I. INTRODUCTION

Aurivillius phase structures family, with the general formula $\text{Bi}_2\text{A}_{m-1}\text{B}_m\text{O}_{3m+3}$ are mostly ferroelectric oxides, consisting of alternating, along the c-axis, of $\text{A}_2\text{BO}_2$ layers and perovskite-like $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{-2}$ blocks, with, $A= \text{Ca}^{2+}, \text{Ba}^{2+}, \text{Sr}^{2+}, \text{Bi}^{3+}, ..., B= \text{Fe}^{3+}, \text{Ti}^{4+}, \text{Nb}^{5+}, \text{W}^{6+}, ...,$ and $m$ is the number of BO$_6$ octahedra in the perovskite-like block ($m=1-8$) and is independent with $A$ and $B$ cations oxidation states to always provide right number of electrons to oxygen atoms [1–6]. Typically, oxide Aurivillius phase structures crystalize at high temperature into centrosymmetric $I4/mmm$ tetragonal phase and adopt at room temperature a polar orthorhombic ground state involving in-plane polar displacement and in-plane and out-of-plane octahedral tilts about [110], and [001], directions, respectively ($t$ referring to the tetragonal parent structure). They are also known to exhibit a large spontaneous polarization $P_s \approx 30-50 \mu\text{C/cm}^2$ and high Curie temperature ($T_c > 350^\circ\text{C}$). Bi$_2$W0$_6$ is the smallest member with $m=1$. It is a one-layer strong ferroelectric with A cation deficiency in the perovskite block, with $P_s = 50 \mu\text{C/cm}^2$ and $T_c = 950^\circ\text{C}$.

Oxyfluoride Aurivillius phases are also naturally occurring. The $m=1$ Bi$_2$TiO$_4$F$_2$, isostructural to Bi$_2$NbO$_5$F$_6$ and Bi$_2$TaO$_5$F$_2$, was first reported in 1952 [7] and has been intensively studied because of its ferroelectric and photocatalysis properties [8, 9]. The first experimental study claimed that Bi$_2$TiO$_4$F$_2$ was ferroelectric with a Curie temperature $T_c \approx 12^\circ\text{C}$ and that the ferroelectric phase transition was accompanied with an orthorhombic distortion of the high temperature tetragonal paraelectric $I4/mmm$ parent phase, that lead to polar $Immm$ phase [10]. Later Ñães et al. [11], by using the combined refinement of the powder X-ray and neutron diffraction, refined Bi$_2$TiO$_4$F$_2$ and Bi$_2$NbO$_5$F$_6$ into centrosymmetric tetragonal $I4/mmm$ symmetry and the fluorine anions assigned to the equatorial sites. No evidence of an orthorhombic distortion of the crystal structure was observed. Furthermore, E. McCabe et al. [12] showed that Bi$_2$NbO$_5$F$_6$ adopts a distorted structure with octahedral tilts about [110] and [001], axis. The absence of SHG signal led them to conclude that the structure was centrosymmetric Pbea and the bond valence sum calculations indicated that fluorine anions prefer the apical sites. However, all these efforts and numerous investigations have not dispelled, so far, the doubts about ferroelectricity and fluoride ordering in Bi$_2$TiO$_4$F$_2$.

Here, we have explored different anions ordering configurations for Bi$_2$TiO$_4$F$_2$ Aurivillius phase, with the aim to examine the effect of fluoride positions on the structural, dielectric and dynamical properties of this compound. We have generated three key configurations: the centrosymmetric tetragonal $I4/mmm$ phase with fluoride anions at the octahedral equatorial sites of the perovskite-like blocks ($I4/mmm$ ($F_{eq}$), see Fig. 1(a)), the centrosymmetric tetragonal $I4/mmm$ phase with fluoride anions at the octahedral apical sites ($I4/mmm$ ($F_{ap}$), see Fig. 1(b)) and the polar orthorhombic Pnma$_2$ ($F_{eq}$+$F_{ap}$) with $fac$-arrangement, consisting of fluoride anions occupying the three corners of one face of the octahedron (see Fig. 1(c)). Recent calculations have recently found this latter configuration as the most stable among twenty tested ones [13].

Our study shows that Bi$_2$TiO$_4$F$_2$ adopts a polar ground state of monoclinic $Pc$ symmetry with the fluorine anions distributed over the octahedral equatorial and apical sites ($F_{eq}$+$F_{ap}$) in a $fac$-arrangement. Phonon
computational details

This work have been performed within density functional theory [14, 15] as implemented in ABINIT package [16–18]. The exchange and correlation functional was evaluated with the generalized gradient approximation GGA-PBEsol as parameterized by perdew, Burke and Ernzerhof [19] where Bi (5d, 6s, 6p), Ti (3d, 4s), O and F (2s, 2p) levels were treated as valence states. Wave functions were expanded up to a kinetic energy cutoff (Ecut) of 42 Hartrees. Integrals over the Brillouin zone approximated by sums on 4 × 4 × 1 Monokhorst-Pack mesh of special k points [20] was enough for good convergence of structural optimization and phonons calculations (tests on 6 × 6 × 1 were also performed for validation). The Broyden-Fletcher-Goldfarb-Shanno [21] minimization algorithm was used to give the structural optimisation. We relaxed the position of each individual atom until the absolute values of the forces on these atoms were converged to less than 10−5 Ha/Bohr. Phonons, Born effective were calculated with a variational approach to density functional perturbation theory (DFPT) [22, 23] and the spontaneous polarization was calculated using the Berry phase formalism [24].

II. COMPUTATIONAL DETAILS

As mentioned in the introduction, we generated three high symmetry hypothetical reference structures for Bi2TiO4F2, with different fluorine anions ordering into the octahedral sites: I4/mmm (Feq), I4/mmm (Fap) and Pma2 (Feq+Fap). Cells parameters and atomic coordinates are given in Table I. After fully relaxation, phonons calculations were performed to identify the kind of instabilities that can lower the internal energy of the different systems.

A. High symmetry I4/mmm (Feq) paraelectric phase

Phonon calculations were performed in this parent phase and numerous mode instabilities were identified at high-symmetry points. They include (i) two [110]t in-plane polar modes (Γ5): one consisting of polar displacements of Bi against Oeq and Ti against Oap, Ti and Feq displace in the same direction at variance of what is commonly observed in oxide Aurivillius phases, where B cations displace against Oeq− (Γ5 at 163i cm−1) and a second polar rigid layer mode (RL-mode), in which, perovskite blocks displace against (Bi2O2) layers -as commonly observed in oxide Aurivillius phases- (Γ5 at 33i cm−1). (ii) [110]t in-plane antipolar modes (M5−, M5+, X5− and X5+), consisting of inter-perovskite antipolar motion of Oeq (M5− at 137i cm−1) and inter-perovskite antipolar motion of Feq (M5+ at 27i cm−1); inter-(Bi2O2) layers antipolar motion of Bi (M5+); antipolar motion of Oap between in-plane linked octahedra (X5− and X5+), and (iii) octahedral tilts about [110]t direction of Oap and Feq (X5− and X5+) and about [001]t direction of Feq (X5−).

Considering the condensation of individual modes, reported in Table I we see that the octahedral tilt about [110]t axis, X5− (Cmca) drives the largest energy gain, followed by the polar distortion Γ5− (Fmm2), the antipolar M5− (Cmcm) and the octahedral tilt about [100]t axis X5+, (Pbam). M5+ (Cmca) and X5+ (Cccm) distortions give also a sizeable energy gain. This hierarchy differs from what is noticed in the m = 1, Bi2WO6 in which the polar Γ5− distortion gives the largest energy gain followed by the [001]t axis tilt, X5− [25].

Considering the condensation of combined unstable modes, we identified many additional metastable phases.
 TABLE I: Calculated cell parameters for high symmetry tetragonal I4/mmm (F_{eq}) and I4/mmm (F_{ap}) and orthorhombic Pma2 (F_{eq}+F_{ap}) phases. Here, the tetragonal phases are doubled along the [110] diagonale $\sqrt{2} \times \sqrt{2} \times 1$, to allow the atomic positions to match those of the orthorhombic metastable phases. Our results are in good agreement with the experimental cell parameters for the I4/mmm phase obtained by Needs and al. [11] with a=5.37Å and c=16.32Å and experimental atomic coordinates between brackets.

| Structure | Atom | x  | y  | z  |
|-----------|------|----|----|----|
| I4/mmm (F_{eq}) | Bi  | 0.0000 | 0.0000 | 0.32654 |
| a=5.41Å  | Ti  | 0.0000 | 0.0000 | 0.32829 |
| c=16.4Å  | F_{eq} | 0.2500 | 0.7500 | 0.0000 |
| O_{ap}   | 0.0000 | 0.0000 | 0.11208 |
| O_{f1}   | 0.2500 | 0.7500 | 0.25000 |
| I4/mmm (F_{ap}) | Bi  | 0.0000 | 0.0000 | 0.33317 |
| a=5.42Å  | Ti  | 0.0000 | 0.0000 | 0.32829 |
| c=15.2Å  | F_{eq} | 0.2500 | 0.7500 | 0.0000 |
| O_{ap}   | 0.0000 | 0.0000 | 0.11614 |
| O_{f1}   | 0.7500 | 0.5000 | 0.25000 |
| Pma2 (F_{eq}+F_{ap}) | Bi_{1} | 0.75000 | 0.22394 | 0.49213 |
| a=5.41Å  | Bi_{2} | 0.75000 | 0.25675 | 0.07642 |
| b=5.37Å  | Ti  | 0.75000 | 0.28640 | 0.74983 |
| c=16.25Å | O_{eq} | 0.0000 | 0.50000 | 0.25601 |
| O_{ap}   | 0.25000 | 0.17128 | 0.35827 |
| O_{ap}   | 0.25000 | 0.67704 | 0.64230 |
| F_{eq}   | 0.50000 | 0.00000 | 0.12847 |
| F_{ap}   | 0.75000 | 0.18477 | 0.87569 |
| O_{f1}   | 0.75000 | 0.70640 | 0.12499 |
| O_{f1}   | 0.00000 | 0.00000 | 0.49981 |

at lower energy (see Table I]. The most stable phase is polar of Pca21 symmetry, resulting from the combination of $\Gamma_5^-$, $X_{3}^+$ and $X_{2}^+$ ($M_5^-$ mode is brought by trilinear coupling $X_{2}^+ \otimes X_{3}^+ \otimes M_5^+$). This Pca21 phase is closely followed by polar Pc phase, resulting from the combination of $M_5^-$, $X_{3}^+$ and $X_{2}^+$ and containing insignificant contributions from $M_5^-$ and $\Gamma_5^-$ mode, not reported in Table I.

The mode-by-mode contributions to the atomic distortion $\Delta$ of each metastable phase with respect to I4/mmm parent reference structure are also reported in Table I. These contributions are evaluated with qAgate software 26, by expressing the distortion $\Delta$ in the basis of phonon eigendisplacements vectors $\eta_i$ of the I4/mmm phase (such that $<\eta_i|M|\eta_j> = \delta_{ij}$), following the scheme explained in Ref. 25: $\Delta = A \sum_i \alpha_i \eta_i$, where $A$ is the total distortion amplitude and $\alpha_i$ are the relative mode contributions such that $\sum_i \alpha_i^2 = 1$. Contributions of distinct phonon modes $i$ to the distortion $\Delta$ of a given phase correspond therefore to the amplitudes $\alpha_i$. From Table I (up part), we notice a strong cooperation between $\Gamma_5^-$ [163$\delta$] and $X_{3}^+$ (in Aba2) and $M_5^-$ [137$\delta$] and $X_{2}^+$ (in Pc), revealed from the distortion amplitudes of these modes, which when combined, became almost the double of those of single ones ( for $\Gamma_5^-$, 7.5 Å in Fmmm2 to 11.8 Å in Aba2 or 13 Å in Pca21; for $X_{3}^+$, 11.1 Å in Cmca to 22.1 Å in Aba2; for $M_5^-$, 8.2 Å in Cmca to 12.7 Å in Pc). These strong modes cooperations lead to the most stable Pca21 and Pc phases. Pca21 phase does not exhibit any further phonon instabilities, so can be considered as the hypothetical ground state for I4/mmm (F_{eq}) configuration.

B. High symmetry I4/mmm (F_{ap}) paraelectric phase

Phonon calculations performed in the parent I4/mmm (F_{ap}) phase with fluorine anions sitting in apical positions, showed the same pattern of unstable modes as frequently found in oxide Aurivillius phases (see [27]), such as: a polar $\Gamma_5^-$ mode (the softest) that consists of polar motion of Ti against both O_{eq} and F_{ap} in perovskite blocks and Bi against O_{f1} in (Bi_{2}O_{2}) layers (the Rigid-Layer mode is stable at 66 cm$^{-1}$); an antipolar $M_5^-$ mode that consists of inter-perovskite antipolar motion of Ti; out-of-plane octahedral tilt of O_{eq} and F_{ap} about [110]$_i$ axis ($X_{3}^+$ and $X_{2}^+$) and in-plane octahedral tilt of O_{eq} about [001]$_i$ axis ($X_{2}^+$). In-plane twists of O_{eq} ($\Gamma_4^-$ and $M_5^-$) were also found. More importantly, an unstable polar mode of $\Gamma_3^-$ symmetry, polarized along the out-of-plane [001]$_i$ direction was also found at a frequency of 65i cm$^{-1}$. This mode usually exists in Aurivillius phases, but is never found unstable [28] (e.g. at 98 cm$^{-1}$ in I4/mmm (F_{eq}), at 88 cm$^{-1}$ in I4/mmm phase of Bi$_2$WO$_6$ and at 65 cm$^{-1}$ in I4/mmm phase of Bi$_2$W$_2$O$_9$). Its eigendisplacement involves mainly a rigid layer motion of the (Bi$_2$O$_2$) layer against the perovskite block along the [001]$_i$ direction, with a domination of Bi motion against O_{eq} (see Fig. 2).

As for I4/mmm (F_{ap}), we condensed individual and combined unstable modes into the parent paraelectric phase I4/mmm (F_{ap}) and the results are also reported in Table I. It is worth noting that both total amplitude of distortions and energy gain are very small compared to I4/mmm (F_{eq}). This is consistent with previous works on Bi$_2$NbO$_5$F compound [29], that showed that the energy to substitute O_{ap} with fluorine anions is much lower than the energy to substitute O_{eq}. The condensation of individual modes gave, equally, the larger energy gain to $\Gamma_3^-$ (I4mm) and $X_{2}^+$ (Cmca), followed by polar $\Gamma_5^-$ (Fmmm2) and antipolar $M_5^-$ (Ccmcm). The condensation of combined modes showed that the most stable phase is associated to $\Gamma_3^-$ and $\Gamma_5^-$ polar modes in addition to $X_{2}^+$ and $X_{3}^+$ octahedral tilts. This phase of Pc symmetry is polar along the in-plane [110]$_i$ direction and out-of-plane [001]$_i$ direction and is considered as the ground state for the (F_{ap}) configuration, since further phonon
TABLE II: Modes contributions $a_{ii}$ (A in Å) (see the text) of metastable phase, derived from condensation of individual and combined unstable modes, wrt. paraelectric $I4/mmm$ ($F_{eq}$) (up table) and $I4/mmm$ ($F_{ap}$) (down table) parent phases. Energy difference $\Delta E_i$ (in meV/f.u) wrt. paraelectric $I4/mmm$ ($F_{eq}$) (up table) and $I4/mmm$ ($F_{ap}$) is also reported. Frequencies $[\omega]$ are in cm$^{-1}$ and Space group are given in a conventional setting.

| $I4/mmm$ ($F_{eq}$) | irreps | $\Gamma_5$ | $M_5$ | $X_5^+$ | $X_5^-$ | $X_7^+$ | $X_7^-$ | $\Delta E$ |
|---------------------|---------|------------|--------|----------|----------|----------|----------|-----------|
| $Pmm2(42)$          | $\Gamma_5$ | 11.3 [7.5 8.0] |        |          |          |          |          | 1.5       |
| $Cmcm(63)$          | $M_5^-$ | 10.7 [8.2 5.5] |        |          |          |          |          | 1.5       |
| $Pbam(55)$          | $X_7^+$ | 7.2 [5.2] |        |          |          |          |          | 1.5       |
| $Cmca(64)$          | $X_7^+$ | 11.6 [11.1] |        |          |          |          |          | 1.5       |
| $Cccm(66)$          | $X_7^+$ | 8.1 [7.6] |        |          |          |          |          | 1.5       |
| $Cmcn(63)$          | $X_7^+$ | 10.1 [9.6] |        |          |          |          |          | 1.5       |
| $Cmca(64)$          | $M_5^-$ | 29.2 [29.0] |        |          |          |          |          | 1.5       |
| $Cmma(67)$          | $X_7^+$ | 1.2 [1.2]  |        |          |          |          |          | 1.5       |

| $I4/mmm$ ($F_{ap}$) | irreps | $\Gamma_5$ | $M_5$ | $M_5^-$ | $M_5^+$ | $X_5^+$ | $X_5^-$ | $\Delta E$ |
|---------------------|---------|------------|--------|----------|----------|----------|----------|-----------|
| $Pmm2(42)$          | $\Gamma_5$ | 2.2 [1.9]  |        |          |          |          |          | 27        |
| $Cmcm(63)$          | $M_5^-$ | 2.1 [1.8]  |        |          |          |          |          | 24        |
| $P4_2/nmc(137)$     | $X_5^+$ | 2.4 [2.3]  |        |          |          |          |          | 15        |
| $I4/mmm(119)$       | $\Gamma_5$ | 2.3 [2.3]  |        |          |          |          |          | 14        |
| $Cmca(64)$          | $X_5^+$ | 5.4 [5.2]  |        |          |          |          |          | 56        |
| $Pbam(55)$          | $X_5^+$ | 2.8 [2.0]  |        |          |          |          |          | 14        |
| $I4/mmm(107)$       | $\Gamma_5$ | 8.2 [8.1]  |        |          |          |          |          | 56        |
| $Cmcm(63)$          | $X_5^+$ | 3.7 [3.7]  |        |          |          |          |          | 10        |

In an aim to explore the origin of out-of-plane instability, the ferroelectricity being directly related to the length and covalency of cations-anions bonds, we examined the selected bonds lengths given in Table III. We noticed that $F_{eq}$ is moving away from $Ti$ and getting closer to Bi (Ti-F$_{ap}$=1.95 Å and Bi-F$_{ap}$=2.77 Å in $I4/mmm$ ($F_{ap}$), in contrast to Ti-O$_{eq}$=1.83 Å and Bi-O$_{eq}$=2.88 Å in $I4/mmm$ ($F_{eq}$)). Accordingly, the calculations of the Born effective charges ($Z^*$), reported in Table IV, showed that, on the other hand, the ionic character of the Ti-F$_{ap}$ bonding, marked by $Z^*_zz$ Ti(+4.18e) that is close to its nominal value along the apical direction, can explain the elongation of the Ti-F$_{ap}$ bonds and the non hybridization between F-$2p$ and Ti-$d$ orbitals and, on the other hand, the strongly anomalous $Z^*$ Bi(+4.2e) and anomalous $Z^*$ Bi(+4.2e) can be linked to an increasing hybridization between F-$2p$ and Bi-$6p$-$6s$ orbitals and hence, to a shortening of Bi-F$_{ap}$ bonds.

The ionic character of the Ti-F$_{eq}$ is also confirmed in $I4/mmm$ ($F_{eq}$) with $Z^*_zz$ Ti(+4.7e), that is close to its nominal value along the equatorial octahedral plane. However, here, the Ti-F$_{eq}$ bond length is equal to Ti-O$_{eq}$ bond length in $I4/mmm$ ($F_{ap}$), although Ti and O$_{eq}$ are highly hybridized ($Z^*_zz$ Ti(+8.4e) and $Z^*_zz$ O$_{eq}$(-4.3e)). This equivalence in bond lengths, despite the clear difference in hybridization between Ti and F$_{eq}$/O$_{eq}$ could be explained by the constrain on bond lengths in the equatorial plane due to the mismatch between the perovskite-like block and the (Bi$_2$O$_2$) layer.
TABLE III: Interatomic bond lengths (Å) for selected atoms.

| structure   | pairs of atoms | distance(Å) |
|-------------|---------------|-------------|
| I4/mmm (F_{eq}) | Bi-O_{eq}     | 2.88        |
|             | Bi-F_{eq}     | 3.42        |
|             | Bi-O_{fl}     | 2.28        |
|             | Ti-O_{eq}     | 1.83        |
|             | Ti-F_{eq}     | 1.91        |
| I4/mmm (F_{ap}) | Bi-F_{ap}     | 2.77        |
|             | Bi-O_{eq}     | 3.17        |
|             | Bi-O_{fl}     | 2.29        |
|             | Ti-F_{ap}     | 1.95        |
|             | Ti-O_{eq}     | 1.91        |

FIG. 2: Out-of-plane, [001]_t direction polar mode, Γ_{-1}. The atomic displacement is showing a Rigid-Layer mode along the polar direction: (Bi$_2$O$_2$) layers displace against Perovskite-like blocks, with a domination of O_{eq} motion against Bi cations. Bi atoms in Purple, Ti in blue, F in light grey and O in red.

Moreover, the calculation of the interatomic force constants (IFCs), $C_{\alpha,\beta}(l, l')$, through the expression $F_{\alpha}(l) = -C_{\alpha,\beta}(l, l')\tau_{\beta}(l')$ [31] which relates $\alpha$-component of the force $F_{\alpha}(l)$ on atom $k$ in cell $l$, to the induced displacement $\tau_{\beta}(l')$ of atom $k'$ in cell $l'$, as defined in Refs [32], allow us to identify which driving forces lead the system to structural instabilities [31, 33]. By convention when the IFC is positive it corresponds to a destabilizing interaction. Accordingly, our results on IFC, reported in Table V, showed that the shortening of the Bi-F_{ap} bonds in I4/mmm (F_{ap}) configuration decreases the distance between Bi and O_{eq} atoms, thus, increases their hybridization, as reflected by the large and positive IFC of Bi-O_{eq} interaction (+0.011 Ha/Bohr$^2$), in contrast to the IFC of Bi-F_{eq} that is positive but vanishingly small (+0.002 Ha/Bohr$^2$).

TABLE IV: Nonzero elements of the Born effective charges tensor $Z^*$ (in Cartesian coordinates) for Bi$_2$TiO$_3$F$_2$ in the paraelectric tetragonal I4/mmm phase. The nominal charges of Bi, Ti, O and F are +3, +4, −2 and −1, respectively.

| structure  | Atom | $Z^*_{xx}$ | $Z^*_{yy}$ | $Z^*_{zz}$ | $Z^*_{xy}$ | $Z^*_{xz}$ | $Z^*_{yz}$ |
|------------|------|------------|------------|------------|------------|------------|------------|
| I4/mmm (F_{eq}) | Bi  | 5.2        | 5.2        | 4.0        | 0.0        | 0.0        | 0.0        |
|             | Ti  | 4.7        | 4.7        | 9.0        | 0.0        | 0.0        | 0.0        |
|             | F_{eq} | −2.0      | −2.0      | −0.9      | −1.3       | −1.3       | 0.0        |
|             | O_{eq} | −2.4      | −2.4      | −4.9      | 1.0        | 0.0        | 0.0        |
|             | O_{fl} | −3.0      | −3.0      | −2.6      | 0.0        | 0.0        | 0.0        |
| I4/mmm (F_{ap}) | Bi  | 4.8        | 4.8        | 4.2        | 0.0        | 0.0        | 0.0        |
|             | Ti  | 8.4        | 8.4        | 4.2        | 0.0        | 0.0        | 0.0        |
|             | O_{eq} | −4.3      | −4.3      | −2.0      | −2.3       | 0.0        | 0.0        |
|             | F_{ap} | −1.7      | −1.7      | −2.3      | 0.0        | 0.0        | 0.0        |
|             | O_{fl} | −2.9      | −2.9      | −2.0      | 0.0        | 0.0        | 0.0        |

TABLE V: Interatomic force constants (IFC) in (Ha/bohr$^2$) between different selected pairs of atoms in their local coordinates system along the longitudinal (∥) direction. Dipole-Dipole (DD) and Short-Range (SR) contributions are also reported.

| structure  | Total | DD  | SR   |
|------------|-------|-----|------|
| I4/mmm (F_{ap}) | Bi-F_{ap}(∥) | 0.011 | 0.013 | −0.002 |
|             | Bi-O_{eq}(∥) | 0.011 | 0.012 | −0.001 |
| I4/mmm (F_{eq}) | Bi-O_{ap}(∥) | 0.015 | 0.022 | −0.007 |
|             | Bi-F_{eq}(∥) | 0.002 | 0.004 | −0.002 |

C. Spontaneous polarization

In order to estimate the spontaneous polarization $P_s$ for the different metastable polar phases derived from I4/mmm (F_{eq}) and I4/mmm (F_{ap}) parent phases, we used two methods: from the Berry phase approach [24], with the careful determination of the polarization quantum (see [25]) and from the knowledge of $Z^*$ and atomic displacements following the expression.

$$P_{s,\alpha} = \frac{e}{\Omega} \sum_{k,\beta} Z^*_{k,\alpha\beta} \delta \tau_{k,\beta}$$

where $\delta \tau_{k,\beta}$ is the displacement of atom $k$ along direction $\beta$ from the paraelectric to the ferroelectric phase, $Z^*_{k,\alpha\beta}$ the Born effective charge tensor of atom $k$, and $\Omega$, the unit cell volume. The results, reported in Table VI showed that, in the structure with (F_{eq}) configuration, the polar phases display $P_s$ along the [110]_t direction. $P_s$ in Fmmm2 phase (with only Γ⁺−− polar mode) is smaller than $P_s$ in Aba2 (Γ⁻− and X^+⁺), and Pca2₁ (Γ⁻, X^+⁻, X^+⁺ and M^+⁻) phases. This is in contrast to the results obtained in Bi$_2$WO$_6$ [23], in which the polarization decreases from Fmmm2 to Aba2 to Pca2₁. The increasing
TABLE VI: Spontaneous polarization $P_s$ (in μc/cm$^2$) of different metastable polar phases of Bi$_2$TiO$_4$F$_2$. $P_s$(BP) refers to the polarization computed using the Berry-phase approach, and $P_s(Z')$ corresponds to the polarization deduced from the knowledge of the Born effective charges and atomic displacements.

| structure | phase | direction $P_s(Z')$ | $P_s$(BP) |
|-----------|-------|---------------------|-----------|
| I4/mmm (F$_{eq}$) | Fm$ar{m}$m(42) | [110]$_t$ | 71 | 72 |
| | Aba2(41) | [110]$_t$ | 136 | 138 |
| | Pca2$_1$(29) | [110]$_t$ | 112 | 110 |
| I4/mmm (F$_{ap}$) | Fm$ar{m}$m(42) | [110]$_t$ | 34 | 30 |
| | I4mm(107) | [001]$_t$ | 45 | 41 |
| | Pc(7) | [110]$_t$ | 39 | 44 |
| | | [001]$_t$ | 37 | 35 |

of $P_s$ in Aba2 of Bi$_2$TiO$_4$F$_2$ with (F$_{eq}$) is due to the strong cooperation between $\Gamma_4^+$ and $X_3^+$ modes, as mentioned in section A, which is weak in the case of Bi$_2$WO$_6$ (see [25]). The polarization can reach, in this case, a very large value of 138 μc/cm$^2$ (see Table VI). In the structure with (F$_{ap}$) configuration, $P_s$ expands along both $[110]_t$ and [001]$_t$ directions. $P_s$ in I4mm phase (with only $\Gamma_4^+$ polar mode) is larger than $P_s$ in Fm$ar{m}$m2 (Γ$^*_4$). In this (F$_{ap}$) configuration, the value of $P_s$ is almost constant in the different polar phases, in agreement with the weak cooperative coupling observed between the polar modes and octahedral tilts, as mentioned in section B. Finally, the ground state Pc displays $P_s$ along two directions: 44 μc/cm$^2$ along [110]$_t$ direction and 35 μc/cm$^2$ along [001]$_t$ direction. This finding is of valuable importance since ferroelectricity in Aurivillius phases is usually in-plane [110], oriented and not very suitable for thin film applications, such as nonvolatile memory devices, that would prefer a polarization switching along out-of-plane [001]$_t$ direction to detect the switching states during read and write operations [35].

D. High symmetry Pma2 (F$_{eq}$+F$_{ap}$)

When fluorine anions are distributed over apical and octahedral sites in facc-arrangement, the highest symmetry phase is polar with orthorhombic Pma2 symmetry, with always the same sort of anion (O$_{ap}$ or F$_{ap}$) on both sides of (Bi$_2$O$_4$) layer. Phonon calculations performed in this Pma2 phase showed four unstable modes: three modes of $\Gamma_4$ symmetry at frequencies of 68i, 61i and 33i cm$^{-1}$ and one mode of $\Gamma_2$ symmetry at 44i cm$^{-1}$. $\Gamma_4$ [68i] and $\Gamma_4$ [61i] are octahedral tilts about [001] direction. Because of absence of inversion center and mirror plane perpendicular to [001] direction, octahedral tilts within the two perovskite blocks are decoupled: each $\Gamma_4$ mode defines tilts of octahedra within one single block. $\Gamma_4$ [33i] corresponds to a translation of (Bi$_2$O$_4$) layer against O$_{ap}$ and $\Gamma_2$ is an octahedral tilt about [110] direction.

We reported in Table VII the metastable phases arising from the condensation of individual and combined modes. We noticed that the energy gain in this (F$_{ap}$+F$_{eq}$) configuration is very small in comparison to (F$_{ap}$) and (F$_{eq}$) configurations. The condensation of one $\Gamma_4$ mode brought the contribution of the other $\Gamma_4$ modes and the larger energy gain (21 meV/f.u) is attributed to the phase Pc involving the largest contribution of $\Gamma_4$ [61i]. Here, we notice, that contrary to I4/mmm (F$_{eq}$) and I4/mmm (F$_{ap}$) configurations, the condensation of [001] and [110] octahedral tilts together ($\Gamma_4$ + $\Gamma_2$) in Pma2 does not increase the system stability. In this case, the ground state is polar of Pc symmetry derived from the condensation of unstable $\Gamma_4$ [001] octahedral tilt mode, but, we were unable to calculate the spontaneous polarization, since no related centrosymmetric parent phase was available in this configuration [35].

TABLE VII: Modes contributions $A_0$ (in Å) (see the text) of metastable phase, derived from condensation of individual and combined unstable modes, wrt. Pma2 orthorhombic parent phase. Energy difference $\Delta E$ (in meV/f.u) wrt. Pma2 is also reported. Frequencies [$\omega$] are in cm$^{-1}$ and Space group are given in a conventional setting.

| phase | $A_0$ | $\Delta E$ |
|-------|------|-----------|
| Pca2$_1$(7) | 8.2 [2.3 1.9 6.8] | -19 |
| Pca2$_1$(7) | 5.4 [2.7 2.4 5.6] | -11 |
| Pca2$_1$(7) | 7.2 [2.7 1.9 5.5] | -21 |
| Pca2$_1$(7) | 7.6 [2.7 1.9 5.5] | -17 |

In previous sections, we have discussed independently the key configurations of fluorine sites ordering in Bi$_2$TiO$_4$F$_2$. In Figure 3, we provided a global view recapitulation, comparing the internal energies of the three parent phases and the metastable phases resulting from the condensation of their unstable modes. We found that I4/mmm (F$_{eq}$) is the less stable configuration, followed by I4/mmm (F$_{ap}$) to finally identify the orthorhombic Pma2 (F$_{ap}$+F$_{eq}$) as the most stable configuration (consistently with the calculations of K. Morita [13]) and its derived polar monoclinic Pc phase as the most stable among the different metastables phases explored herein. Our calculations do not fit the I4/mmm experimental model of Needs et al. [31] with fluorine assigned to equator-lateral sites thanks to Bond Valence Sum calculations. However, it is important to point out that these authors mentioned the possibility of symmetry lowering to polar I4mm, via a phase transition occurring with a very small perturbation that is not apparent to diffraction techniques [36][39]. In particular, these authors exclude the possible assignment of an equal mixture of oxide and fluorine anions over apical and equatorial sites, although
When fluorine anions are positioned at equatorial sites only (F

symmetry, deriving from small distortions of the parent I4/mmm phase, involving in-plane polar and antipolar displacements of Bi and Ti cations and in-plane and out-of-plane octahedral tilts. Whereas, when fluorine anions are at apical sites only (F$_{ap}$), the most favorable phase is polar of Pc symmetry, also deriving from parent I4/mmm phase and involving in-plane polar displacement of Bi and Ti cations, out-of-plane polar displacement of Bi against O$_{eq}$ and in-plane and out-of-plane octahedral tilts. In particular, this Pc phase is displaying two distinct spontaneous polarizations: in-plane $P_x = 44 \mu C/cm^2$ and out-of-plane $P_z = 35 \mu C/cm^2$. This phase is of great importance in FeRAM’s thin films applications and appropriate strain engineering on this phase should be investigated to increase its stability.

IV. CONCLUSION

We have shown in the $m=1$ oxyfluoride Aurivillius phase Bi$_2$TiO$_4$F$_2$, that the ground state is polar of Pc symmetry and that the ordered distribution of fluorine anions over both apical and equatorial octahedral sites in the perovskite-like blocks (F$_{eq}$+F$_{ap}$) is favored. When fluorine anions are positioned at equatorial sites only (F$_{eq}$), the most favorable phase is polar of Pca2$_1$ symmetry, deriving from small distortions of the parent I4/mmm phase, involving in-plane polar and antipolar displacements of Bi and Ti cations and in-plane and out-of-plane octahedral tilts. Whereas, when fluorine anions are at apical sites only (F$_{ap}$), the most favorable phase is polar of Pc symmetry, also deriving from parent I4/mmm phase and involving in-plane polar displacement of Bi and Ti cations, out-of-plane polar displacement of Bi against O$_{eq}$ and in-plane and out-of-plane octahedral tilts. In particular, this Pc phase is displaying two distinct spontaneous polarizations: in-plane $P_x = 44 \mu C/cm^2$ and out-of-plane $P_z = 35 \mu C/cm^2$. This phase is of great importance in FeRAM’s thin films applications and appropriate strain engineering on this phase should be investigated to increase its stability.

[1] B. Aurivillius, Arkiv for Kemi 1, 463 (1949).
[2] J. M. Perez-Mato, P. Blaha, K. Schwarz, M. Aroyo, D. Orobengoa, I. Etxebarria, and A. García, Phys. Rev. B 77, 184104 (2008), URL https://link.aps.org/doi/
