

Hydrogen positions in hydrous ringwoodite determined by pulsed neutron powder diffraction

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The transition zone in the Earth's mantle has been considered potentially large water reservoir. It was experimentally evidenced that its main constituent minerals can uptake significant amount of water as hydroxyl groups in their crystal structures. The ringwoodite $[(\gamma\text{-Mg,Fe})_2\text{SiO}_4]$ is one of the high pressure polymorph of olivine, which is the most major phase in the lower part of the transition zone, between 525 to 660 km in depth. It was reported that ringwoodite can incorporate up to 2.6 wt.% of water (Kohlstedt et al., 1996). The hydration of ringwoodite strongly affects its physical and chemical properties such as electrical conductivity, compressibility and seismic velocities. However, crystallographic sites of hydrogen and its incorporation mechanism are still unclear mainly due to insensitiveness of X-ray probe for hydrogen. The previous studies of its structure refinement by X-ray diffraction demonstrated that hydrous ringwoodite has cubic spinel structure with $Fd\text{-}3m$ space group (Kudoh et al., 2000; Smyth et al., 2003). Here we applied neutron diffraction for hydrous ringwoodite for the first time to analyze its hydrogen positions.

Deuterated ringwoodite powder samples were synthesized at 1300 °C and 18 GPa for 5 minutes using a scaled-up Kawai-type multi anvil apparatus. The run products were evaluated by micro-focused X-ray, Raman spectroscopy and powder X-ray diffractometer to confirm their purity.

Neutron powder diffraction patterns were taken at BL-19 (TAKUMI) at Materials and Life Science Experimental Facility, J-PARC. The two representative deuterated ringwoodite samples were with identical composition mixed and measured together in a sample holder made of TiZr "null" alloy. The obtained diffraction pattern has been analyzed by Rietveld refinement using the "Z-Rietveld" code in order to determine positions and site occupancies of deuterium atoms in the ringwoodite structure.

We can propose two possible models for the deuterium atomic positions, 96g and 192i. These refined models were given with almost identical R factors. They also gave similar site occupancies and temperature factors for the elements except for the deuterium. However, in terms of deuterium temperature factor, the 192i model is more preferable than the 96g model. The refinement results also showed that the (Mg+Fe)/Si ratio is lower than the ideal ratio of dry ringwoodite [(Mg+Fe)/Si = 2.0] while Si in T sites are fully occupied, which demonstrates that deuterium only substitutes Mg and Fe in M sites and Si in T sites is not affected.

References:

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Keywords: ringwoodite, neutron diffraction, Rietveld refinement