Functional materials design: octahedral tilts in hybrid $n = 1$ Ruddlesden–Popper phases

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The importance of hybrid perovskites and more recently their layered analogues [e.g. the high efficiency and stable Ruddlesden–Popper (RP) phases (Stoumpos et al., 2016; Tsai et al., 2016)] is undisputed with significant research resources dedicated to these functional materials. Recently several excellent studies of the structural chemistry of hybrid layered perovskite-related materials have been published (Saparov & Mitzi, 2016; Mao et al., 2019) including an in-depth exploration by McNulty and Lightfoot of several families of layered hybrid perovskite-related materials (McNulty & Lightfoot, 2021). Understanding the precise structure (and symmetry) of these systems is essential for designing and optimizing functional materials, but until recently, there have been few studies on specific families: Li et al. provide an interesting comparison of hybrid Dion–Jacobson materials (Li et al., 2019) with their all-inorganic analogues (Aleksandrov & Bartolomé, 2001), but the $n = 1$ RP family has not received a systematic crystallographic investigation until now. In this issue of *IUCrJ*, Liu et al. take on this challenge with gusto, mapping out the structures expected for the hybrid $n = 1$ RP materials (Liu et al., 2023). This builds on the excellent work of McNulty & Lightfoot (2021), but by focusing on only a single family, Liu et al. can identify specific drivers for tilts and structure types, and even go some way to providing a blueprint for designing hybrid $n = 1$ RP phases with targeted symmetries.

In order to fully appreciate the authors’ work, it is useful to briefly consider the wider field of structural chemistry of perovskites (and related phases). The mineral perovskite, CaTiO$_3$, named after Count Perovski, gives its name to this structure type and well known family of materials (Attfield et al., 2015). Perovskites have long been an important research focus, from the all-inorganic phases [e.g. ferroelectric BaTiO$_3$ (Megaw, 1952)] to the recent ‘hybrid’ perovskites [e.g. CH$_3$NH$_3$PbI$_3$ (Kojima et al., 2009)] known for their impressive photovoltaic properties (NREL, 2023). With the general formula $ABX_3$ ($A$, $B$ are cations; $X$ are anions), the typical perovskite structure can be described in terms of cubic-close-packed $AX_3$ layers with smaller $B$ cations in between (West, 2014) to give the familiar three-dimensional network of corner-linked $BX_6$ octahedra [Fig. 1(a)]. What makes the perovskite family of materials so important is their compositional flexibility: this allows the design of functional perovskite materials with a huge range of properties.

The relatively simple topology of corner-linked $BX_6$ shown in Fig. 1(a) belies the rich structural complexity of this family: the aristotype structure is of $Pm3m$ symmetry, but few materials adopt this ideal structure and several types of distortion (driven by geometric or electronic factors) are possible (Salje et al., 1989). An important type of distortion involves rotation of essentially rigid $BX_6$ octahedra (Glazer, 1972; Howard & Stokes, 1998; Woodward, 1997) to optimize bonding for the various ions. The resulting change in structure (and symmetry) has an enormous impact on properties and so tuning these rotations has been a powerful method of optimizing properties.

Alongside the perovskite with its three-dimensional connectivity of $BX_6$ octahedra, several families of perovskite-related materials with layered structures are known, including the RP (Ruddlesden & Popper, 1957, 1958) and Aurivillius families (Aurivillius, 1950a,b, 1952) [Figs. 1(b), 1(c)]. The connectivity of $BX_6$ octahedra is maintained in two dimensions, but perovskite blocks are separated along the third direction by either $AX$ rocksalt layers (for the RP phases) or by fluorite-like [Bi$_2$O$_2$]$^{2+}$ layers for the Aurivillius phases. As for the $ABX_3$ perovskites, these phases readily undergo distortions from their aristotype structures (of $I4/mmm$ symmetry) involving rotations of the $BX_6$ octahedra. These have been systematically explored in the context of all-inorganic materials (Aleksandrov & Bartolome, 1994; Aleksandrov & Bartolomé, 2001; Hatch & Stokes, 1998; Woodward, 1997) to optimize bonding for the various ions. The resulting change in structure (and symmetry) has an enormous impact on properties and so tuning these rotations has been a powerful method of optimizing properties.

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1987; Hatch et al., 1989) and this understanding has been key in designing complex functional materials (Pitcher et al., 2015; de Araujo et al., 1995; Oh et al., 2015).

The hybrid analogues adopt structures with the same topology, comprising networks of corner-linked $BX_6$ octahedra (such as the lead halide systems), but with molecular cations on the $A$ site, such as ammonium and methylammonium. The hybrid systems have similar structural degrees of freedom to the all-inorganic materials but with added complexity due to the shape and different bonding characteristics of the molecular $A$ cations (Saparov & Mitzi, 2016; Mao et al., 2019; McNulty & Lightfoot, 2021). Understanding the structures and symmetries of these hybrid layered perovskite-related systems, with significant dispersion forces and hydrogen bonding distinguishing them from their all-inorganic counterparts, will be key for designing optimized functional materials.

Liu et al. focus on the $n = 1$ RP [Fig. 1(b)] and their work (Liu et al., 2023) will be valuable to those studying both on hybrid and all-inorganic materials. Their approach is to use the extremely powerful web-based ISODISTORT software (Stokes et al., 2006; Stokes et al., 2022) to identify the symmetry-adapted distortion modes to describe possible rotations of $BX_6$ octahedra about both in-plane and out-of-plane axes. The authors then determine the resulting space groups and basis vectors that allow these degrees of freedom (individual tilts and combinations of tilts). Crucially this work builds on earlier studies by including in-phase tilts about an in-plane axis [$\psi$ tilts, in Aleksandrov notation (Aleksandrov et al., 1987)]. These tabulated results alone will be an important resource for those working on the structural characterization of $n = 1$ RP (and Aurivillius) phases.

Surveying structural databases (the Cambridge Structural Database and the Inorganic Crystal Structure Database) allowed the authors to identify common structures and tilt patterns in hybrid $n = 1$ RPs and to make comparisons with the all-inorganic analogues. Their findings highlight the importance of hydrogen bonding and dispersion forces – both in explaining the relative energy scales (and therefore temperatures) of the distortions, and in understanding the different tilt patterns observed.

A key highlight for me are the findings regarding loss of inversion symmetry in these $n = 1$ materials. Both out-of-phase tilts about an in-plane axis ($\phi$ tilts) and tilts about an out-of-plane axis ($\theta$ tilts) do not break inversion symmetry – either alone, or in combination [as emphasized by McNulty & Lightfoot (2021)] giving centrosymmetric structures (see Table 1 in Liu et al.). The $n = 1$ Aurivillius phases provide all-inorganic examples of this, with the common tilt pattern $\phi\theta\phi\theta\phi\theta\phi\theta\phi\theta\phi\theta\phi\theta\phi\theta\phi\theta\phi\theta\phi\theta\phi$ giving centrosymmetric structures of $Pbca$ symmetry:

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**Figure 1**

In this figure (a) shows the ideal aristotype structure of the cubic perovskite with general formula $ABX_3$; (b) shows the ideal structure of an $n = 1$ RP phase (e.g. Sr$_2$TiO$_4$) and (c) shows the aristotype structure of an $n = 1$ Aurivillius phase [e.g. Bi$_2$TiO$_4$F$_2$ (Needs et al., 2005)]. $A$, $B$ and $X$ ions are shown in green, blue and red, respectively with $BX_6$ octahedra shown in blue and the [Bi$_2$O$_2$]$^{2+}$ fluorite-like layers in the Aurivillius structure shown in red.
(a) with only tilts [e.g. $\text{Bi}_2\text{NbO}_5\text{F}$ (McCabe et al., 2007)], the structure is of $\text{Pbca}$ symmetry;

(b) additional polar displacements are needed to break inversion symmetry [e.g. to $\text{Pca}_2\text{I}$ symmetry with in-plane polarization as for $\text{Bi}_2\text{WO}_6$ (Knight, 1992, 1993) and $\text{Bi}_2\text{MoO}_6$ (Teller et al., 1984); see also the clear discussion by McNulty & Lightfoot (2021), and the symmetry map for $\text{Bi}_2\text{TiO}_6\text{F}_2$ (Giddings et al., 2021)].

This contrasts with the $n = 2$ RP and Aurivillius phases for which equivalent tilt patterns may break inversion symmetry (Aleksandrov & Bartolome, 1994) [e.g. $\text{A}_2\text{LaTaTiO}_7$ (Mallick et al., 2021), $\text{Sr}_3\text{Zr}_2\text{O}_7$ (Yoshida et al., 2018)].

On the other hand, if in-phase ($\psi$) tilts about an in-plane axis are included, inversion symmetry is often broken (see Table 2 in Liu et al.). There are few examples of systems including $\psi$ tilts. The authors explain this in terms of the different cation environments that result, and suggest cation-ordering strategies to design such non-centrosymmetric systems among the hybrid $n = 1$ RP phases.

This systematic crystallographic study of the possible tilt combinations and structures for $n = 1$ RP phases will be a key reference for those working on both hybrid and on all-inorganic systems. It will be particularly exciting to see researchers apply this understanding of the molecular A cation bonding to realize specific tilt combinations (and symmetries) as they seek to prepare new functional materials with optimized properties.

References


