

Stability and compressibility of the high-pressure phases of Al_2O_3 up to 200 GPa: Implications for the electrical conductivity of the base of the lower mantle

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Abstract

We have used a laser-heated diamond anvil cell to investigate the stability and compressibility of *Cmcm* CaIrO_3 -type (post-perovskite structure) Al_2O_3 at pressures up to 200 GPa. A phase transformation from the *Pbcn* $\text{Rh}_2\text{O}_3(\text{II})$ -type to the CaIrO_3 -type structure was observed at 130 GPa, which is consistent with previous theoretical studies. The observed CaIrO_3 -type structure in Al_2O_3 is the same as that in MgSiO_3 post-perovskite, the main mineral of Earth's lowermost mantle. We also calculated the Raman shifts of CaIrO_3 -type Al_2O_3 and MgSiO_3 using density-functional perturbation theory. The similarity of the crystal structures and Raman spectra of CaIrO_3 -type Al_2O_3 and MgSiO_3 suggests that the other physical properties of the two phases could be similar as well. Based on the high electrical conductivity of CaIrO_3 -type Al_2O_3 , we predicted a profile of electrical conductivity at the bottom of the lower mantle, which can explain Earth's rotation period changes of a few milliseconds in Earth's length of day on decadal timescales, if the exchange of angular momentum between the solid mantle and fluid core occurs by an electromagnetic coupling between the conducting core and mantle.

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1. Introduction

The structural and electronic properties of alumina are of considerable importance due to the diverse applications of this material, particularly in high-pressure science. It is used as a window material in shock-wave experiments,

and the Cr^{3+} -doped form called ruby, serves as a pressure standard in diamond anvil cell experiments, through measurement of the pressure-dependent shift of its fluorescence lines. Alumina, in common with a range of A_2O_3 oxides, crystallizes under ambient conditions into the corundum structure with space group *R-3c*, in which all the cations are in a six-coordinate state. On increasing pressure, some A_2O_3 compounds transform into a $\text{Rh}_2\text{O}_3(\text{II})$ -type structure with space group *Pbcn*. For Al_2O_3 , the $\text{Rh}_2\text{O}_3(\text{II})$ -type structure has been reported in both

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theoretical and experimental studies [e.g., 1–6]. Some theoretical studies have also predicted that Al_2O_3 can further transform into a perovskite structure with space group $Pbnm$ at pressures above 200 GPa [2,6,7]. Recently, Oganov and Ono [8] synthesized CaIrO_3 -type (post-perovskite structure) Al_2O_3 with space group $Cmcm$ in high-pressure experiments. First-principle calculations also showed that CaIrO_3 -type Al_2O_3 is stable at high pressures when compared to the perovskite structure [8–10]. However, the stability and physical properties of CaIrO_3 -type Al_2O_3 have not been investigated in high-pressure experiments.

Although Earth's rotation period changes over different timescales, changes occurring over several years and also over very long timescales can be explained by changes in Earth's moment of inertia due to a coupling between the atmosphere and oceans and the tidal friction, respectively [11]. Measured changes of a few milliseconds in Earth's length of day on decadal timescales are attributed to the exchange of angular momentum between the solid mantle and fluid core. A review of core–mantle coupling and angular momentum exchange has been published by Bloxham [12]. To explain the length-of-day type of variations on decadal timescales, the following

mechanisms have been proposed: (1) gravitational coupling between changes in density and/or topographic inhomogeneities of the inner core and mantle [13,14], (2) topographic coupling from fluid pressure on the deformed core–mantle boundary [15–17], and (3) electromagnetic coupling between the core and a weakly conducting mantle [18–22].

Although the third mechanism can reasonably explain the observed changes of a few milliseconds in Earth's length of day on decadal timescales, this mechanism requires a highly conductive layer at the base of the lower mantle. However, it is known that magnesium silicate perovskite, which is the dominant mineral in the lower mantle, does not have such a high electrical conductivity [23,24]. Even if molten iron, which has a high electrical conductivity, can penetrate from the outer core into the solid mantle, the depth of penetration of molten iron into the solid mantle would be short [25]. This indicates that the enhancement of the electrical conductivity of the solid mantle by penetration of molten iron would not be enough to explain the electromagnetic coupling between the core and the mantle.

Therefore, this mechanism was considered unrealistic if the lowermost part of the lower mantle is composed

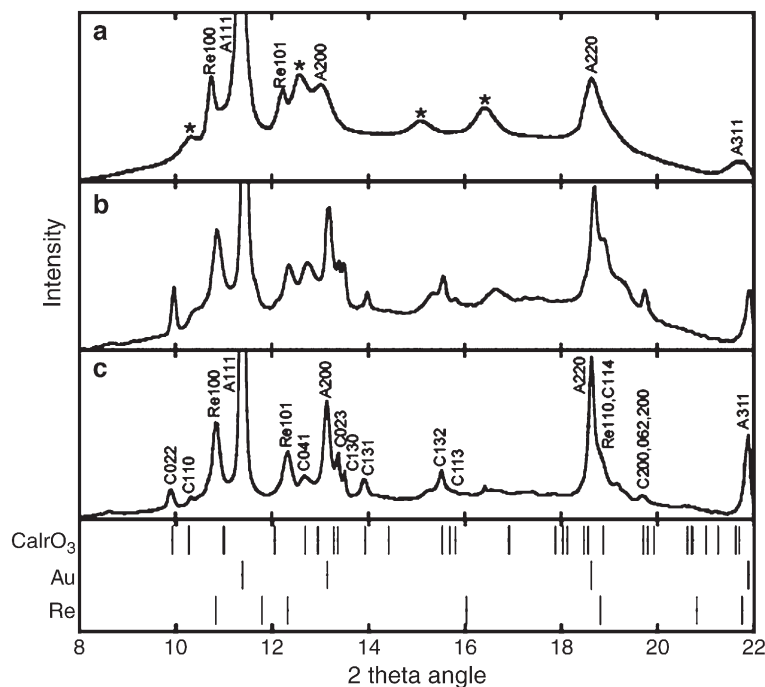


Fig. 1. Examples of diffraction patterns of CaIrO_3 -type Al_2O_3 . These diffraction patterns were obtained at a pressure of about 150 GPa. a, Before the laser heating at 300 K; b, during the heating at about 2000 K; c, after the temperature quench. Abbreviations for peaks are as follows: C, CaIrO_3 -type Al_2O_3 ; A, gold; Re, rhenium gasket. The stars denote the broad peaks of the starting material. The vertical bars denote the calculated positions of the diffraction lines of each phase. The unit cell dimensions are CaIrO_3 -type Al_2O_3 , $a=2.4307\text{ \AA}$, $b=7.925\text{ \AA}$, $c=6.053\text{ \AA}$; gold, $a=3.634\text{ \AA}$; and rhenium, $a=2.546\text{ \AA}$, $c=4.051\text{ \AA}$. The wavelength of the monochromatic incident X-ray beam was 0.4159 \AA .

only of magnesium silicate perovskite. Buffett [26] also discussed the possibility that a high electrical conductive layer may exist at the core–mantle boundary region after observing periodic variations (nutations) in Earth's rotation. Although Buffett et al. [27] argued the possibility that the sedimentation at the top of the outer core forms a layer of high electrical conductivity, there is no experimental evidence that supports this assertion.

Recently, the possibility of CaIrO_3 -type Al_2O_3 with high electrical conductivity has been reported [8]. First principle studies show that CaIrO_3 -type MgSiO_3 phase, which is likely to have analogous high electrical conductivity, can exist at the base of the lower mantle [e.g., 28,29]. The possibility of a highly conductive D' layer requires a reappraisal of the electromagnetic coupling mechanism to understand the observed changes in Earth's length of day.

We used a laser-heated diamond anvil cell (DAC) and intense X-rays from a synchrotron radiation source to acquire precise data on Al_2O_3 under high pressure, and directly observed a phase transformation between $\text{Rh}_2\text{O}_3(\text{II})$ -type and CaIrO_3 -type Al_2O_3 . We also investigated the pressure–volume equation of state (EOS) of CaIrO_3 -type Al_2O_3 over the pressure range

120 to 180 GPa. Ab initio calculations were performed to investigate the Raman shifts of the CaIrO_3 -type phases at high pressure, and we investigated the similarities in physical properties between CaIrO_3 -type Al_2O_3 and MgSiO_3 based on experimental and theoretical data. This allowed us to estimate the profile of the electrical conductivity at the bottom of the lower mantle.

2. Methods

2.1. High-pressure experiments

Powdered Al_2O_3 corundum was used as the starting material. Gold powder was mixed with the sample to absorb the laser radiation for efficient laser heating and for use as an internal pressure calibrant. Gel-type MgSiO_3 powder was also used to investigate the similarities in physical properties between Al_2O_3 and MgSiO_3 . The powders were comminuted in an agate mortar to ensure homogeneity and a small grain size. High-pressure X-ray diffraction experiments were performed in a laser-heated symmetric-type diamond anvil cell with a 60° conical aperture [30]. The diamonds had an inner culet of 100 μm and an outer culet of 600 μm ,

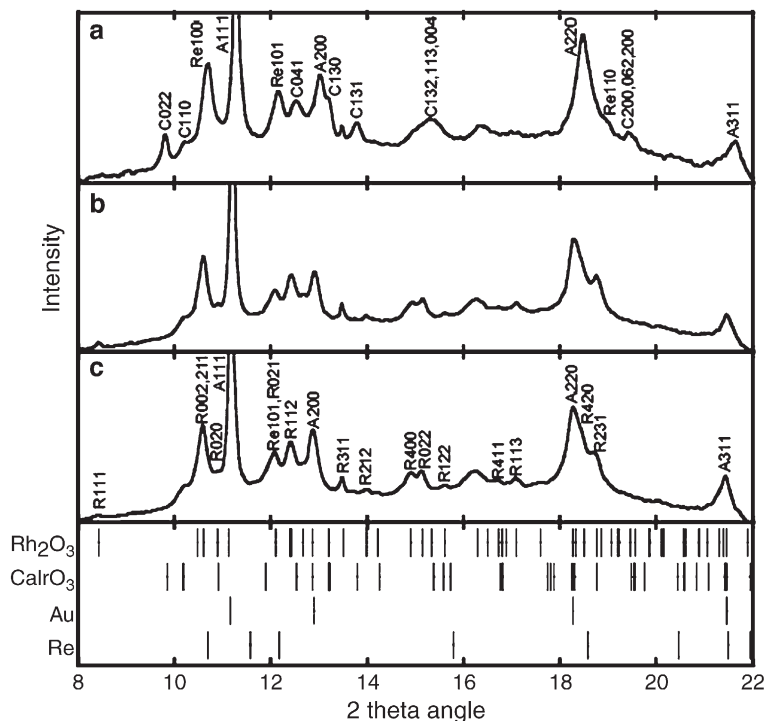


Fig. 2. The phase transition from $\text{Rh}_2\text{O}_3(\text{II})$ -to CaIrO_3 -type Al_2O_3 . a, Before the laser heating; b, on heating; c, after the temperature quench. Abbreviations for peaks are as follows: R, $\text{Rh}_2\text{O}_3(\text{II})$ -type Al_2O_3 ; C, CaIrO_3 -type Al_2O_3 ; A, gold; and Re, rhenium gasket. The vertical bars denote the calculated positions of the diffraction lines of each phase. The unit cell dimensions are $\text{Rh}_2\text{O}_3(\text{II})$ -type Al_2O_3 , $a=6.412\text{ \AA}$, $b=4.380\text{ \AA}$, $c=4.551\text{ \AA}$; CaIrO_3 -type Al_2O_3 , $a=2.449\text{ \AA}$, $b=8.029\text{ \AA}$, $c=6.082\text{ \AA}$; gold, $a=3.703\text{ \AA}$; and rhenium, $a=2.564\text{ \AA}$, $c=4330\text{ \AA}$.

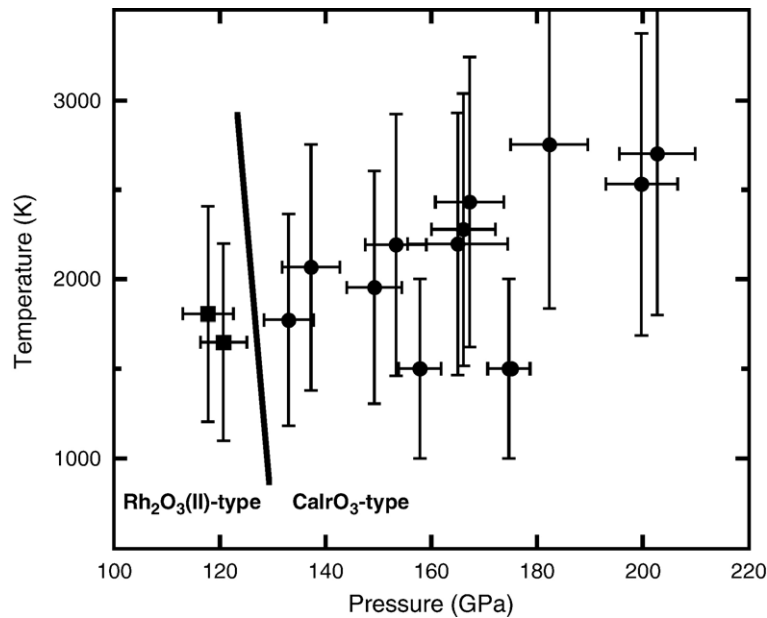


Fig. 3. Experimental results and the phase boundary determined from in situ X-ray observations. Solid squares and circles denote conditions where $\text{Rh}_2\text{O}_3(\text{II})$ -type and CaIrO_3 -type Al_2O_3 were stable. The error bars in pressure include the uncertainty of at temperature, because the EOS is used to calculate the sample pressure. The thick line denotes the inferred phase boundary between the two high-pressure phases. The gradient of dP/dT of this phase boundary was reported by a theoretical study [8].

with a beveled angle of 17° . The powdered sample was loaded into a 40 μm diameter hole drilled into a rhenium gasket, and no pressure-transmitting medium was used. The samples were heated with either a YLF or YAG laser to overcome any potential kinetic effect on the phase transition. The size of the heated spot was 20–30 μm .

The sample was initially compressed to the desired pressure at room temperature, and then the load on the DAC was kept constant during laser heating. After being kept at the desired pressure and temperature for a given period, the sample was quenched by shutting off the laser. The sample temperature was measured using the spectroradiometric method [31]. The spectroradiometric system consisted of a thermoelectrically cooled CCD detector and a spectrograph. The use of the spectrometer allowed us to measure the temperature profile across the laser-heated spot. The temperature was determined by fitting the thermal radiation spectrum between $\lambda=600$ and 800 nm to the Planck radiation function [e.g., 31–33]. The system response was calibrated using a tungsten filament lamp of known radiance that was calibrated relative to an NIST standard. The heated samples were probed using angle-dispersive X-ray diffraction using at the monochromatic incident X-ray synchrotron beam lines BL10XU, SPring-8 [34], and BL13A, Photon Factory [35] in Japan. The X-ray beams were collimated to a diameter of 10–20 μm , and the

angle-dispersive X-ray diffraction patterns were obtained on an imaging plate or on an X-ray CCD detector. The detector-to-sample distances were calibrated using a standard CeO_2 . The uncertainties of the distances were $<0.1\%$. The observed intensities on the imaging plates were integrated as a function of 2θ using the ESRF Fit2d software code [36] to obtain one-dimensional diffraction profiles. The diffraction peak positions were determined using a peak-fitting program. The pressure was estimated from the observed unit cell volumes

Table 1
Lattice parameters and volumes of Al_2O_3 phases at 300 K

P (GPa)	a (Å)	b (Å)	c (Å)	Volume (Å ³)
$\text{Rh}_2\text{O}_3(\text{II})$				
102.8(11)	6.412(5)	4.380(5)	4.551(4)	127.79(21)
CaIrO_3				
124.0(4)	2.449(5)	8.029(16)	6.082(12)	119.59(41)
137.9(6)	2.423(7)	7.965(23)	6.053(43)	116.82(96)
140.8(7)	2.431(1)	7.925(6)	6.053(5)	116.60(14)
148.4(8)	2.425(2)	7.908(12)	6.001(15)	115.11(35)
163.3(17)	2.406(2)	7.936(8)	6.014(6)	113.38(17)
166.5(10)	2.407(2)	7.843(9)	5.989(7)	113.06(20)
181.4(9)	2.389(2)	7.821(8)	5.936(8)	110.87(22)

Numbers in parentheses represent the error of lattice parameter and volume of Al_2O_3 phases. Pressures were determined from the observed unit cell volume of gold using the gold equation of state [37].

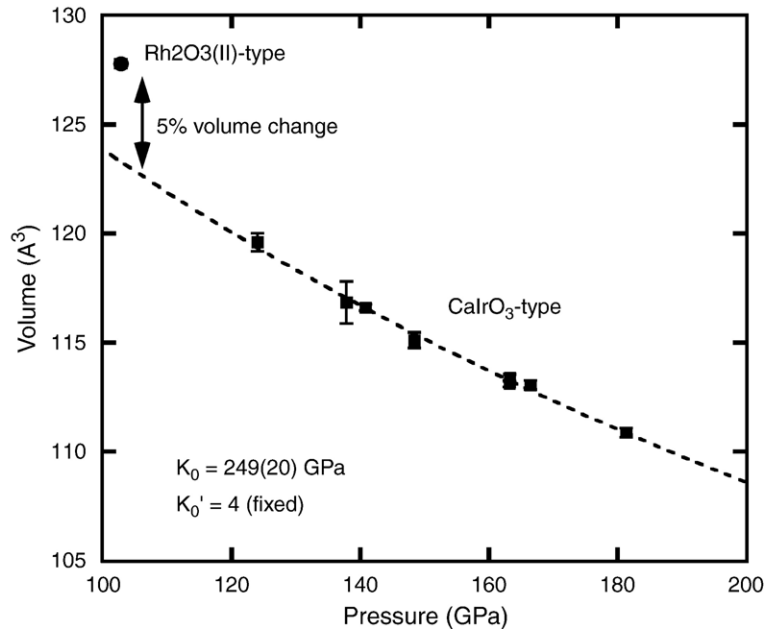


Fig. 4. Pressure–volume data for Al_2O_3 high-pressure phases at 300 K. The solid circle and squares denote the volume data of $\text{Rh}_2\text{O}_3(\text{II})$ -type and CaIrO_3 -type Al_2O_3 , respectively. The dashed curve is the third-order Birch–Murnaghan equation fit with parameters $K_0=249$ GPa and $K'_0=4$ using Jamieson's EOS of Au.

using the equation of state (EOS) of gold [37]. Because we used the EOS, the uncertainty in the pressure was dependent on the experimental temperature. The temperature error at high temperatures was greater than 500 K. The estimated pressure errors at high temperatures included the uncertainty of temperature in the sample.

2.2. Theoretical calculations

We performed calculations based on the plane wave pseudopotential methodology and the local density approximation (LDA), as implemented in the ABINIT code [38], a common project of the Université Catholique de Louvain, Corning Inc., and other contributors (URL <http://www.abinit.org>). Non-local Troullier–Martins pseudopotentials [39] with partial core corrections [40] were used. A plane wave kinetic energy cut-off of 45 Ha and $6 \times 6 \times 4$ Monkhorst–Pack meshes for the Brillouin zone were used, and produced highly converged results. Primitive 10-atom cells were used in all the calculations. CaIrO_3 -type Al_2O_3 and MgSiO_3 were optimized at 130 GPa using the steepest-descent method. For more technical details on the pseudopotentials and convergence tests, see Oganov and Ono [8,29]. The phonon frequencies were computed at the Γ -point for the optimized structures using density-functional perturbation theory [41–43]. From group-

theoretical considerations, we found that twelve modes in the Brillouin zone centre were Raman-active ($4A_g + 3B_{1g} + B_{2g} + 4B_{3g}$).

3. Results

The in situ high-pressure and high-temperature X-ray diffraction patterns are shown in Fig. 1. The pressure was increased directly to about 150 GPa at room temperature, and an X-ray diffraction pattern of the sample was recorded. A strain-broadening of the diffraction peaks of the starting material was observed, because a large differential stress was induced in the diamond anvil cell as the pressure increased. However, no phase transition from corundum to a high-pressure phase was observed (Fig. 1a). Next, the sample was

Table 2
Comparison of the bulk modulus of CaIrO_3 -type Al_2O_3

	K_0 (GPa)	K'_0	V_0 (\AA^3)
Theoretical			
Oganov and Ono [8]	241.6	4.464	161.17
Caracas and Cohen [9]	231	4.38	155.12
Experimental			
This study	249(20)	4 (fixed)	158.4(26)

V_0 , K_0 , and K'_0 are the volume, the isothermal bulk modulus, and the first pressure derivative of the isothermal bulk modulus, respectively. Experimental data were acquired at 300 K.

Table 3
Comparison of X-ray diffraction patterns of CaIrO₃-type Al₂O₃ and MgSiO₃

hkl	Al ₂ O ₃				MgSiO ₃				
	<i>d</i> _{obs} , Å	<i>d</i> _{cal} , Å	<i>d</i> _{obs} / <i>d</i> _{cal} - 1	<i>I</i> _{obs}	<i>I</i> _{cal}	<i>d</i> _{obs} , Å	<i>d</i> _{cal} , Å	<i>d</i> _{obs} / <i>d</i> _{cal} - 1	<i>I</i> _{obs}
020		3.9296			<1		4.0173		
002		2.9950			1		3.0408		
022	2.3876	2.3876	0.0023	100	100	2.4241	2.4246	-0.0002	43
110	2.2951	2.2951	-0.0011	17	21	2.3473	2.3475	-0.0001	6
111	*				4	2.1874	2.1900	-0.0012	1
040	1.9567	1.9567	-0.0041	6	4		2.0087		
041	1.8664	1.8664	-0.0003	20	9	1.9028	1.9073	-0.0024	6
023	1.7842	1.7801	0.0023	36	48	1.8102	1.8098	0.0002	100
130	1.7715	1.7706	0.0005	67	74	1.8102	1.8096	0.0004	100
131	1.6979	1.6980	-0.0001	78	100	1.7348	1.7344	0.0002	54
042		1.6428			1	1.6736	1.6760	-0.0014	4
132	1.5263	1.5242	0.0014	62	64	1.5552	1.5550	0.0001	23
113	1.5073	1.5071	0.0001	32	53	1.5366	1.5343	0.0015	23
004	1.4945	1.4975	-0.0020	14	30	1.5206	1.5204	0.0001	14
133	1.3252	1.3252	0.0003	6	19	1.3485	1.3500	-0.0011	5
150		1.3153			3		1.3391		
151	1.2833	1.2847	-0.0011	13	22	1.3133	1.3128	0.0004	13
114	*	1.2545			29	*	1.2761		
152		1.2043			27	1.2277	1.2296	-0.0016	17
200	1.2012	1.2001	0.0009	42	31	1.2277	1.2273	0.0003	17
062	1.2012	1.2012	0.0000	42	44	1.2277	1.2255	0.0017	17

Calculated *d*-spacings of Al₂O₃ and MgSiO₃ phases are based on orthorhombic unit cell dimensions of *a*=2.402(2) Å, *b*=7.859(6) Å, *c*=5.990(6) Å and *a*=2.455(2) Å, *b*=8.035(6) Å, *c*=6.082(6) Å. Wyckoff symbols and positions of each atom in calculated CaIrO₃-type Al₂O₃; Al1, 4a, (0, 0, 0); Al2, 4c, (0, 0.2514, 0.25); O1, 4c, (0, 0.9092, 0.25); O2, 8f, (0, 0.6448, 0.4289). *Peaks are overlapped by those of gold and rhenium.

heated to 1500–2500 K to relax the differential stress and to overcome potential kinetic effects on the possible phase transition. Many new peaks appeared in the diffraction pattern during heating (Fig. 1b). Thus, the corundum starting material was transformed into a new high-pressure phase. After heating, the diffraction patterns showed no extra change. This implies that the new high-pressure phase can be temperature-quenched (Fig. 1c). The new phase was reasonably indexed to an orthorhombic cell with four formula units (*Z*=4). The space group of this phase was consistent with the *Cmcm* symmetry, which is adopted by CaIrO₃-type Al₂O₃ [8]. The CaIrO₃-type phase was not pressure-quenchable because only the X-ray diffraction pattern of corundum was observed after decompression to ambient pressure.

In the next run, the pressure and temperature of the sample were varied to investigate the stability of the CaIrO₃-type phase after synthesis. During decompression, the CaIrO₃-type phase was stable at pressures higher than 130 GPa. However, the phase transition from the CaIrO₃-type to the Rh₂O₃(II)-type phase was observed below 130 GPa. Fig. 2 shows changes in the X-ray diffraction patterns during this phase transition. Before heating, the X-ray diffraction pattern of the CaIrO₃-type phase was observed (Fig. 2a). A change in

the diffraction pattern was observed during heating (Fig. 2b). The diffraction peaks of the CaIrO₃-type phase disappeared, and new peaks were observed. These new peaks remained after the temperature quenching (Fig. 2c). The new peaks were indexed based on an Rh₂O₃(II)-type structure.

The phases observed in this study are shown in Fig. 3. The CaIrO₃-type phase was stable up to 200 GPa. The phase boundary between the Rh₂O₃(II)-type phase and

Table 4
Comparison of the calculated Raman frequencies (cm⁻¹) of the CaIrO₃-type phases of Al₂O₃ and MgSiO₃ at 130 GPa

Mode	MgSiO ₃	Al ₂ O ₃
A _g	474.12	472.96
A _g	587.58	730.11
A _g	889.60	883.89
A _g	998.17	984.65
B _{1g}	373.53	345.74
B _{1g}	627.72	807.73
B _{1g}	787.87	661.63
B _{2g}	742.78	719.80
B _{3g}	531.15	378.96
B _{3g}	606.96	646.38
B _{3g}	929.65	892.11
B _{3g}	1161.64	1065.88

the CaIrO_3 -type phase is located at about 130 GPa. The boundary determined in this study is in good agreement with that calculated theoretically [8]. Caracas and Cohen [9] reported a theoretical phase boundary at 156 GPa at 0 K, whereas Tsuchiya et al. [10] found a transition pressure of 150–172 GPa at 0 K. These values are somewhat higher than our experimental data. Lin et al. [5] reported that the $\text{Rh}_2\text{O}_3(\text{II})$ -type Al_2O_3 (doped with Cr^{3+}) remained stable up to 136 GPa and 2350 K. The stability field of the $\text{Rh}_2\text{O}_3(\text{II})$ -type phase observed in their study was stable at slightly higher pressures than those observed in our study. As our experimental uncertainty was large under extreme high-pressure conditions, this discrepancy is likely to be insignificant.

Table 1 shows the cell parameters and volumes of the observed phases. As can be seen in Fig. 4, a discontinuity in the volume between the $\text{Rh}_2\text{O}_3(\text{II})$ -type phase and the CaIrO_3 -type phase indicates that this is a first-order phase transition, with a relative volume change of about 5%. A refinement of the volume data of the CaIrO_3 -type phase yields the third-order Birch–Murnaghan equations of state parameters. The bulk modulus, K_0 , was $249(\pm 20)$ GPa and the volume, V_0 ,

was $158.4(\pm 2.6)\text{Å}^3$ when the first pressure derivative of the bulk modulus, K'_0 , is fixed at $K'_0=4$. A comparison of the elastic parameters between theoretical studies and our experimental observations are shown in Table 2. The experimental values are in good agreement with those of theoretical studies.

4. Discussion

4.1. Similarities between CaIrO_3 -type Al_2O_3 and MgSiO_3

Previous high-pressure studies have shown that high-pressure phases of MgSiO_3 form solid solutions with Fe_2O_3 and Al_2O_3 . McCammon [44], and Frost et al. [45] have reported that a significant amount of Fe_2O_3 dissolves into MgSiO_3 perovskite. An incorporation of Al_2O_3 into MgSiO_3 perovskite has also been reported [46]. The solubility of these components is facilitated by the structural similarities between Fe_2O_3 , MgSiO_3 , and Al_2O_3 . From the viewpoint of the similarity in the sequence of pressure-induced phase transitions, Fe_2O_3 , Al_2O_3 , and MgSiO_3 transform into a CaIrO_3 -type

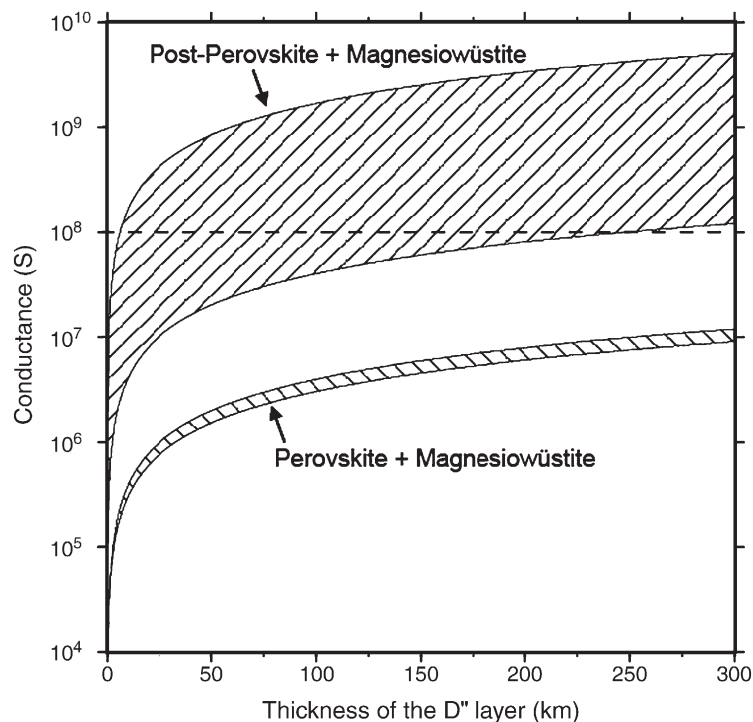


Fig. 5. Electrical conductivity of perovskite+magnesiowüstite, and CaIrO_3 -type phase+magnesiowüstite rocks. The electrical conductivity of CaIrO_3 -type (post-perovskite) MgSiO_3 was assumed to be one to two orders of magnitude higher than that of MgSiO_3 perovskite. The shaded denote the area between the upper and lower bounds of the two-phase materials [51]. If the conductance is $>10^8$ S/m, which is a product of the electrical conductivity and the thickness of the conductive layer, then the decadal variation of the length of day can be explained by an advective electromagnetic toroidal torque [21].

structure at high pressures. Similarities between these isostructural phases are important for understanding the physical properties of Earth's lowermost mantle, the mineralogy of which is dominated by CaIrO_3 -type MgSiO_3 .

Table 3 shows a comparison of the observed X-ray diffraction patterns of CaIrO_3 -type Al_2O_3 and MgSiO_3 . The cell parameters and peak intensities of Al_2O_3 are similar to those of MgSiO_3 . Although it is difficult to determine the atomic positions of both phases using experimental data, the similarity in cell parameters and peak intensities indicates that the atomic positions are nearly the same. The lower limit of the stability field of CaIrO_3 -type Al_2O_3 is almost the same as that of MgSiO_3 . These simple observations strengthen the analogy between the two materials, which is further supported by the similarity of their Raman frequencies.

Table 4 shows the calculated Raman frequencies of these phases at 130 GPa and their symmetry assignments. It can be seen that in most cases, the agreement between the frequencies was within 10%. This, in turn, implies that the strength of the interatomic interactions (and hence, many other properties) between the two materials is not dissimilar. Since Raman spectroscopy is

one of the most convenient probes of matter at ultrahigh pressures, the data in Table 4 can be used to identify CaIrO_3 -type Al_2O_3 and MgSiO_3 .

4.2. Electrical conductivity of the D'' layer

As Earth's mantle consists of elements in addition to Mg, Si, Fe, and O, knowing the effect of minor elements is important in understanding the physics and chemistry of Earth's lower mantle. For example, Xu et al. [24] reported that incorporation of Al_2O_3 increases the electrical conductivity of MgSiO_3 perovskite. Recently, Oganov and Ono [8] hypothesized that the electrical conductivity of the D'' layer was much higher than that of other parts of Earth's mantle, because the CaIrO_3 -type (post-perovskite structure) Al_2O_3 has a high conductivity, and the D'' layer consists of isostructural CaIrO_3 -type MgSiO_3 . On the other hand, observations of changes in Earth's rotation period imply that there is the possibility of the existence of a highly conducting layer at the base of the lower mantle [e.g., 20,21]. Therefore, we assessed the highly conductive layer model predicted by observations on changes in Earth's rotation period.

Fig. 5 shows the relationship between the conductivity predicted by the observations on changes in

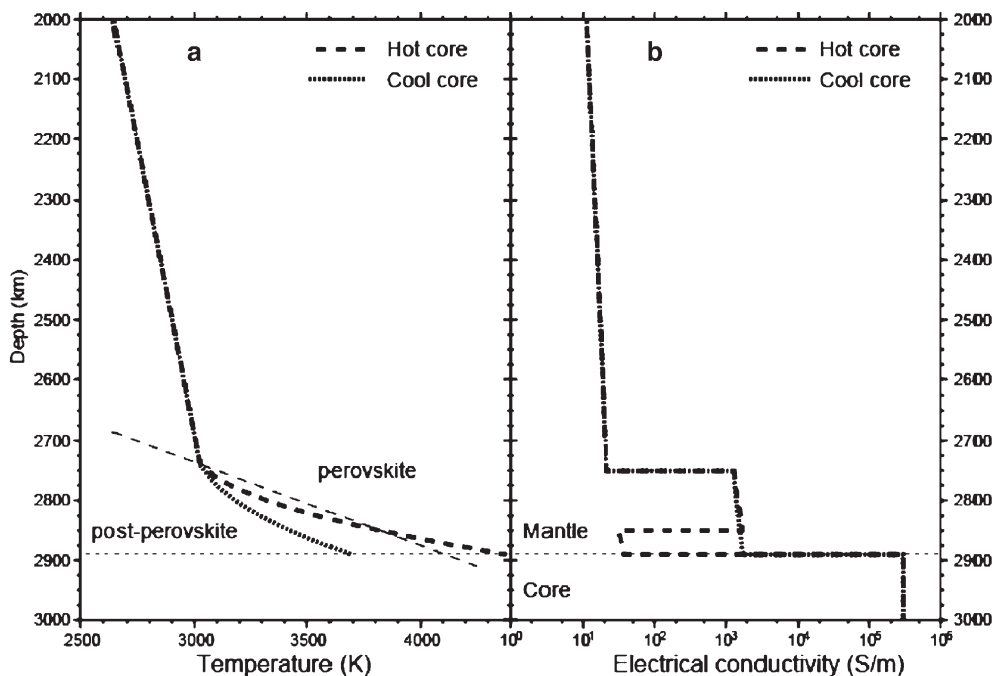


Fig. 6. Temperature and electrical conductivity profiles in the lowermost mantle. a, The temperature models used to estimate the conductivity profile were taken from Hemlund et al. [49]. b, The electrical conductivity model derived from the perovskite, CaIrO_3 -type (post-perovskite) phase, and magnesiowustite [47], were estimated using the effective medium theory [52]. The electrical conductivity of the CaIrO_3 -type phase was assumed to be two orders of magnitude higher than that of perovskite.

Earth's rotation and the conductivity of mantle rock estimated from mineral physics. Holme [21] suggested the conductance of the highly conductive layer was $>10^8$ S. The conductance depends on the electrical conductivity of the rock and the layer thickness. If the conductive layer corresponds to the D'' layer, then the layer thickness is 100–300 km. Xu et al. [47] estimated that the electrical conductivity of perovskite-bearing rock is $10\text{--}10^2$ S/m, but the electromagnetic coupling model cannot explain the conductance of deep mantle based on perovskite-bearing rock [21].

Since the electrical conductivity of CaIrO_3 -type MgSiO_3 has not been measured, we have to rely on the analogy between MgSiO_3 and Al_2O_3 . When the thickness of the highly conductive layer is <5 km, it is difficult to explain the electromagnetic coupling model using CaIrO_3 phase-bearing rock. However, the typical thickness of the D'' layer is 100–300 km. If the electrical conductivity of CaIrO_3 -type MgSiO_3 is an order of magnitude higher than MgSiO_3 perovskite, then the electromagnetic coupling model is reasonable. This change in the electrical conductivity in MgSiO_3 is consistent with the observed change in Al_2O_3 [48]. This implies that the base of the lower mantle corresponding to the D'' layer may be a highly conductive layer. Thus, the exchange of angular momentum between the solid mantle and the fluid core by an electromagnetic core–mantle coupling may be the dominant mechanism for the observed change in the length of Earth's day on a decadal timescale. To discuss our quantitative analysis, it is necessary to perform direct measurements of the electrical conductivity of CaIrO_3 -type MgSiO_3 .

Based on the above, we estimated the profile of the electrical conductivity of the bottom of the lower mantle. Fig. 6 shows the estimated profile of the electrical conductivity. A marked change in the conductivity profile occurs, depending on the geotherm. According to the sandwich-structure (or double-crossing) model [49,50], the lowermost D'' layer does not consist of a post-perovskite-bearing rock. We have calculated two profiles of the electrical conductivity corresponding to hot and cold geotherms (Fig. 6a). When the temperature at the top of the outer core is lower than 4000 K, the D'' layer consists of only a post-perovskite-bearing rock. Thus, the discontinuity in electrical conductivity only occurs at the top of the D'' layer. In contrast, in this scenario, two discontinuities occur at both the top and the bottom of the D'' layer, when the temperature of the outer core is >4000 K, and a thin layer of low electrical conductivity should exist at the bottom of the D'' layer.

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