

**Inelastic neutron scattering and theoretical studies on strontium tungstate, SrWO<sub>4</sub>**

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We report inelastic neutron scattering measurements, lattice dynamics calculations, and molecular dynamics simulations on SrWO<sub>4</sub>. At ambient conditions, this compound crystallizes in a body-centered tetragonal unit cell (space group  $I4_1/a$ ) popularly known as the scheelite structure. We have developed transferable interatomic potentials to study the lattice dynamics of this class of tungstate compounds. The model parameters have been fitted with respect to the experimentally available Raman and infrared frequencies, elastic constants, and the equilibrium unit cell parameters. Phonon dispersion curves of acoustic branches along [100] symmetry direction have been measured using the Triple Axis Spectrometer at Dhruva reactor, India. The measured dispersion is in very good agreement with our calculated results. Phonon density of states has been measured for a polycrystalline sample using IN4C spectrometer at Institut Laue-Langevin, Grenoble. The measured phonon density of states is in excellent agreement with the theoretical calculations, thus validating the interatomic potential developed. Molecular dynamics simulations have been carried out to study the pressure-driven transformation of the scheelite phase of SrWO<sub>4</sub>. We have studied the behavior of the tungstate up to 100 GPa. Our calculated equation of state is in very good agreement with the reported experimental and first principles calculations. In our calculations, there appears to be a second transformation at around 45 GPa with a volume drop of about 8%, which hitherto had not been observed experimentally in this compound.

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**I. INTRODUCTION**

Alkalineearth tungstates MWO<sub>4</sub> (M = Ba, Ca, Sr, Pb) are important for their scientific and technological applications. These compounds find their use in solid-state scintillators and optoelectronic devices. Tungstate SrWO<sub>4</sub> finds use in solid-state laser applications and in geology, apart from various other technological applications. These compounds exhibit a rich phase diagram. Recently, crystal structures of these compounds have been studied at high pressures by means of x-ray diffraction and spectroscopic methods [1–6]. Extensive Raman and infrared scattering [4, 7] techniques have been used to study the zone centre phonon modes. *Ab initio* calculations [2, 4] of the zone centre phonon modes have

been reported for BaWO<sub>4</sub> and PbWO<sub>4</sub>.

Tungstates MWO<sub>4</sub> (M = Ca, Ba, Pb, Sr) crystallize in the scheelite structure (I4<sub>1</sub>/a, Z = 4). The primitive unit cell has two MWO<sub>4</sub> units. Each W is surrounded by four equivalent oxygen atoms in a tetrahedral symmetry. Each M site is surrounded by eight oxygen atoms in an octahedral symmetry. The compounds undergo a scheelite to fergusonite (space group I2/a) phase transition at a high pressure. The study of the phonon properties of these compounds is important in order to improve the knowledge and control of their thermal and optical properties as well as for understanding their thermodynamic behavior under high pressure and temperature conditions. Using interatomic potential models, several studies [8] have been carried out previously, in the ambient pressure as well as high pressure phases. Experimental phonon density of states measurements provide a reliable means to validate the accuracy of the theoretical model developed. Measurement of the phonon dispersion relation and phonon density of states using the inelastic neutron scattering technique combined with theoretical interatomic potential calculations form an ideal combination for a microscopic study of the vibrational and thermodynamic properties. The developed interatomic potential may be used for classical molecular dynamics simulations to gain microscopic insights into a variety of phenomena, such as pressure-induced phase transitions *etc.*

In this paper, we report the study of strontium tungstate using experimental inelastic neutron scattering technique. The experimental findings have been compared with the results of theoretical lattice dynamics model developed [9]. The interatomic potential thus developed has further been used in classical molecular dynamics technique to understand the behavior of room-temperature ambient-pressure scheelite phase of SrWO<sub>4</sub> under increasing hydrostatic pressure.

## II. THEORY

Lattice dynamics calculations of the equation of state and vibrational properties have been carried out by an atomistic approach [10] involving semi-empirical interatomic potentials. The interatomic potential consists of Coulombic and short-ranged BornMayer-type interactions along with a van der Waals interaction term (only between the oxygen atoms). The parameters used in this study have been adjusted to satisfy the conditions of static and dynamical equilibrium. These calculations have been carried out using the current version of the software DISPR [11] developed at Trombay. The form of the interatomic potential is as follows:

$$V(r_{ij}) = \frac{e^2}{4\pi\epsilon_0} \frac{Z(k)Z(k')}{r_{ij}} + a \exp \left[ \frac{-br_{ij}}{R(k) + R(k')} \right] - \frac{C}{r_{ij}^6}, \quad (1)$$

where,  $r_{ij}$  is the separation between the atoms of a type  $k$  and  $k'$  and  $R(k)$  and  $Z(K)$  are, respectively, the effective radius and charge of the atom of type  $k$ . The parameter  $a = 1822$  eV and  $b = 12.364$  have been treated as constants; this choice has been successfully used in earlier phonon studies of several complex solids [8, 12]. The van der Waals interaction terms

( $C = 80 \text{ eV}(\text{\AA})^6$ ) have been introduced only between the oxygen atoms. The polarizability of the oxygen atoms has been introduced in the framework of the shell model with the shell charge  $Y(\text{O})$  and shell-core force constant  $K(\text{O})$ . A covalent potential of the following form is also included between W and O to characterize the W-O stretching frequencies.

$$V(r) = -D \exp \left[ -n(r - r_0)^2 / (2r) \right], \quad (2)$$

where  $n$ ,  $D$ , and  $r_0$  are empirical parameters of the potential.

The equilibrium crystal structure has been calculated by minimizing the Gibbs free energy with respect to the structural parameters. Corresponding to 12 atoms in the primitive cell, a total of 36 phonon modes occur at every wave vector. At the zone center, the phonon modes are classified into the following irreducible representations:

$$\Gamma : 3\mathbf{A}_g + 5\mathbf{B}_g + 10\mathbf{E}_g + 5\mathbf{A}_u + 3\mathbf{B}_u + 10\mathbf{E}_u.$$

The modes  $\mathbf{A}_g$ ,  $\mathbf{B}_g$ , and  $\mathbf{E}_g$  are Raman active;  $\mathbf{A}_u$  and  $\mathbf{E}_u$  are infrared active; and  $\mathbf{B}_u$  is optically inactive. These modes have been experimentally [4, 7] studied, and they compare very well with our calculated values. The group theoretical distribution of phonons along high symmetry [001] and [100] directions is as follows:

$$\Lambda(001) : 8\Lambda_1 + 8\Lambda_2 + 10\Lambda_3 \quad (\Lambda_3 \text{ is doubly degenerate}),$$

$$\Sigma(100) : 18\Sigma_1 + 18\Sigma_2.$$

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. The shell model developed was used to compute the one-phonon neutron cross-section for scattering from a single crystal for each phonon mode. The computed cross-section table was used to identify regions in reciprocal space with maximum probability (and minimum ambiguity) in assignment of the measured phonon frequencies to various group theoretical representations.

Molecular dynamics simulations have been used to study the response of the tungstate to increasing pressure. A supercell of dimension  $4\mathbf{a} \times 4\mathbf{b} \times 2\mathbf{c}$  was used to study the evolution of the room temperature ambient pressure scheelite phase ( $I4_1/a$ ) with increasing pressures up to 100 GPa. At each pressure, the super cell evolution was studied up to 20 ps with a time step of 1fs.

### III. EXPERIMENT

The measurements of the phonon dispersion relations in strontium tungstate were carried out on the Triple-Axis-Spectrometer (TAS) at ambient pressure and room temperature at the Dhruva reactor, Trombay. This TAS uses a Cu(111) monochromator and pyrolytic graphite (PG) (0002) analyser. A PG filter was used to remove the second-order

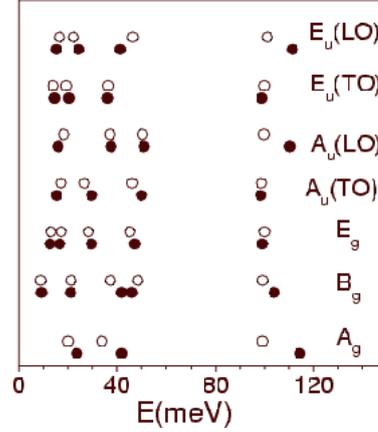


FIG. 1: Comparison between the experimental phonon Raman and IR frequencies (filled circles) [3, 7] with the computed values (open circles).

contributions. A single crystal of strontium tungstate was used to measure the phonon branches. The measurements were undertaken using the constant Q mode with fixed  $E_f$ , the scattered neutron energy fixed at 14.8 meV. The phonon measurements were made in the (100) direction and the acoustic branches between 3–12 meV were measured using incident neutron energies varying from 15–32 meV.

The phonon density of states over a broad energy range up to 130 meV have been determined by neutron scattering experiments on a powder sample under ambient conditions using the IN4C time-of-flight spectrometer at Institut Laue Langevin, (ILL), Grenoble. A polycrystalline sample of about 50 gms was used for the measurement.

#### IV. DISCUSSION

We have developed a model for  $\text{SrWO}_4$  based on our knowledge about related compounds and on some optical data of  $\text{SrWO}_4$ . Figure 1 shows the comparison of the zone centre calculated phonons with the reported Raman and IR values [3, 7]. In our calculation, the highest  $A_g$  and the highest LO modes of the  $A_u$  and  $E_u$  representation have been underestimated. The average deviation of our calculated values with respect to those reported is about 5%.

The partial densities of states obtained through model calculations have been shown in Fig. 2. The strontium atoms contribute only in the lower energy range below 40 meV, tungsten contributes mainly in the lower energy range along with a small contribution above 90 meV, which corresponds to the high energy W-O bond stretching. Oxygen has a contribution throughout the energy spectrum from 0–40 meV and above 90 meV. There is a band gap between 50 meV and 90 meV.

The computed partial density of states have been used for obtaining neutron-weighted

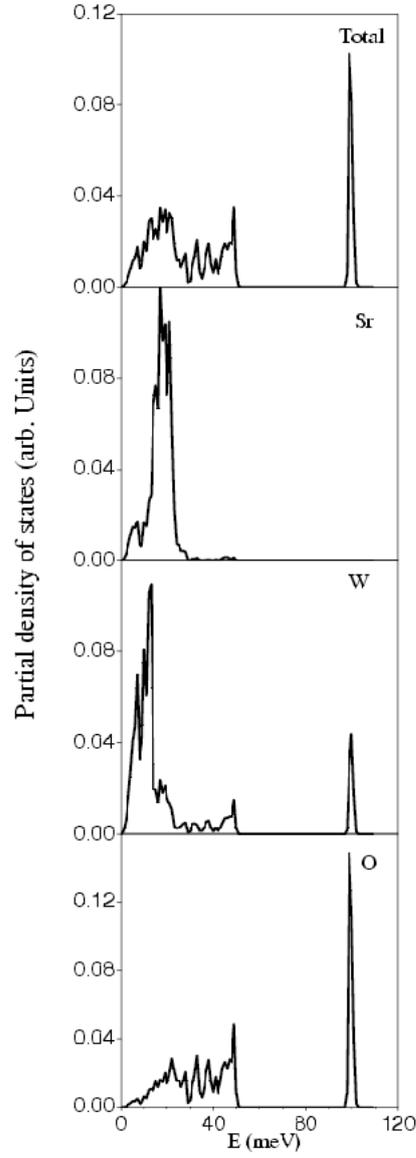


FIG. 2: The calculated total and partial densities of the constituent atoms in  $\text{SrWO}_4$ .

phonon density of states  $g^{(n)}(E)$ ,

$$g^{(n)}(E) = B \sum_k \frac{4\pi b_k^2}{M_k} g_k(E). \quad (3)$$

Here,  $B$  is the normalization constant while  $b_k$ ,  $M_k$ , and  $g_k(E)$  are the neutron scattering length, mass, and partial density of states of the  $k^{\text{th}}$  type of atom. We calculate the

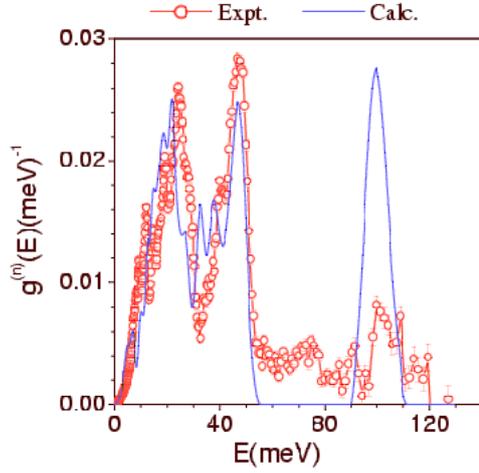


FIG. 3: Comparison between experimentally measured phonon density of states (red full line with open circles) and the calculated spectrum.

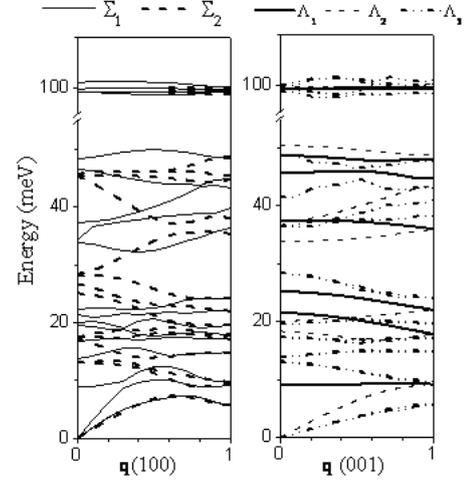


FIG. 4: Calculated phonon dispersion along the [100] and [001] directions in SrWO<sub>4</sub>.

one phonon density of states  $g(E)$  in the following way:

$$g(E) = \sum_k g_k(E). \quad (4)$$

The multiphonon scattering estimated using the Sjolander formalism [13] has been subtracted from the experimental data. Figure 3 gives the comparison between the experimental data and the calculated phonon spectrum. The agreement between the measured and the calculated phonon spectrum is very good, thus validating the reliability of the model parameters obtained.

The calculated phonon dispersion along high symmetry directions is given in Fig. 4. The experimental studies of the phonon dispersion of the acoustic branches along the [100] direction are given in Fig. 5. There is a good agreement between the measured phonon dispersion and our calculated curves.

Alkaline-earth scheelites exhibit an interesting phase diagram [1–6] with respect to increasing pressure. SrWO<sub>4</sub> has been found to undergo a displacive phase transition from ambient scheelite phase to a monoclinic fergusonite phase at around 10 GPa. This new monoclinic phase is a slightly distorted version of the original tetragonal phase. The lattice parameter  $a$  ( $a = b$ , in the I4<sub>1/a</sub> phase) changes [5] from  $a = 5.4136 \text{ \AA}$  and  $c = 11.942 \text{ \AA}$  to  $a = 5.263 \text{ \AA}$ ,  $c = 5.231 \text{ \AA}$ , and  $b = 11.182 \text{ \AA}$ , with the monoclinic angle  $\beta = 90.3$  at 10.1 GPa. There are no other changes in the phase beyond this pressure up to 21 GPa studied experimentally [5]. Our molecular dynamics studies exhibit a similar behavior of the P-V curve as reported experimentally. The calculated equation of state of SrWO<sub>4</sub> from  $P = 0$  to 100 GPa is given in Fig. 6. There seems to be a very miniscule change in the volume of the compound going from scheelite to fergusonite phase, as can be observed in the Fig. 6.

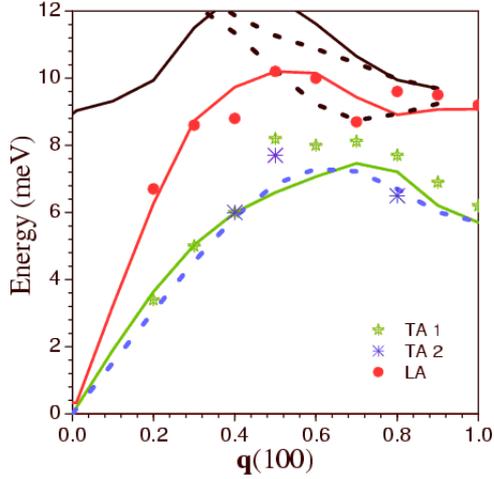


FIG. 5: Measured phonon dispersion of the acoustic phonon branches along the [100] direction. TA1 and TA2 correspond to transverse acoustic phonon branches while LA corresponds to the longitudinal acoustic phonon branch along the given symmetry direction.

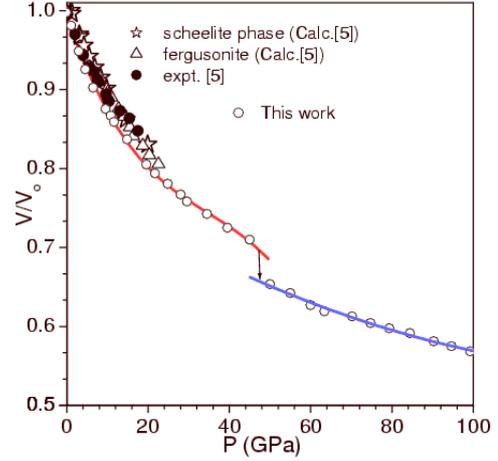


FIG. 6: Pressure dependence of the fractional volume ( $V_0$  being the volume of the ambient  $P = 0$  GPa scheelite phase) as reported by P. Rodríguez-Hernández *et al.* [5] and as obtained in our molecular dynamics simulations. The red and blue lines are polynomial fits to the calculated data below and above the transition indicated by the arrow.

In our calculations, there appears to be a further phase change into a new phase at around 45 GPa with a volume drop of  $\sim 8\%$ . This appears to be consistent with recent reported data [14, 15] on  $\text{ZnWO}_4$  and  $\text{CdWO}_4$ . Lopez-Solano *et al.* [3] have proposed theoretically a dense orthorhombic phase at around 30 GPa in  $\text{SrWO}_4$ , whereas we seem to observe a change in the slope of the P-V curve between 45 and 50 GPa. Further studies to exactly determine this first order phase change at 45 GPa is in progress.

## V. CONCLUSIONS

The lattice dynamical model for  $\text{SrWO}_4$  has been computed, and inelastic measurements have been carried out on both a single crystal and a polycrystalline sample of  $\text{SrWO}_4$ . The experimentally measured phonon density of states is in very good agreement with our theoretically calculated density of states. Single crystal neutron scattering measurements of the low-energy acoustic phonon branches along [100] are reported. The measured values of the phonons are in good agreement with the values that were theoretically predicted by our shell model. The calculated neutron cross-sections have played a vital role in the planning, execution, and analysis of the experimental results. Our molecular dynamics simulations seem to indicate a new post-fergusonite phase at a high pressure of 45 GPa not

studied experimentally so far. The interatomic potential developed can be used to study similar compounds and may be used to give a microscopic picture of their vibrational and thermodynamic properties under varying conditions.

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