High Pressure Phase Transitions in Yttria, Y$_2$O$_3$

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We have carried out neutron inelastic scattering measurement of the phonon density of states and lattice dynamic calculations for Y$_2$O$_3$ using ab-initio density functional perturbation theory and interatomic potential model. The calculations are found to be in good agreement with experimental data, indicating that the potential model can be used for the calculation of phase diagram of Y$_2$O$_3$. The model is then used for free energy calculation to understand the stability of various phases as a function of pressure and temperature.

1. Introduction

Yttria (Y$_2$O$_3$) is an industrially and technologically very useful ceramic material used to increase the ductility of aluminum oxide (alumina ceramics) and to stabilize the cubic and tetragonal phases of zirconia, which is particularly important in the design of solid oxide fuel cells. Dense polycrystalline form of yttria is used in nuclear applications. Raman spectroscopy measurements [1] on yttria single crystals reported two phase transitions, namely, cubic to monoclinic and monoclinic to hexagonal at 12 and 19 GPa respectively. Recent high pressure X-ray diffraction experiments [2] on cubic Y$_2$O$_3$ at room temperature showed coexistence of the cubic, monoclinic and hexagonal phases in a pressure range from 15 GPa to 25.6 GPa. Kinetics seems to play a major role in determining the sequence of phase transitions.

We have carried out extensive lattice dynamical studies to provide insight into the phase transition mechanism of yttria. The phonon spectrum has been calculated using the shell model as well as ab-initio approach. We have also performed inelastic neutron scattering investigations to derive the phonon density of states (PDOS) of Y$_2$O$_3$ at ambient pressure and temperature. The shell model calculations results are in good agreement with the inelastic neutron data and ab-initio calculations. This allowed testing of our model, which is used to explore the high pressure and high temperature regime of the phase diagram. The model has been used for calculation of free energy in various phases of Y$_2$O$_3$. Our approach allows us to calculate the pressure dependence of the vibrational energy contribution to the Gibbs free energy, which is computationally expensive to calculate using ab-initio approach as cubic and monoclinic phase of Y$_2$O$_3$ has 40 and 30 atoms/primitive cell. The details of work have been published elsewhere [3].
2. Experiment

The polycrystalline sample in the cubic phase of Y$_2$O$_3$ was characterized using X-ray diffraction. The analysis of powder diffraction data indicated that sample is in single phase. The inelastic neutron scattering experiments were performed using the thermal time-of-flight neutron spectrometer IN4 at the Institute Laue Langevin (ILL) located in Grenoble (France). A quantity of 25 grams of polycrystalline Y$_2$O$_3$ sample was placed inside a thin aluminum sample holder. The incident neutron wavelength of 2.4 Å (14.2 meV) was chosen which allowed the spectra to be obtained in the neutron energy gain mode at 300 K. We used a Fermi chopper speed of 28000 RPM to allow for a time focusing condition in the inelastic regime (Inelastic time focusing). The detector bank of IN4 covers scattering angles up to 120°. After usual correction, the spectra at all detector angles were summed up to increase the statistics and to average out the coherent effect which is necessary to allow for a correct estimation of the phonon density of states (the so called “incoherent approximation”).

3. Computational Details

We have performed calculations using potential model and first principles. The pseudopotential generated by PBE exchange correlation functional [4] under generalized gradient approximation (PBE-GGA) has been used for ab-initio calculations in cubic phase of Y$_2$O$_3$. The calculations have been carried out using plane wave basis sets and Quantum Espresso software package [5]. We have chosen 4×4×4 k mesh for self-consistent field calculations with energy cutoff of 45 Rydberg, which is found to be sufficient for convergence of the order of meV. The k point mesh has been generated using Monkhorst-pack method [6] Dynamical matrices were calculated on a 3×3×3 mesh in the irreducible Brillouin zone.

The shell model is based on a transferable potential which consists of long-range Coulombic interaction, short range Born-Mayer type repulsive terms, and weakly attractive van der Waals terms. The form of the interatomic potential used in our model is given by the following expression:

\[
V(r) = \frac{e^2}{4\pi\varepsilon_0} \frac{Z(k)Z(k')}{r} + a \exp\left(-\frac{br}{R(k)+R(k')}\right) - \frac{C}{r^6}
\]

Where, \(a=1822\text{eV}\) and \(b=12.364\) are empirical constants. We have successfully used [25, 26] this set of parameters in the lattice dynamical calculations of several complex solids. The term \(C_0 = 100\ eVÅ^6\) accounts for the vander Waals interaction between O-O pairs. The effective charge \(Z(k)\) and radii \(R(k)\) parameters used in our calculations are \(Z(Y)= 2.4\ , \ Z(O)=-1.6\ , \ R(Y)= 1.931Å\) and \(R(O)= 1.89 Å\). The polarizability of the oxygen atoms is introduced in the framework of the shell model [27, 28]. The shell charge and shell core force constants for oxygen atoms are \(-3.75\) and \(170\ eV/Å^2\) respectively. The calculations are carried out using the software DISPR [7] developed at Trombay.

4. Results and Discussions

4.1 Phonon density of states

The comparison between the experimental and calculated neutron-weighted phonon density of states of yttria in the cubic phase using the potential model as well as ab-initio approach is shown in figure 1a. The experimental spectrum can be divided into two parts: the low frequency part (below 40 meV) consists of a series of weak features (14, 17 and 20 meV) superimposed to a general curve having a maximum at 20 meV. The high frequency part features intense contributions at 45 meV (a multi-component peak), 60 meV and 72 meV. No modes have been observed for frequencies higher than 80 meV. The general characteristics of the experimental features are well reproduced by the calculations. Both the calculations agree very well with the experimental data. In particular, the
calculations reproduce very well the low frequency part of the spectrum where the modes involving mainly Y vibrations dominate the dynamics, as indicated by the partial density of states (see Fig. 1b). The comparison of calculated partial density of states (Fig. 1b) of various atoms in cubic $Y_2O_3$ from both the potential as well as ab-initio calculations indicates slight difference in the phonon spectra for oxygen atoms above 40 meV.

![Figure 1](image1.png)

Figure 1 (a) The comparison of the calculated and experimental neutron weighted phonon density of states for cubic phase of yttria at ambient pressure [3]. The ab-initio as well as potential model calculations in the cubic phase are carried out at 0 K, while the measurements were performed at 300 K. (b) The calculated partial densities of states in various phases of $Y_2O_3$. The calculations in the cubic phase at 0 GPa are carried out using both the ab-initio and potential model.

4.2 Free energy and phase diagram

The calculated phonon spectra from the model as well as ab-initio calculations agree very well with the experimental data, indicating that potential model can be used to obtain the phase diagram of yttria. The Gibbs free energy was calculated using the model potential in the various phases of $Y_2O_3$. The Gibbs free energy of the $n^{th}$ phase is given by

$$G_n = \phi_n + PV_n - TS_n$$

Where, $\phi_n$, $V_n$, and $S_n$ respectively relate to internal energy, lattice volume and vibrational entropy of the $n^{th}$ phase. The Gibbs free energy of the various phases of $Y_2O_3$ are compared at different pressures for a fixed temperature, which allows deriving the phase diagram presented in figure 2(a). We find that above 15 GPa at 300 K the monoclinic phase has lower free energy as compared to the cubic phase, and the phonon modes are stable. The calculations therefore predict the transition from cubic to monoclinic phase at this critical pressure, while experimental data [1] report this transition at 12 GPa at room temperature.

The difference between the free energies of the competing monoclinic and hexagonal phases of $Y_2O_3$ as a function of pressure (at 300 K) is reported in figure 3a. The calculations show that the transition from the monoclinic to the hexagonal phase at 48 GPa (Fig. 2(b)) is of first order in nature, as can be seen from the non zero slope of the free energy difference (Fig. 2(b)) between the two phases at the transition pressure. The experimental data [12] show that the hexagonal phase is stable at pressures above a pressure of 26 GPa. The Gibbs free energy calculation qualitatively reproduces the
phase diagram of yttria. This is satisfactorily since it is very difficult to reproduce free energy differences with requisite high accuracy for phase diagram calculation. It is also difficult task to identify equilibrium phases from experiments at high pressure due to large hysteresis. The transition pressure is also affected by the kinetics and also depends on the doping [8] of rare earth ions in Y2O3. Such effects are not accounted for in our investigations.

![Figure 2. (a) The calculated phase diagram obtained from free energy calculations [3]. The closed and open circles are the experimental data [1,2] for the cubic to monoclinic and monoclinic to hexagonal phase transitions respectively. (b) The difference in the free energies of hexagonal and monoclinic phases of Y2O3 as a function of pressure at 300 K.]

As shown in Fig. 2 (b) the difference becomes zero above 62 GPa suggesting the presence of a second order transition between the two phases. The small difference in free energy can be tuned by the incorporation of a small amount of impurity if the first order transition does not already occur at lower pressure. This might be the origin of the coexistence of the monoclinic and hexagonal phases at high pressure [2] or for the two different sequences of phase transition [8] for pure Y2O3 (cubic-hexagonal) and Eu-doped Y2O3 (cubic-monoclinic-hexagonal) with temperature.

5. Conclusions
We have reported inelastic neutron scattering measurements on polycrystalline samples of Y2O3 in the cubic phase. The measurements are in agreement with ab-initio as well as shell model calculations. The free energy calculations in various phases of Y2O3 help us to study the relative stability of high-pressure phases.

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