# Experimental and theoretical study of the phase transition between perovskite polytypes of BaPtO<sub>3</sub> under high pressure and temperature

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APtO<sub>3</sub> (A = Ca, Sr, Ba) is a unique family in the complex transition metal oxides with the AMO<sub>3</sub> formula. Most 3*d* and 4*d* AMO<sub>3</sub> compounds adopt the perovskite structure when synthesized at ambient or high pressure; however, APtO<sub>3</sub> perovskites have not been reported, even if their geometric tolerance factor, *t*, falls in the range suitable for the perovskite structure. Herein, we studied the crystal structures of BaPtO<sub>3</sub> by performing the *in situ* x-ray diffraction over a broad range in the pressure (*P*)–temperature (*T*) phase diagram. The perovskite BaPtO<sub>3</sub> can be stabilized at *P* > 35 GPa and *T* > 1100 K. A variety of crystal structures, including the perovskite structure and its hexagonal polytypes, observed in the *P*–*T* phase diagram of BaPtO<sub>3</sub> match the structure predictions from the first-principles calculations reasonably well.

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# I. INTRODUCTION

The perovskite phase ABX<sub>3</sub> is the major form of matter in the Earth's lower mantle and was believed to have the highest density in oxides and fluorites [1] until the post-perovskite phase was found in MgSiO<sub>3</sub> at 125 GPa and 2500 K in 2004 [2]. Due to their ability to incorporate a wide range of cations at the A and B sites, ABO<sub>3</sub> oxides constitute a large family for fundamental studies and technical applications. The A site's coordination number (CN) varies from 8 to 12 depending on the structural symmetry, while the B site's CN is 6 in most cases. In the perovskite structure, the corner-sharing BO<sub>6</sub> layers form a 3D network with A atoms occupying the voids formed by BO<sub>6</sub> octahedra. The stability of the perovskite structure is determined using the Goldschmidt tolerance factor [3,4]. The tolerance factor *t* for ABO<sub>3</sub> compounds is defined as

$$t = (r_{\rm A} + r_{\rm O}) / [\sqrt{2}(r_{\rm B} + r_{\rm O})],$$
 (1)

where  $r_A$ ,  $r_B$ , and  $r_O$  are the radius of A, B, and O ions, respectively. The perovskite structure of ABO<sub>3</sub> stabilizes in a cubic (3C) form when *t* is equal to unity (t = 1). However, for perovskites with t < 1, the mismatch between equilibrium bond lengths can be accommodated by cooperative octahedral-site

rotations, leading to the tilting systems with reduced symmetries [5]. Among the tilting systems, *Pbnm* (No. 62) is a very common perovskite structure. However, if synthesized at ambient pressure, hexagonal polytypes of ABO<sub>3</sub> form when t > 1 [6]. In this case, high-pressure treatment is necessary to stabilize the perovskite structure. In addition to the density consideration, the compressibility of A–O bonds is usually larger than that of B–O bonds and high pressure can reduce the tolerance factor t to near unity. Therefore, the ABO<sub>3</sub> compounds adopt different hexagonal polytype or perovskite structures at different pressures.

The sequence of BaRuO<sub>3</sub> polytypes under high pressure has been reported in the literature [7–11]. BaRuO<sub>3</sub>, which has a nine-layer rhombohedral (9R) structure at ambient pressure, adopts a four-layer hexagonal (4H) structure and a six-layer hexagonal (6H) structure in the quenched products after synthesizing at 1 and 3 GPa, respectively, and a mixture of 3C cubic phase and 6H phase was obtained in the quenched products which was synthesized above 12 GPa [7]. In the quenched products treated at 18 GPa, the 3C cubic phase of BaRuO<sub>3</sub> was obtained [11]. BaIrO<sub>3</sub>, adopting a monoclinically distorted 9R structure as it is synthesized at ambient pressure, shows a similar series of phase transitions in the quenched products after heat treatments under high pressure, a five-layer hexagonal (5H) structure at approximately 4 GPa and a 6H structure at 5 GPa [12]. Instead of the expected cubic perovskite, BaIrO<sub>3</sub> adopts a lower symmetry tetragonal I4/mcm structure in the quenched product after high-pressure and high-temperature treatment at 25 GPa [13]. Recently, the 3C phase BaOsO<sub>3</sub> has also been reported in the products of treating 6H BaOsO<sub>3</sub> at 17 GPa [14].

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FIG. 1. Unit cells of (a) 10c2h 12H, (b) 6c6h 12H, (c) 12R, (d) 9R, (e) 6H, (f) 4H BaPtO<sub>3</sub> polytypes, and (g) the cubic 3C BaPtO<sub>3</sub> phase.

The polytypes have different ratios of corner-sharing stacking (c) and face-sharing stacking (h) octahedra along the caxis, such as chhchhchh in 9R, chch in 4H, chchc in 5H, and cchcch in 6H. Pressure favors the structures in the quenched products with a higher ratio of corner-sharing stacking in the structure. Therefore, a series of phase transitions, changing from 1:2 in the 9R structure, to 1:1 in the 4H structure, to 3:2 in the 5H structure, to 2:1 in the 6H structure, and eventually to  $\infty$  in the 3C structure, would take place as treatment pressure increases. The structural models of polytypes and cubic perovskite are displayed in Fig. 1. It is worth noting that the crystal structure of a given ABO<sub>3</sub> oxide is not solely determined by t. Other factors, such as the local preferred coordination and Coulomb interactions between ions, must be considered. For example, some RMnO<sub>3</sub> and RGaO<sub>3</sub> (R = rare earths) compounds adopt the hexagonal phase despite their t being in the range suitable for the *Pbnm* perovskite structure (t < 1) [15,16]. Some A<sup>+</sup>B<sup>5+</sup>O<sub>3</sub> compounds with  $t \approx 1$  crystalize in the  $Fd\overline{3}m$  (No. 227) KSbO<sub>3</sub> structure [17] due to a strong Coulomb interaction between  $B^{5+}$  ions [18].

In comparison with other ABO<sub>3</sub> transition metal oxides, the APtO<sub>3</sub> (A = Ca, Sr, Ba) family presents peculiar crystal chemistry. For instance, the tolerance factor t = 0.9568 for CaPtO<sub>3</sub> calculated using the program SPuDS [19] suggests the orthorhombic perovskite structure. Instead, a CaIrO<sub>3</sub>-type post-perovskite structure was reported in the products of high-pressure synthesis [20,21]. The synthesis of CaPtO<sub>3</sub> at ambient pressure resulted in a mixture of CaPt<sub>2</sub>O<sub>4</sub>, Ca<sub>4</sub>PtO<sub>6</sub>, and Pt [20]. A tolerance factor t of 0.9917 for SrPtO<sub>3</sub> suggests the cubic perovskite structure. Attempts to obtain the perovskite SrPtO<sub>3</sub> at ambient pressure resulted in Sr<sub>4</sub>PtO<sub>6</sub> with an  $R\overline{3}m$  (No. 166) structure [22]. The synthesis under high pressure has not been reported. As for the BaPtO<sub>3</sub>, hexagonal polytypes are expected from the tolerance factor t = 1.0511 > 1. A hexagonal BaPtO<sub>3</sub> phase was synthesized by Gallagher *et al.* [23]. So far, no investigation about treating BaPtO<sub>3</sub> polytypes under high pressure has been reported.

In this work, we employed both theoretical and experimental approaches for a thorough investigation of the crystal chemistry of BaPtO<sub>3</sub> and the phase transitions with the treatment under high pressure and high temperature as well as the *in situ* structural determination. In addition, the structural stability has been evaluated by first-principles calculations in terms of enthalpy, tolerance factor, and density at different pressures.

#### **II. EXPERIMENTS AND RESULTS**

The hexagonal polytype phase of BaPtO<sub>3</sub> was synthesized using the precursor approach, as reported in Ref. [23]. Aqueous solutions of Na<sub>2</sub>Pt(OH)<sub>2</sub> (Sigma-Aldrich, 51.2%–62.5% Pt) and BaCl<sub>2</sub> 2H<sub>2</sub>O (99.6%, J.T.Baker) were mixed in the mole ratio of 1:1 to obtain the BaPt(OH)<sub>6</sub> yellow precipitate. The precipitate was decomposed at 823 K for 12 h to form BaPtO<sub>3</sub>. X-ray diffraction (XRD) patterns of the resulting brown powder were collected with Cu-K $\alpha$  radiation in a Rigaku Miniflex 600 X-ray Diffractometer. As depicted in Fig. 2(a), the XRD pattern matches well with the BaPtO<sub>3</sub> pattern reported in Ref. [23], in which the authors indexed the diffraction peaks with a hexagonal unit cell of a = 5.64 Å and



FIG. 2. (a) Representative XRD pattern of the obtained hexagonal BaPtO<sub>3</sub> phase, collected with Cu-K $\alpha$  radiation, and the diffraction peaks calculated from the hexagonal cell from Ref. [23]. (b) The simulated XRD patterns of several structural models of polytypes and the observed XRD pattern of the hexagonal BaPtO<sub>3</sub> phase.

c = 27.44 Å. There are three 12-layer hexagonal polytypes reported previously [24–29] as shown in Figs. 1(a)–1(c). The simulated patterns based on the polytypes of three 12-layered polytypes as well as the 9R, 4H,and 6H phases appear not to match the XRD pattern observed, as shown in Fig. 2(b). Since the XRD pattern of the synthesized BaPtO<sub>3</sub> can be indexed by a hexagonal cell with the *c* axis consistent with other 12-layer polytypes, we assign the BaPtO<sub>3</sub> as a hexagonal 12-layer polytype.

#### A. High-pressure synthesis with a multianvil apparatus

High-pressure high-temperature (HPHT) treatments on the hexagonal BaPtO<sub>3</sub> were performed using a Walker-type multianvil apparatus. The hexagonal BaPtO<sub>3</sub> powder was loaded and sealed into a Pt capsule, which also served as the heater. Several HPHT treatments were conducted at pressures of 10–20 GPa, and the samples were heated at temperatures of 873–1473 K for 10 min. In the case of a phase transition, rather than a solid-state reaction, a 10-min dwelling time is normally sufficient. The samples were quenched to room temperature to preserve the high-pressure phases. The obtained samples were pulverized for powder XRD measurements using Cu-K $\alpha$  radiation in the Rigaku Miniflex 600 X-ray Diffractometer.



FIG. 3. Representative XRD patterns of BaPtO<sub>3</sub> sample obtained after HPHT treatments in the multianvil apparatus. (a) The hexagonal phase as a product after a 873 K heat treatment at 10 GPa. (b) C2/c (No. 15) BaPtO<sub>3</sub> phase after a 1273 K heat treatment at 14 GPa. (c) The pattern of the product after a 1273 K heat treatment at 20 GPa, in which some broad peaks could be indexed to a  $Pm\overline{3}m$  cubic perovskite phase.

The XRD patterns of products from the HPHT treatments are displayed in Fig. 3. The hexagonal phase of BaPtO<sub>3</sub> remained stable at 10 GPa with a heat treatment of 873 K. However, at higher temperatures, the hexagonal BaPtO<sub>3</sub> decomposed into Pt metal and some complex Ba-Pt-O compounds, such as Ba<sub>3</sub>Pt<sub>2</sub>O<sub>7</sub>. Some peaks belonging to the C2/c (No. 15) phase can be identified at 14 GPa after a heat treatment above 1273 K. Using the C2/c model, the refinement of the XRD pattern shown in Fig. 3(b) yielded lattice parameters of a = 5.7860 Å, b = 9.9591 Å, c = 14.4652 Å, and  $\beta = 92.0265^{\circ}$ . The C2/c structure, denoted as 6M, is a monoclinically distorted variant of the 6H structure, similar to the case of  $BaIrO_3$  [12]. The treatments at pressures above 20 GPa and a heating temperature of 1273 K resulted in a nearly amorphous phase, and some broad peaks could be indexed by the 3C phase of BaPtO<sub>3</sub> with a = 4.0712 Å as shown in Fig. 3(c). The HPHT treatment results reveal a structural transformation from hexagonal to 6H above 14 GPa, and a trace of the 3C phase at pressures above 20 GPa.



FIG. 4. (a) Schematic illustration of the laser-heated DAC setup. (b) The optical image of the sample loaded in the DAC, and spots S1–S12 for the *in situ* structural study. The sample had a dimension of approximately  $130 \times 120 \times 20 \,\mu\text{m}^3$ , with an approximately  $10 \,\mu\text{m}$  thick KCl layer on both sides of the sample. The laser spot measured about  $20 \,\mu\text{m}$  in diameter.

#### B. In situ structural study with a diamond anvil cell

The in situ study of phase transitions in a broader range of pressure and temperature was conducted in a DAC using the online double-sided laser heating system and in situ XRD measurements at the beamline 13ID-D GSECARS of the Advanced Photon Source (APS), Argonne National Laboratory (ANL). In the in situ XRD measurements using an X-ray beam  $(\lambda = 0.3344 \text{ Å})$ , an area detector (Dectris Pilatus 1MCdTe) was used to collect two-dimensional diffraction images, and the position and orientation of the detector was calibrated using a LaB<sub>6</sub> NIST standard. As shown in Fig. 4, a DAC equipped with 300 µm culet anvils was used for the study. A Re gasket with an initial thickness of 260 µm was preindented to approximately 40 µm thick and a hole with a diameter of 190 µm was drilled in the central area of the preindented area to serve as a sample chamber. The hexagonal BaPtO<sub>3</sub> phase and the pressure manometer KCl were dried at 473 K in vacuum overnight before loading into the DAC. The starting powder was pressed into a pellet with a dimension of about  $130 \times 120 \,\mu\text{m}^2$  in the lateral direction and 20  $\mu\text{m}$  in thickness and sandwiched between two KCl pellets of around 10 µm thickness, resulting in an approximately 40 um thick sample assembly loaded in the sample chamber. The KCl layers also serve as the thermal insulator [30]. No significant changes were observed in the KCl peaks between laser heated and unheated areas during the experiments, indicating no signs of reactions between KCl and BaPtO<sub>3</sub> under the pressures and temperatures used in this study. The sample pressure was determined by the equation of state of KCl given by Dewaele, et al. [31] at room temperature (T = 300 K).

The experimental configuration is shown in Fig. 4(a); a small area of the loaded sample in the DAC can be subjected to a high temperature with a pair of 1064 nm laser beams focused on a spot of a 20  $\mu$ m diameter on both sides of the sample. The relatively smaller laser spot size in comparison with the sample size loaded in the DAC allows for the laser heating treatments that can be carried out on the pristine starting area

within the same pellet at different pressures. At each spot selected for testing the effect caused by the HPHT treatment, a monochromatic x-ray beam was focused onto a  $2 \times 3.5 \,\mu\text{m}^2$  area within the laser heating spot. As shown in Fig. 4(b), a total of 12 spots, labeled S1 to S12 in the order of increasing pressure, were investigated. The sample pressure for each spot is listed in Table I. XRD patterns taken before turning on laser heating indicate that the hexagonal phase remains stable up to 70 GPa at room temperature as shown in Fig. 5(a). Although it is difficult to refine a full pattern of the hexagonal BaPtO<sub>3</sub> phase, the lattice parameters as shown in Table II can be determined using the indexed (1 1 0) and (1 0 12) peaks.

Synchrotron XRD patterns were collected *in situ* at different temperatures ranging from  $\sim$ 800 to  $\sim$ 2200 K and at different time intervals at a given temperature to monitor the structure of the sample. The laser was applied for about 10–15 min until no discernible change was seen in the XRD pattern. Once a new phase appeared, we slightly moved the sample stage by approximately 2 µm in horizontal and vertical

TABLE I. Sample pressure P and laser heating temperature T range for spots S1–S12.

Spot	P (GPa)	<i>T</i> (K)
S1	$9.18\pm0.02$	1468
S2	$18.87\pm0.15$	836-955
S3	$26.55\pm0.05$	908-1072
S4	$34.73 \pm 0.06$	1008-1278
S5	$39.62 \pm 0.27$	1068-1305
S6	$43.08 \pm 0.22$	994-1303
S7	$49.44 \pm 0.20$	1059-1362
S8	$55.46 \pm 0.21$	1003-1405
S9	$57.94 \pm 0.23$	1014-1404
S10	$60.97 \pm 0.26$	923-1473
S11	$66.10 \pm 0.28$	837-1707
S12	$69.83 \pm 0.26$	907-2246



FIG. 5. Synchrotron XRD patterns of (a) the hexagonal 12-layer polytype phase under different pressure before laser heating and (b) the quenched phase after laser heating at room temperature at the spots S1–S12 at different pressures. The peaks for hexagonal BaPtO<sub>3</sub> (dot), 4H or 6H BaPtO<sub>3</sub> (triangle), 3C BaPtO<sub>3</sub> (dotted circle), KCl (star), and unknown impurities (cross) are labeled at the initial pressure, lower intermediate pressures, and the highest pressure to show the evolution of the peak positions. The peaks of metal Pt in (a) and peaks indexed with (1 1 0) and (1 0 12) of the hexagonal lattice in panel (b) are indicated by arrows. In panel (b), the pattern in black was taken at 18.87 GPa at the spot S1, which was heated at 9.18 GPa. The pattern in gray dotted line shows the hexagonal phase at the spot S1 before heating as a reference. (c) A pressure–temperature phase diagram by summarizing the structural information of the *in situ* structural study at S1 to S12.

directions to ensure thorough heating of the sample at each spot from S1 to S12. Thermal radiation spectra were collected and fitted using the Planck radiation function to determine the temperature during the heating from both sides of the sample. The temperature difference between the two sides varied from 20 to 100 K, and the sample temperature was taken as the average of the readings from both sides. Table I shows the temperature and pressure for each spot on the sample pellet. The Pb beam stopper behind the laser mirrors blocked the low-angle diffractions for all the *in situ* XRD patterns. The XRD patterns over a full range of  $2\theta$  for all the quenched phases at different pressures shown in Fig. 5(b) were measured with a 10-s exposure after the mirrors were removed from the pathway of x-ray diffraction.

Heating the sample to 1468 K at the initial pressure of 9.18 GPa resulted in the decomposition of the hexagonal

TABLE II. Lattice parameters of the hexagonal  $BaPtO_3$  phase determined by the (1 1 0) and (1 0 12) peak positions in the patterns collected at room temperature.

P (GPa)	<i>a</i> (Å)	<i>c</i> (Å)
$9.18 \pm 0.02$	$5.5422 \pm 0.0010$	$29.2427 \pm 0.0100$
$18.87\pm0.15$	$5.3534 \pm 0.0006$	$28.7683 \pm 0.0163$
$26.55\pm0.05$	$5.3066 \pm 0.0006$	$28.4503 \pm 0.0094$
$34.73\pm0.06$	$5.2562 \pm 0.0012$	$28.1530 \pm 0.0068$
$43.08 \pm 0.22$	$5.1740 \pm 0.0006$	$27.7283 \pm 0.0145$
$49.44 \pm 0.20$	$5.1416 \pm 0.0008$	$27.5848 \pm 0.0063$
$55.46 \pm 0.21$	$5.1312 \pm 0.0006$	$27.4714 \pm 0.0077$
$57.94 \pm 0.23$	$5.1348 \pm 0.0012$	$27.2704 \pm 0.0068$
$60.97 \pm 0.26$	$5.2080 \pm 0.0024$	$26.9652 \pm 0.0131$
$66.10 \pm 0.28$	$5.0754 \pm 0.0006$	$27.2638 \pm 0.0111$
$69.83 \pm 0.26$	$5.0568 \pm 0.0006$	$27.1519 \pm 0.0094$

sistent with the observation in the quenched products from the multianvil experiments. At 18-35 GPa, a mixture of possible 3C, 4H, and 6H phases with remaining starting hexagonal phase was observed; the peak intensity of the 3C phase increases relative to those of 4H and 6H phases as the pressure increases. Above approximately 40 GPa, the 3C phase was found to dominate. The results of the in situ HPHT XRD study and the phases quenched to room temperature at different pressures as shown in Appendix C are summarized in the P-Tphase diagram of Fig. 5(c). The 4H and 6H phases are stable below 40 GPa to 1300 K. The perovskite phase (Pv) appears at P > 40 GPa and as low as 800 K. The phase percentage of Pv phase increases as temperature increases; the Pv phase dominates above 1200 K. The Pv phase can be quenched to room temperature under pressure. At P > 65 GPa, shoulders at peaks (110), (200), and (211) of the cubic phase and extra peaks appear at temperatures above  $T^*$  ( $T^* > 1630$  K at P =66.10 GPa and  $T^* > 1700$  K at P = 69.83 GPa). The same diffraction pattern remains as the sample is guenched to room temperature while the pressure is retained. Attempts to fit the pattern with a single phase of perovskite structure failed. However, the fitting quality on the peaks from the original cubic phase and the Pt:Ba ratio from the fitting do not show significant changes for the patterns collected as temperature is raised across  $T^*$ , as shown in Appendix C. The extra peaks and shoulders appear to result from the partial decomposition during recrystallization on crossing  $T^*$ .

phase into metal Pt and other unknown phases, which is con-

The quality of the patterns obtained at P < 40 GPa was not sufficient for a sound refinement. For patterns above 40 GPa, the Rietveld refinements using the structural models of 3C BaPtO<sub>3</sub> and B2 KCl were performed using the program FULLPROF [32]. A refinement result for the phase at 58 GPa which is typical for phase at P > 40 GPa and quenched to



FIG. 6. Rietveld refinement result of the synchrotron XRD pattern collected at the spot S9 at 57.94 GPa at room temperature after laser heating. The unidentified peaks near 8°,  $11.5^{\circ}$ , and  $13.5^{\circ}$ , as labeled in the figure, were from the unknown impurities in the as-made hexagonal BaPtO<sub>3</sub> phase which remained unchanged during the laser heating under different pressures.

room temperature is shown in Fig. 6. It should be noted that the refinement on the diffraction patterns under high pressure, along with some unknown peaks, especially those patterns with extra peaks and shoulders appearing at  $T > T^*$  and at P > 65 GPa, has a relatively high  $\chi^2$  value as shown in Appendix C. Nonetheless, the lattice parameters for 3C BaPtO<sub>3</sub> and B2 KCl are still highly reliable. The lattice parameters for these two phases at different pressures are listed in Table III.

#### C. First-principles Calculations on BaPtO<sub>3</sub>

Geometry optimizations for various BaPtO<sub>3</sub> phases at 0 K from 1 atm to 100 GPa with 5 GPa increments were performed by using density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP) version 5.4.1 [33,34], with the gradient-corrected exchange and correlation functional of Perdew-Burke-Ernzerhof (PBE) revised for solids (PBEsol) [35]. The PBEsol functional yielded lattice volumes that were in excellent agreement with the experimental results for the cubic  $Pm\overline{3}m$  (No. 221) BaPtO<sub>3</sub> phase within the pressure range of 40-65 GPa, with the difference smaller than 0.7% [see Fig. 11(a)]. In contrast, the Perdew-Burke-Ernzerhof (PBE) functional predicted lattice volumes that were 2-3% larger than the experimental results. The projector augmented wave (PAW) method [36] was applied, and the valence electron configurations Ba  $5s^25p^66s^2$ , Pt  $5p^66s^15d^9$ , and O  $2s^22p^4$  were treated explicitly. The plane-wave basis set energy cutoff was 1000 eV. The k-point meshes were gen-

TABLE III. Lattice parameters of 3C BaPtO<sub>3</sub> and B2 KCl obtained from the Rietveld refinements.

P (GPa)	a <sub>BaPtO3</sub> (Å)	$a_{\rm KCl}$ (Å)
$39.62 \pm 0.27$	$3.84130 \pm 0.00143$	$3.17382 \pm 0.00115$
$43.08 \pm 0.22$	$3.83514 \pm 0.00158$	$3.15367 \pm 0.00124$
$49.44 \pm 0.20$	$3.81386 \pm 0.00129$	$3.12008 \pm 0.00101$
$55.46 \pm 0.21$	$3.80154 \pm 0.00114$	$3.09161 \pm 0.00094$
$57.94 \pm 0.23$	$3.78658 \pm 0.00088$	$3.08069 \pm 0.00100$
$60.97 \pm 0.26$	$3.77637 \pm 0.00107$	$3.06786 \pm 0.00109$
$66.10 \pm 0.28$	$3.76777 \pm 0.00127$	$3.04744 \pm 0.00109$
$69.83 \pm 0.26$	$3.75365 \pm 0.00194$	$3.03344 \pm 0.00166$

TABLE IV. Calculated bulk modulus (*B*), shear modulus (*G*), and Vickers hardness ( $H_V$ ) using the Teter model of the cubic BaPtO<sub>3</sub> perovskite under pressure (*P*).

P (GPa)	B (GPa)	G (GPa)	H <sub>V</sub> (GPa)
0	159.10	74.42	11.2
5	160.00	75.17	11.4
10	165.34	77.58	11.7
15	168.05	79.94	12.1
20	171.26	81.85	12.4
25	171.57	82.34	12.4
30	172.33	82.26	12.4
35	173.02	84.02	12.7
40	174.81	83.88	12.7
45	177.46	83.94	12.7
50	181.37	85.03	12.8
55	181.91	85.24	12.9
60	182.16	89.07	13.4
65	182.30	90.91	13.7
70	183.00	91.41	13.8
75	184.76	91.55	13.8
80	185.33	91.73	13.9
85	185.75	92.03	13.9
90	185.99	92.48	14.0
95	187.15	93.07	14.0
100	187.15	94.04	14.2

erated through the  $\Gamma$ -centered Monkhorst-Pack scheme while the number of divisions along each reciprocal lattice vector was selected so that the product of this number with the real lattice constant was 55 Å.

Phonon calculations were carried out through a supercell approach [37,38] using the VASP package coupled to the PHONOPY code [39], and the Pm3m structure was found to be dynamically unstable at 0 K as shown in Fig. 7(a). The dynamically stable structural models were obtained from molecular dynamics (MD) simulations based on a constant number (N), constant-volume (V), and constant-temperature (T) (NVT) ensemble for  $Pm\overline{3}m$  BaPtO<sub>3</sub> supercells at 300 K and 60 GPa, with temperature and volume controlled via a Nose-Hoover thermostat [40-43]. The thermal phonons at 300 K and 60 GPa of the  $Pm\overline{3}m$  phase could not be computed, since the structure decomposed into a larger cubic cell with P1 space group in MD simulations performed on  $2 \times 2 \times 2$ or  $3 \times 3 \times 3$  supercells as shown in Appendix E. The *Pbnm* structure was obtained from the geometry optimizations of the P1 structure at 60 GPa, and then further optimized from 0 to 100 GPa. Phonon calculations were performed on the Pbnm structure as shown in Fig. 7(b). The phonon soft modes of the  $Pm\overline{3}m$  structure were modulated with displacements along the corresponding eigenvectors at high symmetry q points  $(\Gamma \text{ or } R)$  to search for lower energy structures, which were subsequently optimized and whose phonons were calculated. As shown in Fig. 7(c) and Appendix E, only the  $Pca2_1$  structure is dynamically stable, with its enthalpy 5 meV/atom higher than the *Pbnm* structure (see Table V). Additionally, the Gibbs Free Energy of these phases were estimated using the harmonic approximation and neglecting the imaginary phonon modes at 300 K and 60 GPa, and the Pbnm structure



FIG. 7. Phonon band structure and density of states (DOS) of BaPtO<sub>3</sub> with (a)  $Pm\overline{3}m$ , (b) Pbnm, (c)  $Pca2_1$ , and (d)  $P2_1/m$  space group at 60 GPa.

was found to be thermodynamically preferred as shown in Table V.

Crystal structure prediction (CSP) searches were performed using the open-source evolutionary algorithm (EA) XTALOPT [44–46] version 12 [47] with the BaPtO<sub>3</sub> stoichiometry at 60 GPa using 1-6 formula units in the simulation cell. The initial structures were generated by the RANDSPG algorithm [48] with both *Pbnm* and  $Pm\overline{3}m$  as seeded structures. The minimum interatomic distance between Ba-Ba, Ba-Pt, Ba-O, Pt-Pt, Pt-O, and O-O atoms were constrained to 2.53, 2.15, 1.51, 1.77, 1.13, and 0.48 Å using a uniform scaling factor of 0.5 multiplied by tabulated covalent radii. Duplicate structures were identified via the XTALCOMP algorithm [49] and discarded from the breeding pool. The plane-wave basis set energy cutoff was 520 eV. The crossover evolutionary operator was not considered, but the stripple and permustrain

TABLE V. Enthalpy of various BaPtO<sub>3</sub> phases, which were found via phonon modulations at 0 K and 60 GPa and the enthalpy ( $\Delta H$ ) or Gibbs Free Energy ( $\Delta G$ ) difference of various phases at 60 GPa with respect to *Phnm* BaPtO<sub>3</sub> at 0 and 300 K. The thermal effects were not computed for the *P*1 phase due to the high computational cost. The cutoff frequency is set to zero in Phonopy for thermal effects.

Space group	H (eV/atom) T = 0  K	$\Delta H/\Delta G$ with respect to	$\Delta H/\Delta G$ with respect to <i>Pbnm</i> (meV/atom)	
		T = 0  K	T = 300  K	
Initial model				
$Pm\overline{3}m$	-1.903	46.0	28.1	
Mode modulation				
R3m	-1.923	25.8	19.2	
Amm2	-1.926	22.5	40.0	
P4/mmm	-1.915	34.1	25.7	
I4/mcm	-1.936	12.8	5.6	
Fmm2	-1.928	21.4	15.5	
Pbcn	-1.944	5.2	2.7	
$Pca2_1$	-1.944	5.1	3.1	
MD simulation				
Pbnm	-1.949	0.0	0.0	
<i>P</i> 1	-1.898	50.5	_	



FIG. 8. Structure analysis on the 12R BaPtO<sub>3</sub> polytype structure calculated by DFT using PBEsol. (a) The bonding structure in the 12R phase. (b) The Ba–O bond lengths versus pressure. (c) The Pt–O bond lengths versus pressure. (d) The geometric tolerance factor t calculated with average bond lengths of Ba–O and Pt–O bonds versus pressure.

operators were increased to 50 percent. The number of exchanges for permustrain was set to zero, so that effectively this operation only strained the structure. A dynamically stable  $P2_1/m$  structure was found as shown in Fig. 7(d).

The first-principles calculation results are used to discuss the bulk modulus of  $Pm\overline{3}m$  BaPtO<sub>3</sub>, the high-pressure sequence of BaPtO<sub>3</sub> hexagonal polytypes, and the critical pressure to stabilize the perovskite phase in the following sections. The outputs of the DFT calculations were uploaded to the NOMAD database [50]; the calculated structures were deposited to the CCDC database [51].

## **III. DISCUSSIONS**

### A. Crystal chemistry of ABO<sub>3</sub> oxides and its response to high pressure

The studies of BaMO<sub>3</sub> (M = Ru, Ir, Os) under high pressure in the literature, discussed in Sec. I, provide information on the phases at particular locations in the P-Tphase diagram, which are quenchable to ambient pressure. The reason why the polytypes become unstable under high pressure and the essential parameters that trigger the phase transition to the perovskite structure remain unknown. In the ABO<sub>3</sub> polytypes, layered structures of face-sharing octahedra and corner-sharing octahedra, which are stacking along the c axis, are developed to accommodate a larger A–O bond length, which makes t > 1. Taking the 12R BaPtO<sub>3</sub> structure illustrated in Figs. 1(c) and 8(a) as an example, the simulated structure parameters as a function of pressure show a much steeper pressure dependence of the averaged Ba–O bond length than that of Pt–O in the pressure range of 0–65 GPa, as shown in Fig. 8(d). The bond length changes lead to a crossover of t factor from t > 1 to t < 1 at a critical pressure  $P_c \approx 35$  GPa. Although the quality of the synchrotron diffraction data is not good enough for a sound refinement, the lattice parameters behave similar to the simulated 12R phase as a function of pressure, as indicated in Fig. 9(a).

The enthalpy of the polytypes of BaPtO<sub>3</sub> and the 3C BaPtO<sub>3</sub> structure as a function of pressure are shown in Fig. 10. The 3C refers to the cubic perovskite structure in the  $Pm\overline{3}m$  space group. The 6H and 4H polytype models in the  $P6_3/mmc$  (No. 194) space group have a *cchcch* and *chch* stacking [Figs. 1(e) and 1(f)], respectively. The 12R and 9R polytype models adopt an  $R\overline{3}m$  structure with a *hcchhchcchhc* (6h6c) and *hchhchhch* stacking [Figs. 1(c) and 1(d)], respectively. Two 12H polytype models are proposed in the  $P6_3/mmc$  space group with different stackings: *ccchccccchcc* (10*c*2*h*) and *cchhhccchhc* (6*c*6*h*) [Figs. 1(a) and 1(b)]. For a



FIG. 9. (a) Pressure dependence of lattice parameters of the hexagonal BaPtO<sub>3</sub> phase and simulated 12R and 6*c*6*h* 12H structures. (b) The density of the observed BaPtO<sub>3</sub> perovskite (Pv) phase and simulated 3C ( $Pm\overline{3}m$ ), *Pbnm*, 12R, and 6*c*6*h* 12H structures as a function of pressure.





better comparison, the calculated enthalpy for the 3C structure model is used as a reference, and the relative enthalpies of other polytype models are shown in Fig. 10. It should be noted that other structures with even lower enthalpy appeared during the structure optimization using the first-principles calculations as shown in Appendix F. For example, a  $Cmc2_1$  (No. 36) structure appeared with a lower enthalpy than  $P6_3/mmc$ in the whole pressure range during the optimization of the 4H BaPtO<sub>3</sub> structure. However, the orthorhombic  $Cmc2_1$  structure is neither a hexagonal polytype for ABO<sub>3</sub> with t > 1 nor a tilting system that the ABO<sub>3</sub> perovskites with t < 1 can adopt [5]. Therefore, considering BaPtO<sub>3</sub> has a t = 1.0511 > 1 and adopts the hexagonal structure at ambient pressure, we restrict the data to the hexagonal polytypes and the 3C structure for a clear understanding on the high-pressure sequence of BaPtO<sub>3</sub> polytypes and the  $P_c$  for converting the polytypes to the 3C phase in BaPtO<sub>3</sub>. The phases with lower enthalpy can potentially be obtained using an appropriate synthesis route to overcome energy barriers.

Based on the stacking sequence in the polytypes, it is expected that the the 10c2h 12H model will be stabilized at a higher pressure than the 4c2h 6H phase in the highpressure sequence of polytypes, as it has a higher ratio of corner-sharing stacking (5:1). Consistent with this expectation, the simulated results show that the relative enthalpy of the 10c2h 12H model is the highest among the investigated hexagonal polytypes at ambient and low pressures. The 6c6h 12H model and the 12R (6h6c) model have the same 1:1 ratio, which should be less stable than the 9R model with a 1:2 ratio at ambient pressure. However, the 12R structure is likely to be more stable as the block of face-sharing octahedra (h) is shorter in the 12R structure. A shorter block of face-sharing octahedra reduces the expense of electrostatic Madelung energy during the formation of hexagonal stacking [6]. The DFT results show the 12R model is more stable than the 6c6h 12H model throughout the whole pressure range considered. Although the simulated patterns of the 9R, 12R, and 12H models do not match well the XRD pattern of BaPtO<sub>3</sub>, it is reasonable to assume that the hexagonal polytype of BaPtO3 should behave the same as the 9R, or 6c6h 12H, or 12R phase under high pressure. At ambient pressure, the 9R model, 6c6h 12H model, and 12R model are more stable than the 4H and 6H models according to DFT calculations. Notably, the 3C structure model only becomes more stable above approximately 46 GPa compared to the 12R polytype model and above 55 GPa compared to the 10c2h 12H polytype model.

Although there are crosses in the enthalpy versus pressure curves between two polytypes or between polytypes and the 3C phase, the transition to the phase having a lower enthalpy only takes place after the laser heating is applied to overcome the energy barrier for restructuring. The starting material of BaPtO<sub>3</sub> with a 12-layer polytype structure remains stable at room temperature up to 67 GPa, the highest pressure in our experiment. Below 35 GPa, both the 4H and the 6H polytype models have a lower enthalpy than the 3C structure model, and the 6H polytype model is more stable than the 4H model above approximately 8 GPa. The 6H model has the lowest enthalpy among the 9R, 4H, 6H, 6*c*6*h* 12H, and 3C models between 18 to 35 GPa. The DFT calculation results are consistent with the observations that peaks from 4H, 6H and 3C phases are observed in the synchrotron XRD patterns in Fig. 5(b) between 18–35 GPa in the *in situ* structural study with DAC and laser heating, and the monoclinically distorted 6H phase is found in the multianvil HPHT treatment at 14 GPa. Peaks from the 6H phase disappear and peaks from the 3C structure phase dominate in the patterns for pressures above 40 GPa after laser heating, which is close to the  $P_c \approx 35$  GPa from the DFT calculations.

In addition, the pressure induced phase transition from the polytypes to the 3C phase can be rationalized by the density consideration. High pressure prefers the phase with a higher density. Figure 9(b) shows the density as a function of pressure a variety of structures. The perovskite structure, either with a cubic symmetry or orthorhombic symmetry has a higher density than that of polytype phases. More importantly, the density of perovskite phase from experiment matches the results of DFT calculations reasonably well.

The post-perovskite CaPtO<sub>3</sub> phase stabilized at high pressures may provide a useful clue to understand a much higher  $P_{\rm c}$  for converting the polytypes to the 3C phase in BaPtO<sub>3</sub>. The post-perovskite has a layered structure. PtO<sub>6</sub> octahedra share the corners along the c axis with a significant buckling angle, and share the edges along the a-axis. The coupling between layers along the b axis is much weaker compared to those along the a and c axes. This structural feature reflects that Pt<sup>4+</sup> favors a structure with relatively short Pt-Pt distances along a crystallographic axis. The distances are 3.126 Å between the edge-sharing octahedra and 3.675 Å between the corner-sharing octahedra in the post-perovskite CaPtO<sub>3</sub> [21], which are shorter than the approximately 3.95 Ådistance along one direction in the network formed by cornersharing PtO<sub>6</sub> octahedra in a hypothetical cubic perovskite CaPtO<sub>3</sub>. BaPtO<sub>3</sub> polytype structures consist of different ratios of corner-sharing layers and face-sharing layers, and a shorter Pt-Pt distance can be found along the direction of the facesharing octahedra. For example, in the proposed 6H BaPtO<sub>3</sub> structure, the Pt-Pt distance between corner-sharing octahedra is 4.01 Å, while it is only 2.78 Å between face-sharing octahedra. The hexagonal polytype structure, which presumably has a high percentage of face-sharing layer in polytypes, is reminiscent of the preferred local structure with a short Pt-Pt distance found in the post-perovskite structure. In comparison, Ru<sup>4+</sup> does not show any preference for such a local structure. The 3C phase CaRuO<sub>3</sub> and SrRuO<sub>3</sub> can be formed at ambient pressure.  $P_c$  for converting the 9R to 3C phase in BaRuO<sub>3</sub> is as low as 12 GPa although its t is the largest among  $BaMO_3$ compounds that are considered. Therefore, in addition to reduce the t factor to 1, the pressure effect is also to overcome the resistance from the preferred local structure in platinum oxides, resulting in a higher  $P_c$ .

#### **B.** Bulk modulus

To obtain the bulk modulus of 3C BaPtO<sub>3</sub>, the volumes obtained from the refinement results at different pressures were fitted to the Birch-Murnaghan (B-M) equation of state in Eq. 2, where  $\eta = V/V_0$ ,  $B_0$  is the bulk modulus, and  $B'_0$  is the derivative of bulk modulus with respect to pressure [52]:

$$P(V) = \frac{3}{2}B_0\eta^{5/3}(\eta^{2/3} - 1)\left[1 + \frac{3}{4}(B'_0 - 4)(\eta^{2/3} - 1)\right].$$
 (2)



FIG. 11. (a) Pressure dependence of the cell volume for 3C BaPtO<sub>3</sub> and the fitting results to the B-M equation. The observed/calculated structures are shown in circles/squares and the curve in red/blue shows the corresponding B-M fitting results. (b) The bulk moduli of  $A^{2+}B^{4+}O_3$  (A = Ca, Sr, Ba, Pb; B = Ti, Zr, Pt, Si, Ge, Cr, V) with the  $Pm\overline{3}m$  (No. 221) cubic structure. The solid green circle is the DFT calculated bulk modulus of BaPtO<sub>3</sub> and the crossed green circle is the bulk modulus of BaPtO<sub>3</sub> obtained by AFLOW at ambient pressure.

The fitting result is presented in Fig. 11(a), and the bulk modulus of 3C BaPtO<sub>3</sub> is  $224 \pm 18$  GPa, which falls within the typical bulk modulus range for perovskites, using the default value of 4 for  $B'_0$ . The structures of 3C BaPtO<sub>3</sub> at different pressures ranging from 0 to 100 GPa were also calculated using DFT at 0 K. The B-M fitting result for the DFT calculated cell volume versus pressure is shown in Fig. 11(a). The bulk modulus obtained from the fitting is 188 GPa. For comparison, the bulk modulus obtained via a machine-learning model [53] trained on the materials within the AFLOW repository [54,55] was 159 GPa. Both of these are lower than the experimental result, but conform to Anderson's rule discussed below; the discrepancy between the calculated and experimental results is due to the uncertainty



FIG. 12. (a) Dynamically stable structures of BaPtO<sub>3</sub> with P1 space group. (b) The dynamically stable structures of BaPtO<sub>3</sub> with Pbnm space group. Both P1 and Pbnm structures are from molecular dynamics (MD) simulations. (c) The dynamically stable  $Pca2_1$  BaPtO<sub>3</sub> structure from phonon modulations at high symmetry q points. (d) The dynamically stable  $P2_1/m$  BaPtO<sub>3</sub> structure from crystal structure prediction (CSP) searches. (e) The synchrotron XRD pattern of BaPtO<sub>3</sub> at 60.97 GPa and the simulated XRD patterns of the P1, Pbnm, and  $Pca2_1$  structural models. The normalized intensity is in the logarithmic scale to show the minor peaks which fall into the background in linear scale as in Fig. 6.

from fitting the data in a narrow pressure range in our experiments.

Anderson and Nafe proposed an empirical relationship between the bulk modulus  $B_0$  and the specific volume  $V_0$  in the form of  $B_0 \propto 1/V_0$ , which is referred to as Anderson's rule [56]. The experimental bulk moduli for the cubic perovskite A<sup>2+</sup>B<sup>4+</sup>O<sub>3</sub>, including BaTiO<sub>3</sub> [57,58], BaZrO<sub>3</sub> [59], BaSnO<sub>3</sub> [60], SrTiO<sub>3</sub> [61], SrSiO<sub>3</sub> [62], CaSiO<sub>3</sub> [63,64], PbGeO<sub>3</sub> [65], PbCrO<sub>3</sub> [66], PbVO<sub>3</sub> [67], and BaPtO<sub>3</sub> (this work), are plotted as  $B_0$  versus  $1/V_0$  as shown in Fig. 11(b). Most of the bulk moduli fall in the gray rectangle, which is in line with Anderson's rule. However, the bulk moduli of cubic BaPtO<sub>3</sub> and BaZrO<sub>3</sub> are much higher than that predicted by Anderson's rule. It should be noted that our experimental data on BaPtO<sub>3</sub> were obtained in a narrow pressure range, which adds some uncertainty for the bulk modulus from the fit. The DFT calculated bulk modulus of the cubic BaPtO3 is close to the aforementioned gray rectangle, and the cubic BaPtO<sub>3</sub> bulk modulus obtained by AFLOW falls within the area, which agree with Anderson's rule.

## C. Structural complexity of the BaPtO<sub>3</sub> perovskite

Phonon calculations indicate that the cubic BaPtO<sub>3</sub> perovskite phase with a  $Pm\overline{3}m$  space group has several imaginary-frequency phonon branches, which implies that the cubic phase is dynamically unstable from 1 atm to 100 GPa. Moreover, the minor peaks observed in the XRD patterns shown in Fig. 12(e) are not accounted for by the cubic BaPtO<sub>3</sub> perovskite structure, indicating a more distorted structure than the 3C phase. The NVT MD simulations for a  $3 \times 3 \times 3$ supercell of 3C BaPtO<sub>3</sub> perovskite at 300 K and 60 GPa resulted in a larger cubic structure with a = 11.324 Å with P1 space group, characterized by tilted octahedra as shown in Fig. 12(a). As depicted in Fig. 12(e), the comparison between the simulated XRD pattern from the P1 structure and the experimentally obtained XRD pattern at 60.97 GPa indicates that the P1 structural model can account for some of the unknown minor peaks. Refining the XRD pattern at 60 GPa by using the P1 structural model does not lead to any meaningful outcome since the differences between the calculated and observed diffractions for small peaks are negligible compared with that for the major peaks. An MD simulation was also performed on a  $2 \times 2 \times 2$  supercell of 3C BaPtO<sub>3</sub> perovskite, and the resulting structure was optimized to the nearest stationary state. This yielded a Pbnm structure with a = 5.334 Å, b = 5.322 Å, and c = 7.562 Å as shown in Fig. 12(b). Another dynamically stable  $Pca2_1$  structure, as shown in Fig. 12(c), was obtained from phonon modulations at high symmetry q points, adopting an orthorhombic



FIG. 13. Collected thermal radiation spectra and their fits to Planck's radiation function from (a) downstream and (b) upstream directions for a 1380 K laser heating treatment (S9-150) at the heated spot S9.

lattice with a = 5.345 Å, b = 5.261 Å, and c = 7.631 Å. Like the P1 phase, the Pbnm and Pca2<sub>1</sub> structures also provide weak peaks with their positions close to the unknown weak peaks from the experiment. The CSP searches on BaPtO<sub>3</sub> provides a dynamically stable candidate with a P2<sub>1</sub>/m structure. However, the P2<sub>1</sub>/m structure is a layered structure with edge-sharing PtO<sub>6</sub> octahedra along a axis and was not further considered due to the significant difference from the cubic BaPtO<sub>3</sub> perovskite structure.

The newly found dynamically stable *Pbnm* structure was reoptimized from 1 atm to 100 GPa, and its enthalpy relative to the *Pm* $\overline{3}m$  perovskite is plotted in Fig. 10. Overall, the *Pbnm* phase has a lower enthalpy than *Pm* $\overline{3}m$  up to at least 100 GPa. Therefore, the phase transition from the polytypes to the perovskite structure appeared at a lower pressure than expected from the *Pm* $\overline{3}m$  structure. For example, the transition between the *Pbnm* and 6H phases occurs at 15 GPa, which is consistent with the experimental observation that peaks for the perovskite phase appear at a pressure as low as 18 GPa as shown in the *P*-*T* phase diagram of Fig. 5(c). In Table V, we provide the relative enthalpies of a plethora of the



FIG. 14. Progressive change of d-spacing with increasing pressure. (a) The enlarged synchrotron XRD pattern focusing on the (110) peak of the cubic BaPtO<sub>3</sub> and the adjacent unknown impurity peak. (b) The d-spacing of the two aforementioned peaks at different pressures. (c) The relative d-spacing of the two aforementioned peaks with the reference d-spacing at 39.62 GPa set to 1. Compared to the decrease in d-spacing for the cubic BaPtO<sub>3</sub> (110) peak, a slightly smoother decrease in d-spacing is observed for the unknown impurity peak.

phases considered, some obtained from phonon modulations, at 60 GPa and 0 K, as well as at 300 K within the harmonic approximation. The *Pbnm* phase is the most stable in all cases.

The *P*1 or the *Pbnm* phase with tilted octahedra suggests a t < 1 in the perovskite phase of BaPtO<sub>3</sub> stabilized under high pressure and high temperature. Since the ionic Ba–O bonds are more compressible than the relatively covalent Pt–O bonds in BaPtO<sub>3</sub> polytypes, *t* factor would reduce continuously under pressure. Taking the 12R polytype as an example, the behavior of these bond lengths under pressure in the simulated phase as computed using the PBEsol functional is shown in Fig. 8. The *t* factor crosses 1 at  $P \approx 35$  GPa, which matches well with the critical pressure from the enthalpy consideration in Fig. 10. A t < 1 at P > 40 GPa is consistent with the lower symmetry structures of either the *P*1 or the *Pbnm* phase which has tilted octahedra.

#### **IV. CONCLUSION**

The BaPtO<sub>3</sub> phase with the 3C perovskite structure was successfully synthesized in a DAC with laser heating from the hexagonal BaPtO<sub>3</sub> polytype, with an exceptionally high critical pressure  $P_c$  of about 40 GPa. The *in situ* structural study at high temperature and high pressure provides comprehensive information of the pressure effect on the crystal structure of ABO<sub>3</sub> compounds with a t > 1, completing what had been extracted before from the quenched phases at ambient condition. We argue that the unusually high  $P_c$  for converting the hexagonal phase to the 3C phase found in BaPtO<sub>3</sub> reflects that the platinum oxide prefers the structures with a short Pt–Pt distance as in the face-sharing octahedra in the polytypes. The local structural preference creates the resistance for converting the polytypes with a lower c/h ratio to



FIG. 15. Typical *in situ* XRD patterns at different temperatures and pressures at (a) P = 34.73 GPa, (b) P = 39.62 GPa, (c) P = 43.08 GPa, and (d) P = 69.83 GPa.

a higher c/h ratio. The density functional theory calculations performed on BaPtO<sub>3</sub> supports the phenomenological rules



FIG. 16. Raw images of typical *in situ* XRD patterns below and above  $T^*$  at high pressure. (a) The XRD pattern at P = 69.83 GPa and T = 1572.1 K, containing smooth diffraction rings. (b) The XRD pattern at P = 69.83 GPa and T = 2228.0 K, containing grainy diffraction rings with diffraction spot clusters. The diffraction spots at high angles are from the diamond anvils, and the dark area at low angles is blocked by the Pb beam stoppers behind the mirrors.

of (1) polytypes are preferred over the perovskite structure if the geometric tolerance factor is larger than 1 and (2) the perovskite phase can be stabilized under a sufficiently high pressure in the ABO<sub>3</sub> compounds with t > 1. Specifically, the DFT calculations predict a critical pressure  $P_c > 35$  GPa for stabilizing the perovskite phase in BaPtO<sub>3</sub>, which matches our experimental observation. The minor peaks in XRD patterns at 60 GPa, which cannot be refined with the cubic perovskite model, suggest a structure with a lower symmetry, such as the *Pbnm* perovskite. The computed phonon band structures illustrate that the *Pbnm* phase is dynamically stable, whereas the *Pm*3*m* phase is not, supporting the argument of a lower symmetry phase. Moreover, the enthalpy calculated for the lower symmetry phase of either *P*1 or *Pbnm* phase is lower than that of cubic perovskite.

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FIG. 17. (a) Seven-peak Smith-Snyder figure of merit and (b) the Pt:Ba ratios at spot S12 (P = 69.83 GPa) at different temperatures. The estimated  $T^*$  (> 1700 K) is indicated by the gray vertical bar.

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## APPENDIX A: TEMPERATURE DETERMINATIONS IN LASER-HEATED DIAMOND ANVIL CELL

In the experiments conducted in the laser-heated diamond anvil cell (DAC), the temperature was determined by collecting the thermal radiation spectra using a PI-MAX 3 Intensified CCD camera (Princeton Instruments). The spectra were then fitted to the Planck radiation function [69] in terms of the spectral energy density, which is represented by Eq. (A1):

$$u_{\lambda}(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/(\lambda k_{\rm B}T)} - 1}.$$
 (A1)

In this equation,  $u_{\lambda}(\lambda, T) = [4\pi B_{\lambda}(\lambda, T)]/c$  is the spectral energy density,  $B_{\lambda}(\lambda, T)$  is the spectral radiance of a body,  $\lambda$  is the per unit wavelength, T is the absolute temperature, h is the Planck constant,  $k_{\rm B}$  is the Boltzmann constant, and c is the speed of light in the medium. The fitting with calibrations was performed using T-Rax software [70].

In particular, during the laser heating treatment at the heated spot S9, referred to as S9-150, the temperature determination process is described below. The thermal radiation spectrum from the downstream laser direction was fitted to Eq. (A1), resulting in a downstream temperature of  $T_{ds} = 1402.94$  K. Similarly, a fitting was performed on the upstream spectrum, yielding an upstream temperature of  $T_{us} = 1356.17$  K. The sample temperature at S9 during the laser heating was determined to be the average of  $T_{ds}$  and  $T_{us}$ , resulting in  $T_{S9-150} = 1379.56$  K  $\approx 1380$  K. The corresponding thermal radiation spectra and the fitting spectra are shown in Fig. 13. Temperatures at other heated spots were determined using the same methodology.

## APPENDIX B: UNKNOWN IMPURITIES IN THE SAMPLE

The progressive shift of the (110) peak of cubic BaPtO<sub>3</sub> and the adjacent unknown impurity peak at increasing pressure, as depicted in Fig. 14(a), is examined in terms of their respective d-spacing. The dashed line in Fig. 14(a) indicates that the *d*-spacing of the unknown impurity peak undergoes a slower rate of shrinkage compared to that of the cubic BaPtO<sub>3</sub> (110) peak as pressure increases. To clearly demonstrate this trend, the relative *d*-spacing of both peaks, presented in Fig. 14(c), is calculated by using the *d*-spacing at 39.62 GPa as a reference and setting it to 1. The decrease in d-spacing of the unknown impurity is much smoother than that of the cubic BaPtO<sub>3</sub>, indicating that they are from two different phases. A straight line is drawn across the reference point at 39.62 GPa to show the decrease trend of the two phases. The trend suggests a slightly smaller bulk modulus for the unknown impurity in comparison to the bulk modulus of 224 GPa for the cubic BaPtO<sub>3</sub>. Considering the high symmetry of the unknown impurity, as indicated by the small number of peaks observed, and the relatively low purity of the starting material Na<sub>2</sub>Pt(OH)<sub>6</sub>, it is possible that the unknown impurity is a heavy metal such as Pd with a bulk modulus around 200 GPa.



FIG. 18. Rietveld refinement result for synchrotron XRD patterns above 40 GPa. (a)–(h) The Rietveld refinement results for synchrotron XRD patterns collected at S5–S12, respectively.

## APPENDIX C: *IN SITU* X-RAY DIFFRACTION PATTERNS AT DIFFERENT TEMPERATURES AND PRESSURES

The typical *in situ* x-ray diffraction (XRD) patterns at different temperatures and pressures are shown in Fig. 15. It should be noted that there is no change except for peak shift due to lattice thermal expansion between the XRD pattern at the highest temperature and the XRD pattern at room temperature after laser heating, indicating that the heat treatment product is quenchable to room temperature under pressure.

The appearance of extra peaks and shoulders above  $T^*$  is coupling with a change from smooth diffraction rings to grainier diffraction rings with diffraction spot clusters as

shown in Fig. 16. We were unable to index these extra peaks and shoulders using the structural models from the tilting systems of perovskites. To confirm whether the main phase remain 3C perovskite structure when BaPtO<sub>3</sub> is heated above  $T^*$ , we conducted cell refinements in MDI Jade to search for possible changes in peak distribution across  $T^*$ . The cell refinements are based on 7 peaks in the *Pm*3*m* structure, including (100), (110), (200), (211), (220), and (310); they were done on the *in situ* XRD patterns collected at spot S12 at P = 69.83 GPa and T = 1508.3-2245.4 K. The Smith-Snyder figure of merit [71] of the 7-peak refinement, F(7) shown in Fig. 17(a), does not show a significant change across  $T^*$  and remains above 200 ( $|\Delta 2\theta| \leq 0.005^\circ$ ). Additionally,



FIG. 19. Energy (eV/cell) versus molecular dynamics simulation time (ps) for the (a)  $2 \times 2 \times 2$  and (b)  $3 \times 3 \times 3$  supercells of  $Pm\overline{3}m$  BaPtO<sub>3</sub> and at 60 GPa and 300 K. The inserts illustrate initial structure at 0 ps and final structure at 20 ps.

the Pt:Ba ratio obtained in FULLPROF in Fig. 17(b) remains almost constant within the error margin, slightly declining as the temperature increases across  $T^*$ , which indicates loss of Pt from the structure across  $T^*$ . Therefore, the 3C perovskite structure remains, and we believe the extra peaks and shoulders are a result of partial decomposition during recrystallization on crossing  $T^*$ .

For patterns above 40 GPa, the Rietveld refinements using 3C BaPtO<sub>3</sub> and B2 KCl models were performed using FULLPROF [32]. The refinement results are shown in Fig. 18.



FIG. 20. Illustrations of phonon modulations from  $Pm\overline{3}m$  at various q points ( $\Gamma$  or R). For each modulation, at least 10–15 different displacements along the corresponding eigenvectors were performed and the resulting structure was reoptimized. Phonons were computed for modulated structures that differed from the initial geometry. The enthalpies and free energies computed at 300 K and 60 GPa within the harmonic approximation of the modulated phases with respect to *Pbnm* are provided in Table V.



FIG. 21. Relative enthalpy for BaPtO<sub>3</sub> polytypes of (a) 12R, (b) 10c2h 12H, (c) 6H and 6c6h 12H, and (d) 4H, as well as their corresponding lower-enthalpy structures. The calculated enthalpy of 3C BaPtO<sub>3</sub> is used as a reference.

The contribution from the 6H BaPtO<sub>3</sub> model was included in the refinements for the pattern collected at S5 (P = 39.62 GPa).

## APPENDIX D: FIRST-PRINCIPLES CALCULATION OF BULK MODULUS USING AFLOW

The mechanical properties of the cubic BaPtO<sub>3</sub> perovskite, including bulk modulus and shear modulus, were determined using a machine-learning model [53] trained on materials from the AFLOW repository [54,55]. The Vickers hardness was estimated with the Teter equation using the machine learning based shear modulus. The results are presented in Table IV.

# APPENDIX E: PHONON CALCULATIONS AND MOLECULAR DYNAMICS SIMULATIONS

The structure transitioned into *P*1 symmetry phases in MD simulations performed on  $2 \times 2 \times 2$  or  $3 \times 3 \times 3$  supercells as shown in Fig. 19. The phonon soft modes of the  $Pm\overline{3}m$  structure were modulated with displacements along the corresponding eigenvectors at high symmetry *q* points ( $\Gamma$  or *R*) to search for lower energy structures. For each modulation, at least 10–15 different displacements along the corresponding

eigenvectors were considered. The results shown in Fig. 20 indicate that only the  $Pca2_1$  is dynamically stable. The thermal contribution was calculated using Phonopy within the harmonic approximation for all the potential candidates found for BaPtO<sub>3</sub> via the aforementioned phonon modulations, and *Pbnm* phase remains the ground state with the lowest free energy as shown in Table V.

## APPENDIX F: ADDITIONAL STRUCTURES IN THE STRUCTURE OPTIMIZATIONS

During the structure optimization for each structure model using the first-principle calculation with VASP, additional structures with lower enthalpy were observed. The detailed structural information of the additional structures was deposited in the NOMAD databased [50] and the CCDC database [51]. These phases were computed to have lower enthalpy, as shown in Fig. 21, suggesting that they could potentially be obtained by employing suitable synthesis conditions to overcome energy barriers and meet kinetic requirements. Since many of the polytype structure models do not encompass the entire pressure range of the optimization, the enthalpy of the 3C BaPtO<sub>3</sub> model is used as a reference value.

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