Inelastic neutron scattering and lattice dynamics of ZrO_2, Y_2O_3 and $ThSiO_4$

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Abstract. Zirconia (ZrO_2), yttria (Y_2O_3) and thorite ($ThSiO_4$) are ceramic materials used for a wide range of industrial applications. The dynamical properties of these materials are of interest as they exhibit numerous interesting phase transitions at high temperature and pressure. Using a combination of inelastic neutron scattering and theoretical lattice dynamics we have studied the phonon spectra and thermodynamic properties of these compounds. The experimental data validate the theoretical model, while the model enables microscopic interpretations of the observed data. The calculated thermodynamic properties are in good agreement with the experimental data.

1. Introduction

Zirconia (ZrO_2), yttria (Y_2O_3) and yttria-stabilized zirconia (YSZ) are highly useful [1–8] ceramic refractory materials that find a wide range of industrial applications. Zirconia is used in thermal barrier coatings, as optical coatings to absorb harmful ultraviolet radiation, paint additives and is an important nuclear material. Thorite ($ThSiO_4$) is a natural host for U and Th inclusions in the Earth's crust. These advanced oxide ceramics exhibit numerous interesting phase transitions [3,4] at high temperature and pressure. It is of interest to understand how these phase transitions manifest in the phonon spectra and thermodynamic properties.

The crystal structure of zirconia was studied using X-rays [1]. *Ab initio* [2–6] and lattice dynamical studies [7,8] have been carried out to study the phonon properties and phase stability in various phases of ZrO_2. Raman and infra-red scattering techniques [9–12] have been used to study the zone centre phonon modes. Yttria has been studied using X-ray [13], neutron diffraction [14] and Raman and infra-red spectroscopy [15]. *Ab-initio* calculations and molecular dynamics simulations of the structural and dynamical properties of yttria [16] and zirconia [3,17] have also been

reported. Accurate interatomic potentials of the end-members zirconia and yttria are required for multiscale modelling of complex YSZ composites used in fuel cells. Furthermore, development of accurate interatomic potentials for ZrO_2 and Y_2O_3 can help one to understand their complex thermodynamic properties and the phase transitions. The study of orthosilicates like thorite ($ThSiO_4$), zircon ($ZrSiO_4$) and hafnon ($HfSiO_4$) are particularly important [18], since these compounds are effective radiation-resistant materials suitable for fission reactor applications and for storage of nuclear waste.

In continuation of our extensively reported lattice dynamics studies of zircon structured materials [19–21], we have also carried out theoretical calculations of the phonon spectra, thermodynamic properties and phase diagram of $ThSiO_4$.

We have measured the phonon density of states of zirconia and have carried out theoretical calculations of the phonon spectra and thermodynamic properties of zirconia, yttria and $ThSiO_4$. The phonon density of states is the key quantity required to derive the thermodynamic properties. The experimental data validate the theoretical model, while the model enables microscopic interpretations of the observed data. The calculated thermodynamic properties are in good agreement with the experimental data. Molecular dynamics simulations using these interatomic potentials can be effectively used to study the mechanisms and high pressure–temperature phase transitions of these ceramics.

2. Experiment and calculations

Inelastic neutron scattering techniques have been employed to measure the phonon density of states of zirconia. These measurements were carried out using the triple-axis spectrometer at Trombay. About 100 g each of polycrystalline powder samples were used for the measurements. The incident neutron energy was varied by rotating the Cu(1 1 1) monochromator. The measurements were carried out in the energy loss mode. Final energy of the neutrons were analysed using a Be-filter. The phonon spectra in the range of 10–100 meV were measured with fixed scattering angles between 90° and 110°. The data from all the runs were averaged to obtain the final spectrum.

We have carried out theoretical lattice dynamics calculations using interatomic potentials having Coulombic and short-ranged terms. These calculations used the current version of the program DISPR [22]. The polarizability of the oxygen atoms has been introduced in the framework of shell model [23]. The procedure for the calculations of the phonon spectra and thermodynamic properties are as given in our previous publications [20,21]. The parameters of the potentials for zirconia, yttria and thorite are determined from the dynamic and static equilibrium conditions of the crystal.

3. Results and discussion

The experimental data on monoclinic ZrO_2 obtained for different fixed values of scattering angles have been averaged to obtain the neutron-weighted phonon
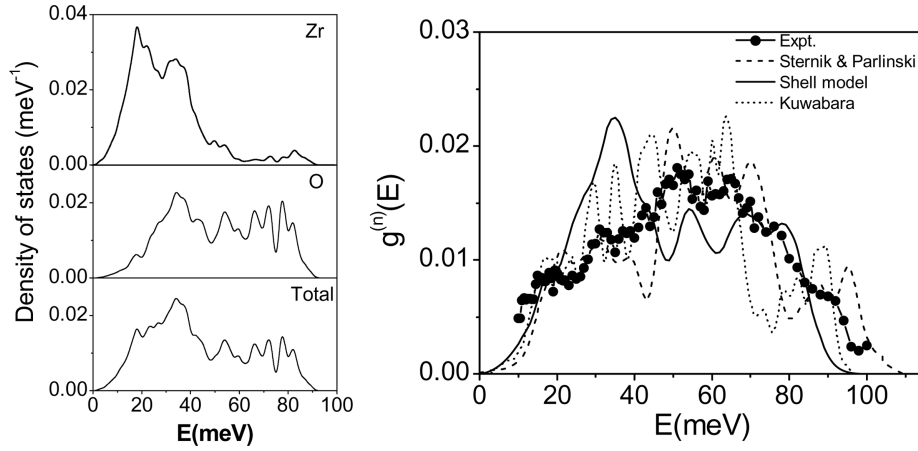
Figure 1. Left: Calculated partial density of states of various atoms in monoclinic ZrO_2 using the shell model. Right: The comparison between the measured ($T = 300$ K) and calculated ($T = 0$ K) neutron cross-section weighted phonon density of states in monoclinic ZrO_2. The calculated phonon spectra using the *ab-initio* partial density of states given by Sternik and Parlinski [2] and Kuwabara [3] are also shown. The calculated spectra have been broadened corresponding to the energy resolution of the experiment.

density of states $g^{(n)}(E)$ (figure 1). The multiphonon scattering estimated using the Sjolander formalism [24] has been subtracted from the experimental data. The estimated experimental one-phonon spectrum is shown in figure 1. The computed partial density of states (figure 1) reveals that the Zr atoms contribute in the 0–45 meV range, while the oxygen vibrations span the entire spectral range (0–100 meV). Our experimental data are in fair agreement with the neutron weighted phonon spectra $g^{(n)}(E)$ obtained from the shell model calculations (figure 1).

Sternik and Parlinski [2] and Kuwabara [3] have reported the first principle calculations of the total and partial density of states of ZrO_2. Using these partial density of states [2,3], we computed neutron weighted phonon density of states, which are compared with our measured data and shell model calculations in figure 1. Although the shell model is less accurate, it enables the calculation of various thermodynamic properties (figure 2) as a function of temperature and pressure.

The bulk modulus value for monoclinic ZrO_2 as obtained from fitting the Birch–Murnaghan equation to the calculated equation of state is 222 GPa, while the experimental value [17] is 212 ± 24 GPa. For cubic yttria the calculated bulk modulus value is 157 GPa. The calculated bulk modulus values in the zircon and monoclinic phases of $ThSiO_4$ are 190 GPa and 185 GPa, respectively. Their experimental values are presently not available for comparison.

Thermal expansion is related to the anharmonicity of lattice vibrations. The energy dependence of Gruneisen parameter is used in the calculations of thermal expansion. The quasiharmonic approximation [20,21] is valid when the effect of explicit anharmonicity is not very significant. Due to very large Debye
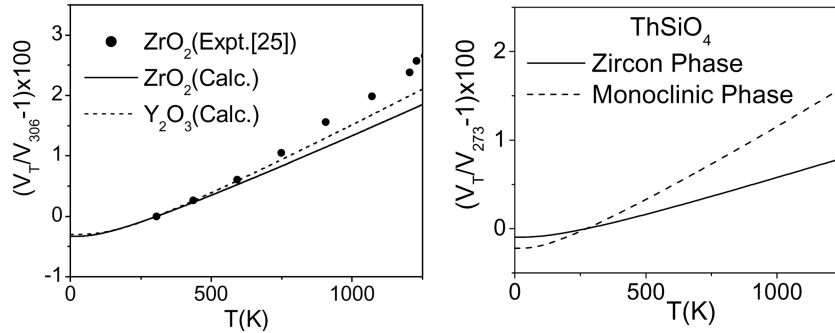
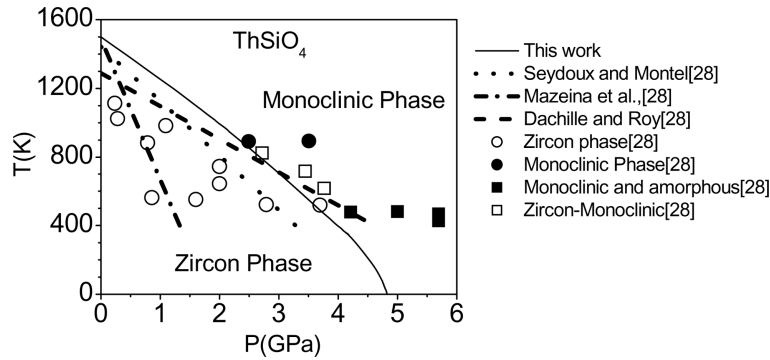**Figure 2.** The calculated (full and dashed lines) and experimental [25] thermal expansion behaviour.

Figure 3. The calculated phase diagram of ThSiO$_4$ as obtained from the free energy calculations. The experimental [28] observations of stable phases and phase boundary are also shown.

temperatures of the compounds we studied, the quasiharmonic approximation seems to be suitable up to fairly high temperatures. Figure 2 shows the calculated thermal expansion as also the experimental values for those available.

Thorium silicate (ThSiO$_4$) has a highly symmetric body centred tetragonal unit cell (I4$_1$/amd) at low temperature [26], whereas the high temperature form of ThSiO$_4$ has monoclinic structure (P2$_1$/n). The tetragonal to monoclinic transition is unusual [27,28] since a less dense phase usually occurs at high temperature. The phase diagram of a compound can be calculated by comparing the Gibbs free energies in various phases. A comparison of the free energy in the phases suggests that the monoclinic phase is the stable phase at high pressure and at high temperature for ThSiO$_4$, which is in good agreement (figure 3) with the experimental observations [28]. The free energy changes due to vibrational energy and entropy play an important role in the zircon to the monoclinic phase transition. The larger density of sates of low energy phonons in the monoclinic phase of ThSiO$_4$ is responsible for the larger entropy contribution.

4. Conclusion

We report inelastic neutron scattering measurements of the phonon density of states of zirconia. Using a combination of inelastic neutron scattering and theoretical lattice dynamics, we have studied the dynamical behaviour and thermodynamic properties of zirconia, yttria and ThSiO$_4$. The calculated thermodynamic properties are in good agreement with the experimental data. The lattice dynamical model for ThSiO$_4$ is further used to calculate the free energies as a function of pressure and temperature in the zircon as well as the high-pressure monoclinic phase. The calculated free energies reproduce the relative stability of the two phases across the observed phase transition pressure of ThSiO$_4$. Molecular dynamics simulations using these interatomic potentials can be effectively used to study the mechanisms and high pressure–temperature phase transitions of these compounds.

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