

Spin State of Ferric Iron in Mg-perovskite up to 200 GPa by X-ray Emission Spectroscopy and Its Implication to the Lower Mantle

Kiyoshi Fujino¹, Daisuke Nishio-Hamane², Yusuke Seto³,
Nagayoshi Sata⁴, Takaya Nagai⁵, Tomoki Ishido⁵, Lin Li⁵, Toru Shinmei¹,
Tetsuo Irifune¹, Hirofumi Ishii (石井 啓文)⁶, Nozomu Hiraoka (平岡 望)⁶,
Yong-Qiang Cai (蔡永強)⁶, and Ku-Ding Tsuei (崔古鼎)⁶

¹Geodynamics Research Center, Ehime University, Matsuyama, Japan

²Institute for Solid State Physics, University of Tokyo, Kashiwa, Japan

³Department of Earth and Planetary Sciences, Kobe University, Kobe, Japan

⁴Institute for Research on Earth Evolution, Jamstec, Yokosuka, Japan

⁵Department of Natural History Sciences, Hokkaido University, Sapporo, Japan

⁶National Synchrotron Radiation Research Center, Hsinchu, Taiwan

Pressure-induced high spin – low spin transition of iron in the lower mantle minerals has been attracting many researchers' interest because the spin transition of iron largely affects the mineralogy and dynamics of the lower mantle. Among the previous reports on the spin transition of iron in the minerals stable in the lower mantle, so far most of the reports on ferropervicite (Mg,Fe)O demonstrate nearly the same tendency that the spin transition of ferrous iron in ferropervicite with 10 – 20 mole% iron occur at pressures around 50 – 70 GPa and the transition pressure increases with the iron content [1, 2]. However, the experimental reports of iron in Mg-perovskite are inconsistent with each other and show a large discrepancy from the theoretical reports. We think that most of inconsistency in the experimental studies originates from the poor qualities (such as coexistence of ferrous and ferric irons) or poor characterizations (such as ambiguous site occupancies of cations) of the samples used for the experiments.

We performed the spin state measurement of ferric iron in Al-bearing Mg-perovskite by X-ray emission spectroscopy (XES) at SPring-8, using the well qualified samples. We used the samples which contain ferric iron because the recent studies indicate that the predominant valence state of iron in Mg-perovskite in the lower mantle is ferric rather than ferrous (MacCammon, 2005).

The measured samples with the composition $\text{Mg}_{0.85}\text{Fe}^{3+}_{0.15}\text{Al}_{0.15}\text{Si}_{0.85}\text{O}_3$ were synthesized from gel of the same composition at 27 GPa and 2000 K by a multi-anvil cell. The XES patterns of the perovskite samples were measured at pressures up to 200 GPa, the highest pressure ever reported for Mg-perovskite, at room temperature (Fig. 1). The observed spin state of ferric iron is almost in the high spin state from 0 to ~ 120 GPa, and it gradually decreases at higher pressures. However, even at 200 GPa, the XES pattern is still intermediate between the patterns of high spin and low spin states. These XES patterns are well fitted by the linear combination of the patterns of high spin and low spin states of ferric iron in Fe_2O_3 , indicating the coexistence of ferric iron of high spin and low spin states. The gradual change of the refined ratios of high spin and low spin states with pressure suggests that partial disordering of Fe^{3+} and Al between the A- and B-sites with the different spin states of ferric iron occurs by the annealing of the

samples at high pressure before the XES measurements.

The present result indicates that the spin state of ferric iron in the A-site of Mg-perovskite is in the high spin state for the whole lower mantle, while that in the B-site is in the low spin state from relatively low pressure, and the ratio of the low spin state of ferric iron would be significant by the disordered distribution of ferric iron and Al between the A- and B-sites at high pressure and high temperature in the lower mantle.

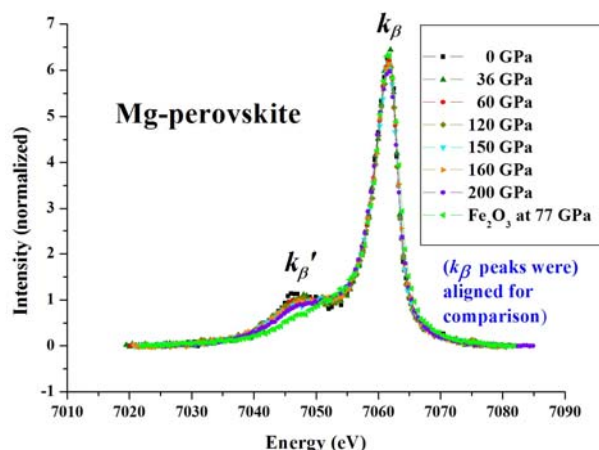


Fig. 1: X-ray emission spectra of ferric iron in Mg-perovskite at pressures up to 200 GPa and Fe_2O_3 in the low spin state at room temperature. The k_β peaks are aligned for comparison.

References

- [1] J. Badro, G. Fiquet, F. Guyot, J. P. Rueff, V. V. Struzhkin, G. Vanko, and G. Monaco, *Science* **300**, 789 (2003).
- [2] J. F. Lin, V. V. Struzhkin, S. D. Jacobsen, M. Y. Hu, P. Chow, J. Kung, H. Liu, H. K. Mao, and R. J. Hemley, *Nature* **436**, 377 (2005).
- [3] C. A. McCammon, *Science* **308**, 807 (2005).