

## High-pressure syntheses and crystal structure analyses of a new low-density CaFe<sub>2</sub>O<sub>4</sub>-related and CaTi<sub>2</sub>O<sub>4</sub>-type MgAl<sub>2</sub>O<sub>4</sub> phases

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### ABSTRACT

Three single crystals of CaTi<sub>2</sub>O<sub>4</sub> (CT)-type, CaFe<sub>2</sub>O<sub>4</sub> (CF)-type, and new low-density CaFe<sub>2</sub>O<sub>4</sub> (LD-CF) related MgAl<sub>2</sub>O<sub>4</sub> were synthesized at 27 GPa and 2500 °C and also CT-type MgAl<sub>2</sub>O<sub>4</sub> at 45 GPa and 1727 °C using conventional and advanced multi-anvil technologies, respectively. The structures of CT-type and LD-CF related MgAl<sub>2</sub>O<sub>4</sub> were analyzed by single-crystal X-ray diffraction. The lattice parameters of the CT-type phases synthesized at 27 and 45 GPa were  $a = 2.7903(4)$ ,  $b = 9.2132(10)$ , and  $c = 9.3968(12)$  Å, and  $a = 2.7982(6)$ ,  $b = 9.2532(15)$ , and  $c = 9.4461(16)$  Å, respectively, ( $Z = 4$ , space group: *Cmcm*) at ambient conditions. This phase has an AlO<sub>6</sub> octahedral site and an MgO<sub>8</sub> bicapped trigonal prism with two longer cation-oxygen bonds. The LD-CF related phase has a novel structure with orthorhombic symmetry (space group: *Pnma*), and lattice parameters of  $a = 9.207(2)$ ,  $b = 3.0118(6)$ , and  $c = 9.739(2)$  Å ( $Z = 4$ ). The structural framework comprises tunnel-shaped spaces constructed by edge- and corner-sharing of AlO<sub>6</sub> and a 4+1 AlO<sub>5</sub> trigonal bipyramid, in which MgO<sub>5</sub> trigonal bipyramids are accommodated. The CF-type MgAl<sub>2</sub>O<sub>4</sub> also has the same space group of *Pnma* but a slightly different atomic arrangement, with Mg and Al coordination numbers of 8 and 6, respectively. The LD-CF related phase has the lowest density of 3.50 g/cm<sup>3</sup> among MgAl<sub>2</sub>O<sub>4</sub> polymorphs, despite its high-pressure synthesis from the spinel-type phase (3.58 g/cm<sup>3</sup>), indicating that the LD-CF related phase formed via back-transformation from a high-pressure phase during the recovery. Combined with the previously determined phase relations, the phase transition between CF- and CT-type MgAl<sub>2</sub>O<sub>4</sub> is expected to have a steep Clapeyron slope. Therefore, CT-type phase may be stable in basaltic- and continental-crust compositions at higher temperatures than the average mantle geotherm in the wide pressure range of the lower mantle. The LD-CF related phase could be found in shocked meteorites and used for estimating shock conditions.

**Keywords:** Single-crystal X-ray diffraction, crystal structure, high pressure, phase transition, spinel, post-spinel, calcium titanate, calcium ferrite