First Principles and Raman Spectroscopic Investigation on some Geologically Important Materials

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Introduction

Studying the behaviour of Earth-forming materials at conditions relevant to earth's interior allows one to understand better the properties of the Earth's interior and provides clues to important geological problems [1-2]. The knowledge of water recycling and storage in Earth is critical to understand the physical and rheological properties of the mantle. Subduction zones play a fundamental role in the cycling of minerals from the surface of the Earth into the Earth's interior. Minerals that are subducted experience high pressure and temperature as they are transported to greater and greater depths. Therefore, understanding of high pressure-temperature behaviour of hydrous minerals at conditions relevant to Earth's mantle is crucial. Our understanding or processes at depths > 150 km is limited since geologic samples from this region are rare, and experiments in this pressure and temperature regime are difficult. The work presented here takes advantage of pressure as a thermodynamic variable in order to gain insight into the physics and chemistry of subduction zone related mineral phases. The work is divided into three major parts (1) high pressure study of structural, mechanical and vibrational properties of hydrous mineral δ-AlOOH (2) Pressure induced changes in hydrogen sublattice in layered hydroxides taking $Mg(OH)_2$, $Ca(OH)_2$, $Co(OH)_2$ and $Ni(OH)_2$ as model systems (3) Determining the stability limit of lawsonite ($CaAl_2Si_2O_7(OH)_2 \cdot H_2O$).

The δ-AlOOH phase is a high-pressure polymorph of the natural aluminous hydrous minerals of diaspore (α-AlOOH) and boehmite (γ-AlOOH) [3-4]. Many attempts have been made to estimate the pressure at which hydrogen bond symmetrization occurs, but there exists a discrepancy in predicting the hydrogen bond symmetrization pressure among experimental and theoretical results and also among theoretical results particularly on hydrogen bond symmetrization pressure [5-8]. The high pressure study of δ-AlOOH and the effect of hydrogen bond symmetrization in its structural, vibrational and mechanical properties needs to be investigated.

The crystal structure of compounds belonging to $M(OH)_2$ compounds, where M is a divalent cation, consists of layers of MO_6 octahedra. Within the interlayer separation, the hydroxyl group are directed along the layer-stacking direction and is attached to three metal atoms. This gives rise to two parallel planes of hydrogen atoms. Under pressure, the interlayer spacing and hence the non-bonded H--H distance decreases which increase the H--H repulsion. At a critical bond distance, the H--H repulsion destabilizes the initial structure and the structure will no longer remain in ordered structure. Hence a transition from order to

the disordered structure under pressure is most likely to occur in all these compounds with increase in pressure. Even though these materials have been subjected to several high pressure experimental and theoretical studies, their structural behaviour has been controversial. The debate centres around the hydrogen order-disorder transition in these compounds, indeed, ambiguity exist in determining the ground state structure of $Mg(OH)_2$ [9-11]. A systematic investigation probing the pressure response of hydrogen sublattice in these layered compounds enables to address this challenging issue.

One of the few minerals that could transport water to depths of > 300 km is lawsonite whose high pressure monoclinic phase was recently being solved experimentally [12]. It is a unique mineral that has a high overall water content and a large pressure/temperature stability field. It is believed to be. Since hydrous minerals are believed to exist in oceanic plates and subduct into the mantle together with the slab components [13], the stability field of hydrous minerals at high pressures and high temperatures is critical for the proposed transportation of hydrogen into the deep mantle. Hence, the structural properties of lawsonite in monoclinic phase at high pressure and its stability limit needs to be investigated.

This work provides a systematic investigation on high pressure studies on $M(OH)_2$ family, δ-AlOOH and lawsonite shed light on pressure response of dominant hydrous minerals which will have vast geophysical implications. To address the pressure response of crystal structure of hydrous minerals, high pressure studies using first principles calculations based density functional theory were carried on δ-AlOOH, lawsonite and combined DFT and synchrotron diffraction measurements on $M(OH)_2$ family which serves as prototype for complex hydrous mineral taking Mg(OH)2, $Ca(OH)_2$, $Co(OH)_2$ and $Ni(OH)_2$ as model systems.

Objectives

- To investigate pressure response of hydrous mineral δ-AlOOH and study the evolution of hydrogen bond.
- To study the Raman spectroscopic signature of structural transition in δ-AlOOH involving change in hydrogen sites under pressure
- To address the challenging problem of hydrogen order-disorder transition in layered hydroxides
- To investigate the structural behavior and stability limit of high pressure phase of hydrous mineral lawsonite.

Outline of the thesis

The thesis presents high pressure structural behaviour of hydrous minerals δ-AlOOH and lawsonite, and further addresses the issue of pressure induced hydrogen order-disorder transition in layered hydroxides. The thesis structure consists of six chapters among which three chapters discuss the main research outcomes. The content of each chapters are described below.

Chapter 1: The thesis begins with a broad introduction to the need of high-pressure research and its implications towards geophysical phenomenon with particular focus on the role played by hydrous minerals. The sections followed will give a detailed literature review highlighting the discrepancies reported in results of high-pressure studies on δ-AlOOH and layered hydroxides.

Chapter 2: This chapter is devoted to the theoretical and experimental methods employed during the work. Section corresponding to theoretical methods includes brief outline of density functional theory and theoretical background of methods used for calculating structural, mechanical and vibrational properties will be discussed. In experimental section, background of synchrotron x-ray powder diffraction (XRPD) and details of experimental setup used for high pressure x-ray powder diffraction measurement in conjunction with diamond anvil cell (DAC) will be presented.

Chapter 3: This chapter presents the high-pressure study on hydrous mineral δ-AlOOH using first principles calculations based on density functional theory. The chapter begins by addressing the issue of determining hydrogen bond symmetrization pressure among reported experimental and theoretical studies. After discussing the optimized and converged parameters used for theoretical calculations, the calculated structural, mechanical and vibrational properties are discussed. Raman spectroscopic signatures of hydrogen bond symmetrization are also discussed which serves as an observable for the transition.

Chapter 4: This chapter presents high pressure study of layered hydroxides belonging to the family of $M(OH)_2$ compounds taking $Mg(OH)_2$, $Ca(OH)_2$, $Co(OH)_2$ and $Ni(OH)_2$ as model systems. The pressure response of these materials was studied using synchrotron XRD measurements and DFT based calculations. In case of $Mg(OH)_2$, density functional theory shows the hydrogen order-disorder transition to occur at very small volume perturbation, owing to which, the behaviour of $Mg(OH)_2$ were also studied at low temperatures using

synchrotron XRPD in order to probe the effect of volume compression caused by thermal contraction. These studies also resolve many of the discrepancies reported in literature there by highlighting the success of adopted methodology of combining synchrotron XRPD and density functional theory based calculations. This chapter also shed light on the challenging problem of pressure induced hydrogen sublattice disordering in layered hydroxides.

Chapter 5: This chapter discuss the high pressure structural behaviour of hydrous mineral lawsonite ($CaAl_2Si_2O_7(OH)_2 \cdot H_2O$) which is known for its water carrying property. The structural properties of monoclinic phase of lawsonite are discussed along with analysis of calculated Raman spectrum. The phonon dispersion curves calculated at high pressure are discussed and the stability limit of lawsonite is determined.

Chapter 6: This chapter provides a summary of research outcomes of chapter 3, 4 and 5. The chapter will generalise the importance of the work carried out in terms of studies contributed to high pressure study of hydrous minerals and layered hydroxides with potential geophysical implications.

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List of publications related to thesis

1. **S. B. Pillai**, P. K. Jha, A. Padmalal, D. M. Maurya, and L. S. Chamyal, *J. Appl. Phys* **123**, 115901 (2018)
2. **S. B. Pillai**, B. Joseph, D. Upadhyay, C. Marini and P. K. Jha, *J. Phys. Chem. C*, **125**, 4, 2785–2792 (2021)
3. **S. B. Pillai**, D. Upadhyay, P. K. Jha and B. Joseph *EPL*, (In press)
4. **S. B. Pillai**. B. Joseph and P. K. Jha, *J. Phys. Chem. Solids (In communication)*