Physics of the Earth and Planetary Interiors 221 (2013) 15–21

Contents lists available at SciVerse ScienceDirect

Physics of the Earth and Planetary Interiors

journal homepage: www.elsevier.com/locate/pepi

Metastable high-pressure transformations of orthoferrosilite Fs_{82}

Przemyslaw Dera[a,e,*], Gregory J. Finkelstein[b], Thomas S. Duffy[b], Robert T. Downs[c], Yue Meng[d], Vitali Prakapenka[a], Sergey Tkachev[a]

[a] *Center for Advanced Radiation Sources, University of Chicago, Argonne National Laboratory, 9700 S. Cass Ave., Bldg. 434, Argonne, IL 60439, USA*
[b] *Department of Geosciences, Princeton University, USA*
[c] *Geology Department, University of Arizona, USA*
[d] *High Pressure Collaborative Access Team, Carnegie Institution of Washington, USA*
[e] *Hawaii Institute of Geophysics and Planetology, School of Ocean and Earth Science and Technology, University of Hawaii at Manoa, USA*

ARTICLE INFO

Article history:
Received 3 February 2013
Received in revised form 11 June 2013
Accepted 13 June 2013
Available online 27 June 2013
Edited by K. Hirose

Keywords:
Ferrosilite
Enstatite
Pyroxenes
High-pressure phase transition
Upper mantle
Synchrotron single-crystal X-ray diffraction

ABSTRACT

High-pressure single-crystal X-ray diffraction experiments with natural ferrosilite Fs_{82} $(Fe^{2+}_{0.82}Mg_{0.16}Al_{0.01}Ca_{0.01})(Si_{0.99}Al_{0.01})O_3$ orthopyroxene (opx) reveal that at ambient temperature the sample does not transform to the clinopyroxene (cpx) structure, as reported earlier for a synthetic Fs_{100} end-member (Hugh-Jones et al., 1996), but instead undergoes a series of two polymorphic transitions, first above 10.1(1) GPa, to the monoclinic $P2_1/c$ phase β-opx (distinctly different from both $P2_1/c$ and $C2/c$ cpx), also observed in natural enstatite (Zhang et al., 2012), and then, above 12.3(1) GPa to a high-pressure orthorhombic *Pbca* phase γ-opx, predicted for $MgSiO_3$ by atomistic simulations (Jahn, 2008). The structures of phases α, β and γ have been determined from the single-crystal data at pressures of 2.3(1), 11.1(1), and 14.6(1) GPa, respectively. The two new high-pressure transitions, very similar in their character to the $P2_1/c$–$C2/c$ transformation of cpx, make opx approximately as dense as cpx above 12.3(1) GPa and significantly change the elastic anisotropy of the crystal, with the [1 0 0] direction becoming almost twice as stiff as in the ambient α-opx phase. Both transformations involve mainly tetrahedral rotation, are reversible and are not expected to leave microstructural evidence that could be used as a geobarometric proxy. The high Fe^{2+} content in Fs_{82} shifts the α–β transition to slightly lower pressure, compared to $MgSiO_3$, and has a very dramatic effect on reducing the (meta) stability range of the β-phase.

1. Introduction

Pyroxenes are among the most important minerals of the Earth's upper mantle and account for approximately 20% of the composition of this layer by volume (Frost, 2008). The pyroxene structure is composed of close-packed layers of O atoms with alternating tetrahedral and octahedral layers that accommodate a variety of different cations ranging from the typical divalent Mg^{2+}, Fe^{2+}, Ca^{2+}, Mn^{2+}, through monovalent Na^{+}, to trivalent Al^{3+}, Fe^{3+} and Cr^{3+} without inducing major rearrangements to the topology and connectivity within the crystal. The structural and compositional flexibility is a consequence of the ability of the infinite corner-linked tetrahedral chains extending along the [0 0 1] direction to stretch or compress by rotation of the individual tetrahedra without affecting the tetrahedral bond lengths, following the rigid unit mode model (Dove et al., 1995). Because of the tetrahedral layer flexibility cations with very different ionic radii coordinated by 4 to 8 oxygen atoms can be accommodated in the M2 sites of the octahedral layers.

Four distinct ambient polymorphs of pyroxene are known, differing in crystal symmetry and layer stacking topology, including $C2/c$ diopside-type, $P2_1/c$ clinoenstatite-type (lp-cpx), *Pbca* orthoenstatite-type (α-opx), and *Pbnm* protoenstatite. Their structures, while easily distinguishable, are very closely related. For some compositions, e.g. in $C2/c$ spodumene, $P2$ and $P2/n$ omphacites and $P2_1ca$ lunar orthopyroxene, small symmetry distortions are found, but their topological relations to the four basic ambient structural types are easily recognizable. Because of the distinct layer stacking patterns, transitions between the principal pyroxene polymorph types are in general reconstructive and involve significant activation barriers, which lead to metastability (Downs, 2003; Thompson and Downs, 2003).

The main geologically-relevant subset of pyroxene composition space is the $MgCaSi_2O_6$ (diopside)–$MgSiO_3$ (enstatite)–$FeSiO_3$ (ferrosilite)–$CaFeSi_2O_6$ (hedenbergite) quadrilateral. Significant (above 10%) Ca^{2+} content strongly favors the monoclinic diopside-type cpx arrangement, while at low Ca^{2+}-contents the preference between the cpx and opx structures is controlled by the pressure and

---

[*] Corresponding author. Address: Hawaii Institute of Geophysics and Planetology, School of Ocean and Earth Science and Technology, University of Hawaii at Manoa, 1680 East West Road, POST Bldg, Office 819 EHonolulu, Hawaii 96822, USA. Tel.: +1 808 956 6347.

E-mail address: dera@cars.uchicago.edu (P. Dera).

0031-9201/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.pepi.2013.06.006

temperature of crystallization (Lindsley, 1983). The compositions richest in Ca^{2+} do not crystallize in the pyroxene structure, but instead assume a $CaSiO_3$ wollastonite structure.

It is widely accepted that the stable high P–T phase diagram along the enstatite-ferrosilite join is composed only of the four principal pyroxene polymorphs. However, a number of recent experimental results and theoretical predictions indicate that the orthorhombic phases if compressed at ambient temperature, rather than transforming to cpx tend to undergo a different kind of structural transformations. Raman spectroscopic experiments indicate one such transition in En_{100} at a pressure of about 10 GPa (Lin, 2003, 2004; Lin et al., 2005). A similar discontinuity in the behavior of hyperfine parameters was noted in a synchrotron Mössbauer study (Zhang et al., 2011). First principles molecular dynamics simulations of the phase behavior of En_{100} starting from the opx structure, conducted at a simulation temperature of 1000 K also revealed a lack of transformation to the monoclinic cpx form, resulting from the large activation barrier for this reconstructive transition. Instead, two possible new metastable displacive polymorphic transitions to HP-OEn2 with space group $P2_1ca$ at 9 GPa and further, to HP-OEn1 with space group $Pbca$ (different than the ambient structure) at 20 GPa were predicted (Jahn, 2008).[1] The two metastable transformations involve gradual rotation of the tetrahedra in the O-type tetrahedral chains, characteristic of the low pressure OEn phase to the S-type. Finally, a recent single crystal study using natural samples with OEn_{87} composition revealed that the phase above 10 GPa is monoclinic (space group $P2_1/c$), but preserves the opx structure topology, with the main structural change being conversion of 25% of the Si-chains from the O to S configuration (Zhang et al., 2012).

The two main processes limiting the geophysical occurrence of pyroxenes in the Earth lower mantle at depths below the transition zone are believed to be dissolution of pyroxene into the garnet structure and the decomposition reaction to free SiO_2 and high-pressure phases of $(Mg, Fe)_2SiO_4$ (Akimoto and Syono, 1970; Ming and Bassett, 1975; Liu, 1976). The boundary of the decomposition reaction coincides with the coesite-stishovite transition of SiO_2, which increases the density of the SiO_2 decomposition product phase by about 30%. At about the same pressure where coesite transforms to stishovite the spinel-type Fe-ringwoodite becomes the stable form of Fe_2SiO_4, however, the volume change associated with this transition (~8%) is smaller than in SiO_2. The decomposition reaction is characterized by a significant activation barrier, and temperatures above 1000 K are needed to initiate the process. The temperature required for decomposition also increases with pressure.

Pyroxenes are abundant in the oceanic crust, which is subducted into the upper mantle at convergent margins (Poli and Schmidt, 2002). While the displacive polymorphic transformations of opx are most likely only between metastable phases, they may have some relevance for deep Earth environments that significantly depart from the standard continental geotherm, such as cold subducted slabs. Some geophysical models (e.g. Bina et al., 2001) assume that subduction can extend to depths greater than 800 km (corresponding to pressures above 30 GPa), with the coldest part of the slab remaining below 1000 K. Orthopyroxene, once stably formed in the oceanic crust, could be metastably transported within the subducting slab to these very significant depths, and experience pressures higher than 10 GPa while still at temperatures lower than the metastable boundaries of polymorphic conversion, dissolution or decomposition (e.g. Nishi et al., 2008 recently demonstrated significant kinetic inhibition of the pyroxene dissolution in garnet at cold subducted slab conditions, at depths exceeding 500 km). As a consequence, understanding of the nature and properties of the high-pressure opx polymorphs may be important in modeling the geophysical behavior of subduction zones (e.g. Bina et al., 2001; Akashi et al., 2009).

$FeSiO_3$ ferrosilite (Fs) is an end-member of the principal pyroxene quadrilateral, and as such is very important in understanding the general crystal chemical and phase stability trends. Pure $FeSiO_3$ has not been reported to occur in nature, but minerals with high Fe/Mg ratios are not uncommon in high-pressure rocks (Bown, 1965; Jaffe et al., 1978; Schreyer et al., 1978; Brothers and Yokoyama, 1990; Young and Cuthbertson, 1994).

Thus far only three polymorphs of synthetic Fs_{100} have been observed at ambient conditions, including opx, lp-cpx and Fs-III (Lindsley et al., 1964). Subsequent structural investigation of these polymorphs revealed that Fs-III (space group P-1) has a pyroxenoid structure (Weber, 1983). High temperature Brillouin scattering study with natural low-Fe OEn at ambient pressure revealed existence of a possible reversible displacive transition to yet unknown high temperature phase at ~1100 °C (Jackson et al., 2004). Unlike OEn, pure OFs was found to convert to cpx at about 4.2 GPa at ambient temperature through a reconstructive transition (Hugh-Jones et al., 1996). An OFs sample with intermediate composition, $Fs_{45}En_{46}Ts_9$ (Ts indicates Tschermak substitution), on the other hand, did not undergo the opx-cpx conversion at ambient temperature up to 9.5 GPa (Nestola et al., 2008). To understand the effect of high Fe^{2+} content on the opx-cpx and α–β-opx transitions we conducted diamond anvil cell single-crystal synchrotron X-ray diffraction experiments with a natural OFs_{82} sample to 32 GPa.

2. Experimental methods

The natural Fs_{82} sample used in our study is from the University of Arizona RRUFF project collections (RRUFF.info/R070386) from a locality in Greenland. This sample was previously used in the thermodynamic study of Mg–Fe order–disorder in orthopyroxenes by Saxena and Ghose (1971), and was referred to as sample XYZ in the Ramberg and DeVore (1951) study of Fe-Mg distribution between olivines and pyroxenes. Electron microprobe analysis (EMPA) indicated a composition $(Fe^{2+}{}_{0.82}Mg_{0.16}Al_{0.01}Ca_{0.01})(Si_{0.99}Al_{0.01})O_3$. Unit cell parameters determined on a single crystal fragment of the sample using a Bruker D8 diffractometer at the University of Arizona were $a = 18.383(1)$ Å, $b = 9.012(1)$ Å, $c = 5.2344(6)$ Å, with a volume of $867.2(3)$ Å^3. This volume is approximately 1% smaller than for pure synthetic OFs_{100} end member (Bass and Weidner, 1984). The bulk composition of the sample was close to the sample S95 of Nestola et al. (2008), $(Fe^{2+}{}_{0.91}Mg_{0.93}Ca_{0.01}Mn_{0.02}Al_{0.08}Fe^{3+}{}_{0.07})(Si_{0.85}Al_{0.15})O_3$, with $a = 18.2920(3)$ Å, $b = 8.8637(4)$ Å, $c = 5.2179(3)$ Å, and $V = 845.99(6)$ Å^3, however, our sample had much higher Fe^{2+}/Mg^{2+} ratio, almost no ferric iron, much lower Al content (the S95 sample contained 15 mol% of trivalent cations incorporated via Tschermak substitution), and a more uniform distribution of Fe between the M1 and M2 octahedral sites, as determined by single crystal structure refinement.

Three separate in situ single-crystal X-ray diffraction experiments were carried out at experimental stations 16IDB (experiments 1 and 2) and 13IDD (experiment 3) of the Advanced Photon Source (APS), Argonne National Laboratory. In each experiment, two crystals with different orientations were loaded into the diamond anvil cell, as shown in Supplementary Fig. 1. The same 4-pin type diamond anvil cell was used in all three experiments. Diamond anvils with culets of 0.3 mm were mounted on asymmetric backing plates (cubic boron nitride towards the X-ray source

---

[1] Jahn (2008), and later Zhang et al. (2012) named the new phases of orthoenstatite HP-OEn1, HP-OEn2 and HPCN2, however, we prefer to adopt a naming convention in which the high-pressure polymorphs of opx will be referred to as α-opx (ambient), β-opx γ-opx etc., to emphasize the topological relationship, which seems more important than the crystal symmetry.