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Geometric Ferroelectricity in Fluoro-Perovskites

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We used first-principles calculations to investigate the existence and origin of the ferroelectric instability in the $ABF_3$ fluoro-perovskites. We find that many fluoro-perovskites have a ferroelectric instability in their high symmetry cubic structure, which is of similar amplitude to that commonly found in oxide perovskites. In contrast to the oxides, however, the fluorides have nominal Born effective charges, indicating a different mechanism for the instability. We show that the instability originates from ionic size effects, and is therefore in most cases largely insensitive to pressure and strain, again in contrast to the oxide perovskites. An exception is NaMnF$_3$, where coherent epitaxial strain matching to a substrate with equal in-plane lattice constants destabilizes the bulk $Pnma$ structure leading to a ferroelectric, and indeed multiferroic, ground state with an unusual polarization/strain response.

Since its discovery in BaTiO$_3$, ferroelectricity in perovskite-structure oxides has attracted tremendous interest, ranging from fundamental studies to technological applications\textsuperscript{1}. Indeed, the transition-metal/oxygen bond, with its large polarizability, is particularly favourable for promoting the transition-metal off-centering that can result in a ferroelectric ground state\textsuperscript{2,3}. Ferroelectrics also exist, of course, in many material chemistries that do not contain oxygen, with a particularly extensive range of fluorne-based examples, including both polymers\textsuperscript{4} and ceramics in many crystal classes (for a review see Ref. 5). Perhaps not surprisingly given the low polarizability of bonds with fluorine, the mechanisms for ferroelectricity in fluorne-based ferroelectrics are distinct from those in oxides, ranging from molecular reorientation in polymers\textsuperscript{6}, to geometric reconstructions in ceramics\textsuperscript{7}. These alternative mechanisms are of particular interest because, again unlike the oxides, they are not contra-indicated by transition metal $d$ electrons, and so allow simultaneous ferroelectricity and magnetic ordering (multiferroism). Interestingly, however, none of the known perovskite-structure fluorides is reported to be ferroelectric.

In this letter we use first-principles density functional calculations to investigate computationally the tendency towards ferroelectricity in perovskite-structure fluorides. Our goals are two-fold: First, by comparing to the behaviour of ferroelectric perovskite-structure oxides, we further understanding of the driving forces for, and competition between, polar and non-polar structural distortions in both systems. Second, we aim to identify conditions, for example of strain or chemistry, under which ferroelectricity, and perhaps multiferroism, could be stabilized in the fluoride perovskites.

A systematic study of the structural instabilities in the high symmetry cubic halide perovskites was carried out in the 1980’s using interionic potentials\textsuperscript{8}. Phonon frequencies were calculated at the $\Gamma$, $X$, $M$ and $R$ high symmetry points of the cubic Brillouin zone for $ABX_3$, with $A = $ Li, Na, K, Rb or Cs, $B = $ Be, Mg or Ca, and $X$ a halide (F, Cl, Br or I). While none of the perovskites has a ferroelectric ground state (although some, mostly Li, members of the series have the non-perovskite ferroelectric LiNbO$_3$ structure as their ground state), 24 of the 60 cases were found to show a ferroelectric (FE) instability. The instability was usually absent in compounds of the larger $A$ cations (which anyway usually form in a non-perovskite hexagonal structure) and so it was concluded that the Na compounds should be the most promising candidates for ferroelectricity. It was found, however, that in all cases a competing antiferrodistortive (AFD) zone boundary instability corresponding to rotations and tilts of the X octahedra around the $B$ cation, dominated over the weaker polar instability, resulting in a centrosymmetric AFD ground state\textsuperscript{9}. Such competition between AFD and FE instabilities has been widely discussed in the perovskite oxides literature\textsuperscript{9–12} and recently shown, in the case of $Pnma$ perovskites to result from a mutual coupling to an $X_\parallel^+$ mode involving antipolar displacements of the $A$-cations and $X$ sites along the [101] axis as shown in Fig. 1. Indeed artificially removing the $X_\parallel^+$ mode in the calculations for perovskite oxides was shown to induce a ferroelectric ground state\textsuperscript{11}.

Our density functional calculations of the electronic and structural properties were performed using the PAW VASP code\textsuperscript{13}, with the GGA PBEsol exchange correlation functional\textsuperscript{14}, an energy cutoff of 700 eV on the plane wave expansion and a Brillouin-zone k-point sampling of $8 \times 8 \times 8$ within the five 5-atom unit cell. Born effective charges and phonons were calculated using density functional perturbation theory\textsuperscript{15} in a $2 \times 2 \times 2$ supercell. The dynamical matrix was unfolded using the Phonopy code\textsuperscript{16} and the phonon dispersion curves were interpolated from the interatomic force constants (IFCs) using the anaddb module provided with the Abinit software\textsuperscript{17}.

In Fig. 1 we show our calculated phonon dispersion for cubic NaMnF$_3$ with its ground state $G$-type antiferromagnetic (AFM) order. Unstable phonons are shown as negative frequencies. We find a polar instability (of $\Gamma_4$ symmetry) at the zone center with eigendisplacement $\eta$
As a next step in the analysis, we decompose the structural distortions that map the high symmetry cubic perovskite structures into their fully relaxed \( \Gamma_{4} \) ground states into linear combinations of the unstable phonons of the cubic structure\(^{22}\). Our results are shown in Fig. 2 for the \( \text{NaBF}_3 \) series with \( B = \text{Mn}, \text{V}, \text{Zn} \) and \( \text{Ni} \). As expected, and as is the case for \( \text{Pnma} \) perovskite oxides, we find that the strongest contributions come from the two \( (R_{4}^{+} \) and \( M_{3}^{+} \)) unstable AFD modes. The absolute magnitudes of the contributions decrease across the series as the \( B \) site cation becomes smaller, consistent with the reduction in the amount of the tiltings and rotations when the tolerance factor increases. The next largest contribution is from the \( X_{5}^{+} \) mode with its anti-polar \( A \)-site motions; notably its contribution to the relaxed ground state is approximately double that of the same mode in the perovskite oxides. Again, the magnitude of its contribution is smaller for smaller \( B \) site cations. There are also small contributions from the \( R_{5}^{+} \) and \( M_{4}^{+} \) modes which are roughly constant across the series and which we do not show.

In Table I we list the frequencies of the unstable modes at the high symmetry points for the \( \text{NaMnF}_3 \) case of Fig. 1 as well as for series obtained by first changing the \( B \) site, then the \( A \) site. We note that the \( R_{3}^{+} \) and \( M_{3}^{+} \) instabilities (which are the AFD out-of-phase and in-phase rotations of the octahedra) are almost unaffected by the change of the \( B \) site. However, the frequencies of the ferroelectric \( \Gamma_{4}^{+} \), and the antiferroelectric \( X_{5}^{+} \) and \( R_{5}^{+} \) instabilities vary with the \( B \) site, with larger radius \( B \) cations having larger cell volumes and in turn stronger FE and AFE instabilities. Interestingly, we find quite different behaviour for the \( A \) sites: Both \( R_{4}^{+} \) and \( M_{4}^{+} \) AFD modes, and \( X_{5}^{+} \) and \( R_{5}^{+} \) AFE modes show a strong dependence on the \( A \)-site, with smaller \( A \)-site cations having softer (or unstable) AFE and AFD phonons, in spite of the reduced cell volume. The volume dependence of the AFD modes follows the same trend as in perovskite oxides, in which rotational instabilities are suppressed as the tolerance factor increases\(^{11}\). The \( \Gamma_{4}^{-} \) mode shows no obvious trend with \( A \)-site radius, but is strongly unstable in \( \text{LiNiF}_3 \). This behavior is distinct from the oxides, where the increase of volume associated with larger \( A \) cations tends to strengthen the FE instability\(^{21}\).

As a next step in the analysis, we decompose the structural distortions that map the high symmetry cubic perovskite structures into their fully relaxed \( \text{Pnma} \) ground states into linear combinations of the unstable phonons of the cubic structure\(^{22}\). Our results are shown in Fig. 2 for the \( \text{NaBF}_3 \) series with \( B = \text{Mn}, \text{V}, \text{Zn} \) and \( \text{Ni} \). As expected, and as is the case for \( \text{Pnma} \) perovskite oxides, we find that the strongest contributions come from the two \( (R_{4}^{+} \) and \( M_{3}^{+} \)) unstable AFD modes. The absolute magnitudes of the contributions decrease across the series as the \( B \) site cation becomes smaller, consistent with the reduction in the amount of the tiltings and rotations when the tolerance factor increases. The next largest contribution is from the \( X_{5}^{+} \) mode with its anti-polar \( A \)-site motions; notably its contribution to the relaxed ground state is approximately double that of the same mode in the perovskite oxides. Again, the magnitude of its contribution is smaller for smaller \( B \) site cations. There are also small contributions from the \( R_{5}^{+} \) and \( M_{4}^{+} \) modes which are roughly constant across the series and which we do not show.

\[
\eta = [0.174, -0.003, -0.015, -0.094] \text{ for [Na, Mn, F}_\perp, F}_\parallel] \text{ respectively, and frequency 107}^i \text{ cm}^{-1}. \text{ The dispersion of this instability is small along } \Gamma - X - M, \text{ similar to the behavior of typical perovskite oxide ferroelectrics}\(^{18}\). In complete contrast to the oxides, however, this branch remains unstable at the \( R \)-point (\( R_{2}^{+} \) mode) where it corresponds to antiferroelectric (AFE) atomic displacements with each “up” dipole surrounded by neighboring “down” dipoles in all three cartesian directions. Interestingly, this type of AFE instability has not been previously explored in perovskite systems\(^{19}\). The composition of the mode also differs from the perovskite oxides, as it is dominated by displacement of the \( A \)-site cation, whereas in the oxides \( B \)-site displacements dominate. The eigendisplacement of the soft polar mode at \( \Gamma \) in \( \text{BaTiO}_3 \), for example, is \( \eta = [0.001, 0.098, -0.071, -0.155] \text{ for [Ba, Ti, O}_\perp, O}_\parallel] \text{. In addition to the unstable polar mode, we find strong AFD instabilities}\(^{20}\) at the \( M \) (in-phase rotation of the octahedra) and \( R \) (out-of-phase rotation of the octahedra around) points, which have similar counterparts in many perovskite oxides.

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\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline
system & \( a_0 \) (Å) & \( B \)-radius & \( \Gamma_{4}^{+} \) & \( X_{5}^{+} \) & \( R_{3}^{+} \) & \( M_{3}^{+} \) & \( R_{5}^{+} \) & \( M_{4}^{+} \) \\
\hline
\text{NaMnF}_3 & 4.144 & 97 & 107i & 96i & 94i & 123i & 131i \\
\text{NaVF}_3 & 4.112 & 93 & 93i & 95i & 92i & 131i & 132i \\
\text{NaZF}_3 & 4.000 & 88 & 85i & 70i & 59i & 129i & 130i \\
\text{NaNiF}_3 & 3.925 & 83 & 50i & 47i & 15 & 126i & 127i \\
\text{BaTiO}_3 & 3.955 & 75 & 220i & 189i & — & 165i & — \\
\hline
\end{tabular}
\end{table}
We also show in Fig. 2 our calculated frequency for the unstable FE mode in the cubic structure (white triangles) as well as the frequency of the FE soft mode in the \textit{Pnma} ground state (white squares). We see that the frequencies of the soft modes in both the cubic and the ground state structures scale with the tolerance factor: the smaller the tolerance factor, the smaller the FE mode frequency in the \textit{Pnma} structure, and the stronger the FE instability in the cubic phase. We note also that a strong ferroelectric instability correlates with a large antipolar \( X_\parallel ^{\perp} \) mode contribution, in complete contrast to the case of perovskite oxides\textsuperscript{11}.

To understand the differences that we have found between oxide and fluoride perovskites, we next calculate the Born effective charges of selected \( ABF_3 \) cubic perovskites, and compare them in Table II with the values for \( BaTiO_3 \). As expected for ionic compounds, the Born effective charges of the fluoro-perovskites are close to the nominal Born effective charges. We address this next.

We saw previously that the eigendisplacements of the ferroelectric instability in \( NaMnF_3 \) are strongly dominated by displacement of the Na ion. In Table II we report the eigendisplacements\textsuperscript{24} \( \eta \) of the FE unstable mode for the series of \( NaBF_3 \) compounds, again comparing with \( BaTiO_3 \). In all fluoride cases we find a strong \( A \)-site contribution, with a substantial contribution also from \( F_\parallel \) but negligible contribution from the \( B \)-site ion. The dominance of the \( A \)-site displacement can also be seen in Fig. 3, where we show with red arrows the eigendisplacements for the FE-mode in \( NaMnF_3 \). The trend in \( A \)-site displacement magnitude reflects the \( A \) and \( B \)-site relative masses: the \( A \)-site contributions to the FE mode eigendisplacements for \( A = Li, Na, K, Rb \) and Cs in \( ANiF_3 \) are 0.347, 0.186, 0.138, 0.081 and 0.057 respectively while the contributions from Ni across the same series are 0.003, -0.019, -0.053, -0.073, -0.096.

To explore the origin of the unstable mode, we report in Table III the on-site interatomic force constants (IFC) for the cubic \( NaBF_3 \) series. The on-site IFC gives the force on an individual atom when it is displaced in the crystal while all the other atoms are kept fixed\textsuperscript{25}. Even in high symmetry phases with structural instabilities, the on-site IFC are usually positive (indicating a restoring

\begin{table}[h]
\centering
\begin{tabular}{llllll}
\hline
\textbf{system} & \textbf{A} & \textbf{B} & \textbf{X} & \textbf{X} & \textbf{X} & \textbf{X} \\
\hline
Nominal & 1 & 2 & -1 & -1 & -1 & -1 \\
\hline
\textbf{NaMnF}_3 & 1.17 & 2.21 & -0.83 & -1.72 & 0.174 & -0.005 & -0.020 & -0.088 \\
\textbf{NaVF}_3 & 1.18 & 1.99 & -0.71 & -1.75 & 0.181 & -0.018 & -0.019 & -0.077 \\
\textbf{NaZnF}_3 & 1.15 & 2.22 & -0.84 & -1.69 & 0.177 & -0.005 & -0.025 & -0.084 \\
\textbf{NaNiF}_3 & 1.15 & 2.05 & -0.74 & -1.73 & 0.186 & -0.002 & -0.025 & -0.068 \\
\textbf{BaTiO}_3 & 2.75 & 7.37 & -2.14 & -5.86 & 0.001 & 0.098 & -0.071 & -0.155 \\
\hline
\end{tabular}
\caption{Born effective charges, \( Z^* (\epsilon) \), and eigendisplacements of the FE unstable mode, \( \eta \), in \( NaBF_3 \) and \( BaTiO_3 \). \( X_\parallel \) and \( X_\perp \) indicate the Born effective charge of the anion (\( F \) or \( O \)) when it is displaced parallel or perpendicular to the \( B - X \) bond.}
\end{table}
force) as a periodic crystal is stable under the displacement of only one atom due to the breaking of the translational invariance. This is indeed the case in all of the NaBF₃ compounds studied, however we note that the Na and F⊥ on-site IFCs are unusually small. This indicates a small energy cost to displace an individual Na or F atom away from its high symmetry position and is consistent with the large contribution of these atoms to the unstable eigendisplacements. We find that the magnitude of the on-site Na IFC depends on the size of the B cation, with the smallest Na on-site IFCs found in perovskites with larger B cations and hence larger cell volumes and a roomier coordination cage around the Na atom. This size effect is confirmed by substituting other alkali atoms on the A site. The progressively larger K, Rb and Cs atoms give on-site IFCs of 2.88 eVÅ⁻², 4.16 eVÅ⁻² and 5.34 eVÅ⁻² respectively, while in LiNiF₃, with its smaller Li A-site ion, the on-site IFC is negative (-0.34 eVÅ⁻²). The A-site on-site IFCs then follow the same volume trends as we observed previously for the FE mode frequencies.

TABLE III. On-site IFCs (first four columns) and largest interatomic IFCs (last three columns) of ABF₃ (eV/Å). X⊥ and X∥ are defined as in Table II.

<table>
<thead>
<tr>
<th>system</th>
<th>A</th>
<th>B</th>
<th>X⊥</th>
<th>X∥</th>
<th>B − X∥</th>
<th>B − B ∥</th>
<th>A − A ∥</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaMnF₃</td>
<td>0.17</td>
<td>13.14</td>
<td>0.76</td>
<td>13.35</td>
<td>-4.62</td>
<td>-2.77</td>
<td>-0.51</td>
</tr>
<tr>
<td>NaVF₃</td>
<td>0.23</td>
<td>19.00</td>
<td>0.88</td>
<td>17.29</td>
<td>-6.78</td>
<td>-1.96</td>
<td>-0.52</td>
</tr>
<tr>
<td>NaZnF₃</td>
<td>0.43</td>
<td>12.63</td>
<td>1.22</td>
<td>13.81</td>
<td>-4.39</td>
<td>-3.21</td>
<td>-0.56</td>
</tr>
<tr>
<td>NaNiF₃</td>
<td>0.60</td>
<td>17.07</td>
<td>1.63</td>
<td>16.13</td>
<td>-5.69</td>
<td>-2.62</td>
<td>-0.59</td>
</tr>
</tbody>
</table>

While the on-site IFCs of Na in NaBF₃ are all positive, we find that displacing all periodically repeated Na ions in the same direction (while keeping the B and F atoms fixed) lowers the energy of the system. In Fig. 3 (green squares) we show the calculated total energy as a function of the magnitude of this collective Na displacement in NaMnF₃. The ferroelectric characteristic double well shape is clear, with an energy lowering of ~200 meV (in the 40 atoms cell) The difference in behaviour between the collective displacement and that of an individual Na ion is due to the negative A − A∥ IFC that is sufficient to destabilize the very small Na on-site IFC. We find the opposite situation for all ions other than Na in the fluorides (the example of Mn in NaMnF₃ is shown in Fig. 3, purple circles). We suggest, therefore, that the FE instability is driven by an instability dominated by the A-site cations. Note, however, that while collectively displacing the Na ions lowers the energy in NaMnF₃, freezing in the full FE soft mode (blue triangles in Fig. 3) leads to an energy lowering that is four times larger indicating that the FE instability is a collective motion.

Pursuing our comparison between oxides and fluoride perovskites, we next analyze the dependence of the FE instability on hydrostatic pressure. In Fig. 4 we show our calculated FE mode frequency (ω²) versus the cubic lattice parameter for NaBF₃ with B = Mn, V, Zn and Ni as well as for BaTiO₃. We see immediately that the FE instability in the fluorides is much less sensitive to volume than in oxides. For example, in BaTiO₃ a change of cell parameter of -2% shifts ω² by 40000 cm⁻² while the same change for NaNpF₃ gives a shift of only 2000 cm⁻². Second, the response of the fluorides is highly non-linear, and in some cases not even monotonic. And finally, for all compounds except NaNpF₃, compression enhances the FE instability, in stark contrast to the behavior in oxides.

In Fig. 5 we report the evolution of the four possible on-site IFCs of cubic NaBF₃ (B = Mn, V, Zn and Ni) versus the pressure in order to explain this unusual pressure enhancement of the FE instability. As expected from a simple ionic picture, the A on-site IFC is stabilized under compression and further softened or destabilized on increasing the volume. The same trend is observed for the B and F⊥ on-site IFCs while the F∥ on-site IFCs show the opposite behaviour. Having a negative on-site IFC means there is no restoring force on the atom, thus the ABF₃ cubic structure is unstable to transverse on-site fluorine movements. This softening of the F∥ IFC is transferred into the FE mode by changing the character of its eigendisplacement, which evolves from A-site dominated toward F∥ dominated under pressure. We note again a striking difference with BaTiO₃, were none of the calculated on-site IFCs become unstable even at extremely high pressure where ferroelectricity has been found to reappear.

Finally, we investigate whether it is possible to exploit this unusual ferroelectric instability to induce multiferroism in ABF₃. It is well established that epitaxial strain can induce ferroelectricity in non-ferroelectric perovskite oxides of Pnma and other symmetries. Therefore
we explore whether similar strain-induced ferroelectricity can occur in Pnma NaBF$_3$ taking the ac-plane as a plane for epitaxial strain. We assume a cubic substrate that forces the $a$ and $c$ lattice constants to be equal, and we relax the out-of-plane lattice parameter (orthorhombic $b$-axis) and internal atomic positions for each value of the in-plane lattice constant. Note that the 0% strain case corresponds to $a_{\text{substrate}} = \frac{a + c}{2}$, where $a$ and $c$ are the relaxed lattice parameters of the bulk Pnma phase. For all cases we find that the lowest FE mode has B$_{2u}$ symmetry (with frequencies 22, 69, 79 and 92 cm$^{-1}$ for $B = \text{Mn, V, Zn and Ni}$ respectively, see Fig. 2.) and is polarized perpendicular to the biaxial constraint. We find that for all of them, this soft B$_{2u}$ mode is slightly sensitive to the value of strain, consistent with our earlier findings under pressure. However, we find that only for $B = \text{Mn}$, the B$_{2u}$ is sufficiently low in frequency to be destabilized by the epitaxial strain, and thus even at zero strain. Performing structural relaxations yields a ferroelectric ground state (space group Pnma) with a $G$-type AFM and a polarization of 6 $\mu$C.cm$^{-2}$ at 0% strain. Interestingly, negative or positive strain both enhance the polarization up to values of 12 $\mu$C.cm$^{-2}$ at +5% and 9 $\mu$C.cm$^{-2}$ at -5% strain, again in contrast with the behaviour of perovskites oxides. This also means that the ground state of coherent epitaxially constrained NaMnF$_3$ is always multiferroic. We note that the polarization develops perpendicular to the antipolar motions of the $X_{\pm}$ mode, in which the $A$ cations move in opposite directions in the ac-plane.

In conclusion, we have investigated from first principles the origin of the FE instability in fluoro-perovskites. We found that the FE instability in these ionic systems originates from the softness of the $A$-site displacements which in turn is caused by a simple geometric ionic size effect. Due to its geometric origin, the fluoride FE instability is rather insensitive to pressure or epitaxial strain and most fluorides remain non-ferroelectric at all reasonable strain values. An exception is Pnma NaMnF$_3$, in which the FE mode is particularly soft, so that it becomes ferroelectric and indeed multiferroic through coherent heteroepitaxy even at zero strain. We hope that our results will motivate experimentalists to revisit the FE behavior of perovskite-structure fluorides.

We thank Ph. Ghosez for fruitful discussions. This work was supported by the ETH-Zürich, CONACYT Mexico under project 152153 and FRS-FNRS Belgium (EB). The computational resources provided by the TACC supercomputer center and ETH-Zürich Brutus Cluster are recognized.

The eigendisplacements are normalized as follows: $\langle \eta | M | \eta \rangle = 1$. $M$ is the atomic mass matrix $M_{ij} = \sqrt{M_i M_j}$ where $M_i$ is the mass of atom $i$.

The IFC matrix is defined by $C_{\alpha \beta ij} = \frac{\partial F_\alpha}{\partial r_\beta j}$ where $i$ and $j$ refer to the directions, $\alpha$ and $\beta$ to the atoms, $F$ is the force on an atom and $r$ the atomic position. The acoustic sum rule imposes $\sum_\beta C_{\alpha \beta ii} = 0$. The on-site IFC of atom $\alpha$ along direction $i$ corresponding to the matrix element $C_{\alpha \alpha ii}$ is thus equal to $C_{\alpha \alpha ii} = - \sum_{\beta \neq \alpha} C_{\alpha \beta ii}$ and so it can be seen as the resulting force on the atom $\kappa$ induced by all the other atoms when this atom $\kappa$ is displaced.