Synthesis and crystal structure of Mg-bearing Fe_9O_{11}: New insight in the complexity of Fe-Mg oxides at conditions of the deep upper mantle

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The Fe-O system is fundamental for understanding redox processes operating in the Earth’s interior. Recent experimental studies have revealed several new mixed-valence Fe-oxides to be stable at high pressures and temperatures, such as the orthorhombic-structured phases $Fe^{2+}{}_2Fe^{3+}{}_2O_5$ and $Fe^{2+}{}_3Fe^{3+}{}_2O_6$. and the monoclinic-structured $Fe^{2+}{}_3Fe^{3+}{}_4O_9$. It has been also demonstrated that Fe_4O_5 and Fe_7O_9 form solid solutions with the Mg-endmembers such as $Mg_2Fe_2O_5$ and $Mg_3Fe_4O_9$, suggesting possible existence of complicated Mg-Fe oxides in the deep mantle. We synthesized a new Mg-Fe oxide with a composition of $Mg_{0.9}Fe_{8.1}O_{11}$. We report the synthesis and crystal structure analyzed by the Rietveld method.

A novel Mg-bearing iron oxide $Mg_{0.87(1)}Fe^{2+}{}_{4.13(1)}Fe^{3+}{}_4O_{11}$ was synthesized at 12 GPa and 1300 ˚C using a large volume press. Rietveld structural analysis was conducted with a laboratory X-ray diffraction pattern obtained at ambient conditions.
The crystal structure, which has one oxygen trigonal prism site and four octahedral sites for the cations, was found to be isostructural with $Ca_2Fe_7O_{11}$. The unit-cell lattice parameters are a = 9.8441(5) Å, b = 2.8920(1) Å, c = 14.1760(6) Å, β = 99.956(4)˚, V = 397.50(3) Å, and Z = 2 (monoclinic, $C2/m$). Mg and Fe cations are disordered on the trigonal prism site and on two of the four octahedral sites, and the remaining Fe is accommodated at the other two octahedral sites. The present structure is closely related to the other recently discovered Fe oxide structures, e.g. Fe_4O_5 and Fe_5O_6, by distortion derived either from incorporation (Fe_4O_5) or removal (Fe_5O_6) of an edge-shared FeO_6 single octahedral chain in their structures. The present synthesis at deep upper mantle conditions and the structural relationships observed between various novel Mg-Fe oxides indicate that a series of different phases become stable above 10 GPa and that their relative stabilities (Fe^{2+}/Fe^{3+}) must be controlled by oxygen fugacity.

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