The effect of Ca substitution on the elastic and structural behavior of orthoenstatite

FABRIZIO NESTOLA,* G. DIEGO GATTA,† AND TIZIANA BOFFA BALLARAN

Bayerisches Geoinstitut, Universitaet Bayreuth, Universitaetstrasse 30, D-95447, Bayreuth, Germany

INTRODUCTION

Orthopyroxenes, and in particular the pure end-member orthoenstatite (Oen, Mg2Si2O6, space group $Pbca$), are among the most studied silicates in Earth Sciences. Such interest is due to their abundance into the Earth’s lower crust and upper mantle. They are also among the most abundant phases present in volcanic rocks and in meteorites as mesosiderites (Ganguly et al. 1994), loderanites, acapulocites, diogenites, howardites, ureilites, and shergottites (Molin et al. 1994; Zema et al. 1996, 1997; Domenechetti et al. 2000; Goodrich et al. 2001; Goodrich 2003). Knowledge of their thermodynamic properties allows us to determine accurately the temperature and pressure conditions at which these minerals are formed and to constrain the formation conditions of important rock assemblages in the Earth’s deep interior. The crystal chemistry of more than 200 natural orthopyroxenes has been determined by Domenechetti et al. (1995a) who obtained linear equations that allow the prediction of cell parameters and interatomic distances for any orthopyroxene, starting from its chemical formula. Several studies of the crystal chemistry and elastic properties at room conditions have been performed on pure orthoenstatite (Morimoto and Koto 1969; Hawthorne and Ito 1977; Weidner et al. 1978; Ohashi 1984; Yang and Ghose 1995a; Duffy and Vaughan 1998; Jackson et al. 1999) and along the join Mg2Si2O6–Fe2Si2O6 (orthoferrrosilite), since Fe$^{2+}$/Mg is the major cation substitution occurring in orthopyroxenes (Bass and Weidner 1984; Domenechetti and Steffen 1992; Skogby et al. 1992; Yang and Ghose 1995b). Numerous investigations along this join have also been carried out both at high-pressure (Frisillo and Barsch 1972; Ito et al. 1977; Weidner et al. 1978; Ralph and Ghose 1980; Webb and Jackson 1993; Angel and Hugh-Jones 1994; Hugh-Jones et al. 1997; Woodland 1998; Chai et al. 1997; Flesch et al. 1998; Jackson et al. 1999; Angel and Jackson 2002; Lin 2003; Kung et al. 2004) and at high temperature (Chopelas and Boehler 1992; Yang and Ghose 1994; Zhao et al. 1995; Hugh-Jones 1997; Chopelas 2000; Jackson et al. 2001, 2004). The elasticity and equation of state (EoS) of orthopyroxenes have been the subject of controversy for the last few decades. In a recent study, Angel and Jackson (2002) addressed the discrepancies among EoS parameters previously reported for orthoenstatite. They re-analyzed published measurements of compression and elasticity of Oen, and showed that the revised room pressure bulk modulus ($K_0$) and its pressure derivative ($K’$) are indeed consistent with one another as well as with new single-crystal compression data presented in the same paper. The best estimates of $K_0 = 105.8(5)$ GPa and of $K’ = 8.5(3)$, using a third-order Birch-Murnaghan (BM3; Birch 1947) EoS, confirm that orthoenstatite (and very likely also orthoferrrosilite; Hugh-Jones et al. 1997) has an “anomalously” high value of $K’$ at room temperature. It appears, therefore, that Fe$^{2+}$ substitution has little effect on the compressibility of orthoenstatite (Hugh-Jones et al. 1997). However, some investigations indicate that the Fe$^{3+}$ substitution has an effect on the elasticity of orthoenstatite (Bass and Weidner 1984; Duffy and Vaughan 1988; Jackson et al. 1999), although the effect seems to be more pronounced for shear elasticity and there is some debate concerning its effect on the bulk modulus (Jackson et al. 1999).

Natural orthopyroxenes, however, seem to behave differently, probably due to the presence of other cations, like Al or Ca, which may play a crucial role in determining the elastic and compressional behavior of these minerals. A few studies have

ABSTRACT

A single crystal of orthopyroxene with composition Ca$_{0.07}$Mg$_{1.93}$Si$_2$O$_6$ (space group $Pbca$) has been investigated at high pressure and room temperature by in-situ X-ray diffraction using a diamond anvil cell. The unit-cell parameters have been determined at ten different pressures up to 10.16(5) GPa. In the pressure range investigated no evidences of phase transitions have been found. The pressure-volume data have been fitted with a third-order Birch-Murnaghan equation of state resulting in the following parameters: $V_0 = 838.26(8)$ Å$^3$, $K_0 = 110(1)$ GPa, $K’ = 6.6(4)$. The Ca substitution in the pure orthoenstatite Mg$_2$Si$_2$O$_6$ structure causes a slight increase in $K_0$ and a decrease in $K’$. The compressibility of $a$, $b$, and $c$ unit-cell parameters is strongly anisotropic with a compressibility scheme $\beta_a >> \beta_b >> \beta_c$. The structure evolution as a function of pressure has been determined at five different pressures up to 6.25(5) GPa. The M2 polyhedron undergoes the largest volume variation (~7.7%), whereas the volume variation of M1 is ~6.1%. The TA and TB tetrahedral volumes decrease by about 3% and 1.2%, respectively, without a discontinuity in the pressure range investigated.

Keywords: Orthopyroxene, high-pressure, compressibility, equation of state
been performed at room conditions on natural Ca-orthopyroxenes (Chatillon-Colinet et al. 1983; Domenechetti et al. 1995b; Zema et al. 1999; Stimpfl et al. 1999). Zema et al. (2003) showed that Ca occupies the M2 sites causing an enlargement of this polyhedron but it does not affect the kinetics of the Fe-Mg non-convergent ordering process. Single-crystal structure determinations up to 6 GPa of a natural orthopyroxene (Hugh-Jones et al. 1997) show that chemical substitution of Al and Ca into the structure of orthopyroxene inhibits the initial rapid compression of M2-O3 bonds and the significant tetrahedral compression above 4 GPa observed in synthetic (Mg,Fe)SiO3 samples. In natural samples, however, it is difficult to discriminate among the effects of the different cations, and only the overall effect of minor cations can be described.

The first study focusing on the effect of Ca alone on the orthoenstatite structure was performed along the synthetic join diopside (CaMgSi2O6)–enstatite (Nestola and Tribaudino 2003). That study demonstrated that substitution of Ca in the P63/mmc structure of orthoenstatite induces local distortions of the tetrahedral chains, which destabilize the structure. This suggests that the orthoenstatite structure cannot contain more than 9–10% of Ca apfu, as observed in natural samples (Domenechetti et al. 1995a). For Ca contents of ~15%, the stable phase appears to be that of pigeonite with P2_1/c symmetry at room conditions (Tribaudino and Nestola 2002).

In this study, high-pressure experiments have been performed on one of the samples synthesized by Nestola and Tribaudino (2003), an iron-free orthopyroxene with composition Ca0.07Mg1.93Si2O6. The purpose is to determine if Ca alone may be responsible for the difference between the high-pressure behavior of natural orthopyroxenes and orthoenstatite (Hugh-Jones et al. 1997).

**EXPERIMENTAL METHODS**

The orthopyroxene sample used in this study has been accurately characterized by means of transmission electron microscopy (TEM), X-ray diffraction, and SEM-EDS (Nestola and Tribaudino 2003). Two single crystals of different sizes were formed on one of the samples synthesized by Nestola and Tribaudino (2003) as starting parameters in the refinement. Anisotropic displacement parameters were obtained for all atoms only in the structure refinement based on room pressure data, which was obtained from the crystal in air. In the structure refinements at high-pressure, anisotropic displacement parameters were determined only for the M2 and M1 sites, with occupancy of Mg and Ca of the M2 site constrained to the values obtained from the chemical analysis (0.93 and 0.07 apfu, respectively; Nestola and Tribaudino 2003). Refinement details, atom coordinates, displacement parameters, and interatomic distances and angles are reported in Tables 2, 3, and 4.

**RESULTS**

**Elastic behavior**

The unit-cell parameters measured at ten different pressures up to 10.16(5) GPa are reported in Figure 1. The data points at 9.40, 7.49, and 2.80 GPa were measured while decompressing and they do not show any deviation from the trends obtained during compression. No evidence of a phase transition was found. The pressure-volume data were fitted by a BM3 EoS (Birch 1947) refining simultaneously unit-cell volume, V0, bulk modulus, K0, and its first pressure derivative, K0'. The refinement was performed using the program EOSFIT 5.2 (Angel 2001), which yielded the following EoS parameters: V0 = 838.26(8) Å³, K0 = 110(1) GPa, K0’ = 6.6(4). The normalized strain vs. finite strain plot (F_t/F_0 plot; Angel 2000) confirms that the P-V data are adequately described by a BM3 fit (Fig. 2).

The compressibility of a, b, and c unit-cell parameters is strongly anisotropic (Fig. 1). Linearized F_t/F_0 plots, obtained by substituting the cube of the unit-cell lattice parameters for the volume in the normalized strain and finite strain equations.

**TABLE 1.** Variation of unit-cell parameters with pressure for the Ca-orthoenstatite sample

<table>
<thead>
<tr>
<th>P (GPa)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000(1)</td>
<td>18.2718(4)</td>
<td>8.8323(2)</td>
<td>5.1914(4)</td>
<td>838.24(8)</td>
</tr>
<tr>
<td>1.51(5)</td>
<td>18.2150(6)</td>
<td>8.7859(3)</td>
<td>5.1719(6)</td>
<td>827.60(8)</td>
</tr>
<tr>
<td>2.80(5)*</td>
<td>18.1659(6)</td>
<td>8.7459(7)</td>
<td>5.1545(1)</td>
<td>818.93(14)</td>
</tr>
<tr>
<td>3.81(5)</td>
<td>18.1684(4)</td>
<td>8.7460(3)</td>
<td>5.1539(6)</td>
<td>818.84(8)</td>
</tr>
<tr>
<td>5.35(5)</td>
<td>18.1342(6)</td>
<td>8.7176(4)</td>
<td>5.1400(7)</td>
<td>812.57(8)</td>
</tr>
<tr>
<td>7.28(5)</td>
<td>18.0789(5)</td>
<td>8.6750(3)</td>
<td>5.1221(6)</td>
<td>803.29(8)</td>
</tr>
<tr>
<td>9.40(5)*</td>
<td>17.9563(5)</td>
<td>8.5796(5)</td>
<td>5.0801(8)</td>
<td>782.62(12)</td>
</tr>
<tr>
<td>1.00(5)</td>
<td>17.9416(5)</td>
<td>8.5642(7)</td>
<td>5.0740(7)</td>
<td>779.64(7)</td>
</tr>
</tbody>
</table>

Note: The uncertainties in pressure is from Mao et al. (1986).

* Data measured under decompression.

**TABLE 2.** Structure refinement results for the Ca-orthoenstatite sample

<table>
<thead>
<tr>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.2588(5)</td>
<td>18.201(1)</td>
<td>8.768(1)</td>
<td>8.750(1)</td>
</tr>
<tr>
<td>18.203(2)</td>
<td>18.108(2)</td>
<td>8.723(2)</td>
<td>8.7201(9)</td>
</tr>
<tr>
<td>18.206(2)</td>
<td>18.108(2)</td>
<td>8.724(2)</td>
<td>8.7201(9)</td>
</tr>
<tr>
<td>18.203(2)</td>
<td>18.108(2)</td>
<td>8.723(2)</td>
<td>8.7201(9)</td>
</tr>
<tr>
<td>18.203(2)</td>
<td>18.108(2)</td>
<td>8.723(2)</td>
<td>8.7201(9)</td>
</tr>
</tbody>
</table>

Note: The data at 1.76 and 3.94 GPa were measured during decompression. The refinement at 0 GPa is for the crystal in air.
Structural behavior

The structure of orthopyroxenes consists of alternating layers of silicate tetrahedra and M^2O_4 octahedra parallel to the (100) plane (see, for example, Cameron and Papine 1981). The tetrahedra form infinite chains (A- and B-chains) parallel to the c axis. The A-chain is more extended and tetrahedra in the chain are characterized by smaller volumes. Of the two octahedral sites, the M2 site is larger and more distorted than M1. Large cations, like Ca, can only occupy the M2 site, whereas smaller cations (mainly Fe^{2+} and Mg) reside in both M2 and M1 sites. The sample studied in this work contains 7% of Ca in the M2 sites, with Mg occupying both the M2 (93%) and M1 (100%) sites. From the refinement of the intensity data collected with the crystal in air, we obtain atomic coordinates that are not significantly different from those reported by Nestola and Tribaudino (2003).

Structural refinements at high-pressure confirm that the M2 octahedron is the most compressible polyhedron in the structure (Hugh-Jones and Angel 1994; Hugh-Jones et al. 1997). The M2 volume decreases by about 7.7% up to 6.25 GPa (Table 4, Fig. 3a) with a linear compressibility \( \beta_{M2} = 0.0123(1) \) GPa\(^{-1}\), the average \( \Delta V \) bond distances undergo a shortening of about 2.6%, as a result of a relatively small shortening of the six M2-O distances (from –0.3% down to –1.6%), and a very strong compression of the longest M2-Oa and the M2-Ob (2000) indicate that the evolution of the unit-cell lattice parameters also is well described by a BM Eos, which has, therefore, been used. The resulting Eos parameters are: \( \beta_0 = 18.2719(6) \) Å, \( K_{\theta0} = 150(3.3) \) GPa, \( K_{\phi0} = 7.3(9) \) GPa, \( K_{\gamma0} = 88.2(1.1) \) GPa, \( K_{\delta0} = 4.7(3) \), \( c_0 = 5.1942(4) \) Å, \( K_{\phi0} = 108.09(2.4) \) GPa, \( K_{\gamma0} = 8.2(8) \) GPa.

The linear axial compressibilities \( \beta_x = -1/(d \theta/d \beta)_{Eos} \), with \( d = a, b, \) and \( c \) are \( \beta_0 = 0.0018(1) \) GPa\(^{-1}\), \( \beta_y = 0.0030(1) \) GPa\(^{-1}\), and \( \beta_z = 0.0023(1) \) GPa\(^{-1}\), with a compressibility scheme \( \beta_a > \beta_b > \beta_c \).

**Notes:**

1. The data at 1.76 and 3.94 GPa were measured during decompression, that one at 0 GPa is for the crystal in air. For the HP-refinements the isotropic thermal parameters, \( U_{iso} \), are reported, whereas for the room condition refinements \( U_{iso} \) are shown.

2. The structure of orthopyroxenes consists of alternating layers of silicate tetrahedra and M^2O_4 octahedra parallel to the (100) plane.
bond distances (−3.4% and −7.4%, respectively). The M1 octahedron, which is smaller and more regular than M2 (Table 4), shows a smaller volume variation with pressure (−6.1%; Table 4 and Fig. 3a) with a linear compressibility \( \beta_{M1} = 0.0097(1) \) GPa\(^{-1}\). The average \(<M1-O>\) bond distances show a variation of about −2.1% with all six M1-O bond distances decreasing between 0.6% (M1-O2A) and 3% (M1-O1B).

The pressure dependence of the volumes of the SiO\(_4\) tetrahedra TA and TB of the A-chain and B-chain, respectively, is shown in Figure 3b. The volumes of TA and TB decrease by about 3% and 1.2%, respectively, vary linearly with pressure and exhibit no discontinuities in the pressure range investigated. The chain kinking expressed in terms of the O3-O3-O3 angle decreases by 1.4% for the A-chain and by 3.5% for the B-chain (Table 4).

The basal tilt, defined as the angle between the basal plane of the tetrahedron (defined by O3-O2-O3) and (100), decreases linearly as a function of pressure, with a variation by about 1.4° for the A-chain and about 0.7° for the B-chain (Table 4).

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**Figure 1.** Evolution of the unit-cell parameters (a) and volume (b) as a function of pressure for Ca-bearing orthoenstatite. The open symbols refer to the measurements performed during decompression. Uncertainties are smaller than the symbols used.

**Figure 2.** \( f_E: f_E \) plot. From the linear fit one obtains \( f_E = K_T = 112(1) \) GPa for \( f_E = 0 \) and \( K' = (\text{slope}/3K_T) \times 2 + 4 = 6 \). The value of \( K_T \) and \( K' \) so calculated are in good agreement with those obtained by fitting the \( P-V \) data with a BM3 EoS.

**Figure 3.** Evolution of the octahedral (a) and tetrahedral (b) volumes as a function of pressure for Ca-bearing orthoenstatite of this study. The values at 0.0001 GPa are from the structure refinement with the crystal in air. The open symbols refer to the measurements during decompression.
**DISCUSSION**

Effect of Ca on the elastic behavior of pure orthoenstatite

A comparison between the EOS parameters obtained for pure orthoenstatite (Angel and Angel 2002) and those obtained in this study reveals that the substitution of 7% of Ca for Mg gives rise to a slight increase of the $K_{0}$ value (about 3.6%) and to a decrease of the $K'$ value (about 22%). This variation of the elastic behavior of orthoenstatite due to Ca substitution is very similar to that observed for a natural orthopyroxene, which contains both Ca and Al and is stiffer than our sample (Hugh-Jones et al. 1997). We, therefore, exclude the possibility that such effects might be due to clinopyroxene lamellae, which are present at practically negligible levels (estimated to be less than 0.1% by volume based on TEM observations).

Ca substitution in monoclinic pyroxenes has the opposite effect on bulk modulus and its pressure derivative. For $P2_{1}/c$ clinopyroxenes along the join diopside-clinoenstatite (Angel and Hugh-Jones 1994; Nestola et al. 2004) it has been found that the substitution of 15% Ca into the pure clinopyroxene structure decreases the value of $K_{0}$ from 111.1(3.3) to 102(2) GPa and increases the value of $K'$ from 6.6(1.1) to 8(1).

Structural evolution of orthopyroxenes with pressure

To understand the effect of Ca substitution on the deformation mechanism of the orthopyroxene structure, we can compare our results with those obtained for a synthetic pure orthoenstatite (Hugh-Jones and Angel 1994), for a synthetic sample with composition Mg$_{0.6}$Fe$_{0.4}$SiO$_3$ (En60) (Hugh-Jones et al. 1997) and for a natural orthopyroxene with composition (Mg$_{0.83}$Fe$_{0.12}$Ca$_{0.006}$Al$_{0.04}$)(Si$_{0.97}$Al$_{0.03}$)O$_3$ (Oen-nat; Hugh-Jones et al. 1997). For all samples, the M2 polyhedron undergoes the formation mechanism of the orthopyroxene structure, we can compare our results with those obtained for a synthetic pure orthoenstatite (Hugh-Jones and Angel 1994), for a synthetic sample with composition Mg$_{0.6}$Fe$_{0.4}$SiO$_3$ (En60) (Hugh-Jones et al. 1997) and for a natural orthopyroxene with composition (Mg$_{0.83}$Fe$_{0.12}$Ca$_{0.006}$Al$_{0.04}$)(Si$_{0.97}$Al$_{0.03}$)O$_3$ (Oen-nat; Hugh-Jones et al. 1997). For all samples, the M2 polyhedron undergoes the largest deformation. This is mainly due to the very large variation shown by the M2-O3A and M2-O3B bond distances. The M2-O3B bond distance decreases at a greater rate than M2-O3A for all the samples except Oen-nat (Fig. 4). The stiffening of the M2-O3B bond in the natural sample may be a consequence of its smaller tetrahedral B-chain kinking with respect to the synthetic pyroxenes, which gives rise to a shorter M2-O3B distance. It appears therefore that the stiffening of the M2-O3B bond in the natural orthopyroxene is not directly related to the Ca substitution into the M2 site, but more likely to some secondary effect such as the presence of Al at the M1 site.

The other major difference between the high-pressure structural behavior of the Oen-nat and (Mg,Fe)$_3$SiO$_5$ orthopyroxenes is related to the compressibility of the TA and TB tetrahedra (Hugh-Jones et al. 1997). Whereas the tetrahedra of the Oen-nat sample are relatively incompressible up to 6 GPa, the tetrahedra of pure orthoenstatite (Hugh-Jones and Angel 1994) and En60 show a change in their compressibility behavior at about 3–4 GPa. Our Ca-bearing sample shows an intermediate behavior: both TA and TB are more compressible, but do not show any discontinuity in the evolution of their volumes with pressure (Fig. 3b). Thus, although the Ca substitution clearly affects the tetrahedral behavior with respect to that observed for synthetic (Mg,Fe)$_3$SiO$_5$ and natural orthopyroxene, it cannot be the only factor because the presence of other cations (e.g., Al in natural orthopyroxene) can contribute to polyhedral compressibility.

High-pressure phase transition in orthopyroxenes

High-pressure Raman spectroscopic studies have reported the occurrence of a phase transformation in orthoenstatite above 10 GPa (Chopelas 1999; Lin 2003), which appears to be first order and reversible with a slight hysteresis. Chopelas (1999) suggests that the new phase is the monoclinic high-pressure C2/c phase of clinoenstatite; however, it is well known that C2/c clinoenstatite reverts to $P2_{1}/c$ clinoenstatite rather than orthoenstatite with decreasing pressure. For this reason, Lin (2003) suggests that the high-pressure phase is a metastable intermediate polymorph between orthoenstatite and the high-pressure clinoenstatite. Kung et al. (2004) observe an anomalous behavior of the elastic wave velocities $V_p$ and $V_s$ for orthoenstatite above 9 GPa, which appears to be associated with a reversible phase transformation. On the basis of their X-ray powder-diffraction patterns, they suggest that this high-pressure polymorph is a metastable phase related to the kinetics of the phase transition from orthoenstatite to HP-clinoenstatite at room temperature. However, this phase is different from the $Cmca$ phase suggested by Jackson et al. (2004) from their high-temperature experiments of orthoenstatite at room pressure. The $Pbca \rightarrow HP-C2/c$ phase transition has indeed been observed for orthoferrosilite by in-situ single-crystal X-ray diffraction above 4.2 GPa (Hugh-Jones et al. 1996), and it appears to be highly time-dependent. No discontinuity in the unit-cell parameter evolution was observed for our sample up to 10.16 GPa, suggesting that no phase transition occurs in the pressure range investigated. The crystal, however, was kept at pressure above 9.4 GPa only for a total of 7 days, therefore it is not possible to determine if the Ca substitution increases the stability field of pure orthoenstatite, or if the time-scale of our experiment was too short to observe any anomaly in our crystal.

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