The Phase Boundary Between α- and β-Mg_2SiO_4 Determined by in Situ X-ray Observation

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The stability of Mg_2SiO_4, a major constituent in the Earth's mantle, has been investigated experimentally by in situ observation with synchrotron radiation. A cubic-type high-pressure apparatus equipped with sintered diamond anvils has been used over pressures of 11 to 15 gigapascals and temperatures of 800° to 1600°C. The phase stability of α-Mg_2SiO_4 and β-Mg_2SiO_4 was determined by taking account of the kinetic behavior of transition. The phase boundary between α-Mg_2SiO_4 and β-Mg_2SiO_4 is approximated by the linear expression $P = (9.3 \pm 0.1) + (0.0036 \pm 0.0002)T$, where P is pressure in gigapascals and T is temperature in degrees Celsius.

The mineral $(Mg_{0.9},Fe_{0.1})_2SiO_4$ olivine is a major component of the Earth's upper mantle, and its pressure-induced phase transition into modified spinel structure (β-phase) is believed to be responsible for the 400-km seismic discontinuity. Precise determination of the α-β phase transition boundary could constrain the thermal structure of the mantle on the basis of seismic observations. Moreover, the mode of mantle convection and the dynamics of subducting slabs and mantle plumes are expected to be influenced by the significant contrast in the density and elastic properties of the α and β phases (*1*).

Transformations in the system Mg_2SiO_4-Fe_2SiO_4 at 5 to 15 GPa, corresponding to depths of 160 to 440 km, have been experimentally investigated by many authors (*2–6*). In most of these experiments, a quenching method was used to determine the boundary lines [Yagi *et al.* (*6*) used an in situ method]. An accurate determination of phase boundary requires correct measurement of pressure and temperature together with identification of the stable phase during both progressive experiments and reversals across the boundary. We used a high pressure in situ diffraction technique. This technique has two advantages: (i) pressure values during the run can be monitored by use of an equation of state for a pressure marker material and (ii) phase identification of the sample can be made by diffraction under high pressure and high temperature so that we can observe the kinetic behavior.

We made our high-pressure experiments at National Laboratory of High Energy Physics, using a single-stage cubic-type apparatus installed across the synchrotron radiation lines (*7*). The in situ measurements are made with synchrotron radiation x-ray source. Such an intense incident x-ray beam allows a short acquisition time of the diffraction profile; it took less than one minute to identify phases present. Thus we could measure pressure and identify phases virtually at the same time, and we could study the kinetic behavior of the transition.

Temperature was recorded with a W3%Re–W25%Re thermocouple located at the center between the upper and lower halves of the assembly (Fig. 1). The temperature reading was made without any correction for pressure. The starting and pressure marker material were filled in the upper part and lower part of the sample chamber, respectively. Diffraction profiles of the sample and the pressure marker material were taken separately just below and above the thermocouple junction by changing the position of the incident beam.

Pressure values were determined from unit cell volume of NaCl measured at each experimental conditions on the basis of Decker's equation of state for NaCl (*8*). The unit cell volume was calculated from at least two diffraction lines or, in most cases, more than three diffraction lines.

We used a starting material of a fine powder of α phase or β phase (*9*). In experiments over about 1100°C, we used a powder mixture of α phase and BN to prevent rapid grain growth, which distorted the relative intensities of diffraction lines of α and β phase.

The starting material was heated at high pressure until a single phase of α or β phase was partly transformed to a mixture of α and β phases (*10*). We then made in situ measurements on this two-phase mixture at desired conditions. We observed the change of relative intensity of α and β phases with time, without any delay resulting from nucleation kinetics. Thus the stable phase can be clearly identified (Fig. 2). The data points of the stable phases were taken only when we found the relative change of diffraction lines under constant pressure and temperature. To compare relative intensity, we chose five diffraction lines—(021), (101), (111 + 120), (121 + 002), and (130)—for the α phase, and six—(211), (040), (310 + 112), (112), (400), and (042)—for the β phase; these peaks did not overlap under the experimental conditions. It took up to 30 min to confirm the change of the relative intensity at each condition.

In the experiments lower than about 1100°C, temperature was kept within 10°C of a desired value. Errors in pressure resulting from the combined uncertainty of the unit cell volume of NaCl and the temperature fluctuation were smaller than 0.1 GPa in these runs. Temperature fluctuations increased to about 50°C in experiments at temperatures above 1100°C. Uncertainty of pressure associated with this temperature variation is about 0.2 GPa. However, as it can be shown from the equation of state of NaCl, ambiguity of the run temperature should result in the shift of the data almost parallel to the α-β phase boundary. Therefore uncertainty of the run temperature has little effect on the determination of the phase boundary. The results show that the transformation pressure in Mg_2SiO_4 is ap-

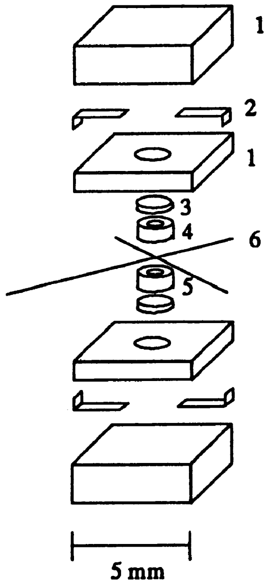

Fig. 1. Furnace and sample assembly of the single-stage sintered diamond-anvil system with 3-mm edge length of the anvil head. 1, pressure medium (boron + epoxy); 2, electrode (Mo); 3, heater (graphite or TiC + diamond); 4, a container of sample (boron + epoxy); 5, a container of pressure marker (boron + epoxy); and 6, thermocouple (W3%Re–W25%Re).

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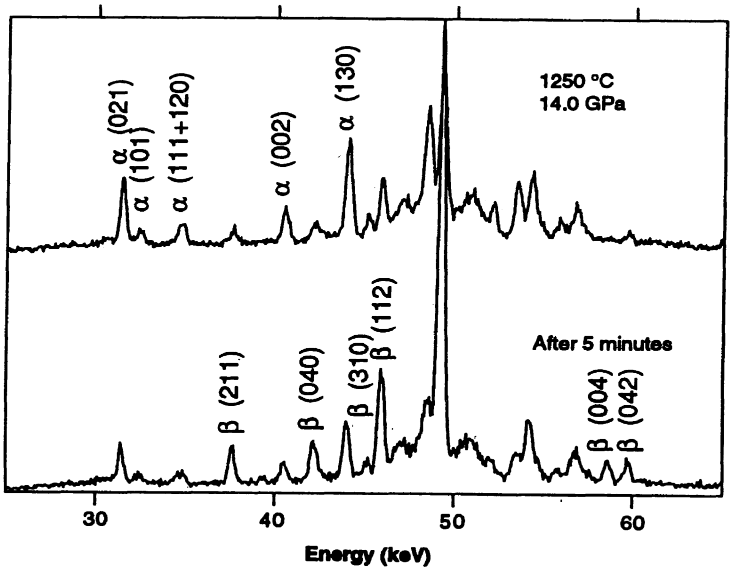

Fig. 2. Time variation of diffraction profile of the sample at 14.0 GPa and 1250°C. Counting time is 100 s and 2θ angle is 5.988°. All peaks with higher energy than 30 keV are diffraction lines of α or β phase. Diffraction lines of sample, which do not overlap with that of another phase, are labeled. Intensity of diffraction lines of α phase became weaker than those of β phase with time, which indicates that the transition from α to β phase has progressed. Then α phase was found to be unstable. From these observations, we conclude that β phase is stable at 14.0 GPa and 1250°C.

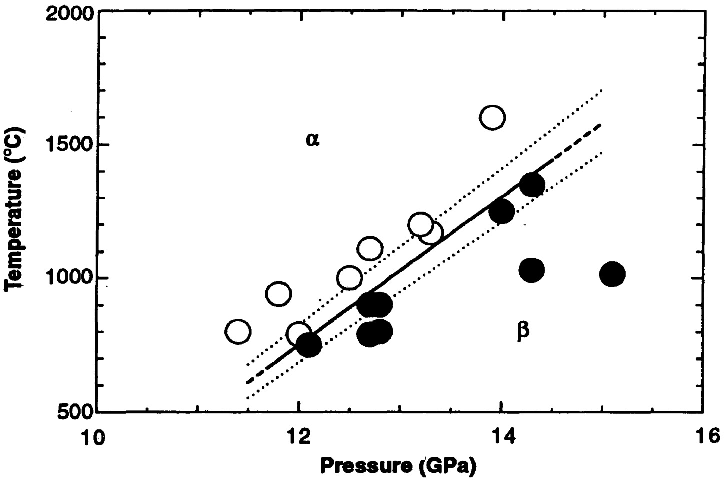

Fig. 3. Phase diagram of Mg_2SiO_4 determined by the present in situ experiments. Open and solid circles represent conditions where α and β phase was stable, respectively. All of the circles show conditions where we observed coexistence of α and β phases and then we confirmed increase of α or β phase peaks with time. Error in pressure and temperature is less than or equal to the size of the circle. Solid line is the inferred phase boundary between α and β phase, dotted lines show the estimated error.

proximately given by the linear expression: $P = (9.3 \pm 0.1) + (0.0036 \pm 0.0002)T$, where P is pressure in gigapascals and T is temperature in degrees Celsius (Fig. 3).

Previous determinations of the α-β phase boundary (*3–5*) generally implied that the transition took place at higher pressures than we found (Fig. 4). The slope of the phase boundary, dP/dT, we determined is intermediate between those of Kawada (*4*) and Katsura and Ito (*5*). Thermodynamic calculations based on the various physical parameters gives the slope dP/dT = 0.0015 to 0.0027 GPa °C^{-1} (*12*), which is smaller than our result of 0.0036 GPa °C^{-1}. Katsura and Ito (*5*) estimated the temperature at the depth of 380 to 425 km to be 1400° to 1750°C based on their phase diagram in the system Mg_2SiO_4-Fe_2SiO_4. Our result suggests that the temperature at the same depth range is expected to be higher by about 100°C (*11*). Moreover, significant difference in the slope of the α-β phase boundaries between our results and thermodynamic calculations implies that thermodynamic parameters of α and β phase (for example, heat capacities, thermal expansivities and compressibilities) still involves large uncertainties.

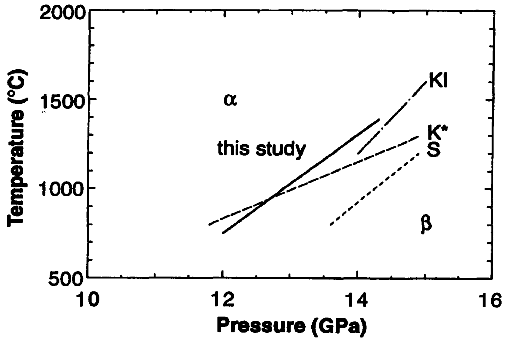

Fig. 4. Phase diagram of Mg_2SiO_4. Solid line is our phase boundary between α and β phase. Other lines are: S, Suito (*3*); K*, Kawada revised by Akimoto (*4*); KI, Katsura and Ito (*5*).

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8. D. L. Decker, *J. Apple. Phys.* **42**, 3239 (1971); A fine powder mixture of NaCl, Au, and BN was filled in the lower part of the sample chamber. NaCl was used as a pressure marker. The diffraction lines of NaCl and Au were used to calibrate the 2θ angle of solid state detector at ambient pressure. Addition of BN prevents the powdered material from grain-growth, so that we could obtain a powder diffraction profile even at high temperatures.
9. The α phase material was prepared from synthetic single crystal. The β phase material was synthesized at about 15 GPa and 1300°C using an MA8 high-pressure apparatus.
10. The sample was loaded and heated in two ways. In one case, pressure was applied first by loading at room temperature; next, the sample was heated until a single phase of α or β was partly transformed to make a mixture of α and β phases. In the other case, the sample was heated at lower pressure than the α-β phase boundary; next, pressure was increased from stability field of α phase to that of β phase at constant temperature. Then temperature was increased again to make a mixture of α and β phases, since α phase did not transform to β phase when only pressure was increased even at temperatures higher than 1000°C within the limited experimental time.
11. We assumed that Katsura and Ito (*5*) overestimated pressures when we reevaluated their phase diagram in the system of Mg_2SiO_4-Fe_2SiO_4. Consequently, we found that the temperature at around 400 km is expected to be higher than the estimation based on the original diagram of Katsura and Ito (*5*).
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