# Recipes for Improper Ferroelectricity in Molecular Perovskites

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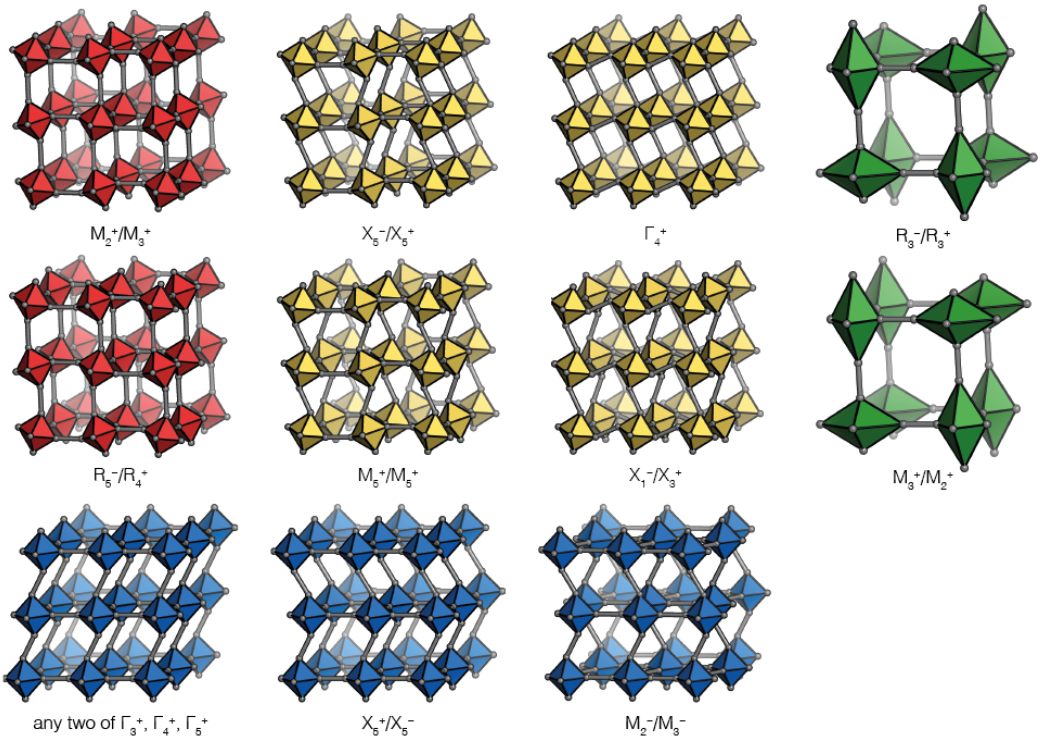
Supplementary Information




**Supplementary Figure 1.** Common structural distortions of the molecular perovskites. Conventional tilting is shown in red, unconventional tilting in yellow, columnar shifts in blue and Jahn-Teller distortions in green. The pictures are accompanied by the irrep in the setting with the A-site/B-site at the origin.

**Supplementary Table 1.** Conversion of irreps for the different settings of the perovskite unit cell.

| Distortion | Origin at A | Origin at B |
|---|---|---|
| Symmetric strain | $\Gamma_1^+$ | $\Gamma_1^+$ |
| Tetragonal strain | $\Gamma_3^+$ | $\Gamma_3^+$ |
| Unconventional tilt | $\Gamma_4^+$ | $\Gamma_4^+$ |
| Orthorhombic strain | $\Gamma_5^+$ | $\Gamma_5^+$ |
| Acoustic polar mode | $\Gamma_4^-$ | $\Gamma_4^-$ |
| Octahedral deformation | $\Gamma_5^-$ | $\Gamma_5^-$ |
| Out-of-phase shift | $X_1^+$ | $X_3^-$ |
| Octahedral deformation | $X_2^+$ | $X_4^-$ |
| Columnar shift | $X_5^+$ | $X_5^-$ |
| Unconventional tilt | $X_1^-$ | $X_3^+$ |
| Octahedral deformation | $X_2^-$ | $X_4^+$ |
| Jahn-Teller distortion | $X_3^-$ | $X_1^+$ |
| Jahn-Teller distortion | $X_4^-$ | $X_2^+$ |
| Unconventional tilt | $X_5^-$ | $X_5^+$ |
| Octahedral deformation | $M_1^+$ | $M_4^+$ |
| Conventional tilt | $M_2^+$ | $M_3^+$ |
| Jahn-Teller distortion | $M_3^+$ | $M_2^+$ |
| Jahn-Teller distortion | $M_4^+$ | $M_1^+$ |
| Unconventional tilt | $M_5^+$ | $M_5^+$ |
| Octahedral deformation | $M_1^-$ | $M_4^-$ |
| Columnar shift | $M_2^-$ | $M_3^-$ |
| A-site displacement | $M_3^-$ | $M_2^-$ |
| Out-of-phase shift | $M_5^-$ | $M_5^-$ |
| Octahedral deformation | $R_4^+$ | $R_5^-$ |
| Out-of-phase shift | $R_5^+$ | $R_4^-$ |
| B-site cation order | $R_2^-$ | $R_1^+$ |
| Jahn-Teller distortion | $R_3^-$ | $R_3^+$ |
| Octahedral deformation | $R_4^-$ | $R_5^+$ |
| Conventional tilt | $R_5^-$ | $R_4^+$ |

**Supplementary Table 2.** Third-order couplings with polarisation ($\Gamma_4^-$). The coupling of one irrep from each column in a given row will generate a polar distortion, provided that crystal momentum is conserved (*e.g* $X_1^+[½,0,0] + X_3^-[½,0,0]$ but not $X_1^+[½,0,0] + X_3^-[0,½,0]$). Coupling schemes satisfying the restrictions for the conservation of parity and crystal moments NOT listed here may still give piezoelectric space groups.

| | |
|---|---|
| $R^+_{4,5}$ | $R^-_{1,2,3,4,5}$ |
| $R^-_{4,5}$ | $R^+_{1,2,3,4,5}$ |
| $M^+_5$ | $M^-_{1,2,3,4,5}$ |
| $M^-_5$ | $M^+_{1,2,3,4,5}$ |
| $M^+_{1,2}$ | $M^-_{3,4}$ |
| $M^-_{1,2}$ | $M^+_{3,4}$ |
| $X_5^+$ | $X^-_{1,2,3,4,5}$ |
| $X_5^-$ | $X^+_{1,2,3,4,5}$ |
| $X^+_{1,2}$ | $X^-_{3,4}$ |
| $X^-_{1,2}$ | $X^+_{3,4}$ |

**Supplementary Table 3.** Fourth-order couplings with polarisation ($\Gamma_4^-$). The coupling of one irrep from each column in a given row will generate a polar distortion, provided that crystal momentum is conserved (*e.g* $X_1^+[0,½,0]$ + $M_5^-[½,0,½]$ + $R_2^+[½,½,½]$, but not $X_1^+[0,½,0]$ + $M_5^-[0,½,½]$ + $R_2^+[½,½,½]$). Coupling schemes satisfying the restrictions for the conservation of parity and crystal moments NOT listed here may still give piezoelectric space groups.

| | | |
|---|---|---|
| $X^+_{1,2}$ | $M^+_{3,4,5}$ | $R^-_{1,2,3,4,5}$ |
| $X^+_{1,2}$ | $M^-_{3,4,5}$ | $R^+_{1,2,3,4,5}$ |
| $X^-_{1,2}$ | $M^+_{3,4,5}$ | $R^+_{1,2,3,4,5}$ |
| $X^-_{1,2}$ | $M^-_{3,4,5}$ | $R^-_{1,2,3,4,5}$ |
| $X^+_{3,4}$ | $M^+_{1,2,5}$ | $R^-_{1,2,3,4,5}$ |
| $X^+_{3,4}$ | $M^-_{1,2,5}$ | $R^+_{1,2,3,4,5}$ |
| $X^-_{3,4}$ | $M^+_{1,2,5}$ | $R^+_{1,2,3,4,5}$ |
| $X^-_{3,4}$ | $M^-_{1,2,5}$ | $R^-_{1,2,3,4,5}$ |
| $X_5^+$ | $M^+_{1,2,3,4,5}$ | $R^-_{1,2,3,4,5}$ |
| $X_5^+$ | $M^-_{1,2,3,4,5}$ | $R^+_{1,2,3,4,5}$ |
| $X_5^-$ | $M^+_{1,2,3,4,5}$ | $R^+_{1,2,3,4,5}$ |
| $X_5^-$ | $M^-_{1,2,3,4,5}$ | $R^-_{1,2,3,4,5}$ |
| $X^+_{1,2,3,4,5}$ | $M^+_{1,2,3,4,5}$ | $R^-_{4,5}$ |
| $X^+_{1,2,3,4,5}$ | $M^-_{1,2,3,4,5}$ | $R^+_{4,5}$ |
| $X^-_{1,2,3,4,5}$ | $M^+_{1,2,3,4,5}$ | $R^+_{4,5}$ |
| $X^-_{1,2,3,4,5}$ | $M^-_{1,2,3,4,5}$ | $R^-_{4,5}$ |