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High-pressure Raman studies on post-perovskite solid solution CaIr_{0.5}Pt_{0.5}O₃ and room-pressure Raman studies on CaIr_{1-x}Pt_xO₃ (x = 0, 0.3, 0.5, 0.7) & CaIr_{0.5}Rh_{0.5}O₃

Shigeto Hirai^{*}, Yohei Kojima^{**}, Hiroaki Ohfuji^{**}, Norimasa Nishiyama^{**}, Tetsuo Irifune^{**}, Stephan Klemme^{***}, Geoffrey Bromiley^{*} and J. Paul Attfield^{****}

^{*}Centre for Science at Extreme Conditions and School of Geosciences, University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, UK

^{**} Geodynamics Research Center, Ehime University, 2-5 Bunkyo-cho, Matsuyama, Ehime 790-8577, Japan

^{***} Institut für Mineralogie, Corrensstr. 24, Universität Münster, 48149 Münster, Germany

^{****} Centre for Science at Extreme Conditions and School of Chemistry, University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, UK

Abstract: High-quality polycrystalline samples of CaIr_{1-x}Pt_xO₃ (x = 0.3, 0.5, 0.7) and CaIr_{0.5}Rh_{0.5}O₃ have been obtained at a pressure of 15 GPa, and high-pressure Raman studies on CaIr_{0.5}Pt_{0.5}O₃ and room-pressure Raman studies on CaIr_{1-x}Pt_xO₃ series (x = 0, 0.3, 0.5, 0.7) and CaIr_{0.5}Rh_{0.5}O₃ are reported. A new phase of CaIr_{0.5}Pt_{0.5}O₃ synthesized at 60GPa, 1900K has Raman modes which resemble those of CaIrO₃ perovskite, suggesting this phase has a perovskite structure. Pt-O covalent bonding stabilizes the post-perovskite structure and destabilizes the perovskite structure, whilst pressure and the replacement of Pt-O by Ir-O bonding also stabilises the perovskite structure. The instability of the perovskite phase of CaIr_{0.5}Pt_{0.5}O₃ reveals why the post-perovskite to perovskite phase transition has not been observed for CaPtO₃ unlike the case for CaIrO₃, CaRhO₃ and CaRuO₃.

I. Introduction

Since the discovery of the perovskite to post-perovskite transition in MgSiO_3 in a laser-heated diamond anvil cell¹, wide attention has been focussed on the post-perovskite phase of MgSiO_3 . This is because the post-perovskite phase is likely to play a key role in processes occurring in Earth's lower mantle, and the perovskite to post-perovskite transition can explain many features of the D'' seismic discontinuity there. While it is important to conduct further studies on MgSiO_3 , this post-perovskite phase cannot be quenched to ambient conditions; this is also the case for the post-perovskite type transition metal oxides Fe_2O_3 ² and Mn_2O_3 ³. Thus, it is useful to investigate structural analogues of the MgSiO_3 post-perovskite that are quenchable to ambient conditions.

The post-perovskite phase of MgSiO_3 adopts the layered structure CaIrO_3 -structure containing corner-linked chains of edge-sharing octahedra (Fig.1). Four quenchable CaIrO_3 -type oxides have been reported to date: CaIrO_3 ⁴, CaPtO_3 ⁵, CaRhO_3 ⁶ and CaRuO_3 ⁷. Polycrystalline CaIrO_3 can be synthesized at ambient pressure from binary oxides heated to 1273 K in an evacuated silica tube, and single crystals of CaIrO_3 were synthesized at 1223 K using a CaCl_2 flux.⁴ The other three oxides were obtained using a multi-anvil apparatus to achieve high pressure-temperature conditions; CaPtO_3 (4GPa, 1073K),⁵ CaRhO_3 (6GPa, 1473K)⁶ and CaRuO_3 (23GPa, 1223K).⁷ need high pressure/temperature condition for synthesis. Further studies on these materials have revealed post-perovskite to perovskite structural phase transitions at high P-T. The post-perovskite phase of CaIrO_3 transforms to the perovskite structure at 2GPa, 1673K⁸ and this transformation was also observed for CaRhO_3 (6GPa, 1873K) and CaRuO_3 (23GPa, 1343K), while CaPtO_3 remained post-perovskite at higher temperatures⁹. The former observations show that the perovskite type is the high temperature phase and this was supported by a Raman spectroscopy study of CaIrO_3 up to 30GPa¹⁰ and a synchrotron X-ray diffraction of CaPtO_3 up to 40GPa¹¹ which show that the phase transition from post-perovskite to perovskite transition does not occur at room temperature.

The presence of heavy transition metal ions in the above CaMO_3 post-perovskites suggests that such phases might have interesting electronic or magnetic properties. A study of $\text{Ca}_{1-x}\text{Na}_x\text{IrO}_3$ solid solutions (synthesized at 4GPa, 1073K)¹² revealed a metal-insulator transition at $x = 0.37$. To investigate such properties further, we have explored the $\text{CaIr}_{1-x}\text{Pt}_x\text{O}_3$ series and the synthesis, structural and physical properties of these solid solutions are reported here. We

have also demonstrated that $\text{CaIr}_{1-x}\text{Rh}_x\text{O}_3$ materials are accessible and we report the $x = 0.5$ member of this series.

II. Experimental Section

Polycrystalline samples of CaIrO_3 post-perovskite were synthesized by solid state reaction from CaO and IrO_2 . CaO powder was prepared from CaCO_3 by heating in air at $1000\text{ }^\circ\text{C}$ for 24 hrs. Well-ground mixtures of the starting material in a stoichiometric molar ratio were sealed in an evacuated silica tube, and heated in air at 1273K over 20 hrs. CaIrO_3 post-perovskite single crystals were synthesized by flux method⁴. Polycrystalline samples of the perovskite phase of CaIrO_3 were synthesized by solid state reaction from CaO and IrO_2 . Well-ground mixtures of the starting material in a stoichiometric molar ratio were sealed in an evacuated silica tube, and heated in air at $930\text{ }^\circ\text{C}$ over 60 hrs.

Polycrystalline samples of $\text{CaIr}_{1-x}\text{Pt}_x\text{O}_3$ and $\text{CaIr}_{0.5}\text{Rh}_{0.5}\text{O}_3$ were synthesized at high pressure-temperature conditions. $\text{CaIr}_{1-x}\text{Pt}_x\text{O}_3$ ($x = 0.3, 0.5, 0.7$) were synthesized by solid-state reaction from CaO , IrO_2 , and PtO_2 powders. Well-ground mixtures of the starting material in a stoichiometric molar ratio were placed into an Au capsule ($\phi = 2.5\text{ mm}$) sandwiched by BN composite disks ($\phi = 2.7\text{ mm}$). $\text{CaIr}_{0.5}\text{Rh}_{0.5}\text{O}_3$ was synthesized by solid-state reaction from CaO , IrO_2 , and Rh_2O_3 , with KClO_4 as an oxidizer. A well-ground mixture of the starting materials at a ratio of $1/0.5/0.5/4.07$ ($\text{Ca}/\text{Ir}/\text{Rh}/\text{O}$) was placed into an Au capsule ($\phi = 2.5\text{ mm}$) sandwiched by MgO disks ($\phi = 2.7\text{ mm}$), to avoid reducing conditions within the cell. The capsules were heated in a multi-anvil apparatus at $1300\text{ }^\circ\text{C}$ and 15GPa pressure for 40 min, followed by rapid quenching to ambient temperature, and then release of pressure. Considerably high-pressure (15GPa) was needed since the reduction of PtO_2 followed by the phase separation of solid solutions (for example, the Ir/Pt ratio varied from 0.4 to 0.6 for $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$) was detected by SEM/EDX and a large amount of IrO_2 impurity was detected by XRD when synthesis pressures were at $\sim 3\text{ GPa}$ and $\sim 10\text{GPa}$. Extremely high-pressure (15GPa) was needed in order to maximize the high oxygen pressure within the capsule in case of $\text{CaIr}_{0.5}\text{Rh}_{0.5}\text{O}_3$. Dense black pellets were obtained and that of $\text{CaIr}_{0.5}\text{Rh}_{0.5}\text{O}_3$ was washed with distilled water to remove KCl .

High pressure Raman spectroscopy studies on $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ were conducted using a laser-heated diamond anvil cell with NaCl pressure medium and Renishaw RS-SYS 1000 (Ar laser: $\lambda = 514.5\text{ nm}$) at GRC. The sample was heated to $\sim 1900\text{ K}$ for more than 10 minutes by using double-sided laser heating system ($\lambda = 1072\text{ nm}$) installed at GRC. Pressures were estimated from diamond Raman shift¹³, and temperatures were determined by spectroradiometric measurements of the light emitted from the sample under heating. Ambient condition Raman

spectra on $\text{CaIr}_{1-x}\text{Pt}_x\text{O}_3$ ($x = 0.3, 0.5, 0.7$) and $\text{CaIr}_{0.5}\text{Rh}_{0.5}\text{O}_3$ were collected using Lab-Raman (HeNe laser: $\lambda = 632.8$ nm) at CSEC.

III. Results and Discussion

Post-perovskite and perovskite type polymorphs of CaMO_3 ($M = \text{Ir/Pt}$) can be identified and distinguished at high pressure from their Raman spectra. Fig. 3 shows representative spectra of the polycrystalline CaIrO_3 post-perovskite and $\text{CaIr}_{0.7}\text{Pt}_{0.3}\text{O}_3$ post-perovskites and for the perovskite phase of polycrystalline CaIrO_3 prepared at 930°C in an evacuated silica tube, which is noisier as this phase is metallic¹⁴. The post-perovskite phases are characterised by five prominent Raman modes, the frequencies of which are shown in Table 2. All of the modes harden at similar rates with pressure, as shown in the plot in Fig. 4. The asymmetry and the broadening of the Raman mode peaks observed for $\text{CaIr}_{1-x}\text{Pt}_x\text{O}_3$ series ($x = 0, 0.3, 0.5, 0.7$) and $\text{CaIr}_{0.5}\text{Rh}_{0.5}\text{O}_3$ imply the beginning of the photo-induced metallization of these compounds since they only have a small band gap¹⁵.

The post-perovskite to perovskite structural transformation at the mid-point of the CaIrO_3 - CaPtO_3 solid solution was explored through a high pressure Raman spectroscopy study. $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ retains the post-perovskite structure on compression to 60 GPa in a DAC (diamond anvil cell) and the changes of Raman frequencies of shown in Table 2. Fig. 2 shows the room temperature Raman spectra of the sample at 60 GPa before and after laser-heating to ~ 1900 K, and at several pressures during subsequent decompression to ambient pressure. Before heating the sample up to ~ 1900 K, heating at lower temperatures (~ 1500 K and ~ 1700 K) were tried, but their Raman spectra showed no indication of phase transition. Comparison with the spectra in Fig. 2, and that of CaHfO_3 perovskite,¹⁶ shows that $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ transforms from post-perovskite (CaIrO_3) type to perovskite type on heating at 60 GPa. The perovskite phase persists on decompression to 20 GPa, but reverts to the post-perovskite structure between 20 and 9 GPa. The Raman modes of the perovskite phase of $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ are shown in Table 3 and are plotted against pressure in Fig. 5.

As the perovskite phase of $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ transformed back into post-perovskite at ~ 9 GPa, we conclude that Pt-doped CaIrO_3 favours the post-perovskite structure over the perovskite structure at moderate pressures.

High pressure Raman spectroscopy studies on $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ revealed that the five prominent Raman modes for post-perovskite phase show positive pressure dependence: 1.6 to 4.3 ($\text{cm}^{-1}/\text{GPa}$) (Fig.4, Table 2). According to the group theory, there are 12 Raman-active modes

($4A_g + 3B_{1g} + B_{2g} + 4B_{3g}$) out of 30 phonon modes ($4A_g + 2A_u + 3B_{1g} + 6B_{1u} + B_{2g} + 6B_{2u} + 4B_{3g} + 4B_{3u}$) for *Cmcm* symmetry in post-perovskite regime. Thus, 5 out of 12 Raman-active modes were observed for each of the pressures in our study. The number of modes and their frequency are similar to the previously reported CaIrO_3 high-pressure Raman spectra¹⁰, apart from the newly observed Raman mode near 700cm^{-1} , which was in fact detectable in our study for $\text{CaIr}_{1-x}\text{Pt}_x\text{O}_3$ series ($x = 0, 0.3, 0.5, 0.7$) and $\text{CaIr}_{0.5}\text{Rh}_{0.5}\text{O}_3$ by adopting the appropriate orientation of grains. The Ir and Pt atoms do not participate in the Raman-active phonon modes due to its atomic site symmetry (: 4a), while post-perovskite structure has 4 structural degree of freedom out of 12 atomic coordinates. As a reference, the Ir atoms in CaIrO_3 post-perovskite and CaIrO_3 perovskite do not participate in the Raman-active phonon modes either.

High pressure Raman spectroscopy studies on $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ revealed that the seven prominent Raman modes for perovskite phase show positive pressure dependence: 1.0 to 2.8 ($\text{cm}^{-1}/\text{GPa}$) (Fig.5, Table 3). However, the fifth Raman mode (ν_5) of the perovskite phase does not follow this trend. The anomalous pressure dependence of this Raman mode around 28 GPa implies a possible second-order phase transition. It is worthwhile to note that when the Raman modes of the perovskite phase of $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ are extrapolated to ambient pressure, they have the same number of Raman modes below 400cm^{-1} and similar mode frequencies with CaMnO_3 perovskite¹⁷ in *Pbnm* space group. This is reasonable since CaIrO_3 perovskite is also in the space group of *Pbnm*. Therefore, the perovskite phase of $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ is likely to be in the orthorhombic regime with GdFeO_3 -type structure (space group: *Pbnm*) having its octahedron less distorted and tilted compared to that of CaIrO_3 perovskite, since the presence of Pt^{4+} suppresses Jahn-Teller effect of Ir^{4+} in orthorhombic perovskite.

As the values of bulk modulus at ambient pressure for the post-perovskite phase of CaIrO_3 ¹⁸ (K_0 : 180.2(28) GPa) and CaPtO_3 ¹¹ (K_0 : 174.0(5) GPa) calculated by in-situ X-ray diffraction studies are close to each other, it is a good estimation to assume that the bulk modulus of the post-perovskite phase of $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ has the average value of these two values, K_0 : 177.1 GPa. As the mode Grüneisen parameters ($\gamma_{i,0}$) of each Raman mode is defined in the equation as follow, where $\gamma_{i,0}$ is the mode Grüneisen parameter, K_{T_0} is the bulk modulus at ambient temperature and $\nu_{i,0}$ is the wavenumber of the ν_i Raman mode at ambient pressure:

$$\gamma_{i,0} = K_{T_0}/\nu_{i,0} * (d\nu_i / dP)$$

Table 2 shows the mode Grüneisen parameters ($\gamma_{i,0}$) of the post-perovskite phase of $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$, which can be calculated using the estimated bulk modulus at ambient conditions. The mode Grüneisen parameters ($\gamma_{i,0}$) varied from 0.869 to 1.10 and $\langle \gamma_{i,0} \rangle$ is 0.971 (Table 2), showing similar values and isotropy with those of MgGeO_3 ¹⁹ instead of those of CaIrO_3 ¹⁰. $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ has much smaller and much more isotropic mode Grüneisen parameters compared with CaIrO_3 ¹⁰. It is well known²⁰ that the weighted average of mode Grüneisen parameters by the Einstein heat capacity is in good match with the thermodynamic Grüneisen parameter γ_{th} (this is also the case for CaIrO_3 post-perovskite). The weighted average of mode Grüneisen parameters [$\gamma_{i,0}$] for $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ post-perovskite is 0.952 (Table 2), which is much smaller than the case of CaIrO_3 post-perovskite ([$\gamma_{i,0}$]: 1.66). Thus, the weight average of mode Grüneisen parameters implies that $\gamma_{\text{th}} \sim 0.952$ for $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ post-perovskite. Such results suggest that $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ is a better analogue of the post-perovskite phase of MgSiO_3 than CaIrO_3 as the triply degenerate ground state of low spin $5d^5 \text{Ir}^{4+}$ is replaced by non-degenerate $5d^6 \text{Pt}^{4+}$. In addition, its estimated bulk modulus K_0 : 177.1 GPa has similar a value with that of MgSiO_3 ²¹ (K_0 : 231 GPa) and MgGeO_3 ²² (K_0 : 205 GPa).

As the thermodynamic Grüneisen parameter γ_{th} can be calculated as:

$$\gamma_{\text{th}} = \alpha K_{\text{T}0} V / C_V \quad (\alpha: \text{thermal expansion parameter, } V: \text{cell volume, } C_V: \text{heat capacity})$$

, the thermal expansion and the heat capacity of $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ post-perovskite will be very different from those of CaIrO_3 post-perovskite due to the large gap in γ_{th} . The parameter q , which is the logarithmic volume derivative of Grüneisen parameters was also calculated for $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ in order to compare it with that of CaIrO_3 ¹⁰ and MgGeO_3 ¹⁸. The parameter q varied from 2.86 to 3.93, showing similar values with those of MgGeO_3 ¹⁸ perovskite. It is worthwhile to note that unlike the case of the mode Grüneisen parameters, the parameter q has similar values with that of CaIrO_3 ¹⁰, especially for v_3 .

As the experimentally derived bulk modulus at ambient pressure for perovskite phase of CaIrO_3 is K_0 : 198(3) GPa, which is not so far away from the bulk modulus of the post-perovskite phase of CaIrO_3 either, it is constructive to assume that the extrapolated ambient pressure bulk modulus of the perovskite phase of $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ is ~ 200 GPa. Then, the mode Grüneisen parameters ($\gamma_{i,0}$) of the perovskite phase of $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ can be calculated as shown in Table 3.

The mode Grüneisen parameters ($\gamma_{i,0}$) varied from 0.912 to 1.96 and the simple average $\langle \gamma_{i,0} \rangle$ is 1.29, showing similar values and isotropy with those of MgGeO_3 ¹⁸ perovskite. As the weighted average of mode Grüneisen parameters is $[\gamma_{i,0}]$: 1.27, we estimate that $\gamma_{\text{th}} \sim 1.27$ for $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ perovskite. Therefore, the thermodynamic Grüneisen parameter increases by 33 % across the post-perovskite to perovskite phase transition in $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$. A similar magnitude of increase in γ_{th} is reported for $(\text{Mg,Fe})\text{SiO}_3$ ²³ (27 %) and MgGeO_3 ¹⁸ (33 %). In addition, the perovskite phase of $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ has the same number of prominent Raman modes as MgGeO_3 ¹⁸ perovskite. Therefore, $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ is a promising analogue of MgSiO_3 system in the lowermost mantle. The parameter q was not calculated since the pressure dependence of Raman modes of the perovskite phase of $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ were close to linear, having similar feature with the MgGeO_3 ¹⁸ perovskite. It would be useful to conduct CaIrO_3 perovskite high-pressure Raman studies for comparison, but this is extremely difficult since the Raman peaks are very noisy due to its metallic¹⁴ feature.

The Raman mode near 563 cm^{-1} , which is present for $\text{CaIr}_{1-x}\text{Pt}_x\text{O}_3$ ($x = 0.3, 0.5, 0.7$) and not visible for CaIrO_3 , indicates that the strong attraction of O atoms toward the Pt atoms plays an important role in the vibration regarding PtO_6 octahedron. In other words, the strengthening of the vibration modes that are responsible for O atoms due to the slightly stronger attraction of O atoms toward the Pt atoms gives rise to the Raman mode near 563 cm^{-1} .

IV. Discussion

The newly synthesized phase at 60GPa, ~1900K for $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ has Raman modes which resemble those of CaIrO_3 perovskite and CaHfO_3 perovskite, suggesting this phase has a perovskite structure. However, this perovskite phase transformed back into a post-perovskite phase when the pressure was released down to ~9GPa. According to the previous studies on phase transition from post-perovskite to perovskite in CaIrO_3 ⁸, the phase equilibrium boundary is calculated to be $P \text{ (Gpa)} = 0.040 T \text{ (K)} - 67.1$. Thus, the phase equilibrium boundary condition for CaIrO_3 at $T = 1900\text{K}$ is predicted to be $P = 8.9\text{Gpa}$ from the strongly positive P/T slope. Therefore, assuming the gradient of the P/T slope is uniform over the $\text{CaIr}_{1-x}\text{Pt}_x\text{O}_3$ series, the theoretical phase boundary between post-perovskite and perovskite phase for CaPtO_3 is estimated as ~111Gpa for ~1900K and ~87Gpa for ~1300K by extrapolating the P/T phase boundary for CaIrO_3 (8.9Gpa, 1900K) and $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ (60Gpa, 1900K). Taking such estimations into

consideration, the observation that CaPtO_3 ⁹ did not transform into perovskite phase at 7GPa and ~1300K suggests the lack of synthesis pressure for a perovskite phase. Thus, even though the phase transition from post-perovskite to perovskite may take place at extremely high pressures (above 80GPa), it is likely that the perovskite phase reverts back to post-perovskite structure at lower pressures. In other words, the instability of the perovskite phase of CaPtO_3 has been revealed by the destabilization of newly synthesized perovskite phase of $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$.

The conflict between the strong Pt-O covalent bonding that favours large octahedral tilting and the Jahn-Teller inactive Pt^{4+} in perovskite regime which favour cubic perovskite is one possible reason for destabilization of the perovskite-structure. A similar destabilization mechanism of perovskite- against ilmenite-structure has been previously explained in the case of NaSbO_3 -type oxides²⁴. In conclusion, the conflict between the strong Pt-O covalent bonding that favours large octahedral tilting and the Jahn-Teller inactive Pt^{4+} in perovskite structure which favour cubic regime is one possible reason for destabilization of the perovskite-structure, while pressure and the replacement of Pt-O by Ir-O bonding can play a role in sustaining perovskite structure. In the case of CaIrO_3 , CaRhO_3 and CaRuO_3 , this conflict does not exist since the B-site cation (Ir^{4+} : $5d^5$, Rh^{4+} : $4d^5$, Ru^{4+} : $4d^4$) in each compound is Jahn-Teller active. In other words, the instability of the perovskite phase of $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ has revealed why post-perovskite to perovskite phase transition has not been observed for CaPtO_3 unlike the case for CaIrO_3 , CaRhO_3 and CaRuO_3 . The stability condition of post-perovskite/perovskite regime is very sensitive since Ir^{4+} and Pt^{4+} in CaMO_3 ($\text{M} = \text{Ir/Pt}$) have similar ionic radii (Ir^{4+} : 0.625, Pt^{4+} : 0.625) and similar electronegativity (χ_{Ir} : 2.2, χ_{Pt} : 2.28). The strong Pt-O covalent bonding that stabilizes post-perovskite regime comes from the high electronegativity of Pt. The post-perovskite phase of CaIrO_3 , CaPtO_3 , CaRhO_3 and CaRuO_3 can be quenched to ambient pressure since the electronegativity of Ir, Pt, Rh and Ru are 2.20, 2.28, 2.28 and 2.20, while that of Si, Ge, Al, Fe and Mn are 1.90, 2.01, 1.61, 1.83 and 1.55, respectively. Therefore, MgSiO_3 ¹⁹, MgGeO_3 ²⁰, Al_2O_3 ²⁵, Fe_2O_3 ² and Mn_2O_3 ³ can take the post-perovskite structure at high pressures, but when the compression of bonds due to high confining pressure is removed, the strong M-O covalent bonding ($\text{M} = \text{Si/Ge/Al/Fe/Mn}$) disappears and it can no longer sustain the post-perovskite structure. It has been reported that Al^{3+} incorporation²⁶ in the Si-site of the post-perovskite phase of MgSiO_3 is much more difficult than in the Si-site of MgSiO_3 perovskite and requires stabilization pressure higher than 130GPa. This is in good agreement with the fact that Si has higher electronegativity than Al. In other words, the incorporation of Al^{3+} in the Si-site will stabilize the perovskite-regime and destabilize the post-perovskite regime. Si has higher electronegativity than any existing elements of M^{3+} or M^{4+} ($\text{M} = \text{Al, Fe, Ti, Mn, Zr}$) in the

lowermost mantle. Therefore, substitutions of the Si-site by M (M = Al, Fe, Ti, Mn, Zr) will be destabilized at lowermost mantle conditions and can only be stabilized by pressures higher than in the lowermost mantle. Thus, the high electronegativity which plays a key role in the stability of post-perovskite phase of $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ leads to an important implication: the Si-site of the post-perovskite phase of MgSiO_3 is free from any substitution in the lowermost mantle.

V. Conclusions

The new phase synthesized at 60GPa, 1900K for $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ has Raman modes which resemble those of CaIrO_3 perovskite, suggesting this phase has a perovskite structure. Pt-O covalent bonding due to the high electronegativity of Pt stabilizes the post-perovskite structure and destabilizes the perovskite structure, while pressure and the replacement Pt-O by Ir-O bonding can play a role in sustaining the perovskite structure. The instability of the perovskite phase of $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ reveals why the post-perovskite to perovskite phase transition has not been observed for CaPtO_3 unlike the case for CaIrO_3 , CaRhO_3 and CaRuO_3 . Furthermore, we predict that the Si-site of the post-perovskite phase of MgSiO_3 is free from any substitution in the lowermost mantle. High pressure Raman spectroscopy studies on $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ reveal that the five primary Raman modes for post-perovskite phase and seven primary Raman modes for perovskite phase show positive pressure dependence: 1.6 to 4.3 ($\text{cm}^{-1}/\text{Gpa}$) for post-perovskite phase and 1.0 to 2.8 ($\text{cm}^{-1}/\text{Gpa}$) for perovskite phase. We estimated the increase in γ_{th} across the post-perovskite to perovskite transition, which is in similar magnitude with $(\text{Mg,Fe})\text{SiO}_3$ and MgGeO_3 , suggesting that $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ is a promising analogue for investigating MgSiO_3 system in the lowermost mantle.

Table 1: The five primary Raman modes of $\text{CaIr}_{1-x}\text{Pt}_x\text{O}_3$ and $\text{CaIr}_{0.5}\text{Rh}_{0.5}\text{O}_3$

Wavenumber (cm^{-1})	CaIrO_3	$\text{CaIr}_{0.7}\text{Pt}_{0.3}\text{O}_3$	$\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$	$\text{CaIr}_{0.3}\text{Pt}_{0.7}\text{O}_3$	$\text{CaIr}_{0.5}\text{Rh}_{0.5}\text{O}_3$
ν_1	309	322	320	334	301
ν_2	444	452	451	452	449
ν_3	552	543	544	553	546
ν_4	-----	562	559	568	565
ν_5	712	688	692	703	648

Table 2: The five primary Raman modes of post-perovskite phase of $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ at high pressures along with the mode Grüneisen parameters ($\gamma_{i,0}$) and its logarithmic volume derivative q

P (GPa)	$\nu_1(\text{cm}^{-1})$	$\nu_2(\text{cm}^{-1})$	$\nu_3(\text{cm}^{-1})$	$\nu_4(\text{cm}^{-1})$	$\nu_5(\text{cm}^{-1})$
0	322	448	545	565	692
9	337	467	586	599	733
30	378	534	651	681	840
50	403	569	693	748	917
60	416	582	714	766	943
$\gamma_{i,0}$	0.869	0.913	0.894	1.08	1.10
q	2.86	3.84	3.93	2.93	3.11

Simple average of $\gamma_{i,0}$, $\langle\gamma_{i,0}\rangle$: 0.971

Weighted average of $\gamma_{i,0}$, $[\gamma_{i,0}]$: 0.952

Table 3: The seven primary Raman modes of perovskite phase of $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ at high pressures along with the mode Grüneisen parameters ($\gamma_{i,0}$)

P (GPa)	$\nu_1(\text{cm}^{-1})$	$\nu_2(\text{cm}^{-1})$	$\nu_3(\text{cm}^{-1})$	$\nu_4(\text{cm}^{-1})$	$\nu_5(\text{cm}^{-1})$	$\nu_6(\text{cm}^{-1})$	$\nu_7(\text{cm}^{-1})$
20	164	181	208	263	295	314	377
28	178	193	233	268	282	340	389
38	190	203	258	282	306	364	408
60	206	223	292	312	349	426	445
$\gamma_{i,0}$	1.23	1.13	1.96	0.966	1.05	1.76	0.912

Simple average of $\gamma_{i,0}$, $\langle\gamma_{i,0}\rangle$: 1.29

Weighted average of $\gamma_{i,0}$, $[\gamma_{i,0}]$: 1.27

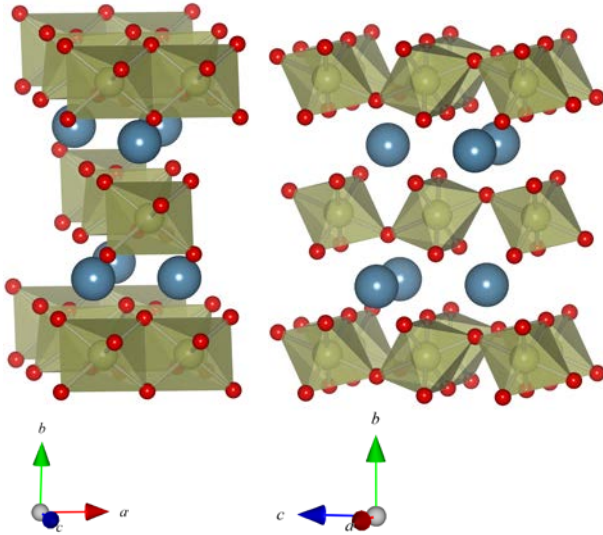


Fig.1: Crystal structure of CaIrO_3 in edge-sharing and corner-sharing projection
 Fig.2: Raman spectra of $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ at high pressure conditions for (a) 60GPa, RT before heating the sample by laser, (b) 60GPa, RT after heating the sample upto 1900K by laser, (c) pressure released down to 38GPa after laser heating, (d) pressure released down to 20GPa after laser heating, (e) pressure released down to 9GPa after laser heating

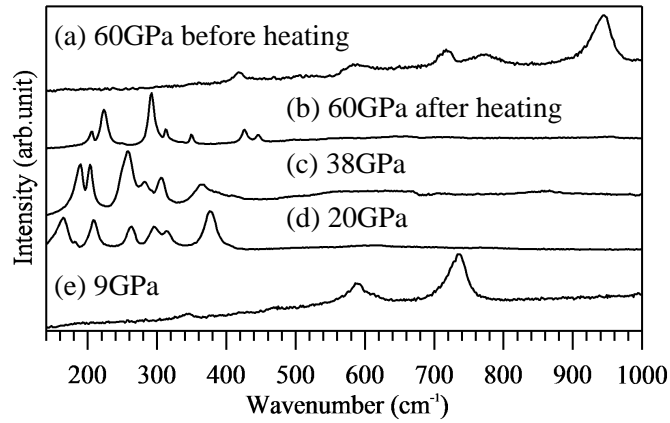


Fig.3: Raman spectra of (a) CaIrO_3 perovskite, (b) CaIrO_3 post-perovskite and (c) $\text{CaIr}_{0.7}\text{Pt}_{0.3}\text{O}_3$

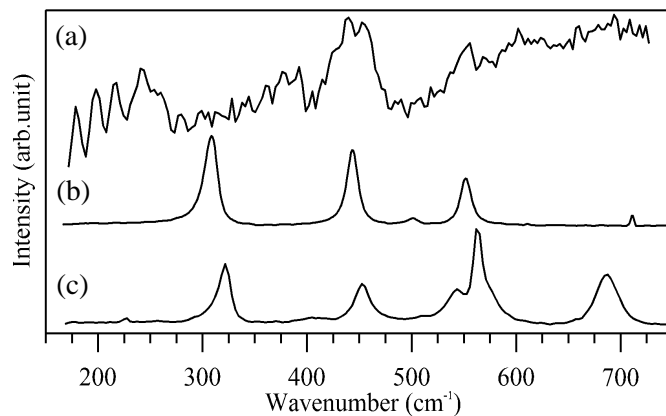


Fig.4: Pressure dependence of the five primary Raman modes of $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ post-perovskite ($\nu_1: n, \nu_2: l, \nu_3: s, \nu_4: t, \nu_5: \Lambda$)

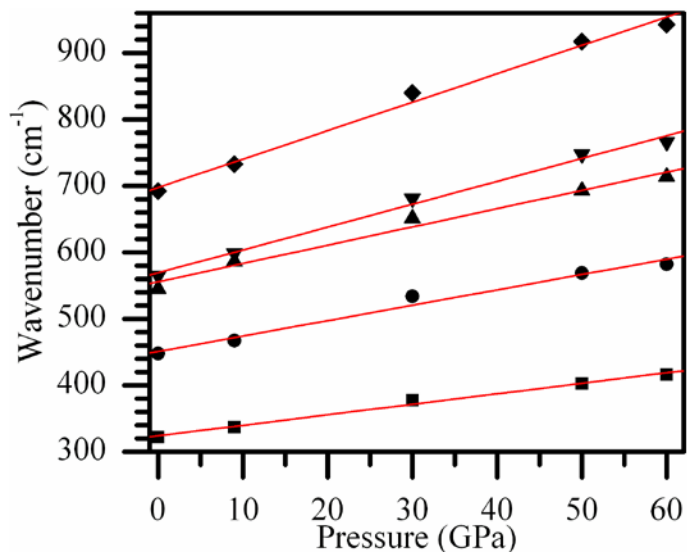
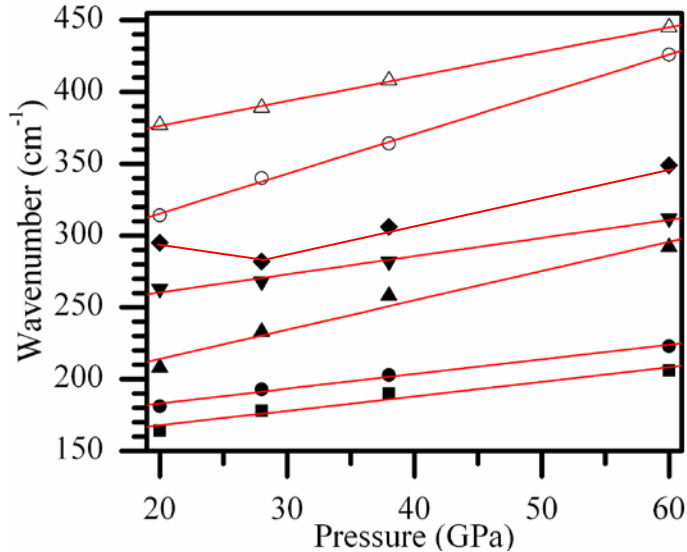


Fig.5: Pressure dependence of the seven primary Raman modes of $\text{CaIr}_{0.5}\text{Pt}_{0.5}\text{O}_3$ perovskite ($\nu_1: n, \nu_2: l, \nu_3: s, \nu_4: t, \nu_5: \Lambda, \nu_6: m, \nu_7: 8$)



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