High pressure generation and investigation of the spin transition of ferropericlase (Mg_{0.83}Fe_{0.17})O

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Abstract. High pressure generation has been tried by using the Kawai-cell equipped with sintered diamond cubes in conjunction with investigation of the spin transition in Fe^{2+} of (Mg_{0.83}Fe_{0.17})O (ferropericlase, Fp). The Kawai-cell was squeezed in the DIA type press SPEED mkII installed at SPring-8. The volumes of the Fp and Au pressure standard were simultaneously determined by in situ X-ray diffraction using the synchrotron radiation. The maximum attainable pressure has reached 90 GPa at 300 K based on Anderson et al.’s Au scale [4]. The P-V data of (Mg_{0.83}Fe_{0.17})O were acquired at 300 K and 700 K up to 90 GPa. From detailed analysis of the compression data, it is suggested that the spin transition proceeds over pressure ranges from 50 to 70 GPa at 300 K and from 50 to 75 GPa at 700 K.

1. Introduction

A marked advantage of the Kawai-type multi anvil apparatus (KMAA) over the diamond anvil cell (DAC) is its much larger sample volume, which makes it possible to conduct experiments under much precisely controlled P-T conditions. A disadvantage of the KMAA, on the other hand, is that the accessible pressure is limited to ca. 28 GPa so far as tungsten carbide (WC) is used as the anvil material. However, recently the maximum attainable pressure of the KMAA has progressively been rising by adopting sintered diamond (SD) for the cubic anvils [1].

High spin (HS) to low spin (LS) transition of Fe^{2+} in (Mg_{1-x}Fe_{x})O ferropericlase (Fp) occurring under lower mantle conditions have been attracted special attention, because the transition is considered to considerably affect geophysical and geochemical processes there [2]. The transition can be detected by observing an anomaly in the compression curve due to a drastic change in effective ionic radius of Fe^{2+} accompanied with the HS-LS transition [3]. In the present study, we have carried out high pressure generation in conjunction with acquisition of pressure (P)-volume (V) data of (Mg_{0.83}Fe_{0.17})O Fp. The spin transition in (Mg_{0.83}Fe_{0.17})O was reported to proceed over a pressure range ca. 40-70 GPa at room temperature [4], and theoretical calculation that higher temperature expands the range of transition pressure [5]. As recent our target in pressure generation is reaching 100 GPa, detection of the spin transition in Fp is most convenient subject to be carried out at the same time.
2. Experimental

High pressure experiments were conducted by squeezing the Kawai-cell equipped SD cubic anvils with 14 mm edge length and 1.0 mm truncation in the DIA-type press (SPEED Mk II) installed at SPring-8. An octahedral pressure medium of MgO + 5%Cr$_2$O$_3$ with an edge length of 4.7 mm was adopted. A cross section of the sample assembly is schematically shown in Fig. 1. A powdered mixture of (Mg$_{0.83}$Fe$_{0.17}$)O + 0.1 Au (in weight ratio) was directly put into a cylindrical heater of TiB$_2$ which was set at the center of the octahedron normal to the opposed triangle surfaces. Energy dispersive method was adopted for X-ray diffraction study to determine unit cell volumes for both the (Mg$_{0.83}$Fe$_{0.17}$)O and Au. Pressure was determined from the volume of Au based on the Anderson et al.’s [6] scale. The volume data were acquired first at 700 K and then at 300 K at constant press load up to 90.4 GPa.

3. Results and discussion

3.1 Pressure generation

We can see X-ray images of the sample and the thermocouple by the CCD camera through the TiB$_2$ heater. The anvil gap between the SD anvils is closing with increasing pressure, which, however, is still 0.4 mm at 57 GPa.

Performances of pressure generation at 300 K obtained in several runs are shown in Fig. 2. The maximum pressure 90.4 GPa was attained in run M726 which is read as 87.6 GPa and 95.5 GPa based on Shim et al.’s [7] and Tsuchiya’s [8] Au scales, respectively. Runs M139 and M456 were carried out by adopting SD cubes with a truncated edge corner of 1.5 mm. It should be noticed that the maximum pressure has been rising...
year by year; i.e., 63 GPa in 2004, 72 GPa in 2006, and 90 GPa in 2008.

However, in some runs, after pressure reached a limit of 65-70 GPa, it suddenly dropped by more than 5 GPa and the run blew out on further increase in load. Inspection of the recovered anvils of such runs revealed that serious subsidence occurred at the top portion close to the truncation of one or two anvils. The observation suggests that the subsidence causes the pressure drop and the blow out. Therefore improvement of toughness of SD is the most important factor to generate higher pressure safely.

3.2 Spin transition on compression curves of (Mg$_{0.83}$Fe$_{0.17}$)O Fp

![Graphs showing compression data for (Mg$_{0.83}$Fe$_{0.17}$)O Fp and fitting the 3rd Birch-Munaghan EoS’s.](image)

Fig. 3. Compression data for (Mg$_{0.83}$Fe$_{0.17}$)O Fp and fitting the 3rd Birch-Munaghan EoS’s. In the left-hand figures, all the data for both 300 and 700 K were well fitted to single EoS’s. However, the resultant $K_0$ and $K'_0$ values are contradictory to the literature [9]. In the right-hand figures, fitting up to 40 GPa assuming $K_0 = 4.0$ yield reasonable $V_0$ and $K_0$ values for both 300 and 700 K data. The data for higher pressures clearly deviates towards lower direction, indicating occurrence of the spin transition. For the LS regime of 70-90 GPa at 300 K and 75-90 GPa at 700 K, we tried to fit various EoS’s as shown in the insertion in the right-hand figures (see text for the details).
The P-V data for (Mg$_{0.83}$Fe$_{0.17}$)O acquired at 300 K and 700 K up to 90 GPa are shown in Fig. 3. Errors in determination of volume pressure are less than ±0.006 Å$^3$ and 0.4 GPa, respectively.

At first glance conspicuous ‘shift’ of the compression curves towards lower volume associated with the HS to LS transition of Fe$^{2+}$ [2,3] are not conspicuous at both 300 and 700 K. Therefore we tried to fit all the data to a single 3rd order Bich-Murnaghan (B-M) EoS. Actually the fitting was carried out fairly well over all data points to 90 GPa as shown by the solid lines in two left-hand side figures of Fig. 3. However, the fits result in unacceptably larger bulk moduli ($K_0$) and smaller its pressure derivatives ($K_0'$) compared to the literature values [9] for both the data at 300 and 700 K (see the insertion).

We tried to fit the B-M EoS with $K_0'$ = 4 to the data up to 40 GPa, which are successfully performed resulting in reasonable values of zero pressure volume $V_0$ and $K_0$ for Fp (Mg$_{0.83}$Fe$_{0.17}$)O in the HS regime at 300 and 700 K [10]. However the volume data at pressures higher than 50 GPa at 300 and 700 K clearly deviate towards smaller volume as shown in two right-hand side figures of Fig. 3. The feature can be regarded as the sign of onset of spin transition following the previous works [2, 3]. For the data at 70-90 GPa and 300 K and those at 75-90 GPa in the LS regime, we tried to fit various EoS’s with resultant parameters indicated as insertions in the figures. The broken line (LS) in the upper left figure (300 K) represents EoS proposed for the LS regime by Lin et al. [4], and that in the lower left figure (700 K) is result of fitting of the B-M EoS with $K_0'$ = 4, which yields $V_0$ = 74.15 Å$^3$ and $K_0$ = 172.2 GPa. We also tried to fit the EoS’s of MgO to the LS data following the Fei’s view [3] that the effective ionic radius of Fe$^{2+}$ in the LS state is close to that of Mg$^{2+}$. We adopted $V_0$ and $K_0$ values recently reported by Jacobsen et al. [11] together with their temperature dependence [9, 12]. These EoS’s are shown as the dotted curves in the figures. All the fittings seem to represent the LS data fairly well. It is evident that, in order to specify the parameters of Fe$^{2+}$ in the LS state, acquisition of LS data up to still higher pressure is required.

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References

[1] Ito, E. 2007, Theory and Practice-Multianvil Cells and High-Pressure Experimental Methods, In: Treatises on Geophysics, 2, edited by G. D. Price and G. Schubert, Elsevier B. V. 197-230.
[2] Lin, J-F and Tsuchiya, T, 2008, Phys. Earth Planet. Inter., 170, 248-259.
[3] Fei, Y et al., 2007, Geophys. Res. Lett., 34, doi: 10.1029/2007GL030712.
[4] Lin, J.-F., et al., 2005, Nature, 436, doi: 10.1038/nature03825.
[5] Tsuchiya T et al., 2006, Phys. Rev. Lett., 96, 198502.
[6] Anderson, O L, 1989, J. Appl. Phys., 65, 1534-1543.
[7] Shim, S-H et al., 2002, Earth Planet. Sci. Lett., 203, 729-739.
[8] Tsuchiya, T. 2003, J. Geophys. Res., 108, doi: 10.1029/2003JB002446.
[9] Anderson, O L and Isaak D G1995, Elasticity of Minerals, Glasses, and Melts, In: Mineral Physics & Crystallography, A Handbook of Physical Constants, edited by T. J. Ahrens, AGU Reference Shelf 2, 64-97.
[10] Lin, J-F et al., 2005, Nature, 436, 377-380.
[11] Jacobsen, S D et al., 2008, Am. Min., 93, 1823-1828.
[12] Fei, Y, D G1995, Elasticity of Minerals, Glasses, and Melts, In: Mineral Physics & Crystallography, A Handbook of Physical Constants, edited by T. J. Ahrens, AGU Reference Shelf 2, 29-44.