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The Isothermal Equation of State of CaPtO₃ Post-perovskite to 40 GPa

Alex Lindsay-Scott^a, Ian G. Wood^{*a}, David P. Dobson^a, Lidunka Vočadlo^a, John P. Brodholt^a, Wilson Crichton^{b, a}, Michael Hanfland^b and Takashi Taniguchi^c

^a*Department of Earth Sciences, University College London, Gower Street, London, U.K.*

^b*European Synchrotron Research Facility, Grenoble, France*

^c*National Institute for Materials Science, Tsukuba, Ibaraki, Japan*

^{*} Corresponding author. *Email address:* ian.wood@ucl.ac.uk

Abstract

ABX₃ post-perovskite phases that are stable (or strongly metastable) at room-pressure are of importance as analogues of post-perovskite MgSiO₃, a deep-Earth phase stable only at very high pressure. Commonly, CaIrO₃ has been used for this purpose, but it has been suggested that CaPtO₃ might provide a better analogue. We have measured the isothermal incompressibility, at ambient temperature, of orthorhombic post-perovskite structured CaPtO₃ to 40 GPa by X-ray powder diffraction using synchrotron radiation. A third-order Birch-Murnaghan equation of state fitted to the experimental data yields $V_0 = 228.10(2) \text{ \AA}^3$, $K_0 = 168.2(8) \text{ GPa}$ and $K'_0 = 4.51(6)$. Similar fits to the cube of each axis of the unit cell shows that the *b*-axis is the most compressible ($b_0 = 9.9191(5) \text{ \AA}$, $K_0 = 123.3(5) \text{ GPa}$, $K'_0 = 2.37(3)$); the *a*-axis ($a_0 = 3.12777(8) \text{ \AA}$, $K_0 = 195.7(8) \text{ GPa}$, $K'_0 = 6.63(8)$) and *c*-axis ($c_0 = 7.3551(4) \text{ \AA}$, $K_0 = 192(2) \text{ GPa}$, $K'_0 = 12.2(3)$) are both much stiffer and have almost identical incompressibilities when the material is close to ambient pressure, but the *c*-axis shows greater stiffening on compression. Comparison of these axial incompressibilities with those of CaIrO₃ shows that CaPtO₃ is slightly less anisotropic under compression (possibly

because of the absence of Jahn-Teller distortion), suggesting that CaPtO_3 may be a somewhat better analogue of MgSiO_3 .

Our sample also contained minor amounts of a cubic $\text{Ca}_x\text{Pt}_3\text{O}_4$ phase, for which the third-order Birch-Murnaghan equation of state parameters were found to be: $V_0 = 186.00(3) \text{ \AA}^3$, $K_0 = 213(1) \text{ GPa}$ and $K'_0 = 4.9(1)$.

Keywords:

CaPtO_3

CaPt_3O_4

Post-perovskite

Equation of state

X-ray powder diffraction

1. Introduction

Perovskite-structured (PV) MgSiO_3 transforms to an orthorhombic CaIrO_3 -structured post-perovskite (PPV) phase at around 120 GPa (Murakami et al., 2004; Oganov and Ono, 2004). The atomic arrangement in the PPV-phase of MgSiO_3 differs greatly from that found in PV- MgSiO_3 and thus one might expect that the physical properties of the two phases will also differ appreciably. The perovskite phase of MgSiO_3 contains the 3-dimensional network of corner-linked octahedra found in all perovskites. In contrast, the structure of ABO_3 post-perovskites is commonly described in terms of sheets of corner- and edge-sharing octahedra, lying parallel to (010), separated by planar A-cation interlayers. These features are illustrated in Figure 1, which shows the crystal structure of the post-perovskite phase of CaIrO_3 , viewed down the a -axis; however, as discussed further below (Section 4) this view of the post-perovskite structure in terms of layers is almost certainly too simplistic.

The pressure at which the phase transition in MgSiO_3 occurs implies that post-perovskite MgSiO_3 might be the majority phase in the D'' region that extends into the mantle from the core-mantle boundary. If this is the case, then the physical and chemical properties of post-perovskite are likely to dominate the dynamics of much of the core–mantle boundary region. Measurements of the physical and chemical properties of post-perovskite MgSiO_3 are difficult to perform because it is stable only at megabar pressures and so it has been more practical to obtain some of the experimental results required for comparison with computer simulations of PPV-structured MgSiO_3 from isostructural analogues whose compressive and thermal distortion at lower temperature and pressure are similar to those of MgSiO_3 .

Analogues studied to date include CaIrO_3 (Boffa Ballaran et al., 2007; Lindsay-Scott et al., 2007; Martin et al., 2007, 2007a; Martin, 2008; Sugahara et al., 2008; Hirai et al., 2009) and CaPtO_3 (Inaguma et al., 2008; Ohgushi et al., 2008). CaIrO_3 may be synthesised at atmospheric pressure (see e.g. Lindsay-Scott et al., 2007). To date, synthesis of CaPtO_3 has

been reported only at high pressures, in the range 4 GPa (Ohgushi et al., 2008) to 7 GPa (Inaguma et al., 2008). However, after synthesis, CaPtO_3 is readily recoverable to atmospheric pressure, where it remains stable, or at least very strongly metastable; for example, high-temperature X-ray powder diffraction measurements in our laboratory (unpublished) have shown that it persists, in air, for periods of longer than one hour at temperatures as high as 800 °C. CaPtO_3 is of interest because, unlike CaIrO_3 , it does not exhibit structural distortion due to the Jahn-Teller effect and thus it has been suggested that it might provide a better analogue of MgSiO_3 (Ohgushi et al., 2008). Boffa Ballaran et al. (2007) and Martin et al. (2007) have measured the bulk and axial incompressibilities of CaIrO_3 , but CaPtO_3 has been studied only at ambient pressure and temperature (Ohgushi et al., 2008; Inaguma et al., 2008). In this paper we report measurements of CaPtO_3 to 40 GPa in order to assess the similarity of its behaviour under compression to that of CaIrO_3 and MgSiO_3 .

2. Experimental method

The sample was synthesized under high pressure and high temperature using a belt-type high-pressure apparatus at the National Institute for Materials Science, Tsukuba, Ibaraki, Japan. The starting material was a stoichiometric powder mixture of PtO_2 and CaO , ground together in a mortar and sealed in a Pt capsule. This was then compressed to 4 GPa, heated to 800 °C for 24-hours and then quenched to room temperature prior to slow decompression. The recovered dark-yellow powder was characterized by X-ray powder diffraction. The sample for this X-ray analysis was prepared as a thin smear on an “off-axis” silicon plate (i.e. one cut so as to produce no Bragg reflections) and the powder pattern was recorded using a PANalytical X’Pert Pro diffractometer with $\text{Co K}\alpha_1$ radiation (40 kV, 30 mA), scanning over the range $10^\circ < 2\theta < 90^\circ$. The sample was found to contain orthorhombic CaPtO_3 ($Cmcm$; $a = 3.12612(2)$ Å, $b = 9.91709(6)$ Å, $c = 7.34952(5)$ Å, $V = 227.850(2)$ Å³), with

minor amounts of cubic $\text{Ca}_x\text{Pt}_3\text{O}_4$ ($Pm\bar{3}n$; $a = 5.7064(1) \text{ \AA}$, $V = 185.82(1) \text{ \AA}^3$; Bergner and Kohlhaas, 1973) and traces of cubic Pt ($Fm\bar{3}m$; $a = 3.9262(2) \text{ \AA}$, $V = 60.52(1) \text{ \AA}^3$; Holmes et al., 1989). The lattice parameters for the CaPtO_3 (estimated from a LeBail refinement of the data, see below) were found to be in reasonable agreement with those previously reported at ambient pressure and temperature (see Table 1a). Our values are much closer to those of Ohgushi et al. (2008) than those of Inaguma et al. (2008); however, when comparing these results it should be remembered that, due to the lack of an internal standard and limited 2θ range, they are likely to be less accurate on an absolute scale than their precision might otherwise suggest (although it should, in principle, have been possible to use the platinum present in our sample as an internal standard, in practice there was insufficient platinum present to allow this to be done reliably in any of our experiments).

A selected portion of the sample was loaded, with a helium pressure medium, into a $150 \mu\text{m}$ diameter hole in a $40 \mu\text{m}$ thick steel gasket mounted between two opposed $300 \mu\text{m}$ diamond culets of a Boehler-Almax-type membrane-driven diamond anvil cell. Pressures were determined from the shift of the wavelength of the ruby- R_1 fluorescence line, using the recent pressure-scale calibration of Jacobsen et al. (2008) for helium pressure media. Ruby fluorescence measurements were made before and after collection of each diffraction pattern, with the ruby- R_1 wavelength at the data point taken as the mean value of these two readings. The uncertainty in the pressure, due to relaxation of the cell during the collection of each diffraction pattern, was estimated from the difference in the two ruby measurements, in combination with the quoted uncertainty in the B -parameter in the equation relating the pressure to the ruby- R_1 wavelength-shift (Jacobsen et al., 2008); see Table 1 for further details.

117 Diffraction patterns were collected on the ID09 beamline at the ESRF, using a
 118 monochromatic wavelength of 0.41456 Å on a mar555 image plate detector. The detector
 119 was positioned at 358.71 mm from the sample, so as to cover a range $0^\circ < 2\theta < 37.9^\circ$; the
 120 exposure time was ~ 1 second. Data were collected with increasing pressure from 2.90(2)
 121 GPa to 42.50(4) GPa, with a final pattern recorded at 1.21(1) GPa after decompression. The
 122 2θ vs Intensity patterns used in the powder refinement were obtained by integrating around
 123 the Debye-Scherrer rings, after correction for detector distortion and tilt, using the Fit2D
 124 package (Hammersley et al., 1995). The diffraction patterns were then fitted, over the range
 125 $3.16^\circ < 2\theta < 33.2^\circ$, to obtain unit-cell parameters using the Le Bail method (Le Bail et al.,
 126 1988) implemented in the GSAS suite of programs (Larson and Von Dreele, 1994) with the
 127 EXPGUI graphical interface (Toby, 2001). The lineshape used in the GSAS refinements was
 128 “profile function number 2”, which is based on a pseudo-Voigt function (Larson and von
 129 Dreele, 1994). At pressures above 12.6 GPa diffraction peaks characteristic of hexagonal
 130 ($P6_3/mmc$) He crystals were observed (Mao et al., 1988) and so this phase was also included
 131 in the refinements. Examples of the fitted diffraction patterns at 2.90(2) GPa and 42.50(4)
 132 GPa are shown in Figure 2. It can be seen that the Bragg reflections in Fig. 2B are broader,
 133 due to the development of non-hydrostatic stresses; after decompressing the sample the
 134 widths of the reflections returned to their original low-pressure values. The onset of this line
 135 broadening is clearly indicated in the refined values of the GSAS profile parameters; these
 136 are effectively invariant until ~16 GPa, but at higher pressures the values of some of the
 137 profile coefficients alter systematically. In particular, the coefficient U (which affects the
 138 Gaussian variance of the Bragg peaks via a term in $U \tan^2(\theta)$; Caglioti et al., 1958) increases,
 139 with the increase becoming marked above ~22 GPa, an effect that can be attributed to non-
 140 uniform strain in the crystallites (Larson and von Dreele, 1994). Possible sources of non-
 141 hydrostatic stresses in the experiment are solidification of the He pressure medium and
 142 grain-grain interactions in the CaPtO₃ sample. This line broadening does not appear to lead

to any systematic errors in the refined values of the cell parameters (see Figs 3 and 4), but it does increase their estimated uncertainties, which are greater by about a factor of seven at ~40 GPa than at pressures below ~7 GPa (Table 1b).

3. Results

The observed unit-cell parameters and unit-cell volume of CaPtO₃ between 1.21(1) GPa and 42.50(4) GPa are listed in Table 1b. Figure 3 shows the change in volume with pressure and Figure 4 shows the relative compression of the three unit-cell edges, plotted as the cube of the axial compression ratios. It can be seen from Figure 4 that the compression is strongly anisotropic, being greatest for the *b*-axis (i.e. for the direction perpendicular to the sheets of PtO₆ octahedra and Ca-ion interlayers) and smallest for the *c*-axis (i.e. along the chains of apex-linked PtO₆ octahedra). The data, including the decompression data point, both for the unit-cell volume and for the cubes of the unit-cell axes, were fitted to third-order Birch-Murnaghan equations of state (Birch, 1978) by non-linear least-squares using the EOS-fit program (Angel, 2000, 2001); the weighting scheme in the refinement used weights calculated from the errors in both the pressure and in the unit-cell volume and lattice parameters. The resulting values of the three equation-of-state parameters for each of the four fits are listed in Table 2. The values of V_0 , a_0 , b_0 , and c_0 thereby obtained are consistent both with the lattice parameters of CaPtO₃ from previous powder diffraction studies at ambient pressure (Ohgushi et al., 2008; Inaguma et al., 2008) and with those that we obtained in the present study during the sample characterisation (there is, however, clearly a slight systematic offset between our two diffraction experiments as all of the values from the high-pressure study are slightly higher, by 0.1% for the unit-cell volume and 0.02 – 0.07 % for the unit-cell edges). The good internal consistency of the high-pressure data sets can be demonstrated in two ways. Firstly, the values from the non-linear least-squares fit of the volumetric incompressibility (K_0) and of its first derivative with respect to pressure (K'_0) of

168.2(8) GPa and 4.51(6), respectively, are in good agreement with the corresponding values of 168.4(4) GPa and 4.47(4) obtained by weighted linear regression from the f - F plot (see e.g. Angel, 2000) that is shown as an inset in Figure 3. In this method of analysis, the incompressibility at zero pressure is obtained from a weighted linear fit of the normalised stress $F_E = \frac{P}{3f_E(1+2f_E)^{5/2}}$ against finite strain, $f_E = 0.5 \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right]$. Secondly, the value of V_0 obtained from the product of a_0 , b_0 , and c_0 is 228.19(2) Å³, which differs by 0.09(3) Å³ from that obtained when the volume is fitted directly.

In addition to the CaPtO₃, there was sufficient of the cubic Ca_xPt₃O₄ phase present in the sample to allow reliable determination of its cell parameter. By fitting the unit-cell volume to a third-order Birch-Murnaghan equation of state, as described above, we obtained the following values: $V_0 = 186.00(3)$ Å³; $K_0 = 213(1)$ GPa; $K'_0 = 4.9(1)$. When considering these results, which are reported here for completeness, it should, however, be remembered that this material has been reported to be of variable stoichiometry, with $0 \leq x \leq 1$ (Bergner and Kohlhaas, 1973).

4. Discussion

The only equation-of-state parameters for CaPtO₃ with which to compare the results of the present study are those of Matar et al. (2008) who carried out an investigation of both PPV- and PV-structured CaPtO₃ by athermal *ab initio* computer simulations within the local density approximation (LDA). The agreement of our experimental values { $V_0 = 228.10(2)$ Å³; $K_0 = 168.2(8)$ GPa; $K'_0 = 4.51(6)$ } with those from this simulation is surprisingly poor, as Matar et al. (2008) obtained $V_0 = 212.14(5)$ Å³ and $K_0 = 222(1)$ GPa, with $K'_0 = 4.59(8)$.

Although LDA calculations commonly overestimate the binding of the atoms and hence lead to calculated unit-cell parameters that are smaller than the experimental values, the discrepancy of 7% in V_0 is very large; similarly the value of K_0 from the computer simulations is over 30% greater than our experimental value (note, however, that if the equation-of-state parameters of Matar et al. are used to calculate K at the experimental value of V_0 a value of 157 GPa is obtained, in much closer agreement with our experimental result). The reasons for this poor agreement are not clear, especially as Matar et al. (2008) also state that test calculations carried out using the generalised gradient approximation (GGA), which commonly leads to an overestimate of the unit-cell volume, did not produce any significant improvement in the agreement between their calculated volume and the available experimental results. It is, perhaps, possible that the discrepancy is simply due to the lack of state points in the calculations, which appear to have been carried out at only six volumes, of which only two were for the material under compression. Unfortunately, no lattice parameters are given by Matar et al. (2008), only unit-cell volumes, and so it is impossible to determine whether their calculations produced a general underestimate of all three cell parameters or whether they failed to reproduce correctly the axial ratios of the crystal.

It is also of interest to compare the present results with the experimental values of the equation-of-state parameters for the other low-pressure post-perovskite analogue phase, CaIrO_3 . We have found that PPV- CaPtO_3 has a slightly larger unit-cell volume and lower value of K_0 than PPV- CaIrO_3 . Boffa Ballaran et al. (2007) fitted a third-order Birch-Murnaghan equation to single-crystal X-ray data from PPV- CaIrO_3 , obtaining $V_0 = 226.38(1) \text{ \AA}^3$ and $K_0 = 181(3) \text{ GPa}$, with $K'_0 = 2.3(8)$. Although the uncertainty is large, the value of K'_0 for CaIrO_3 is significantly lower than our corresponding value for CaPtO_3 . Boffa Ballaran et al. (2007) used methanol-ethanol as their pressure medium, and the ruby scale of Mao et al. (1986); however, the difference in K'_0 cannot be attributed simply to differences

in the pressure scale, since if we apply the ruby scale of Mao et al. (1986) to our data (see Table 2) we still obtain a value of K'_0 that is significantly higher than that of CaIrO_3 . Other previous measurements of the compression of PPV- CaIrO_3 are those obtained using X-ray powder diffraction by Martin et al. (2007) who fitted a second-order Birch-Murnaghan equation, giving $V_0 = 226.632(45) \text{ \AA}^3$ and $K_0 = 180.2(3) \text{ GPa}$; our corresponding values for PPV- CaPtO_3 ($V_0 = 227.95(2) \text{ \AA}^3$, $K_0 = 174.0(5) \text{ GPa}$, with K'_0 fixed at 4; see Table 2) show an increase in V_0 and decrease in K_0 similar to that discussed above, although, as K'_0 is fixed at 4 in both cases, the differences in the two fitted parameters are now not as large.

A further contrast in the behaviour of CaPtO_3 and CaIrO_3 lies in the relative unit-cell volumes and incompressibilities of the PPV- and PV-structured forms of the two materials. For CaIrO_3 , Boffa Ballaran et al. (2007) found experimentally that, at zero pressure, the ratio of the volumes of the PPV- and PV-structured phases was 0.98656(6) and that the PV-structured phase, with $K_0 = 198(3) \text{ GPa}$ and $K'_0 = 1.2(8)$, was stiffer (at ambient pressure) than the PPV-structured phase. For CaPtO_3 , the computer simulations of Matar et al. (2008), showed that, at zero pressure, the PPV- and PV-structured phases have a similar volume ratio to that of CaIrO_3 , 0.9878(13), but in this case the PV-structured material is softer, with $K_0 = 205(1) \text{ GPa}$ and $K'_0 = 4.42(5)$. However, this apparent difference in behaviour should probably be treated with caution. No experimental data for a PV-structured phase of CaPtO_3 have, as yet, been presented and in view of the discrepancy of the *ab initio* results with our experimental values for PPV- CaPtO_3 it is probably unwise to rely upon them too closely.

The axial incompressibilities of CaPtO_3 are similar in form to those of CaIrO_3 . The a -axis and c -axis of CaPtO_3 have the same incompressibility (within experimental uncertainty) at ambient pressure, but the c -axis stiffens faster than the a -axis, having a value of K'_0 that is greater by almost a factor of two; in contrast, the b -axis is much softer. If the crystal

structure of PPV-CaPtO₃ is viewed in a naive way in terms of layers of PtO₆ octahedra separated by planar Ca-cation interlayers, a ready explanation is afforded for the relative softness of the *b*-axis by reduction of the interlayer spacing. However, on this basis it is difficult to explain why the *c*-axis is the least compressible direction in the crystal, since this axis should then be readily shortened by buckling of the planes of corner-linked octahedra, whereas to reduce the length of the *a*-axis must involve distortion of the PtO₆ octahedra through shortening of the O-O distances aligned parallel to the *a*-axis. Clearly, therefore, this view of the response to compression of post-perovskite structures in terms of layers and interlayers is too simplistic, but to properly address this question requires an accurate set of atomic coordinates as a function of pressure, which is not yet available. In connection with this discussion, it is interesting to note also that, at least in the case of CaIrO₃, the response of the PPV-structure to heat is not simply the inverse of the response to pressure; thus, although the *b*-axis of CaIrO₃ expands most on heating, the expansion of the *c*-axis is far larger than that of the *a*-axis (Lindsay-Scott et al., 2007; Martin et al., 2007).

In Table 3, the ratios of the axial incompressibilities with respect to that of the *c*-axis, for both CaPtO₃ and CaIrO₃, are compared to those for MgSiO₃ and Mg_{0.6}Fe_{0.4}SiO₃. The low incompressibility ratio of the *b*-axis relative to that of the *c*-axis, found in both CaPtO₃ and CaIrO₃, is similar in magnitude to that reported for MgSiO₃ at pressures and temperatures comparable to those that would obtain in the D'' region of the Earth's mantle (Guignot et al., 2007). However, much worse agreement is found with the axial incompressibility ratios for Mg_{0.6}Fe_{0.4}SiO₃ at 140 GPa and ambient temperature (Mao et al., 2010); in this case, although the value for K_a/K_c agrees well with that from CaPtO₃, neither CaPtO₃ nor CaIrO₃ give a similar value for K_b/K_c (though the agreement for CaPtO₃ is somewhat better than for CaIrO₃). A more detailed comparison of the axial compressions of CaPtO₃ with previously published results for CaIrO₃ (Boffa Ballaran et al., 2007) is shown as an inset to Figure 4.

Clearly, at all pressures, CaPtO_3 is slightly less elastically anisotropic than CaIrO_3 . This difference in anisotropy may be due to distortion of the IrO_6 octahedra in CaIrO_3 , caused by the Jahn-Teller effect (Ohgushi et al., 2008); the absence of this effect in CaPtO_3 may indicate that it is, therefore, a somewhat better analogue for MgSiO_3 post-perovskite at low pressure and temperature.

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Figure Captions

Figure 1: The CaIrO_3 post-perovskite type-structure viewed along the a -axis. This structure is commonly described in the following way. Rods of edge-shared octahedra running parallel to the a -axis are linked into corrugated sheets by corner-sharing parallel to the c -axis, so as to produce sheets of PtO_6 octahedra lying parallel to (010); these sheets are then separated along the b -axis by planar interlayers of Ca ions. However, this view of the structure in terms of layers is almost certainly too simplistic (see Section 4 for further discussion).

Figure 2: Observed (points), calculated (line) and difference (lower trace) X-ray powder diffraction patterns ($\lambda = 0.41456 \text{ \AA}$) for CaPtO_3 at: (A) 2.90(2) GPa and (B) 42.50(4) GPa. The tick marks show the positions of the Bragg reflections of (from the bottom upwards): CaPtO_3 , CaPt_3O_4 , Pt and (Fig. 2B only) He.

Figure 3: Unit-cell volume of CaPtO_3 between 1.21(1) GPa and 42.50(4) GPa.

Experimental values are shown as points (error bars are smaller than the symbols used). The full line shows the fit of the data to a third-order Birch-Murnaghan equation of state (see text for details). The inset shows the f - F plot for these data, calculated using the value of V_0 , $228.10(2) \text{ \AA}^3$, from this fit (Table 2). The solid line shown in the inset is a weighted linear fit with $F_E = 120(11)f_E + 168.4(4) \text{ GPa}$. The value of the incompressibility, K_0 , is equal to the intercept on the y -axis of the f - F plot; the value of its first derivative with respect to pressure, K'_0 , is obtained *via* the relationship that the slope of the f - F plot is equal to $3K_0(K'_0 - 4)/2$ (Angel 2000; see Section 3 for further details).

Figure 4: Axial compressions, i/i_0 (where $i = a, b$ or c unit-cell parameter), of CaPtO_3 , plotted as the ratios $(i/i_0)^3$. The symbols denote the experimentally-observed axial and volumetric values. The lines are derived from the axial equations of state, plotted against values of V/V_0 calculated from the volumetric equation of state (Table 2). The inset to the figure shows a comparison of the values for CaPtO_3 (solid symbols and lines) with those for CaIrO_3 (open symbols and broken lines), as determined by Boffa Ballaran et al. (2007).

Table 1: (a) Unit-cell parameters and unit-cell volume for CaPtO_3 at ambient pressure and temperature; the numbers in parentheses are estimated standard uncertainties and refer to the least-significant digits. The value quoted for the present work is that measured in our laboratory at UCL with $\text{Co K}\alpha_1$ radiation (see Section 2).

	a(Å)	b(Å)	c(Å)	Volume (Å ³)
Present work	3.12612(2)	9.91709(6)	7.34952(5)	227.850(2)
Ohgushi et al. 2008	3.12607(1)	9.91983(4)	7.35059(3)	227.942(2)
Inaguma et al. 2008	3.1232(4)	9.912(1)	7.3459(9)	227.41(5)

(b) Unit-cell parameters and unit-cell volume for CaPtO_3 as a function of pressure, as measured in the diamond-anvil cell at the ESRF. The data were recorded in the order shown. The numbers in parentheses are estimated standard uncertainties and refer to the least-significant digits.

P (GPa)	a(Å)	b(Å)	c(Å)	Volume (Å ³)
2.90(2)	3.11291(2)	9.84590(9)	7.32129(6)	224.393(4)
3.45(1)	3.11050(2)	9.83073(9)	7.31545(6)	223.695(4)
3.98(1)	3.10794(2)	9.81702(9)	7.31008(6)	223.036(4)
4.59(1)	3.10502(2)	9.80079(7)	7.30368(5)	222.263(2)
5.05(3)	3.10275(2)	9.78895(9)	7.29884(6)	221.685(4)
5.69(2)	3.09984(2)	9.77312(9)	7.29270(6)	220.933(4)
6.20(2)	3.09763(2)	9.76146(9)	7.28801(6)	220.370(4)
6.71(2)	3.09572(2)	9.75077(9)	7.28391(6)	219.869(4)

7.22(2)	3.09357(3)	9.73904(10)	7.27951(7)	219.320(4)
7.84(1)	3.09084(3)	9.72520(10)	7.27384(6)	218.645(4)
8.37(2)	3.08839(3)	9.71204(11)	7.26870(7)	218.021(5)
9.02(2)	3.08566(3)	9.69559(11)	7.26296(7)	217.288(5)
9.55(3)	3.08358(3)	9.68384(10)	7.25855(7)	216.747(5)
10.04(2)	3.08195(3)	9.67358(10)	7.25490(7)	216.290(4)
10.55(3)	3.08001(3)	9.66289(10)	7.25109(7)	215.805(4)
11.08(3)	3.07811(3)	9.65200(11)	7.24707(7)	215.310(5)
11.59(3)	3.07627(3)	9.64136(11)	7.24333(7)	214.833(5)
12.10(2)	3.07409(3)	9.62936(12)	7.23903(8)	214.287(5)
12.62(3)	3.07204(3)	9.61759(12)	7.23493(8)	213.761(5)
13.70(5)	3.06793(4)	9.59463(13)	7.22645(9)	212.715(6)
14.38(2)	3.06576(4)	9.58160(13)	7.22187(9)	212.142(6)
15.43(3)	3.06221(4)	9.56182(16)	7.21496(11)	211.256(7)
16.46(2)	3.05840(4)	9.54021(15)	7.20764(11)	210.303(7)
17.52(3)	3.05471(5)	9.51746(18)	7.20009(12)	209.329(8)
19.06(4)	3.04976(6)	9.48918(22)	7.19095(15)	208.104(10)
20.62(3)	3.04465(6)	9.45945(23)	7.18141(15)	206.830(10)
22.22(4)	3.03963(7)	9.42972(28)	7.17183(18)	205.565(12)
24.79(2)	3.03231(9)	9.38640(37)	7.15781(25)	203.729(17)
27.46(2)	3.02459(11)	9.33593(40)	7.14297(30)	201.699(19)
30.30(2)	3.01617(13)	9.28288(52)	7.12716(33)	199.551(23)
33.61(4)	3.00811(14)	9.22671(55)	7.11284(37)	197.416(26)
37.98(5)	2.99721(16)	9.15550(64)	7.09562(42)	194.710(29)
40.02(3)	2.99209(16)	9.11863(64)	7.08734(43)	193.369(29)
42.50(4)	2.98668(15)	9.08541(61)	7.07981(42)	192.112(28)

1.21(1) 3.12155(4) 9.88679(14) 7.33933(9) 226.507(6)

431

432

433 In **(b)** above, the pressure values were obtained from the relative shift of the wavelength of
434 the ruby- R_1 fluorescence line ($\Delta\lambda/\lambda_0$), using the equation $P \text{ (GPa)} = (A/B)\{[1 + (\Delta\lambda/\lambda_0)]^B - 1\}$,
435 where $A = 1904 \text{ GPa}$ and $B = 10.32(7)$ (Jacobsen et al., 2008). Ruby measurements were
436 made before (λ_a) and after (λ_b) each diffraction pattern was recorded and the value of $\Delta\lambda$ was
437 then calculated using their mean. The uncertainties in the pressure values were derived
438 assuming that the uncertainty in the fluorescence wavelength was $(\lambda_a - \lambda_b)/4$ (i.e. that the
439 observations corresponded to a mean value $\pm$ two standard uncertainties); the uncertainty
440 in the parameter B given by Jacobsen et al. (2008) was also included in the calculation.

441

442 Note that in both **(a)** and **(b)** the lattice parameter values listed are probably less accurate
443 than might be expected from the stated uncertainties, which are as reported by the Le Bail
444 fits using GSAS; for further discussion of the importance of systematic errors in profile
445 refinement of X-ray powder data see e.g. Thompson and Wood (1983).

446

447

Table 2: Equation of State parameters obtained by fitting the data shown in Table 1 to third-order Birch-Murnaghan equations of state. For the unit-cell edges, the values of K_0 and K'_0 are those obtained by fitting to the cubes of the lengths of the unit-cell edges (for details see text).

	V_0 ($\text{\AA}^3$)	K_0 (GPa)	K'_0
Volume	228.10(2)	168.2(8)	4.51(6)
<i>a</i> -axis	3.12777(8)	195.7(8)	6.63(8)
<i>b</i> -axis	9.9191(5)	123.3(5)	2.37(3)
<i>c</i> -axis	7.3551(4)	192(2)	12.2(3)

For comparison with the results of Martin et al. (2007) the unit-cell volumes were also fitted to a second-order Birch-Murnaghan equation of state. The resulting values of V_0 and K_0 were 227.95(2) $\text{\AA}^3$ and 174.0(5) GPa respectively (with K'_0 fixed at 4).

(Note that if the commonly-used ruby fluorescence pressure scale of Mao et al. (1986) is employed, instead of that of Jacobsen et al. (2008), the volumetric equation of state parameters then become $V_0 = 228.09(2) \text{\AA}^3$, $K_0 = 168.8(8)$ GPa and $K'_0 = 4.16(6)$ respectively. The more recent ruby scale of Dewaele et al. (2004), gives values that are not significantly different from those shown in the Table above, with $V_0 = 228.10(2) \text{\AA}^3$, $K_0 = 168.5(8)$ GPa and $K'_0 = 4.39(6)$).

465 **Table 3:** Axial incompressibility ratios of some post-perovskite phases.

466

	K_a/K_c	K_b/K_c
CaPtO ₃ (ambient P, T) ^a	1.02(1)	0.64(1)
CaIrO ₃ (ambient P, T) ^b	0.94(3)	0.51(1)
MgSiO ₃ (135 GPa, 4000 K) ^c	0.84(6)	0.58(4)
Mg _{0.6} Fe _{0.4} SiO ₃ (140 GPa, ambient T) ^d	1.05*	0.91*

467

468 ^aThis work

469 ^bBoffa Ballaran et al. (2007)

470 ^cGuignot et al. (2007)

471 ^dMao et al. (2010); *uncertainties not given.

Figure 1
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