NMR measurement and lattice parameter determination of Al-containing MgSiO3 perovskite

Hiroshi Kojitani[1], Jonathan F. Stebbins[2], Masaki Akaogi[3], Alexandra Navrotsky[4]

[1] Dept. of Chemistry, Gakushuin Univ., [2] Geological and Environmental Sci., Stanford Univ., [3] Dept. of Chem., Gakushuin Univ., [4] UC Davis, Chem. Eng. and Materials Sci.

High-pressure and high-temperature experiments have shown the existence of Al- containing MgSiO3 perovskite with Mg/Si ratio grater than unity. EPMA observation of such Al-containing MgSiO3 perovskites that total cation number for the three oxygen basis exceeds two suggested that they contain oxygen vacancy. However the direct evidence for the oxygen vacancy has not been reported yet. Furthermore, it is not clear how the crystal structure of Al containing MgSiO3 perovskite is deformed by the oxygen vacancy. In this study, NMR measurement was performed to know oxygen coordination environment around Al3+ which gives the direct evidence for the oxygen vacancy. Also XRD measurement was made for investigating an effect of oxygen vacancy on deformation of the crystal structure of the perovskite.

Samples for NMR and XRD measurements were synthesized by using a Kawai-type multianvil high-pressure apparatus at Gakushuin University. NMR samples were prepared by heating the mixture of MgO, Al2O3 and SiO2 with the bulk composition of MgSi0.9Al0.1O2.95 at 27 GPa and 1873 K for 3 hours. XRD samples were synthesized by heating the mixture of MgO, Al2O3 and SiO2 with bulk compositions of MgSi0.9Al0.1O2.95 and 0.9Mg0.95Si0.95Al0.1O3 + 0.1MgO at 27 GPa and 1873-2073 K for 3 to 6 hours. XRD results of recovered samples showed that they consisted of single phase of perovskite. Compositions of them were also measured by EPMA.

In the NMR measurement, total 1.4 mg of polycrystalline samples were used. NMR spectra were collected at the high magnetic fields of 14.1 and 18.8 Tesla at Stanford University to enhance sensitivity for the small samples. Determination of lattice parameters of Al-containing MgSiO3 perovskites was made by using a powder X-ray diffractometer (Rigaku RINT-2500V, Cr K-alpha, 45 kV, 250 mA) at Gakushuin University. Synthetic samples were cooled by liquid nitrogen and then were powdered by crushing in a die. XRD measurements were performed with a scan step of 0.02 degree and a holding time of 10 seconds/step in the 2theta range of 20 to 140 degree.

Our NMR results indicate a new peak at chemical shift of about 15 ppm of which was not observed in the NMR spectra of a stoichiometric (Tschermakitic) Mg0.95Si0.95Al0.1O3 perovskite by Stebbins et al. (2001). It was also observed that relative intensity of a peak at about -20 ppm (from the dodecahedral site) to a peak at 5 ppm (from the octahedral site) was smaller than that by Stebbins et al. (2001). These results suggest that Al abundance in the eight-coordinated site in the nonstoichiometric perovskite is lower than that in the Tschermakitic perovskite of the same Al content and that new five coordination site produced by oxygen defect possibly exists in the nonstoichiometric perovskite.

Lattice parameters of the nonstoichiometric perovskite with the composition of MgSi0.9Al0.12.95 were determined to be a=4.7783(18), b=4.9351(8) and c=6.9142(22) angstrom. On the other hand, lattice parameters of the stoichiometric perovskite with Mg0.95Si0.95Al0.1O3 composition were obtained as a=4.7796(11), b=4.9370(5), c=6.9141(7) angstrom. The comparison between them shows that b-axis of the nonstoichiometric perovskite is smaller than that of the Tschermakitic perovskite without oxygen vacancy. Furthermore, XRD pattern of the nonstoichiometric perovskite sysntesized at 27 GPa, 2073 K indicates decrease of relative intensity of the (020) diffraction peak. Hence it is expected that oxygen vacancy might cause change of atomic arrangements on a plane which is perpendicular to b-axis.