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Lattice dynamics of strontium tungstate

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Abstract. We report here measurements of the phonon density of states and the lattice dynamics calculations of strontium tungstate ($SrWO_4$). At ambient conditions this compound crystallizes to a body-centred tetragonal unit cell (space group $I4_1/a$) called scheelite structure. We have developed transferable interatomic potentials to study the lattice dynamics of this class of compounds. The model parameters have been fitted with respect to the experimentally available Raman and infra-red frequencies and the equilibrium unit cell parameters. Inelastic neutron scattering measurements have been carried out in the triple-axis spectrometer at Dhruva reactor. The measured phonon density of states is in good agreement with the theoretical calculations, thus validating the interatomic potential developed.

Keywords. Inelastic neutron scattering; lattice dynamics; phonons.

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1. Introduction

Alkaline-earth tungstates, MWO_4 (M = Ba, Ca, Sr, Pb) are important because of their scientific and technological applications. These compounds find their use [1] in solid-state scintillators and optoelectronic devices. Tungstate divalent scheelite compound strontium tungstate ($SrWO_4$) finds use in solid state laser applications and various other technological applications. These compounds exhibit a rich phase diagram. Recently, crystal structures of these compounds have been studied [2–4] at high pressures by means of X-ray diffraction and spectroscopic methods. The compounds undergo a scheelite to fergusonite (space group $P2_1/n$) phase transition at high pressure and temperature. Extensive Raman and infra-red scattering techniques [5] have been used to study the zone centre phonon modes. The acoustic phonons have been measured using a single crystal of $CaWO_4$ [6]. *Ab initio* calculations [3,4] of the zone centre phonon modes have been reported for $BaWO_4$ and $PbWO_4$.

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

Table 1. Calculated elastic constants and bulk modulus of $SrWO_4$ in GPa units.

C_{11}	115
C_{33}	98
C_{44}	26
C_{66}	41
C_{12}	77
C_{13}	55
Bulk Modulus	78

well as for understanding their thermodynamic behaviour under high pressure and temperature conditions. Earlier, we have used extensive measurements [7,8] of the phonon dispersion relation in $ZrSiO_4$ up to 80 meV and data for $LuPO_4$ from the literature [9] for development of transferable interatomic potential models for ASiO$_4$ (A = Zr, Hf, Th, U) and (RPO$_4$, R = rare earth atom) and (RVO$_4$, R=rare earth atom). Using these models we could calculate [7,10–12] high pressure and temperature phase diagrams as well as thermodynamic properties for ASiO$_4$, RPO$_4$ and RVO$_4$ in the ambient pressure as well as high pressure phases. Now in order to validate the lattice dynamical model developed for $SrWO_4$ we have measured phonon density of states using a polycrystalline powder of $SrWO_4$.

2. Experimental and lattice dynamical calculations

The inelastic neutron scattering experiment was carried out using the triple-axis spectrometer at Dhruva reactor. A polycrystalline powder sample of 50 g was placed inside a sealed aluminum container. Cu(1 1 1) has been used as the monochromator while Be-filter has been used as the analyzer. The measurements were carried out in the neutron energy loss mode.

A shell model potential consisting of Coulombic terms and short range terms has been used. A covalent term is used to explain the stretching frequencies of the WO_4 molecular unit. The parameters of the potentials satisfy the conditions of static and dynamic equilibrium. The polarizability of the oxygen atoms has been introduced in the framework of the shell model [13]. The calculations have been carried out using the current version of DISPR [14]. The model has been used to calculate the partial density of states, elastic constants, bulk modulus and variation of specific heat with temperature. The procedure for the calculations of thermodynamic properties is given in our previous publications [15,16].

3. Results and discussion

We have developed a model for $SrWO_4$ based on our knowledge about related compounds and on some optical data [5] of $SrWO_4$. Figure 1 shows the comparison of the zone centre calculated phonons with that of the reported Raman and IR values. The average deviation between calculated and experimental long wavelength

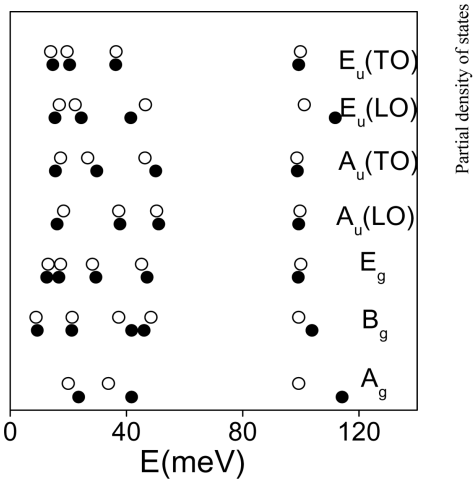

Figure 1. Comparison between experimental (filled circles) [3,5] (Raman and IR) data with computed (open circles) phonon frequencies.

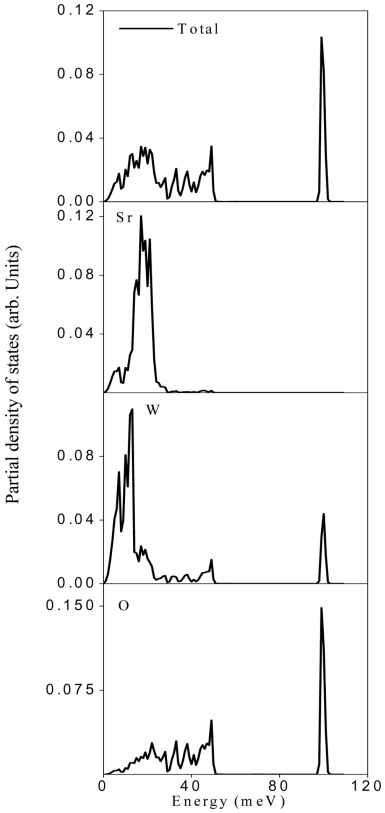

Figure 2. Partial phonon densities of Sr, W and O atoms in $SrWO_4$.

Raman and infra-red modes for $SrWO_4$ is 6.4%. Table 1 gives the calculated values of the elastic constants and the bulk modulus.

The partial densities of states obtained through model calculations are shown in figure 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 smaller contribution above 90 meV, and oxygen has a contribution throughout the energy spectrum from 0 to 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 phonon density of states $g^{(n)}(E)$ (figure 3) and total density of states $g(E)$ (figure 2) via

$$g^{(n)}(E) = B \sum_k \frac{4\pi b_k^2}{M_k} g_k(E). \tag{1}$$

Here, B is the normalization constant while b_k, M_k and $g_k(E)$ are the neutron

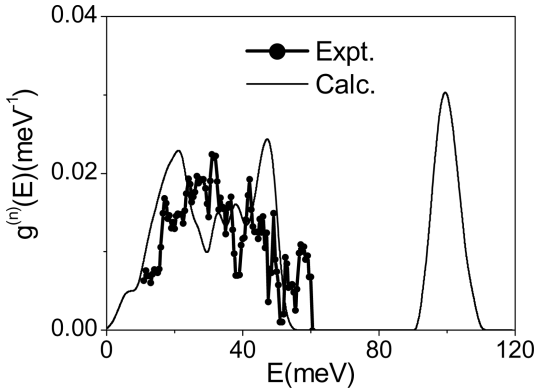

Figure 3. Inelastic neutron scattering spectra of the phonon density of states compared with model calculations. The band around 100 meV has not been measured.

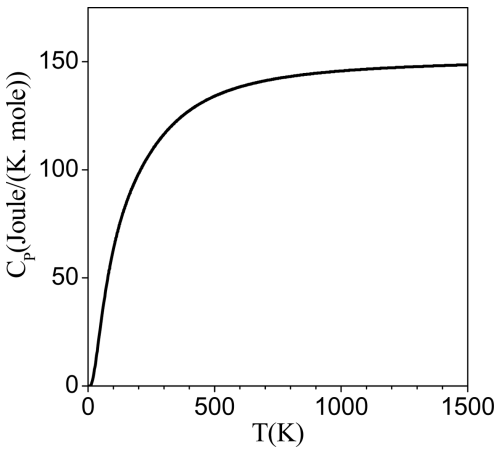

Figure 4. Calculated specific heat of $SrWO_4$ at constant pressure.

scattering length, mass and partial density of states of the kth type of atom. We calculate the one-phonon density of states $g(E)$ using the relation

$$g(E) = \sum_k g_k(E). \tag{2}$$

The multiphonon scattering estimated using the Sjolander formalism [17] has been subtracted from the experimental data. Figure 3 gives the comparison between experimental data and the calculated phonon spectrum. Owing to instrumental limitations, the highest band is not seen in the collected data. The agreement between the measured and the calculated phonon spectrum is satisfactory, thus validating the reliability of the model parameters obtained. The model has further been used to calculate the thermal properties (figure 4) of the compound such as the specific heat, thermal expansion, etc.

4. Conclusions

The lattice dynamical model for $SrWO_4$ has been validated by comparing the experimentally measured phonon density of states with theoretically calculated density of states. The interatomic potential formulated has been used to calculate the vibrational and thermodynamic properties. There are no reported experimental data on elastic constants in $SrWO_4$. The model may be further extended to study the high pressure and temperature thermodynamic properties of this class of compounds like $BaWO_4$, $PbWO_4$, $SnWO_4$, etc.

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