Study of Phonons in CaSiO$_3$ Perovskite at Lower Mantle Pressure

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CaSiO$_3$ perovskite is thought to comprise between 6 and 12 weight % of the lower half of the earth's transition zone and lower mantle (depths between 500 and 2900 km). Its structure throughout this regime is generally assumed to be cubic because x-ray diffraction studies have found no detectable deviation from Pm3m symmetry. Theoretical studies based on ionic models, periodic Hartree-Fock, and pseudopotential calculations have supported this picture. In this work, we are reporting the results of our theoretical investigation on the phonon properties of CaSiO$_3$ in its cubic phase by using lattice dynamical simulation method based on de Launey angular force (DAF) constant model to understand the role of phonon in this system. The calculated zone center phonon frequencies agree well with available results.

Key Words: Lattice dynamics, zone centre phonons, CaSiO$_3$, Silicates

INTRODUCTION

Silicate perovskites dominate the mineralogy of the earth's lower mantle. An understanding of the fundamental physics of the earth's interior requires information about the phase transitions and thermodynamic properties of key constituent mineral phases. Information about the earth's interior is only in-directly inferred from seismic observations. Compositional modelling based on accurate data about the structure and thermodynamic properties of minerals is essential to interpret the complex seismic data. Of particular interest is an understanding of mineral behaviour in terms of its microscopic structure and dynamics[1-5]. These characteristic properties are conveniently studied using neutron scattering-based techniques. Inelastic neutron scattering measurements have been used to study key lattice dynamical properties like the phonon dispersion relations and density of states, which govern a wide range of material behaviour, including structural phase transitions, thermodynamic properties, elasticity and melting. These, in combination with theoretical first principles calculations and atomistic simulations, have helped one to study the phonon spectra and associated physical properties of a wide variety of minerals

CaSiO$_3$ perovskite is thought to constitute between 6 wt% and 12 wt% of the Earth's lower mantle and is the third most abundant phase after (Mg,Fe)SiO$_3$

perovskite (~70%) and magnesiowustite (Mg,Fe)O (~20%), under the assumption that the lower mantle is pyrolytic[6-8]. It is, however, very difficult to perform detailed structural studies at lower-mantle pressures (up to 136 GPa) in the laboratory. A feasible solution to these problems is to use theoretical simulations. Here we investigate the interatomic interactions and zone center phonons of $CaSiO_3$ at high pressures. These results are important for the understanding of the physics and chemistry of the mantle phase; its phase stability, elasticity, and its ability to incorporate other cations such as Mg, Fe, and Al. Phase transitions in lower-mantle constituents have important implications for the understanding of recent seismological observations of reflective features within the lower mantle near 700, 900, 1,200 and 1,700 km depths[9].

STRUCTURE AND METHODOLOGY

The structure of $CaSiO_3$ perovskite in the pressure regime of the lower mantle is disputed; some claim it to be cubic with no detectable deviations of the diffraction pattern from cubic symmetry[10-11]. However there are studies which find the cubic structure to be unstable[12-13]. There is almost no doubt that even if the cubic phase is dynamically unstable at low temperatures, at mantle temperatures it will be stabilized by entropy. However, the ability to reproduce the small structural distortion (or its absence) is an interesting test of theoretical methods.

At ambient conditions, $CaSiO_3$ forms the mineral wollastonite, which has a pyroxenoid structure. Under pressure, it transforms to walstromite, then to a mixture of larnite (Ca_2SiO_4) and titanite-structured $CaSi_2O_5$[1415]. The perovskite structure appears at about 10 GPa and 1100 K. At lower mantle conditions $CaSiO_3$ has an ideal cubic perovskite structure, while at lower temperatures it is distorted. The small amplitude of the distortions is hardly observable by current high-temperature and high-pressure X-ray techniques and several orthorhombic and tetragonal structures have been proposed[12]. In the present study we have studied interatomic interactions and zone center phonons of $CaSiO_3$ in its high temperature cubic phase by applying lattice dynamical theoretical model.The ideal cubic perovskite $CaSiO_3$ is a simple cubic cell which is formed by corner - shared SiO_6 octahedra (in all three dimensions) and stuffed with a large Ca atom in the center of the cube of eight SiO_6 octahedra with a stoichiometric $CaSiO_3$ formula. From the point of view of lattice dynamics, the unit cell contains five atoms give rise to 15 phonons (three acoustics and 12 optic). The symmetry of these phonons at the Γ point (in terms of the O_h representation) is

$$\Gamma (O_h) = 4T_{1u} + T_{2u}$$

Where T_{1u} and T_{2u} represent the normal modes with triple degeneracy. One T_{1u} mode is acoustic and the rest are optical modes. The T_{2u} mode is inactive, while T_{1u} modes are only IR active. The compound in cubic phase has no Raman mode

In the present investigation a de Launey angular force (DAF) constant model[16] has been used to study the zone center phonons in the CaSiO$_3$. In DAF model, the relative displacement of the reference atom and one of the neighbors is considered. The restoring force on the reference atom is taken to be proportional to the component of the relative displacement perpendicular to the line joining the two atoms at their equilibrium positions. The forces due to all neighbors are calculated separately and summed up together. Different force constants are used for the various categories of neighbors and the net force on the reference atom is obtained by summing over the contribution from all the neighbors. The present calculation involves four central force constants α_1, α_2, α_3, α_4 and four angular force constants $\alpha_1{}'$, $\alpha_2{}'$, $\alpha_3{}'$ and $\alpha_4{}'$ between Si-O, Ca-O, Ca-Si and O-O atoms respectively up to third nearest neighbor.

RESULTS AND DISCUSSION

In the present calculation the interatomic force constants are obtained by fitting the calculated results of Stixrude et al.[17] at the ZC for transverse infrared active phonon frequencies. The force constants thus calculated are listed in table 1. Taking these force constants as input parameters, the dynamical matrix is solved at the zone center (ZC) The ZC phonons thus obtained are listed in table 2.

Table 1: Values of force constants (10^3 dyne cm^{-1})

Force constant	CaSiO$_3$
α_1 (Si–O)	102.8
$\alpha_1{}'$ (Si-O)	6.0
α_2 (Ca-O)	-7.0
$\alpha_2{}'$ (Ca-O)	24.0
α_3 (Ca–Si)	18.0
$\alpha_3{}'$ (Ca–Si)	4.5
α_4 (O-O)	19.7
$\alpha_4{}'$ (O-O)	-4.85

Table 2: Calculated zone center phonon frequencies in cm^{-1}

ZC-phonons	Present work	Stixrude et al.[17]
T_{1u}(TO1)	197.1	197
T_{1u}(TO2)	393.5	393
T_{1u}(TO3)	691.2	691
T_{2u}(inactive)	327.2	327

It is clear from table 1 that the calculated force constant α_1 between Si-O is strongest among all other interatomic interactions. This suggests that the covalent bonding between (Si-O) is strongest than that between (Ca-Si), (O-O) and (Ca-O). The larger force constant corresponds to stronger bond give rise to larger value of frequency. Two of the central force constant α_2 between Ca-O and $\alpha_4{}'$ between (O-O) are negative. The negative force constant corresponds to motion along modes that lead to energy lowering and it gives the indication of phase transition of $CaSiO_3$ and is in agreement with other study. The calculated zone center phonons are in agreement with other calculation[17].

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