

Synchrotron XRD and Mossbauer spectroscopic study on $\text{Ca}_2\text{MgSi}_2\text{O}_7$ - $\text{Ca}_2\text{Fe}^{3+}$ series melilite at high pressures

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Synthetic $\text{Ca}_2\text{MgSi}_2\text{O}_7$ (akermanite: Ak)- $\text{Ca}_2\text{Fe}^{3+}\text{AlSiO}_7$ (ferrialuminium gehlenite: FAGeh) series melilites were investigated using synchrotron X-ray diffraction and synchrotron-radiation-based Mossbauer spectroscopic methods to determine the distribution of Fe^{3+} between two structurally independent tetrahedral sites (T1 and T2), and the relationship between ionic substitution and incommensurate structure in melilite at high pressures. ^{57}Fe -doped Ak-FAGeh melilites were synthesized from starting material with composition of $\text{Ak}_{50}\text{FAGeh}_{50}$ by sintering technique at 1140-1180 °C and 1 atm for high pressure experiment. The average chemical composition of the synthetic melilites was $\text{Ca}_{2.00}\text{Mg}_{0.56}\text{Fe}^{3+}_{0.42}\text{Al}_{0.44}\text{Si}_{1.57}\text{O}_7$. The site populations at the T1 and T2 sites at the synthetic condition were determined by X-ray Rietveld analysis and ^{57}Fe Mossbauer spectroscopy (340MBq ^{57}Co source) to be $[0.557\text{Mg}+0.280\text{Fe}^{3+}+0.237\text{Al}]_{\text{T1}}$ $[0.197\text{Fe}^{3+}+0.176\text{Al}+1.574\text{Si}]_{\text{T2}}$ (apfu: atoms per formula unit), which is consistent with that by Hamada and Akasaka (in press).

The experiments at high pressures were performed using a diamond anvil cell (DAC) with culet size of 0.3 mm. A Rhenium gasket was pre-indented to 0.06 mm in thickness, and a hole with 0.1 mm in a diameter was drilled in the gasket as the sample chamber. NaCl was used as pressure medium. In addition to the powder sample, several ruby tips (0.01-0.02 mm in diameter) were put into the chamber as a pressure marker. The pressure was estimated based on Ruby fluorescence (Mao et al., 1978). Mossbauer spectra and X-ray diffraction were taken at the beamline BL11XU of SPring-8. The energy of used gamma-ray for Mossbauer spectroscopy was 14.4125 keV. Mossbauer spectra were measured at 0.8, 1.6, 14.1, 18.7 GPa. The spectra were fitted to Lorentzians with widths and intensities constrained to be equal at each site, using synchrotron-based-Mossbauer analysis program S8QBMOSS (Hamada and Akasaka, in prep.).

At 0.8 and 1.6 GPa, Mossbauer spectra consisted of two doublets assigned to T1 and T2 sites. However, Isomer Shifts (*I.S.*) of T1 and T2 sites at 1.6 GPa (0.11(5) and 0.05(5) mm/s, respectively) were smaller than those at ambient condition. Area ratio of $\text{Fe}^{3+}(\text{T1}):\text{Fe}^{3+}(\text{T2})$ at ambient condition was 47(1):53(2) (Hamada and Akasaka, in press). Whereas, area ratio at 0.8 and 1.6 GPa were 52(10):48(9) and 44(9):56(8), respectively. Mossbauer spectra at 14.1 and 18.7 GPa consisted of only one doublet assigned to Fe^{3+} at T2 site. However, the half width was broad, suggesting that the spectrum consists of strongly superimposed doublets.

The variation of the Mossbauer hyperfine parameters (*I.S.* and quadrupole splitting *Q.S.*) suggests that covalencies of T1-O and T2-O bonds increase and difference of geometric properties (site distortion and mean T-O distance) between T1O_4 and T2O_4 tetrahedra becomes smaller with increasing pressure. Yang et al. (1997) reported the incommensurate (IC)-normal (N) phase transition at 1.7 GPa. The smaller *I.S.* values may be caused by IC-N phase transition.

Keywords: Synchrotron X-ray diffraction, Synchrotron Mossbauer spectroscopy, Synthetic melilite, Incommensurate structure, High pressure