Local Oxygen-Vacancy Ordering and Twinned Octahedral Tilting Pattern in the Bi$_{0.81}$Pb$_{0.19}$FeO$_{2.905}$ Cubic Perovskite

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Supporting Information

ABSTRACT: The structure of Bi$_{0.81}$Pb$_{0.19}$FeO$_{2.905}$ was investigated on different length scales using a combination of electron diffraction, high-resolution scanning transmission electron microscopy, synchrotron X-ray powder diffraction, and Mössbauer spectroscopy. In the 80–300 K temperature range, the average crystal structure of Bi$_{0.81}$Pb$_{0.19}$FeO$_{2.905}$ is a cubic Pm$3m$ perovskite with $a = 3.95368(3)$ Å at $T = 300$ K. The (Pb$^{2+}$, Bi$^{3+}$) cations and O$^{2−}$ anions are randomly displaced along the (110) cubic directions, indicating the steric activity of the lone pair on the Pb$^{2+}$ and Bi$^{3+}$ cations and a tilting distortion of the perovskite framework. The charge imbalance induced by the heterovalent Bi$^{3+}$ → Pb$^{2+}$ substitution is compensated by the formation of oxygen vacancies preserving the trivalent state of the Fe cations. On a short scale, oxygen vacancies are located in anion-deficient (FeO$_{1.23}$) layers that are approximately 6 perovskite unit cells apart and transform every sixth layer of the FeO$_6$ octahedra into a layer with a 1:1 mixture of corner-sharing FeO$_4$ tetrahedra and FeO$_2$ tetragonal pyramids. The anion-deficient layers act as twin planes for the octahedral tilting pattern of adjacent perovskite blocks. They effectively randomize the octahedral tilting and prevent the cooperative distortion of the perovskite framework. The disorder in the anion sublattice impedes cooperative interactions of the local dipoles induced by the off-center displacements of the Pb and Bi cations. Magnetic susceptibility measurements evidence the antiferromagnetic ordering in Bi$_{0.81}$Pb$_{0.19}$FeO$_{2.905}$ at low temperatures.

KEYWORDS: perovskite, multiferroic, BiFeO$_3$, Pb, doping, oxygen vacancy, octahedral tilting, ordering, transmission electron microscopy, HRTEM, ED, HAADF-STEM, ABF-STEM

1. INTRODUCTION

At room temperature, the well-known perovskite BiFeO$_3$ is both ferroelectric ($T_C \approx 1100$ K) and antiferromagnetic ($T_N \approx 640$ K). This makes it one of the rare single-phase materials that are multiferroic at room temperature. BiFeO$_3$ crystallizes in a rhombohedral $R3c$ unit cell, with an antiphase tilt of the FeO$_6$ octahedra represented by the $a\bar{a}c$ pattern in Glazer’s notation. The displacement of both the Fe$^{3+}$ and Bi$^{3+}$ cations from their different coordination environments along the cubic $[111]$ directions (here, the subscript $p$ refers to the parent perovskite cell) results in the appearance of switchable electric polarization. To make the material suitable for applications, the polarization should be further coupled to the net magnetization, which is, however, very weak in the canted antiferromagnetic structure of BiFeO$_3$.

Numerous isovalent and heterovalent substitutions on the A site of BiFeO$_3$ have been attempted, in order to induce the net magnetization and improve magnetoelastic coupling. The Bi$^{3+}$ → Pb$^{2+}$ replacement holds a special place in this row, because the electronic structures of Pb$^{2+}$ and Bi$^{3+}$ are similar, with both cations having a lone pair. However, the Bi$^{3+}$ → Pb$^{2+}$ substitution requires charge compensation that occurs through the formation of oxygen vacancies. The formation of oxygen vacancies is promoted by the Fe$^{3+}$ cation, which is able to adopt different coordination environments—tetrahedral, pyramidal or octahedral—because of the $d^5$ high-spin electronic configuration and zero crystal-field energy that reduces the energetic difference between the different coordination polyhedra.

In low amounts ($x \leq 0.075$), the substitution of Bi$^{3+}$ by Pb$^{2+}$ maintains the $R3c$ structure of Bi$_{1−x}$Pb$_x$FeO$_3$ while at higher $x$ the rhombohedral distortion slowly decreases within a two-phase region (cubic and rhombohedral). From $x \geq 0.15$ up to $x = 0.20$, the cubic $Pm3m$ perovskite structure is formed. At a higher Pb content, antiferroelectric (Pb,Bi)$_{1−x}$Fe$_{1+x}$O$_3$ perovskites are obtained, with compositions ranging from Bi$_{0.894}$Pb$_{0.106}$Fe$_{0.046}$O$_{3.572}$ to Bi$_{0.05}$Pb$_{0.95}$Fe$_{0.025}$O$_{2.796}$. In these compounds, the oxygen vacancies are partially eliminated by periodically spaced crystallographic shear planes. The Pb$_3$Fe$_2$O$_7$ ($x = 1$) end member of the series does not exist as an individual compound, but consists of an intergrowth of domains, with perovskite blocks modulated by crystallographic...
shear planes featuring variable orientation and interplanar spacing. The functioning of such domains is therefore variable. The prevailing composition is \( \text{Bi}_0.81\text{Pb}_{0.19}\text{FeO}_{2.905} \).

At first glance, the cubic phase at \( 0.15 < x < 0.20 \) is rather bland compared to other solid solutions and \( \text{BiFeO}_3 \) itself. The cubic symmetry forbids the formation of electric polarization and is clearly detrimental for the multiferroic behavior. However, the local structure of the “cubic” \( \text{Bi}_{0.81-x}\text{Pb}_{x}\text{FeO}_{3-x/2} \) perovskite may be more complex than initially perceived. First, a strong interaction between the oxygen vacancies should be operative already at \( 0.15 < x < 0.20 \). Above \( x = 0.4 \), such interactions eventually lead to the formation of ordered arrays of crystallographic shear planes, and at \( x = 0.2 \), interactions and ordering at least on a local scale can be expected. Second, the low tolerance factor \( (t = 0.93) \) for the \( x = 0.2 \) composition implies the possibility of an octahedral tilting distortion of the perovskite framework. Third, the lone-pair A cations are an additional source of structural distortions. Both the ordering of oxygen vacancies, the tilting distortion, and the displacements of the lone-pair A cations will break the cubic symmetry and enable the formation of local dipoles as a prerequisite of bulk ferroelectricity.

Therefore, the cubic symmetry of the \( \text{Bi}_{0.81-x}\text{Pb}_{x}\text{FeO}_{3-x/2} \) solid solutions remains controversial. For example, Khomchenko et al. proposed a rhombohedrally distorted polar \( R3c \) structure with the \( a' a'a' \) tilting distortion for \( x = 0.2 \), 0.3, but Chaigneau et al. reported the cubic symmetry. In this contribution, we resolve this controversy and provide a complete characterization of the long-range and short-range structural order in \( \text{Bi}_{0.81-x}\text{Pb}_{x}\text{FeO}_{3-x/2} \). Although we unequivocally establish the cubic symmetry of the average crystal structure, electron microscopy and Mössbauer spectroscopy evidence complex local distortions related to the ordering of oxygen vacancies and tilting distortions of the perovskite framework.

2. EXPERIMENTAL SECTION

The single crystal with the nominal composition \( \text{Bi}_{0.81-x}\text{Pb}_{x}\text{FeO}_{3-x/2} \) was provided by Chaigneau et al. \(^6\) The \( \text{Bi}_{0.81-x}\text{Pb}_{x}\text{FeO}_{3-x/2} \) sample for the synchrotron X-ray powder diffraction (SRXD) experiment was synthesized by a solid-state reaction of \( \text{Bi}_2\text{O}_3 \), \( \text{PbO} \), and \( \text{Fe}_2\text{O}_3 \). The oxides were mixed in a stoichiometric ratio, rigorously ground in an agate mortar under acetone, pressed into pellets, and annealed in air at 800 °C for 50 h with an intermediate regrinding. The completeness of the reaction was controlled by powder X-ray diffraction taken with a Huber G670 Guinier image plate camera (Cu Kα radiation).

The high-resolution synchrotron X-ray powder diffraction patterns were measured at the ID31 beamline of the European Synchrotron Radiation Facility (ESRF) with a constant wavelength of about 0.4 Å. The data were collected by eight scintillation detectors, each preceded by a Si (111) analyzer crystal, in the angle range \( 2θ = 1−40° \). The powder sample was contained in a thin-walled borosilicate glass capillary with an external diameter of 0.5 mm. To achieve good statistics and to avoid the effects of the preferred orientation, the capillary was spun during the experiment. The sample was cooled below RT with a liquid-nitrogen cryostream (temperature range 100–300 K). Diffraction data were analyzed by the Rietveld method with the JANA2006 program. \(^18\)

Samples for electron microscopy were prepared by dispersing the powder in ethanol and depositing it on a holey carbon grid. Selected area electron diffraction (SAED) patterns were obtained on a Philips CM20 transmission electron microscope. High-resolution transmission electron microscopy images (HRTEM) were obtained on a JEOL-2000 transmission electron microscope, high-angle annular dark-field scanning transmission electron microscopy images (HAADF-STEM) on a Tecnai G2 transmission electron microscope, and annular bright-field scanning transmission electron microscopy (ABF-STEM) images were obtained using a Titan G3 electron microscope operated at 300 kV and equipped with an aberration corrector. The composition of the samples was determined with energy dispersive X-ray (EDX) analysis performed on a JEDM JSM5510 scanning electron microscope on 50 different crystallites and on the Philips CM20 transmission electron microscope for each crystallite studied by electron diffraction; both instruments are equipped with the Oxford INCA system. HAADF-STEM and ABF-STEM image simulations were made using the QSTEM software. \(^17\)

The oxidation state of iron in the \( \text{Bi}_{0.81-x}\text{Pb}_{x}\text{FeO}_{3-x/2} \) material with the natural abundance of \( ^5\text{Fe} \) has been tested in a Mössbauer absorption study. Mössbauer spectra were collected using a conventional constant acceleration spectrometer consisting of a Rh matrix \(^{57}\)Co radioactive source mounted on an oscillating drive, a sample stage, and a gas proportional detector. An absorption spectrum of 25 μm thick iron foil was used for calibration. Absorption spectra were fitted within a thin absorber approximation using the commercially available program NORMOS written by R.A. Brand and distributed by Wissenschaftliche Elektronik GmbH, Germany. The isomer shift values are calculated relative to the value of the \( α\text{-Fe} \) calibration foil.

The magnetic susceptibility of \( \text{Bi}_{0.81-x}\text{Pb}_{x}\text{FeO}_{3-x/2} \) was measured with the Quantum Design PPMS SQUID magnetometer in the temperature range 2–380 K in fields up to 5 T. No differences between the data collected in the field-cooling and zero-field-cooling regimes were detected.

3. RESULTS

Laboratory powder XRD analysis of the \( \text{Bi}_{0.81-x}\text{Pb}_{x}\text{FeO}_{3-x/2} \) sample indicated the presence of a cubic perovskite phase only. The EDX analysis shows an atomic ratio of \( \text{Bi/Pb/Fe} = 0.41(8):0.08(5):0.50(9) \), and according to the Mössbauer study, all iron in the material is present as \( \text{Fe}^{3+} \) only. The low values of the Mössbauer isomer shifts for all hyperfine components contributing to the absorption spectrum are the distinctive signature of \( \text{Fe}^{3+} \) iron (discussed later). These results are in agreement with the nominal composition \( \text{Bi}_{0.81-x}\text{Pb}_{x}\text{FeO}_{3-x/2} \).

Synchrotron X-ray powder diffraction in the 80–300 K temperature range did not reveal any extra reflections or reflection splitting that could be attributed to either a superstructure or impurity phases. The SXPD pattern was completely indexed in a primitive cubic unit cell with \( a = 3.95368(3)Å \) at 300 K. The crystal structure of \( \text{Bi}_{0.81-x}\text{Pb}_{x}\text{FeO}_{3-x/2} \) was refined within the \( Pm\overline{3}m \) space group using the atomic coordinates of the cubic perovskite as a starting model (\( \text{PbBi}:1/2,1/2,1/2 (1\text{a}); \text{Fe}:0,0,0(1\text{b}); \text{O}:1/2,0,0(3\text{d}) \)). The 1b position was assumed to be occupied jointly by \( \text{Bi}^{3+} \) and \( \text{Pb}^{2+} \) cations with an occupancy factor 0.81 \( \text{Bi}^{3+} \) + 0.19 \( \text{Pb}^{2+} \). The occupancy factor for the O position was set to \( g = 0.968 \) in order to satisfy the \( \text{Bi}_{0.81-x}\text{Pb}_{x}\text{FeO}_{3-x/2} \) formula. The refinement with the ideal perovskite structure revealed abnormally large atomic displacement parameters \( \overline{U}_{iso} \) (ADP) of 0.065 Å\(^2\) and 0.074 Å\(^2\) for the \( \text{Pb}-\text{Bi} \) and \( \text{O} \) atoms, respectively, whereas \( \overline{U}_{iso} \) for the \( \text{Fe}^{3+} \) cations has a reasonable value of 0.016 Å\(^2\). This indicates random displacements of the \( \text{Pb}^{2+} \)–\( \text{Bi}^{3+} \) and \( \text{O}^{2-} \) ions from the high-symmetry positions.

The displacements of the \( \text{Pb}^{2+} \)–\( \text{Bi}^{3+} \) cations along the \( 100 \), \( 110 \), and \( 111 \) directions of the cubic unit cell were tested in the refinement against the SXPD data at \( T = 80 \) K, in order to minimize the impact of the thermal motion. The reliability factors \( (R_p) \) and \( U_{iso} \) values \( R_p = 0.0536, U_{iso} = 0.032(2) Å^2 \) for the \( 100 \)-displacement, \( R_p = 0.0295, U_{iso} = 0.016(1) Å^2 \) for the \( 110 \)-displacement, and \( R_p = 0.0295, U_{iso} = 0.020(1) Å^2 \) for the \( 111 \)-displacement clearly disfavor displacements along \( 100 \). Although the \( 110 \) - and \( 111 \) -oriented displacements provide the same reliability factors, the former was selected for

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the final refinement due to the lower ADP. The same tendency in $R_p$ and $U_{	ext{iso}}$ for the Pb2+–Bi3+ position was observed for all temperatures up to $T = 300$ K. Based on the same arguments, the displacement of the O2− anions from the $\frac{1}{2}, 0, 0$ 3d position to $\frac{1}{4}, 0.5, 0$ 12j position with the corresponding occupancy reduction are suggested. The experimental, calculated, and difference SXPD patterns after the Rietveld refinement are shown in Figure 1 for $T = 80$ K and Figure S1 of the Supporting Information for $T = 300$ K. This can be attributed to an anisotropic strain, monotonic at all temperatures (Figure S2 of the Supporting Information). The tilt series of electron diffraction patterns of $\text{Bi}_{0.81}\text{Pb}_{0.19}\text{FeO}_{2.905}$ was recorded from a large number of crystallites. Representative patterns are shown in Figure 2.

Table 1. Selected Parameters from the Rietveld Refinements for $\text{Bi}_{0.81}\text{Pb}_{0.19}\text{FeO}_{2.905}$

<table>
<thead>
<tr>
<th>temp., K</th>
<th>80</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>space group</td>
<td>$Pm\overline{3}m$</td>
<td>$Pm\overline{3}m$</td>
</tr>
<tr>
<td>$a$, Å</td>
<td>3.94815(2)</td>
<td>3.95368(3)</td>
</tr>
<tr>
<td>$Z$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>cell volume, Å³</td>
<td>61.5435(4)</td>
<td>61.8024(4)</td>
</tr>
<tr>
<td>calculated density, g/cm³</td>
<td>8.387</td>
<td>8.352</td>
</tr>
<tr>
<td>radiation</td>
<td>synchrotron X-rays, $\lambda = 0.39491$ Å</td>
<td></td>
</tr>
<tr>
<td>$2\theta$ range and step, deg.</td>
<td>$4 \leq 2\theta \leq 35$, 0.002</td>
<td>$4 \leq 2\theta \leq 35$, 0.002</td>
</tr>
</tbody>
</table>

Table 2. Positional and Atomic Displacement Parameters for $\text{Bi}_{0.81}\text{Pb}_{0.19}\text{FeO}_{2.905}$ at $T = 80$ K (first row) and 300 K (second row)

<table>
<thead>
<tr>
<th>atom</th>
<th>site</th>
<th>$x/a$</th>
<th>$y/b$</th>
<th>$z/c$</th>
<th>$U_{	ext{iso}}$, Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiPb⁺</td>
<td>12j</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>0.5606(7)</td>
<td>0.5606(7)</td>
</tr>
<tr>
<td></td>
<td>$\frac{1}{4}$</td>
<td>0.5633(7)</td>
<td>0.5633(7)</td>
<td>0.016(1)</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>1a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0089(4)</td>
</tr>
<tr>
<td>O²⁻</td>
<td>12j</td>
<td>$\frac{1}{2}$</td>
<td>0.058(2)</td>
<td>0.058(2)</td>
<td>0.033(3)</td>
</tr>
<tr>
<td></td>
<td>$\frac{1}{4}$</td>
<td>0.053(3)</td>
<td>0.053(3)</td>
<td>0.042(4)</td>
<td></td>
</tr>
</tbody>
</table>

The set of strong reflections corresponds to the perovskite parent structure with $a_p = 3.95$ Å. In addition to these strong reflections, there are weak satellite reflections running along the $b_p^*$ direction, which cannot be indexed using the perovskite cell parameters. The satellite reflections can be indexed assuming an average unit cell with the parameters $a' = b' = c' = 2a_p$, together with a modulation vector $q \approx 0.16b^\|$. Alternatively, the positions of the satellite reflections can be approximately fitted with a commensurate $I$-centered orthorhombic supercell with $a = 2a_p$, $b = 12a_p$, $c \approx 46.8$ Å. $c = 2a_p$ (see the indexation of the ED patterns in Figure S3 of the Supporting Information). The tilt series made by the tilting along [110]c evidenced further weak reflections that, at first sight, seem to be in disagreement with this $I$-centering (Figure S4 of the Supporting Information). However, part of these reflections are due to the intersection of the reciprocal plane of the ED pattern with the streaks that run along the $b^*$-axis, and the remaining reflections are related to double diffraction, as clarified by the schematic representation at the bottom of Figure S4 in the Supporting Information.

Although no reflection splitting was observed on the SXPD patterns in the 100–300 K temperature range, the angular dependence of the full-width-at-half-maximum is apparently non-monotonic at all temperatures (Figure S2 of the Supporting Information). This can be attributed to an anisotropic strain, caused for example by a large concentration of planar defects in the sample, or to local ordering. In the Rietveld refinement, the broadening anisotropy was taken into account using the axial method with the [111] anisotropy axis. To get insight into the local structure of $\text{Bi}_{0.81}\text{Pb}_{0.19}\text{FeO}_{2.905}$, a transmission electron microscopy investigation was undertaken.

Table 3. Main Interatomic Distances (Å) for $\text{Bi}_{0.81}\text{Pb}_{0.19}\text{FeO}_{2.905}$ at $T = 80$ and 300 K

<table>
<thead>
<tr>
<th></th>
<th>80 K</th>
<th>300 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiPb−→O × 12: min 2.14(1)</td>
<td>BiPb−→O × 12: min 2.130(9)</td>
<td></td>
</tr>
<tr>
<td>BiPb−→O × 12: max 3.45(1)</td>
<td>BiPb −→O × 12: max 3.453(9)</td>
<td></td>
</tr>
<tr>
<td>Fe−O × 6: 1.999(2)</td>
<td>Fe−O × 6: 2.000(1)</td>
<td></td>
</tr>
</tbody>
</table>

∗Due to random nature of the atomic displacements of the Pb2+–Bi3+ and O2− ions, only minimum and maximum interatomic distances are shown.
these defects is variable, but on average over a large area they are separated by a distance of about 23 Å, as deduced from the Fourier transform of this image (see the insert in the bottom right corner of Figure 3). This Fourier transform shows the same characteristics as the [001]p ED pattern in Figure 2 and confirms that the superstructure reflections in the experimental diffraction patterns originate from these defects.

Figure 4 shows a [001]p HAADF-STEM image of Bi$_{0.81}$Pb$_{0.19}$FeO$_{2.905}$. The brightness of the dots corresponding to a particular projected atomic column in HAADF-STEM images is proportional to $Z^n$ ($n \approx 1-2$), with $Z$ being the average atomic number along the column. The columns seen in the [001]p projection are A-cation columns occupied by Pb ($Z = 82$) and Bi ($Z = 83$) (brighter dots in Figure 4) and BO columns occupied by alternating Fe ($Z = 26$) and O ($Z = 8$) (fainter dots in Figure 4). The columns consisting of only oxygen anions are not seen as separate dots on the image because of their low $Z$ contribution. The only defects that can be faintly observed on the HAADF-STEM images are lines running along the $a_p$ direction (indicated by a white arrow) with a slightly darker background between the cation columns. This suggests that oxygen vacancies might be at the origin of these defects. Therefore, ABF-STEM images were obtained to visualize the oxygen sublattice.

ABF-STEM images demonstrate an “absorptive” type of contrast, where the regions of higher atomic potential look darker on a bright background. Due to the impact of elastic scattering, columns of light elements can be observed more easily together with the heavy atomic columns on ABF-STEM images, in contrast to HAADF-STEM images. A low pass filtered [001]p ABF-STEM image of Bi$_{0.81}$Pb$_{0.19}$FeO$_{2.905}$ is shown in Figure 5. In this image, the darker dots are associated with the projection of Bi and Pb columns, the less dark ones are

Figure 3. HRTEM image of Bi$_{0.81}$Pb$_{0.19}$FeO$_{2.905}$ along the [001]p direction, a Fourier transform of the image is included in the bottom right corner. The area indicated in the top right by a rectangle is shown enlarged in the top left corner.

Figure 4. HAADF-STEM image of Bi$_{0.81}$Pb$_{0.19}$FeO$_{2.905}$ along [001]p direction. Calculated image (sample thickness $t = 72$ Å) is indicated with a white border.

Figure 5. ABF-STEM image of Bi$_{0.81}$Pb$_{0.19}$FeO$_{2.905}$ along [001]p direction. A part of the defect layer is indicated by the black rectangle. Complete and incomplete oxygen columns along the defect plane are marked with the black and white arrows, respectively.
associated with the projection of FeO columns, whereas the weakest ones are related to the oxygen-only columns. The defect (a part of which is indicated by the rectangle) appears in this image as an alternation of brighter and darker dots at the oxygen column positions. The black arrows point to the darker dots, while the white ones show the positions of the less dark dots. The weaker dots correspond to the oxygen-depleted columns. These columns are arranged into planes perpendicular to the b-axis, which agrees with the extra reflections observed on the ED patterns being directed along b*. and which also agrees with the defects seen on the HRTEM and HAADF-STEM images. Therefore, we suggest that all observed effects originate from the ordering of oxygen vacancies in the structure.

The alternation of the columns with different oxygen content along the a-axis (as seen on the ABF-STEM images) causes the doubling of the periodicity along the a-axis relative to the perovskite subcell. The fact that a less bright dot is still seen at the position of the incomplete columns on the ABF-STEM image implies the presence of residual oxygen anions in this position. The possible models for the oxygen-vacancy ordering were constructed using a combination of the TEM and Mössbauer spectroscopy data.

The fit of the room temperature Mössbauer absorption spectrum for Bi0.81Pb0.19FeO2.905 is shown in Figure 6. The spectrum is decomposed into two components: the sextet (blue) and doublet (pink) subspectra originate from the (FeO1.5) composition and consists of corner-sharing FeO5 pyramids. However, the most plausible situation is a mixture of these two limiting cases (Figure 7b), where clusters of four FeO4 tetrahedra are surrounded by partially filled oxygen positions. Mössbauer spectroscopy requires an occupancy factor of \( \delta \approx 0.2 \) for these positions to fulfill the O2.905 stoichiometry. However, from the modulation vector \( \mathbf{q} = \beta \mathbf{a}^* + \delta \mathbf{b}^* \) the oxygen content can be calculated using the \( 3 - \beta (1 - \delta) \) formula (see the Supporting Information for derivation), that requires \( \delta \approx 0.4 \). Since both the fraction of low-coordinated iron from the Mössbauer data and the \( \beta \) component of the modulation vector from the electron diffraction data are determined with relatively low precision, \( \delta \approx 0.25 \) seems to be a good approximation. For this \( \delta \) value the anion-deficient layer has the (FeO1.5) composition and consists of corner-sharing FeO5 pyramids. Such an atomic arrangement was proposed earlier for the Co-, Fe-, and Mn-based perovskites with composition \( \text{Sr}_1-x \text{R}_x \text{Co}_y \text{O}_{10+y} \) with \( R = \text{La}, Y, \text{Sm–Yb}, 0.4 \leq x \leq 1.33 \), and \(-0.02 \leq \delta \leq 0.74, x = 1.0, \text{Sr}_2 \text{RFe}_4 \text{O}_{10.5} (R = Y, \text{Ho, Dy})^{29} \) and \( Y_{0.3} \text{Sr}_{0.7} \text{Mn}_2 \text{GaO}_6 \).
As deduced from the ABF-STEM images, the oxygen anions in the (FeO$_3$)$_2$ (010)$_2$ layers on both sides of the anion-deficient plane demonstrate an antiphase out-of-plane shift. This shift results in a buckling of the (FeO$_3$) layers. Such buckling corresponds to a tilting of the FeO$_6$ octahedra around the c-axis. Taking into account the approximate 6σ$_p$ separation between the anion-deficient planes along the b-axis and the I-centering of the commensurate supercell, we constructed a model for the local oxygen-vacancy ordering in Bi$_{0.81}$Pb$_{0.19}$FeO$_{2.905}$. The projected tilted FeO$_6$ octahedra and FeO$_4$/FeO$_5$ polyhedra are shown schematically on the enlarged ABF-STEM image of the defect plane (Figure 8). The calculated ABF-STEM image (computed using the model of the (FeO$_{1.3}$) layer in Figure 7b at a thickness t = 72 Å) is inserted at the right side of Figure 8 and agrees well with the experimental image. The HAADF-STEM image calculated with the same model and same thickness is also in good agreement with the experimental one (Figure 4).

Magnetization measurements reveal a marginal temperature dependence of the magnetic susceptibility in the 2–380 K range (see Figure 9). No anomalies related to possible magnetic transitions are observed. Such behavior is characteristic of an ordered antiferromagnet well below the Néel temperature. The pronounced field dependence of the susceptibility signifies the presence of net magnetization, which is also visible as a tiny hysteresis in the magnetization loop measured at 2 K. The respective magnetic moment is about 0.001 $\mu_B$/f.u. and only 0.02% of the total magnetic moment of 5 $\mu_B$/f.u. anticipated for Fe$^{3+}$. The observed uncompensated moment is well below expectations for a net magnetization arising from a typical canted antiferromagnetic structure (e.g., 0.06 $\mu_B$/Fe in BiFeO$_3$). Therefore, the small uncompensated moment should rather be attributed to a tiny amount of ferromagnetic impurity. For example, the moment of 0.001 $\mu_B$/F.u. can be induced by less than 0.01 wt % of PbFe$_2$O$_4$. Such amount of the impurity cannot be detected by X-ray diffraction and/or Mössbauer spectroscopy.

The slight decrease in the susceptibility upon heating is somewhat unusual for ordered antiferromagnets. This temperature dependence might be related to the iron sites with a lowered coordination (FeO$_{2.8}$) layers, which, according to the Mössbauer data, experience zero magnetic field and do not take part in the static long-range magnetic order at room temperature. However, these spins are also not paramagnetic, because the susceptibility data do not follow the Curie law expected for noninteracting Fe$^{3+}$ cations. Considering the weak susceptibility upturn below 20 K, we estimate the maximum amount of paramagnetic spins as 0.1%. At low temperatures, most of the Fe$^{3+}$ cations should take part in the long-range antiferromagnetic order or, at least, experience strong antiferromagnetic interactions that prevent the paramagnetic behavior. A more detailed picture of the magnetic interactions in this compound would require temperature dependent Mössbauer and neutron powder diffraction investigations.

4. DISCUSSION

The SXPD data and electron diffraction patterns allow us to rule out the R3c polar structure for Bi$_{0.81}$Pb$_{0.19}$FeO$_{2.905}$ and unequivocally establish the cubic symmetry of the average crystal structure. Neither reflection splitting nor superstructure reflections characteristic for the $a' a' a$ hexagonal tilt system have been observed by either technique. No signs of a rhombohedral structure distortion are seen down to $T = 80$ K. Although the cubic Pm$ar{3}$m crystal structure was deduced for Bi$_{0.81}$Pb$_{0.19}$FeO$_{2.905}$ from the bulk SXPD data in the $T = 80–300$ K temperature range, the local structure is far from cubic. Oxygen vacancies are not randomly distributed, but form anion-deficient planes appearing approximately every six perovskite unit cells. Such anion-deficient planes have the idealized composition (FeO$_{2.5}$), transforming one layer of FeO$_6$ octahedra into a layer consisting of a 1:1 mixture of corner-sharing FeO$_4$ tetrahedra and FeO$_5$ distorted tetragonal pyramids. Thus, the oxygen-vacancy ordering within the anion-deficient layers in Bi$_{0.81}$Pb$_{0.19}$FeO$_{2.905}$ is incomplete in comparison with that in the (FeO$_{1.3}$) layers observed in Bi$_{0.75}$Sr$_{0.25}$FeO$_{2.75}$ and Bi$_{0.85}$Ca$_{0.15}$FeO$_{2.875}$, where all Fe$^{3+}$ cations are supposed to have the tetragonal pyramidal coordination.

The slightly larger ionic radius of Pb$^{2+}$ (1.29 Å for CN = 8) in comparison with that of Bi$^{3+}$ (1.11 Å for CN = 8) results in an increase in the tolerance factor from 0.915 for BiFeO$_3$ to 0.93 for Bi$_{0.81}$Pb$_{0.19}$FeO$_{2.905}$ (as calculated with the SPUdS software using the bond valence sum method$^{32}$). Nevertheless, the tolerance factor for Bi$_{0.81}$Pb$_{0.19}$FeO$_{2.905}$ is still well below 1 and implies a tendency toward tilting distortions of the perovskite octahedral framework. Indeed, random displacements of the O$^{2-}$ anions along $\langle 110 \rangle$ occur, as determined from the Rietveld refinement against the SXPD data. The direct ABF-STEM observations confirm that the FeO$_6$ octahedra are tilted in Bi$_{0.81}$Pb$_{0.19}$FeO$_{2.905}$. The displacement of the O$^{2-}$ anions along $\langle 110 \rangle$ suggests at least two nonzero tilting components. According to the ABF-STEM image, the octahedral tilt definitely occurs around the c-axis and has an in-phase character. The available data do not allow to make an
Anion-deficient \((\text{FeO}_{1.25})\) planes act as twin planes mirroring the \(c’\) tilt component in the perovskite blocks on both sides of the \((\text{FeO}_{1.25})\) plane. Taking into account that for \(\beta \approx 0.16\) the average number of complete \((\text{FeO}_2)\) layers between two adjacent anion-deficient \((\text{FeO}_{1.25})\) layers is 5.25, one can assume that the structure is built by uniformly distributed perovskite blocks with a thickness of 5 and 6 \((\text{FeO}_2)\) layers occurring in a \(\sim 3:1\) ratio. However, opposite absolute configuration patterns of the tilted octahedra will be observed in neighboring perovskite blocks depending on whether the perovskite block contains an odd or an even number of \((\text{FeO}_2)\) layers (Figure 10). Thus, the incomplete ordering of

\[ \text{Figure 10. Models showing the octahedral tilting patterns in Bi}_{0.81}\text{Pb}_{0.19}\text{FeO}_{2.905} \text{along [001]}_p \text{. Top structure shows the stacking of the perovskite blocks with an odd number of octahedral layers. Bottom structure demonstrates stacking of the perovskite blocks with a mixture of even and odd numbers of octahedral layers. Note the reversal of the tilt direction of the FeO}_2 \text{octahedra in comparison with the top structure (shown by curved arrows). The Pb}^{2+} \text{and Bi}^{3+} \text{cations are shown as large spheres. Small spheres indicate the oxygen positions with the occupancy}\ \delta = 0.25. \]

the anion-deficient \((\text{FeO}_{1.25})\) layers will also effectively randomize the octahedral tilting. Since the anion-deficient planes occur equivalently along all three cubic perovskite axes, \(\text{Bi}_{0.81}\text{Pb}_{0.19}\text{FeO}_{2.905}\) retains the average cubic symmetry on a large scale, in spite of the noticeable octahedral tilting at the local level.

The electron diffraction patterns of \(\text{Bi}_{0.81}\text{Pb}_{0.19}\text{FeO}_{2.905}\) are very similar to the patterns of \(\text{NaLaMgWO}_6\), where the satellite skite,\(^{35,36}\) which also adopts the cubic perovskite structure. In contrast to \(\text{Bi}_{0.81}\text{Pb}_{0.19}\text{FeO}_{2.905}\), no octahedral tilting has been observed in \(\text{PbFeO}_2\text{F}\), in agreement with the tolerance factor \(t = 1.01\). The off-center displacements of the A cations are very similar in both compounds: they randomly occur along all twelve \((110)\) directions, resulting in one short \(A-O\) distance \((d(\text{PbBi-O}) = 2.13\ \text{Å} \text{in } \text{Bi}_{0.81}\text{Pb}_{0.19}\text{FeO}_{2.905} \text{and } d(\text{Pb-(O,F)}) = 2.54 \text{Å in } \text{PbFeO}_2\text{F})\). This is an indication of the steric activity of the lone pair on the A cations, which is associated with intermixing the \(6s\) A-states and the \(2p\) states of the anions with the formation of highly covalent bonds and shortening of some of the 12 initially equivalent interatomic distances.\(^{7,38}\) Such displacements have a polar character and might lead to ferroelectricity and multiferroic properties, but in both compounds, they are oriented in a random manner, thus resulting in the absence of net polarization. Apparently, a long-range disorder in the anion sublattice effectively cancels the cooperative dipolar interactions, irrespective of the exact nature of the disorder: the \(O/F\) mixing or the \(O/vacancy\)-mixing at the anion site.

## ASSOCIATED CONTENT

### 3 Supporting Information

Experimental, calculated, and difference SXPD profiles at \(T = 300\ K\). Angular dependence of full-width-at-half-maximum (fwhm) for the reflections at \(T = 80\ K\) (SXPD data). Representative electron diffraction patterns from a tilt series around the \(b^*_p = b^*-a^*_p\) with all reflections indexed in the commensurate \(2a^*_p \times 12a^*_p \times 2a^*_p\) supercell. Representative electron diffraction patterns from a tilt series around the \([110]_p^* = [160]^*_p\) direction indexed in the commensurate \(2a^*_p \times 12a^*_p \times a^*_p\) supercell. This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

### Author Contributions

The manuscript was written through contributions of all authors.

### Notes

The authors declare no competing financial interest.

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