Lattice dynamics and high pressure phase stability of zircon structured compounds

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Abstract. Lattice dynamics calculations of the phonon spectra, thermodynamic properties and phase diagram of the zircon-structured compounds (body centered tetragonal, \textit{I4}/_{amd}) have been carried out. The compounds are known to transform to the scheelite phase (body centered tetragonal, \textit{I4}/_{a}) and monoclinic phase (\textit{P2}/_{1}/n) at high pressure and temperature. We have used our extensive measurements of the phonon dispersion relation and density of states, and data from the literature for development of transferable interatomic potential models for MSiO$_4$ (M=Zr, Hf, Th, U) and (RPO$_4$, R=Rare earth atom). Using these models we have calculated Gibbs free energies including the vibrational contributions as a function of pressure and temperature. The calculated phase diagrams are in fair agreement with the experimental observations.

1. Introduction
The zircon structure consists of four formula units of ABO$_4$ in a body-centered tetragonal unit cell (space group \textit{I4}/_{amd}). This structure is common to a variety of optical materials, including natural mineral zircon (ZrSiO$_4$) and rare earth orthophosphates (RPO$_4$, R=Rare earth atom), vanadates (RVO$_4$) and arsenates (RAsO$_4$). The high melting temperature, structural and chemical stability along with long term corrosion resistance of these compounds has prompted the suggestion of their use as a nuclear waste storage media [1]. These compounds in general have good optical quality, high hardness and large refractive index. Zircon structured compounds (ZrSiO$_4$, ThSiO$_4$, LuPO$_4$ etc.) are known to transform [2-4] to the scheelite phase (body centered tetragonal, \textit{I4}/_{a}) and monoclinic phase (\textit{P2}/_{1}/n) at high pressure and temperature. The \textit{c}/\textit{a} in scheelite phase is almost twice in comparison of the zircon phase. Scheelite phase of ZrSiO$_4$ and HfSiO$_4$ is known as one of the most incompressible compounds containing SiO$_4$ tetrahedra. We have carried out lattice dynamical calculations to study their high pressure and temperature phase diagram.

2. Lattice dynamical calculations
The force constants between various pairs of atoms can be computed using quantum-mechanical first principles techniques or by using semiempirical interatomic potentials. The interatomic potentials [5, 6] consist of Coulombic and the short ranged Born-Mayer-type interaction terms, van der Waals interactions, and (Si, P)-O bond-stretching potential. The polarizibility of the oxygen atoms is introduced in the framework of the shell model [7]. The empirical parameters are optimized to reproduce the minimum enthalpy structure close to that determined by the diffraction experiments at zero pressure. Further the potential parameters are chosen such that they satisfy the condition of dynamic equilibrium, and long wavelength phonon modes and elastic constants are close to their

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experimental values. The potential reproduces the structure of compounds quite satisfactorily. The calculations are performed using the latest version of the program DISPR [8] developed at Trombay.

3. Results and discussion

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Figure 1. (Left) The experimental phonon data along [100] direction with the lattice dynamical calculations (solid lines - shell model, dashed lines- \textit{ab initio}) for zircon [11]. The open rectangles, solid circles and open circles give the phonon peaks identified in the experiments at LLB (France) [11], ISIS (UK) [12] and Dhruva (India) [13], respectively. (Right) The comparison of the measured [14] (solid circles) and calculated (solid line – shell model) neutron-cross-section-weighted phonon density of states in LuPO$_4$. The multiphonon contribution has been subtracted from experimental data to obtain the experimental one-phonon spectrum.

The comparison between the calculated and experimental long wavelength Raman and infrared modes for ZrSiO$_4$ and LuPO$_4$ shows that average deviation of our shell model calculations from the experimental data is about 4%. The large LO-TO splitting for the infra red active $A_{2u}$ and $E_u$ modes has been correctly described by our calculation. The comparison between the calculated [11] and experimental data [11-13] of phonon dispersion relation for ZrSiO$_4$ along [100] direction is shown in figure 1. The calculations for ZrSiO$_4$ [11] have been done using ab-initio LDA as implemented in the code ABINIT [10] as well as a shell model, and both are in reasonably good agreement with the experimental data.

The experimental [14] neutron weighted one phonon density of states (figure 1) is obtained by subtracting the calculated multiphonon contribution from the experimental data. The multiphonon contribution is obtained using the Sjolander formalism [28]. The spectra consist of phonon bands centered at about 24, 40, 68, 83 and 125 meV. There is a band gap in the energy range of 90-115 meV. The calculated partial density of states shows that vibrations of oxygen and phosphate atoms span the entire 0-145 meV range. Above 115 meV the contributions are mainly due to P-O stretching modes.

We have also calculated phonon spectra in scheelite phase of LuPO$_4$. The total density of states in both zircon and scheelite phases is similar. However, the band gap (85-120 meV) of the zircon phase is shifted towards lower energy in the scheelite phase.
Several of the zircon structure compounds are known to transform to the scheelite phase ($I4_1/a$) at high pressure. LuPO$_4$ showed a phase transition [2] at 22 GPa at ambient temperature in Raman scattering experiments carried out at Trombay. The c/a ratio in scheelite phase is found almost twice in comparison with that of the zircon phase. Thorium silicate, ThSiO$_4$ has a high symmetry body centered tetragonal unit cell ($I4_1/amd$) at low temperature, whereas the high temperature form [3] of ThSiO$_4$ has monoclinic structure ($P2_1/n$). Tetragonal to monoclinic transition [3] is unusual since a less dense phase usually occurs at high temperature.

The computed phonon density of states g(E) is used to derive [15] Gibbs free energy. The phase diagram of a compound can be calculated by comparing the Gibbs free energies in various phases. In quasiharmonic approximation, Gibbs free energy of $n^{th}$ phase is given by

$$G = \Phi_n + PV_n - TS_n$$

where $\Phi_n$, $V_n$, and $S_n$ refer to the internal energy, lattice volume and the vibrational entropy of the $n^{th}$ phase. By minimizing the Gibbs free energy with respect to the structure variables (lattice parameters and atomic positions) while keeping the space group unchanged, the optimum crystal structure and volume at a fixed pressure and zero temperature can be obtained. We have also included the vibrational contributions in the phase diagram, by calculating the phonon frequencies in all the phases of MSiO$_4$ and RPO$_4$. A comparison of the free energy in the ambient and high pressure phase suggest that scheelite and monoclinic phases are the stable phases at high pressure for LuPO$_4$ and ThSiO$_4$ respectively, which is in good agreement (figure 2) with the experimental observations [2,3]. The free energy changes due to volume are important in zircon to scheelite phase transition, while vibrational energy and entropy plays an important role in zircon to monoclinic phase transition.

3. Conclusions
We have developed a lattice dynamical model for zircon structured compounds MSiO$_4$ and RPO$_4$ and validated it by our extensive measurements of the phonon density of states and phonon dispersion relation, and data available in the literature. Further, we employed the lattice dynamical model for calculations of various high pressure and temperature thermodynamic properties of MSiO$_4$ and RPO$_4$ in their zircon, scheelite and monoclinic phase. The lattice dynamical models are further used to calculate the free energies as a function of pressure and temperature in the zircon as well as the high-pressure scheelite (or monoclinic) phase. The calculated free energies reproduce the relative stability of the two phases across their observed phase transition pressure.
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