Perspective
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Understanding ferroelectricity in layered perovskites: new ideas and insights from theory and experiments
Understanding ferroelectricity in layered perovskites: new ideas and insights from theory and experiments

Nicole A. Benedek,*a James M. Rondinelli,b Hania Djani,c Philippe Ghosezd and Philip Lightfoote

ABO₃ perovskites have fascinated solid-state chemists and physicists for decades because they display a seemingly inexhaustible variety of chemical and physical properties. However, despite the diversity of properties found among perovskites, very few of these materials are ferroelectric, or even polar, in bulk. In this Perspective, we highlight recent theoretical and experimental studies that have shown how a combination of non-polar structural distortions, commonly tilts or rotations of the BO₆ octahedra, can give rise to polar structures or ferroelectricity in several families of layered perovskites. We discuss the crystal chemical origin of the polarization in each of these families – which emerges through a so-called ‘trilinear coupling’ or ‘hybrid improper’ mechanism – and emphasize areas in which further theoretical and experimental investigation is needed. We also consider how this mechanism may provide a generic route for designing not only new ferroelectrics, but also materials with various other multifunctionalities, such as magnetoelectrics and electric field-controllable metal-insulator transitions.

1. Introduction

Solid-state scientists have devoted decades of effort to searching for and designing polar materials, owing to their fascinating physical properties – ferroelectricity, piezoelectricity, and non-linear optical activity, for example – and important technological applications. Such materials must satisfy strict crystallographic requirements, since only a limited number of point groups can support polar symmetry. Hence, the challenge for the materials designer is to determine which chemistries and structure types will give rise to the desired structure and properties. Of the inorganic materials families, complex oxides have perhaps been one of the most fertile families of materials in which to search for new polar compounds, particularly perovskites and perovskite-related phases. Indeed, the perovskite BaTiO₃ is considered the archetypal ferroelectric, or even polar.13

In contrast to bulk ABO₃ perovskites, the family of layered perovskite-like phases contains a number of polar and ferroelectric materials. For example, the Aurivillius phase SrBi₂Ta₂O₇ has been extensively investigated as a fatigue-free ferroelectric for ferroelectric memories.18,19 Bi₂Ti₃O₁₀, Bi₂TiNbO₉ and Bi₂WO₆ are also Aurivillius ferroelectrics.22 The Ruddlesden–Popper phases Ca₃Ti₂O₇,23 Ca₃Mn₂O₇,26,27 and Ca₃Ru₂O₇ are all polar, although the parent materials Ca₃TiO₅, Ca₃MnO₃ and Ca₃RuO₃ are not. The Dion–Jacobson phases29,30 CsBiNb₂O₇ and CsNdNb₂O₇ have been experimentally observed31,32 to be polar and ferroelectricity has been demonstrated in RbBiNb₂O₇.33 and, very recently, in CsBiNb₂O₇.34 First-principles calculations have predicted that several other Dion–Jacobson phases may also be polar.35 A number of AA′B₂O₆ double perovskites36,37 are either known experimentally to be polar (for example, NaLaMnWO₆,38 which exhibits simultaneous A- and B-site cation ordering) or have
been predicted to be polar from first-principles calculations. Ferroelectricity has also been demonstrated in various artificial superlattices grown as thin-films, even in cases it was unexpected. Why is ferroelectricity – and acen
tricity in general – much more common among the layered perovskites than their ABO₃ counterparts?

In this Perspective, we review recent progress in understanding the crystal chemistry of layered perovskites, particularly the mechanisms by which polar structures emerge in various families of materials; see Fig. 1. In contrast to SOJT-driven materials like BaTiO₃ and BiFeO₃, the origin of the transition from a non-polar to a polar structure in many layered perovskites is not the instability of a polar mode driven by charge transfer or hybridization. Instead, the transition involves two non-polar lattice distortions (commonly ‘rotations’ or ‘tilts’ of the BO₆ octahedra), which couple to a polar lattice mode in a so-called ‘trilinear coupling’ mechanism. The importance of octahedral rotations (which are generally driven by electrostatic or ion size mismatch effects) in giving rise to polar structures was emphasized in several experimental studies of Aurivillius phases, Dion-Jacobson phases and double perovskites. These works essentially anticipated the trilinear coupling mechanism as the origin of ferroelectricity, the microscopics of which was first revealed by Bousquet et al. and further formally elucidated in a series of papers using theory and first-principles calculations. We begin by briefly reviewing the basics of this mechanism from the perspective of theory, and discuss how it manifests in different families of layered perovskites. In particular, we aim to highlight advances in understanding made possible by synergistic interactions between theory and experiment. Finally, we discuss the possibilities for exploiting the trilinear coupling mechanism as a generic route to creating various types of multifunctionalities,

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such as metal-insulator transitions and magnetoelectric effects.

2. Trilinear coupling: polar structures from non-polar lattice distortions

Before discussing the specifics of the trilinear coupling mechanism, it is useful to briefly review the manner in which polar structures and ferroelectricity emerge in prototypical ferroelectrics like BaTiO$_3$ and PbTiO$_3$. In these materials, ferroelectricity is driven by a single, zone-center polar lattice distortion (phonon), which gives rise to a spontaneous polarization. The cooperative acentric displacements associated with this polar lattice mode (sketched in Fig. 2a), completely account for the symmetry lost between the paraelectric parent phase and the ferroelectric ground state. A convenient approach to understand the loss of inversion symmetry at the atomic scale involves treating the electric polarization that results from the displacements as an order parameter, and expanding the free energy $F$ of the paraelectric phase in powers of the polarization $P$ (to fourth order) as:

$$F = F_0 + \alpha P^2 + \beta P^4,$$

where $F_0$ is the energy of the undistorted paraelectric phase and $\alpha$ and $\beta$ are coefficients. Ferroelectric transitions for which the polarization is the primary order parameter are known as ‘proper’. Below the Curie temperature ($\alpha < 0$), eqn (1) produces the double-well potential energy curve that is shown in Fig. 2c, and is characteristic of proper ferroelectrics.

The polarization is not the primary order parameter in all ferroelectric transitions, as in the case of ‘improper’ ferroelectrics such as the hexagonal multiferroic YMnO$_3$. The polarization is instead coupled to another primary cooperative atomic displacement pattern $R$, which occurs at the zone-boundary of the paraelectric phase and thus leads to an enlargement of the unit cell at the transition. For example, Fig. 2b depicts such a mode in the 5-atom cubic perovskite, which manifest as rotations of the BO$_6$ octahedra. In hexagonal YMnO$_3$, a similar type of zone-boundary mode, which triples the unit cell of the paraelectric phase and leads to a tilting of the MnO$_6$ polyhedra and a buckling of the Y–O planes, acts as the primary order parameter driving the transition into the ferroelectric ground state. In other words, the polar zone-center mode is not intrinsically unstable in improper ferroelectrics and only appears due to its coupling with the zone-boundary mode (Fig. 2e).

In the specific case of YMnO$_3$, (or rather, any isostructural hexagonal manganite and even BaMnO$_3$, in spite of its very different crystal structure), the free energy expansion in terms of $P$ and $R$ can be written as,

$$F = F_0 + \alpha_{20} R^2 + \alpha_{02} P^2 + \beta_{40} R_4^2 + \beta_{04} P^4 + \beta_{31} R^2 P + \beta_{22} R^2 P^2. \quad (2)$$

The key detail is the second-last term, which couples the polarization at linear order to the primary order parameter and, even when $\alpha_{02} > 0$, allows YMnO$_3$ to develop an (ionic) polarization when the MnO$_6$ polyhedra have tilted and the Y–O planes have buckled. The free energies of all typical improper ferroelectrics will contain such a term linear in $P$, although it may have a slightly different form. Since $P$ is no longer the primary order parameter, as shown in Fig. 2e, the conventional double-well minimum does not exist ($\alpha_{02} > 0$; in some nominally improper ferroelectrics the polarization may be unstable and produce a double-well minimum by itself, but the energy lowering will be minimal compared to that found for the polarization coupled to the primary order parameter). Rather, the free energy exhibits a single-well minimum shifted to a nonzero value of $P$ owing to the coupling term in which $-\beta_{31} R^2$ acts as an effective electric field that induces $P$ (Fig. 2f).
Fig. 2 Schematic energy contours reveal the change in the energy profile upon cooling (lighter colors correspond to lower temperatures) for (c) a proper and (f) an improper ferroelectric transition driven by a non-polar mode $R$, such as the oxygen rotation mode shown in (b). Panels (c) and (e) and panels (d) and (f) show the polarization well in the absence ($R = 0$) and presence ($R = 1$) of the non-polar distortion $R$, respectively. In a proper ferroelectric, the coupling between the polarization and rotation is frequently bi-quadratic, and renormalizes the potential energy landscape such that the interaction leads to a less pronounced double-well potential (d). The effect of the odd coupling of the polar and non-polar modes on the energy surface for an improper ferroelectric is shown in panel (f), where the minimum shifts to a non-zero value of the polarization amplitude. Note that a symmetry-related energy profile exists, but is not depicted for (f), with a parabola that has a minimum at an equivalent negative polarization amplitude.

also note that one convenient way of assessing unambiguously the improper ferroelectric behavior of a compound is from calculations under open-circuit electrical boundary conditions, which has recently been made possible with advances owing to the modern theory of electric polarization.

Physically, the coupling term (odd in $P$ and $R$) indicates that when an electric field is applied to an improper ferroelectric, the primary order parameter will switch direction in addition to the polarization. As we discuss below, this has important consequences for the design of multifunctional materials. van Aken and co-workers used first-principles calculations to show that, unlike the ferroelectric transitions of BaTiO$_3$ and PbTiO$_3$, the transition in YMnO$_3$ is accompanied by little to no charge transfer or rehybridization. They thus concluded that, “the mechanism is driven entirely by electrostatic and [ion] size effects, rather than the usual changes in chemical bonding associated with ferroelectric phase transitions in perovskite oxides.”

Materials that undergo ferroelectric transitions (or more generally, transitions to a polar structure) through a trilinear coupling mechanism contain a term in their free energies in which the polarization is linearly coupled to two other non-polar order parameters $P_1$ and $P_2$ viz., $F = \gamma P_1 R P_2$, where $\gamma$ is a coefficient and $R_1$ and $R_2$ are non-polar structural distortions of different symmetry. The origin of the term ‘trilinear coupling’ should now be apparent. This mechanism is somewhat peculiar since it does not appear to fulfill one of the basic postulates of Landau theory, that of a single order parameter. The question of which structural distortion -- $P$, $R_1$ or $R_2$ -- drives the transition and the order in which the phase transitions actually take place is somewhat complicated and differs for different materials. In the Aurivillius phase SrBi$_2$Nb$_2$O$_9$, a polar mode (transforming like the irreducible representation $E_u$) and a zone-boundary mode ($X_5^-$) first condense simultaneously in a so-called avalanche transition (which is first-order), accompanied by another zone-boundary mode ($X_5^+$) that is coupled to the first two and appears as a secondary order parameter. In this case, the primary order parameter actually consists of two different distortions, $E_u$ and $X_5$. The fact that both modes condense at the same temperature is highly unusual, since two lattice distortions of different symmetries would not be expected to have the same temperature dependence. Another possibility is when the primary order parameter consists of two non-polar (zone-boundary) lattice distortions, which in combination give rise to a macroscopic polarization. This scenario – nowadays known as “hybrid improper” ferroelectric – was first proposed to be the origin of ferroelectricity in artificial PbTiO$_3$/SrTiO$_3$ superlattices, NaLaMnWO$_6$ double perovskites and a Ca$_3$Mn$_2$O$_7$ Ruddlesden–Popper compound.

In the remainder of this Perspective, we will highlight the manner in which the trilinear coupling mechanism gives rise to ferroelectricity or polar structures in different families of layered perovskites. In particular, we aim to show that this mechanism can provide a unifying framework for rationalizing the crystal chemistry of polar structures across many families of materials. We also highlight the possibility of using the trilinear coupling mechanism as a generic tool to design new multifunctional materials.

Before beginning our review of layered perovskites, we make a few notes here regarding terminology. First, we use the term ‘ferroelectric’ to describe a material that displays a spontaneous macroscopic polarization (that is, the material is polar), which may in principle be switched to a symmetry-equivalent state with an applied electric field. Materials for which polarization switching has been demonstrated experimentally...
will be noted explicitly. Second, we use the terms octahedral ‘rotation’ and ‘tilt’ interchangeably to mean the same thing: a structural distortion involving rotation of the BO₆ octahedra about one or more crystallographic axes. Finally, although we will make frequent mention of various structural distortions, any discussions of phase transitions or critical behavior will be limited to experimental observations only, as detailed information concerning the dynamics of phase transitions is not really available from first-principles calculations.

3. Trilinear coupling in action

3.1. Double perovskites and superlattices

The early 2000s saw many efforts devoted to understanding the effects of dimensionality and finite-size on ferroelectricity in thin-films of various ABO₃ perovskite materials. Initially, the focus was mostly on thin-films of a single material, playing with electrical and mechanical boundary conditions, but the interests of the community naturally evolved to artificial superlattices built from the repetition of two or more different ABO₃ perovskite layers alternately stacked one over the other in a manner akin to Lego blocks. This includes so-called ‘bicolor’ superlattices such as SrTiO₃/BaTiO₃, SrTiO₃/PbTiO₃, KNbO₃/KTaO₃ and even tricolor systems, such as (ABO₃)/2-(A′BO₃)ₘ₋(A″BO₃)ₙ that were shown to naturally break inversion symmetry. This activity gave rise to many fundamental discoveries fueled by the combination of first-principles calculations based on density functional theory and experimental investigations relying on advanced layer-by-layer growth deposition techniques and local probe measurements.

Artificial superlattices appeared at first glance as merely a nice playground for finely tuning ferroelectric properties through appropriate control of layer thickness. For example, SrTiO₃ is nominally not ferroelectric but undergoes a transition to a structure with octahedral rotations at 103 K, whereas PbTiO₃ is a good ferroelectric with no octahedral rotations. In SrTiO₃/PbTiO₃ superlattices the polarization and phase transition temperature can be tuned systematically and scale predictably with the PbTiO₃ volume fraction. Hence, if the thickness of the SrTiO₃ layers is held constant at 3 unit cells, the polarization increases as the PbTiO₃ layer thickness increases, as expected. However, Dawson and co-workers made a surprising and intriguing discovery: the polarization decreases as the PbTiO₃ layer thickness decreases, but re-appears unexpectedly when there are only one or two PbTiO₃ unit cells in the PbTiO₃ layer. Why does ferroelectricity re-appear in the limit of ultra-thin PbTiO₃ layers, precisely where it is least favorable?

A superlattice consisting of alternating layers of undistorted ABO₃ and A′BO₃ has tetragonal P4/emm symmetry (one can think of such a superlattice as an A-site ordered double perovskite with cation order along [001]). Focusing on a PbTiO₃/SrTiO₃ superlattice in which one layer of PbTiO₃ alternates with one layer of SrTiO₃, Bousquet et al. showed that the lowest-energy structure has polar P4/emm symmetry and that this atomic structure can be reached from the P4/emm structure via a combination of three different structural distortions: (i) a polar distortion (transforming the irreducible representation Γ₋₀ involving displacements of the Pb, Sr and Ti cations against the oxygens along [001]) (ii) an octahedral tilting distortion (M₁₋₀) corresponding to the Glazer tilt pattern a₀d₀c₀, and (iii) a second octahedral tilting distortion (M₂₋₀) corresponding to the Glazer tilt pattern a₀d₀c₀. Using Landau theory and a group theoretical analysis, Bousquet and co-workers showed that there is a term in the free energy, \( f = PR_{1} R_{2} \), where \( P \) is the \( \Gamma₋₀ \) polar mode and \( R_{1} \) and \( R_{2} \) are the M₁₋₀ and M₂₋₀ octahedral tilting distortions. As we discussed above, this means that if \( R_{1} \) and \( R_{2} \) are present (that is, if the structure contains the two octahedral tilting distortions) then a polarization will automatically appear because \( P \) is coupled to \( R_{1} \) and \( R_{2} \) through the trilinear term. The conclusion was thus that this trilinear coupling is responsible for the re-appearance of the polarization and the improper ferroelectric behavior observed experimentally (linear temperature dependence of \( P \) and absence of divergence of the dielectric constant at the phase transition).

The SrTiO₃ substrate on which the superlattices are grown imposes an epitaxial strain on the film such that the P4/emm phase is only just stable. Under slightly greater tensile strain, a Pmc2₁ phase is preferred, which again can be reached from P4/emm via a combination of three different structural distortions: (i) an octahedral tilting distortion corresponding to a₀d₀c₀, as above, (ii) an octahedral tilting distortion corresponding to a₀d₀c₀(\( M₂₋₀ \)) and, (iii) a polar distortion transforming like the irrep \( \Gamma₋₀ \), which produces a polarization in the [110] direction, i.e. in the plane of the substrate, instead of perpendicular to it. Amazingly, the symmetry of these three modes is also compatible with a trilinear coupling term of exactly the same form as above. In contrast to the polar mode in the superlattices with P4/emm symmetry, here the crystal chemical origin of the polarization can be traced back to anti-polar displacements of the A-site cations. The microscopics of this mechanism were elucidated on studies of both A-site ordered double perovskites and Ruddlesden–Popper phases, as described below.

Rondinelli and Fennie showed using symmetry arguments and first-principles calculations that the presence of identical A-site cations in A₂B₂O₆ double perovskites with layered ordering along [001] (again, these systems can be thought of as (ABO₃)₂/3-(A′BO₃)₁ superlattices) shifts the location of the inversion centers in the undistorted P4/emm paraelectric structure such that a combination of two octahedral rotations can globally lift inversion symmetry and allow a macroscopic polarization to arise. Note that no combination of octahedral rotations can globally lift inversion symmetry in a bulk ABO₃ perovskite. Hence, as for the superlattices above, the free energies of these double perovskites contain a trilinear term that couples the polarization to the two octahedral rotation modes.
This understanding was used to formulate a set of design guidelines, whereby polar A-site ordered double perovskites were constructed by layering two non-polar \textit{Pnma} perovskites; the \textit{Pnma} structure is composed of the two tilt patterns \(a'\overline{a}a'c\) and \(a'\overline{a}ac\), i.e., \(a'\overline{a}a'c\) (these rotations transform like the irreps \(M_3^1\) and \(R_{4}^1\), respectively). These guidelines were stated in the form of a chemical criterion and an energetic criterion. The chemical criterion merely states that the A-sites of the double perovskite must be occupied by two chemically distinct cations. The energetic criterion requires that the two perovskites used to construct the layered material have a strong energetic tendency towards the \(a'\overline{a}a'c\) tilt pattern (subsequent work\textsuperscript{34} also showed that the layered ordering must be along the direction of the \(c^+\) tilt, or inversion symmetry lifting does not occur). The resulting double perovskite has polar \textit{Pmc2}_1 symmetry.

The crystal chemical origin of the polarization in these double perovskites was identified by Mulder and co-workers\textsuperscript{40} as arising from anti-polar displacements of the A-site cations (transforming like the irrep \(X_5^4\)). Not all octahedral rotation patterns allow the A-site to shift from its ideal position in the cubic perovskite structure. The \(a'\overline{a}a'c\) tilt pattern that produces the \textit{Pnma} space group does allow such A-site displacements (along the [110] direction with respect to the cubic perovskite axes) and they in fact produce a polarization in the A-O layers of \textit{Pnma} perovskites, as shown in Fig. 4a. However, the A-sites are related by inversion symmetry through the B-site and hence the induced polarizations are of exactly equal and opposite magnitude such that they cancel each other out. If there are two chemically distinct A-sites however, as in A-site ordered double perovskites, then the induced polarizations are no longer exactly equal and the cancelation is incomplete, leaving a residual macroscopic polarization (Fig. 4b). This makes such materials ferrielectrics, or electronic analogues of ferrimagnets.\textsuperscript{85}

What determines the magnitude of the polarization in these A-site ordered double perovskites? The A-site cation displacements are coupled to the octahedral rotations such that the larger the magnitude of the rotations, the larger the A-site cation displacements. One might then naïvely expect that the polarization should be maximized for double perovskites built from components with large octahedral rotation distortions. However, if both ABO\textsubscript{3} and A'BO\textsubscript{3} have large octahedral rotations, then the A-site cation displacements will be similar in magnitude and though they may not completely cancel (and the A and A' Born effective charges may be slightly different), the total polarization will be small. In addition, the barrier to switch the polarization will be large. A better strategy, outlined here as a simplified version of the theory presented in ref. 40 is to select ABO\textsubscript{3} and A'BO\textsubscript{3} such that “the average tolerance factor is maximized and the difference in their tolerance factors is also large.”\textsuperscript{40} In other words, the difference in the tendency of the A-site cations to displace will be maximized (if A prefers to displace very little, while the A' cation displaces a lot), leading to a minimal cancelation of layer polarizations, a large total polarization and a smaller switching barrier. The stannate ASnO\textsubscript{3}/A'SnO\textsubscript{3} superlattices (A,A' = Ca, Sr, and Ba) are predicted to best satisfy these design guidelines;\textsuperscript{86} however, experimental realization of the system remains to be reported. The design rules also allow for the design and prediction of the net polarization in (ABO\textsubscript{3})\textsubscript{m}/(A'BO\textsubscript{3})\textsubscript{n} superlattices of arbitrary thickness. Most importantly, for a given A and A', the polarization is maximized if both m and n are odd (and it will be exactly zero if both m and n are even). Another key outcome from these analyses is that the size of the polarization is directly proportional to the degree of A-site ordering; hence, the maximum polarization is obtained when the A-site cations are completely ordered with a square-wave like composition variation along the [001] direction. Bellaiche and Íñiguez have also shown that the coupling between the anti-polar A cation displacements and octahedral tilt modes is a general feature in perovskite oxides due to induced interatomic forces.\textsuperscript{53,87} Interestingly, if a proper ferroelectric is used as a building block in these superlattices, e.g., as in BaTiO\textsubscript{3}/CaTiO\textsubscript{3}, then a proper out-of-plane polarization results that reduces the \textit{Pmc2}_1 symmetry to \textit{Pn}.\textsuperscript{88}

Since inversion symmetry is broken in the layered 1/1 superlattices by the combination of two octahedral rotation modes, such oxides can readily exhibit long-range magnetic order by selecting transition metal B cations with open d-shell configurations. One of the first multiferroic systems proposed to fulfill these conditions includes the \((\text{BiFeO}_3)_1/(\text{LaFeO}_3)_1\) superlattice epitaxially grown on a (001)-SrTiO\textsubscript{3} substrate.\textsuperscript{89} Although, the thermodynamically stable phase of BiFeO\textsubscript{3} is a rhombohedral \textit{R3c} structure with the \(a'\overline{a}a'c\) tilt system, and thus does not immediately satisfy the guidelines provided by Rondinelli and Fennie, it does have a strong tendency to the \textit{Pnma} tilt system.\textsuperscript{90} In contrast, LaFeO\textsubscript{3} does exhibit the \(a'\overline{a}ac\) tilt at room temperature. Both compounds are also G-type antiferromagnets with Neél temperatures well-above room temperature. First-principles calculations found that the equilibrium structure of the ferrate superlattice is indeed polar, \textit{Pmc2}_1, owing to trilinear coupling among the octahedral tilt and polar modes with a sizable polarization of 11.6 \(\mu\text{Cm}^{-2}\) along the [110] direction. Because the magnetic spins of the B cations in orthorhombic perovskites are not required to be collinear,\textsuperscript{91} a small spin canting can support a net magnetization in the AFM phases. In this case, the easy axis for the spins was computed to be along the [011] direction, which is perpendicular to the direction of the net polarization. The net spin-canted moment of \(\sim 0.40\mu_B\) is induced by the polar displacements and aligned along the [001] direction, i.e., orthogonal to both the polarization and the easy magnetization axis. The sign of the canting moment is controlled by the \(a'a'c\) tilt, and electric switching the direction of the weak magnetization requires reversing both the polarization direction and sense of the out-of-phase tilts. It was proposed that in-plane rotation of the polarization might be a possible low-energy switching path allowing this.\textsuperscript{89}

This concept was extended to other \((\text{LaFeO}_3)_m/(\text{LnFeO}_3)_m\) (Ln = lanthanide) ferrate\textsuperscript{92} and the \((\text{LaCrO}_3)_m/(\text{YCrO}_3)_m\) chromate\textsuperscript{53} superlattices with odd periodicities. Remarkably, electronic-
structure calculations on the ferrates demonstrate that electrical switching of magnetization should be feasible through the coupling of multiple lattice modes with weak ferromagnetism, circumventing the complications with finding single phase materials with coexisting ferroic orders that originate from conventional mechanisms. In fact, the magnetoelectric response in the (LaFeO$_3$)$_1/(YFeO$_3$)$_1$ superlattice was found to be two-to-three times larger than that of the prototypical magnetoelectric Cr$_2$O$_3$. Recently these first-principles derived guidelines have been realized in the [001] ordered odd period superlattice (LaFeO$_3$)$_5/(YFeO$_3$)$_5$ grown using pulsed-laser deposition. Second-harmonic generation polarimetry plots indicate the film is polar (point group mm2 consistent with the theoretical predictions), and room temperature magneto-optical Kerr experiments reveal long-range order consistent with the bulk components, but the weak-ferromagnetism remains to be reported. Although the superlattice was not digitally ordered a net polar structure results from the uncompensated layer polarizations as predicted by Mulder et al.$^{40}$

Generalization of the design guidelines discussed above shows that layering of both A and B sites along additional directions besides [001] makes it possible to lift inversion symmetry with octahedral rotations. Fig. 3 shows the multitude of simple orderings possible in double perovskites; many more may be accessible using non-equilibrium thin film growth methods.$^{94,95}$ The manner in which inversion can be removed depends on the details of the octahedral tilt system, and here we describe some of those most promising order schemes, which should be experimentally accessible owing to coordination-driven cation order.

Ordering of cations along the [111]-direction as in AA'B$_2$O$_6$ perovskites and depicted in Fig. 3c, requires tilts consisting of two modes (such as $a^-a^-c^+$) as already described,$^{41,96}$ or alternatively a single mode as recently pointed out by Young and Rondinelli.$^{97}$ In the latter case, only out-of-phase rotations are required: first-principles calculations on a series of aluminates, including LaNdAl$_2$O$_6$, LaPrAl$_2$O$_6$, and CePrAl$_2$O$_6$ found that while only LaPrAl$_2$O$_6$ and CePrAl$_2$O$_6$ are polar (Imm2), LaNdAl$_2$O$_6$ is chiral and non-polar (space group R32). Interestingly, all are predicted to undergo a transition to the R32 chiral phase at higher temperatures, which possesses relatively large piezoelectric coefficients, comparable to those of common lead-free piezoelectric materials such as BaTiO$_3$ and LiNbO$_3$. Unlike the Pnma orthorhombic perovskites, inversion symmetry in the rhombohedral aluminates with tendencies to only out-of-phase rotations results from coupling between a single tilt mode and the ‘polar’ displacements. Comparing the polarization of AA'B$_2$O$_6$ with [001] and [111] ordering and $a^-a^-c^+$, the former are always found to exhibit larger polarizations. Interestingly, if the A cations are ordered along [110] (Fig. 3b), there is no combination of octahedral rotations that will lift inversion symmetry. This was shown using representation theory and supported by first-principles calculations on gallate, zirconate, and hafnate superlattices$^{97}$ (note that if B cation ordering is included, this restriction is lifted).

![Diagram](image_url)

**Fig. 3** Cation ordered variants of double perovskite without octahedral distortions: AA'B$_2$O$_6$ with (a) layered, (b) columnar, (c) rock-salt ordering of A and A' cations, and A$_2$BB'O$_6$ (d) layered, (e) columnar, (f) rock-salt ordering of B and B' cations. (g) The common ordering adopted by AA'B'B'O$_6$ double perovskites (left) owing to valence preferences and the requirement to alleviate under and over-coordinated cations. The layered A-site order with rock salt B-site order and the orthorhombic tilt pattern (right) leads results in a polar-chiral space group P2$_1$.

![Diagram](image_url)

**Fig. 4** (a) Layer-resolved polarization of Pnma SrSnO$_3$ and (b) BaSrSn$_3$O$_6$ double perovskite (in polar space group Pmc2$_1$) from first-principles calculations.$^{40}$ Notice that the polarizations induced in the Sr–O layers in SrSnO$_3$ are exactly equal and opposite and hence cancel each other out such that the macroscopic polarization is zero. This cancelation is incomplete in the double perovskite, and a residual polarization remains.
Double perovskites with the AA’BB’O6 stoichiometry tend to exhibit layered ordering of the A and A’ cations and rocksalt ordering of the B and B’ (Fig. 3g), because these arrangements best optimize the electrostatic interactions. Examples of such compounds include NaLaMgWO6 or NaLaScNbO6. A magnetic version of the former, NaLaMnWO6, was first reported in 2009 by Woodward and co-workers98 to be polar (P21/n), and subsequently first-principles calculations elucidated the atomistic origin of the inversion symmetry to arise from the coupling of the octahedral tilt modes in the presence of the cation order.31 Recent experimental study, however, found no spontaneous electric polarizations in samples of NaLaMnWO6 and NaNdMnWO4, which was attributed to difficulty in making dense ceramics required for electrical poling measurements.59

The design of new multiferroics based on this cation-ordering concept was extended to double perovskites with the same cation order on the A and B sites, but included magnetic Ni and Mn cations on the B-site to stabilize ferromagnetic order.100 (Recall that the double order and a’ a c’ tilt is sufficient to provide for an electric polarization, yet if only B-site order is present then the structure is non-polar P21/n, consistent with the guidelines of Rondinelli and Fennie). In the RLaNiMnO6 perovskites, where R is a rare-earth ion, the R32NiO7– phases built from A1+ B3+O3 perovskites, the valence state of the B-site cation varies with n, e.g. the valence state of Ni in La2NiO4 (n = 1) is formally 2+, whereas it is 2.5+ in La3NiO7 (n = 2). Nowadays, Ruddlesden–Popper phases can be epitaxially grown on perovskite substrates, with perfect control of the perovskite block thickness n, also opening the way to epitaxial strain engineering in this class of compounds.94,95

The mechanism by which ferroelectricity arises in Ruddlesden–Popper phases was first explained for n = 2 Ca3Ti2O7.25 and CaMn2O7.26,27 Neither of the parent perovskites of these materials (CaTiO3 and CaMnO3) are polar in bulk, forming instead in the non-polar Pnma space group. Ca3Ti2O7 has only been reported in the polar A2/am space group whereas CaMn2O7 undergoes a structural phase transition from a non-polar tetragonal I4/mmm phase to A2/am in the range 200–300 °C.27 Benedek and Fennie50 showed that for both materials, the polar A2/am phase could be reached from I4/mmm by a combination of octahedral rotation distortions corresponding to a’ a c’ (this distortion transforms like the irreps X4) and a’ a c’ (X5). Both modes combined again give the familiar a’ a c’ tilt pattern of Pnma perovskites and couple trilinearly to a zone-center polar mode of Γ5 symmetry. Hence, the Ruddlesden–Popper phases ‘inherit’ the structural distortions of their parent perovskites, like the AAB’O6 family discussed above, and despite any differences in lattice topology between these two families of materials, the microscopic mechanism that gives rise to the polarization in Ca3Ti2O7 and Ca3Mn2O7 is identical to the double perovskites.

In an exciting development, Oh and co-workers106 recently demonstrated that the polarization in Ca3Ti2O7 single crystals can be switched with an applied electric field (although switching was not demonstrated, experimental support for the hybrid improper mechanism was also provided by Senn et al.107). The work of Oh et al. is significant for several reasons. Firstly, it was not apparent from the theoretical studies40,50 whether the polarization could be switched experimentally or what the switching mechanism might be. In particular, there were concerns that the switching barrier (and hence the switching field) may be impractically high. Related to this, one of the most intriguing features of hybrid improper ferroelectricity is the possibility of coupling other lattice distortions or physical properties to the polarization, such that when the polarization is switched with an electric field, the other structural distortions or properties are switched also. For example, Benedek and Fennie showed28 that the magnetism in CaMn2O7 is coupled to the polarization such that (a) when inversion symmetry is broken and the polarization condenses, the magnetization also switches on, and (b) when an electric field is used to switch the polarization, the magnetization also switches 180°. That is, the magnetization is electric field-controllable. Although this prediction has not been confirmed experimentally, recent work by Pitcher et al.,108 has shown that the polarization and magnetization can co-exist in double perovskite (Ca3Sr1−yTby)1.15Tb1.85Fe2O7 at room temperature, whereas Ca3Mn2O7 is only magnetically ordered below 115 K; the polarization in this double perovskite compound arises...
tolerance factor of the parent ABO$_3$ phase: as the tolerance
phases containing only a single A-site cation relies only on the
mechanism), since only even-
this limitation. In fact, ref. 40 showed that the same general
skites, ordering multiple cations can be used to circumvent
polarization also increases. As in the cation ordered perov-

Figure 5 shows the layer-resolved polarization for Ca$_3$Mn$_2$O$_7$
from first-principles calculations.$^{199}$ As in the double perov-
skites, the polarization arises from anti-polar displacements of
the A-site cations. The rocksalt interface breaks the inversion
center at the B-site such that the A-site cations in the AO layer
directly adjacent to the interface are crystallographically
different to the A-site cations in the middle of the perovskite
block. Hence, the rocksalt interface satisfies the chemical
criterion by creating symmetry-inequivalent A-sites. In addition,
the interface breaks the connectivity of the BO$_6$ octahedra
along [001] such that there is an odd number of AO layers in
the perovskite block, which ensures that the induced layer
polarizations do not completely cancel. It follows that only
even-$n$ Ruddlesden–Popper phases will be polar (through this
mechanism), since only even-$n$ phases contain an odd number
of AO layers in the perovskite block.

Recent work by Balachandran and co-workers$^{110}$ has also
provided a more exhaustive set of guidelines for lifting inversion
symmetry in $n =$ 1 Ruddlesden–Popper phases, which
tend to form in centrosymmetric structures compared to the
$n =$ 2 family. Three distinct cases were discussed: (i) no cation
order, (ii) A-site order, and (iii) B-site order. The consequence
of the cation ordering in combination with various octahedral
tilt patterns, including those beyond the most familiar $a' \ a' \ c'$,
was then treated with group-theoretical methods. Interestingly
and unlike the three-dimensional perovskites, there are combi-
inations of tilt patterns that will lift inversion symmetry in the
absence of cation order in A$_2$BO$_4$ materials (case i). The syn-
thetic challenge, however, is choosing the optimal cations that
will simultaneously favor two distinct tilt modes. In ref. 110
the authors provided a data-driven model founded on Bayesian
inference that allows for the chemical selections. Case ii with
A and A' was also suggested to be a promising strategy and rea-
alyzed experimentally by Akamatsu et al.$^{111}$ in a new RNaTiO$_4$
family of piezoeactive $n =$ 1 Ruddlesden–Popper phases. These
experimental findings increased considerably the number of
known $n =$ 1 Ruddlesden–Popper materials and demonstrate
the power of combining predictive theories based on symmetry
arguments with first-principles calculations and dedicated
experimentation.

3.3. Aurivillius phases

Aurivillius phases of generic formula Bi$_2$AM$_{n-1}$B$_n$O$_{3n+1}$
form another interesting family of naturally-occurring layered perov-
skites.$^{14}$ Their structure is made of fluoro-like Bi$_2$O$_2$ layers,
alternating along the c-axis with perovskite-like AM$_{n-1}$B$_n$O$_{3n+1}$
blocks, where $m$ is the number of BO$_6$ octahedra in the perov-
skite-like blocks; see Fig. 1. As in the Ruddlesden–Popper
phases, the BO$_6$ octahedra are only connected in two direc-
tions. Typically, the A-site (12-coordinated) is occupied by
mono-, di- or trivalent cations such as Na$^+$, K$^+$, Ba$^{2+}$, Sr$^{2+}$, Ca$^{2+}$,
Pb$^{2+}$, Bi$^{3+}$ or Ln$^{3+}$, and the B-site (6-coordinated) by d$^0$ tetra-,
penta- or hexavalent cations such as Ti$^{4+}$, Nb$^{5+}$, Ta$^{5+}$, W$^{6+}$. The
case of non-d$^0$ cations like Fe$^{3+}$, Ru$^{4+}$, Cr$^{3+}$, Ir$^{5+}$ or Mn$^{4+}$ at the
B site has also been considered in the search for magnetic and
multiferroic Aurivillius phases.$^{112-116}$

At the structural and functional levels, most Aurivillius
phases share common characteristics. At high temperatures,
they crystallize in the tetragonal I4/mmm space group (except
for Bi$_2$WO$_6$, see later), which can be seen as the prototypical
high-symmetry reference structure for the whole family. At low
temperatures, the majority of Aurivillius phases adopt a polar
orthorhombic (or monoclinic) ground-state with a and b cell
parameters remaining very close. Typically, this ground-state is
ferroelectric (except for Bi$_2$W$_2$O$_9$ and Sb$_2$WO$_6$ and exhi-
bits a large spontaneous polarization ($\approx$30–50 $\mu$C cm$^{-2}$) and
high Curie temperature ($T_c > 600$ K). Combined with fatigue-
free behavior and low leakage currents, these features make
these compounds very attractive for ferroelectric applications.
They usually behave as normal ferroelectrics but systems with
large atomic disorder between the Bi and A sites can also show
relaxor behavior.$^{119}$ The other functional properties (piezoelec-
tric, electro-optics, etc.) of Aurivillius phases have not been extensively investigated so far but have been predicted to be comparable to conventional ferroelectrics, such as PbTiO$_3$. Aurivillius phases appear attractive also in view of their high ionic conductivity and photocatalytic activity. They were also proposed as potential candidates for superconductivity.

The experimentally observed orthorhombic or monoclinic ground-state structures result always from only small distortions of the $I4/mmm$ reference phase. Their symmetry is, in each case, a subgroup of $I4/mmm$ but not an isotropy subgroup, which means that modes transforming like more than one irreducible representation must be invoked to explain the observed symmetry breaking. The parent $I4/mmm$ phase of these compounds typically exhibits numerous unstable phonon modes and the numbers and types of atomic motions involved in the symmetry lowering leading to the ground state can depend on the chemical composition but usually they include (i) tilts of the oxygen octahedra around the $a$-axis, (ii) rotations of the oxygen octahedra around the $c$-axis and (iii) polar cation motions along the $a$-axis, i.e., the (110) direction of the tetragonal reference structure. Recent studies shed new light on the way these distortions couple together to produce the ground state. In addition, in contrast to the double perovskites and Ruddlesden–Popper phases discussed above, the lattice dynamics of the Aurivillius phases cannot be linked to any parent perovskite phase. This is because the thickness $m$ of the perovskite-like block cannot be systematically increased while keeping the same A and B cations. The only exception is in the absence of A cations, as in the $Bi_2WmO_{4m+1}$ series. The reason originates in the formal charges of the $[Bi_2O_5]$ and $[A_{m-1}B_mO_{4m+2}]^{2-}$ layers which requires the combination of $A^{3+}$ and $B^{7+}$ cations satisfying: $(m-1)x+y-2(3m-1)=-2$ or equivalently $(x+y-6)m=x$. For $m=1$, the only possibility is $x=0$ and $y=6$, which appears also as a generic solution for any value of $m$. At $m=2$ and $m=3$, another integer solution is $(x=2,y=5)$ and $(x=3,y=4)$ respectively. Those with larger $m$ typically combine different cations at either A or B site, in order to provide an appropriate average fractional formal charge. As illustrated in Table 1, various phases are known and have been investigated extensively. Aurivillius can also form mixed layered structures in which Bi$_2$O$_3$ planes alternate with two or more perovskite-like blocks of different thicknesses and composition. Examples of such intergrowths are Bi$_2$Ti$_4$NbO$_{13}$ and Bi$_2$Ti$_3$Nb$_2$O$_{13}$, which can be viewed as the stacking of Bi$_2$Ti$_4$NbO$_{13}$ and Bi$_2$Ti$_3$Nb$_2$O$_{13}$, respectively. Bi$_2$WO$_6$ (m = 1, BWO) is unique amongst the Aurivillius phases in that it adopts, at high temperatures, an unusual $A2/m$ paraelectric monoclinic phase with edge-shared oxygen octahedra. On cooling, it exhibits a phase transition at 950 °C to an intermediate ferroelectric phase of $B2cb$ symmetry and then a second transition at 670 °C to a ground-state ferroelectric phase of $P2_1ab$ symmetry. Both these ferroelectric phases appear as small distortions of the aristotype $I4/mmm$ phase, although this latter is never reached at high temperature (the system instead undergoes a first-order transition to the $A2/m$ phase). Nonetheless, we can still consider $I4/mmm$ as a hypothetical reference structure, which first-principles calculations have shown to be unstable to numerous structural distortions. The strongest instability is a polar $E_u$ ($\Gamma_5^-$) mode dominated by a displacements of W against the oxygen octahedra in the perovskite layers. Two other relevant instabilities are a $X_1^+$ mode related to rotations of oxygen octahedra around the $c$-axis and a $X_3^+$ mode related to tilts of oxygen octahedra around the $a$-axis. The intermediate $B2cb$ phase is reached from the combination of $\Gamma_5^-$ and $X_1^+$ motions, while the $P2_1ab$ phase requires the additional appearance of a $X_3^+$ distortion. Although the co-existence of these modes allows a priori for additional kinds of atomic displacements through different trilinear coupling terms, the structures of the ferroelectric phases are dominated by displacements arising from the initial instabilities ($\Gamma_5^-$, $X_1^+$ and $X_3^+$). Inspection of the energy landscape highlights that the bi-quadratic couplings between $\Gamma_5^-$, $X_1^+$ and $X_3^+$ motions are positive but very weak so that these modes behave rather independently. The spontaneous polarization $P_s = 48 \mu C \cdot m^{-2}$ is mainly produced by the unstable $\Gamma_5^-$ mode and so arises from the motion of W and O in the perovskite block. An additional contribution could also come from a rigid motion of the Bi$_2$O$_2$ layers relative to the perovskite-like blocks, associated with a harder mode.

$$\text{SrBi}_2\text{Ta}_2\text{O}_6 (m = 2, \text{SBT})$$ crystallizes at high temperature in the prototype $I4/mmm$ phase. Similarly to BWO, this phase exhibits various structural instabilities including a polar $E_u$ mode associated with an anti phase displacement of the Bi atoms and the perovskite blocks (sometimes referred to as a rigid layer mode) and a $X_1^+$ mode associated with tilts of the oxygen octahedra along the $a$-axis. In SBT, the strongest instability is the $X_3^+$ mode and its condensation brings the system to an intermediate non-polar $Amam$ phase. The $X_3^+$ and $E_u$ modes have a strong positive biquadratic coupling – the condensation of both modes simultaneously is energetically unfavored – which suggests that $Amam$ should be the ground-state. It was shown however that a strong trilinear coupling between $X_1^+$, $E_u$ and a hard $X_3^+$ mode, involving only oxygen motion within the [Bi$_2$O$_3$] layer, drives the system into a ground-state ferroelectric structure $A2_1am$ combining all three modes. Sr$_2$Bi$_4$Nb$_2$O$_{13}$, isomorphous to SBT, has the same ground-state space group but does not go through an intermediate phase: it displays a direct phase transition from $I4/mmm$. 

<table>
<thead>
<tr>
<th>Example</th>
<th>$m$</th>
<th>$x$</th>
<th>$y$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Bi}_2\text{WO}_6$, $\text{Bi}_2\text{MoO}_6$</td>
<td>1</td>
<td>6</td>
<td>6</td>
<td>118, 126, 128, 132</td>
</tr>
<tr>
<td>$\text{Bi}_2\text{WO}_6$</td>
<td>2</td>
<td>6</td>
<td>6</td>
<td>117</td>
</tr>
<tr>
<td>$\text{CaBi}_2\text{Nb}<em>2\text{O}</em>{10}$, $\text{SrBi}_2\text{Ta}_2\text{O}_6$</td>
<td>3</td>
<td>5</td>
<td>15, 125, 127, 133</td>
<td></td>
</tr>
<tr>
<td>$\text{Bi}_2\text{W}<em>3\text{O}</em>{12}$</td>
<td>3</td>
<td>4</td>
<td>134</td>
<td></td>
</tr>
<tr>
<td>$\text{Bi}_2\text{Ti}<em>3\text{O}</em>{12}$</td>
<td>4</td>
<td>3</td>
<td>22, 123, 124, 127</td>
<td></td>
</tr>
<tr>
<td>$\text{Bi}_2\text{WO}_6$</td>
<td>4</td>
<td>6</td>
<td>6</td>
<td>—</td>
</tr>
<tr>
<td>$\text{SrBi}_2\text{Ti}<em>4\text{O}</em>{15}$</td>
<td>8/3</td>
<td>4</td>
<td>135</td>
<td></td>
</tr>
<tr>
<td>$\text{SrBi}_2\text{Ti}<em>4\text{O}</em>{15}$</td>
<td>3</td>
<td>15/4</td>
<td>135</td>
<td></td>
</tr>
</tbody>
</table>
Intermediate phases have also not been detected in Bi$_2$Tl$_3$FeO$_{15}$ or Bi$_3$Tl$_2$O$_{12}$, both of which seem to exhibit a direct phase transition from the high-temperature tetragonal to a ferroelectric phase. Similarly, an $Ammm$ intermediate phase has been detected experimentally in SrBi$_2$Ti$_3$O$_{12}$, in the region 550–650 °C, but not in its analogue Bi$_2$Ti$_3$FeO$_{15}$.\(^{61}\)

Bi$_3$Tl$_2$O$_{12}$ ($m = 3$) was originally suggested to exhibit a single phase transition from the $I4/mmm$ high temperature phase to a $B1a1$ ferroelectric monoclinic ground-state.\(^{123}\) However this study lacked the small temperature interval necessary to detect the possible intermediate phases. Indeed, two more recent studies have suggested differing phase transition sequences\(^{139,140}\) and the mechanism of the phase transition is not yet fully understood. Theoretical studies suggest that it may involve a complex interplay of six different normal modes, belonging to four different irreducible representations. The primary instabilities consist of a polar $E_u$ mode located in the center of the perovskite block and dominated by Bi and O motions, a $X_3^+$ mode related to tilts of the oxygen octahedra along $a$ and a $X_2^+$ mode associated with oxygen rotations around $c$. These three modes have the correct symmetry properties to lower the symmetry from $I4/mmm$ to $B1a1$. Harder modes nevertheless do appear in the ground-state. The assumption of simultaneous condensation of the different order parameters through the so-called avalanche transition was made, but first-principles energy and phonon calculations of this compound failed to show any features that would favor such a mechanism.\(^{141}\) The true nature of any intermediate phases in Bi$_3$Tl$_2$O$_{12}$ is thus yet to be established.

### 3.4. Dion–Jacobson phases

The crystal chemistry of the Dion–Jacobson phases has not been as extensively investigated as the Ruddlesden–Popper and Aurivillius phases. However, inspired by earlier experimental work, there has been a recent resurgence of interest (both from theorists and experimentalists) in Dion–Jacobson materials. Similar to Ruddlesden–Popper phases, the Dion–Jacobson phases also form a homologous series with general formula $A'[A_{n-1}B_nO_{3n+1}]$ for $n > 2$, whereas the $n = 1$ member has the formula ABO$_4$ (most known $n = 1$ materials are fluorides, however).\(^{142}\) The $A'$ cation separates the perovskite-like blocks in Dion–Jacobson phases with $n > 1$ and is typically an alkali cation, but can also be a transition metal halide complex, such as [MnCl].\(^{143-146}\) Among the oxide $n > 1$ Dion–Jacobson phases we focus on below, compositions with $A$ = a rare earth or Bi\(^{147}\) and $B$ = Nb or Ta have been synthesized (oxy-fluoride Dion–Jacobson phases are also known).\(^{147-149}\)

As with the Aurivillius phases above, the lattice dynamics of the Dion–Jacobson phases cannot be linked to that of a parent perovskite phase because the material that makes up the perovskite-like blocks as $n \to \infty$ in the Dion–Jacobson phases does not exist independently as a bulk perovskite. For example, for a Dion–Jacobson phase with formula Cs[La$_{n-1}$Nb$_n$O$_{3n+1}$] the perovskite-like blocks are composed of La–O and Nb–O layers, but there is no perovskite with formula LaNbO$_3$. A composition with LaNbO$_3$ would be allowed and indeed this is the hypothetical $n = 1$ member of the series; this stoichiometry is known to adopt a different structure. Hence, there does not seem to be any simple choice of fundamental building block for the Dion–Jacobson phases in the same sense that there is for the A-site ordered double perovskites and Ruddlesden–Popper phases. However, we can still obtain information about trends by comparing the behavior of different members of the family and this is the approach we take here.

The undistorted prototype structure for the Dion–Jacobson phases varies according to the identity of the $A'$ cation. For smaller $A'$ cations (Li, Na), the perovskite blocks in adjacent layers are offset from each other by $1/2[110]$ and the undistorted prototype has $I4/mmm$ symmetry, like the Ruddlesden–Popper phases. The prototype has $Cmcm$ symmetry for slightly larger cations (such as K), in which case the perovskite blocks in adjacent layers are offset by $1/2[100]$ or $1/2[010]$. All of the materials discussed below contain Cs or Rb at the $A'$ site and here the prototype has $P4/m/mmm$ symmetry with the perovskite blocks in adjacent layers directly aligned.

CsBiNb$_2$O$_7$ and RbBiNb$_2$O$_7$ are perhaps the most well-studied polar Dion–Jacobson materials. They were first synthesized relatively recently by Subramanian and co-workers\(^{150}\) and characterized as orthorhombic with $a_0 \sim b_0 \sim 2a_0$ and $c_0 \sim 2c_T$, where $a_0$, $b_0$ and $c_0$ refer to the lattice parameters of the orthorhombic structure and $a_0$ and $c_0$ refer to the lattice parameters of the undistorted $P4/m/mmm$ prototype. Although CsBiNb$_2$O$_7$ and RbBiNb$_2$O$_7$ were identified as having a larger unit cell and lower symmetry than the prototype phase, neither of the materials was initially reported as polar. The subsequent powder neutron diffraction study of Snedden et al.\(^{31}\) showed that CsBiNb$_2$O$_7$ is indeed polar (along with CsNdNb$_2$O$_7$) with space group $Pmc2_1$ and lattice parameters $a_0 \sim b_0 \sim \sqrt{2} a_0$ and $c_0 \sim c_T$, i.e., the $a$ and $b$ lattice parameters are enlarged compared to the undistorted phase but in a different sense to that reported by Subramanian. In their analysis of the structures of CsBiNb$_2$O$_7$ and CsNdNb$_2$O$_7$ Snedden noted the “large polar displacements of the perovskite A cation with cooperative octahedral tilting” corresponding to the $a' a' c'$ Glazer tilt pattern. The first-principles calculations of Fennie and Rabe\(^{151}\) confirmed the importance of octahedral rotations in giving rise to the polar structure, but the mechanism through which the polar phase emerges from the undistorted $P4/m/mmm$ prototype was not elucidated. In addition, although experiments had confirmed that both CsBiNb$_2$O$_7$ and CsNdNb$_2$O$_7$ belong to polar space groups, neither material appeared to be ferroelectric (polarization switching was not demonstrated). Goff\(^{132}\) reported a structural study of CsBiNb$_2$O$_7$ by powder neutron diffraction up to 900 °C, but saw no significant change in the orthorhombic or polar distortion; the recent study of dielectric properties by Chen et al.\(^{34}\) suggests a $T_c$ of 1033 °C, so a further diffraction-based study is now prompted in order to elucidate the details of this transition.

The polarity of both CsBiNb$_2$O$_7$ and RbBiNb$_2$O$_7$ is most often ascribed to the stereoactive Bi$^{3+}$ lone pair. However, this
cannot explain why CsNdNb$_2$O$_7$ adopts a polar structure since this material does not contain any lone pair cations. It is also somewhat curious that of the many known $n = 2$ Dion–Jacobson phases, only a few have been definitively identified as belonging to polar space groups. A recent first-principles study$^{35}$ of a series of $n = 2$ Dion–Jacobson phases (A’ = Rb, Cs, A = La, Nd, Y, Bi, B = Nb) predicted that all of these materials should adopt the same polar Pmc$_2$$_1$ space group as the Bi-containing compounds, even CsLaNb$_2$O$_7$, which has only ever been characterized in the undistorted P4/mmm phase and is often considered the archetype of this structure. Ref. 35 also showed that the transition from P4/mmm to Pmc$_2$$_1$ is driven by the same trilinear coupling mechanism found in the materials families discussed above: two octahedral rotation distortions, one similar to the $a^0a^0c^c$ Glazer tilt pattern (transforming like the irrep M$_2^+$) and the other to $a^a c^c$ (M$_1^-$), couple to a polar mode ($\Gamma_5^+$) to give rise to a macroscopic polarization. As with the other layered materials discussed in this Perspective, the octahedral rotations optimize the A-site coordination environment, which is under-bonded in P4/mmm. This is the case even in the Bi-containing compounds, i.e., although the lone pair on Bi enhances the magnitude of the polarization in the polar phase, these Dion–Jacobson materials can undergo polar distortions even in the absence of stereoeactive cations.

Fig. 6 shows the layer-resolved polarization for Pmc$_2$$_1$ CsLaNb$_2$O$_7$ from first-principles calculations. In contrast to the pattern of anti-polar displacements found in the double perovskites and Ruddlesden–Popper phases, here the layer polarizations are all aligned and hence the macroscopic polarization does not arise from an incomplete cancelation of oppositely oriented A–O layer polarizations. The reason for this is not difficult to understand: there is only one A–O layer in the $n = 2$ Dion–Jacobson phases, as opposed to at least two in the double perovskites and Ruddlesden–Popper phases. Hence, even though A-site under bonding is ultimately responsible for driving the transition from P4/mmm to Pmc$_2$$_1$, the main contribution to the polarization actually comes from the B–O layers, simply because there are two B–O layers per unit cell. In addition, similar to the Ruddlesden–Popper phases, only even $n$ Dion–Jacobson phases will be polar, i.e., the $a^a c^c$ tilt pattern does not give rise to a polar space group in odd-$n$ Dion–Jacobson phases,$^{152,153}$ but a polar structure may emerge through some other mechanism.

The recent flurry of results and interest in Dion–Jacobson phases has reinvigorated experimental efforts. Polarization switching has now been demonstrated in both CsBiNb$_2$O$_7$ and RbBiNb$_2$O$_7$ and the experimentally observed polarizations are generally in good agreement with those predicted from theory. Several Dion–Jacobson materials that had previously only been reported in the undistorted P4/mmm structure have been re-examined and preliminary results suggest that the list of polar Dion–Jacobson phases may be growing. However, the nature of the high-temperature structural behaviour of the Dion–Jacobson family is also much less well studied than that of the Ruddlesden–Popper and Aurivillius phases. Apart from the study of CsBiNb$_2$O$_7$ by Goff et al.,$^{32}$ which unfortunately did not reach TC, we are only aware of one other variable temperature crystallographic study: Geselbracht et al.$^{154}$ reported from powder XRD that RbCa$_2$Nb$_3$O$_{10}$ retains tetragonal symmetry throughout the range RT $<$ T $<$ 1000 $^\circ$C. In addition, the presence of alkali metals in the inter-layer regions makes these materials intrinsically susceptible to ion-exchange and water-uptake phenomena, thus exacerbating the difficulties in obtaining robust ferroelectric behavior. Further studies might therefore target compositions with, for example, Ba$^{2+}$ in the interlayer A’ sites. Examples of such materials are known, such as BaSrTa$_2$O$_7$; previous studies$^{155}$ have suggested non-polar symmetry (Immm) at ambient temperature.

4. Summary and outlook

Hybrid improper ferroelectricity and the trilinear coupling mechanism are much more than a simple academic curiosity. Rather, they provide a unifying framework for understanding the crystal chemistry of polar structures in many families of layered perovskites and a powerful pathway to engineer new or enhanced functional properties. Independent of the primary order parameters and the improper nature of the phase transition, the trilinear coupling of lattice modes in the low-symmetry phase appears in itself as a key feature to be exploited. As anticipated by Bousquet et al.,$^{37}$ the linear coupling between polar and non-polar distortions offers a unique opportunity to tune with an electric field non-polar distortions and the properties linked to them. A concrete realization of this is, for example, the predicted electric field-controllable magnetization in Ruddlesden–Popper Ca$_3$Mn$_2$O$_7$.$^{50}$

From the experimental side, the present overview shows that a combination of first-principles calculations, guided by symmetry analysis of all possible distortion mode pathways provides an essential guide for the experimental inorganic chemist in targeting suitable compositions likely to display ferroelectricity in the various families of layered perovskites. Crystallographic studies must become more detailed and...
reliable, both in characterizing the ambient temperature phases and the nature of the high-temperature phase transitions towards and into the paraelectric state. Such studies require either single crystal X-ray or the highest quality powder neutron diffraction data. In addition, care must be taken in processing of ceramics suitable for robust and reliable dielectric data to be obtained.

Most efforts so far have focused on specific trilinear terms involving the polarization and antiferrodistortive oxygen motions linked to Glazer’s tilt patterns \( \rho^{\alpha} \rho^{\beta} \rho^{\gamma} \) and \( \rho^{a} \rho^{b} \rho^{c} \). Trilinear terms can also couple the polarization to other types of atomic motions like Jahn–Teller distortions. In the highly strained \( Pmc_2_1 \) phase of BiFeO\(_3\) for instance,\(^{159}\) a trilinear term involving the polarization, oxygen rotations and anti-polar distortion was predicted to allow for electric control of the magnetization. In AVO\(_3\)/AVO\(_1\) superlattices,\(^{160}\) a term linking two Jahn–Teller distortions to the polarization was recently shown to be able to produce an out-of-plane polarization and to allow for electric-field induced magnetic phase transitions. Layered perovskites allow for various trilinear mechanisms and offer a still widely unexplored playground for the coupling of functional properties and the appearance of unexpected phenomena.

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