Synthesis and structural analysis of CaFe$_2$O$_4$-type single crystals in the NaAlSiO$_4$-MgAl$_2$O$_4$-Fe$_3$O$_4$ system

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ABSTRACT

Orthorhombic CaFe$_2$O$_4$-structured (Cf) Na-rich aluminous silicate (space group Pbnm) is a major mineral of metabasaltic rocks at lower mantle conditions and can, therefore, significantly affect the physical properties of subducted oceanic crusts. We attempted to synthesize single crystals of Cf-type phases in the systems NaAlSiO$_4$, NaAlSiO$_4$-MgAl$_2$O$_4$, NaAlSiO$_4$-MgAl$_2$O$_4$-Fe$_3$O$_4$, and NaAlSiO$_4$-MgAl$_2$O$_4$-Fe$_3$O$_4$-H$_2$O at 23–26 GPa and 1100–2200 °C. Under dry conditions, single crystals of Cf-type phase up to 100–150 μm in size were recovered from 23 GPa and 2000–2200 °C. Single-crystal X-ray diffraction and composition analyses suggest that the synthesized Cf-type phases have a few percent of vacancies in the eightfold-coordinated site with Na, Mg, and Fe$^{3+}$ and partially disordered Al and Si in the octahedral sites. Iron-bearing Cf-type phases have 32–34% Fe$^{3+}$ that is hosted both in the octahedral sites and in the eightfold-coordinated site. In NaAlSiO$_4$-MgAl$_2$O$_4$-Fe$_3$O$_4$-H$_2$O system, no formation of Cf-type phase was observed at 24 GPa and 1100–2000 °C due to the formation of hydrous Na-rich melt and Al-rich oxides or hydroxides, suggesting the possible absence of Cf-type phase in the hydrous basaltic crust. The single-crystal syntheses of Cf-type phases will be useful for investigating their physical properties, potentially improving models of lower mantle structure and dynamics.

Keywords: Calcium ferrite, single crystal, multi-anvil press, high pressure, basaltic crust

INTRODUCTION

CaFe$_2$O$_4$-type (Cf) phase is a major mineral phase (~25% in volume fraction) of subducted basaltic crusts at lower mantle conditions (e.g., Ishii et al. 2019a, 2022). The chemical formula of Cf-type phases is generally expressed as A$^2$+B$^2$+O or X(Y$^{3+}$Z$^{4+}$)O$_4$. The Cf structure is orthorhombic (space group Pbnm) and consists of double chains of edge-sharing B$^{6+}$O$_4$ or (Y$^{3+}$Z$^{4+}$)O$_4$ octahedra running parallel to the c-axis. The octahedral double chains are linked to one another by sharing vertices and form channel-like cavities that extend parallel to the c-axis where relatively large A$^{2+}$ or X$^+$ cations are accommodated (Yamada et al. 1983; Ishii et al. 2018). In a basaltic crust composition, Cf-type phases are constituted by a solid solution approximately expressed by the end-members NaAlSiO$_4$, MgAl$_2$O$_4$, FeAl$_2$O$_4$, and Fe$_3$O$_4$.

Recent seismological and geodynamic studies suggest that significant amounts of basaltic crusts have been subducted and accumulated in the lower mantle (e.g., Kaneshima 2019; Ballmer et al. 2015), stressing the importance of determining the chemical and physical properties of the Cf phase for better understanding of the lower-mantle structure and dynamics. Experimental studies of physical properties of single-crystal samples generally provide more information than those of polycrystalline aggregates because they allow constraining the anisotropic properties of the material of interest. For instance, relatively large single crystals (~100 μm) of high quality are required to determine physical properties such as the full elastic tensor, sound wave velocities anisotropy, and thermal conductivity (e.g., Hsieh et al. 2020; 2022; Satta et al. 2021). To date, the structural and physical properties of Cf-type phase have been poorly constrained as measurements were conducted in limited systems and using polycrystalline samples.

Additionally, defects in minerals can significantly affect their transport properties, such as electrical conductivity and viscosity, because these properties are controlled through defects. Because of the large fraction of Cf phase in basaltic crusts, defect chemistry of Cf phase can play an important role in understanding the physical properties of lower-mantle basaltic crusts and, therefore, the lower-mantle structure and dynamics. It has been suggested that Cf phase may have A-site vacancies based on electron microprobe analysis (e.g., Ono et al. 2009; Wu et al. 2017). Because of the difficulty in accurately determining Na content by electron microprobe due to its volatilization during measurement, it is still under debate whether Cf phase has vacancies.

In this study, we attempted to synthesize large single crystals of Cf-type phase in the systems NaAlSiO$_4$, NaAlSiO$_4$-MgAl$_2$O$_4$, NaAlSiO$_4$-MgAl$_2$O$_4$-Fe$_3$O$_4$, and NaAlSiO$_4$-MgAl$_2$O$_4$-Fe$_3$O$_4$-H$_2$O at 23–26 GPa up to 2000–2200 °C by high pressure-temperature experiments. Single crystals of Cf-type phases with dimensions up to 150 μm were recovered in the dry systems and characterized by electron microprobe, Mössbauer spectroscopy, and X-ray structural analysis. We examined their vacancy concentrations by combining electron microprobe measurements and single-crystal structural refinements of high-quality single crystals. Based on these results, we discuss the crystal chemistry, molar volume systematics, and stability of Cf-type phase in a subducted basaltic crust.