High-pressure synthesis of skiagite-majorite garnet and investigation of its crystal structure

LEYLA ISMAILOVA1,2,*, ANDREY BOBROV3, MAXIM BYKOV1, ELENA BYKOVA1,2, VALERIO CERANTOLA2, INNOKENTY KANTOR4, ILYA KUPENKO4, CATHERINE MCCAMMON2, VADIM DYADKIN4, DMITRY CHERNYSHOV4, SAKURA PASCARELLI4, ALEKSANDR CHUMAKOV4, NATALIA DUBROVINSKAIA1 AND LEONID DUBROVINSKY2

1Laboratory of Crystallography, Universität Bayreuth, 95447 Bayreuth, Germany
2Bayernisches Geoinstitut, Universität Bayreuth, 95447 Bayreuth, Germany
3Department of Petrology, Geological Faculty, Moscow State University, 119234 Moscow, Russia
4ESRF, European Synchrotron Radiation Facility, CS40220 38043 Grenoble Cedex 9, France

ABSTRACT

Skiagite-rich garnet was synthesized as single crystals at 9.5 GPa and 1100 °C using a multi-anvil apparatus. The crystal structure [cubic, space group Ia3d, a = 11.7511(2) Å, V = 1622.69(5) Å3, Dcalc = 4.4931 g/cm3] was investigated using single-crystal synchrotron X-ray diffraction. Synchrotron Mössbauer source spectroscopy revealed that Fe2+ and Fe3+ predominantly occupy dodecahedral (X) and octahedral (Y) sites, respectively, as expected for the garnet structure, and confirmed independently using nuclear forward scattering. Single-crystal X-ray diffraction suggests the structural formula of the skiagite-rich garnet to be Fe3+Fe2+3Fe3+3Si2O12(OH), in agreement with electron microprobe chemical analysis. The formula is consistent with X-ray absorption near-edge structure spectra. The occurrence of Si and Fe in the octahedral Y-site indicates the synthesized garnet to be a solid solution of end-member skiagite with ~23 mol% of the Fe-majorite end-member Fe3+(Fe2+Si3+)2(SiO4)3.

Keywords: Skiagite, majorite, garnets, single-crystal X-ray diffraction, Mössbauer spectroscopy, nuclear forward scattering, XANES

INTRODUCTION

Garnet is a common mineral in mantle assemblages and often occurs as inclusions in natural diamonds. Due to the compositional complexity of natural garnets, the relationship between their composition and the pressure-temperature conditions of their formation is still not well constrained (Akaogi and Akimoto 1977; Irfune 1987; Stachel 2001; Collerson et al. 2010).

Sicate garnets have the general formula [X]3[Y2]SiO12 where [X] and [Y] are cations occupying the dodecahedral and octahedral sites, respectively. In garnets from the crust and upper mantle the dodecahedral site is occupied by a divalent cation (e.g., Fe2+, Mg2+, Ca2+) and the octahedral site by a trivalent cation (e.g., Fe3+, Al3+, Cr3+). Garnets from mantle xenoliths and inclusions in diamonds contain both ferrous (Fe2+) and ferric (Fe3+) iron. Thus information about the properties and high-pressure behavior of the iron end-member skiagite, Fe3+Fe2+3(SiO4)3, is important for mineral physics and the geochemistry of the Earth’s upper mantle and transition zone. Moreover, the fate of iron-rich silicate material incorporating a skiagite component is unknown at conditions of the deep lower mantle and the core-mantle boundary.

The stability field of skiagite has been investigated in several studies. Karpinskaya et al. (1982) were probably the first to synthesize skiagite, which was produced at 12 GPa and 800 °C. Woodland and O’Neill (1993) measured the variation of garnet unit-cell parameter along the almandine-skiagite solid solution join. Woodland and Ross (1994) studied the crystal chemistry of skiagite solid solutions along the joins Fe3Al(SiO4)3–Fe3Fe2Fe3Si(OH)4 (almandine-skiagite) and Ca3Fe2Si3O12–Fe3Fe2Fe3Si(OH)4 (andradite-skiagite) at pressures between 1.7 and 9.7 GPa and temperatures of 1080 to 1100 °C. Woodland and O’Neill (1995) investigated the stability of Ca-bearing garnets on the join Ca3Fe2Si3O12–Fe3Fe2Fe3Si(OH)4 (andradite-skiagite) as a function of pressure at 1100 °C. Simple Cr2+–Fe2+ exchange in the octahedral sites of the skiagite–Fe-knorringite [Fe3Fe2Si3O12–Fe3Cr2Si3O12] binary join was studied by Woodland et al. (2009). However, so far the iron-skiagite end-member has not yet been synthesized so that it can be investigated by mineral physics methods, including single-crystal X-ray diffraction and Mössbauer spectroscopy.

Here we report the high-pressure high-temperature synthesis of single crystals of skiagite-rich garnet, Fe3+Fe2+3Fe3+3Si2O12(OH), and the results of its characterization using single-crystal synchrotron X-ray diffraction, synchrotron Mössbauer source (SMS) spectroscopy, nuclear forward scattering (NFS), and X-ray absorption near-edge structure (XANES) spectrosopies.

EXPERIMENTAL METHODS

Synthesis experiments were performed using a split-sphere type multi-anvil apparatus at 9.5 GPa and 1100 °C at Bayernisches Geoinstitut (Bayreuth, Germany) (BGI). The starting material (corresponding to the nominal composition Fe3+Fe2+3SiO4) was a powdered mixture of chemically pure oxides (Fe2O3, Fe3O4, and SiO2) homogenized at room temperature by milling in a mortar using ethanol and then dried in a furnace at 100 °C for 24 h. The prepared mixture was placed in a capsule of 3.5 mm length and 2 mm diameter made of platinum foil. High temperature was generated using a LaCrO3 heater and the capsule was insulated from the heater by a MgO cylinder. The cell assembly with the sample was compressed to the target pressure between eight cubic tungsten carbide anvils with corners truncated to 11.0 mm edge lengths. The accuracy in determination of pressure and temperature is estimated to be ±0.5 GPa and ±50 °C, respectively (Frost et al. 2004).

* E-mail: leyla.isml@gmail.com