Chapter 4

Inelastic Neutron Scattering Studies of Phonon Spectra and Simulations in Tungstates, AWO₄ (A = Ba, Sr, Ca and Pb) and LuVO₄

4.1 INTRODUCTION

Compounds of the form MWO₄ (M = Mn, Cu, Ba, Sr etc) are studied [1-11] extensively for their interesting properties and usefulness. This thesis reports lattice vibrational studies on AWO₄ type tungstates with A = Ba, Sr, Ca and Pb, which are important for their scientific and technological applications [12-18]. These compounds in nano or bulk state find applications in solid- state scintillators [16-19], optoelectronic devices, solid state laser applications etc as well as in understanding of geological aspects. They also form a part of oxide ceramic composites useful for cryogenic detectors. These possible applications have motivated extensive interest in understanding the fundamental physical properties [20-31] of the AWO₄ tungstates. Rare-earth vanadates RVO₄, phosphates and arsenates whose crystal structure is the tetragonal zircon-type [29] with space group I4₁/amd have received much attention in modern laser physics and non-linear optics. When doped with suitable ions, these vanadates serve as excellent host material for laser application. These materials have been employed as
model systems for the investigation of polymorphism among ABO$_4$ type compounds. Sections 4.2 and 4.3 report studies done on tungstates and vanadates respectively.

4.2 Inelastic Neutron Scattering Studies of Phonom Spectra and Simulations in Tungstes

The compounds under normal conditions crystallize in the tetragonal scheelite [28] structure (CaWO$_4$ mineral structure). The scheelite structure (space group 88, Z = 4) adopted by AWO$_4$ has a body centered unit cell, with A atoms occupying $S_4$ symmetry while the sixteen oxygen atoms occupy $C_1$ sites. Each W is surrounded by four equivalent oxygen atoms in a tetrahedral symmetry and A is surrounded by eight oxygen atoms. Along a-axis the WO$_4$ units are directly aligned whereas along the c-axis, AO$_8$ dodecahedra are interspersed between two WO$_4$ tetrahedra. Hence, different arrangement of hard WO$_4$ tetrahedra along the c and a-axis accounts for the difference in compressibility of the two unit-cell axes. These compounds exhibit a rich phase diagram with respect to change in pressure and temperature [23]. Several experimental and theoretical efforts have been undertaken to obtain understanding of the phase diagram of the compounds [20-27], which still remains elusive. Extensive Raman [27,28,29] and infrared [30] scattering techniques have been used to study the zone centre phonon modes in several of these tungstates. Experimental studies using angle dispersive X-ray diffraction (ADXRD), x-ray absorption near edge structure measurements (XANES) have observed that upon compression at high pressures AWO$_4$ undergoes a scheelite to
fergusonite phase transition at room temperature. This transformation is a displacive in nature [23]. The $\beta$ angle of the high pressure monoclinic cell of the fergusonite phase is only a little different from 90°. Upon further compression the compounds change into denser monoclinic and orthorhombic phases, before amorphizing. In the meanwhile, experiments like Raman scattering suggest [27-29] that there is a possibility of a reconstructive, first order transition to $P2_1/n$ phase which coexists with the fergusonite phase. But this competing phase is kinetically hindered.

The author reports a complete and comparative details of the inelastic scattering experiments and theoretical studies on a series of tungstates as $\text{AWO}_4$ ($A = \text{Ba, Sr, Ca and Pb}$). The measurement of phonons density of states is carried out by using neutron inelastic scattering. The transferable interatomic potential has been developed and further used in molecular dynamics studies to understand the mechanism of pressure driven phase changes of $\text{AWO}_4$ ($M = \text{Ba, Ca, Sr and Pb}$). The author has looked at the changes occurring in the lattice under increasing pressure. The simulations have enabled us to understand the behavior of various polyhedra under compression.

### 4.2.1 Experimental details

Polycrystalline samples of the $\text{AWO}_4$ ($A= \text{Ba, Sr and Ca}$) were prepared by solid state reaction of appropriate amounts of alkaline earth carbonate ($\text{ACO}_3$) and $\text{WO}_3$. $\text{PbWO}_4$ was prepared by heating the precipitates obtained from $\text{Pb(NO}_3)_2$ and $(\text{NH}_4)_2\text{WO}_4$ solutions. The phonon density of states measurements of all $\text{AWO}_4$ ($A= \text{Ba, Sr, Ca, Pb}$) were performed in the neutron-energy gain mode with incident neutron energy of 14.2 meV. The data were taken over the scattering angle 10° to 113°. The signal is corrected for the contributions from the empty cell and suitably averaged over the angular range.
using the available software package at ILL. The incoherent approximation [32,33] was used in the data analysis. The data were suitably averaged over the angular range of scattering using the available software package at ILL to obtain the neutron-cross-section weighted phonon density of states. The multiphonon contribution has been calculated using the Sjolander [34] formalism and subtracted from the experimental data.

4.2.2 Theoretical Formalism

We have used a transferable interatomic potential to study the vibrational properties of the tungstates using lattice dynamics calculations. An interatomic potential as described in equation (1.25) consisting of short range and Coulombic terms is used. The radii parameters for M atoms are \( r_{\text{Ca}} = 2.06 \, \text{Å}, \, r_{\text{Ba}} = 2.4 \, \text{Å}, \, r_{\text{Pb}} = 2.25 \, \text{Å} \) and \( r_{\text{Sr}} = 2 \, \text{Å} \) respectively. The van der Waals interaction between O-O pairs is 80 eVÅ\(^6\). The parameters of the WO\(_4\) stretching potential described in equation (1.26), are \( D = 3.2 \, \text{eV}, \, r_o = 1.75 \, \text{Å} \) and \( n = 26.2 \, \text{Å}^{-1} \). The polarizibility of the oxygen and alkali earth atoms has been considered in the framework of shell model with shell charge and shell core force constants for oxygen atoms as \(-2.0\) and \(50 \, \text{eV/Å}^2\) and for alkaline atoms as \(3.0\) and \(50 \, \text{eV/Å}^2\) respectively.

Molecular dynamics (MD) simulations have been carried out using the model parameters obtained from the lattice dynamics calculations. A super cell consisting of 8×8×4 unit cells (6144 atoms) has been used to study the response of the compounds on compression. Rigid ion model has been used in the MD simulations. Calculations have been carried out from ambient pressure to around 50 GPa at room temperature. Equation of state has been integrated for about 1400 picoseconds using a timestep of 0.002 picoseconds.
4.2.3 Results and Discussion

The neutron inelastic scattering experiments have been performed using powder samples of the AWO₄ (M = Ba, Sr, Ca and Pb) at ambient conditions. The measurements have been carried out on the time of flight (TOF) instrument IN4C, ILL, Grenoble.

The measured phonon density of states of the four tungstates in comparison with potential model calculations is given in Fig. 4.1. The potential model calculations results are in good agreement with the inelastic neutron data. This has allowed validation of our model, which is further used to explore the phase stability of the compounds using molecular dynamics simulations as discussed below. The measured spectra show that phonons occur in two distinct regions in these compounds. The first region extends from 0 to 60 meV, while there is another region between 90-120 meV. The higher energy component corresponds to the internal vibrations of the WO₄ tetrahedra.

The calculated partial phonon densities of each atom of AWO₄ compounds are given in Fig. 4.2. It can be seen that the contribution from the A atoms extends up to 20 meV. The contribution of Pb atom is at the lowest energy while that of Ca at the highest energy. This is in commensurate with their relative atomic mass. The contribution from W atoms is confined within 20 meV, with a very small contribution up to 60 meV. There is another contribution above 90 meV in the band between 90-110 meV from W atoms. In case of oxygen, contribution is in the complete range 0-60 meV and in the band between 90 to 110 meV. The partial phonon densities ascertain that the contribution above 90 meV in the measured spectra is from the internal stretching modes of the W-O tetrahedra.
Fig. 4.1  Neutron inelastic scattering data of the phonon density of states in $\text{AWO}_4$ ($A = \text{Ba, Ca, Sr and Pb}$) compared with shell model calculations.

Fig. 4.2. Calculated partial phonon density of states in all the three compounds
Fig. 4.3. Calculated phonon dispersion in SrWO$_4$ along with measured phonon branches along [100] and [001] directions in single crystal of SrWO$_4$ using TAS, Dhruva, India. Solid symbols are the measured phonons. The full, dashed and dotted lines are the calculated phonon branches belonging to different representations as carried out by the author.
Phonon dispersion relation in single crystal of SrWO$_4$ has been measured along [100] and [001] directions. Only the low energy acoustic modes have been measured. The calculated phonon dispersion along with measured phonon branches in the [100] and [001] directions is given in Fig. 4.3. The measurements have been carried out using TAS, Dhruva. The agreement between the measured and calculated phonon dispersion is good.

![Graphs showing specific heat for different tungstates](image)

**Fig.4. 4** Experimental and computed (using potential model) specific heat in AWO$_4$ ($A =$ Ba, Sr, Ca and Pb). The experimental data for CaWO$_4$ is from Ref. [35].

The group theoretical distribution of phonons along high symmetry [001] and [100] directions is as follows:

Λ (001): $8 \Lambda_1 + 8 \Lambda_2 + 10 \Lambda_3$ ($\Lambda_3$ is doubly degenerate)

Σ (100): $18 \Sigma_1 + 18 \Sigma_2$

The symmetry vectors obtained through detailed group theoretical analysis along the two high symmetry directions and the zone centre point were employed to classify the phonon frequencies obtained into their irreducible representations.
Fig. 4.5. Calculated (using potential model) and experimental equation of state of AWO$_4$ (A = Ba, Ca, Sr and Pb). V and V$_0$ are the unit cell volume at high and ambient pressure respectively. ‘a’, ‘b’ and ‘c’ correspond to the experimental data from references [13], [24] and [27]. The full and dash lines correspond to calculations at T=300 K and 0 K respectively.

The computed density of states has been used to determine the specific heat capacity of the four oxides as shown in Fig. 4.4. The available data on CaWO$_4$ [35] has been compared and is found to be in very good agreement with our calculated data. Using the interatomic potential developed, we have studied the pressure evolution of the tungstates. Fig. 4.5 gives the equation of state of the four compounds. These compounds are found to undergo initial transformation from scheelite (I$\bar{4}$$_{1}$/a) to fergusonite (I2/a). According to experimental XANES [23,24] and ADXRD [23,24] studies, it is now well known that BaWO$_4$ transforms from scheelite to fergusonite phase at 7.5 GPa, PbWO$_4$
transforms at 9 GPa, CaWO₄ undergoes the above said transition at 11 GPa, and SrWO₄ at 10 GPa.

The pressure driven transition to fergusonite phase is of displacive in nature, it is known to be a second order phase transition with almost no discernable volume discontinuity. The change in the β angle is only feeble; change in the ‘b’ lattice parameters is also negligible. This change is not evident from our MD calculations.

In our molecular dynamics calculations we can see that there is a discontinuity in the pressure-volume curve (Fig. 4.4), which suggests a change in phase. In case of CaWO₄, this change is seen around 30 GPa, around 34 GPa in SrWO₄, in case of PbWO₄ it is around 38 GPa while in case of BaWO₄ it is around 45 GPa. Detailed studies were done to understand this sudden change in the equation of state. Fig. 4.5 gives the structural arrangement of the different polygons at different pressures (in BaWO₄) as obtained from our computations. At P = 0 GPa, the atoms are arranged in the scheelite structure, A atom is in AO₈ coordination while W is in tetrahedral WO₄ coordination. Regions B and C are identified to depict the coordination of A and W atoms. As pressure is increased, at 43 GPa, there is no visible change in the structural arrangement of the various polygons. There is no change in the coordination around A and W atoms. Beyond 45 GPa, there is a volume drop in BaWO₄. This observation coincides with the volume discontinuity observed around 45 GPa in BaWO₄ in Fig.4.5. The structure at 47 GPa shows several obvious changes as compared to earlier structures. In region C, it can be seen that A atoms are no longer in perfect bisdisphenoids, instead it is now seen in a highly distorted polygon. In region B, W atoms show significant changes, the co-ordination number has increased. Most of the WO₄ tetrahedra have changed in to distorted WO₆.
Fig. 4.6. The structure of BaWO₄ super cell evolving under pressure. Regions B and C are marked to depict and understand the change in coordination around A and W atoms. (c-axis is perpendicular to the plane of the paper)

Further credence to this observation is obtained from the O-W-O bond angle distribution given in Fig. 4.7. At ambient pressure, all WO₄ tetrahedra are regular with O-W-O angle equal to 109°. At 43 GPa, WO₄ tetrahedra are still regular. But on amorphization, the increase in coordination has resulted in the change in the bond angle.

Majority of the O-W-O angle is around 90° which corresponds to an octahedral arrangement. Not all the W’s have attained a coordination of 6; hence, distortion of the tetrahedra has given rise to a range of angles for the O-W-O bond as seen in Fig. 4.7. Similar behavior is seen in all the remaining tungstates. In order to obtain a deeper understanding into this volume discontinuity, we have studied the local order in the lattice between various atomic pairs. The pair correlations have been computed in these compounds with increasing pressure. Fig. 4.8 shows the pair-correlation function between A-W, A-O, A-A, W-W, W-O and O-O at various pressures. We find that with increasing pressure, there are subtle and small changes in the correlations between the different atomic pairs. In case of BaWO₄, the correlations broaden beyond 47 GPa, as seen from
the plots in Fig. 4.8. This is in very good agreement with the reported value [24] of 45 GPa for amorphization in BaWO$_4$. In case of CaWO$_4$, the broadening of peaks appear around 32 GPa, while the experiments show [28] amorphization around 40 GPa. Our molecular dynamics calculations predict that in case of SrWO$_4$, at 36 GPa the peaks in the calculated pair correlations broaden, implying that the discrete ordering is lost. In PbWO$_4$, similar trend is observed at 40 GPa. These observations are in tandem with the equation of states (Fig. 4.5) computed in each of the compounds.

![Fig. 4.7: Intratetrahedral bond angle O-W-O with changing pressure in BaWO$_4$.](image)

Careful investigations of the various atomic pairs reveal some interesting observations. In case of A-O pair distribution, we find that changes due to increase in pressure is seen to occur gradually, as can be seen in the inset of the Ba-O pair distribution. There is gradual decrease in the bond length on going from 0 GPa to 43 GPa. The BaO$_8$ units are able to withstand the increased pressure with gradual rearrangements of the Ba-O bonds, but beyond 43 GPa, the polyhedra distorts considerably. This leads to the broadening of peaks, suggesting the loss of long range order. In case of WO$_4$ tetrahedra, there is almost no change in the bond-length (changes by about 0.015 Å) as pressure is increased from 0 to 43 GPa (Inset Fig. 4.8).
However further increase in pressure beyond a threshold of 45 GPa leads to an abrupt increase in the W-O bond by about 0.1 Å. Hence it can be inferred that WO$_4$ tetrahedra is almost immune to changes in pressure up to an upper threshold of pressure, whose value is different for each of the tungstate. Beyond this threshold, WO$_4$ tetrahedra distort and W atom’s coordination increases.

Our above said observations are in tandem with experimentally [24] observed amorphization around 45 GPa in BaWO$_4$ and at around 40 GPa in CaWO$_4$ [28]. The equation of state for various compounds has also been obtained (Fig. 4.5) from minimization of the enthalpy at 0 K. Table 4.1 gives the bulk modulus and its pressure derivative for the four compounds in comparison with the available reported experimental data [24]. The values are obtained from fitting of the Birch equation of state [36] to the calculated equation of states.

**TABLE 4.1 :** Comparison between the experimental and calculated bulk modulus (B) (in GPa units) and its pressure derivate (B’). The experimental values at 300 K are from Ref. [24]. The B values at 300 K has been obtained using the B’ values estimated at 0 K.

<table>
<thead>
<tr>
<th></th>
<th>BaWO$_4$</th>
<th>CaWO$_4$</th>
<th>SrWO$_4$</th>
<th>PbWO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B</td>
<td>B’</td>
<td>B</td>
<td>B’</td>
</tr>
<tr>
<td>Expt. (300 K)</td>
<td>52(5)</td>
<td>5(1)</td>
<td>74(7)</td>
<td>5.6(9)</td>
</tr>
<tr>
<td>Calc. (0 K)</td>
<td>55.8(8)</td>
<td>4.4(1)</td>
<td>80.1(5)</td>
<td>4.5(1)</td>
</tr>
<tr>
<td>Calc. (300 K)</td>
<td>46.8(4)</td>
<td>4.4</td>
<td>62.1(4)</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Earlier studies [23] surmise that large ratio of ionic radii (WO$_4$/A) accommodates increased stresses through larger and more varied displacement from their average
positions. This results in the loss of translational periodicity at high-pressure. Larger the WO₄/A ratio, lower the pressure threshold for pressure induced amorphization. This ratio decreases as per the following order: WO₄/Ca>WO₄/Sr>WO₄/Pb>WO₄/Ba. As per this notion, CaWO₄ should have the lowest value of pressure for amorphization to occur, followed by SrWO₄, PbWO₄ and BaWO₄ respectively. Our computed results are in full agreement with this expected trend.

**Fig. 4.8** Pair correlations between various atomic pairs as obtained from molecular dynamics simulations.
4.3 Inelastic Neutron Scattering, Lattice Dynamics and High Pressure Stability of LuVO₄

4.3.1 Introduction

Rare-earth vanadates RVO₄, phosphates and arsenates whose crystal structure is the tetragonal zircon-type [29] with space group $I4_1/amd$ have received much attention in modern laser physics and non-linear optics. When doped with suitable ions, these vanadates serve as excellent host material for laser application. In this each R ion is coordinated by 8 oxygen atoms, forming dodecahedral cages and the V ion is coordinated by 4 oxygen atoms, forming VO₄ tetrahedra. The unit cell consists of four formula units. These materials have been employed as model systems for the investigation of polymorphism among ABO₄ type compounds.

LuVO₄ has been found to transform to a pressure quenchable scheelite phase ($I4_1/a$) with approximately 10% reduction in volume at around 8 GPa [37]. This reduction is due to a more efficient polyhedral packing when the ambient phase is pressurized well above the equilibrium transition pressure. This section deals with studies on the lattice dynamics of this vanadate in the quasiharmonic approximation. The presence of several atoms in the unit cell (in this case the primitive cell contains two formula units $i.e.$, 12 atoms) justifies the use of an atomistic approach to study the vibrational and thermodynamic properties. The inelastic neutron scattering studies have been carried out on a polycrystalline sample to obtain the phonon density of states in the entire Brillouin zone.
4.3.2 Experiment and theoretical calculations

The inelastic neutron scattering studies on a polycrystalline sample of LuVO$_4$ was carried out using the High Resolution Medium Energy Chopper Spectrometer (HRMECS) at the intense pulsed neutron source of Argonne National laboratory (ANL), USA. It is a time of flight spectrometer equipped with a large detector bank covering a wide-range (-10$^0$ to 140$^0$) of scattering angles. The measurements were performed in collaboration with Dr. C. -K. Loong, ANL, USA.

A shell model potential (as described in equation (1.25) chapter 1) consisting of Coulombic terms and short range terms has been used for the calculations of the lattice dynamics of these vanadates. A covalent term (equation (1.26)) is used to explain the stretching frequencies of the VO$_4$ molecular unit. The radii and charge parameters for Lu, V and O atoms are $r_{\text{Lu}} = 2.161$ Å, $r_{\text{V}} = 0.953$ Å, $r_{\text{O}} = 1.855$ Å and $Z_{\text{Lu}} = 2.971e$, $Z_{\text{V}} = 3.013e$ respectively. The van der Waals interaction between O-O pairs is 22 eVÅ$^6$. The parameters of the WO$_4$ stretching potential described in equation (1.26), are $D = 1.96$ eV, $r_o = 1.7$ Å and $n = 26.2$ Å$^{-1}$. The parameters of the potentials satisfy the conditions of static and dynamic equilibrium. The polarizibility of the oxygen atoms has been introduced in the framework of shell model.

4.3.3 RESULTS AND DISCUSSION

4.3.3.1 Phonon density of states

The zircon structure adopted by the compound at ambient condition with two formula units per primitive cell, supports 36 zone-center phonon modes. Group theoretical considerations lead to the following vibrational representation at the $\Gamma$ point.
(zone-centre, \( \Gamma = 2A_{1g} + 2B_{1u} + 4B_{1g} + 4A_{1u} + A_{2g} + B_{2u} + B_{2g} + A_{2u} + 5E_{g} + 5E_{u} \)), A and B modes are nondegenerate, whereas the E modes are doubly degenerate. The modes \( A_{1g}, B_{1g}, B_{2g} \) and \( E_{g} \) are Raman active, while \( A_{u} \) and \( E_{u} \) are infrared active.

**Fig. 4.9** Comparison of experimentally reported data of optically active modes with calculated values. Open and closed symbols correspond to the calculated and experimental [38,39] results.

The calculated phonon frequencies with mode assignments are compared with the available Raman and infrared data [48,49] in Fig. 4.9. The comparison between the experimental and calculated density of states is shown in Fig. 4.10. The peak around 40 meV in the experimental data has been shifted to higher energies in our calculations while all other phonon peaks agree well.
Fig 4.10 Inelastic neutron scattering data in comparison with the calculated density of states.

4.3.3.2 High Pressure Phase Transition in LuVO₄

Gibb’s free energy of a given crystalline phase includes contributions from enthalpy and vibrational entropy at a given temperature and pressure. In our calculations, along with enthalpy changes, we have also taken into consideration vibrational entropy contribution by calculating the phonon density of states in the entire Brillouin zone. During phase transitions, the stability of a crystalline phase is determined by the minimum free energy of the competing phases.

The Gibbs free energy of the two phases has been compared (Fig. 4.11) at different pressures at 300 K. The results indicate that transition to scheelite phase occurs around 8 GPa, which is in excellent agreement with the reported transition pressure of 7.9 GPa.
The computed drop in volume is around 8% while experimental studies [37] indicate a drop of about 11%. In this displacive phase transition, author finds that the change in free energy due to volume is dominant in comparison to changes due to vibrational entropy.

4.4 CONCLUSIONS

A combination of potential model and neutron inelastic scattering has been used to study the vibrational properties in the four tungstates. Molecular dynamics simulations have been employed to understand their evolution with increasing pressure. Inelastic neutron scattering experiments have been carried out to phonon dispersion in single crystal of SrWO$_4$, and to measure the phonon density of states in all the four compounds. The calculations are in good agreement with experimentally measured data. With increasing pressure, tungstates undergo transition from scheelite to fergusonite phase, it is a second order displacive transition with no apparent volume discontinuity. This transition is not evident in our calculations. But with further increase in pressure, these
tungstates show pressure induced loss of translational ordering, which is seen by the sudden drop in volume in all the four tungstates studied, using molecular dynamics simulations. On amorphization WO$_4$ tetrahedra deform, the coordination of W atoms increases from 4. The AO$_8$ polyhedra show considerable distortion. The calculated amorphization pressures for BaWO$_4$ and CaWO$_4$ are in agreement with the available experimental data. The molecular dynamics simulations facilitates in predicting the amorphization in SrWO$_4$ and PbWO$_4$ at high pressures.

Further we have also studied lattice dynamics and high pressure studies on LuVO$_4$. Our model calculations are able to explain the obtained density of states very well. Our calculations reproduce the pressure-driven phase transition from zircon to scheelite in LuVO$_4$ with excellent accuracy. This study indicates that similar investigations on rare earth vanadates and arsenates would be rewarding, particularly in establishing the systematics of crystal-chemical aspects of the pressure-induced transition in zircon-type structured compounds.
References


[34] A. Sjolander, Arkiv fur Fysik 14, 315 (1958).


