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Thermal equation of state and stability of $(Mg_{0.06}Fe_{0.94})O$

June K. Wicks [a,c,*], Jennifer M. Jackson [a], Wolfgang Sturhahn [a], Kirill K. Zhuravlev [b], Sergey N. Tkachev [b], Vitali B. Prakapenka [b]

[a] *Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, USA*
[b] *Center for Advanced Radiation Sources, University of Chicago, Chicago, IL 60637, USA*
[c] *Department of Geosciences, Princeton University, Princeton, NJ, USA*

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ABSTRACT

We present the pressure–volume–temperature (P–V–T) equation of state of polycrystalline $(Mg_{0.06}Fe_{0.94})O$ (Mw94) determined from laser-heated X-ray diffraction experiments up to 122 GPa and 2100 K, conditions approaching those of the deep mantle. We conducted two sets of experiments, one with an *in situ* Fe metal oxygen fugacity buffer and one without such a buffer. The internal pressure markers used in these experiments were *B*2-NaCl and *hcp*-Fe in the buffered experiment and *B*2-NaCl in the unbuffered experiment. In the sampled P–T range of the high temperature part of this study, only the *B*1 structure of Mw94 was observed, indicating that the addition of Mg to FeO stabilizes the *B*1 phase with respect to the *B*8 phase at these conditions. Both datasets were fit to a Birch–Murnaghan and Mie–Grüneisen–Debye thermal equation of state using a new open-source fitting routine, also presented here. Analysis of these data sets using the same internal pressure marker shows that the P–V–T data of Mw94 obtained in the unbuffered experiment are well explained by the equation of state parameters determined from the buffered data set. We have also compared the thermal equation of state of Mw94 to that of wüstite and conclude that Mw94 has measurably distinct thermoelastic properties compared with those of wüstite. We use the results obtained in the buffered experiment to determine the density and bulk sound velocity of Mw94 at the base of the mantle and compare these values to geophysical observations of ultralow-velocity zones.

1. Introduction

1.1. Motivation

Iron-poor members of the periclase–wüstite (MgO–FeO) solid solution may comprise up to 20% of the Earth's lower mantle. According to the "pyrolite" model, the chemistry of this phase contains 10–20% FeO (Ringwood, 1975). The simplest assumption is that the lower mantle is homogeneous, yet seismic studies reveal discontinuities and lateral heterogeneity in the deep mantle that suggest lateral chemical inhomogeneities (Garnero et al., 2007). Chemical analyses of magma associated with hotspot volcanism from mantle plumes reportedly sourced from the lower mantle also give evidence for chemical heterogeneity, promising a more complex lower mantle (Mukhopadhyay, 2012). To understand the role of (Mg,Fe)O in these variations, the thermodynamic and elasticity systematics of ferropericlase, $(Mg_{1-x}Fe_x)O$ with $x < 0.5$, has been extensively studied as a function of composition, pressure, and temperature. However, more iron-rich compositions of (Mg, Fe)O have not been explored in the same detail.

Ultralow-velocity zones (ULVZs) at the core–mantle boundary give insight into the chemical heterogeneity of the lowermost mantle. As their name implies, ULVZs are characterized by very low seismic wave velocities (10–30%) (e.g. Garnero and Helmberger, 1998; Helmberger et al., 2000; Rost et al., 2006; Sun et al., 2013). Requiring concomitant density increase and sound velocity decrease with respect to the surrounding mantle, ULVZs are best explained by Fe-enrichment. Recent considerations of a crystallizing primordial magma ocean show that enrichment of Fe in the lowermost mantle is possible, preserved as either iron-rich solids or residual melt (Labrosse et al., 2007; Lee et al., 2010; Nomura et al., 2011).

Incorporation of 40% Fe into magnesium silicate post-perovskite has been found to reduce shear wave velocities to 33% lower than that of the 1D Preliminary Reference Earth Model (PREM) (Mao et al., 2006; Dziewonski and Anderson, 1981). An iron-rich oxide, namely $(Mg_{0.16}Fe_{0.84})O$, also has low shear wave velocities—50% lower than that of PREM (Wicks et al., 2010). Partial melting has

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* Corresponding author at: Department of Geosciences, Princeton University, Princeton, NJ, USA.

E-mail address: jwicks@princeton.edu (J.K. Wicks).

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also been suggested as a plausible mechanism (Williams et al., 1998; Lay et al., 2004; Labrosse et al., 2007).

Dynamic models have been used to explore the stability and topology of ULVZs to differentiate the observable characteristics of various candidate assemblages. Hernlund and Tackley (2007) found that the amount of partial melt required to decrease the sound velocities of a phase assemblage to match ULVZs would percolate and pool at the base of the mantle, a result that could be prevented if the ULVZ were stirred (Hernlund and Jellinek, 2010). Dynamic models exploring solid ULVZs show that ULVZ shape can be correlated to chemical density anomaly, which in turn can be used to explore the tradeoff between density and sound velocities of (Mg,Fe)O and bridgmanite (Bower et al., 2011; Sun et al., 2013).

We are motivated, therefore, to measure the pressure–volume–temperature equation of state of iron-rich (Mg,Fe)O, so that the density of iron-rich ULVZs can be properly modeled, and the relationship between sound velocity and density can further constrain the composition of ULVZs.

1.2. Previous experimental studies

Previous pressure–volume–temperature (*P*–*V*–*T*) studies have shown that the MgO–FeO solid solution is complicated by the existence of phase transitions, a spin transition, and defect clustering as a function of FeO component (e.g. Lin et al., 2003; Fei et al., 2007a; Lin et al., 2005; Speziale et al., 2005; Kantor et al., 2009; Mao et al., 2011). The MgO endmember is known to be cubic beyond the pressure and temperature conditions of the Earth's mantle (Duffy and Ahrens, 1993). The FeO endmember is thought to be cubic at the pressures and temperatures of the interior of the Earth, but at lower temperatures is found to transform to a rhombohedral structure at moderate pressures (e.g. Shu et al., 1998) and to the *B*8 NiAs structure at higher pressures (e.g. Fei and Mao, 1994; Fischer et al., 2011b).

At 300 K, iron-rich (Mg,Fe)O undergoes a cubic to rhombohedral phase transition at 8–40 GPa, with a phase transition pressure sensitive to both composition and hydrostaticity. Studies of the bulk modulus at 0 GPa as a function of composition show differing trends due to sample stoichiometry. Studies of non-stoichiometric, iron-rich (Mg,Fe)O show that both K_S and K_T decrease as a function of Fe concentration (Jacobsen et al., 2002; Richet et al., 1989), where K_S is determined from measurements of volume, composition, and of V_P and V_S using ultrasonic interferometry, and K_T is determined in a *P*–*V* compression study. The trend is opposite for stoichiometric samples, where ultrasonic interferometry studies for iron-poor samples display a positive trend of K_S with increasing iron content (Jacobsen et al., 2002). In the iron endmember, K_T does indeed depend on stoichiometry, with $Fe_{0.99}O$ being much less compressible than $Fe_{<0.98}O$ (Zhang and Zhao, 2005).

Thermal expansion, $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$, has been shown to be insensitive to Fe content for Mg-containing ferropericlase (Zhang and Kostak, 2002; Westrenen et al., 2005; Komabayashi et al., 2010; Mao et al., 2011). Yet, it appears to be sensitive to defect concentration. In the Fe end member, α is about 30% larger for $Fe_{0.942}O$ than $Fe_{0.987}O$ at pressures and temperatures up to 5.4 GPa and 1073 K (Zhang and Zhao, 2005). In this study, we aim to determine the *P*–*V*–*T* equation of state for $(Mg_{0.06}Fe_{0.94})O$ at conditions approaching those of the deep mantle to constrain the thermoelasticity of iron-rich (Mg,Fe)O and to see if these aforementioned trends apply to iron-rich (Mg,Fe)O.

1.3. Experimental considerations

In this paper we discuss two types of experiments, "buffered" and "unbuffered". In previous high-*PT* experiments on wüstite, an *in situ* Fe metal oxygen buffer has been used (Fischer et al., 2011b; Seagle et al., 2008; Ozawa et al., 2010). The motivation of using such a buffer has been to decrease the vacancy population of wüstite at high pressures and temperatures, as some studies indicate that the thermoelastic properties of wüstite vary as a function of vacancy concentration (Zhang and Zhao, 2005).

2. Materials and methods

Polycrystalline $(Mg_{0.06}{}^{57}Fe_{0.94})O$ was synthesized from ^{57}Fe (95% enriched, *Isoplex*) and MgO powders in a 1 atm gas-mixing furnace at 1673 K for two runs of 20 h each. A H_2/CO_2 gas mixture was used to control the oxygen fugacity of the synthesis to just above that of the iron-wüstite fugacity buffer ($\log f_{O_2} = -9$). Sample composition was measured using a JEOL-JXA-8200 electron microprobe, reporting a composition of $(Mg_{.058(1)}Fe_{.942(1)})O$, where the number in parentheses is the error on the last digit. A conventional Mössbauer spectrum (Fig. 1, inset) caps the ferric content at 5% of the total iron, thus capping the vacancy concentration at 5%.

Two experiments were conducted in this study. For the unbuffered experiment, a symmetric diamond anvil cell with 300 μm-culet diamonds was prepared. $(Mg_{0.06}Fe_{0.94})O$, hereafter referred to as Mw94, was lightly ground with NaCl powder (1:1 by volume) in an agate mortar under ethanol, allowed to dry, then pressed into a pellet. This mixture was loaded between two thin NaCl plates (<10 μm), and the remaining space in the rhenium gasket sample chamber was filled with neon using the COMPRES/GSECARS gas-loading system (Rivers et al., 2008). To keep the NaCl dehydrated, the pellet was consistently stored in a desiccator when not in use, and the loaded diamond anvil was placed under vacuum for about one hour and purged with argon before being put into the gas-loading system.

We conducted a second experiment with an *in situ* Fe metal oxygen buffer for comparison. In this second, buffered, high pressure experiment, 250 μm-culet diamonds were used. Otherwise, the preparation differed in that the sample pellet (Mw94 and NaCl) also included Fe metal (1:1 Mw94:Fe by weight) as an *in situ* oxygen buffer and pressure marker. Thus, both experiments contained an intimate mixture of Mw94 and NaCl in the sample pellet, so that NaCl may be used as a common pressure marker to compare the results of the buffered and unbuffered experiments.

The high temperature powder X-ray diffraction (XRD) experiments were conducted at the 13-ID-D beamline (GeoSoilEnviroCars) at the Advanced Photon Source, Argonne National Laboratory. Using an incident X-ray beam of $\lambda = 0.3344$ Å and focus spot size of 4 μm × 4 μm, angle-dispersive X-ray diffraction patterns were recorded onto a MAR165 CCD detector and subsequently integrated using Fit2D (Hammersley et al., 1996). CeO_2 was used to calibrate the sample to detector distance at 1 bar. Samples were compressed to about 35 GPa at room temperature before heating. High temperatures were achieved *in situ* by laser heating from both sides by 1.064 μm Yb fiber lasers with 'flat top' profiles (Prakapenka et al., 2008) and temperatures were determined spectroradiometrically (e.g. Heinz and Jeanloz, 1987; Shen et al., 2001) using the gray body approximation over the 600–800 nm range of thermal emission. Temperatures were measured during the collection of the diffraction patterns. In the buffered experiment, only the upstream temperatures were used due to technical difficulties with the downstream temperature determinations. The diffraction peaks were relatively sharp compared to ambient temperature data, indicating that temperature gradients are likely small. Example XRD patterns are shown in Fig. 1.

The 2θ angles corresponding to lattice reflections of $(Mg_{0.06}Fe_{0.94})O$, NaCl, Fe, and Ne were determined by fitting the patterns with Voigt peaks using Igor Pro (WaveMetrics, Lake