Pressure-induced phase transitions in Ni-bearing ferrosilite (Ni-En$_{31}$Fs$_{65}$)

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ABSTRACT

Orthopyroxene is an abundant mineral in subducting slabs. Studying its phase transitions at high pressure is important to the understanding of mineralogy of subducting slabs in the deep Earth. Synchrotron-based single-crystal X-ray diffraction experiments were conducted on a synthetic Ni-bearing ferrosilite (Ni-En$_{31}$Fs$_{65}$) at pressures up to 33.8 GPa. Three phase transitions were observed at 12.1(6), 15.6(6), and 31.3(25) GPa. The first two phase transitions in Ni-En$_{31}$Fs$_{65}$ resemble the previously described phase transitions in Ni-free Fe-rich orthopyroxenes, i.e., the initial α-opx (Pbca) transforms to β-opx (P$_2$1/c), then the latter transforms to γ-opx (Pbca). This indicates that the incorporation of a few mol% NiSiO$_3$ does not influence the phase transition path of Fe-rich orthopyroxene. After the third phase transition, the structure (P$_2$1,c2a) of Ni-En$_{31}$Fs$_{65}$ resembles the previously reported β-popx observed in En$_{30}$ at high pressure, although the onset pressure of the phase transition in Ni-En$_{31}$Fs$_{65}$ is ~7 GPa lower than that in En$_{30}$. β-popx has a post-pyroxyene structure that contains fivefold- and sixfold-coordinated Si cations. Our results indicate that the post-pyroxyene structure is β-popx (P$_2$1,c2a) for either Fe-poor or Fe-rich orthopyroxenes, although the phase transition path before the pyroxene → post-pyroxyene is compositionally dependent. Additionally, unlike the second and third transitions, whose onset pressures are monotonously decreased by increasing Fe content, the Fe effect on shifting the first transition is much more significant for orthopyroxenes within En <50 mol% than that within En >50 mol%.

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

INTRODUCTION

Orthopyroxene is a major rock-forming mineral in the subducting oceanic slabs. A typical subducting slab is composed of three layers, with the basaltic crust layer atop, and the residual harzburgite and lherzolite at the middle and bottom, respectively (Ringwood 1982). Harzburgite and lherzolite commonly contain more than 20 vol% orthopyroxene (Bodinier and Godard 2007). It has been proposed that pyroxene minerals could survive as metastable phases in cold subducting slabs as the low-temperature conditions largely inhibit the pyroxene-majorite transition (Nishi et al. 2013; van Mierlo et al. 2013). Therefore, investigating the phase transitions of orthopyroxene at high pressures and high temperatures is important to the understanding of the mineralogy of subducting slabs.

In recent years, room-temperature high-pressure single-crystal X-ray diffraction (SCXRD) has revealed several high-pressure phases of orthopyroxene. The initial orthopyroxene (α-opx, Pbca space group) transforms into a monoclinic structure (β-opx, P$_2$1/c) at pressures ranging from 6 to 16 GPa depending on the contents of Fe, Al, and Ca (e.g., Lin et al. 2005; Dera et al. 2013a; Zhang et al. 2012, 2013a, 2013b; Finkelstein et al. 2015; Xu et al. 2020; Li et al. 2022). With increasing pressure, β-opx transforms into α-opx (P$_2$1,c2a; Finkelstein et al. 2015) when the molar percentage (M; mol%) of enstatite (En, MgSiO$_3$) of the sample is higher than ~80 mol%, otherwise it transforms into γ-opx (Pbca; Dera et al. 2013a). The onset pressure (12–31 GPa) of the β-opx → γ-opx transition is also dependent on the contents of Fe, Al, and Ca (Xu et al. 2020; Xu et al. 2022). After the β-opx → γ-opx transition, no further phase transitions have been observed; in comparison, the α-opx → β-popx (P$_2$1,c2a, post-pyroxyene structure; Finkelstein et al. 2015) transition in En$_{30}$Fs$_{70}$ (Fs is ferrosilite, FeSiO$_3$) has been observed at ~40 GPa. It should be noted that the high-pressure SCXRD measurement (Xu et al. 2018) up to 34 GPa did not observe phase transition in end-member enstatite (En$_{30}$) after the α-opx → β-opx transition but high-pressure Raman spectroscopy experiment (Serghiou et al. 2000) revealed a new phase (at ~40 GPa) whose structure resembles that of the β-popx after the α-opx → β-opx transition. High-pressure and high-temperature SCXRD and Raman spectroscopy studies revealed that the α-opx → β-opx → γ-opx transitions could occur for orthopyroxenes under the pressure-temperature conditions of the cold slab center within the transition zone (Zhang et al. 2014; Xu et al. 2022).

Nonetheless, the compositional effects on the high-pressure phase transitions of orthopyroxene have not yet been well con-