

Pressure-Volume-Temperature (P-V-T) equation of state of CaSiO_3 perovskite to 108 GPa and 2420 K

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Introduction

Calcium oxide is expected to be 3–10 wt% of the Earth's mantle, according to geochemical models [1, 2], and 10–15 wt% of subducting slabs. Thus, the physical properties and the phase transformations of calcium-bearing phases are important for understanding the dynamics and the evolution of the Earth's interior. Calcium is incorporated into the perovskite structure at pressures equivalent to 580–720 km depth [3, 4].

There have been few detailed studies about the phase relationships in the CaO-SiO_2 system at Earth transition zone conditions [e.g., 5, 6]. The stability and the physical properties of CaSiO_3 perovskite have never been examined directly at lower mantle P-T conditions. The stability at lower mantle pressures were confirmed only at 300 K [7, 8, 9, and 10]. The P-V-T equation of state (EOS) was measured using a large volume press (LVP) [6, 11] at low P-T conditions ($P < 12$ GPa and $T = 300\text{--}1600$ K), thus requiring long extrapolation to derive physical properties, such as density and bulk modulus, at lower mantle conditions ($P = 24\text{--}135$ GPa).

In this study, using a stable heating system and $10\ \mu\text{m}$ x-ray beam at GeoSoilEnviroCARS (GSECARS), we were able to confirm the stability of CaSiO_3 perovskite at lower mantle conditions, determine the phase boundary with lower pressure phases, and obtain P-V-T EOS (Figure 1). In addition, we define the temperature and stress condition of the sample at extreme P-T conditions, which is crucial to obtain precise P-V-T EOS.

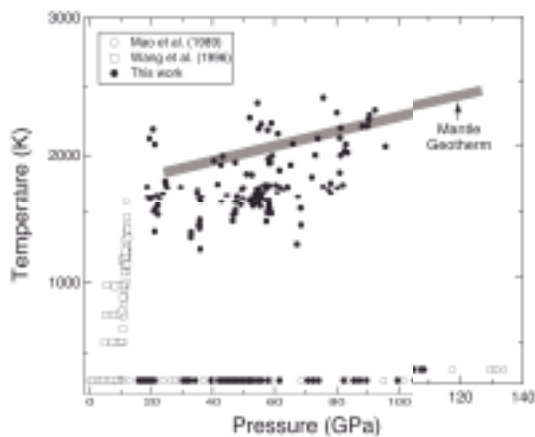


Figure 1: Pressure and temperature conditions of this work and comparison with previous studies.

Methods and Materials

A natural wollastonite was used as the starting material. The wollastonite was mixed with 10 wt% platinum powder (submicron grain size), which was used as a laser beam absorber and pressure standard. A thin ($10\ \mu\text{m}$) foil of the wollastonite-platinum mixture was loaded in a preindented stainless steel or rhenium gaskets and compressed using $300\ \mu\text{m}$ diamond anvils for experiments covering the 10–70 GPa range and beveled diamond anvils with $100\ \mu\text{m}$ central flats were used for higher pressure experiments. A pressure medium and insulation layer of either NaCl or argon was loaded together with the sample foil in such a way that the sample foil was not in contact with the diamond anvils.

Energy dispersive x-ray diffraction (XRD) measurements were carried out at the GSECARS sector. A $10\ \mu\text{m} \times 10\ \mu\text{m}$ beam size was used. This small beam size is especially important to collect the XRD spectra in an area with a homogeneous temperature distribution, since the flat top of the temperature profile is $\sim 20\ \mu\text{m}$.

Using the relative shifts of individual diffraction lines for a sample we were able to describe the differential stress, t , and elastic anisotropy, S [12]. This information was used in fitting an EOS to our data.

Two Nd:YLF laser beams were used to simultaneously heat the sample on both sides of the diamond-anvil cell (DAC). The temperature is also measured on both sides independently. This design reduces the thermal gradient along the stress axis of the DAC significantly [13]. The temperature is determined by fitting the measured visible spectrum of thermal radiation to the Planck equation. Assuming grey body radiation, we fit emissivity and temperature. By measuring temperature across the heated area on both sides of the sample, we obtain information on the three-dimensional temperature distribution within the x-rayed volume.

Results

Since differential stress can produce systematic error in measured volume and pressure, characterizing the uniaxial stress component is crucial to obtain an accurate P-V EOS curve. In this study, we obtain differential stress information on our data points and select the points with lowest differential stress factor. By fitting to a third-order Birch-Murnaghan equation, the isothermal bulk modulus of CaSiO_3 , K_{T_0} , is found to be 236 ± 4 GPa and its pressure derivative, K'_{T_0} is to be 3.9 ± 0.2 . This is significant smaller than earlier DAC studies ($K_{T_0} = 280\text{--}300$ GPa). In addition, in those studies, the data scatter precludes precise determination of the pressure derivative of the bulk modulus,

K'_{T0} . In the LVP study, which covered a limited pressure range, to obtain a constraint on K'_{T0} , Wang *et al.* [6] combined their data with high-pressure DAC data. A large value of K'_{T0} ($= 4.8$) was obtained by reconciling their data with nonhydrostatic DAC measurements.

The LVP measurements reported that the $-Ca_2SiO_4 + CaSi_2O_5$ assemblage, which is disproportionated from walstromite-type $CaSiO_3$, transforms to $CaSiO_3$ perovskite at 9–11 GPa at high temperature. In order to verify the proposed phase boundary, four heating runs covering 8–22 GPa and 300–2200 K were performed. According to our observation, the $Ca_2SiO_4 + CaSi_2O_5$ assemblage is stable to 15 GPa and the phase boundary to $CaSiO_3$ perovskite lies between 15–17 GPa. In contrast, the previous LVP studies reported the phase boundary at much lower pressure, 9–12 GPa [6].

The stability of $CaSiO_3$ perovskite has never been confirmed directly at lower mantle P-T conditions. We measured the XRD patterns at in situ lower mantle conditions ($18 < P < 96$ GPa, $1238 < T < 2419$ K). $CaSiO_3$ perovskite diffraction lines were readily observed in all of our runs (Figure 2). No peak splitting or new peaks were found. This indicates that $CaSiO_3$ perovskite is stable to 2300 km depth in the earth's interior.

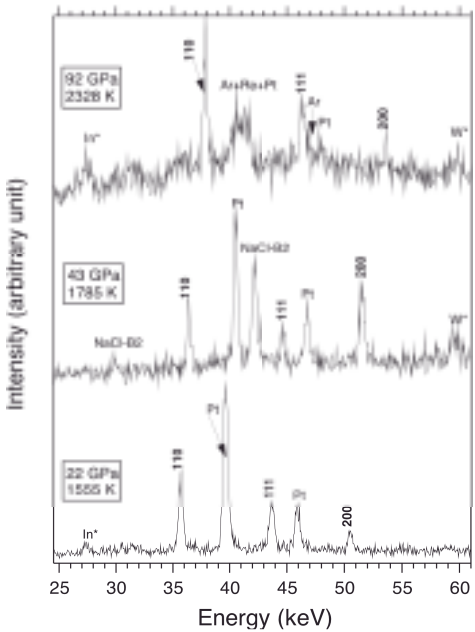


Figure 2: Energy dispersive x-ray diffraction pattern of $CaSiO_3$ perovskite at lower mantle P-T conditions.

The Grüneisen parameter, γ_0 , and its logarithmic volume dependence, q , are fit to our high-temperature data points using the Debye model. The fit for the combined data set (our data set and Wang *et al.* [11]) yields $\gamma_0 = 1.92 \pm 0.05$ and $q = 0.6 \pm 0.3$.

Discussion

Recent improvement of the laser-heated DAC technique opens up new opportunity to measure material properties at the conditions of the deep interior of the earth. However, to use this result for high-precision EOS study, the error sources must be carefully identified. In this study, we were able to describe the differential stress and the temperature gradient which have not been carefully determined in previous studies. It turns out that these two factors can result in significant error for EOS fitting.

We compare the density and bulk modulus profiles of the Earth's lower mantle with calculated profiles using the EOS parameter obtained in this study (Figure 3). In contrast to previous results, both the density and bulk modulus of $CaSiO_3$ perovskite are very close to those of lower mantle seismic models.

In an earlier mantle chemical model [14], a chemically distinct lower mantle was proposed. Bulk sound velocity profiles for upper mantle mineral assemblages were unable to fit the lower mantle seismic models. A major reason for this discrepancy was their choice of high-bulk modulus of $CaSiO_3$ perovskite ($K_{T0} = 301.4$ GPa). Our results indicate that the bulk modulus of $CaSiO_3$ perovskite is much smaller at lower mantle conditions.

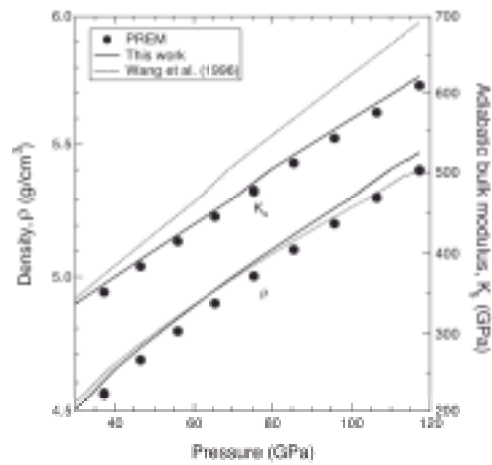


Figure 3: Density and bulk modulus profiles of lower mantle and $CaSiO_3$ at lower mantle P-T conditions.

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