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High-Pressure Synthesis, Structure, and Characterization of a Post-perovskite $CaPtO_3$ with $CaIrO_3$-Type Structure

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A new ternary platinum oxide, $CaPtO_3$ was synthesized under a pressure of 7 GPa and a temperature of 1000 °C. The crystal structure of $CaPtO_3$ was determined by Rietveld analysis of the X-ray powder diffraction data. $CaPtO_3$ has a layered $CaIrO_3$-type structure (orthorhombic, space group: *Cmcm*), which is the same as that of a post-perovskite $MgSiO_3$ in the Earth's lower mantle. The magnetic susceptibility data indicate that the Pt ion in $CaPtO_3$ is tetravalent in the low spin state with an electron configuration of $t_{2g}{}^6e_g{}^0$ ($S = 0$). This finding is consistent with the insulating behavior.

Pt metal and Pt-containing compounds have received much attention because of their excellent catalytic and electrochemical properties. Therefore, binary and ternary platinum oxides have been extensively studied in terms of synthesis, structure, and electronic properties in addition to catalytic properties. A review of the structure and properties has been given by Schwartz and Prewitt.[1] In the Ca−Pt−O system among ternary platinum oxides, three phases, Ca_4PtO_6,[2–8] $Ca_2Pt_3O_8$,[9] and $CaPt_2O_4$,[10] have been well-identified. On the other hand, though the synthesis[2] and the standard Gibbs energies of formation[7,8] of a tetragonal $CaPtO_3$ at ambient pressure have been reported, the phase identification has not been done in detail. When we then attempted to synthesize $CaPtO_3$ in ambient pressure, the phase of $CaPtO_3$ was not obtained, resulting in a mixture of $CaPt_2O_4$, Ca_4PtO_6, and Pt metal (see Figures S1 and S2 in the Supporting Information). We therefore tried to stabilize $CaPtO_3$ under high pressure. It was then found that the high-pressure phase has a layered $CaIrO_3$-type structure[11–14] (orthorhombic, space group *Cmcm*), which is the same as that of a post-perovskite $MgSiO_3$ in the Earth's lower mantle. The Earth's lower mantle is believed to be composed mainly of $(Mg,Fe)SiO_3$ perovskite. Recently, ab initio simulation and high-pressure experiments have demonstrated that, at pressures and temperatures of the lowermost part of the lower mantle called D″ layer (above 125 GPa and 2500 K), $MgSiO_3$ transforms from perovskite into a layered $CaIrO_3$-type phase.[15,16] Therefore, the compounds with a $CaIrO_3$-type structure are generally called "post-perovskite" among geoscientists.

In this Communication, we report on the synthesis, crystal structure, and some properties of a post-perovskite $CaPtO_3$.

$CaPtO_3$ was synthesized by a solid-state reaction under high pressure at elevated temperature. Stoichometric amounts of CaO (Soekawa Chemicals, >99.9% purity) and PtO_2 (Alfa Aesar, >99.95% purity) in the molar ratio of 1:1 were mixed together in a mortar. The mixture was sealed in a gold capsule (0.2 mm in thickness, 3.1 mm in inner diameter, and 3.2 mm in depth). These processes were performed in a glovebox filled with Ar gas to avoid the humidity and CO_2 gas. A pyrophyllite cube block (13 mm in side length) was used as a pressure medium. A cylindrical graphite heater was place in the cube block together with a NaCl sleeve as a thermal insulator. The capsule was put in the heater. NaCl disk plugs were then stuffed at both ends of the heater. The mixture was allowed to react in a TRY cubic multianvil-type high-pressure apparatus (NAMO 2001) at 7 GPa and 1000 °C for 30 min and then was quenched to room temperature. No weight loss in the sample has been observed after the high-pressure and heat treatment.

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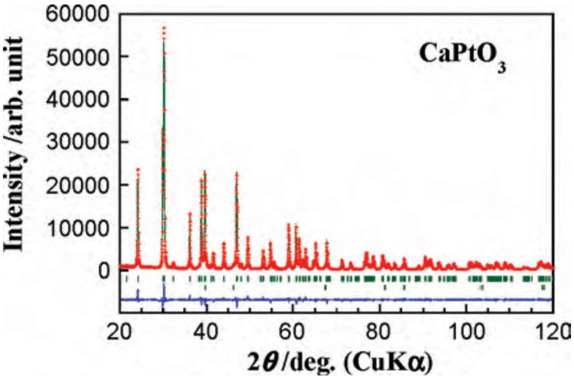

Figure 1. Observed (+) and calculated (solid line on the top) X-ray powder diffraction patterns, difference (solid line on the bottom), and peak positions (|) of $CaPtO_3$ and Pt.

Table 1. Structural Parameters in $CaPtO_3$[a]

atom	site	x	y	z	B/Å^2
Pt	4a	0	0	0	0.71(2)
Ca	4c	0	0.2508(2)	$^1/_4$	1.00(5)
O1	4c	$^1/_2$	0.4160(6)	$^1/_4$	1.3(2)
O2	8f	$^1/_2$	0.1245(4)	0.0447(6)	1.1(1)

[a] Orthorhombic, space group *Cmcm* (No. 63), $Z = 4$, $a = 0.31232(4)$ nm, $b = 0.9912(1)$ nm, $c = 0.73459(9)$ nm. $R_{\mathrm{wp}} = 7.09\%$, $R_{\mathrm{p}} = 5.62\%$, $R_{\mathrm{R}} = 7.52\%$, $R_{\mathrm{e}} = 2.81\%$, $S = 2.52$, $R_{\mathrm{I}} = 2.15\%$, and $R_{\mathrm{F}} = 1.16\%$.

The color of the obtained powder was mustard. The phase was identified by the X-ray powder diffraction method using a Rigaku RINT2100 diffractometer (graphite-monochromatized Cu Kα). The X-ray diffraction data were collected in the range $2\theta = 20-120°$ at 0.02° intervals at room temperature. The X-ray diffraction pattern (Figure 1) showed only the orthorhombic phase and a small residual amount of Pt metal. The X-ray diffraction profile of the orthorhombic phase could be indexed using a C-centered unit cell, implying that $CaPtO_3$ would adopt the $CaIrO_3$-type structure (space group *Cmcm*) with unit cell parameters $a = 0.31232(4)$ nm, $b = 0.9912(1)$ nm, and $c = 0.73459(9)$ nm. The crystal structure of $CaPtO_3$ was refined using the Rietveld analysis program *RIETAN 2000*.[17] Peak profiles were fitted with the pseudo-Voigt function. Figure 1 shows the observed and calculated X-ray powder diffraction patterns and their differences. The scale factors for $CaPtO_3$ and Pt are $6.71(5) \times 10^{-5}$ and $7.3(1) \times 10^{-6}$, respectively. Using the equation by Bish and Howard,[18] the amount of Pt is estimated to be 2.0 wt % (2.8 mol %). The refined structural parameters for $CaPtO_3$ are listed in Table 1. The structure of $CaPtO_3$ shows layers formed from corner-shared (along c axis) and edge-shared PtO_6 octahedra (along a axis) and separated by Ca^{2+} ions (Figure 2). Table 2 lists the selected interatomic distances and bond angles of $CaPtO_3$. The Pt$-$O interatomic distances in $CaPtO_3$ are 0.2016(3) and 0.2017(3) nm and thus are in good agreement with other Pt^{4+}-containing oxides, e.g., Ca_4PtO_6[6] and $Ca_2Pt_3O_8$[9] ($Pt^{4+}-O$ interatomic distance 0.202–0.204 nm). The bond valence sums[19,20] of Ca, Pt, O1, and O2 are calculated to be 2.31, 4.13, 2.28, and 2.08, respectively. The Ca$-$O and Pt$-$O bonds are both overbonded; in particular, the Ca$-$O bond is. This finding implies that the covalency between metal and oxygen, especially Ca$-$O, is strengthened in the high-pressure phase of $CaPtO_3$.

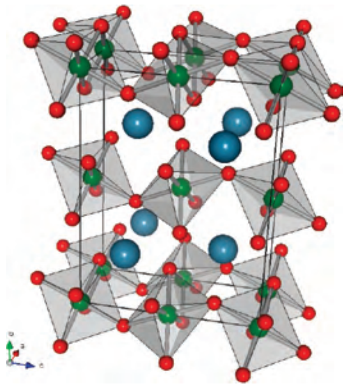

Figure 2. Crystal structure of a post-perovskite $CaPtO_3$.

Table 2. Selected Interatomic Distances (nm) and Bond Angles (deg) in the Crystal Structure of $CaPtO_3$

interatomic distance/nm		bond angle/deg	
Pt$-$O1	$0.2016(3) \times 2$	O1$-$Pt$-$O2	84.0 (2)
Pt$-$O2	$0.2017(3) \times 4$	O1$-$Pt$-$O2	96.0(2)
Ca$-$O1	$0.2263(5) \times 2$	O2$-$Pt$-$O2	78.6(2)
Ca$-$O2	$0.2493(5) \times 2$	O2$-$Pt$-$O2	101.4(2)
Ca$-$O2	$0.2506(4) \times 4$	Pt$-$O1$-$Pt	131.2(3)

In addition, though the Pt$-$O distances are close, the PtO_6 octahedron is not regular in shape. A characteristic of the PtO_6 octahedron is that the oxygen rectangle composed of four O2 surrounding Pt in the ac plain of the PtO_6 octahedron is elongated along the a axis, accompanied by the bond angles of O2$-$Pt$-$O2, which are quite distorted from the 90° values. A similar elongation of the oxygen rectangle along the a axis is also observed in $CaIrO_3$.[11] This characteristic originates from the electrostatic repulsion between the cations with high electric charges, Pt^{4+} or Ir^{4+}, in edge-shared oxygen octahedra along the a axis.

The obtained sample shows very high electronic resistivity at room temperature ($>3 \times 10^7\ \Omega$ cm), as checked by the direct current two-probe method using a Hokuto-Denko potentiostat$-$galvanostat HA-301. The magnetic susceptibility data (see Figure S3 in the Supporting Information) indicate that the Pt ion in $CaPtO_3$ is tetravalent in the low-spin state with an electron configuration of $t_{2g}{}^6e_g{}^0$ ($S = 0$), i.e., a diamagnetic ion. The insulating behavior originates from the localization of t_{2g} electrons. The elongation of the octahedron along the a axis is also attributed to the repulsive electronic interaction between the filled t_{2g} orbitals. The Ir$-$O distances in $CaIrO_3$ are quite different (Ir$-$O1 = 0.194 nm and Ir$-$O2 = 0.207 nm),[11] whereas the Pt$-$O distances in $CaPtO_3$ are regular. This presumably arises from the different bonding associated with the d^5 and d^6 electron configurations.

In this study, we found that $CaPtO_3$ with $CaIrO_3$-type structure, which is thought to be the high-pressure structure post-perovskite, can be stabilized under a pressure of 7 GPa. The perovskite tolerance factor of $CaPtO_3$ is calculated to be 0.880 using Shannon's ionic radii[21] (Ca^{2+}(CN = 8) = 1.12 Å; Pt^{4+}(CN = 6) = 0.625 Å). The value is comparable to or greater than those of $GdFeO_3$-type Ca-containing

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perovskites such as $CaTiO_3$ (0.889), $CaSnO_3$ (0.853), and $CaZrO_3$ (0.841). We can therefore expect that $CaPtO_3$ would adopt the perovskite structure at ambient pressure. However, the perovskite phase is not available by a solid-state reaction at ambient pressure, resulting in dissociation to the mixture of CaO and/or Ca_4PtO_6 and Pt metal at elevated temperature.[2,7,8] In the near future, we will try to synthesize the perovskite phase of $CaPtO_3$ and discuss the stability of perovskite and post-perovskite phases.

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Supporting Information Available: Powder X-ray diffraction patterns for samples obtained by the solid-state reaction of $CaCO_3$ or CaO and PtO_2 in air or in the flow of oxygen and temperature dependence of the magnetic susceptibility of $CaPtO_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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