In-situ Measurement of Elastic Velocity Contrast between $MgSiO_3$ Enstatite Polymorphs at High Pressure

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Introduction

Orthopyroxene is an important mineralogical constituent of petrological models of the Earth's upper mantle. Therefore, the reconstructive (or first-order) phase transformation between orthoenstatite (OEN, orthorhombic symmetry, space group Pbca) and high-pressure clinoenstatite (HP-CEN, monoclinic symmetry, space group C2/c) is of great interest for geophysical applications. In particular, this phase transition was shown to be likely to occur in the deeper portions of the upper mantle [1-3], where the depth is coincident with the reflector observed at ~300 km [4, 5].

However, the HP-CEN phase is unquenchable. The elastic property, therefore, has to be measured within its stability field. Restricted by the techniques that are available, measuring the elasticity has never been done experimentally. The absence of direct measurements of sound velocities of the HP-CEN has made it difficult to ascertain whether the magnitude of the acoustic velocity or the impedance contrast between the OEN and HP-CEN phases of enstatite is sufficiently strong to produce an observable seismic signature.

Contrary to most high-pressure mantle phases (e.g., wadseylite, ringwoodite, and Mg-rich perovskite), HP-CEN cannot be recovered at ambient conditions because it transforms to a low-pressure monoclinic form ($P2_1/c$) upon the release of pressure [3, 6]. Thus the HP-CEN phase has to be synthesized *in situ*, followed by acoustic experiments performed within its stability field. Such acoustic experiments, which basically measure the travel times of sound waves in specimens, require techniques for monitoring the specimen length under elevated pressure and temperature conditions, to obtain velocity data. This is especially important when the specimen is undergoing a first-order phase transformation involving a volume change. Recently, our group (ultrasonic group at SUNY) has adapted x-radiographic imaging techniques for use in simultaneous ultrasonic and *in situ* x-ray diffraction experiments in order to permit direct measurements of the specimen length [7, 8].

The stability field of high-pressure clinoenstatite extends to the transition zone (~15 GPa). The 1000-ton multianvil press (T-25) [9] newly installed at beamline 13-ID at the APS has given us the opportunity to make ultrasonic measurements that cover the pressure-temperature (P-T) space of high-P clinoenstatite in the mantle conditions. Through the collaboration between our group and GSECARS, we have been able to measure elastic velocity across the OEN and unquenchable HP-CEN phases at mantle conditions.

Methods and Materials

Because of its unquenchable nature, HP-CEN was synthesized *in situ* at high pressure and temperature during the acoustic measurements by using the well-sintered OEN sample that was synthesized prior to the high-pressure acoustic experiment. The OEN sample was loaded in the acoustic cell assembly and heated up to ~1000°C at 13 GPa for 2 hours to transform it into the HP-CEN phase.

In order to obtain compressional (P) and velocity (S) wave elastic velocities ($V_{(P,S)} = 2l/t_{(P,S)}$), the round-trip travel times ($t_{(P,S)}$) and specimen lengths (l) were collected simultaneously by using a transfer function method and x-radiographic image technique. In this study, dual-mode transducers, which generate P and S wave stress wave at the same time, were used. The energy-dispersive x-ray method was employed; white radiation was used to collect data on the cell parameters of both NaCl as the pressure marker and the $MgSiO_3$ specimen (including OEN and HP-CEN phases) at each experimental condition. X-ray diffraction patterns of NaCl and the sample and data on the travel times and length images of the specimen were collected at high pressures before and after the OEN specimen transformed to the HP-CEN phase. The data for the OEN phase were collected while the pressure was increasing at room temperature to a maximum of ~17 GPa. After the specimen had been fully transformed to HP-CEN, data were collected as the cell pressure was decreased. The data collection for the HP-CEN phase was stopped at ~6 GPa before the specimen transformed to the LP-CEN phase.

Results

The results from two runs (T354 and T409) are presented in this report. The densities of OEN and HP-CEN were calculated from the pressure-volume (P-V) data in this study and were compared with those measured from previous studies [3, 10-12]. As Fig. 1 shows, the density measurements for OEN and HP-CEN in this study

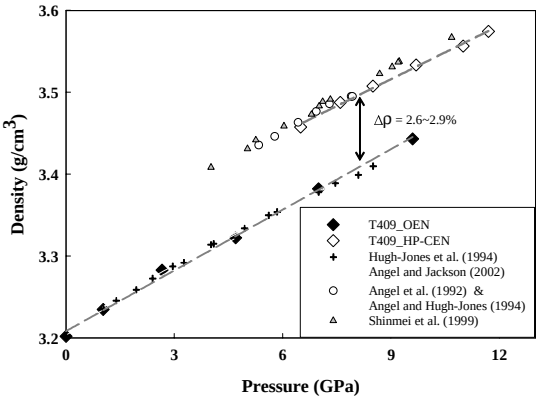

FIG. 1. Density of OEN and HP-CEN as a function of pressure, at room temperature. The densities of OEN (solid diamonds) and HP-CEN (open diamonds) obtained in our study are in good agreement with previous studies. The density jump associated with the phase transformation OEN-HP-CEN is 2.6% to ~2.9% from the pressure range of 7 to 9 GPa.

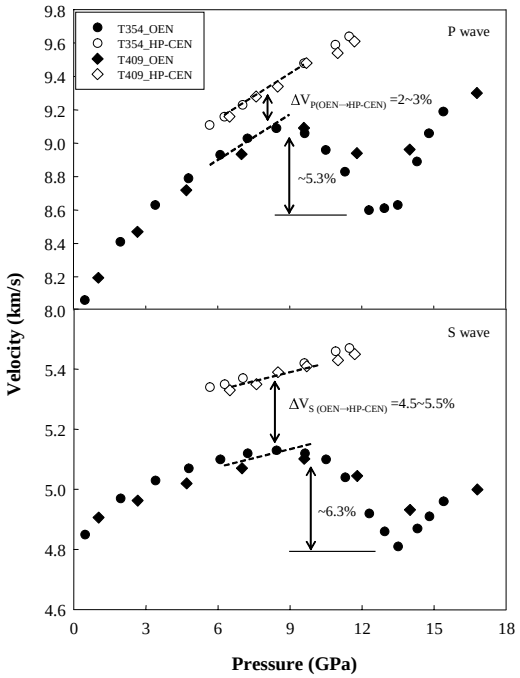

FIG. 2. P and S wave velocity of $MgSiO_3$-enstatite as a function of pressure at room temperature. Measured P and S waves of OEN (solid symbols) up to 9 GPa are remarkably consistent between two experimental runs and two specimens (T354 and T409) but show the characteristic change in behavior above 9 GPa, as the "trough." The velocity reduced by the anomalous behavior is 5.3% for the P wave and 6.3% for the S wave, from a pressure of 9 to 13 GPa. The velocity contrast associated with the phase transformation OEN → HP-CEN is 2% to ~3% for the P wave and 4.5% to ~5.5% for the S wave.

are in good agreement with results from previous studies that were carried out in separate experiments. The density contrast between OEN and HP-CEN in a pressure range from 7 to 9 GPa were calculated to be 2.9% to 2.6% in this study. The magnitude of the density contrast determined in this study is comparable to that at 7.9 GPa (2.7%) calculated by using the data from Angel et al. [2] and Hugh-Jones et al. [10].

Resultant P and S wave velocities of OEN and HP-CEN measured in this study are plotted as functions of pressure in Fig. 2. This figure shows that the P and S wave velocities of OEN made the characteristic change in behavior at 9 GPa. Both the P and S wave velocities from the two runs were remarkably consistent with each other below 9 GPa and increased systematically as the pressure increased. Above 9 GPa, both V_P and V_S decreased dramatically with increasing pressure; the minimum values were attained between 12 and ~14 GPa, then they increased again. The deduced rates of velocity to the minimum in both runs were somehow different from run to run. This scenario may be related to the kinetic process; the slow compression rate caused a larger reduction in velocity in run T354. In the pressure range from 9 to ~13 GPa, the P and S wave velocities decreased by a maximum of 5.3% and 6.3%, respectively (i.e., T354; solid circles in Fig. 2).

In contrast to OEN, the pressure dependencies of the velocities of HP-CEN appear to be linear functions within the pressure range of the data collected (6 to ~12 GPa). The pressure dependencies of the velocities of the HP-CEN phase were subparallel to those of OEN above 6 GPa (Fig. 2). In the pressure range of 7-9 GPa and at room temperature, the velocity contrasts between the OEN and HP-CEN phase transition were 2.0-3.0% for the P wave and 4.5-5.5% for the S wave. The magnitude of the P wave velocity jump measured in this study matched that predicted by the Birch law; a velocity jump of ~3% was associated with a change of ~3% in density [3, 4].

Discussion

The OEN to HP-CEN transition involved a significant density increase of nearly 3%, which has been suggested to be responsible for the reflector observed in the condition of a "depleted" bulk mantle composition at a depth of 200 to ~300 km [3-5]. By using the state-of-the-art experimental setup, we were able to measure the elasticity of OEN and HP-CEN in the same experiment in order to evaluate the elastic velocity contrast between the two phases directly. The density jump across the phase transformation from OEM to HP-CEN was 2.6% to 2.9%

at a pressure range corresponding to a depth of 200 to ~300 km in the upper mantle. The velocity jump associated with this phase transformation was 2% to ~3% for the P wave and 4.5% to ~5.5% for the S wave. The seismic impedance contrast (Z = density × velocity) was 5.6% to ~7.8% for the P wave and 12.6% to ~14.3% for the S wave. For a depleted bulk mantle composition model with ~20 modal % OEN [5, 13] the corresponding seismic impedance contrast is about 1.1% to ~1.5% for the P wave and 2.5% to ~2.9% for the S wave at a depth of 200 to ~300 km. When the thermal effect is taken into account, the impedance contrasts between the two phases was reduced by some degree. Such a small seismic impedance contrast induced by the phase transition in enstatite would likely be smeared out by the other geophysical processes. Therefore, this phase transformation alone may not provide a satisfactory explanation for the reflectors observed at a depth of 200 to 300 km.

An unexpected acoustic velocity softening of OEN was observed in our study at a high pressure (above 9 GPa) and at room temperature. On the basis of a subsequent diamond anvil cell study and Raman measurement, we conclude that the anomaly was caused by a reversible phase transition. The phase transformation and its mechanism remain unknown and will be studied by different techniques.

In summary, with the ultrasonic technique in conjunction with *in situ* x-ray techniques (x-ray diffraction and x-radiographic image) has made it possible to measure the contrast of elastic properties (density and elastic velocity) and the elastic behavior across the phase transition in the same experimental run. Furthermore, the ultrasonic measurement interfaced with high-pressure large volume apparatus also provide the opportunity of measuring the elasticity of mantle phases in their stability field, for example, the unquenchable HP-CEN phase in this study.

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