Thermal Equation of State of MgSiO₃ Ilmenite to 19 GPa and 1373K

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Introduction

The ilmenite form of MgSiO₃ is an important mineral in the Earth's transition zone between depths of 410 and 660 km. Knowledge of the thermoelastic properties of ilmenite is critical in understanding the seismic velocity and density profiles of the transition zone and the constraining composition and mineralogy of this portion of the Earth. Before this study, no pressure-volume-temperature (P-V-T) data were available for ilmenite, mainly because it is stable only at high pressures (above 16 GPa) and temperatures (above 1000K). Here we discuss results on the thermoelastic properties of ilmenite measured by x-ray diffraction up to 19 GPa and 1373K by using the 250-ton large-volume press (LVP) at the GSECARS bending magnet beamline (13-BM-D) at APS. The results will be used to model the seismic structure in the transition zone.

Methods and Materials

Polycrystalline specimens of MgSiO₃ ilmenite, about 1 mm in diameter and 1.5 mm in length, were synthesized at 21 GPa and 1723K by using the offline press (USSA-2000) at the Stony Brook High Pressure Laboratory. Several small disks (about 0.5-mm thick) were cut from the specimens and loaded in a cell assembly specially designed for *in situ* x-ray diffraction studies in the 2.5-MN (250-ton) LVP [1] with a T-cup multi-anvil apparatus [2] at GSECARS beamline 13-BM-D [3]. A pressure standard, either NaCl or Au, was also loaded in the cell as a separate layer (see Fig. 1). The equations of state of NaCl [4] and Au [5] were used to calculate pressures at high temperatures, which were measured by a W/Re thermal couple.

The energy-dispersive diffraction technique is used for P-V-T measurements at a fixed two-theta angle of about 6° by using a Ge solid-state detector. The experiments followed carefully designed P-T paths for two purposes: to (1) obtain P-V-T data within as well as outside the ilmenite stability field while the sample remained metastable and (2) minimize unwanted nonhydrostatic stress, which may introduce systematic uncertainties in the measurement. Prior to the P-V-T measurements, a separate experiment was conducted by heating an ilmenite sample outside its stability field. Conversion to the low-pressure enstatite phase was observed at temperatures as low as 800K. We therefore restricted the maximum temperature to 773K during the P-V-T measurement. Figure 2 shows our P-T condition in reference to the

ilmenite stability field determined in a quench study [6]. Note that our highest temperature point (1473K and 18 GPa) lies outside the stability field. Since ilmenite remains stable at this condition, the lower pressure boundary (between high clinoenstatite and ilmenite) should be at least 2 GPa lower than that previously claimed on the basis of the quench study [6].

Results

A total of 134 P-V-T points were obtained in two runs, after nonhydrostatic stresses were minimized by heating the sample (and its surrounding pressure media) to at least 773K before making the P-V-T measurement. Room temperature data points that were most likely affected by the presence of nonhydrostatic stress were rejected in the following equation of state analyses.
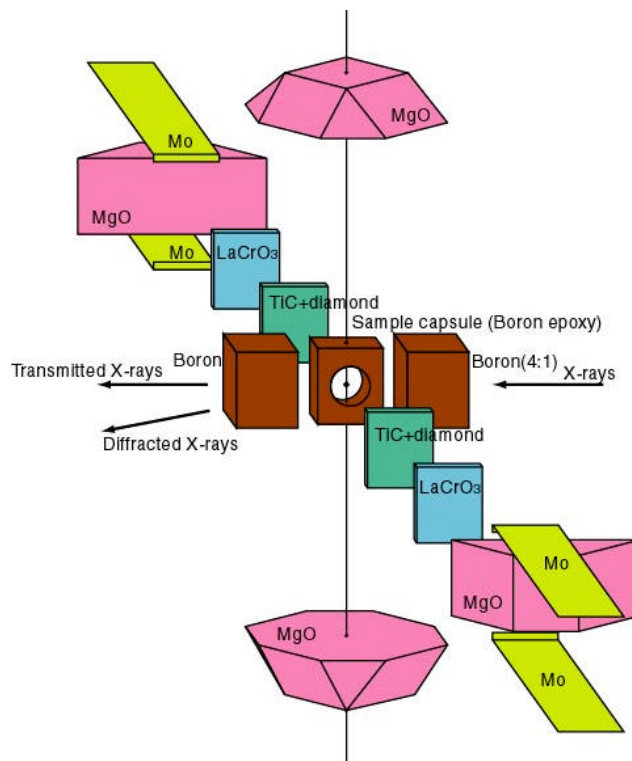

FIG. 1. *Exploded view of the cell assembly used for the present study. The sample chamber (1.0-mm diameter) is divided into two compartments (separated by the thermocouple), for sample and pressure standard.*
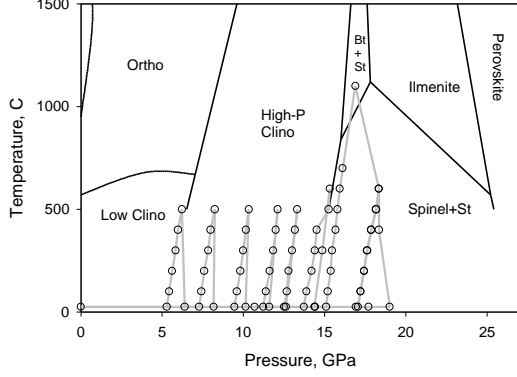
FIG. 2. Typical P-T path (lines with dots) in our P-V-T measurements for MgSiO₃ ilmenite, superimposed on the phase diagram for MgSiO₃ [6]. Ortho = orthoenstatite, Low Clino = low clinoenstatite, High-P Clino = high-pressure clinoenstatite, BT = wadsleyite (beta phase of olivine), Spinel = ringwoodite, and St = stishovite. The garnet phase (majorite) is stable above 1500°C (1773K) in pure MgSiO₃, and at lower temperatures when Al is present.

We first fit the room temperature data with the third-order Birch-Murnaghan equation of state in the following form:

$$P = (3/2) K_{T0} (x^{7/3} - x^{5/3}) [1 + (3/4)(K_{T0}' - 4) (x^{2/3} - 1)] \quad (1)$$

where K_{T0} and K_{T0}' = the room temperature isothermal bulk modulus and its pressure derivative, respectively, and $x = V_0/V$, where V_0 is the ambient unit cell volume. Because of the limited compression range (up to ~7%) and the well-known trade-offs among V_0, K_{T0}, and K_{T0}', the data do not provide a robust constraint on K_{T0} and K_{T0}' simultaneously. We therefore adopted the bulk modulus (210 GPa) determined at ambient conditions by Brillouin scattering [7] and used Eq. (1) to extract the pressure derivative of the bulk to be $K_{T0}' = 5.1 \pm 0.3$. Figure 3 shows the room temperature data and the best fit. This equation of state will be used as the baseline in high-temperature equation of state fits.

The high-temperature data are fit with several thermal equations of state to cross-check the consistency of the results. We first fit the data with a high-temperature Birch-Murnaghan equation of state, which takes the same form as Eq. (1), but K_{T0} = the isothermal bulk modulus at a given temperature T and $x = V_{T0}/V$, where V_{T0} = the zero pressure volume at T.
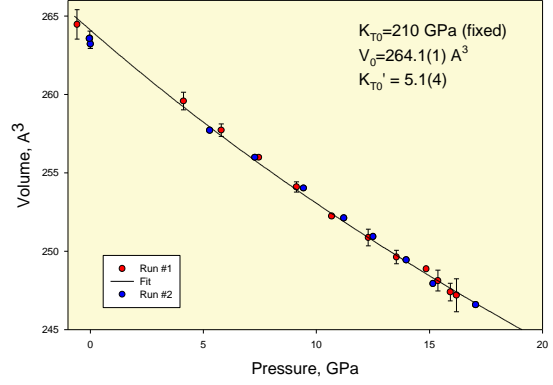
$$V_{T0} = V_0 \exp[\int \alpha_0 dT], \quad (2)$$

FIG. 3. Room temperature equation of state of ilmenite. Curve represents fit using the third-order Birch-Murnaghan equation of state.

where α_0 = the zero-pressure thermal expansion, with the following empirical expression:

$$\alpha_0 = a + b\,T - c\,T^{-2}, \quad (3)$$

where a, b, and c = positive constants. The integration in Eq. (2) is from T_0 (= 298K) to T. Ashida et al. [8] measured the room pressure thermal expansion of ilmenite to 873K. Their data can be best fit by a constant thermal expansion α_0 of $2.44 \pm 0.20 \times 10^{-5}$ K⁻¹. By using this thermal expansion in our high-temperature Birch-Murnaghan fit, we obtain $(\partial K_T/\partial T)_P = -0.040 \pm 0.001$ GPa/K. The fit is shown in Fig. 4.
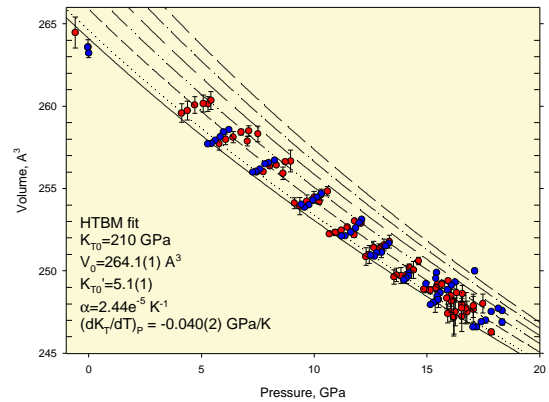

FIG. 4. P-V-T data obtained from this study and the high-temperature Birch-Murnaghan equation of state fit. Different symbols are data from the two runs. Curves (from bottom up) are fit at 298, 373, 573, 773, 973, 1173, and 1373K, respectively.

Discussion

The results on the thermoelasticity of ilmenite are added to the existing database for the most dominant mantle minerals to calculate acoustic velocity and density profiles for candidate mantle mineralogical models and to compare them with seismically derived Earth velocity and density structure, by using the approach outlined in Ref. 9. The new ilmenite data allow us to quantitatively examine the effects of ilmenite-forming phase transformations on seismic signatures near the 660-km seismic discontinuity. Because of the high bulk modulus of ilmenite, a "double-step" discontinuity may occur if the transition zone temperature is relatively low and ilmenite-stable (e.g., near the subduction zone). This effect will be more pronounced in a mantle with a large amount of pyroxene component. Also, lateral mantle temperature variations may cause ilmenite-garnet phase modulations in the transition zone, because ilmenite is stable at low temperatures, whereas majorite garnet is stable at high temperatures. Similarly, lateral composition variations, especially Al content (which tends to stabilize the garnet phase), can also cause phase modulations. The large differences in elastic properties (e.g., $K_{T0} = 210$ GPa for ilmenite and 160 GPa for garnet) may result in large apparent lateral velocity variations, which, in turn, may be misinterpreted as abnormal physical properties (such as $\partial K/\partial T$ and $\partial \mu/\partial T$, where μ = the shear modulus) in the mantle.

References

[1] Y. Wang, M. Rivers, T. Uchida, P. Murray, G. Shen, S. Sutton, J. Chen, Y. Xu, and D. Weidner, "High pressure research using large-volume presses at GeoSoilEnviroCARS, Advanced Photon Source," *Science and Technology of High Pressure,* Vol. 2, pp. 1047-1052 (2000).

[2] M. T. Vaughan, D. J. Weidner, Y. Wang, J. H. Chen, C. C. Koleda, and I. C. Getting, "T-cup: A new high-pressure apparatus for x-ray studies," Rev. High Pressure Sci. Technol. **7**, 1520-1522 (1998).

[3] M. L. Rivers, T. S. Duffy, Y. Wang, P. J. Eng, and S. R. Sutton, "A new facility for high-pressure research at the Advanced Photon Source," in *Properties of Earth and Planetary Materials at High Pressure and Temperature*, edited by M. H. Manghnani and T. Yagi (American Geophysical Union, Washington, DC, 1998), pp. 79-88.

[4] D. L. Decker, "High-pressure equation of state for NaCl, KCl, and CsCl," J. Appl. Phys. **42**, 3239-3244 (1971).

[5] O. L. Anderson, D. G. Isaak, and S. Yamamoto, "Anharmonicity and the equation of state of gold," J. Appl. Phys. 65, 1534-1543 (1989).

[6] T. Gaparik, "Phase relations in the transition zone," J. Geophys. Res. **95**, 15751-15769 (1990).

[7] D. J. Weidner and E. Ito, "Elasticity of $MgSiO_3$ in the ilmenite phase," Phys. Earth Planet. Int. **40**, 65-70 (1985).

[8] T. Ashida, S. Kume, E. Ito, and A. Navrotsky, "$MgSiO_3$ ilmenite: heat capacity, thermal expansivity, and enthalpy of transformation," Phys. Chem. Minerals **16**, 239-245 (1988).

[9] D. J. Weidner and Y. Wang, "Chemical and Clapeyron induced buoyancy at the 660 km discontinuity," J. Geophys. Res. **103**, 7431-7442 (1998).