

Pressure-induced $Pbca$ – $P2_1/c$ phase transition of natural orthoenstatite: The effect of high temperature and its geophysical implications



Jin S. Zhang^{a,*}, Bruno Reynard^b, Gilles Montagnac^b, Jay D. Bass^a

^a Department of Geology, University of Illinois, Urbana, IL 61801, USA

^b Laboratoire de Géologie de Lyon, UMR CNRS 5276, Ecole Normale Supérieure de Lyon, France

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ABSTRACT

In-situ high-pressure (P) high-temperature (T) Raman spectroscopy has been used to investigate the effect of temperature on the high-pressure phase transition of Mg-rich orthoenstatite (OEN) to a newly-discovered $P2_1/c$ phase (HPCEN2) up to 673 K and 18.2(10) GPa. Two natural orthoenstatite samples were used in this study: near end-member Mg orthoenstatite (Zabargad Island, Egypt), and Al + Fe-bearing orthoenstatite (San Carlos, Arizona). For San Carlos OEN (SC-OEN), the experiment was performed at room temperature, 373, 573 and 673 K; For Zabargad Island OEN (Zabg OEN), experiments were performed at 573 and 673 K. The three phases OEN, HPCEN2, and another high-pressure phase with space group $C2/c$ (denoted by HPCEN) are readily distinguished by a characteristic doublet, triplet, or singlet, respectively, in the 660–680 cm^{-1} range. Similarly, splitting of a peak near 1100 cm^{-1} is indicative of an OEN \rightarrow HPCEN2 transition. For both samples, no phase other than OEN and HPCEN2 was observed within the investigated P – T range. The recovered products after slow cooling for over 24 h from 673 K and 16.6(9) GPa were OEN. The Clapeyron slope (dP/dT) of this transition is bracketed between +0.020 to –0.0026 GPa/K for Zabg-OEN, and +0.0023 to –0.0049 GPa/K for SC-OEN. Our results suggest a possible stability field for HPCEN2 at the bottom of the upper mantle.

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1. Introduction

Mg-rich Fe-bearing pyroxene with approximate formula $(\text{Mg,Fe})\text{SiO}_3$, is widely considered to be one of the major minerals in Earth's upper mantle. Four polymorphs of $(\text{Mg,Fe})\text{SiO}_3$ are potentially stable under upper mantle conditions: orthoenstatite (OEN) with space group $Pbca$ (Morimoto and Koto, 1969), low-pressure clinoenstatite (LPCEN) with space group $P2_1/c$ (Morimoto et al., 1960), high-pressure clinoenstatite (HPCEN) with space group $C2/c$ (Angel et al., 1992), and a newly discovered high-pressure monoclinic polymorph (HPCEN2), also with space group $P2_1/c$ (Zhang et al., 2012).

Early studies suggested that OEN transforms into HPCEN between 6–9 GPa at high temperature, and that HPCEN transforms to LPCEN upon cooling and decompression (Pacalo and Gasparik, 1990; Kanzaki, 1991; Ulmer and Stadler, 2001; Angel et al., 1992; Shinmei et al., 1999; Kung et al., 2004; Akashi et al., 2009). These experiments lead to the hypothesis that LPCEN, OEN, and HPCEN are the stable polymorphs over the range of upper mantle conditions (Angel et al., 1992; Woodland, 1998). However, the rarity of LPCEN in nature strongly argues against this view of LPCEN

stability (Anthony et al., 1975; Kirby, 1975; Ito, 1975). Moreover, most previous experiments in the literature used either flux-grown synthetic crystals with impurities from the fluxes incorporated in the structure (e.g. Mo, V, etc.), or were performed under hydrous/flux-bearing/high-shear-stress environments (e.g. Grover, 1972; Ito, 1975). Enstatite has been shown to be very sensitive to those impurities and stress environments (e.g. Coe and Kirby, 1975), thus we must view the phase relations of OEN as a function of P , T , chemical composition (X) and stress state σ (not just P and T). In fact, the product recovered upon slow cooling from temperatures of over 1000 °C at room-pressure was found to be OEN instead of LPCEN (Jackson et al., 2004; Brenizer, 2006; Reynard et al., 2009). The only previous studies utilizing natural enstatite samples under nearly water/stress-free conditions by Zhang et al. (2012, 2013), provided both X-ray and Raman evidences of a new high pressure phase transition (OEN \rightarrow HPCEN2) in the enstatite system, and raised questions about the OEN equilibrium phase relations (e.g. the stability field of HPCEN ($C2/c$) and the newly discovered high pressure phase HPCEN2).

In order to examine the stability of HPCEN2, it is necessary to perform phase identification of Mg-rich Ca-poor pyroxene under in situ high P – T and water/stress-free conditions. As for the effect of composition on the high-pressure phase relations, it has been shown that natural impurities of several percent Fe and Al could

* Corresponding author. Tel.: +1 2174191378.

E-mail address: zhang72@illinois.edu (J.S. Zhang).

change the onset of the OEN \rightarrow HPCEN2 transition by up to 3 GPa at room temperature conditions; however, no other phases were observed during the experiments (Zhang et al., 2013). This indicates that natural compositional variations do not stabilize an additional phase of $(\text{Mg,Fe})\text{SiO}_3$ at room temperature and high pressure. However, the combined effects of temperature and composition are still unknown. Thus, in this study, we have performed in situ high-pressure high-temperature Raman experiments with near end-member Mg orthoenstatite from Zabargad Island, Egypt, and Al, Fe-bearing orthoenstatite from San Carlos, Arizona, to address the effects of temperature and composition on the newly-discovered $Pbca \rightarrow P2_1/c$ phase transition.

2. Sample description and experimental methods

Natural orthenstatite samples from two different locations and with distinct chemical compositions were used in this study: Near end-member MgSiO_3 orthoenstatite from Zabargad Island, Egypt with composition $(\text{Mg}_{0.994}\text{Fe}_{0.002}\text{Al}_{0.004})_2(\text{Si}_{0.996}\text{Al}_{0.004})_2\text{O}_6$; and aluminous Fe-bearing orthoenstatite from San Carlos (SC), Arizona with composition $(\text{Mg}_{0.87}\text{Fe}_{0.08}\text{Al}_{0.03}\text{Ca}_{0.02})_2(\text{Si}_{0.97}\text{Al}_{0.03})_2\text{O}_6$ (analyzed by EPMA). Samples of high optical quality were polished into plate-like samples ($\sim 20\ \mu\text{m}$ thickness) using Al_2O_3 abrasive film (down to grit size $0.3\ \mu\text{m}$). Samples were scratch and inclusion-free under examination by optical microscopy, and were cut into pieces approximately $20\text{--}60\ \mu\text{m}$ wide for DAC loading.

High-pressure experiments were performed with a membrane-type diamond anvil cell for precise pressure control (Chervin et al., 1995). Rhenium metal gaskets with an initial thickness of $250\ \mu\text{m}$ were pre-indented to $0.070\ \text{mm}$ using $500\ \mu\text{m}$ -culet ultra-low fluorescence diamond anvils. A $250\ \mu\text{m}$ diameter hole in the gasket formed the sample chamber. For runs at room temperature and 373 K, 2 pieces of SC-OEN (orientation (010) and (100)) were loaded with several ruby spheres in the sample chamber with an alcohol mixture (methanol (M): ethanol (E) = 4:1) as the pressure-transmitting medium. In the room temperature measurements, we used a heat gun to anneal the pressure medium by heating it to about 333 K before measurement. With a freezing pressure $\sim 18\ \text{GPa}$ for the alcohol mixture at 373 K (Klotz et al., 2009), we expected a hydrostatic stress state within the sample chamber. For runs at 573 and 673 K, one piece of SC-OEN and one piece of Zabg-OEN (both with random orientation) were loaded with several ruby spheres into the same chamber with CsBr as the pressure-transmitting medium. Pressure was determined using the ruby fluorescence pressure scale (Mao et al., 1986) before and after a Raman experiment at each pressure–temperature point. Because the temperature and pressure shifts of the ruby R1 peak are largely independent, the effect of temperature on the ruby peak shift could be calibrated at 1 atm. pressure and at temperatures up to 673 K (Fig. 1). The maximum pressure difference from different ruby spheres in the sample chamber at any given P – T point, from measurements taken both before and after Raman spectra were collected, was less than 1.0 GPa in CsBr at 673 and 573 K, and less than 0.5 GPa in the alcohol mixture at lower temperatures.

For the DAC chamber containing two pieces of SC-OEN and a ME pressure-transmitting medium, high-pressure Raman data were collected at 9 different pressures between 0 and 13.13(20) GPa at room temperature, and at 15 different pressures between 3.29(3) and 16.3(4) GPa at 373 K. For the DAC chamber with SC-OEN and Zabg-OEN loaded with CsBr as pressure-transmitting medium, high pressure Raman data were collected at 24 pressures between 5.8(1) and 18.1(9) GPa at 573 K, at 13 pressures between 5.6(1) and 16.6(10) GPa at 673 K, and finally at 17.9(10) GPa and room temperature after slow cooling.

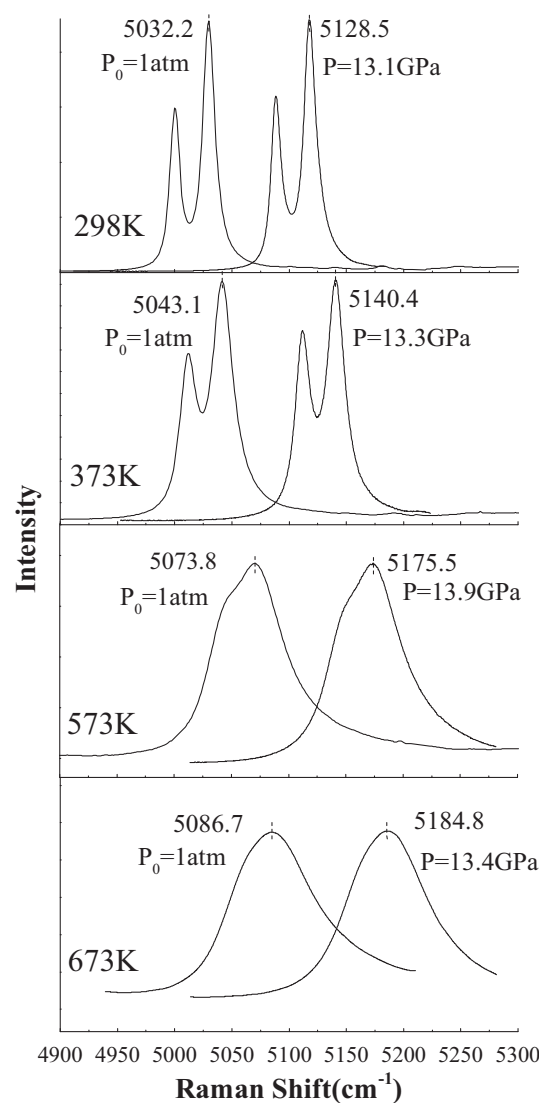


Fig. 1. Ruby spectra at several temperatures.

In-situ high-pressure single-crystal Raman spectroscopy experiments were carried out at Ecole Normale Supérieure de Lyon. Raman spectra were obtained by using a multichannel Raman microprobe (LabRam HR800 from DILOR) equipped with a confocal stage that enhances the signal-to-noise ratio by eliminating most of the parasitic light from the sample and diamond fluorescence. Experiments were conducted in a backscattering geometry with a Mitutoyo objective. The laser spot was focused on the sample to less than $2\ \mu\text{m}$ in diameter. The scattered Raman light is focused through a 100-micron slit into a spectrograph equipped with a 1800 gr/mm grating and analyzed by a CCD detector, giving a resolution of approximately $2.5\ \text{cm}^{-1}$ (Auzende et al., 2004). The accumulation times for Raman spectra were typically 60–120 s over the spectral region from 100 to $1250\ \text{cm}^{-1}$. The precision with which Raman peak positions were determined is typically $0.2\ \text{cm}^{-1}$ (2 sigma) for strong peaks; accuracy is approximately $1\ \text{cm}^{-1}$ for peaks with a full-width at half-maximum (FWHM) of $0.5\text{--}1\ \text{cm}^{-1}$. For weak peaks and overlapped peaks, the peak-position uncertainty is larger but still within $2\ \text{cm}^{-1}$. The 514.5 line of an argon ion laser was used as an excitation source at an output power ranging from 500 to 1500 mW. Only 5–10% of this power reaches the sample, due to absorption or reflection from the objectives, diamonds, and environmental windows in the optical path. Separate spectra were collected with the incident laser beam

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