General Rules for Predicting Phase Transitions in Perovskites due to Octahedral Tilting

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Recent experiments on several oxide perovskites reveal that they undergo tilt phase transitions to higher-symmetry phases on increasing pressure and that $dT_c/dP < 0$, contrary to a general rule previously proposed for such zone-boundary transitions. We show that the negative slope of the phase boundary is a consequence of the octahedra in these perovskites being more compressible than the extra-framework cation sites. Conversely, when the octahedra are stiffer than the extra-framework cation sites, the phase transition temperatures increase with increasing pressure, $dT_c/dP > 0$.

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Compounds with the perovskite structure and its derivatives are perhaps the most widely used ceramics for technological applications because of the excess physical properties that arise as a result of structural phase transitions that distort the ideal cubic perovskite structure. Therefore, the physical principles that govern the structural state of a given perovskite, and how that state may change with intensive variables such as pressure or temperature, have long been the subject of investigation and debate. In particular, it was originally suggested [1] that the phase transition temperatures T_c of zone-boundary transitions in perovskites should always increase with pressure; thus $dT_c/dP = \Delta S/\Delta V > 0$. This "general rule" has recently been challenged by experimental data [2–4] that demonstrates that several oxide perovskites exhibit zone-boundary transitions with $dT_c/dP < 0$. The reversal of the slope and the implied change in sign of one of ΔS and ΔV indicates that these transitions have fundamentally different thermodynamics. In this contribution we combine the results of recent experimental high-pressure measurements of perovskites with a new paradigm for understanding their structural response to pressure to resolve this apparent contradiction and to develop a modified "general rule."

The idealized structural formula of oxide perovskites can be expressed as ABX_3, A and B representing cations and X an anion. The aristotype structure consists of an array of perfectly regular and untilted BX_6 octahedra that share corners to form a three-dimensional framework within the cavities of which lie the A cations in twelvefold coordination by the X anions. This structure has $Pm3m$ symmetry. Under ambient conditions many perovskites exhibit structures with lower symmetries that can be derived from the cubic aristotype structure through the tilting of essentially rigid BX_6 octahedra [5–9]. While we restrict ourselves in this Letter to structures in which tilting alone is the symmetry-breaking process, we note that many other perovskites, including $CaTiO_3$ itself, exhibit structures and symmetries that result from cation displacements in addition to tilting of the octahedra.

Perovskites with lower symmetries at ambient conditions generally exhibit a series of phase transitions with increasing temperature to higher-symmetry structures with smaller tilts, the end point being the cubic structure with no tilts and $Pm3m$ symmetry (see review in [10]). These high-temperature transitions can be mostly understood in terms of the changes in the pattern of tilts of effectively rigid octahedra. If the octahedra are truly rigid, then the connectivity of the structure (Fig. 1) means that a decrease in the magnitude of the tilts of the octahedra, whether continuously within a phase or at a phase transition, must be accompanied by an increase in the unit-cell volume. Conversely, the only way in which the volume of such a structure can be reduced is through an increase in the tilts of the octahedra. Pressure must therefore result in either an increase in tilting of the rigid octahedra without a change of symmetry or a phase transition to a structure of lower symmetry, greater tilts and smaller volume. Pressure therefore has the same effect on these structures as decreasing temperature, and the phase transition boundaries will therefore have slopes $dT_c/dP > 0$ as illustrated in Fig. 2(a). When considered as a transition from the lower-symmetry phase to the higher-symmetry phase, both ΔS and ΔV are positive. As changes in tilt system are normally accompanied by changes in the size of the primitive unit cell, they are zone-boundary phase transitions [8,9]. This structural analysis therefore gives the same result of $dT_c/dP > 0$ that was previously obtained through consideration of the interatomic forces involved [1].

Recent experiments have now provided exceptions to this general rule. $LaAlO_3$ was recently reported to undergo a phase transition at about 14 GPa from a structure with R-$3c$ symmetry to $Pm3m$ symmetry on the basis of *in situ* Raman spectroscopy and x-ray powder diffraction measurements [2]. The same transition was predicted on the basis of first-principles calculations to occur in $NdAlO_3$ at higher pressure [11] and has been observed in $NdNiO_3$ at 6 GPa [4]. Similarly, x-ray diffraction experiments show that $LaGaO_3$ undergoes a phase transition at 2.3 GPa from the ambient-pressure phase with $Pbnm$ symmetry to R-$3c$

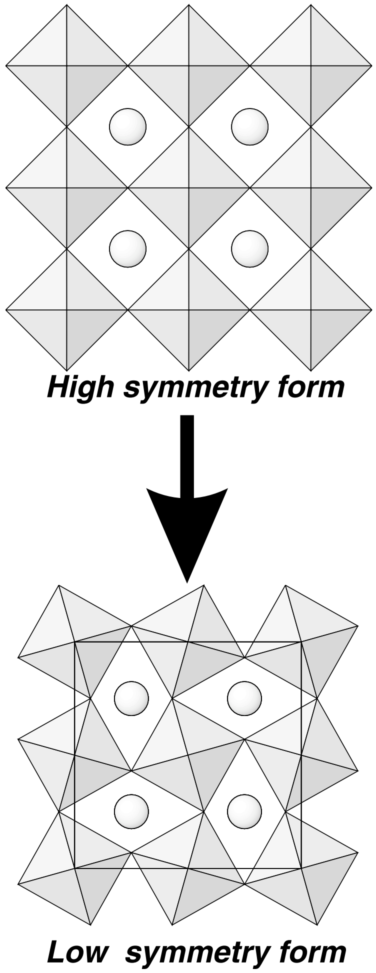

FIG. 1. Perovskites are comprised of a framework of BX_6 octahedra with A cations (shown as spheres) occupying the interstices within the framework. The aristotype structure is cubic and shows no octahedral tilting (top). If the octahedra are completely rigid, the only way in which the unit-cell volume can be reduced is by introducing tilts of the octahedra (bottom).

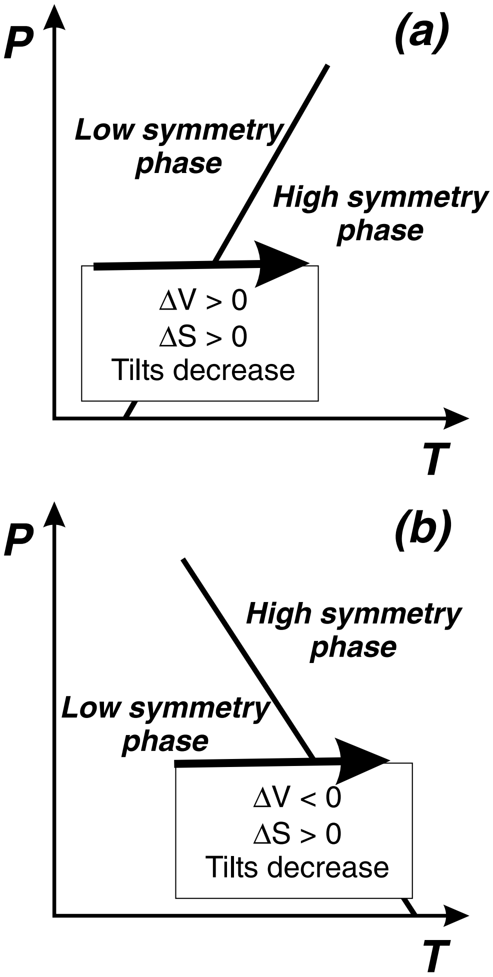

FIG. 2. Schematic P-T phase diagrams for perovskites. (a) $dT_c dP > 0$ when the octahedra are more rigid than the AX_{12} site. (b) $dT_c/dP < 0$ when the octahedra are less rigid than the AX_{12} site.

symmetry (Fig. 3 and [3]). In all of these zone-boundary transitions the same symmetry change occurs on increasing temperature at ambient pressure [4,11–13]. Thus the phase transition temperature decreases with increasing pressure; that is, $dT_c/dP < 0$, as shown in Fig. 2(b). Thermodynamics therefore requires $\Delta S/\Delta V < 0$ for the transition from the more tilted low-symmetry phase to the less tilted high-symmetry phase. Since ΔS must be positive, ΔV must be negative. This is exactly the opposite of the volume change expected for transitions involving a decrease in the tilts of rigid octahedra.

The resolution of this contradiction and the basis for this apparently anomalous transition behavior can be found in recently elucidated principles that govern the general response of the perovskite structure to pressure. While it has long been recognized that the relative compressibility of the AX_{12} and BX_6 sites must play a role in determining whether the perovskite structure becomes more distorted with increasing pressure [14–17], the resolution of high-pressure diffraction measurements has until recently been insufficient to reliably determine whether the BX_6 octahedra undergo significant compression. Now that a number of experimental studies [18–21] have been completed it is no surprise to find that the BX_6 octahedra of all perovskites undergo small but significant amounts of compression. More importantly, these new data also show that the compression of the A-X and B-X bonds induced by increasing pressure are such that the resulting bond-valence strain is distributed equally across the B-X and A-X polyhedra [22]. As a consequence, the ratio of the compressibilities of the AX_{12} and BX_6 polyhedra is given by $\beta_B/\beta_A = M_A/M_B$, in which the M_A and M_B are parameters for the two sites defined as $M_i = \frac{R_i N_i}{B} \exp(\frac{R_0 - R_i}{B})$ [22]. Here R_i is the average bond length and N_i the coordination number of the cation site in the structure at ambient conditions. R_0 is a bond-valence parameter that is dependent only upon the cation-anion pair and can be obtained from published tables [23] and B is a universal constant [23]. The general behavior of all perovskites at high pressures follows immediately from this relationship.

The limiting but unphysical case of completely rigid BX_6 octahedra is represented by $\beta_B = 0$ and thus $M_A/M_B = 0$. In such a structure all of the volume reduction on increasing pressure would be accommodated by increases in the tilts of the octahedra as noted above. Perovskites in which the A cation has a lower formal charge than the B cation, for example $MgSiO_3$ and $CaSnO_3$, have $M_A/M_B < 1$ and thus the AX_{12} sites are more compressible than the BX_6 octahedra. The tilts of the BX_6 octahedra therefore increase on increasing pressure [18,24], thereby reducing the unit-cell volume. Pressure thus drives these perovskites away from the phase transition boundary to higher-symmetry structures; negative pressure would therefore be required to increase their symmetry, consistent with the phase boundaries having $dT_c/dP > 0$, as shown in Fig. 2(a). Higher-symmetry perovskites with $M_A/M_B < 1$ are expected to undergo phase transitions to lower-symmetry structures, as illustrated by the transition of $CaSiO_3$ with $M_A/M_B = 0.97$ from $Pm3m$ to an, as yet, unidentified lower-symmetry structure at pressures above 20 GPa [25].

Perovskites in which the A and B cations have the same formal charge, including $NdNiO_3$, $LaAlO_3$, $LaGaO_3$, $YAlO_3$, $GdFeO_3$, and $GdAlO_3$, have $M_A/M_B > 1$, and the BX_6 octahedra are therefore more compressible than the AX_{12} sites. As a consequence the tilts of the octahedra decrease with increasing pressure and thus evolve back towards the cubic aristotype [4,19–21]. In $LaAlO_3$ experimental difficulties have so far prevented the structure being determined up to the phase transition at 14 GPa. Lower-pressure single-crystal diffraction data [21] do show that the single rotation angle of the octahedra decreases continuously with pressure and extrapolates to zero in the neighborhood of the known transition pressure [2]. The reduction in the unit-cell volume with increasing pressure is provided by the compression of the octahedra, which are softer than the structure as a whole [21] because the reduction in the tilting angle contributes, in the absence of other distortions, an increase to the volume. These principles can be explored in more detail with $LaGaO_3$ that has $Pbnm$ symmetry at ambient conditions, and exhibits the same phase transition to $R\text{-}3c$ symmetry at both high temperature [12] and at high pressures [3] and thus also has $dT_c/dP < 0$. New single-crystal diffraction data show that the high-pressure phase transition is first-order in character with $\Delta V = -0.23\%$ (Fig. 3). Direct measurements of the crystal structure of $LaGaO_3$ on either side of the phase transition show that this overall volume reduction is achieved by a 0.8% compression of the octahedral volumes, but is partially counteracted by the decrease in the average tilt angle of the octahedra (Fig. 3). Similarly, at the $Pbnm$ to $R\text{-}3c$ transition in $LaCrO_3$ at ~525 K under ambient pressure the volume decrease of 0.7% is produced entirely by a decrease in octahedral volume, with no change in the volume of the A site [26].

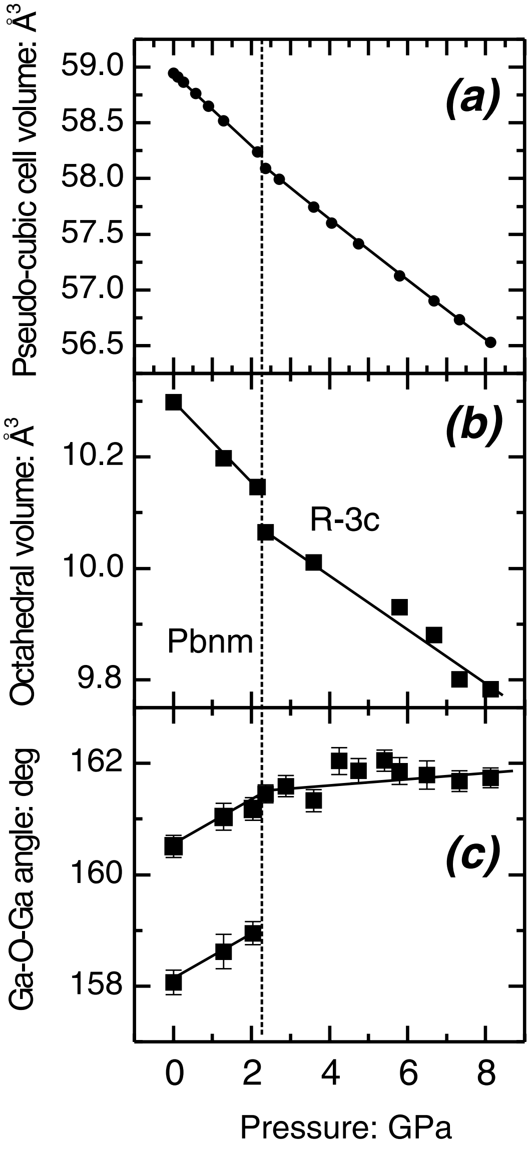

FIG. 3. Data from *in situ* single-crystal x-ray structure determinations of $LaGaO_3$. (a) Unit-cell volume variation with pressure. (b) Octahedral volume variation with pressure. (c) Variation of the Ga-O-Ga angles with pressure. An increase in angle corresponds to a decrease in octahedral tilt. There are two symmetrically distinct Ga-O-Ga angles in the $Pbnm$ phase.

The general rule [1] for predicting the variation in transition temperatures of tilt transitions in perovskites can therefore be modified as follows. In perovskites with $M_A/M_B < 1$, the octahedral tilts will increase with increasing pressure because the AX_{12} sites are more compressible than the BX_6 octahedra. Therefore, phase transitions from the low-symmetry phase stable at low temperatures and high pressures to the high-symmetry phase at high temperatures and low pressures are accompanied by increases in both entropy and volume. Therefore, $dT_c/dP = \Delta S/\Delta V > 0$ as shown in Fig. 2(a). The increase in volume arises from both the decrease in tilts of the octahedra as well as their expansion. In contrast, perovskites with $M_A/M_B > 1$ exhibit decreasing tilts with increasing pressure. In this case the phase transition is from a low-symmetry phase stable at low temperatures and pressures to the high-symmetry phase stable at high temperatures and pressures. It is accompanied by an increase in entropy but a decrease in volume, so $dT_c/dP = \Delta S/\Delta V < 0$ as shown in Fig. 2(b). The volume decrease arises from a significant reduction in the volume of the octahedra, as seen in $LaGaO_3$ (Fig. 3) and $LaCrO_3$ [26] which is partially compensated by a contribution from the decrease in the tilts of the octahedra.

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