Molecular Dynamics Simulations of cubic CaSiO3 at lower mantle conditions

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First-principles projector-augmented wave (PAW) molecular dynamics was used to investigate structure and properties of what is thought to be the third most abundant phase in the Earth's lower mantle, CaSiO₃ perovskite. The commonly assumed cubic structure was found to be stable at high temperatures and unstable at low temperatures at all pressures. On the basis of these results, we predict that the low temperature structure of CaSiO₃ perovskite is tetragonal space group I4/mcm. This phase would transform into an orthorhombic Imma structure under non-hydrostatic conditions. It is also obtained by fast quenching of cubic CaSiO₃ perovskite. This Imma structure explains hitherto puzzling experimental X-ray powder diffraction patterns.



Fig1.(a) Snapshot of MD Simulations at 100GPa and 2500K. One can see clearly the strong deviations from the ideal cubic position because of the strong thermal movement. However, in average the structure remains cubic.

Fig1(b) Quenched structure. At 100 GPa CaSiO₃ was cooled down from 2500 K to 0K.

CaSiO₃ perovskite is thought to comprise between 6 and 12 wt% of the lower half of the Earth's transition zone and lower mantle. Its structure throughout this regime is generally assumed to be cubic [1, 2] because temperature generally increases symmetry. At lower temperature deviations towards a tetragonal structure were found [1, 3].

Using VASP code in the PAW frame the CaSiO3 cubic structures were first optimized at 0 K for pressures of 0, 50, 100, 150 GPa [6]. For MD simulations we used an N-V-T-ensemble with Nosé thermostat [5]. Temperatures of 500, 1500, 2500 and 3500 K were

simulated. The lattice parameters were not relaxed but on the difference of stress in the three spacial directions we could observe a phase transition from the cubic phase at high temperatures to a tetragonal phase at low temperatures. As we observe a significant difference in stress components, we predict that transition takes place between 1500K and 500K.

Experiments [4, 1] indicate a tetragonal structure with c/a = 0.993, in apparent contrast to static energy minimization which gives structures with from c/a = 1.012 to 1.016. To resolve this question, we also performed quenches, which at the end gave new structures. Brute force changes of lattice parameters c/a < 1 and c/a > 1 were also performed. Fast quenching always gave Imma symmetry at the end. Slow quenching gave different results: Imma for c/a > 1 and I4/mcm for c/a < 1. This Imma symmetry structure is the only one explaining experiment as it gives the correct ratio of (440) and (004) intensities.

We suggest that the Imma symmetry phase is energetically more favorable at nonhydrostatic pressures, as it occurs both in experiment and simulations. In experiment non hydrostaticity comes from crystallization of pressure medium at low temperatures. In computations non-hydrostaticity comes from the cubic shape of the box the atoms are enclosed in whereas from their energetics the atoms would prefer a slightly distorted box.

As the Gibbs free energy has a hydrostatic and a non hydrostatic term, we suggest, that in the Imma phase the contribution from the non hydrostatic term is smaller than in the I4/mcm phase, which under hydrostatic condition is energetically preferable in agreement with [6,7].

The non hydrostatic term is given by

$$\frac{1}{2}\sum_{ij,kl}\sigma_{ij}\frac{\partial^2 G}{\partial\sigma_{ij}\partial\sigma_{kl}}\sigma_{kl}$$

where σ_{ij} is the stress tensor and $\frac{\partial^2 G}{\partial \sigma_{ij} \partial \sigma_{kl}}$ is equal to the elastic compliances. By

lowering the symmetry from I4/mcm to Imma under non hydrostatic stress CaSiO₃ perovskite lowers the symmetry of the elastic constants and thus can minimize the non hydrostatic contribution to the Gibbs free energy. Further calculations will include computation of the elastic constants and minimization of Gibbs free energy under non-hydrostatic pressure.



Fig2. Comparison of diffraction patterns at high pressure. (a) Experiment from [1]. Peaks are indexed by phase (C: CaSiO₃) and the corresponding hkl indices. (b) Theory: Computed powder diffraction pattern of optimized I4/mcm structure. (c) Theory: Computed powder diffraction pattern of optimized Imma structure coming from a quench.

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