

High-pressure rhombohedral Fe₂SiO₄ and structure change with spin state

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Motivation High-pressure transformations of various iron bearing spinel solid solutions have been performed by X-ray diffraction measurements (XRD), magnetic measurement, electric conductivity measurement and Raman spectroscopy[1, 2]. Fe₂SiO₄ spinel is decomposed with a reaction of Fe₂SiO₄ (spinel) = 2FeO (wustite) + SiO₂ (stishovite) by high-pressure and temperature experiments [3]. Recently a new structural of a rhombohedral phase has been reported by XRD and Mossbauer spectroscopy measurement at pressures above 30 GPa at ambient temperature [4].

High-pressure transition In the present experiment the structure transition of Fe₂SiO₄ from cubic spinel to rhombohedral (R- Fe₂SiO₄) phase and compression mechanism of spinel phase were elucidated by Rietveld profile fitting analyses and X-ray emission spectra study under high pressure up to 65 GPa at ambient temperature in order to clarify the correlation between structure transition and spin transition.

The rhombohedral-to-cubic back transformation is confirmed by decompression study, indicating the reversible structure transition. Spinel and R- Fe₂SiO₄ were heated to 1500 K by laser heating, proving a decomposition to rhombohedral FeO and SiO₂ stishovite.

New rhombohedral structure A new phase different from spinel was observed above 44 GPa at ambient temperature. Rietveld profile fitting analysis of the pattern taken at 55 GPa confirms the high-pressure rhombohedral structure with R3m space group symmetry and Z=6. There are two Fe sites with six-fold coordination: Fe1 with site symmetry of 2/m (9e) and Fe2 with m (3b). Si atom has a four-fold coordination with 3m (6c). Fe1 site is considerably deformed and Fe1-O average bond distance of 1.935 Å, which is smaller than Fe2-O of 2.001 Å. A topotactic relation between spinel and R- Fe₂SiO₄ is preserved.

Fe₂SiO₄ spinel at 39 GPa, cubic Fd3m, z = 8, a_c = 7.855 Å

R- Fe₂SiO₄ at 55 GPa, hexagonal R3m, z = 6, a_h = b_h = 5.380 Å, c_h = 13.814 Å

a_{h,cal} = b_{h,cal} = d_{c,110} = 5.554 Å, c_{h,cal} = d_{c,111} = 13.685 Å

Compression in the <110> direction of spinel structure and simultaneous elongation to <111> direction creates a high-pressure R- Fe₂SiO₄ phase from the spinel structure. The density of R- Fe₂SiO₄ at 55 GPa is D=5.867 g/cm³, about 5 % larger than D=5.584 g/cm³ of spinel at 39 GPa.

X-ray emission spectra XES of Fe²⁺ (3d⁶) ion at the octahedral site of Fe₂SiO₄ shows an intermediate spin state. The spin transition from high spin (HS) to low spin (LS) started at 23 GPa in Fe₂SiO₄. The transition started at much lower pressure than the most of iron-bearing silicate and oxide structural transitions observed by XRD. The LS electronic state increases with compression. Electron spin state gives a great influence on effective ion radii of the transition elements [5].

Fe²⁺-O distance of Fe₂SiO₄ is 2.16 Å in the high spin state at low pressures and 1.99 Å at low spin state under high pressures. The bond distance changes induce the polyhedral distortion. The Si-O bond is little compressed, while the Fe-O bond is enormously compressive. Fe-O bond distance shows a distinct change in the spinel phase at 23 GPa. It is consistent with the spin transition pressure.

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