American Mineralogist, Volume 106, pages 1105–1112, 2021

High-pressure syntheses and crystal structure analyses of a new low-density $CaFe_2O_4$-related and $CaTi_2O_4$-type $MgAl_2O_4$ phases

Takayuki Ishii[1,2,3,*], Giacomo Criniti[2], Elena Bykova[2], Leonid Dubrovinsky[2], Tomoo Katsura[2,3,†], Hidekazu Arii[1,‡], Hiroshi Kojitani[1], and Masaki Akaogi[1]

[1]Department of Chemistry, Gakushuin University, Mejiro, Toshima-ku, Tokyo 171-8588, Japan
[2]Bayerisches Geoinstitut, University of Bayreuth, 95440 Bayreuth, Germany
[3]Center for High Pressure Science and Technology Advanced Research, Beijing, 100094, China

Abstract

Three single crystals of $CaTi_2O_4$ (CT)-type, $CaFe_2O_4$ (CF)-type, and new low-density $CaFe_2O_4$ (LD-CF) related $MgAl_2O_4$ were synthesized at 27 GPa and 2500 °C and also CT-type $MgAl_2O_4$ at 45 GPa and 1727 °C using conventional and advanced multi-anvil technologies, respectively.The structures of CT-type and LD-CF related $MgAl_2O_4$ 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_6 octahedral site and an MgO_8 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_6 and a 4+1 AlO_5 trigonal bipyramid, in which MgO_5 trigonal bipyramids are accommodated. The CF-type $MgAl_2O_4$ 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^3 among $MgAl_2O_4$ polymorphs, despite its high-pressure synthesis from the spinel-type phase (3.58 g/cm^3), 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 $MgAl_2O_4$ 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