High Pressure Phase Equilibria of Fe2O3

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The maximum attainable pressure of the Kawai-type apparatus has been extended to higher than 63 GPa by employing sintered diamond (SD) cubes instead of the traditional tungsten carbide ones (Ito et al. 2005). The pressure generation was confirmed at room temperature based on in situ X-ray diffraction study of the pressure standard material (MgO) using synchrotron radiation at SPring-8. However, we do not have any conventional pressure fixed point for calibration in each laboratory at pressures higher than the beta-omega transition of Zr (33 GPa). In order to develop fixed points to higher pressures we have examined several candidate materials such as Mg, AlN, GaN etc. Here we report high pressure phase equilibria of Fe2O3 which can serve as a fixed point at higher than 50 GPa.

All the experiments were carried out by compressing the Kawai-cell of SD cubes with edge length of 14 mm and 1.5 truncated corner with the aid of a DIA-type press SPEED mk-II installed at Spring-8. Powdered sample of hematite Fe2O3 (99.9 % purity) loaded into a MgO sleeve (the pressure standard) was put into a cylindrical heater of LaCrO3 or metal which is aligned parallel to the incident X-ray beam in the octahedral pressure medium of MgO5%Cr2O3 with 5.0 mm edge length. Phase identification of the sample and pressure determination was performed by in situ energy dispersive X-ray diffraction method. A polychromatic X-ray collimated to 100 microns vertically and 50 microns horizontally was introduced to the sample and the MgO standard (capsule), independently. The diffracted beam was detected by a Ge solid-state-detector (SSD) through a collimator of 50 microns width to ensure a diffraction angle 2theta which was calibrated at ambient conditions with accuracy of plus minus 0.001degree. Pressure determination was based on the Matsui et al.'s (2000) MgO scale. Phase equilibria was examined up to 50 GPa and 1400 K. Electric resistance was also measured at 300 K and to 58 GPa by the two probe method.

Phase equilibria: Hematite (phase I) transformed successively to phases II and III with increasing pressure. As to the structure of phase II, both the perovskite and Rh2O3 (II) structures were consistent with the observed diffraction profile of phase II in terms lattice parameters and the general trend in the peak intensity. However, the detailed comparison of the observed with the calculated intensity profiles for both the structures suggested the latter structure is more preferable than the former. Structure of phase III has not been determined at present because the diffraction profile was superposed by weak diffractions from phase II. The phase boundaries were determined by observing growth of the next phase in the diffraction pattern. However a reverse transformation from phase II to I was not observed. Phase boundaries between I-II and II-III are expressed by P(GPa) = -0.014T(K) + 43.3 and P(GPa) = -0.006T(K) + 49.8, respectively.

Electric resistance: Electric resistance of Fe2O3 changed from few hundreds mega ohms at several GPa to a few ohms at 58 GPa. The change was generally gradual. However, the change in a pressure range of 2 GPa around 54 GPa is characteristically rapid, extending to about four orders magnitude. It should be noted that the X-ray diffraction of the Fe2O3 sample showed no evidence for occurrence of phase transformation up to 58 GPa. The calculation of the electronic band structure assuming the hematite structure, on the other hand, indicates that the energy gap between valence and conduction bands becomes smaller with pressure and almost closes at 55 GPa. The abrupt resistance change can be usable as a pressure fixed point at ca. 54 GPa.