A new high-pressure phase transition in clinofersilite: In situ single-crystal X-ray diffraction study

Anna Pakhomova1,*, Leyla Ismailova1, Elena Bykova1, Maxim Bykov1, Tiziana Boffa Ballaran1, and Leonid Dubrovinsky1

1Bayerisches Geoinstitute, University of Bayreuth, Universitätsstrasse 30, D-95447 Bayreuth, Germany

ABSTRACT

Synchrotron-based high-pressure single-crystal X-ray diffraction experiments were conducted on synthetic pure clinofersilite, Fe2SiO4, at room temperature to a maximum pressure of 45 GPa. In addition to the previously described P21/c → C2/c phase transition between 1.48 and 1.75 GPa (Hugh-Jones et al. 1994), we observe further transition between 30 and 36 GPa into the high-pressure P21/c phase (HP-P21/c). The C2/c → HP-P21/c transition is induced by rearrangement of half of the layers of corner-sharing SiO4 tetrahedra into layers of edge-sharing SiO4 octahedra. The new configuration of 2Si layers suggests a possibility of a progressive transformation of the pyroxene into an ilmenite-type structure. The persistence of metastable pyroxene up to pressures higher than expected and its feasible direct transformation to ilmenite are of special interest for understanding the dynamics of cold-subducting slabs. We report on structural and compressibility features of both high-pressure phases as well as address thermal stability of HP-P21/c.

Keywords: Pyroxene, single-crystal X-ray diffraction, high-pressure, high-temperature, phase transitions

INTRODUCTION

Pyroxenes belonging to the hedenbergite-diopside-ferrosilite-enstatite, CaFeSi2O6-MgCaSi2O6-Fe2SiO4-MgSi2O6 (Hd-Di-Fs-En), quadrilateral system (Morimoto et al. 1989) are one of the major constituent minerals in the Earth’s upper mantle. Depending on the assumed petrological model, orthopyroxenes compose from 17 to 27% of the upper mantle, whereas the content of clinopyroxenes varies in the range 16–20% (Frost 2008). The significant proportion of pyroxenes results in their inevitable influence on mineralogy, thermodynamics, and geological structure of the upper mantle. Phase transitions in pyroxenes have been repetitively considered as a possible cause or contribution to seismic discontinuities in the mantle such as the Lehmann and the X shallow discontinuities (Woodland 1998; Deuss and Woodhouse 2002; Stixrude and Lithgow-Bertelloni 2005; Akashi et al. 2009; Jacobsen et al. 2010; Ferot and Bolfan-Casanova 2012). Pyroxenes are also a major constituent of the harzburgites that make up a large portion of subducting lithosphere (Ringwood 1982). Under relatively cold temperatures (in comparison with the mantle geotherm away from tectonic plate boundary) of subducting slabs, pyroxenes may be retained down to transition zone depths through slower subduction and/or transient stagnation (Mierlo et al. 2013; Agrusta et al. 2014) as metastable phases add buoyancy to the slabs. Under such conditions, the direct transformation of pyroxene to a dense ilmenite-type phase may occur, possibly promoting penetration of stagnant slab into the lower mantle (Hogrefe et al. 1994).

The occurrence of pyroxenes in different geological locations as well as their rich high-temperature–high-pressure phase diagram may be explained by the flexibility of their crystal structures, which are composed of cubic close-packed layers of O atoms with alternating tetrahedral and octahedral layers (Fig. 1). The octahedral M1 and M2 sites can accommodate various different cations (e.g., Mg2+, Fe3+, Ca2+, Mn2+, Na+, Al3+, Fe2+, Cr3+) as well as vacancies (McCormick 1986; Ma et al. 2015) without introducing pronounced rearrangements to the atomic topology. The structural and chemical flexibility is a consequence of the ability of the corner-sharing tetrahedral chains running along the c axis to rigidly stretch or compress by simple rotation of the individual tetrahedra without affecting the tetrahedral bond lengths.

A well-constrained correlation between chemical composition, crystal structure and elastic properties is extremely important for the modeling of the behavior of pyroxenes in the Earth’s interior. To this end the study of the high-temperature and high-pressure behavior of pyroxene end-members is necessary for constraining the effect of cation substitution at the M1 and M2 octahedra. In the present work we report results from diffraction experiments on the Fe end-member, Fe2SiO4. Three polymorphs of synthetic Fs100 have been observed at ambient conditions, namely orthofersilite (OFs, Pbcn), clinofersilite (CFs, P21/c), and Fs-III (Lindsley et al. 1964). Subsequent structural investigation of these polymorphs demonstrated that Fs-III (PT) has a pyroxenoid structure (Weber 1983). At room temperature pure OFs converts into a C2/c phase at 4.2 GPa through a reconstructive transition (Hugh-Jones et al. 1996) while a natural OFs2 follows two metastable transitions: first, above 10.1(1) GPa, to the monoclinic P21/c phase (β-opx), and then, above 12.3(1) GPa, to a high-pressure orthorhombic phase Pbcn (γ-opx) (Dera et al. 2013). CFs transforms into a C2/c phase between 1.48 and 1.75 GPa with a volume decrease of 3% (Hugh-Jones et al. 1994). Here we report on a further single-crystal X-ray diffraction investigation of the compressional behavior of...