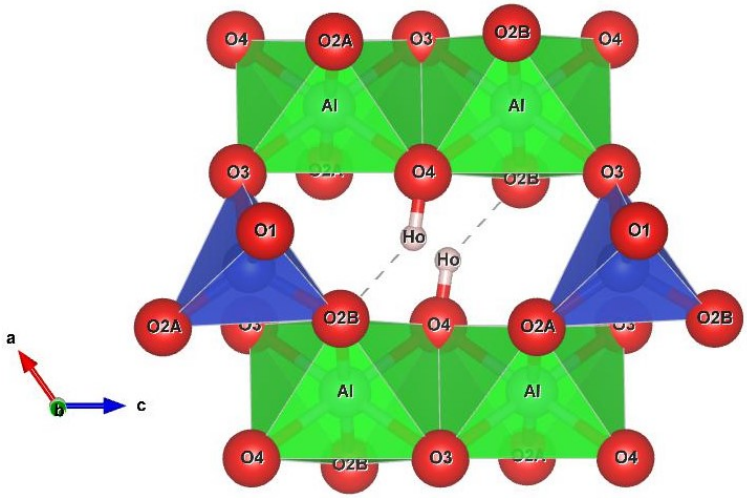
Table 5.1: Calculated structural parameters of monoclinic lawsonite at 10 GPa compared with the available data for the closest pressure value reported.

	This work (10 GPa)	Expt (9.7 GPa) [188]
a (Å)	5.2914	5.2189
b (Å)	12.8444	12.934
c (Å)	5.6486	5.6856
O2A--O4 (Å)	2.972	2.917
O2B--O4 (Å)	2.592	2.733
O4-H--O2B (Å)	114.5	148
O4-H---O2A (Å)	117.66	118
β (°)	125.353	124.47
Vol (Å^3)	313.1143	316.43

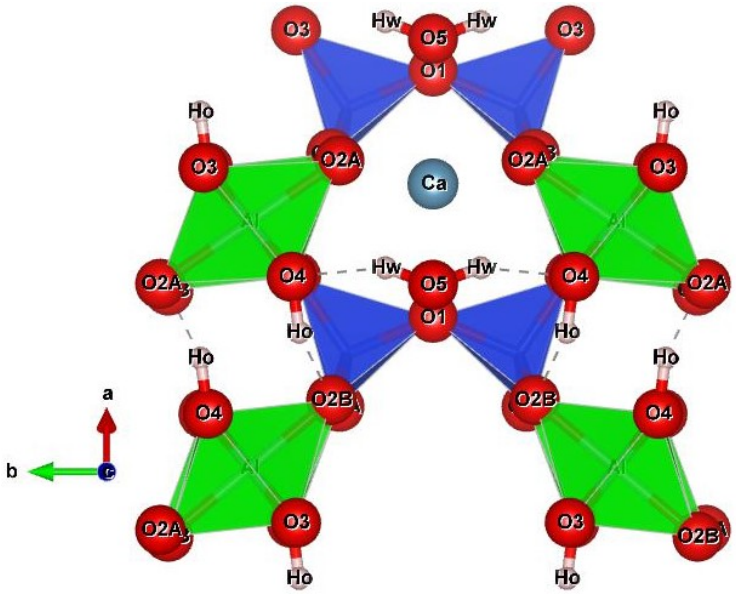
adopted from O'Bannon et al. [188] for making it convenient to compare the results of present study with their XRD study on monoclinic structure. SiO_4 tetrahedra and AlO_6 octahedra are the most basic building block of the aluminosilicate framework in lawsonite. It consists of chains of edge-sharing AlO_6 octahedra which runs parallel to the c-axis (in $P21/m$ setting) and the edges are shared through O3 and O4 oxygen atoms as shown in Fig. 5.2(a) . Two SiO_4 tetrahedra are linked to each other through the bridging O1 atom to form a Si_2O_7 group as shown in Fig. 5.2(b). These Si_2O_7 groups share each corner with one AlO_6 octahedra and the chains of AlO_6 octahedra are thereby interconnected to form a three-dimensional framework. This configuration forms large cavities which is occupied by a Ca atom and a H_2O molecule and remaining smaller cavities are occupied by hydroxyl group (O4-H_O) attached to AlO_6 octahedra.

The two hydrogen atoms of the water molecule (H_W) in the monoclinic lawsonite is hydrogen-bonded to O4 oxygen atoms of two hydroxyl group. In the low-pressure orthorhombic phase, the hydrogen atom associated with the water molecule and these two oxygen atoms lies in the same plane, however, on the transition to monoclinic structure, these two O4 oxygen atoms moves out of the plane causing the water molecule to rotate slightly [188]. Before the transition to the monoclinic phase, the O2A and O2B oxygen atoms were equivalent (O2) and formed two symmetric hydrogen bond with O4-Hw

hydroxyl [188]. In monoclinic lawsonite, O2 sites split into O2A and O2B sites giving rise to asymmetric bond distances from O4 atom making one of the O2 atoms (O2B here) closest to the O4 atom as shown in Fig. 5.2(a) and is consistent with the study of O'Bannon et al. [188]. The calculated unit cell parameters and hydrogen bond distances corresponding to the water molecule and the hydroxyl group are presented in Table. 5.1 and are compared with the experimental data of the closest pressure value reported. Apart



(a)



(b)

Figure 5.2: (a) The hydrogen bonding environment of monoclinic lawsonite when viewed along b-axis. The O4-H_O axis is tilted towards O2B oxygen atoms forming the hydrogen bond (dotted line). (b) Hydrogen bonding of water molecule and hydroxyl group in monoclinic lawsonite.

from the small difference in pressure values, there are two possible factors responsible for the observed variation in bond length and bond angle involving hydrogen atoms, in comparison with the XRD study of O'Bannon et al. [188]: 1) fixed O-H bond lengths for the hydroxyls and water molecule during the refinement of high-pressure single-crystal X-ray diffraction data of O'Bannon et al. [188] and 2) the approximation to the exchange-correlation used in our theoretical study. However, both these studies provide a consistent picture of hydrogen disordered state with asymmetric O4-O2A and O4-O2B distances in the monoclinic phase of lawsonite. This tilted configuration of O4-H_O minimizes the H_O--H_O repulsion between the hydrogen atoms of neighbouring hydroxyl group residing in the same channel. The unusual bond angle has been attributed to the dynamic disordered state [193]. Due to the limitation of static calculation, it is not possible to simulate the dynamics of disordering of hydrogen atoms with the employed unit cell. To confirm the stability of our computed structure, the phonon dispersion curves along the high-symmetry path of the Brillouin zone were calculated at 10 GPa and is presented in Fig. 5.3.

The absence of imaginary frequencies in the phonon dispersion curves confirms the lattice dynamical stability of the monoclinic phase of lawsonite. The calculated structural parameters, diffraction pattern and phonon dispersion curves validate the optimised unit cell of monoclinic lawsonite at 10 GPa to carry out calculations at high-pressure regime. The pressure window for the high-pressure study of the monoclinic phase was determined by searching the stability limit of monoclinic lawsonite. With an increase in pressure, the phonon branch along **A**-**Y** direction and at **Y** symmetry points of the Brillouin zone undergoes softening and turns imaginary above 25 GPa. The phonon dispersion curves of lawsonite calculated at higher pressure showed that the softening of phonon modes drives the monoclinic phase to lattice instability as shown in Fig. 5.3 for 30 GPa. This indicates that the monoclinic phase of the lawsonite becomes unstable above 25 GP and thereby leads to a possible phase transition.

With increase in pressure, the H_W--O4 distance decreases, increasing the hydrogen bond strength, however, this decrease in water-hydroxyl group distance also reduces the distance between hydrogen atoms of the water molecule and the hydroxyl group (See Fig. 5.2(b)). Further, the H_O hydrogen atoms also experience the repulsive force from the H_O hydrogen of the neighbouring hydroxyl group residing in the same cage. The evolution of

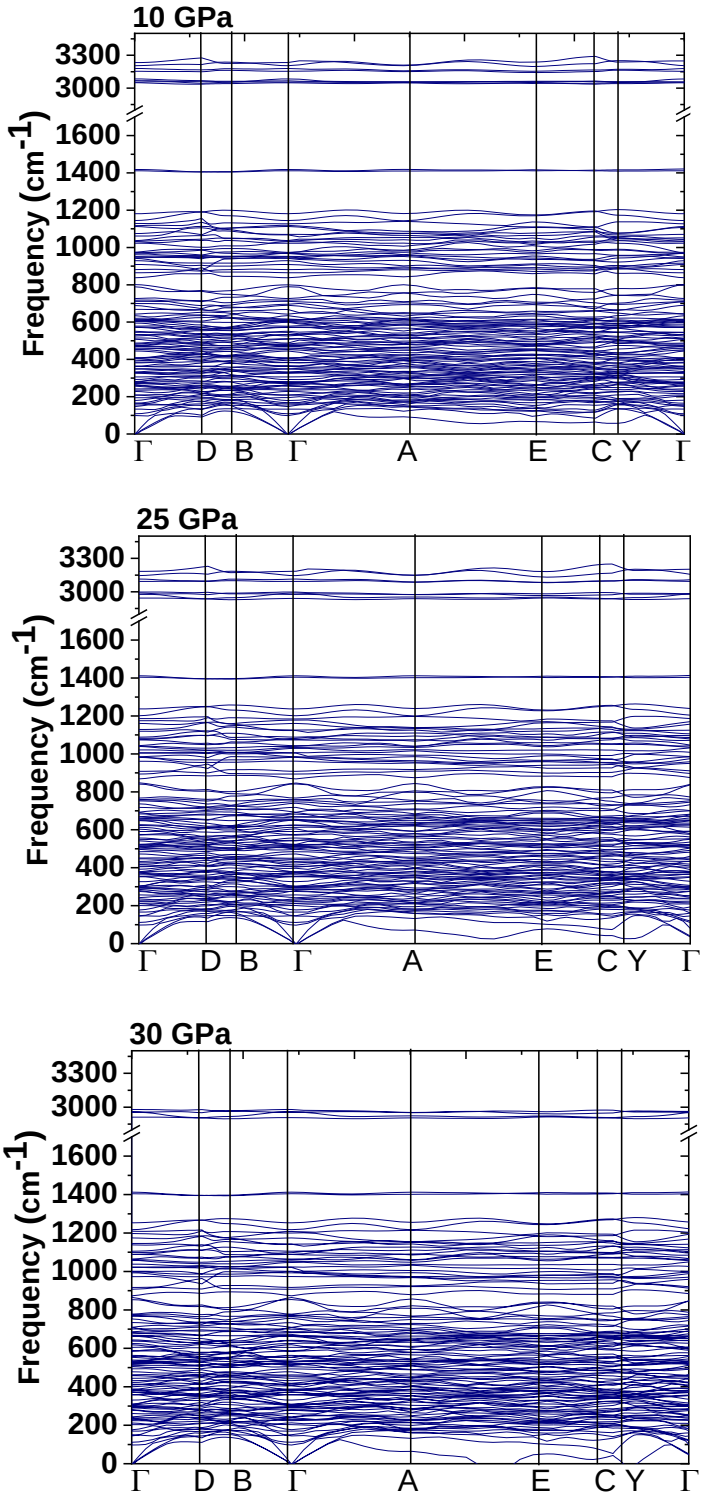
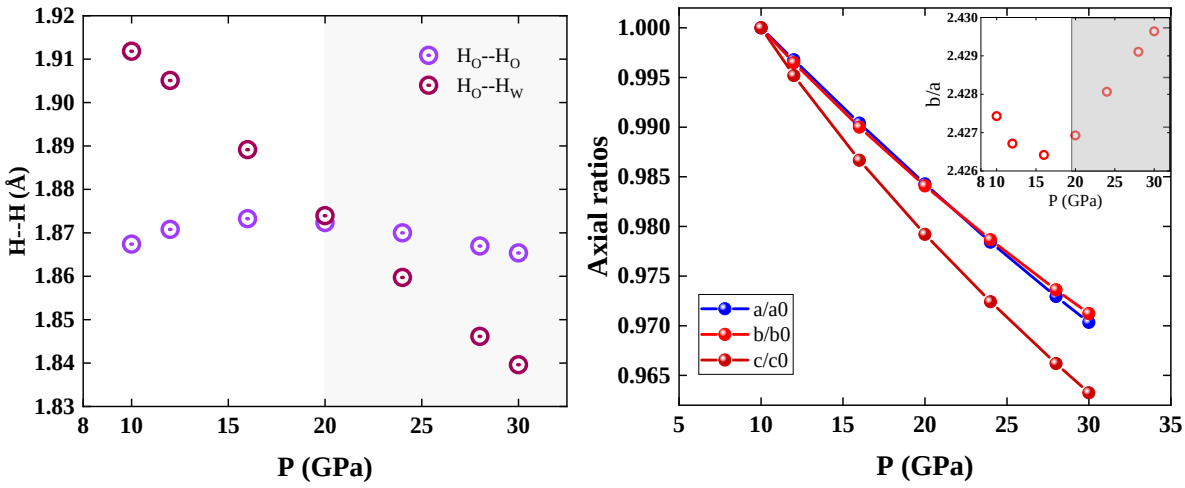


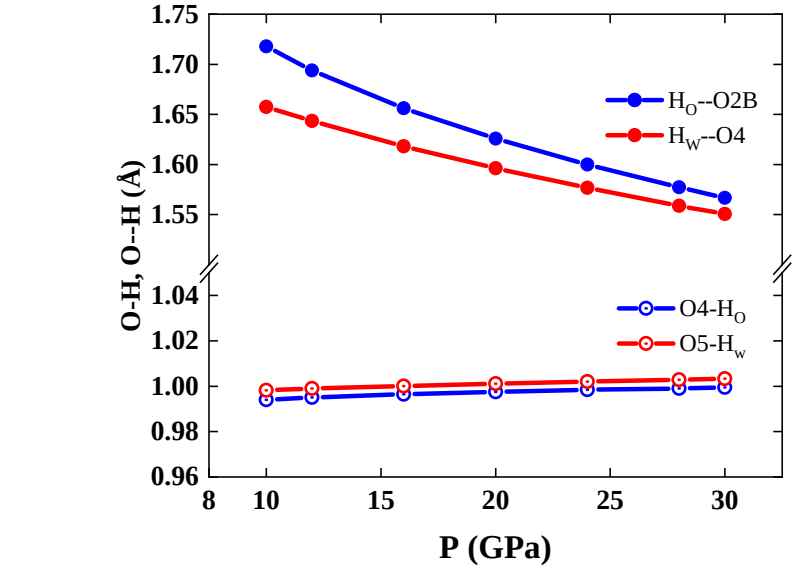
Figure 5.3: Phonon dispersion curves of monoclinic lawsonite calculated at 10, 25 and 30 GPa.

both pairs of H--H separations are plotted in Fig. 5.4(a). Initially, H_O--H_O repulsion is dominant (with smaller H_O--H_O separation). With further increase in pressure, the separation between H_O hydrogen atoms increases minimizing the repulsion between the neighbouring hydroxyl group and increasing the stability of hydrogen bonding environment. With further increase in pressure, the H_O--H_O distance ceases to increase and above 20 GPa, it decreases further increasing the H_O--H_O repulsion. This change in trend occurs when the distance between hydrogen atoms of hydroxyl and the nearby water molecule (H_O--H_W) becomes comparable to that of the nearby hydroxyl group (H_O--H_O) at 20 GPa. At this juncture, there are two competing H--H repulsive force acting on a single hydrogen atom, H_O. With further increase in pressure, both repulsive forces increase reducing both H--H separations, leading to repulsion induced geometrical frustration. The dominant repulsive force above 20 GPa being H_W--H_O is close to the b-axis and hence the compressibility of the b-axis is lower than that of a-axis above 20 GPa. The pressure dependence of axial ratios of monoclinic lawsonite is shown in Fig. 5.4(b). The c -axis is more compressible than the a- and b- axis. Though the compression of the a- and b-axis is isotropic, their relative compressibility changes above 20 GPa. The compressibility along the b-axis decreases as compared to the a-axis above 20 GPa (see inset of Fig. 5.4(b))

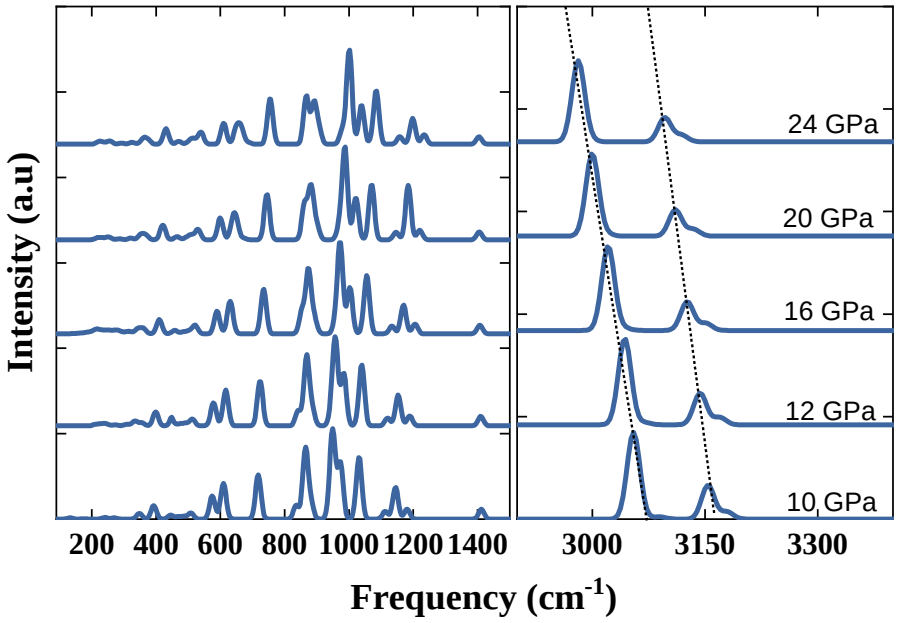


(a) (b)

Figure 5.4: (a) Evolution of separation between hydrogen atom of neighbouring hydroxyl group (H_O--H_O) and that of between water molecule and closest hydroxyl group involved in hydrogen bonding. (b) Plot of axial ratios with pressure showing the compressibility of the crystal structure of monoclinic lawsonite



(a)



(b)

Figure 5.5: (a) Pressure dependence of hydrogen bond length and O-H distance of water molecule and hydroxyl group. (b) Raman spectra calculated at various pressures corresponding to the O-H,O--H bond distance plotted in panel (a).

suggesting the existence of structural anomaly as a precursor to the phase transition in monoclinic lawsonite. The main contributor to the structural anomaly arises from the H--H_W and H--H_O repulsion.

The distance between H_W-O4 (1.657 Å) is shorter than H_O--O2B (1.718 Å), therefore the hydrogen bond of water is stronger than that of the hydroxyl group. The evolution

of O-H--O distance corresponding to both the water molecule and the hydroxyl group is plotted in Fig. 5.5(a). The distance between the hydrogen and the acceptor oxygen anion decreases with pressure which shows an increase in hydrogen bond strength of both the H_2O and O-H group. However, the O-H bond length is nearly constant throughout the studied pressure regime as shown in Fig. 5.5(a). Further, the pressure-induced changes in hydrogen bond strength were confirmed from softening of hydroxyl stretching modes from the calculated Raman spectrum. The evolution of the Raman spectrum with pressure is shown in Fig. 5.5(b). Consistent with this picture, our calculated high-pressure vibrational modes of O-H vibration showed a gradual decrease in frequency with pressure whereas all other lattice modes show slight hardening with the pressure. Pressure dependence of vibrational modes indicates a significant change in the H-bonding environment of water molecule which is different to what reported for orthorhombic lawsonite or across orthorhombic-monoclinic phase transition [184, 185]. This significantly affects the environment of water molecule, particularly of the cavity.

The variation in the relative dimension of the cage was investigated using the O4--O4, O2--O2 and O3--O3 bond distance and is presented in Fig. 5.6(a). It can be seen that the compression of these distances is not isotropic, with larger compression along the O2A--O2A direction. The reduction of O4--O5 distances with pressure was identical implying that both the hydrogen bond of water increases symmetrically with pressure and hence no rotation or freezing of water molecule was observed within the stability limit of lawsonite. This behaviour is different to that observed for the low-temperature phase where the two O4--O5 distances decrease by different amounts and the water molecules drift towards the closer O4 atom [179]. The possibility of the formation of additional weak hydrogen bonds increases with pressure as the distance between the hydrogen atoms and the surrounding oxygen anion decreases. O'Bannon et al. [188] reported that the O2A and O2B are far away from the water molecule (> 3.0 Å), and therefore they are not expected to form hydrogen bonds. We observed that, at higher pressure, the water molecule begins experiencing weak hydrogen bonds due to the presence of O2A and O2B where the distance from H_W hydrogen atom and O5 oxygen to the closest oxygen atom (O2B) becomes 2.418 Å and 2.834 Å respectively at 20 GPa. For the case of water molecule, the increasing hydrogen bond strength with a subtle change in O5-H_W length indicates the drifting of

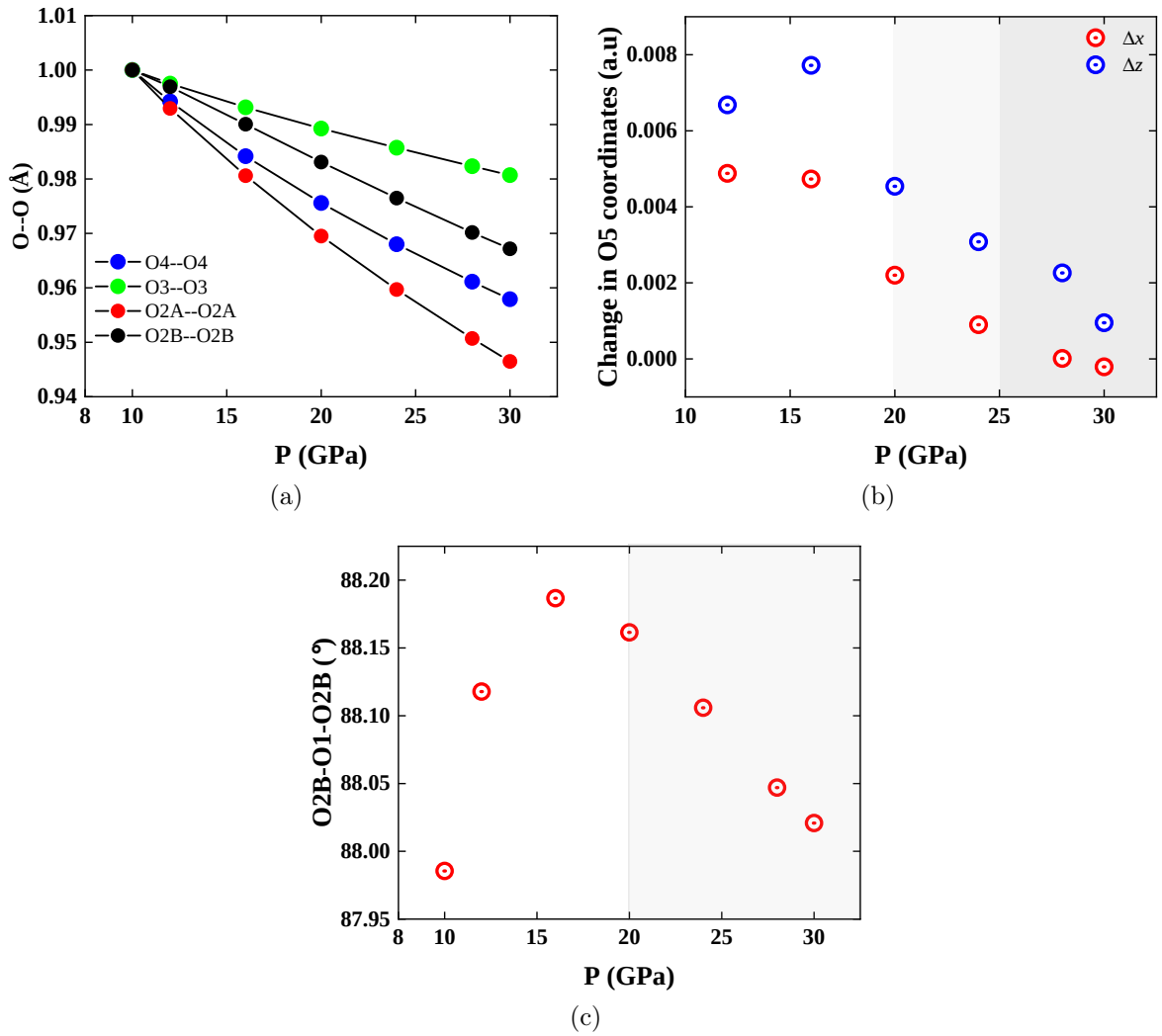


Figure 5.6: (a) The cross channel distance O4--O4, O3--O3, O2A--O2A and O2B--O2B which represents the change in channel dimension with respect to the water molecule (b) Evolution of the position of O5 oxygen atom with pressure, where the change in x and z coordinates are with reference to the position of O5 at for preceding pressure value (c) Change in O2B-O1-O2B angle with pressure, which is one of the angles between two SiO_4 tetrahedra about the O1 bridging oxygen atom.

the water molecule as a whole under compression. The displacement of the water molecule with pressure can be understood by the evolution of the position of O5 oxygen atom, where the change in x and z coordinates are shown in Fig. 5.6(b). The shifting of water molecule decreases as pressure is close to 20 GPa and converges to zero above 25 GPa. The resistive movement of water molecules from ∼20 GPa can be attributed to the combined effect of H_O--H_O and H_O--H_W repulsion and the formation of new hydrogen bonds with the neighbouring O2A and O2B oxygen atoms of the cage. Anomalous behaviour was also

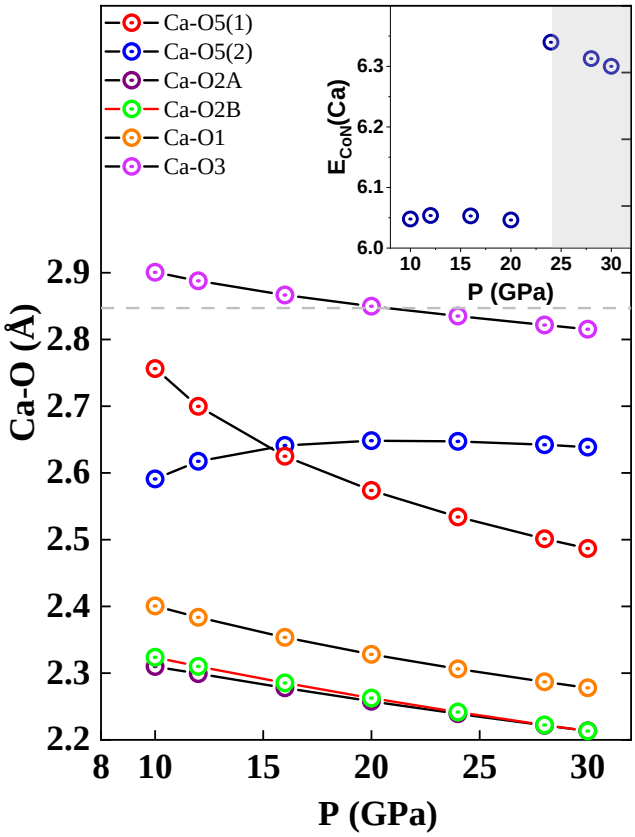


Figure 5.7: Pressure dependence of calculated bond length between calcium and neighbouring oxygen atoms. The reference line is drawn at the maximum bond length estimated for the calcium atom with coordination number 6 according to Ref.[34]

observed in the bending of two SiO_4 groups about the bridging oxygen atom. The pressure evolution of angle O2B-O1-O2B is shown in Fig. 5.6(c). The angle initially increases with pressure and decreases above 20 GPa. We attribute the initial opening of angle to the increase in hydrogen bonding of hydroxyl group and the sudden change in trend thereafter can be attributed to the combined effect of newly formed hydrogen bonding with O2B atom as well as the increase in strength of Ca with O2B bond under compression.

The bond length of calcium with its neighbouring oxygen atoms are shown in Fig. 5.7. There are two different Ca--O5 bond distances corresponding to the interaction between calcium atom and water molecule where the evolution of Ca--O5 bond distance is associated with the position of water molecules with respect to calcium atoms. Initially, the two water molecules are not equidistant from calcium giving rise to two distinct Ca--O5 bonds labelled as Ca--O5(1) and Ca--O5(2) with length 2.591 Å and 2.756 Å respectively. With pressure, the evolution of position of water molecules is such that at

16 GPa, both molecules are equidistant from the calcium atom. The Ca--O3 bond was shown to be least affected by the pressure in the monoclinic phase up to 10 GPa, thereby not including it in the coordination sphere of calcium by O'Bannon et al. [188]. Stating the coordination of the central atom as a single number is somewhat difficult in relatively distorted coordination polyhedral, therefore, it is convenient to use mean or 'effective' coordination number (E_{CoN}) where the surrounding atoms are not counted as full atoms but as fractional atoms with numbers between 0 and 1 added with a weighting scheme. Imposing the criteria of maximum bond length of 2.847 Å for Ca--O in a 6 coordinated calcium [194], the polyhedral and the effective coordination number can be calculated. The plot of E_{CoN} with pressure is shown in the inset of Fig. 5.7. Our study shows that the Ca--O3 bond distance reduces with further increase in pressure and falls within the coordination sphere above 24 GPa. Hence this change in the coordination sphere of calcium will drive the system to lattice instability leading to a phase transition. Based on the decrease of Ca--O3 bond distance within the bonding limit of calcium, we presume that the phase transition to a post-monoclinic structure will have increased coordination number of calcium atom.

5.4 Conclusions

In this work, a high-pressure structural and lattice dynamical study of lawsonite in monoclinic structure was performed to determine its stability limit under high-pressure condition. The structure of lawsonite was initially studied at 10 GPa for validating the DFT calculated geometrical parameters of the monoclinic unit cell. Good agreement between the unit cell parameters and simulated XRD pattern with reported experimental data was obtained. The absence of imaginary phonon frequency confirmed the stability of the simulated unit cell at 10 GPa. The stability limit under pressure was investigated by calculating the phonon dispersion curves of monoclinic lawsonite at higher pressure. Our study showed that the high-pressure monoclinic phase of lawsonite is dynamically stable up to 25 GPa beyond which the phonon modes turn imaginary along **A-E** direction and **Y** symmetry point of the Brillouin zone. The change in compressibility and axial length ratio with pressure showed that the compressibility of the *b*- axis becomes lower

than *a*- axis above 20 GPa, however, well before the stability limit. The anomalous behaviour is attributed to the increasing H_O--H_W repulsion which dominates the H_O--H_O repulsion above 20 GPa, leading the geometry to structural frustration. Under pressure, the hydrogen bond of both the hydroxyl group and water increases. The position of water changes with pressure where we attribute the drifting of water molecule to the combined effect of increased hydrogen bonding, H_O--H_W and H_O--H_O repulsion and the formation of weak hydrogen bonds of the water molecule to the neighbouring OA and O2B oxygen atoms. The increase in hydrogen bond strength is consistent with the high-pressure Raman spectral calculations where the frequency of O-H stretching vibrations decreases with pressure. The structural anomaly at 20 GPa is reflected in the Si_2O_7 framework where the O2B-O1-O2B angle initially increases with pressure and decreases above 20 GPa. Thus, the increasing H--H repulsion and origin of additional weak hydrogen bonds cause the crystal structure to exhibit anomalous behaviour at ∼20 GPa as a precursor to the possible phase transition at 25 GPa. The instability in the monoclinic structure above 25 GPa as shown by phonon dispersion curves is attributed to the increase in coordination number of calcium. At ∼25 GPa, the Ca--O3 bond distance falls below 2.847 Å which has been reported as the maximum bond length of calcium atom with coordination number 6 [194] thereby abruptly increasing the effective coordination number. The post monoclinic structure is likely to have increased coordination number of calcium.