Dislocation microstructures of ferropericlase at high pressures.

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Introduction

The rheological behavior of magnesium silicate perovskite (MgPv) and ferropericlase (Fp) at high pressure and temperature is indispensable for discussing dynamics of the Earth's lower mantle. Deformation of plastically weaker Fp than coexisting MgPv is likely to be responsible for bulk strain of the rock, if it develops a sufficient grain connectivity in a fabric development at high temperature. Particularly, lattice preferred orientations (LPO) of the polycrystalline Fp can be important to explain observed seismic anisotropies in the bottom of Earth's lower mantle, so called "D" layer". For understanding deformation mechanisms to create a LPO pattern, dislocation microstructures of Fp under lower mantle conditions are very important, because dislocation creep mechanisms could become one of dominant mechanisms in the D" layer. To discuss the influence of pressure on the active slip system in Fp, we report dislocation microstructures of Fp in a pyrolite mineral assemblages synthesized at 44 GPa and 2073 K [1], in comparion to those of lower pressure samples, by using TEM.

Results and Conclusion

In the pyrolite mineral assemblage, MgPv contained a few dislocations and Fp displayed a high density of dislocations (Figure 1). In a Fp grain, straight long screw dislocations with $\boldsymbol{b} = 1/2[1-10]$ were nucleated on the (110) and/or (11-1) planes (Figure 1a) and the other dislocations with $\boldsymbol{b} = 1/2[01-1]$ was also along the (011) plane (Figure 1b) in the same grain.

Dislocation microstructures of Fp synthesized at high temperatures and different pressures from 0 to 44 GPa were compared in the TEM images. The highest pressure sample indicate that an active slip system of $1/2 < 110 > \{110\}$ in Fp, consistent with previous experimental studies at lower pressures. The characteristic textures of straight screw dislocations along a specific crystal orientation strongly imply that the Peierls friction for movement of 1/2 < 110 > dislocations in Fp increases with increasing pressure. The dislocation microtextures are compared with a current theoritical study of dislocation mobilities in MgO [2].

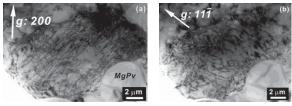


Figure 1: Bright field TEM micrographs of Fp in a pyrolite mineral assemblage at 44 GPa and 2073 K.

[1] Irifune, Shinmei, McCammon, Miyajima, Rubie & Frost (2010) *Science* **327**, 193-195. [2] Cordier, Amodeo & Carrez (2012) *Nature* **481**, 177-180.

Local structure of Al in Al-Zn hydroxide coprecipitates

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Al-Zn hydroxide coprecipitate

Zn²⁺ adsorption onto alumina, which represents the behavior of heavy metal ions in soil systems, can be devided into three processes; adsorption due to formation of inner-sphere complex, desorption of Zn²⁺ accompanied with dissolution of Al³⁺, and then re-adsorption of Zn^{2+} [1]. Recently, the final product of the above three processes was found to have AlO₄ species in its structure [2]. The formation of AlO₄ was induced by Zn²⁺ adsorption and it relats deeply to the dissolution and re-adsorption of Al3+. There are two possible assignement for the AlO4 species; one is Keggin-like structure, and the other is substitution of Zn2+ by Al3+ in the structure of zinc aluminate, ZnAl₂O₄. Because the adsorption experiments were performed at constant pH of 6.5, where Keggin is not stable, the formation of Keggin-like structure seems to be unlikely. On the other hand, ZnAl₂O₄ is a member of the spinel family and Al³⁺ can substitute four coordinated Zn^{2+} in its structure. Zinc aluminate is known to be prepared by calcining Al-Zn hydroxide coprecipitates [3]. In the process of Zn2+ adsorption onto alumina, it is possible that the desorbed Zn2+ and dissolved Al3+ coprecipitate to form zinc aluminate-like structure as the final products of adsorption. In order to examine this possibility, Zn-Al hydroxide coprecipitates having various Zn/Al ratios were prepared and chemical states of Al was compared to the final product of adsorption using ²⁷Al MAS NMR.

²⁷Al MAS NMR spectra of the coprecipitates

Figure 1 shows the ²⁷Al MAS NMR spectra of coprecipitates prepared by hydrolysis of mixed solution of zinc and aluminum nitrates. Peaks at around 60 ppm, which correspond to AlO₄ species, increased by decrease of Zn/Al ratios. Fig. 1 shows that the AlO₄ species can be formed by coprecipitation of Al and Zn, without calcination. AlO₄ species increased by lowering Zn/Al ratios.

Therefore, less Zn^{2+} seems to cause more isomorphic subsbitution by Al³⁺. The shape of ²⁷Al MAS NMR spectra of the coprecipitate with low Zn/Al ratio is almost identical to that of the final product of Zn^{2+} adsorption onto alumina. Therefore, it is highly possible that Zn^{2+} adsorption onto alumina induced the formation of Zn-Al hydroxide coprecipitate having zinc aluminate-like structure.

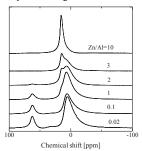


Figure 1: ²⁷Al MAS NMR spectra of the Zn-Al hydroxide coprecipitates

[1] Miyazaki et al, (2003) Geochem. Cosmoshim. Acta **67**, 3833-3844.

[2] Miyazaki et al, (2011) Goldschmidt, 08/3045.

[3] van de Laag et al, (2004) J. Eur. Ceram. Soc. 24, 2417-2424.