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Thermal equation of state of superhydrous phase B to 27 GPa and 1373 K

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Abstract

Pressure–volume–temperature relations have been measured to 27 GPa and 1373 K for superhydrous phase B ($Mg_{10}Si_3O_{14}(OH)_4$) using synchrotron X-ray diffraction with a multi-anvil apparatus at the SPring-8 facility. The analysis of room-temperature data fitted to a third-order Birch–Murnaghan equation of state (EOS) yields $V_0 = 623.38 \pm 0.39$ Å^3; $K_0 = 138.7 \pm 3.0$ GPa and $K' = 4.9 \pm 0.3$, when pressure was calibrated using the Au EOS of Anderson et al. [Anderson, O.L., Issak, D.G., Yamamoto, S., 1989. Anharmonicity and the equation of state for gold. J. Appl. Phys. 65, 1534–1543]. These values are consistent with subsequent thermal EOS analysis and previous estimations for superhydrous phase B. A fit of *P*–*V*–*T* data to high-temperature Birch–Murnaghan EOS yields $V_0 = 623.47 \pm 0.37$ Å^3; $K_0 = 135.8 \pm 2.6$ GPa; $K' = 5.3 \pm 0.2$; $(\partial K_T/\partial T)_P = -0.026 \pm 0.003$ GPa/K and zero-pressure thermal expansion $\alpha = a_0 + a_1 T$ with $a_0 = 3.2\ (1) \times 10^{-5}$ K^{-1} and $a_1 = 1.2\ (4) \times 10^{-8}$ K^{-1}. The Anderson–Grüneisen parameter is estimated to be $\delta_T = 5.4$. A fit to the thermal pressure EOS gives $V_0 = 623.50 \pm 0.36$ Å^3; $K_0 = 135.3 \pm 2.3$ GPa; $K' = 5.3 \pm 0.2$; $(\partial K_T/\partial T)_V = -0.002$ (2) GPa/K and $\alpha_0 = 3.8\ (2) \times 10^{-5}$ K^{-1}. The lattice dynamical approach using a Mie–Grüneisen–Debye EOS yields Grüneisen parameter $\gamma_0 = 1.33 \pm 0.05$ and $q = 2.03 \pm 0.35$, if the Debye temperature θ_0 is fixed at 860 K, as calculated from sound velocities. The analysis of axial compressibility and thermal expansivity indicates that the *a*-axis is more compressible ($K_{Ta} = 126 \pm 3$ GPa) than the *b*-axis ($K_{Tb} = 137 \pm 1$ GPa) and *c*-axis ($K_{Tc} = 143 \pm 1$ GPa). The temperature dependence of K_T is stronger for the *b*-axis, $(\partial K_T/\partial T)_{Pb} = -0.033$ (3) GPa/K, than for the *a*-axis $(\partial K_T/\partial T)_{Pa} = -0.028$ (7) GPa/K and *c*-axis $(\partial K_T/\partial T)_{Pc} = -0.017$ (3) GPa/K. The present EOS enables us to accurately estimate the density of superhydrous phase B in a pyrolitic composition under deep mantle conditions. The density reduction of hydrated subducting slab (∼1 wt.% H_2O) at the top of the lower mantle due to the presence of ∼18% of superhydrous phase B would be 1.9–2.1%. Accordingly, a model slab that is homogeneously hydrated may be buoyant relative to the surrounding mantle rocks and would not penetrate to the deep lower mantle.

Keywords: Superhydrous phase B; Equation of state; Synchrotron X-ray diffraction; Mantle; Subduction

1. Introduction

Recent geophysical data indicates that at least locally, the upper mantle and transition zone may be substantially hydrated. The evidence for this come from (1) electrical

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conductivity anomalies observed in the transition zone and the upper mantle along with studies of hydrogen diffusivity and electrical conductivity of mantle minerals (e.g. Fukao et al., 2004; Tarits et al., 2004; Huang et al., 2005; Koyama et al., 2006; Hae et al., 2006); (2) seismic imaging of changes in depth or broadening of upper mantle discontinuities at 410, 520 and 660 km (e.g. Castle and Creager, 1998; Collier et al., 2001; Van der Meijde et al., 2003), in conjunction with experimental data (e.g. Smyth and Frost, 2002; Frost, 2003; Litasov et al., 2005a, 2006; Ohtani and Litasov, 2006); (3) thermal modeling of subducted slabs (e.g. Kirby et al., 1996; Kerrick and Connolly, 2001), and phase relations in hydrous mantle compositions (e.g. Ohtani et al., 2000, 2001, 2004; Litasov and Ohtani, 2003a, in press; Kawamoto, 2004, 2006; Komabayashi et al., 2004; Komabayashi and Omori, 2006). In addition, observations of low-velocity zones on the top of the 410 km discontinuity may indicate the existence of trapped melt (e.g. Revenaugh and Sipkin, 1994; Song et al., 2004), which is likely to be hydrous according to differences in water solubility between olivine and wadsleyite (e.g. Kohlstedt et al., 1996; Chen et al., 2002; Smyth et al., 2006), and the melting temperatures of anhydrous and hydrous peridotite mantle (e.g. Litasov and Ohtani, 2002, 2003b). In support of the latter statement, Matsukage et al. (2005) and Sakamaki et al. (2006) showed that hydrous basaltic and peridotitic melt is denser than surrounding mantle near 410 km depth and can be accumulated atop of this discontinuity.

High-pressure experiments reveal the existence of several dense hydrous magnesium silicates (DHMS) stable along subduction slab geotherms in a peridotite composition. After the breakdown of serpentine and chlorite at 6 GPa the most important of them, with increasing pressure, are phase A, phase E, superhydrous phase B, and phase D. Although these phases have not been identified in natural samples, they could be important carriers of subducted water to the deep mantle (e.g. Frost, 1999; Ohtani et al., 2004; Komabayashi and Omori, 2006). The stability field of superhydrous phase B (hereafter referred as SuB) suggests that it might be the most important phase in the hydrated parts of the transition zone and the uppermost part of the lower mantle (Gasparik, 1993; Irifune et al., 1998; Ohtani et al., 2001, 2003, 2004).

SuB has a composition $Mg_{10}Si_3H_4O_{18}$, a zero-pressure density of 3.33 g/cm^3, and contains 5.8 wt.% H_2O (Pacalo and Parise, 1992). SuB synthesized at 20 GPa and 1673 K has orthorhombic symmetry with space group *Pnnm* (Pacalo and Parise, 1992). However, Kudoh et al. (1994) determined a lower-symmetry for SuB ($P2_1mn$) in a sample synthesized at 17 GPa and 1000 °C. Recently Koch-Müller et al. (2005) defined two symmetries for SuB synthesized at 22 GPa and different temperatures and noted that SuB synthesized at 1400 °C (HT polymorph) has space group *Pnnm*, whereas that synthesized at 1200 °C (LT polymorph) has space group *Pnn*2, which is slightly different from that of Kudoh et al. (1994), but supports that a lower temperature polymorph of SuB crystallizes in a lower-symmetry space group.

The stability of SuB was studied in the simple MSH systems (Gasparik, 1993; Irifune et al., 1998; Ohtani et al., 2001, 2003, 2004; Litasov and Ohtani, 2003a). Gasparik (1993) observed SuB, coexisting with stishovite, to be stable between 16 and 24 GPa at 1073–1673 K. In hydrous peridotite, SuB is stable together with phase D at pressures above 20 GPa and temperatures up to 1373 K (Kawamoto, 2004; Litasov et al., 2007). Ohtani et al. (2003) determined the decomposition boundary of SuB to phase D, Mg-perovskite, and periclase at high pressures and located it at about 28 GPa and 1400 K.

There are several reports on the thermoelastic properties of SuB (Kudoh et al., 1994; Pacalo and Weidner, 1996; Crichton et al., 1999; Inoue et al., 2006); however, these datasets collectively have covered a limited *P–T* space than is desirable for accurate determinations of physical properties and for constraining the distribution of water in the mantle by comparison with seismic observations. For example, sound velocities and aggregate elastic properties were measured only at ambient conditions (Pacalo and Weidner, 1996). Here we report comprehensive results of measurements of lattice parameters of SuB at pressures to 27 GPa and temperatures to 1373 K using *in situ* X-ray diffraction with synchrotron radiation. Based on the resulting thermoelastic parameters of the EOS, we discuss effect of SuB on the density of subducting slabs at high pressures and temperatures.

2. Experimental procedure

The starting material was a pure oxide mixture corresponding to the composition of SuB. The H_2O was added as $Mg(OH)_2$. Before the experiment, the starting material was powdered with Au in a ratio of 20:1. The composition of SuB after *in situ* X-ray diffraction experiment is shown in Table 1.

In situ X-ray diffraction experiment was conducted at the synchrotron radiation facility 'SPring-8' in Hyogo prefecture, Japan. We used a Kawai-type multi-anvil apparatus, 'SPEED-1500', installed at a bending magnet beam line BL04B1 (Utsumi et al., 1998). Energy-dispersive X-ray diffractometry was conducted with a