Insights in the A- and B-site’s Radii Influence in the Polar Character of ABF$_4$

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Abstract. Here, we present the study of the ferroelectricity in the ABF$_4$ materials with A = (Sr, Ba) and B = (Mg, Zn). This theoretical study was performed based-on first-principles calculations within the density-functional theory, DFT, formalism. We found that the geometric ferroelectricity in ABF$_4$ layered compounds can be tuned by changing the A-site with Sr and Ba cations and B-sites with Mg and Zn atoms. Additionally, we studied the stability of the phases as a function of the A and B cations’ occupation preference. We observed a layer-by-layer disposition, as a ground state, when the A-site has different compositions of Sr/Ba.

1. Introduction

Recently, naturally layered oxide-based compounds have attracted particular attention due to their possibility to hold a strong polar ferroelectric state, well above room-temperature, on top of other properties such as magnetic ordering [1, 2, 3, 4] and Rashba-type spin-splitting [5]. Nevertheless, the ensemble of polar oxide candidates within the layered stoichiometries, such as Ruddlesden-Popper, Aurivillius, and Dion-Jacobson, is quite limited and therefore, similar materials that share this structural feature are on a pursuit. On top of the widely investigated oxides materials, several fluorides have shown to be good candidates for multifunctional applications in the water-splitting process [6, 7], catalysis [8, 9], and transparent ceramics with photonic response [10]. More recently, the reported multifunctional phenomena in fluorides also includes multiferroic and magnetoelectric behavior based-on the ferroelastic-magnetic coupling [11], ferroelectric-magnetic behavior [12, 13] geometrically-driven ferroelectricity [14], and possibly, superconductivity at oxyfluoride interfaces [15, 16]. Within this class of materials, layered structures with stoichiometric relationship $A_nB_nX_{3n+2}$ have been recently highlighted thanks to their structural topology that allows the direct coupling between the polar displacements and the octahedral rotations making them suitable for multifunctional applications involving electrically-controlled magnetization [17, 1]. Consequently, necessary studies focused on the possible tuning of their polar state can shed light into the enhancement of their properties. The latter, to highlight such materials as potential candidates for future applications where the intertwining of the polar character with other features, such as spin-control and magnetic ordering, can be required.

In this work, we show through density-functional theory calculations, the study of the dependence of the ferroelectric behavior as a function radii size when replacing A- and B-sites
in ABF$_4$ compounds. This study was performed mainly in its Cmc2$_1$ polar layered structure. Nevertheless, we also considered the Cmcn high-symmetry structure and the anti-polar P2$_1$/c for comparison. We found that the total energy for the Sr/Ba and Mg/Zn substitutions suggest ground state structures that displace a layer-by-layer (Sr/Ba)MgF$_4$ and Ba(Mg/Zn)F$_4$ disposition. Additionally, we show how smaller cations in the A-site enhance the spontaneous polarization; meanwhile, bigger B-sites increases the polar eigendisplacements.

2. Computational Details
First-principles calculations based on density functional theory, DFT, used to describe the electronic and structural properties. Such calculations were performed using the VASP code [18, 19]. Projected-Augmented Waves, PAW [20], pseudo-potentials were employed to represent the valence and core electrons. The electronic configurations —for valence and semi core electrons— taken into account in the pseudo-potentials are Ba (5s$^2$5p$^6$6s$^2$, version 06Sep2000), Sr (4s$^2$4p$^5$5s$^2$, version 07Sep2000), Mg (2p$^6$3s$^2$, version 13Apr2007), Zn (3d$^{10}$4s$^2$, version 06Sep2000) and F (2s$^2$2p$^5$, version 08Apr2002). The exchange-correlation was represented within the general-gradient approximation, GGA - PBEsol parametrization [21]. The periodic solution of these crystalline structures was represented by using Bloch states with a Monkhorst-Pack k-point mesh of (8×4×8) and 500 eV energy cut-off, which has been tested already to give forces convergence to less than 0.0001 eV/Å and an error in total energy around ± 0.4 meV in the phases of the (Ba/Sr)MgF$_4$ and Ba(Mg/Zn)F$_4$ compounds. Additionally, the vibrational modes were fully converged concerning the energy and k-points mesh to obtain values in error less than 1 cm$^{-1}$. Full phonon-dispersion curves were computed by calculating the dynamical matrix from the 2×2×2 supercell and mapped to the unit cell. The dynamical matrices were obtained by the finite displacement method as implemented in VASP and post-processed with the Phonopy code [22]. Finally, the ferroelectric polarization was obtained employing the Berry-phase approach [23].

3. Results and Discussion
As it is well-known, ABF$_4$ layered materials belong to the stoichiometric formula $A_nB_nX_{3n+2}$, in which $n = 2$. This structure is comprised of $BX_6$ octahedral layers separated by the A-sites along the y-axis as shown in Fig. 1. In the case of fluorides, several examples have been reported and demonstrated to be strong ferroelectrics well above room temperature [25]. In order to understand de A- and B-site’s effect on the structure and ferroelectric polarization in known ABF$_4$ materials, we defined several sites by symmetry and different $A/A'$ and $B/B'$ elements which, in this case, are Sr/Ba and Mg/Zn. It worth mentioning that the bulk compounds formed by the combinations, SrMgF$_4$, BaMgF$_4$, and BaZnF$_4$, are reported to show ferroelectric behavior at room temperature [9]. Moreover, these elements were chosen based on their ionic radii size where $r_{Sr} = 132$ pm, $r_{Ba} = 149$ pm, $r_{Mg} = 86$ pm, and $r_{Zn} = 88$ pm in case of the +2 oxidation state [26]. Thus, A1, A2, and A3 sites were identified with the structural arrangements shown in Fig. 1 for Sr and Ba atoms. Similarly, B1, B2, and B3 combinations were also defined for Mg and Zn sites, as presented in Fig. 1.

In the A-site case, after full atomic and structural relaxation we found that the lowest energy structure was the A3 with a total energy of $E_{A3} = -33.771$ eV/f.u. in comparison to $E_{A1} = -33.765$ eV/f.u. and $E_{A2} = -33.751$ eV/f.u. for A1 and A2 respectively. In the B-site case, we found that the ground state structure is B1 with a total energy of $E_{B1} = -31.992$ eV/f.u. against $E_{B2} = -31.990$ eV/f.u. and $E_{B3} = -31.991$ eV/f.u. for B2 and B3 respectively. We obtain a relaxed lattice parameters of $a = 4.0176$ Å, $b = 14.487$ Å, $c = 5.760$ Å for the (Sr/Ba)MgF$_4$ structure and $a = 4.150$ Å, $b = 14.557$ Å, $c = 5.846$ Å for the Ba(Mg/Zn)F$_4$/BaZnF$_4$. Interestingly, as it can be appreciated from Fig 1, in both of the cases,
Figure 1. (Color online) Possible occupation of the A- and B-sites within the Cmc2\(_1\) phase. Here, Sr, Ba, Mg, Zn, and F sites are depicted in green, blue, orange, dark-grey, and light-grey, respectively. The figures of the structures elaborated with the VESTA code [24].

The ground state structure display a layer-by-layer disposition such as SrMgF\(_4\)/BaMgF\(_4\) and BaMgF\(_4\)/BaZnF\(_4\).

With further analysis of the structures, we found that the polar phase symmetry is reduced from the Cmc2\(_1\) (space group No. 36) to the Pmc2\(_1\) (space group No. 26). The latter, due to the breaking of symmetry introduced by the A- and B-sites replacement. Although, and as commented before, the bulk components are reported to be ferroelectric, we tested the stability of the polar Pmc2\(_1\) phase against the expected high-symmetry structure, Pmma in this case, and the anti-polar phase P2\(_1\)/c (reported in other compounds such as LaTaO\(_4\) [27]). The results, presented in Table 1, confirm that the lowest energy phase, and therefore, the ground state is the polar Pmc2\(_1\) structure.

We found, by using theAMPLIMODES [28, 29] tool, that the phonon mode driving the polar distortion from the expected high-symmetry structure Pmma to the polar Pmc2\(_1\) ground state is the \(\Gamma_{-3}\). This mode comprises the BF\(_6\) octahedral rotation coupled to the A-site polar

|                  | E [eV/f.u.] |
|------------------|-------------|
| Pmma            |            |
| BaMgF\(_4\)/SrMgF\(_4\) | -33.601  |
| BaMgF\(_4\)/BaZnF\(_4\)  | -31.892  |

Table 1. Total energy per formula unit for each when the A- and B-sites are changed. As expected, the ferroelectric phase is the ground state in both cases.
Figure 2. (Color online) Above, the averaged BF$_6$ octahedral rotation angle as a function of the A- and B-sites replacement. Below, computed spontaneous polarization as a function of the A- and B-sites, respectively. As it can be seen, the polarization, as well as the octahedral rotation angle, follow the ionic size trend as expected from the geometrically driven ferroelectric phenomenon.

eigendisplacements. Moving forward, in Fig. 2 we presented the computed values of the spontaneous polarization as well as the averaged BF$_6$ octahedral rotation angle as a function of the A- and B-sites radii size modification through the atomic substitution. Interestingly, we found that as soon as the A-site becomes larger, from Strontium to Barium, the ferroelectric polarization decreases from 13.4 to 9.9 $\mu$C$\cdot$cm$^{-2}$, respectively. Meanwhile, for larger B-sites, from Magnesium to Zinc, the polarization increases from 9.9 $\mu$C$\cdot$cm$^{-2}$ to 12.2 $\mu$C$\cdot$cm$^{-2}$. When analyzing the averaged octahedral rotation in each case, it can be observed that the rotation angle, $\phi$, follows the same trend as the polarization does. Then, for large A-sites, $\phi$ decreases meanwhile for large B-sites, $\phi$ increases. The latter findings are explained in terms of the polar mode that is controlling the ferroelectricity and its relationship with the A- and B-sites radii size. In the A-site’s case, the MgF$_6$ rotations become larger when small A-sites are chosen. Therefore, the A-site’s associated displacements are enhanced, increasing the polarization. On the other side, when large B-sites are placed in the octahedral site, the “free space” of the A-site is increased and with it, the A-site’s polar eigendisplacements. Thereupon, our results are in full agreement with the geometrically-driven ferroelectricity in this layered fluoride compounds.

Finally, in order to corroborate the dynamical stability of the Pmc2$_1$ in both cases, we computed the vibrational modes at the $\Gamma$-point (not shown here). As expected in this high-symmetry point, we did not observe negative phonon frequencies that could be related to unstable modes. Nevertheless, it worth mentioning that further studies focused on the stability
of the phase in another high-symmetry point in the Brillouin zone can be of interest.

4. Conclusions
We studied, employing first-principles calculations, the influence of the A- and B-sites radii size in the geometric ferroelectricity of the ABF$_4$ compounds. After analyzing the possible Sr/Ba and Mn/Zn occupations sites' preference, we observed a layer-by-layer ground state in both cases such as SrMgF$_4$/BaMgF$_4$ and BaMgF$_4$/BaZnF$_4$. Regarding the polar character, we found that smaller A-sites increase the spontaneous polarization, whereas it is reduced by smaller B-sites. Finally, we corroborated the stability of the polar phase by computing the phonons at the Γ-point, and no unstable modes were observed. Then, our results suggest that a possible tuning of the ferroelectric properties, and more interestingly, layer-by-layer heterostructures, might be naturally formed. Therefore, this A-site engineering can be used as a potential design rule for enhanced ferroelectric behavior within the 2D layered materials.

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