

Elastic Behavior and Properties of CaSiO₃ Wollastonite and Perovskites to 15 GPa and 1200K

B. Li,¹ J. Kung,¹ T. Uchida,² Y Wang²

¹State University of New York (SUNY) at Stony Brook, NY, U.S.A.

²The University of Chicago, IL, U.S.A.

Introduction

Seismological observations provide information about the properties and processes of the Earth's interior in the form of profiles of density and velocity as a function of depth. Seismic tomography on a global scale reveals lateral variations in compressional (P) and shear (S) wave velocities and densities at various depths of the Earth's interior, reflecting differences in chemical composition, mineralogy, and/or temperature. The successful interpretation of these seismic observations in terms of those variables requires experimental and theoretical information on the elasticity of deep Earth materials under elevated pressure and temperature (P-T) conditions. In the last decades, major mantle phases have been investigated by using various techniques, including ultrasonic interferometry, Brillouin scattering, shock wave compression, x-ray diffraction, and, most recently, inelastic scattering. Details can be found in Refs. 1 and 2.

CaSiO₃ perovskite is the third-most-abundant phase in the lower mantle of the Earth. The assessment of its visibility in the seismic data has been hampered by the lack of reliable elasticity data. The elastic bulk modulus and its pressure derivative have been constrained in previous compression studies only by using diamond anvil cell (DAC) and large-volume apparatus in conjunction with synchrotron x-radiation [3-5]. Moreover, the crystal structure of CaSiO₃ in the mantle is still controversial. Most experimental studies have reported that CaSiO₃ possesses a cubic structure in the Earth's mantle, but some theoretical calculations have suggested the possibility of tetragonal and even lower symmetry [6-8]. A recent high-resolution x-ray diffraction study reported evidence for the existence of a symmetry lower than cubic at room temperature from the diffraction line splitting (<0.4%) [9]. An attempt to obtain elastic constants by using the radial x-ray diffraction technique at the lower mantle pressures has also been reported; however, the precision and reliability of this technique still need improvement [10].

Methods and Materials

Technical advances in high-pressure ultrasonic interferometry have allowed us to measure sound wave velocities at P-T conditions up to the top of the lower mantle [2]. The combination of ultrasonic measurements with results from a synchrotron x-ray source has enabled

the simultaneous determination of the crystal structure and elasticity of a millimeter-sized solid. In this study, we applied these state-of-art techniques to study CaSiO₃ perovskite by using an MA-8-type high-pressure apparatus installed at the GSECARS facility at the APS [11]. A 14/8 cell assembly modified from Ref. 12 was used in this study. In current experiments, x-ray diffraction spectra, the travel times of acoustic waves in the sample, and x-ray images of the sample were collected simultaneously at each P-T condition. Energy-dispersive x-ray diffraction spectra from the sample and internal pressure standard (NaCl) were recorded by using a solid-state Ge detector. Ultrasonic signals were generated by using a dual-mode piezoelectric transducer made of LiNbO₃, and the waveform data were collected by using a recently developed transfer function method [13]. Sample images at all the P-T conditions were recorded by using a system consisting of a yttrium-aluminum-garnet (YAG) crystal and charge-coupled device (CCD) camera [11].

Unlike some mantle phases that can be synthesized and characterized at ambient conditions before the high-pressure experiment, the unquenchable nature of CaSiO₃ perovskite prohibited us from recovering the cubic structure phase at ambient conditions. Upon the release of pressure, the perovskite phase transforms to an amorphous state. Therefore, in the current experiment, a low-pressure phase of CaSiO₃ (wollastonite) was used as the starting material instead.

The experimental P-T path is plotted in Fig. 1. The pressure was raised to 16 GPa, then the sample was heated to 1200K as monitored by the thermocouple. When heated to about 973K, perovskite peaks started to appear. The sample was then kept at 14 GPa and 1200K for about 2 hours. Full transformation to the perovskite phase was confirmed by x-ray diffraction. Extensive data collection along multiple heating/cooling cycles upon decompression was begun after peak P-T conditions were reached in order to provide wide P-T coverage.

Results and Discussion

Each point shown in the P-T path in Fig. 1 represents the conditions at which x-ray diffraction, acoustic, and x-ray imaging data were collected. Between 350K and 473K, data were collected at 10K temperature intervals. The sample pressure was determined from the x-ray diffraction of NaCl, enclosed in the cell next to the

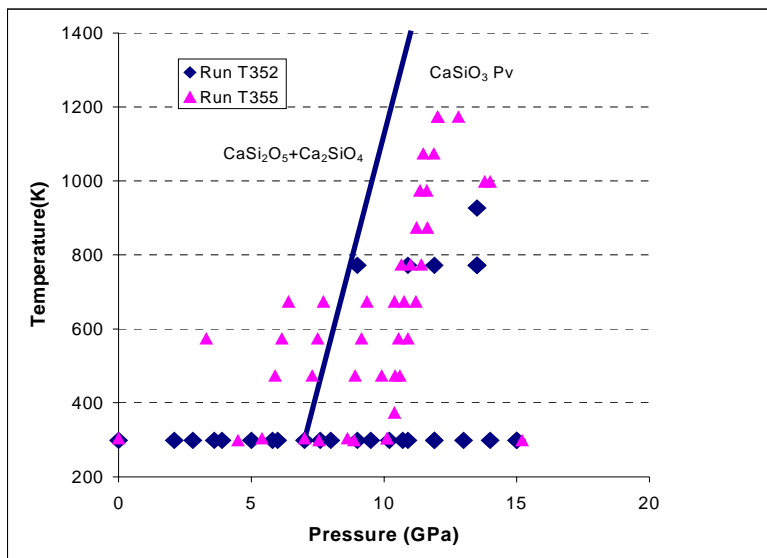


FIG. 1. Experimental P-T conditions for runs T352 and T355, from which x-ray diffraction, acoustic, and x-ray imaging data were collected. Solid line represents the phase boundary of CaSiO_3 from Ref. 4.

sample, while the temperature was measured by using a W3%ReW25%Re thermocouple. A preliminary analysis of the experimental data yielded the following findings.

Velocity Anomaly before Wollastonite Amorphization under Pressure

Pressure-induced amorphization in wollastonite at pressures of >10 GPa was reported on in a previous x-ray diffraction study [14]. However, the physical properties at the amorphous state have not been well characterized. In this study, by monitoring the sample length change with an x-ray imaging system, we were able to obtain a precise measurement of P and S wave velocities as a function of pressure during the amorphization process (Fig. 2). As shown in Fig. 2, the S wave velocity of CaSiO_3 wollastonite decreased linearly with increasing pressure between 2 and 10 GPa, while the P wave velocity showed a slow increase between 2 and 6 GPa and a rapid decrease from 6 to 10 GPa. X-ray diffraction data at this pressure range showed a continuous decrease of diffraction intensity and a broadening of diffraction peaks. A few broader peaks were still present up to the highest pressure in this experiment. It appears that the shear modulus of wollastonite softens with increasing pressure, when the material loses its long-range ordering toward the amorphous state. After 10 GPa, both P and S wave velocities increased rapidly with increasing pressure to 14 GPa.

Velocity Anomaly and Phase Transition in CaSiO_3 Perovskite

The travel-time data for CaSiO_3 perovskite showed an anomalous behavior at 420K when it was heating up to and cooling down from high temperatures. As plotted in Fig. 3, in each heating cycle, the P wave travel time decreased rapidly with increasing temperature between 300K and 400K. Above 425K, the travel time started to increase with increasing temperatures (a “normal” behavior observed for most solids and liquids). Upon cooling, the travel time showed a rapid increase with the decrease in temperature at a range of 300-420K (following the path of increasing temperature but in reversed order). In the same temperature range, the relative change in the magnitude of S wave signals between the buffer rod and sample (featuring an alternative variation to a sequence of disappearance, reappearance, and growth to steady state) indicated an impedance contrast discontinuity across the buffer rod/sample interface, which is normally associated with phase transitions. However, the weak splitting in the (200) and (211) lines in the x-ray diffraction data, as described in a previous study [9], was beyond the resolution of the energy-dispersive method used in this study. Further investigations using monochromatic x-rays to refine the crystal structure at these conditions are underway. Our current explanation is that the observed impedance

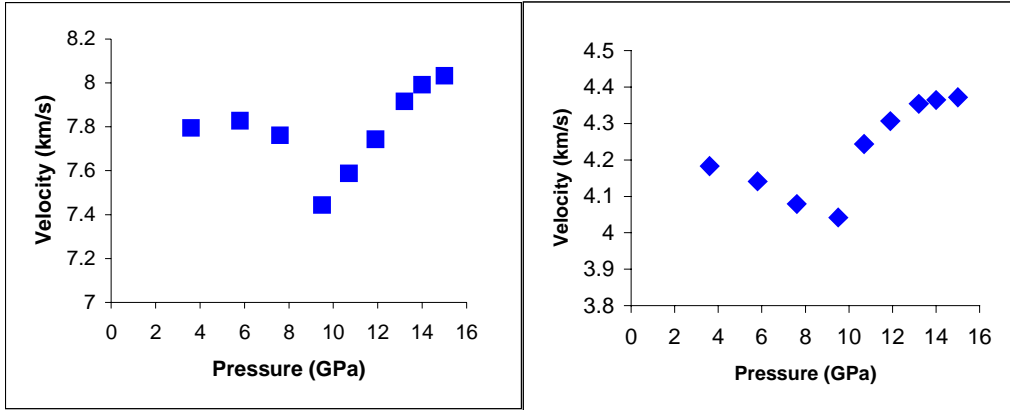


FIG. 2. *P* (left) and *S* (right) wave velocities of wollastonite as a function of pressure.

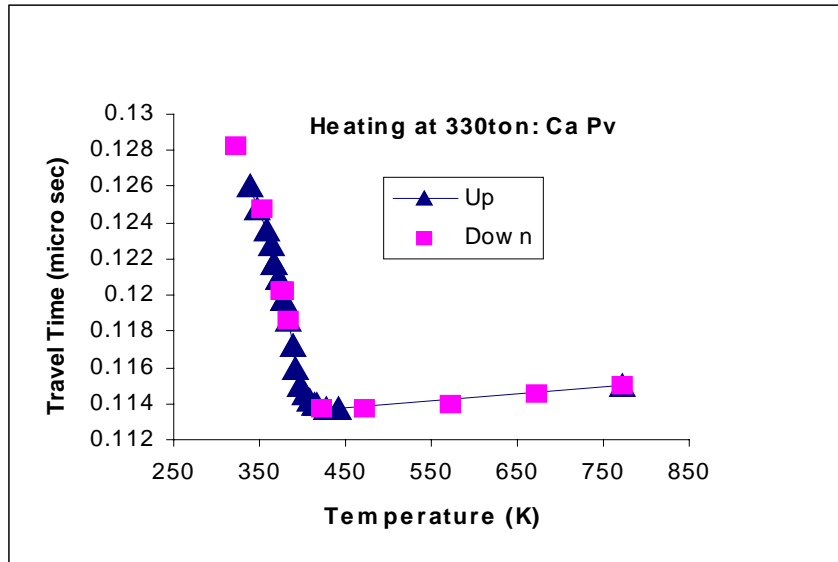


FIG. 3. Variations of *P* wave travel times as a function of temperature during the heating and cooling cycle at 9.6 GPa. Similar behavior was observed at all other heating cycles at a pressure range of 2-12 GPa.

change was primarily caused by a velocity change that resulted from a ferroelastic phase transition from cubic at high temperature to a noncubic distortion at low temperature (a commonly observed feature for ABO_3 perovskite materials) [15]. The reversibility shown in Fig. 3 suggests that the thermal hysteresis of the acoustic velocity around this phase transition is very small. Another softening feature was observed at pressures greater than 12 GPa at room temperature, which might be a transition from the noncubic phase discussed above to the tetragonal phase reported in the previous study [9].

A cubic structure was assumed when all the x-ray diffraction data were fitted to obtain the unit cell volume of the sample at all conditions. The resulting unit cell volumes at high *P* and *T* appeared to be compatible with

those from previous studies [3-5]. A full analysis of the current data will provide complete elasticity data for the perovskite phases observed at high *P* and *T*. The high velocity of the cubic $CaSiO_3$ phase is likely to produce higher-visibility lower mantle conditions than previous calculations that used elasticity results obtained at high pressure and room temperature.

Acknowledgments

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