O/F anion order in Pb$_2$Ti$_4$O$_9$F$_2$ stabilized by the 6s$^2$ lone pair electrons of Pb$^{2+}$

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Understanding the mechanisms of anionic ordering in mixed anion compounds is a crucial factor for designing their structural and functional properties. Some oxyfluorides are known to exhibit the F$^-$ ordering. The ordering is accompanied by a tetragonal distortion, which is believed to be originated by the 6s$^2$ lone pairs of Bi and Pb. To elucidate the role played by the lone pair, we studied isostructural Bi$_2$Ti$_4$O$_{11}$ and Pb$_2$Ti$_4$O$_9$F$_2$ with a combination of synchrotron X-ray diffraction techniques and ab initio calculations. Bi$_2$Ti$_4$O$_{11}$ undergoes antiferroelectric-paraelectric transitions from C2/c to C2/m. Meanwhile, Pb$_2$Ti$_4$O$_9$F$_2$ does not, because F$^-$ selectively occupies the closest anion site to Bi/Pb and reduces the distortion. The question on why a particular site is selectively occupied by F$^-$ in Pb$_2$Ti$_4$O$_9$F$_2$ becomes important to understand the role of 6s$^2$ lone pair electrons for stabilizing the anion order. Our DFT ab initio calculations reproduced the same anionic arrangement in terms of the total energy. However, this energy gain cannot be fully explained by the electrostatic energy, being an exception of Pauling’s second rule. We explain the reason focusing on the steric effects of 6s lone pairs.

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I. INTRODUCTION

The properties of mixed anion compounds strongly depend on the degree of order or disorder of the anions. Anionic ordering can cause heteroleptic coordinations or low-dimensional structure which in turn modify electronic properties. This intriguing possibility to modify a material has attracted significant attention [1–4]. A typical example are ABX$_3$ perovskites. For example, SrTaO$_3$N and BaTaO$_2$N have a high dielectric constant due to the O/N anion order [5–7]. In addition, an oxyhydride SrVO$_2$H shows the two-dimensional electronic conduction and compression anisotropy due to the O/H anion order [8].

Multiple anions and cations are heteroleptically coordinated and their concentrations typically obey valence charge neutrality conditions. When differences in ionic radii, electronegativity or polarizability are large, materials tend to
exhibit ionic ordering [9, 10]. However, although O$^{2-}$ and F$^-$ are neighboring anions in the periodic table, the oxyfluorides exhibit an anionic ordering depending on the structure. While simple cubic perovskites (SrFeO$_3$F [11], BaFeO$_2$F [12], PbScO$_2$F [13], BaScO$_2$F [14], AgFeOF [15], BaInO$_3$F [16], and AgTiOF$_2$ [17]) adopt disordered configurations, a variety of Ruddlesden-Popper type layered perovskites (Sr$_2$CuO$_2$F$_2$ [18], Sr$_2$FeO$_3$F [19, 20], Ba$_2$InO$_3$F [21], Ba$_2$ScO$_2$F [22], Sr$_2$MnO$_3$F [23], Sr$_2$Fe$_{3-}x$O$_x$F$_x$ [19, 24]) exhibit ordered configurations of F$^-$. In layered perovskites, multiple distinct anion sites are present and support anion order. This manner can be interpreted by considering Pauling’s second rule, where a stable ionic structure is arranged to compensate the valence of an anion by the bond strength of coordinated cations. Thus, F$^-$ prefers more open site compared to O$^{2-}$, leading to O/F anion order. On the other hand, there are some perovskites with relatively simple structures showing the partial anion ordering, such as PbFeO$_2$F [26, 27], Pb$_2$Ti$_2$O$_5$F$_2$ [28], PbOF$_2$ [29], and Pb$_2$Ti$_3$O$_5$F$_2$ [30]. Their anion order is considered the consequence of the Jahn-Teller distortion relevant to the 6$s^2$ lone pair [27, 28, 30].

To investigate the role played by the 6$s^2$ lone pair, we concentrate on the oxyfluorides containing Pb or Bi [28–30]. For an ideal analysis, completely isostructural oxyfluoride concentrate on the oxyfluorides containing Pb or Bi [28–30]. To investigate the role played by the 6$s^2$ lone pair, we concentrate on the oxyfluorides containing Pb or Bi [28–30]. For an ideal analysis, completely isostructural oxyfluoride concentrate on the oxyfluorides containing Pb or Bi [28–30].

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Eventually, we found an isostructural pair Pb$_2$Ti$_3$O$_5$F$_2$ [30] and oxide Bi$_2$Ti$_3$O$_11$ [33]. Both Pb$^{2+}$ and Bi$^{3+}$ have the same electron configuration and a 6$s^2$ lone pair. Bi$_2$Ti$_3$O$_11$ undergoes antiferroelectric-paraelectric transitions from C$2/c$ to C$2/m$, while Pb$_2$Ti$_3$O$_5$F$_2$ does not. The high-temperature paraelectric phase of Bi$_2$Ti$_3$O$_11$ (C$2/m$) adopts the same space group symmetry as Pb$_2$Ti$_3$O$_5$F$_2$ [33]. Therefore, the system provides ideal platform to investigate the role of 6$s^2$ lone pair on O/F anion arrangement.

An earlier work by Oka et al. found that F$^-$ selectively occupies the closest anionic site to Bi/Pb site in Pb$_2$Ti$_3$O$_5$F$_2$ [30]. The anionic site was named site-6. They observed that the fluorine occupation elongates the distance between the site-6 and Bi/Pb site. Oka et al. concluded that the elongation caused the disappearance of antiferroelectric transition in Pb$_2$Ti$_3$O$_5$F$_2$.

In this paper, to understand what is unique at site-6, we carefully analyzed and compared Pb$_2$Ti$_3$O$_5$F$_2$ and Bi$_2$Ti$_3$O$_11$. The anion configuration around Bi is more distorted than that of Pb, where the O$^{2-}$ at the site-6 is significantly closer to Bi than the other surrounding oxygen ions. We established that this difference between Pb$_2$Ti$_3$O$_5$F$_2$ and Bi$_2$Ti$_3$O$_11$ attributed to that 6$s^2$ lone-pair more strongly hybridizes with oxygen than fluorine at the site-6. Here, the question is why site-6 is preferred by fluorine ions in Pb$_2$Ti$_3$O$_5$F$_2$. To answer this question, we performed ab initio calculations. Though the total energy is surely stabilized by the site-6 occupation, it is not fully stabilized due to the electrostatic electrostatic energy, being an exception of Pauling’s second rule. Our structural and bonding nature analyses showed that the site-6 occupation weakens the anti-bonding orbital, between Pb and site-6 anion, distributing on the other side of the site-6 across Pb. The change of the anti-bonding orbital reduces the steric effect that hampers Pb bond to the site-2 oxygen on the other side of the site-6. This can be the reason of the deviation from Pauling’s second rule.

We organize the rest of the paper as follows. In Section II, we describe the details of the synthesis and synchrotron X-ray powder diffraction (SXRD) and the calculation conditions. In Section III, we compare and discuss the geometric and electronic structures of Pb$_2$Ti$_3$O$_5$F$_2$ with the isostructural oxide, the high-temperature (HT) phase of Bi$_2$Ti$_3$O$_11$, and the low-temperature (LT) phase of Bi$_2$Ti$_3$O$_11$. In Section IV, we show the total energies and electrostatic energies for the possible five anion orders to show that their lowest energies structures are inconsistent. This is not explained by Pauling’s second rule. We discuss the reason focusing on the orbital hybridizations. We summarize our work in Section V.

II. METHODS

The powder samples of Bi$_2$Ti$_3$O$_11$ and Pb$_2$Ti$_3$O$_5$F$_2$ were prepared by solid-state reaction. As previously reported [30, 33], Bi$_2$Ti$_3$O$_11$ was synthesized from a stoichiometric mixture of Bi$_2$O$_3$ (99.9%, Rare Metallic Co.) and TiO$_2$ (99.9%, Rare Metallic Co.) powders. The pelletized mixture was treated at 1273 K for 12 h in the air. Pb$_2$Ti$_3$O$_5$F$_2$ was synthesized from a mixture of PbO (99.9 %, Rare Metallic Co.), PbF$_2$ (99.9 %, Rare Metallic Co.), and TiO$_2$ (rutile, 99.9 %, Rare Metallic Co.) powders were weighed to be 10 mol% fluorine-rich to compensate the loss of fluorine during the reaction [27]. The pelletized mixture was sealed in an evacuated Pyrex tube and treated at 823 K for 12 h.

SXRD patterns were collected with a large Debye–Scherrer camera installed at beamline BL02B2 of SPring-8 using a glass capillary and a solid state detector [34]. The crystallographic parameters were refined by the Rietveld method using the RIETAN-FP program [35]. The electron density distributions were estimated by the maximum entropy method (MEM) using the Dynamos program [36]. The crystal structures and electron density mappings are visualized using VESTA program [37].

The density functional theory (DFT) calculations were performed with Quantum Espresso [38]. PBE [39] and BLYP [40, 41] semi-local functionals were employed. The core orbitals were described by projector augmented wave (PAW) method [42]. PAW pseudopotentials were taken from the pslibrary [43]. The valence orbitals were expanded with
plane waves. The cutoff energy was 100 Ry and the $k$-point mesh was $7 \times 7 \times 5$ for the unit cell. The LOBSTER code [44] was used to perform the Crystal Orbital Hamiltonian Population (COHP) analyses based on the DFT results with pbeVaspFit2015 basis set [45, 46].

### III. COMPARISON BETWEEN Bi$_2$Ti$_4$O$_{11}$ AND Pb$_2$Ti$_4$O$_9$F$_2$

Production of single phase for both Bi$_2$Ti$_4$O$_{11}$ and Pb$_2$Ti$_4$O$_9$F$_2$ samples were confirmed by SXRD technique. The SXRD patterns and results of Rietveld refinement for the LT (300 K) and HT (600 K) phases of Bi$_2$Ti$_4$O$_{11}$ and Pb$_2$Ti$_4$O$_9$F$_2$ (300 K) are given in the supporting information. Bi$_2$Ti$_4$O$_{11}$ undergoes structural transition from low-temperature (LT) antiferroelectric (Space group: C2/c) to high-temperature (HT) paraelectric phase (Space group: C2/m) at 506 K [33]. As previously reported, Pb$_2$Ti$_4$O$_9$F$_2$ is isostructural with the HT paraelectric phase of Bi$_2$Ti$_4$O$_{11}$ and does not show structural transition down to 5 K [30].

The local coordination environments around Bi/Pb in Bi$_2$Ti$_4$O$_{11}$ and Pb$_2$Ti$_4$O$_9$F$_2$ are shown in Figure 1. The numbers at the anions indicate the site indices. We provide the experimental crystal structures in the CIF format as the supporting information, as one can distinguish the anion sites with their own visualizing softwares. The shortest Bi/Pb-O/F6 bond lengths are largely different between Bi$_2$Ti$_4$O$_{11}$ and Pb$_2$Ti$_4$O$_9$F$_2$. Pb-F6 of Pb$_2$Ti$_4$O$_9$F$_2$ is significantly longer than Bi-O6 of the HT phase of Bi$_2$Ti$_4$O$_{11}$. Here, O6 (F6) indicates an oxygen (fluorine) ion in the site-6. The elongated bond length reduces the degree of anisotropy of the ligand configurations around Bi/Pb as shown in Figure 1. The antiferroelectric transition in Bi$_2$Ti$_4$O$_{11}$ is known to be associated with displacements of the Bi ion from the centrosymmetric position along the $b$ axis [33, 47]. Therefore, the disappearance of antiferroelectric transition for Pb$_2$Ti$_4$O$_9$F$_2$ would be related to the reduced anisotropic character around Pb$^{2+}$ ion.

The changes in local coordination environment around Bi$^{3+}$ or Pb$^{2+}$ were further investigated. Figure 2 shows the electron density distribution obtained by MEM. The differences of covalent character of the Bi-O6 bonds between the HT and LT phases of Bi$_2$Ti$_4$O$_{11}$ are obvious. This anisotropic change in covalency around Bi$^{3+}$ is associated with the anti-parallel displacement of Bi$^{3+}$ ion along the $b$ axis in the LT phase, suggesting 6$^2$c lone pair electrons at play. Therefore, we infer that the absence of antiferroelectric transition in Pb$_2$Ti$_4$O$_9$F$_2$ is a consequence of the reduction on the interaction between the Pb-6s and anion-2p electrons. Figure 3 shows a 2-dimensional electron density mapping sliced along Bi/Pb-O/F6 bond obtained by MEM. The electron density associated to the covalent character of Bi-O6 is observed in Bi$_2$Ti$_4$O$_{11}$ at the HT phase. On the other hand, the covalency between Pb and F6 is less pronounced in Pb$_2$Ti$_4$O$_9$F$_2$. These results suggest that O/F anion order in Pb$_2$Ti$_4$O$_9$F$_2$ occurs to reduce the interaction between 6s and 2p electrons. We confirmed that the

We verified the experimental conclusion theoretically per-forming a COHP analysis to the hybrid orbital of Pb/Bi-6s and O/F-2p. The COHP analysis quantifies the degree of (anti-)bonding strength of the hybrid orbital evaluating the integrated COHP (ICOHP). Positive (negative) ICOHP indicates anti-bonding (bonding) nature. The absolute value indicates a degree of (anti-)bonding strength. We obtained ICOHP(Pb-6s–F6-2p) = -0.032 and ICOHP(Bi-6s–O6-2p) = -0.289; Pb-6s and F6-2p make a significantly weaker bonding hybrid orbital than Bi-6s and O6-2p. The stronger bonding hybridization between Bi-6s and O6-2p makes Bi easily displaces towards the site 6 than Pb. This explains the relatively high temperature of the antiferroelectric transition (C2/m $\rightarrow$ C2/c in Figure 2) of Bi$_2$Ti$_4$O$_{11}$.

We also confirmed that DFT and MEM give qualitatively similar results as shown in the supporting information.

### IV. REASON OF THE F-IN-SITE6 PREFERENCE IN Pb$_2$Ti$_4$O$_9$F$_2$

We performed DFT ab initio calculations to evaluate the energetics of the F$^{-}$ occupation patterns of Pb$_2$Ti$_4$O$_9$F$_2$. We calculated the energy of each pattern with PBE [39] and BLYP [40, 41] functionals as shown in Table I. Here, for example, F-in-site2 indicates the pattern that fluorine selectively occupies the site 2. F-in-site 3 is not considered because the multiplicity of site 3 is 1 per f.u., but there are 2 fluorine atoms per f.u. Both functionals reproduce the experimental F-in-site6 preference. The two results are very close to each other and qualitatively identical. Therefore, the DFT result would not significantly alter depending on the choice of functional. To understand the origin of F-in-site6 stabilization, we compared electrostatic energies using PBE and BLYP functionals, shown as the vertical axis values in Figure 4. To get the electrostatic energies, we used ultrasoft pseudopotentials provided in the pslibrary [43], since we could not get the electrostatic energies from the quantum espresso output with PAW pseudopotential. This is because the one-center term includes both electrostatic and exchange-correlation energies [48]. We confirmed that the relative energies of fluorine occupation patterns are identical between PAW and ultrasoft pseudopotentials within 1 meV/f.u. Figure 4 shows that PBE and BLYP qualitatively agree with each other. The total energies are roughly proportional to the electrostatic energies, consistent with a previous systematic study on NdNiO$_2$F by simulations [49]. Meanwhile, the F-in-site6 cannot be fully

| Site | PBE Energy (meV) | BLYP Energy (meV) |
|------|------------------|-------------------|
| F-in-site1 | 1.019 | 0.965 |
| F-in-site2 | 0.935 | 0.889 |
| F-in-site4 | 0.321 | 0.308 |
| F-in-site5 | 0.061 | 0.066 |
| F-in-site6 | 0.000 | 0.000 |
explained by Pauling’s second rule (structural stabilization via electrostatic gain), requiring us to investigate further the origin of the F-in-site6 stabilization. (In the supporting information, we discussed the electrostatic energies approximated by Madelung potentials with different point charge models.) Later in this paper, we use only PBE functional because PBE and BLYP agree with each other about the total and electrostatic energies.

We focused on the orbital energies to explain the F-in-site6 stabilization. One can understand qualitatively the sta-
orbital channels. TABLE II. Energy differences (F-in-site5 - F-in-site6) of the valence orbital channels.

| Orbital channel | Energy (eV) |
|-----------------|-------------|
| F-2\(\alpha\)   | +0.098      |
| F-2\(p\)        | -0.062      |
| O-2\(s\)        | -0.206      |
| O-2\(p\)        | +1.288      |
| Pb-6\(s\)       | +0.820      |
| Pb-6\(p\)       | +0.078      |
| Ti-3\(s\)       | +0.005      |
| Ti-3\(p\)       | +0.009      |
| Ti-3\(d\)       | +0.095      |
| Ti-4\(s\)       | +0.028      |
| Total           | +2.15       |

The PDOS result indicates that the hybridization occurred mainly between Pb and O6. The energy of orbital \(\alpha\) is given as the integration of \(\epsilon \cdot D_{\alpha}(\epsilon)\), where \(D_{\alpha}(\epsilon)\) is the PDOS of the orbital \(\alpha\) at the energy \(\epsilon\). We performed the PDOS integration for each orbital in the valence band range, \([-10\text{eV}:0\text{eV}]\) \((\epsilon=0\ \text{eV}\ \text{is the Fermi energy})\). Then, we compared the orbital energy differences between F-in-site5 and F-in-site6, as shown in Table II: the orbital energy of O-2\(p\) was significantly higher for F-in-site5 than F-in-site6.

TABLE III. Energy differences (F-in-site5 - F-in-site6) of the 2\(p\) channels of the anions.

| \(\alpha\) (orbital) | \(\epsilon \cdot \Delta D_{\alpha}(\epsilon)\) (eV) |
|---------------------|-----------------------------------------------|
| O1-2\(p\)           | +0.119                                        |
| O2-2\(p\)           | +0.335                                        |
| O3-2\(p\)           | +0.015                                        |
| O4-2\(p\)           | -0.064                                        |
| O5/6-2\(p\)+F6/5-2\(p\) | +0.191                                        |

The 2\(p\) orbital energy difference of each oxygen between F-in-site5 and F-in-site6 is shown in Table III. (For sites 5 and 6, we compared O5-2\(p\)+F6-2\(p\) for F-in-site5 and F5-2\(p\)+O6-2\(p\) for F-in-site6.) The result shows that 2\(p\) orbital energy of O2 differs the most. O2 is located on the other side of O/F6 across the Bi/Pb as shown in Figure 6. The figure shows the distance and ICOHP between Pb and O2 and the values indicate weaker binding strength for the F-in-site5. This would be contributed to that the Pb-O6 hybridization for F-in-site5 is stronger than the Pb-F6 hybridization for F-in-site6. The hybridization makes an anti-bonding orbital distributing in the other side of the O/F6 across the Bi/Pb, i.e., between the Bi/Pb and O2. Therefore, the anti-bonding orbital caused by the 6\(s^2\) lone pair would hamper the binding between Bi/Pb and O2 as a steric effect. Since the hybridization is stronger for F-in-site5 than F-in-site6, the steric effect would be also stronger for F-in-site5. This is a significant origin of the F-in-site6 preference in Pb\(_2\)Ti\(_4\)O\(_8\)F\(_2\), which cannot be fully explained by Pauling’s second rule.

V. CONCLUSION

To understand the cause of the F\(^-\) ordering, preferably occupying a specific site, Bi\(_2\)Ti\(_4\)O\(_{11}\) and Pb\(_2\)Ti\(_4\)O\(_8\)F\(_2\) were simultaneously investigated by SXRD technique and ab initio calculations. In Bi\(_2\)Ti\(_4\)O\(_{11}\), the tetragonal instability and the accompanying anisotropic coordination result in an antiferroelectric transition. Meanwhile, Pb\(_2\)Ti\(_4\)O\(_8\)F\(_2\) undergoes an antiferroelectric transition down to 5 K, because F\(^-\) selectively occupies the closest anion site (site-6) to Bi/Pb, and then F\(^-\) elongates the Bi/Pb-O/F6 distance and reduces the distortion around the Bi/Pb. We found that the binding hybridization between Pb-6\(s\) and F6-2\(p\) is significantly weaker than Bi-6\(s\) and O6-2\(p\), explaining the longer distance of Pb-F6 than Bi-O6. Ab initio calculations were performed to analyze the F-in-site6 preference. Though the F-in-site6 is surely observed experimentally to be the most stable configuration, it is not fully explained by the electrostatic energy, being an exception of Pauling’s second rule. To understand the reason, we focus on the orbital energies. The PDOS analysis shows that the O2-2\(p\) is significantly more stable for F-in-site6 than F-in-site5. From the structural and COHP analyses, we conclude...
that the anti-bonding hybrid orbital between Pb and O/F6, explained by the RLP model [51], hampers the binding between Pb and O2 more strongly for the F-in-site5 than F-in-site6.

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FIG. 5. Partial density of states predicted by DFT. The arrows indicate the peaks accompanied by the anti-bonding hybrid orbitals explained by the lone-pair model.
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