Report for the Joint Use/Research of the Institute for Planetary Materials, Okayama University for FY2024

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Category: ☑International Joint Research ☐General Joint Research ☐Joint Use of Facility ☐Workshop

Name of the research project: Spin transition and thermal elastic properties of Fe-bearing CF Phase at High Pressures and Temperatures

Principal applicant: Xinyue Zhang

Affiliated institution and department: School of Earth and Space Sciences, University of Science and Technology of China

Collaborator

Name: Izumi Mashino

Affiliated institution and department: Okayama University, the Institute for Planetary Materials

Research report:

[Research purpose]

The density and velocity profile of the mid-ocean ridge basalts (MORBs) has not been well constructed because of the lack of the elastic properties of the main minerals. Therefore, the main purpose of this research is to synthesize Fe-bearing CF phase with different compositions, which is a main phase in the MORBs, using large volume press and further determine the electronic spin and valence states of iron ions, sound velocities, and density of CF phase using combined synchrotron Mössbauer spectroscopy (SMS), inelastic X-ray scattering (IXS) and X-ray diffraction (XRD) up to 130 GPa and 2500 K. The experimental results will allow us to detect the effect of compositions on the spin transition and elastic properties of CF phase and better constrain the density and velocity profiles of the MORBs with more realistic composition in the lower mantle. These results will provide new insights into deciphering the role of subducted slabs in the seismic anomalies and material circulation.

[Actual conducted research]

a. Sample synthesis and composition/structure determining

The mixture of 30% ^{57}Fe enriched Fe_2O_3, MgO, and Al_2O_3 powder were used and heated in the furnace to form the spinel with 10%$FeAl_2O_4$-90% $MgAl_2O_4$, 30%$FeAl_2O_4$-70% $MgAl_2O_4$, 5%$MgFe_2O_4$-95%$MgAl_2O_4$, 10%$MgFe_2O_4$-90%$MgAl_2O_4$, and 20%$MgFe_2O_4$-80%$MgAl_2O_4$ composition as the starting materials in dry Fe-bearing system. The mixture of MgO, Al_2O_3, and $Al(OH)_3$ powder were also used as the starting material in the $MgAl_2O_4$-5 wt% H_2O and $MgAl_2O_4$-10 wt% H_2O system. To synthesize CF phase, high-pressure and high-temperature experiments has been performed at ~25 GPa and 1400–1900 °C for 1-6 h using the 1000-ton and 5000-ton Kawai-type multi-anvil apparatus (USSA-1000 and -5000) at the Institute for Planetary Materials, Okayama University at Misasa. The starting mixtures have been packed in Au- or Re-foil capsules for the material in 10%$FeAl_2O_4$-90% $MgAl_2O_4$ and 30%$FeAl_2O_4$-70% $MgAl_2O_4$ system and in Pt-foil capsules for materials in other system. Cr-doped MgO octahedral pressure media with 8-mm edges have been used for experiments in combination with tungsten carbide anvils with 3-mm truncations. The samples were first compressed to a desired press load, and then heated to 1400–1900 °C at 50 °C/min. After keeping the target temperature for the desired time, the samples were quenched by cutting the electrical power supply and decompressed to room pressure for 12 h. The recovered samples have been characterized by microfocus powder XRD for phase identification and scanning electron microscope (SEM) for chemical analysis. One additional analysis using Fourier Transform Infrared Spectroscopy (FTIR) were used to determine the water content of single-crystal CF phase synthesized in $MgAl_2O_4$-5 wt% H_2O system.

b. High-pressure measurements using SMS

The SMS measurement was conducted at Spring-8 for the recovered polycrystalline samples in 5%$MgFe_2O_4$-95%$MgAl_2O_4$ and 20%$MgFe_2O_4$-80%$MgAl_2O_4$ system to determine the pressure of the spin transition. The samples were pressed to get a pellet of 30 μm in thickness and loaded to two diamond anvil cells with 150-and 300-μm culets. Rhenium was used as a gasket and KCl was used as the pressure-transmitting media. The high-pressure measurement was conducted at an interval of 5-10 GPa up to 70 GPa.

c. High-pressure and high-temperature measurements using IXS techniques

To determine the influence of iron content in the sound velocity of CF phase, IXS of the Fe-bearing CF phase synthesized in 10%$FeAl_2O_4$-90% $MgAl_2O_4$, 30%$FeAl_2O_4$-70% $MgAl_2O_4$ system has been collected in a pressure step of 5 GPa up to 25 GPa and 10 GPa, respectively, at 300 K. The samples were pressed to get a pellet of 30 μm in thickness and loaded to two diamond anvil cells with 450-and 300-μm culets. Rhenium was used as a gasket and Ar was used as the pressure-transmitting media. The phonon-dispersion spectra were simultaneously collected by detectors with 16 spherical silicon crystal analyzers with a collection time of about 7 h. To make the fastest transverse acoustic waves (TA) of the diamonds be oriented along the momentum transfer of the IXS measurements, the orientations of the two diamond anvils were measured in advance using the single crystal XRD in Misasa and prealigned. Therefore, sample longitudinal acoustic wave (LA) and TA of diamonds in most directions could be better separated at higher pressures where phonon dispersion curves of the sample are expected to occur at higher energy transfers.

[Research outcomes]

Combined with the results of SEM and SMS measurement, the ratios of Fe^{3+}/Fe of the recovered samples in 5%$MgFe_2O_4$-95%$MgAl_2O_4$ and 20%$MgFe_2O_4$-80%$MgAl_2O_4$ system were 0.4 and 0.7, respectively, which shows that Fe tends to exist in the form of Fe^{2+} in the CF phase. This observation is also consistent with the relatively reduced composition of MORB. As CF phase in MORB composition can contain about 30% Fe, which may strongly affect the velocity, it is necessary to study the influence of Fe^{2+} on the elastic properties of CF phase. Our results show that the increasing iron content in CF phase will decrease its sound velocity. Moreover, the spin transition of Fe^{3+} in CF phase was observed to occur at ~ 35-40 GPa for both two samples, which is consistent with previous results in Na, Fe-bearing samples. The influence of spin transition on the density and elasticity is also needed to construct the velocity profile of the MORB.

In addition, from the synthesis experiment in the water-bearing system, CF phase was not stable in the system of 10 wt% H_2O, while it can exist stably in the system of 5 wt% H_2O. However, FTIR results indicated that the water content in CF phase is about 100 ppm and nearly same for the samples synthesized at different temperatures. Therefore, the CF phase with $MgAl_2O_4$ end-member may not be the main reservoir of water in the Earth's interior. The article about the stability and water solubility of CF phase has been published in *progress in earth and planetary science* with the title “Stability and water solubility of calcium ferrite-type aluminum-rich phase: implications for deep water cycle caused by subducting basaltic crusts”.

[Collaborator’s information]

	Name	Affiliated institute	Department
1	Izumi Mashino	Okayama University	Institute for Planetary Materials
2	Takayuki Ishii	Okayama University	Institute for Planetary Materials

3	**Takashi Yoshino**	**Okayama University**	**Institute for Planetary Materials**

1) Please write the research report with free format, but include followings: research purpose, actually conducted research, and research outcomes. If necessary, you can add another page.
2) For the workshop, please write the report for the workshop. Also, attach the program, abstracts, and list of the participants etc.
3) Please add Collaborator's Name, Affiliated institution and department as needed.
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