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The equation of state of Al,H-bearing SiO₂ stishovite to 58 GPa

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Abstract We have determined the P-V equation of state of Al-rich H-bearing SiO₂ stishovite by X-ray powder diffraction at pressures up to 58 GPa using synchrotron radiation. The sample contained 1.8 wt% Al₂O₃ and up to 500 ppm H₂O, and had a composition that would coexist with Mg-silicate perovskite in a subducted slab. By fitting a third-order Birch-Murnaghan equation of state to our compression data, we obtained a bulk modulus $K_{T0} = 298(7)$ GPa with $K' = 4.3(5)$. With K' fixed to a value of 4, the bulk modulus $K_{T0} = 304(3)$ GPa. Our results indicate that Al³⁺ and H⁺ have a small effect on the elastic properties of stishovite. Compared with data obtained up to 43.8 GPa, peak intensities changed and we observed a decreased quality of fit to a tetragonal unit cell at pressures of 49 GPa and higher. These changes may be an indication that the rutile↔CaCl₂ transition occurs between these pressures. After laser annealing of the sample at 58.3(10) GPa and subsequent decompression to room conditions, the cell volume is the same as before compression, giving strong evidence that the composition of the recovered sample is also unchanged. This suggests that Al and H are retained in the sample under extreme P-T conditions and that stishovite can be an agent for transporting water to the deepest lower mantle.

Keywords Water in the mantle · High pressure · Synchrotron X-ray diffraction · Equation of state · Water-bearing stishovite

Introduction

The equation of state of water-bearing aluminous stishovite has become an important issue in relation to the density of subducting slabs, and the transport and retention of water in the mantle. As shown in numerous high pressure–high temperature (high-P/T) experiments on the phase relations of mid-ocean ridge basalt (MORB) under upper and lower mantle conditions, stishovite can compose up to 20 vol% of the subducted oceanic crust (e.g., Irifune and Ringwood 1993, 1994; Hirose 2002). The composition of stishovite formed in such an Al- and water-rich environment was shown to deviate significantly from pure SiO₂. In particular, it has been observed that several wt% of Al can be accommodated in stishovite via the coupled substitution: $\text{Si}^{4+} \rightarrow \text{Al}^{3+} + \text{H}^{+}$ (e.g. Pawley et al. 1993; Smyth et al. 1995; Panero et al. 2003, 2004). In order to determine the density of subducted slab material under lower mantle conditions, it is important to determine the bulk modulus of stishovite containing its most important minor elements.

A variety of experimental and theoretical studies have been conducted on the high-pressure elasticity and stability of pure stishovite. Most recent elasticity studies have converged on bulk modulus values close to the single-crystal Brillouin scattering result of $K_S = 316$ GPa (Weidner et al. 1982) and the value from the most recent compression study of $K_T = 309.9(11)$, and $\partial K_{T0}/\partial P = K' = 4.59(23)$ (Andraut et al. 2003). However, a review of the available literature shows that the value of K' is highly uncertain and varies from ~ 2 to ~ 6 (Fig. 1). The stability of pure stishovite is also uncertain. Numerous authors have reported a Landau-type phase transition from P4₂/mmm (rutile structure) to a Pnnm

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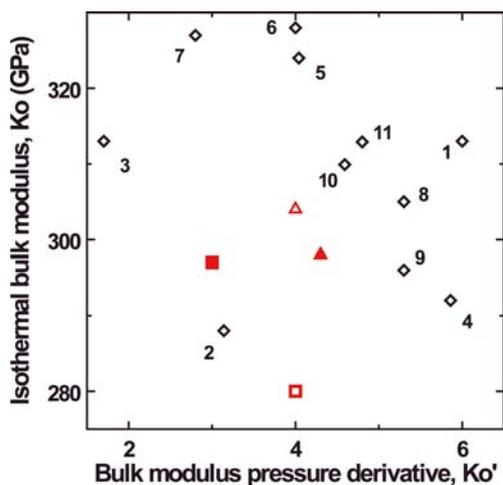


Fig. 1 The isothermal bulk modulus (K_T) and its pressure derivative (K') of pure and Al-bearing stishovite. *Squares* Ono et al. 2002; *triangles* this work (*filled* best fit, *empty* K' fixed at 4). *Empty diamonds* previous experimental and theoretical data on pure stishovite (1 Sugiyama et al. 1987; 2 Park et al. 1988; 3 Ross et al. 1990; 4 Keskar et al. 1991; 5 Cohen 1991; 6 Sherman 1993; 7 Jolly et al. 1994; 8 Li et al. 1996; 9 Liu et al. 1999; 10 Andraut et al. 2003; 11 Panero et al. 2003)

(CaCl₂ structure). However, the pressure at which this transition is reported to occur varies widely from study to study, ranging from ~43 GPa (Mao et al. 1994) to ~60 GPa (Andraut et al. 1998).

Ono et al. (2002) first reported results on the equation of state of Al-bearing stishovite. Their sample contained 2.1 wt% of Al₂O₃ and was compressed in Ar and NaCl pressure media up to 40 GPa. The sample was synthesized from a mixture of SiO₂ and Al(OH)₃ powders. Unfortunately, the water content of the sample was not specified. The resulting K_T and K' were shown to be 297(5) GPa and 3.0(3), respectively ($K_T = 282(2)$ GPa at K' fixed at 4).

In this paper, we report new measurements on the bulk modulus for an Al, H-rich stishovite synthesized from material with a composition analogous to natural MORB, and we discuss the role of Al³⁺ and H⁺ on the compressibility of Al,H-bearing stishovite.

Experimental procedures

A polycrystalline sample of Al–Fe-rich magnesium silicate perovskite + Al,H-bearing stishovite was synthesized at 26–27 GPa and 1,200°C using a Kawai-type (MA8) multi-anvil apparatus at Tohoku University. The sample assembly used in the present experiment is similar to that shown in Litasov and Ohtani (2002).

The starting material for the synthesis was a mixture of the oxides with a bulk composition close to the Al–Fe-rich Mg-perovskite (Al–Fe Pv) that forms from MORB at pressures above 26–27 GPa (Hirose and Fei 2002; Litasov and Ohtani 2004). Water was added to the charge to provide hydrous synthesis conditions, and as a means of promoting reaction kinetics and grain growth.

The resulting sample consisted of a mixture of perovskite and stishovite that are presumably close to or at chemical equilibrium with each other. X-ray diffraction did not reveal any majoritic garnet phase in the resulting mixture. The chemical composition of the Al,H-bearing stishovite was determined by electron microprobe (Jeol Superprobe JXA-8800; Table 1). The H⁺ content was estimated from SIMS analyses of other syntheses at similar conditions that yielded larger crystals (run K161, Table 1) (Litasov et al. 2003).

The synthetic perovskite + stishovite run product was disaggregated into small pieces and compressed between two diamonds to reduce the grains size (which was initially about ~5 μm on average). A rhenium gasket was pre-indented to a thickness of 35 μm and a 78 μm—diameter hole was drilled into it. The sample was cryogenically loaded with argon in a symmetrical type diamond-anvil cell. Small ruby chips were used for pressure measurement. Usually, several ruby chips contributed to the observed fluorescence signal, making it difficult to use the fluorescence peak width to characterize non-hydrostaticity. However, the ruby fluorescence peaks remained remarkably sharp, with clear separation of the R1 and R2 lines, over the pressure range of our experiment. Pressure was measured before and after each data collection. At the maximum pressure of 58.8(10) GPa, a Nd:YLF laser heating system (Shen et al. 2001) was used to heat the sample from both sides of the DAC to 1,500(100) K for less than 10 min. The laser beam was rastered over the entire sample area to ensure uniform heating. After heating the pressure was measured to be 58.3(10) GPa.

High-pressure angle-dispersive X-ray diffraction experiments were performed at the ID-13 GSECARS sector of the Advanced Photon Source (APS), Argonne National Laboratory (ANL). The incident wavelength was 0.3311 Å. The beam was collimated to a diameter of about 5 μm at FWHM. A MAR-CCD detector was used to record the diffraction signal. The observed diffraction patterns were integrated as a function of 2θ using the Fit2D program (Hammersley 1997), and

Table 1 Results of microprobe and SIMS analyses of synthetic stishovites given in wt% and ppm, respectively

n	Hirose et al. 1999	K-239 ^a 1	K-161 ^b 5
SiO ₂	96.82	96.72	96.73(106)
TiO ₂	0.11	0.08	0.04(1)
Al ₂ O ₃	1.26	1.82	2.21(21)
FeO	0.46	0.60	0.53(18)
MgO	0.38	0.09	0.06(3)
Total	99.59	99.31	99.57
n		–	6
H ₂ O, ppm		–	550(160)

Starting compositions are similar for K-239 and K-161. *n* is the number of analyses

^aUsed in this study

^bSee Litasov et al. 2003

showed both (Al, Fe)-Pv and stishovite diffraction peaks. A report on the equation of state of the perovskite phase is given elsewhere (Vanpeteghem et al. 2005). Typically, the diffraction patterns contained five to six clear stishovite peaks. The lattice parameters and unit cell volumes were determined using the program Unit Cell (Holland and Redfern 1997) and also by LeBail refinements using the GSAS package (Larson and von Dreele 1988) (Table 2).

Results and discussion

The zero-pressure volume of Al-bearing stishovite was measured outside the DAC and was found to be $V_0 = 46.782(10) \text{ \AA}^3$, which is slightly lower than that of Ono et al. (2002) ($V_0 = 46.816(13) \text{ \AA}^3$). The difference between the two volumes is probably related to the lower Al_2O_3 content of our sample (1.8 vs. 2.1 wt%). The initial zero-pressure volumes from this study and Ono et al. are both higher than that of pure stishovite reported by Andraut et al. (2003) ($V_0 = 46.5126(61) \text{ \AA}^3$, Fig. 2). To a very good first approximation, the effect of the coupled substitution of $\text{Al}^{3+} + \text{H}^+$ on the unit cell volume of stishovite can be described by a linear relationship: $V_0 = 46.512 + 0.146x$, where x is the Al_2O_3 content in wt%.

Although stishovite constituted only ~5–10% by volume of the bulk sample (the remainder consisting of perovskite), its diffraction peaks were strong and easily distinguished from those of (Al,Fe)-Mg perovskite (Fig. 3). All of the spectra used in our data analysis contained five or more stishovite peaks for determination of the unit cell volumes.

At pressures higher than 43.6 GPa the quality of the stishovite diffraction peaks decreased markedly. Data was collected at pressures of 49.0(18), 53.7(18) and 58.7(21) GPa, but in these patterns the intensities of stishovite diffraction peaks was low, and some of the peaks were broad as compared with the data at lower pressures. In addition, the weaker high- 2θ peaks were not easily

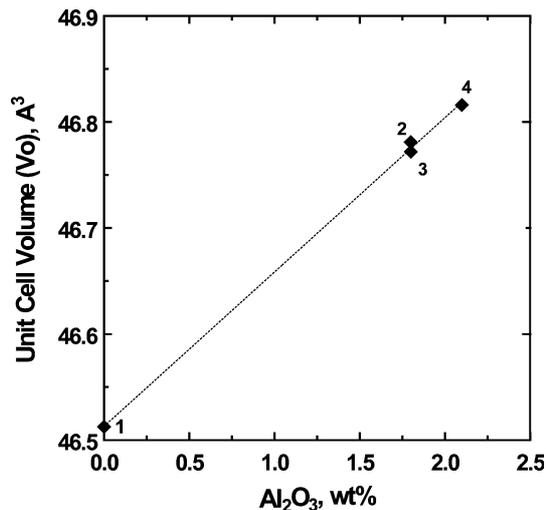


Fig. 2 Stishovite unit cell volume as a function of Al_2O_3 content. 1 Andraut et al. 2003 (pure stishovite); 2 this work (1.82 wt%) before high-pressure; 3 this work, after high-pressure; 4 Ono et al. 2002 (2.1 wt%)

distinguished from neighboring peaks of the (Al, Fe)-perovskite also present in this run. We do not include the data collected at pressures of 49.0(18), 53.7(18) and 58.7(21) GPa in our bulk modulus determination for stishovite, inasmuch as the spectra contained only two to three peaks that could be undoubtedly assigned to stishovite. However, after the sample was laser annealed at $P = 58.8(10)$ GPa, the quality of the stishovite pattern improved markedly, thus allowing us to determine the unit cell volume with greater certainty.

The sudden change of peak intensities observed at pressures higher than 44 GPa, as well as decreased quality of a tetragonal fit, may be indicative of the rutile \leftrightarrow CaCl_2 transition in Al-bearing stishovite. Recent observations in pure SiO_2 have placed this transformation at rather a high pressure of ~60 GPa (Andraut et al. 1998, 2003). In the case of Al-bearing stishovite it is possible that this transition may occur at lower pres-

Table 2 Unit-cell volumes of Al,H-bearing stishovite to 60 GPa

Pressure (GPa)	Unit cell volume (\AA^3)
0.0001	46.782(7)
2.1	46.431(56)
8.8(1)	45.404(38)
14.6(3)	44.745(112)
18.3(3)	44.316(115)
22.4(4)	43.905(120)
37.2(7)	42.409(78)
40.2(8)	41.941(246)
43.6(8)	41.711(174)
58.3(10)	40.559(83)
0.0001 ^a	46.774(5)

Parentheses show standard deviation

^aMeasured on recovered sample

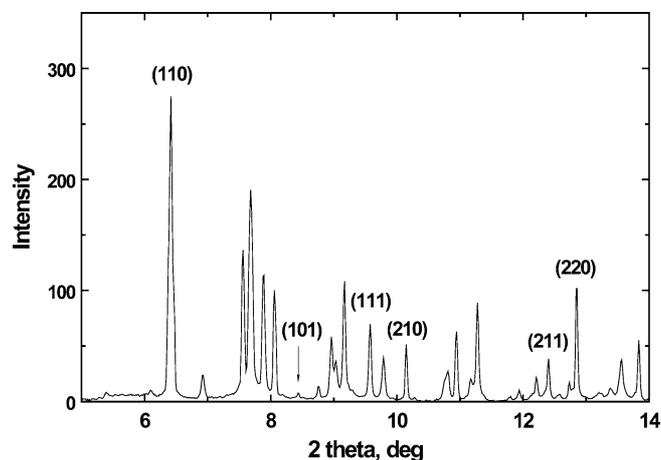
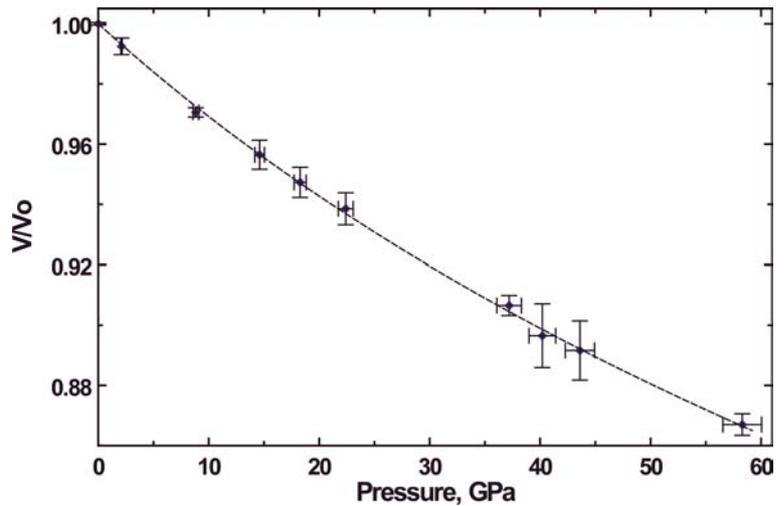


Fig. 3 Ambient pressure spectrum of perovskite and stishovite mixture used in this study. Stishovite peaks are marked

Fig. 4 Al,H-bearing stishovite unit cell volume data (*diamonds*) and third-order Birch-Murnaghan equation of state (*line*)



tures due to the presence of dissolved Al, close to the transition pressure obtained by Mao et al. (1994). As shown by Andraut et al. (2003), the unit cell volumes of CaCl₂-phase and stishovite (extrapolated) probably would not be resolved at $P > 60$ GPa, given our experimental uncertainties. An analysis of the spectrum at 58.3(10) GPa based on the rutile and CaCl₂ structures produced a volume difference of only 0.1 Å³. Thus, although the possibility of a phase transition to a CaCl₂ structure at $P > 43.6$ GPa cannot be excluded, making the structure at 58.3 GPa ambiguous, we present the cell volume obtained by a fit of the diffraction data to the rutile structure.

A least-squares regression of the P-V data to a third-order Birch-Murnaghan equation of state resulted in a bulk modulus of $K_T = 298(7)$ GPa with $K_T' = 4.3(5)$ (Fig. 4). With K_T' fixed at a value of 4, a least-squares fit yielded a value of $K_T = 304(3)$ GPa, which differs negligibly from the solution where K_T' is unconstrained. Our result for K_T is higher than that obtained by Ono et al. (2002) ($K_T = 281$ GPa at $K' = 4$). However our value of K_T is much closer to recent values reported for pure stishovite (which fall in the range $K_T = 309$ – 313 GPa (Andraut et al. 2003; Panero et al. 2003)), and to similar values obtained in a number of other previous studies (Fig. 1).

Recent studies by Ono et al. (2002), Chung and Kagi (2002), Panero et al. (2003, 2004) argue that natural stishovite produced by transformations in basalt would accommodate a few weight percent of trivalent cations such as Al³⁺, Cr³⁺, Fe³⁺, and V³⁺, thus being capable of storing hydrogen by the coupled substitution mechanism. In this case, stishovite can be one of the major carriers of water to the lower mantle.

The bulk modulus of Al,H-bearing stishovite obtained by Ono et al. (2002) is considerably lower than that of pure stishovite. Our result is in qualitative agreement, showing that the presence of Al³⁺ and H⁺ in the stishovite structure does reduce bulk modulus. However, the effect is smaller in magnitude than obtained by Ono

et al. (2002). Nevertheless, a lower bulk modulus would make stishovite denser at the bottom of transition zone (compared with pure SiO₂ stishovite), thus still making the density balance more favorable for slabs to penetrate into the lower mantle. We further note that in our experiments the sample was annealed at far higher pressures and temperatures than the original synthesis conditions of the sample. Nevertheless, the unit cell volume of the recovered sample is the same as before our compression experiment. The equivalence of volumes before and after heating at high pressure is significant, because there is a clear dependence of the cell volume on Al content. This strongly suggests that the Al (and likely H) content of our sample did not change over the course of the laser heating, even in the presence of (Al,Fe)-Pv. Our observations reinforce the notion that considerable amounts of water can be retained in stishovite under lower mantle conditions, and that stishovite can be an important transporting agent of Al and H to the deepest levels of the lower mantle.

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