

Pressure-Induced Phase Transition in PrAlO_3

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PrAlO_3 is shown to undergo a rhombohedral ($\bar{R}\bar{3}c$) to orthorhombic ($Imma$) phase transition upon application of pressures of up to 9.1 GPa. The structures in both phases have been refined from high-resolution synchrotron diffraction data. The structure initially evolves toward a higher-symmetry structure as the pressure is increased before ultimately undergoing a first-order transition to a lower-symmetry orthorhombic structure. This behavior appears to be related to the change in the tilting of the AlO_6 groups.

Introduction

The perovskites are, arguably, the most important class of metal oxides, having both technological and geological importance. Perovskite-related oxides exhibit colossal magnetoresistance, superconductivity, and ferro- and piezoelectric properties, and the perovskite phase of MgSiO_3 is the dominant species in the Earth's lower mantle.

The ideal ABO_3 perovskite structure has cubic ($Pm\bar{3}m$) symmetry, consisting of a framework of corner-sharing BO_6 octahedra with the A-type cation in each resulting cuboctahedral interstice. In the cubic structure, all of the atoms are located at special positions, and with only one variable, the lattice parameter, the archetypal perovskite structure is a very exacting one. The majority of ABO_3 perovskites are not cubic; rather, rotation or tilting of the BO_6 octahedra provides structural flexibility, and a series of distorted structures exist.¹ Tilting of the BO_6 octahedra acts to shorten the A-type ion-to-oxygen distances while preserving the length of the B-type ion-to-oxygen distances. Thus, smaller-than-optimal A-type cations can be accommodated. The most commonly observed distorted structures for the perovskites are the orthorhombic ($Pnma$) and rhombohedral ($\bar{R}\bar{3}c$) structures. Expanding upon the ideas of Glazer² and Alexandsrov,³ Howard and Stokes⁴ described the structural family for ABX_3 perovskites and, importantly, identified allowed pathways by which one structural type can transform into another.

Variable-temperature high-resolution diffraction studies have shown that, for perovskites exhibiting continu-

ous or second-order phase transitions, the tilting of the BX_6 octahedra tends toward zero as the temperature increases; that is, the symmetry of the perovskite structure increases.^{5–8} Even for discontinuous or first-order transitions, increases in temperature invariably increase the symmetry of the perovskite.^{9,11} A recent high-temperature powder neutron diffraction study of SrZrO_3 , for example, shows the sequence of phase transitions from the room-temperature orthorhombic ($Pnma$) structure to a second orthorhombic ($Imma$) structure, followed by a transition to a tetragonal ($I4/mcm$) polymorph and ultimately to the cubic aristotype.⁶ Similarly PrAlO_3 transforms from monoclinic ($C2/m$) symmetry at low temperatures to orthorhombic ($Imma$), rhombohedral ($\bar{R}\bar{3}c$) and cubic at higher temperatures.⁵ Whereas the $Imma \leftrightarrow I4/mcm$ and $Imma \leftrightarrow \bar{R}\bar{3}c$ transitions are first-order, the other transitions all involve a continuous rotation of the BO_6 octahedra.⁴

The effect of pressure on the structures of perovskites is unclear.^{12–18} It has been suggested that, similarly to

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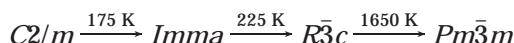
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heating, higher volumes will favor the high-symmetry structures.¹² In other words, the application of pressure should lower the symmetry of the perovskite. Alternatively, Yagi et al. predicted that the symmetry should increase as the pressure is increased.¹³ Experimental studies apparently support both hypotheses. For example, high-pressure diffraction studies of PrNiO_3 ¹⁶ and YAlO_3 ¹⁸ show a trend toward less distorted (higher-symmetry) structures as the pressure is increased, whereas the structure of MgSiO_3 shows¹⁵ a slight increase in distortion as the pressure is increased. In each of these cases, no phase transition is observed. There are also examples of conflicting experimental studies. Raman studies suggest that BaZrO_3 undergoes two phase transitions as the pressure is increased initially above 9 GPa and then above 23 GPa.¹⁹ In contrast, using XAFS, Andrault and Poirier²⁰ concluded that BaZrO_3 remains cubic up to 52 GPa. The effect of temperature on the structure of BaZrO_3 is unknown. It is clear from these very limited examples that there is considerable scope for high-resolution structural studies of perovskites as a function of pressure.

Recent high-resolution powder neutron and synchrotron diffraction studies of PrAlO_3 have shown that it undergoes three phase transitions^{5,7}



upon heating from 20 K. The first two transitions are close to room temperature and involve a measurable change in the volume. Equally importantly all of the structures are accurately known and can be distinguished by examining a small number of diagnostic Bragg reflections. Hence, any pressure-induced transition should be easy to observe and describe. In this paper, we present a high-pressure powder synchrotron X-ray study of the structure of PrAlO_3 at pressures of up to 9.1 GPa at room temperature.

Experimental Section

The polycrystalline sample of PrAlO_3 was prepared by heating Pr_4O_{11} and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as described previously.⁷ A modified Merrill–Bassett diamond-anvil cell was used for the X-ray studies in the pressure range 0.0–9.0 GPa. The powdered sample, together with a few small ruby chips, was loaded into a 200- μm hole in a steel gasket. A methanol/ethanol/water (16:3:1) mixture was used as the hydrostatic pressure-transmitting medium. The pressure was calibrated by measuring the shift of the R_1 fluorescence line of ruby before and after each run. The X-ray diffraction data were collected using synchrotron radiation at the bending magnet beamline, X7A, of the National Synchrotron Light Source at Brookhaven National Laboratory. A wavelength of 0.7054 \AA was selected using a bent Si 220 focusing crystal monochromator. At this wavelength, a small but detectable amount of $\lambda/2$, ca. 0.45%, was also observed. Data were collected using a linear position-sensitive detector mounted ca. 450 mm from the sample. Further information on the instrument configuration and data collection procedure can be found elsewhere.²¹ The program

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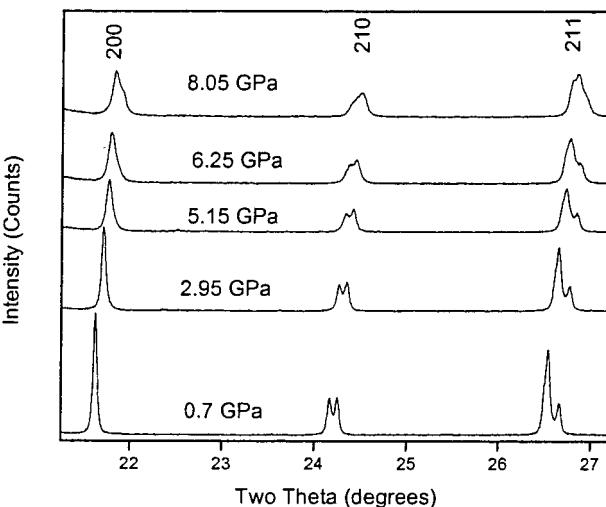


Figure 1. Variation with pressure of the synchrotron diffraction patterns for PrAlO_3 . The rhombohedral-to-orthorhombic structural transition near 7 GPa is clearly visible. The hkl indices of the cubic aristotype are shown.

RIETICA was employed to refine the crystal structures using the Rietveld method.²²

Results and Discussion

Selected areas of the synchrotron X-ray diffraction patterns collected from PrAlO_3 are shown as a function of pressure in Figure 1. There is a small increase in the broadening of the peaks with pressure, presumably because of strains associated with pressure gradients in the sample. However the nicely separated and sharp ruby doublet indicates hydrostatic pressure conditions. The X-ray diffraction patterns of PrAlO_3 measured at pressures of up to 6.25 GPa at room temperature could all be indexed with a cell having rhombohedral symmetry. Despite the presence of additional peaks from the ruby and gasket, it was possible to successfully refine the structures in space group $\bar{R}3c$ with an $a^-a^-a^-$ tilt system, this being the structure adopted by this compound at ambient pressure at temperatures between 225 and 1600 K. The refined lattice parameters are given in Table 1. With increasing pressure, a progressive decrease in the cell parameters (and hence volume) is observed (Figure 2). The variation in volume is well reproduced by the Birch–Murnaghan third-order equation of state. As the pressure was increased to above 8.05 GPa, the cubic 200 reflection was observed to split, indicating a lowering of symmetry from $\bar{R}3c$. The patterns recorded at pressures above 8 GPa were successfully indexed to an orthorhombic cell. There was no evidence for any superlattice reflections indicative of \pm tilts of the AlO_6 octahedra as would occur if the structure were in the Pnma space group ($a^0b^-b^-$ tilt system), although X-ray diffraction methods are less than optimal in this regard. Subsequently, the structure was refined in Imma ($a^0b^-b^-$ tilt system) for patterns recorded at 8.05 and 9.1 GPa, this being the structure observed when PrAlO_3 is cooled below 225 K.⁵ Although

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Table 1. Refined Structural Parameters for the Rhombohedral Phase^a of PrAlO_3 as a Function of Pressure

pressure ^b (GPa)	a^c (Å)	c^c (Å)	x^c
0.00	5.3336(2)	12.9858(4)	0.5427(6)
0.71 ↑	5.3312(2)	12.9812(4)	0.5422(6)
1.25 ↑	5.3243(3)	12.9632(5)	0.5435(7)
1.85 ↑	5.3208(1)	12.9557(3)	0.5396(5)
2.95 ↑	5.3089(2)	12.9284(3)	0.5379(6)
4.57 ↑	5.2998(2)	12.9064(4)	0.5346(7)
5.15 ↑	5.2903(3)	12.8853(5)	0.5308(6)
6.25 ↑	5.2780(3)	12.8590(5)	0.5258(7)
7.14 ↓	5.2610(3)	12.8180(6)	0.5221(9)
6.43 ↓	5.2684(2)	12.8329(5)	0.5257(8)
4.40 ↓	5.2913(2)	12.8834(5)	0.5243(6)
2.50 ↓	5.3024(1)	12.9109(4)	0.5246(6)
0.00 ↓	5.3317(2)	12.9812(4)	0.5360(6)

^a In $\bar{R}3c$, the Pr is on the 6a sites at (0, 0, 0.25), the Al is on the 6b sites at (0, 0, 0), and the O is on the 18e sites at (x, 0, 0.25). ^b ↑ indicates that the data were collected with increasing pressure, whereas ↓ is for data collected as the pressure was released.

^c Values in parentheses are the esd's in the last figure.

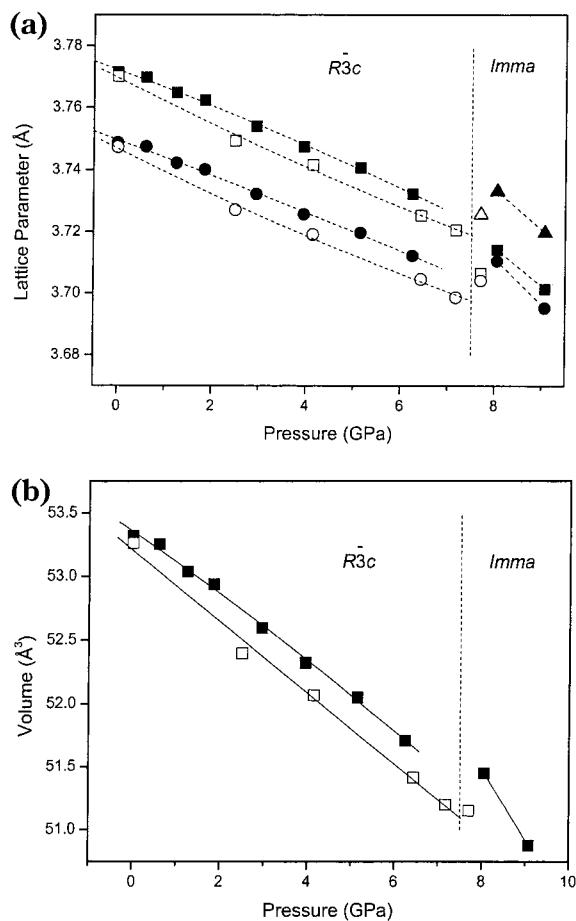


Figure 2. Variation of (a) the reduced lattice parameters (■ and ● c) and (b) the volume for PrAlO_3 with pressure. In all cases, the esd's are smaller than the symbols. The vertical line near 7 GPa indicates the point of the rhombohedral–orthorhombic transition. The closed symbols represent points taken with successively increasing pressure, and the open symbols are data collected as the pressure was reduced from 9.1 GPa. The solid lines serve as a guide to the eye and highlight the hysteresis in the lattice upon partial release of the pressure.

we did not see any evidence for a monoclinic structure in PrAlO_3 , by analogy with the low-temperature studies,⁵ such a structure might be favored at still higher pressures. Releasing the pressure to below 7.2 GPa

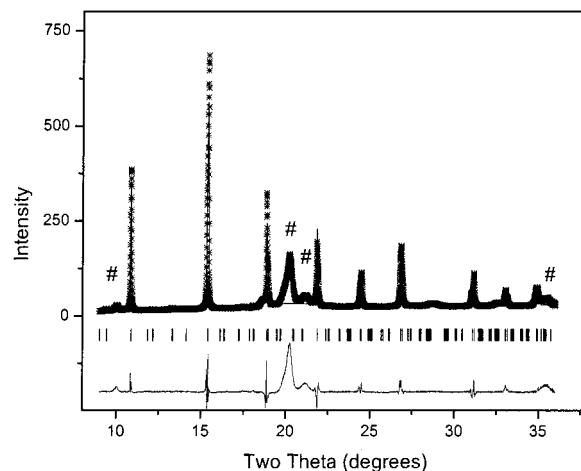


Figure 3. Synchrotron powder diffraction pattern for PrAlO_3 at 8.05 GPa. The crosses are the observed data, and the solid line is the calculated pattern. The short vertical lines show the positions of the allowed Bragg reflections. The peaks marked with # are from the ruby or DAC, and regions containing these peaks were excluded during the structural refinement.

resulted in a transition back to the rhombohedral structure. The pattern collected at 7.2 GPa during the release of pressure was consistent with a two-phase mixture and appears to contain both the *Imma* and $\bar{R}3c$ phases. As seen in Figure 2, there is considerable hysteresis in the lattice parameters as the pressure is initially released. Both the lattice parameters and the volume are noticeably smaller as the pressure is released, although once the pressure is totally released, the lattice parameters rapidly return to the values found prior to the pressure cycle.

In Figure 3, we show the results of Rietveld refinement in the *Imma* phase. The agreement between the observed and calculated patterns is acceptable. The refined structural parameters obtained for PrAlO_3 in *Imma* are given in Table 2. The variations of the lattice parameters and volumes are shown in Figure 2. It is clear that the cell decreases in size upon application of pressure. Whereas there is a noticeable change in the cell parameters associated with the observed rhombohedral–orthorhombic phase transition, the change in cell volumes is much less dramatic. This is consistent with the previous variable-temperature diffraction study.⁵ Group theory shows that the $\bar{R}3c$ -to-*Imma* transition must be first-order.⁴

It is worth stressing that the absolute decrease in cell volume observed here is considerably larger than that found in the variable-temperature studies, which indicated the presence of two phase transitions.⁵ It is common practice to approximate the BO_6 octahedra as rigid bodies when considering perovskite structures, and in general, it is anticipated that the shorter bonds will compress less than the longer ones, leading to more regular polyhedra, although this is not always observed.²³ Within the precision of the present refinements, there is no evidence to suggest that any unusual contraction of the A–O bond distances occurs at the phase transition. An alternate approach, suggested by

Table 2. Refined Structural Parameters for the Orthorhombic Phase^a of PrAlO_3 as a Function of Pressure

pressure ^b (GPa)	a^c (Å)	b^c (Å)	c^c (Å)	Pr z^c	O(1) z^c	O(2) y^c
8.05 \uparrow	5.2526(2)	7.4209(3)	5.2794(2)	0.4998(2)	0.0566(3)	-0.0003(1)
9.07 \uparrow	5.2346(2)	7.3903(4)	5.2605(2)	0.4992(3)	0.0574(3)	0.0009(1)
7.70 \downarrow	5.2418(2)	7.4082(3)	5.2689(2)	0.5004(3)	0.0537(4)	-0.0047(1)

^a In *Imma*, the Pr and O(1) are on 4e sites at (0, 0.25, z), the Al is on 4a sites at (0, 0, 0), and the O(2) is on 8g sites at (0.25, y , 0.25). \uparrow indicates that the data were collected with increasing pressure, whereas \downarrow is for data collected as the pressure was released. ^c Values in parentheses are the esd's in the last figure.

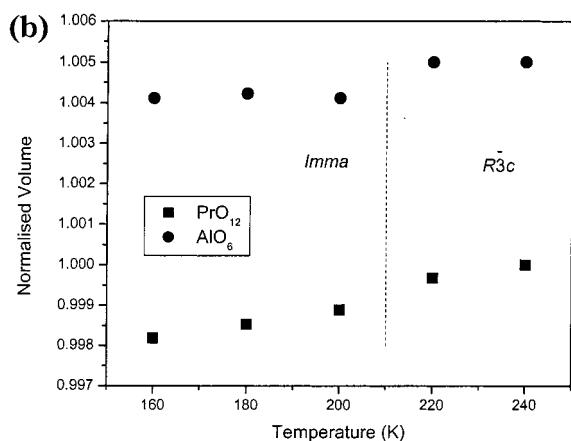
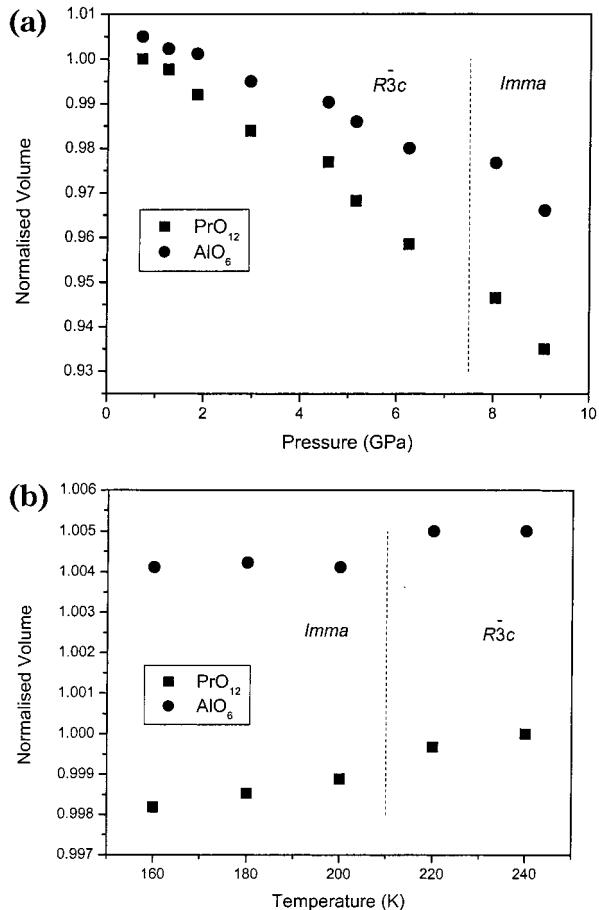


Figure 4. Variation in the normalized AlO_6 and PrO_{12} polyhedron volumes determined as a function of (a) pressure and (b) temperature. The temperature-dependent data are taken from ref 7.

Thomas,^{24,25} is to examine the volume of the AO_6 and BO_6 polyhedra. Using this approach, Hashimoto and co-workers showed that, although both the La–O and Cr–O distances contracted by an equal amount in the thermally induced *Pnma*-to-*R3c* phase transition in LaCrO_3 , the most significant structural change was a large decrease in the volume of the CrO_6 octahedron. As expected in PrAlO_3 , the PrO_{12} polyhedron shows the largest absolute reduction in volume as the pressure is increased, although the percentage decreases of both the PrO_{12} and AlO_6 polyhedron are comparable.²⁶ Both are observed to contract at the *Imma*–*R3c* phase transition, irrespective of whether the transition is induced by increased pressure or reduced temperature, although,

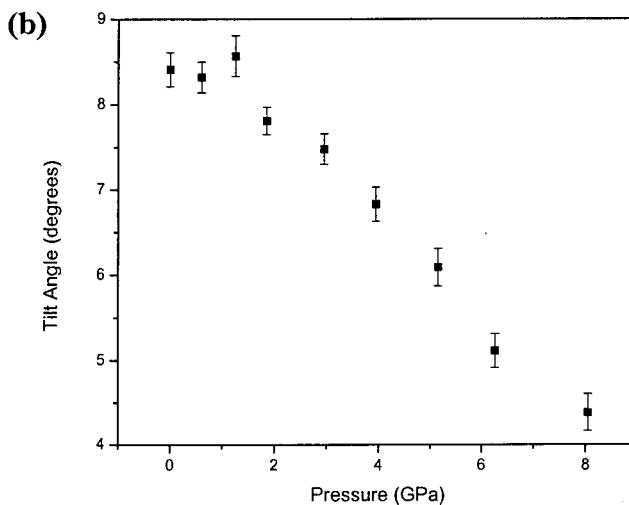
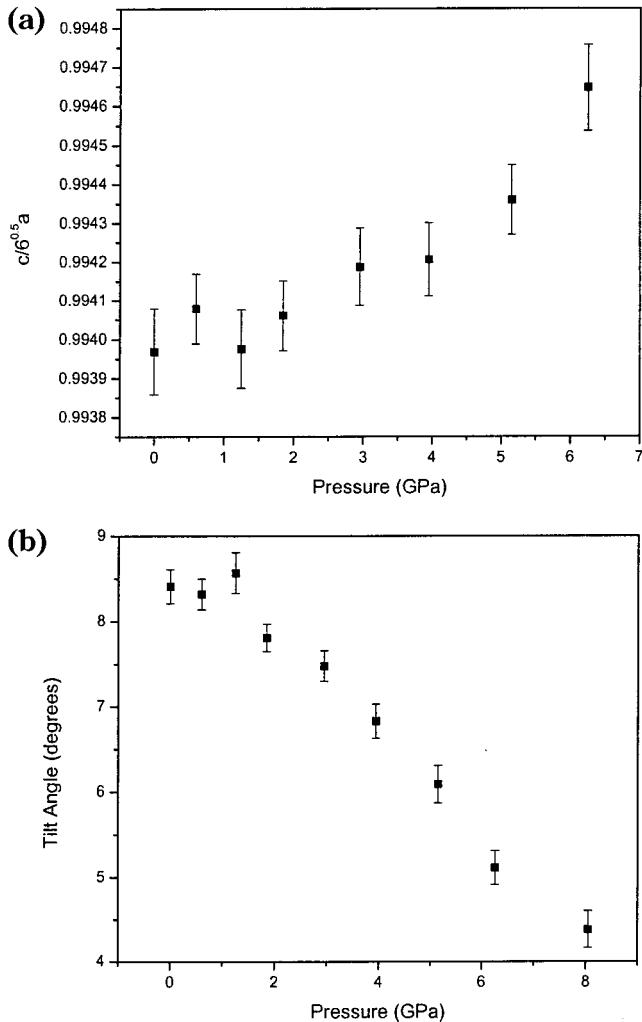


Figure 5. Pressure variation of (a) the ratio $\sqrt{2}c/\sqrt{12}a$ of the rhombohedral lattice parameters (the value would be 1 in the cubic phase) and (b) the angle of rotation of the oxygen octahedron about the 3-fold axis of the rhombohedral phase (this angle would be 0° in the cubic phase). For clarity, only data collected with increasing pressure are shown. The vertical lines show the positions of the phase transitions.

as is evident from Figure 4, there is a change in slope in the volume of the AlO_6 polyhedron at the phase transition. In the temperature-dependent studies, the volume of the AlO_6 octahedron decreases at the phase transition, whereas in the pressure-dependent studies, it remains almost constant. We will return to this point later. A reduction in the rotations of the AlO_6 octahedra can also result in a reduction in the volume of the PrO_{12} polyhedron.

In *R3c*, there are two measures of distortion of the cell from the aristotype cubic structure:⁷ the ratio $\sqrt{2}c/\sqrt{12}a$ and the tilt angle ϕ given by $\tan \phi = 2u\sqrt{3}$, where the x coordinate of the O atom is at $1/2 + u$ and

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$u = 0$ in the cubic perovskite. Both of these measures are plotted in Figure 5 and both indicate a systematic shift toward a higher-symmetry structure upon application of pressure. The high-temperature diffraction study of the $\bar{R}\bar{3}c$ -to- $Pm\bar{3}m$ transition in PrAlO_3 showed both that the modified c/a ratio tended toward unity and that the tilt angle tended toward zero as the transition to cubic was approached. Yet, when it is observed, the pressure-induced phase transition is toward a lower-symmetry structure.

Thus, we are left with the unusual occurrence of the rhombohedral structure initially tending toward a higher-symmetry arrangement before undergoing a first-order phase transition to the lower-symmetry orthorhombic structure. We note that there are numerous reports of pressure decreasing the distortion in orthorhombic (*Pnma*-type) perovskites. However, we are unaware of any high-resolution diffraction studies demonstrating that they undergo a continuous structural phase transition. The most comprehensively studied perovskites, ScAlO_3 ²⁷ and MgSiO_3 ,¹¹ both remain in *Pnma* to the highest pressures studied. Likewise, neither of these compounds undergo a crystallographic phase transition to another perovskite-type structure upon heating.

It is probable that the unusual pressure-dependent variation in the tilt angles is related to the jump in the volume of the AlO_6 octahedron at the phase transition. Hashimoto and co-workers¹⁰ have previously shown that, in LaCrO_3 , the high-temperature *Pnma*- $\bar{R}\bar{3}c$ phase transition is associated with a large change in the volume of the BO_6 polyhedra. For rhombohedral ABO_3 perovskites in $\bar{R}\bar{3}c$, a reduction of the tilt angle of the BO_6 octahedron by movement of the oxygen atom toward $x = 0.5$ results in a small decrease in the volume of the BO_6 octahedron and a concurrent increase in the volume of the AO_{12} polyhedron. This is in addition to

any changes observed as a result of changes in the lattice parameters. At the pressure-induced $\bar{R}\bar{3}c$ -to-*Imma* transition in PrAlO_3 , there is only a very minor change in the cell volume, and the apparent increase in the volume of the AlO_6 octahedron is believed to be due to a rapid increase in the tilting of the AlO_6 octahedron. It should be stressed that, because this is a first-order phase transition, there is no simple relationship between the tilts in $\bar{R}\bar{3}c$ and *Imma*. In the temperature-induced transition, the rotation of the AlO_6 groups is not significantly altered, and the observed reduction in the volume of the AlO_6 octahedron is mainly a result of the changes in the lattice parameters. It is unclear why the degree of rotation of the AlO_6 groups should increase with pressure, although, as mentioned above, there are other examples of perovskites that tend toward higher-symmetry structures as the pressure is increased. It is possible that this reflects the different compressibilities of the A–O and B–O bonds. These, in turn, are presumably related to the polarizabilities of the A and B cations.

In conclusion, we have demonstrated that high pressure induces the same crystallographic phase transition in PrAlO_3 as does cooling. The transition is associated with a measurable change in the volume of the AlO_6 polyhedra. It appears that, as suggested by Hashimoto and co-workers,¹⁰ the change in the relative volumes of the BO_{12} and AO_6 polyhedra is critical in inducing the transition to lower symmetry. Clearly, there remains considerable scope for further studies of pressure-induced phase transitions in simple perovskites.

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