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The spin state of iron in Fe^{3+}-bearing Mg-perovskite and its crystal chemistry at high pressure†

IZUMI MASHINO[1,*], EIJI OHTANI[1,2], NAOHISA HIRAO[3], TAKAYA MITSUI[4], RYO MASUDA[5], MAKOTO SETO[5], TAKESHI SAKAI[1,6], SUGURU TAKAHASHI[1] AND SATOSHI NAKANO[7]

[1]Department of Earth and Planetary Materials Science, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan
[2]V.S. Sobolev Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences, Koptyuga Avenue, 3, Novosibirsk, 630090, Russia
[3]Japan Synchrotron Radiation Institute, Sayo, Hyogo 679-5198, Japan
[4]Japan Atomic Energy Agency, Sayo, Hyogo 679-5148, Japan
[5]Research Reactor Institute, Kyoto University, Kumatori, Sennan-gun, Osaka 590-0494, Japan
[6]Geodynamics Research Center, Ehime University, Matsuyama 790-8577, Japan
[7]National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

ABSTRACT

Valence, spin states, and crystallographic sites of Fe in $(Mg,Fe)SiO_3$ perovskite were investigated using energy-domain ^{57}Fe-synchrotron Mössbauer spectroscopy and powder X-ray diffraction up to 86 GPa. The volumes of Fe^{3+}-bearing perovskite in this study are slightly smaller than those of Mg end-member perovskite. Our Mössbauer data suggest that Fe^{3+} prefers A sites coupled with Mg vacancies, which is consistent with previous data at ambient conditions. Fe^{3+} in the A site remains in a high-spin state up to 86 GPa, and some fraction of the A site is occupied by Fe^{2+} at pressures above 30 GPa. Fe^{2+} in the A sites is also in a high-spin state up to 86 GPa. The coupled substitution from Mg^{2+} to a high-spin state of Fe^{3+} and Mg^{2+} vacancy would make the volume of perovskite smaller than that of Mg end-member perovskite. If the lower mantle is saturated in silica, perovskite containing high-spin Fe^{3+} in A site has a higher density. Such silica oversaturated regions could sink by the density difference.

Keywords: Perovskite, ferric iron, spin state, Mössbauer spectroscopy, X-ray diffraction