PIGEONITE UNDER NON-AMBIENT CONDITIONS

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ABSTRACT

Two natural Ca-poor pigeonite samples with different Fe content and free of exsolved augite, were studied by "in situ" high-pressure single-crystal X-ray diffraction using a diamond anvil cell (DAC). For both samples a first order phase transition from $P2_1/c$ to $C2/c$ was found and a relationship between the transition pressure P_c and the average M2 ionic radius was evidenced.

The Fe-poor sample was also studied by both "in situ" and "ex situ" high-temperature single crystal X-ray diffraction using a micro-furnace and a vertical oven respectively. The character of the $P2_1/c$ to $C2/c$ phase transition was defined and the temperature of the transition was constrained. These data together with the closure temperature of the Fe^{2+}-Mg order-disorder were needed for establishing the temperature range of the annealing "ex situ" experiments required for the further kinetic study.

The results of this work have already been published (Alvaro et al., 2010).

INTRODUCTION

Pigeonites are clinopyroxenes which undergo a $P2_1/c$-$C2/c$ phase transition during compression and on increasing temperature. The only available HP data on $P2_1/c$ pyroxene concern so far synthetic samples of clinoenstatite, $Mg_2Si_2O_6$, clinoferrosilite, $Fe_2Si_2O_6$, and a sample with composition $Ca_{0.15}Mg_{1.85}Si_2O_6$ (Hugh-Jones & Angel, 1994; Hugh-Jones et al., 1994; Nestola et al., 2004). Although these studies have showed that composition affects the pressure of transformation (P_c), the mechanism still has to be fully characterized.

Aim of the present work is the definition of the stability field of two natural pigeonite samples with different composition as a function of P and T using "in situ" single crystal X-ray diffraction. In particular this study will be focused on: i) the variation of the thermoelastic properties as a function of the composition at different P and T conditions; ii) the effect of composition on the critical P and T and on the thermodynamic character of the $P2_1/c \rightarrow C2/c$ phase transition. The measured critical temperature allowed us to know in advance the maximum temperature that could be reached during the HT "ex situ" experiments devoted to the further kinetic study. This was performed to measure the disordering rate constants of the Fe-Mg intracrystalline exchange reaction and to constrain the effect of X_{Fe} by comparison with the kinetic data from literature on the Fe-rich BTS-308 ($W_{10}En_{47}Fs_{43}$) pigeonite sample (Domeneghetti et al., 2005) and on the augite KC ($W_{43}En_{46}Fs_{11}$) sample (Brizi et al., 2001).

EXPERIMENTAL METHODS

Single-crystal X-ray diffraction (XRD) experiments at high-pressure (HP) "in situ" and high-temperature (HT) "in situ" and "ex situ" conditions were performed on two natural pigeonite samples, previously studied at high-T and room pressure (Pasqual et al., 2000; Cámara et al., 2002; Domeneghetti et al., 2005).

Samples

The first sample studied is a Fe-rich natural pigeonite sample from the Paranà ryodacite (labelled BTS-308) with crystal-chemical formula $^{M2}(Ca_{0.19}Mg_{0.09}Fe_{0.69}Mn_{0.03})$ $^{M1}(Mg_{0.75}Fe_{0.23}Fe^{3+}_{0.01}Ti_{0.01})$ $^{T}(Si_{1.97}Al_{0.03})$ O_2. The second sample is a Fe-poor natural pigeonite sample from the Antartic ureilite Pecora Escarpment (labelled PCA-82506-3), with formula $^{M2}(Ca_{0.117}Mg_{0.5618}Fe_{0.3048}Mn_{0.0112})$ $^{M1}(Mg_{0.9146}Fe_{0.0494}Cr_{0.0328}Na_{0.0052})$ $^{T}(Si_{1.9696}Al_{0.0304})$ O_6. The crystals used for the experiments do not contain exolved augite lamellae, the presence of which has been excluded by single-crystal XRD rocking profiles analysis.

High-pressure experiments

The unit cell parameters on the sample labelled BTS-308 were collected at the Bayerisches Geoinstitut (Bayreuth), by XRD at 18 different pressures up to 6.3 GPa using a HUBER four-circle diffractometer and the SINGLE software (Ralph & Finger, 1982; Angel *et al.*, 2000). The BTS-308 N.1 crystal was loaded in a BGI-type diamond anvil cell (DAC; Allan *et al.*, 1996 - see Fig. 1), using a steel gasket (T301), pre-indented to a thickness of 110 µm and with a hole of 300 µm in diameter. Unit-cell parameters were determined at high pressure by the method of eight-position diffracted-beam centering (King & Finger, 1979; Angel *et al.*, 2000).

The unit-cell parameters on PCA82506-3 sample were determined by XRD at 14 different pressures up to about 7.142 GPa using a STOE STADI4 four-circle diffractometer and the SINGLE software (Ralph & Finger, 1982; Angel *et al.*, 2000). The PCA82506-3 N.1 crystal was loaded in an ETH-type DAC (Miletich *et al.*, 2000), using a steel gasket (T301), pre-indented to a thickness of 96 µm and with a hole of 250 µm in diameter. For both experiments a single-crystal of quartz was used as an internal diffraction pressure standard (Angel *et al.*, 1997); a 4:1 mixture of methanol:ethanol and a 16:3:1 mixture of methanol:ethanol:water was used as hydrostatic pressure medium for BTS-308 and PCA82506-3

Fig. 1 - Picture of the ETH-DAC (diamond anvil cell) designed by R. Miletich (photo taken by author).

samples respectively. Unit-cell parameters were determined at high pressure by the method of eight-position diffracted-beam centering (King & Finger, 1979; Angel *et al.*, 2000).

The intensity data devoted to the structural refinements were carried out at the Dipartimento di Geoscienze (University of Padova). The intensity data collection were performed by single-crystal XRD at 11 different pressures up to 9.4 GPa using a STOE Stadi 4 single-crystal diffractometer and an ETH-type DAC (Miletich *et al.*, 2000). A steel gasket (T301), pre-indented to 90 µm and with a hole of 250 µm in diameter was used with a 16:3:1 mixture of methanol:ethanol:water hydrostatic pressure medium. As the unit-cell volumes measured at ambient conditions on crystal N.1 and N.2 and N.3 are in good agreement (with differences less than two e.s.d.'s), no pressure standard was used in this second experiment. The internal pressure of each data point was determined using the equation of state calculated from the unit-cell parameters collected for BTS-308 N.1, following the same experimental procedure used

in (Nestola *et al.*, 2008). For each pressure experiment, the intensity data were collected and used for weighted structure refinement by applying two scale factors, starting from the atomic coordinates of Pasqual *et al.* (2000). The package SHELX-97 (Sheldrick, 1997) was used. Structural refinements were performed in $P2_1/c$ space group for data measured up to 3.15 GPa. Above this pressure, the disappearance of the *b*-type reflections ($h + k = 2n + 1$) was observed, indicating that a transition to a *C* centred lattice had occurred. Therefore, the structure refinements of data measured between 3.6 and 9.4 GPa were performed in $C2/c$ space group, starting from the atomic coordinates of Nestola *et al.* (2004). The atomic scattering curves were taken from the International Tables for X-Ray Crystallography (Wilson, 1995). Neutral *vs.* ionized scattering factors were refined for O and Si while ionized scattering factors were refined for Fe, Ca and Mg. A residual electron-density maximum, located at 0.5-0.6 Å from the M2 site was observed in the difference-Fourier map throughout the entire investigated pressure range. A residual electron-density maximum, located 0.5-0.6 Å from the M2 site, was observed in the difference-Fourier map for all the crystals during the experiments. The same feature had previously been observed by Cámara *et al.* (2002) and Domeneghetti *et al.* (2005) in another BTS-308 pigeonite crystal and by Tribaudino & Nestola (2002) in two synthetic $P2_1/c$ clinopyroxene samples with compositions $Di_{15}En_{85}$ and $Di_{23}En_{77}$. As suggested by these authors, this residual electron density is due to positional disorder of Ca at the M2 site. A M21 split position, with the atomic coordinates of the residual (*ca.* $x = 0.25$, $y = 0.08$, $z = 0.26$), was then introduced in the structure refinements with a soft constraint based on the M2-M21 distance observed in the difference-Fourier map. In the structure refinement, only the atomic displacement parameters of the M1 and M2 sites were treated as anisotropic. Structure refinements carried out in $P2_1/c$ symmetry with the M21 split model resulted in an improvement of the agreement factor with respect to the non-split model. On the contrary, the M21 split model was not applied in the $C2/c$ structure refinements as no further improvement was observed. For all high-pressure data the Mg and Fe site occupancies of the M1 and M2 sites were constrained to those obtained for crystal N.2, for which the structure refinement was performed using diffraction data collected in air.

High-temperature experiments

The Fe-poor pigeonite crystal PCA82506-3 N. 4 was annealed "in situ" during the single crystal XRD experiment using a micro-furnace with a H-shaped resistance heater which has been built specifically for a point detector Philips PW1100 automated four-circle diffractometer (see Fig. 2).

This furnace allows temperatures up to 1100°C to be reached and intensity data to be collected in the 2θ range of 3–58°. It has been calibrated for temperature using the melting points of selected standards (Tribaudino *et al.*, 2002). The crystal was annealed in a sealed quartz vial (inner Ø = 0.5 mm). To avoid any mechanical stress, the crystal was kept steady in the vial, using quartz wool. Some graphite powder was placed inside the sealed vial, at 5 mm from the crystal, to prevent oxidation of Fe. Starting from room temperature, and then heating up to 1093°C, lattice parameters were measured centering 24 selected *hkl* a reflections ($h + k = 2n$) at 19 different temperatures. The intensity of *hkl* *b*-type reflections ($h + k = 2n + 1$) (102, 052, $\overline{7}$02, $\overline{2}\,\overline{3}$3, $\overline{2}$33) present only in the *P*-centred lattice were measured by stepscan profiles of 3° by ω-rotations. They were scaled with respect to the intensities of adjacent reflections in the same reciprocal row (202, 062, $\overline{6}$02, $\overline{1}\,\overline{3}$3, $\overline{1}$33). The ratio I_b/I_a was obtained summing all the data for the intensities of *b*-reflections (ΣI_b) and of the *a*-reflections (ΣI_a). The components of the spontaneous strain due to the phase transition, the strain volume, the scalar strain and the non-breaking strain component of the spontaneous strain tensor have been calculated as described in Cámara *et al.* (2003).

Isothermal annealing experiments were carried out until equilibrium on other three crystals of sample PCA82506-3 at three temperatures ranging between the closure temperature of the Fe-Mg exchange reaction (*ca.* 730°C), calculated from the calibration by Pasqual *et al.* (2000), and the critical temperature obtained by the "in situ" heating experiments of this study (912°C).

Crystal PCA N.16 was heated at 790°C, crystal PCA N.13 at 840°C and crystal PCA N.10 at 865°C. For each annealing experiment the crystal was sealed into silica vial, after alternately washing with nitrogen flux and vacuuming, together with an iron-wüstite buffer to control the fO_2. Inside the silica tube, the crystal and the buffer were put into two small, separate Pt crucibles to avoid contact between them. Heating experiments were quenched by dropping the tubes into cold water. The presence of both iron and wüstite, in a different ratio compared to that in the original powder, was verified at the end of each experiment by X-ray powder diffraction. The "hot spot" of the vertical furnace was calibrated to be ≈ 5 cm long. Before the insertion of the vial the temperature was monitored by a Pt/(Pt-Rh) thermocouple

Fig. 2 - Microfurnace with a H-shaped resistance heater mounted on Philips PW1100 automated four-circle diffractometer.

(±3°C) with its junction placed at the same (±0.5 cm) horizontal section of the furnace as that containing the sample. The temperature of the thermocouple was checked at ≈ 800°C using the melting point of pure NaCl (801°C).

Intensity data were collected on the untreated crystal and after each annealing experiment. The unit-cell parameters were measured with the conventional diffractometer Philips PW1100 using a locally improved version (Cannillo *et al.*, 1983) of the Philips LAT routine.

Structure refinement was performed in the same way as for the high pressure experiments. In the difference-Fourier map the residual electron-density maximum, located 0.5-0.6 Å from the M2 site, found by Cámara *et al.* (2002), Merli & Cámara (2003) and Domeneghetti *et al.* (2005) in BTS-308 crystals was not observed for crystals PCA N.10, N.13 and N.16 before and after all the annealing experiments. This residual electron density maximum had been interpreted as due to positional disorder of Ca at the M2 site and the height of this maximum has been related to the content of this cation (Merli & Cámara, 2003). The lower Ca content of the PCA pyroxene may not be enough to resolve this maximum with the resolution of our data (0.62 Å^{-1}).

Once structure refinement reached convergence, full-matrix least-squares cycles with chemical constraints taken from the electron microprobe analysis (assuming 1σ as error) were carried out to obtain the cation partitioning. The M1 and M2 partitioning was obtained taking into account the stronger preference of Mn for M2 compared to Fe^{2+} observed by (Stimpft, 2005) in a donpeacorite sample (Mn$_{0.54}$Ca$_{0.03}$Mg$_{1.43}$Si$_2$O$_6$). Domeneghetti *et al.* (2005) showed that for pigeonite BTS-308 the "different partitioning methods do not affect the k$_D$ values, as previously observed by (Tribaudino *et al.*, 2003; Stimpfl *et al.*, 2005) for Mn-poor, Fe-rich (X_{Fe} = 0.19-0.75) orthopyroxenes". Therefore, equation (1) by
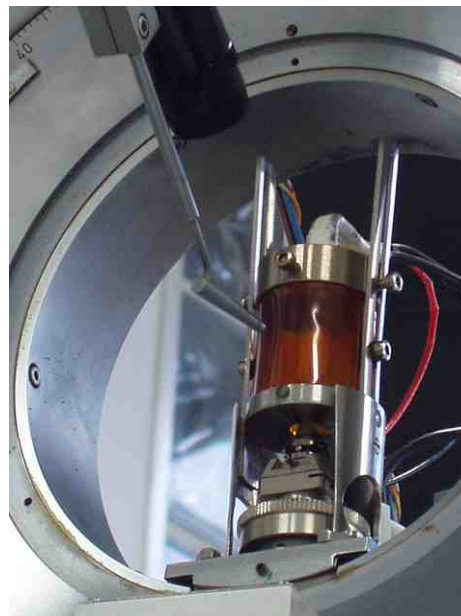
Domeneghetti *et al.* (2005) was not adopted for PCA82506-3 sample, which contains a lower amount of Mn (*ca.* 0.0125 apfu) than BTS-308 sample, and Mn was considered totally ordered at the M2 site. The following constraints were introduced into the refinement: (1) all structural sites were considered fully occupied; (2) Al was distributed between the TB and M1 sites and Cr^{3+}, and Ti^{4+} were considered fully ordered at the M1 site while Mg and Fe^{2+} were allowed to fractionate between the M1 and M2 sites; (3) Na, Ca and Mn were assumed to occupy the M2 site; (4) charge balance in the isomorphous replacements was constrained by the equation $X_{[6]Al} + 2X_{Ti4+} + X_{Cr} = X_{Na} + X_{[4]Al}$.

RESULTS AND DISCUSSION

As it concerns the high-P experiments the obtained results reported in (Alvaro *et al.*, 2010) confirm what expected by the previous literature data (Hugh-Jones *et al.*, 1994; Alvaro *et al.*, 2010). In particular: i) the experimentally measured transition pressure P_c obtained for the low-Fe sample PCA82506-3 is in perfect agreement with the value expected by the average ionic radius of the cation at the M2 site; ii) our values of the bulk modulus K_{TO} compared with the available K_{TO} values of $P2_1/c$ samples from literature (Hugh-Jones *et al.*, 1994; Alvaro *et al.*, 2010) confirms that the $P2_1/c$ phase becomes softer with increasing the Fe content.

As it concerns the high-T "in situ" experiments a first order transition was found for PCA82506-3 sample and the critical temperature measured was higher than the obtained on natural BTS-308 sample $T_c = 758°C$ by Cámara *et al.* (2003). This is in agreement with the recent results on the $P2_1/c$ to $C2/c$ phase transition by Tribaudino *et al.* (2002, 2003) on two different synthetic Fe-free Ca-rich pigeonites samples. These authors found for these samples a switch from first-order to tricritic behaviour with increasing Ca content.

Concerning the high-T "ex situ" experiments, the isothermal annealing carried out at 790, 840, and 865°C until equilibrium allowed us to obtain a linear regression of $\ln k_D$ *vs.* 1/T and to calculate the closure temperature of the Fe^{2+}-Mg order-disorder for PCA82506-3 sample. Analysis of the kinetic data, performed according to Mueller's model, allowed us to retrieve for this sample the disordering rate constants $C_0 K^+_{dis}$ for all three temperatures yielding an Arrhenian relation used to calculate the activation energy (Ea) of the order-disorder process and the cooling rate constants.

The measured very fast cooling rate is clearly in agreement with the interpretation of the cooling history, suggested by Takeda (1987) and already confirmed by Tribaudino *et al.* (1997), of a collisional breakup of the parent body of the ureilite PCA82506-3 into small fragments, subjected to a fast cooling due to radiative heat loss from the crystallization temperature (~ 1200°C) to a temperature lower than the closure temperature. Several works demonstrated that the reequilibration temperature for the Fe/Mg intercrystalline exchange reaction ranging from 1050 to 1200°C obtained for olivine, orthopyroxene, pigeonite and augite suggested a period of slow cooling at lower T for the ureilite parent body (UPB). This period of slow cooling must have been followed by a period of extremely rapid cooling, as evidenced by the Fe^{2+}-Mg intracrystalline partitioning in the orthopyroxene, by the lack of either exsolution lamellae in the augite or nuclei in the glasses in the inclusions (Goodrich *et al.*, 2001) and was confirmed by the cooling rate calculated on PCA82506-3 pigeonite sample.

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