Manipulation of spin orientation via ferroelectric switching in Fe-doped Bi₂WO₆ from first principles

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Atomic-scale control of spins by electric fields is highly desirable for future technological applications. Magnetically-doped Aurivillius-phase oxides present one route to achieve this, with magnetic ions substituted into the ferroelectric structure at dilute concentrations, resulting in spin-charge coupling. However, there has been minimal exploration of the ferroelectric switching pathways in this materials class, limiting predictions of the influence of an electric field on magnetic spins in the structure. Here, we determine the ferroelectric switching pathways of the end member of the Aurivillius phase family, Bi₂WO₆, using a combination of group theoretic analysis and density functional theory calculations. We find that in the ground state P₂₁/a phase, a two-step switching pathway via C₂ and Cm intermediate phases provides the lowest energy barrier. Considering iron substitutions on the W-site in Bi₂WO₆, we determine the spin easy axis. By tracking the change in spin directionality during ferroelectric switching, we find that a 90° switch in the polarization direction leads to a 112° reorientation of the spin easy axis. The low symmetry crystal-field environment of Bi₂WO₆ and magnetoelastic coupling on the magnetic dopant provide a route to spin control via an applied electric field.

I. INTRODUCTION

Multiferroic materials with coupled ferroic orderings (e.g. ferromagnetism, ferroelectricity, ferroelasticity) exhibit intriguing physics and hold potential for enabling new types of future electronic devices.¹ In magneto-electric materials with coupled ferroelectricity and magnetism, the ability to switch the magnetization by an applied electric field is particularly promising for low-power spintronics.² Materials approaches to multiferroicity, for example multiferroic superlattices³, nanocomposites⁴, domain walls⁵ and single phase materials⁶, typically focus on realizing long-range magnetic order for macroscopic devices. However, several recent works have pushed towards the fundamental limits of multiferroic phenomena, including electric field manipulation of molecular magnets⁷,⁸, tuning exchange in a molecular system⁹, and the coherent electric field control of dilute iron dopants in a ferroelectric crystal.¹⁰ These milestones towards full control of isolated spins by electric fields may enable new functionalities in classical electronic devices in the field of spintronics as well as in quantum computing.¹⁰,¹¹

A promising pathway to achieve isolated spin centers with magnetoelectric coupling is to dope a ferroelectric structure with dilute concentrations of magnetic ions.¹⁰ Here, magnetoelectricity arises by coupling the ferroelectric’s polar distortion with the spin dopant through spin-orbit interactions. This approach confers the rich phase space of ferroelectric crystals, in particular of complex oxide materials, for use as hosts for spin dopants. In particular, the versatile structural motifs and distortions in ferroelectric oxides provide a highly tunable local environment for the spin center, allowing control of the magnetocrystalline properties via the crystal field environment. The symmetry lowering caused by the ferroelectric distortion results in magnetocrystalline anisotropies that lead to preferential alignment of spins within a plane (spin easy plane) or along an axis (spin easy axis). Using the prototypical ferroelectric PbTiO₃ as a host for Fe³⁺ spins, some of the present authors recently demonstrated that the tetragonal polar distortion results in a spin easy plane with 90° switching under the application of an electric field.¹⁰ However, preferentially aligning spins along an easy axis and 180° switching would have technical advantages for applications. Ferroelectric hosts providing lower crystallographic symmetries in the vicinity of the spin are more likely to support spin easy axes due to their highly distorted crystal fields, and so are sought for such ferroelectric-mediated spin switching.

The Aurivillius phases are a family of layered ferroelectric materials with low symmetry crystal structures that could satisfy these requirements. The Aurivillius structure is composed of m perovskite-like layers (Aₘ₋₁BₘO₃m+1)²⁻ interspersed with fluorite-like (Bi₂O₂)₂⁺ layers, giving the overall general formula Bi₂Aₘ₋₁BₘO₃m+3. The Aurivillius phases are well known for their robust ferroelectricity, including high Curie temperatures (Tc), large spontaneous polarizations¹²-¹⁴, and fatigue resistance.¹⁵ Furthermore, the
composition has great versatility owing to the different
cations that can be placed on the A and B sites,
which has led to efforts to design multiferroic Aurivilli-
us compounds via incorporation of magnetic ions.\textsuperscript{16-22}
Most work has focused on achieving long range mag-
netic ordering in single phase materials with large por-
portions of magnetic cations, for example in doped
\( \text{Bi}_{n+1}\text{Fe}_{n-3}\text{Ti}_2\text{O}_{3n+3} \) compounds. However, the com-
plex crystal structure and difficulty in synthesis of phase
pure samples has made characterization of the multifer-
roic properties difficult.\textsuperscript{21,23,24} In particular, the ferro-
electric and magnetoelectric switching mechanisms have
not been elucidated.\textsuperscript{25} These limitations hinder the pre-
diction of the behavior of magnetic spins during switch-
ing. Moreover, to the best of our knowledge, magnetoe-
electric coupling of isolated magnetic dopants has not yet
been investigated in this class of materials.

Here, we use group theoretic analysis and first prin-
ciples calculations to explore ferroelectric switching and
control of magnetic dopants in the end member of the
Aurivillus family, \( \text{Bi}_2\text{WO}_6 \) \((m=1, \ B=W)\). We select
\( \text{Bi}_2\text{WO}_6 \) because it exhibits robust ferroelectricity and
also possesses a complex crystal structure which can pro-
vide a low symmetry crystallographic environment for
magnetic dopants. Theoretical and experimental work
has revealed that ferroelectricity in \( \text{Bi}_2\text{WO}_6 \) arises from an
instability to a polar distortion involving large Bi
displacements with respect to the perovskite layer.\textsuperscript{26-30}
It undergoes a two-step paraelectric-ferroelectric phase
transition sequence: at room temperature, \( \text{Bi}_2\text{WO}_6 \) crys-
tallizes in the orthorhombic ferroelectric phase \( P2_1ab \),
then transitions to the polar orthorhombic structure
\( B2cb \) at 670°C, and finally transitions to the paraelec-
tric monoclinic phase \( A2/m \) above 950°C.\textsuperscript{31}

Experiments have reported that ferroelectric switching
in \( \text{Bi}_2\text{WO}_6 \) proceeds via a two-step process\textsuperscript{39}, but the
details of the precise switching pathway taken are still
lacking. We therefore start by determining the likely fer-
roelectric switching pathway, by systematically enumer-
ating and then evaluating the energetics of several possi-
ble symmetry-distinct paths. Here we consider \textit{intrinsic}
ferroelectric switching paths, where we calculate energy
barriers for coherent polarization reversal in a single in-
finite domain.\textsuperscript{32} Although this does not provide a full
description of the dynamic ferroelectric switching process,
work on other ferroelectrics\textsuperscript{33,34} has shown that when
multiple symmetry-distinct switching paths are available,
intrinsic barriers can correctly identify the experimental
switching path. We then introduce \( \text{Fe}^{3+} \) dopants into the
structure at dilute concentrations and track the change
in spin directionality with ferroelectric switching. This
work lends understanding to the magnetoelectric effects
on isolated spins in \( \text{Bi}_2\text{WO}_6 \), demonstrating the potential
for atomic-scale spin control in this class of materials.

II. COMPUTATIONAL METHODOLOGY

We perform density functional theory (DFT) calcula-
tions using the Vienna \textit{Ab initio} Simulation Package
(VASP)\textsuperscript{35-38}, using projector augmented wave
(PAW) pseudopotentials\textsuperscript{39,40} including \( \text{Bi} \ 5d^{10}6s^26p^3 \), \( \text{W} 
5p^65d^46s^2 \), \( \text{O} \ 2s^22p^4 \), and \( \text{Fe} \ 3d^54s^2 \) as valence electrons.
A plane wave cut-off energy of 800 eV is used with a
\( 6 \times 6 \times 2 \) Gamma-centered \( k \)-point grid (for the \( P2_1ab \)
\( \text{Bi}_2\text{WO}_6 \) 36-atom unit cell), which converges the total
energy to 1 meV per formula unit (f.u.). The same
\( k \)-point grid is used for all undoped structures, and a
\( 2 \times 2 \times 2 \) \( k \)-point grid is used for the doped supercells.
All calculations are done using the generalized gradient
approximation (GGA) based exchange-correlation func-
tional PBEsol\textsuperscript{41}, which gives lattice parameters within
1% of experiment\textsuperscript{30} \( a=5.443 \text{Å}, b=5.443 \text{Å}, c=16.557 \text{Å}, \)
for \( P2_1ab \).

For undoped structures, we allow the ionic positions,
cell volume, and cell shape to optimize and apply a force
tolerance convergence of 1 meV Å\(^{-1}\). The nudged elastic
band (NEB) method\textsuperscript{42} implemented in VASP is employed
for the structural parameters and energies of inter-
mediate structures lying along the ferroelectric switching
pathways. For the NEB calculations, the force con-
vergence tolerance is increased to 10 meV Å\(^{-1}\).

We calculated \( \text{Fe}^{3+} \) substitutional defects on W-sites
in \( 2 \times 2 \times 1 \) supercells of \( \text{Bi}_2\text{WO}_6 \) (144 atoms), with three
electrons added for charge compensation. For structures
containing more than one symmetrically inequivalent W-
site, we consider each as a different dopant site. An ef-
ective Hubbard term \( U_{\text{eff}}=U-J=4 \text{ eV} \) is added to the
\( \text{Fe} \) \( d \)-orbitals within the Dudarev approach.\textsuperscript{43} Geometry
optimization of the ions for each defect supercell is com-
piled to a force convergence of 10 meV Å\(^{-1}\), whilst keep-
ing the cell volume and shape fixed. Magnetocrystalline
anisotropy energy (MCAE) surfaces are calculated by in-
cluding spin-orbit coupling self consistently and varying
the spin quantization axes over 194 points. We make
use of the ISOTROPY software suite\textsuperscript{44} for group theo-
retic analysis and VESTA\textsuperscript{45} for the visualization of crys-
tal structures.

III. RESULTS AND DISCUSSION

A. Ground state crystal structure

To set the stage for understanding ferroelectric switch-
ing, we first analyze the structural distortions present
in the ferroelectric \( P2_1ab \) structure. The \( P2_1ab \) space
group is established by the condensation of three dis-
tinct structural distortions that transform like irreducible
representations (irreps) of the high-symmetry reference
structure \( I4/mmm \) (Fig. 1a, b). These distortions are a
polar displacement along the [1 0 0] orthorhombic axis which transforms like the irrep $\Gamma_5^-$, an octahedral rotation about [0 0 1] which transforms like $X_2^+$, and an out-of-phase $X_3^+$ octahedral tilt about [1 0 0] which transforms like $X_3^+$. The axes shown under panel (a) are used for all panels except for (c).

FIG. 1. The (a) high-symmetry reference structure $I4/mmm$ and (b) polar orthorhombic structure $P2_1ab$ of Bi$_2$WO$_6$. A structural decomposition of $P2_1ab$ into symmetry adapted modes of $I4/mmm$ reveals three main structural distortions: (c) a polar displacement along [1 0 0] with symmetry $\Gamma_5^-$, (d) an octahedral rotation about [0 0 1] with symmetry $X_2^+$, and (e) an out-of-phase octahedral tilt about [1 0 0] with symmetry $X_3^+$. The axes shown under panel (a) are used for all panels except for (c).

### Table I. Decomposition of the Bi$_2$WO$_6$ $P2_1ab$ structure (DFT-relaxed and experimental) into symmetry adapted modes of $I4/mmm$. The experimental structure is taken from Ref. 47. The amplitudes are given in Å for a 36-atom computational cell. For the O1 atoms, the coordinates in parentheses indicate the axes along which the atoms displace; there are two distinct O1 displacement patterns in the $xy$ plane that are consistent with the symmetry.

| Atom | $\Gamma_5^-$ | $X_2^+$ | $X_3^+$ |
|------|--------------|--------|--------|
|      | DFT Expt. | DFT Expt. | DFT Expt. |
| Bi   | 0.66 0.68   | 0.33 0.30 |        |
| W    | 0.18 0.25   | 0.00 0.00 | 0.87 0.70 |
| O1(z) | 0.00 0.00   | 0.75 0.85 | 0.00 0.00 |
| O1(xy) | -0.15 -0.11 | 0.75 0.85 | 0.00 0.00 |
| O1(xy) | -0.25 -0.29 | -0.01 -0.02 | 0.00 0.00 |
| O2   | -0.77 -0.74 | 0.00 0.00 | -1.10 -0.89 |
| O3   | 0.27 0.17   | 0.00 0.00 | -0.05 -0.02 |
| Total | 1.10 1.09   | 0.75 0.85 | 1.44 1.17 |

The main contribution to the polar distortion comes from displacement of the Bi cations against the O2 atoms as shown in Fig. 1(c). In addition to the three distortions discussed above, there are several other distortions which are symmetry-allowed in the $P2_1ab$ structure, but they have negligible amplitudes$^{28}$ so we do not consider them in this work.

**B. Ferroelectric switching pathways**

To provide a framework for systematically identifying ferroelectric switching pathways, we next enumerate possible metastable structural phases of Bi$_2$WO$_6$ and compute their energies with DFT. The key to uncovering the metastable structural phases is to recognize that each of the three structural distortions shown in Figure 1 is described by a two-dimensional order parameter $Q\alpha^{16,34}$. Here $Q$ is the order parameter amplitude and $\alpha$ is the phase. For the $X_3^+$ octahedral tilt and the $\Gamma_5^-$ polar distortion, the phase $\alpha$ describes the orientation of the tilt (polar) axis. For the $X_2^+$ octahedral rotation, the phase describes the relative “sense” of the octahedral rotations in adjacent perovskite layers.

Each two-dimensional structural order parameter can lie along three symmetry-distinct directions ($Q \cos \alpha, Q \sin \alpha$) = (a,a), (a,0), or (a,b) where a $\neq b$ are real num-
TABLE II. Subgroups of I4/mmm established by different combinations of the $X_3^+$, $X_2^+$, and $\Gamma_5^-$ order parameter directions. Total energies, distortion amplitudes, and lattice parameters obtained from DFT structural relaxations of Bi$_2$WO$_6$ in each space group are given. The energies are reported relative to the energy of $P2_1ab$, which is set to 0 meV/f.u. If a structure relaxes to a higher symmetry space group, that space group is indicated in the energy column. The distortion amplitudes are obtained by decomposing the distorted structures with respect to I4/mmm and are reported for a 36-atom computational cell.

| Irreps | Order parameter direction | Space group (N°) | Amplitude (Å) | Lattice parameters (Å) | Energy (meV/f.u.) |
|--------|---------------------------|-----------------|---------------|-----------------------|------------------|
| $\Gamma_5^- \otimes X_3^+$ | (a,0) - | $Cm2a$ (39) | 0.44 0.48 | 7.601 7.754 | 16.481 103.46 |
| | (a,0) - | $B2b$ (41) | 1.19 0.76 | 5.442 5.443 | 16.557 -0.08 |
| $\Gamma_5^- \otimes X_2^+$ | (a,0) (b) | $C2$ (5) | 0.49 | 5.750 7.774 | 16.507 96.68 |
| | (a,0) (b) | $P2_1$ (4) | 0.49 0.58 | 5.750 7.740 | 16.507 99.70 |
| $\Gamma_5^- \otimes X_3^+ \otimes X_2^+$ | (a,0) (b) | $Pcm$ (29) | 1.11 0.76 | 5.443 5.443 | 16.557 0 |

We then perform structural relaxations of Bi$_2$WO$_6$ with its symmetry constrained to each space group identified in Table II, and report the resulting energy and structural parameters.

We find two very low energy structures: $B2cb$ (43 meV/f.u.) and $Pc$, and $P2_1ab$ structures exhibit the same $X_3^+$ and $\Gamma_5^-$ distortions, the only difference is the relative "sense" of the $X_2^+$ rotations in adjacent perovskite layers, thus it is unsurprising that these phases are very close in energy. We note that the relative energy of $Pc$ and $P2_1ab$ is quite sensitive to the value of the lattice parameters.

Using these identified structures, we construct the two lowest energy two-step ferroelectric switching pathways.

We next use the results of Table II to enumerate possible Bi$_2$WO$_6$ ferroelectric switching pathways. The simplest way to reverse the polarization is in a single 180° step, where the polarization is brought to zero and then turned on again pointing in the opposite direction, as shown in Figure 2a. At the midpoint of the path, the amplitude of the polarization is zero, and the symmetry of the crystal structure is $Pc$, which is 149.74 meV/f.u. above the $P2_1ab$ ground state structure (see Table II). The $Pc$ crystal structure is shown in Figure 3a.

In addition to the one-step $Pc$ switching path, we identify three “two-step” switching pathways, where the polarization reverses direction by rotating through two 90° steps (while maintaining finite amplitude). Since the $\Gamma_5^-$ order parameter in $P2_1ab$ is oriented along the $(a,a)$ direction, rotating it by 90° takes it to either the $(-a,a)$ or $(a,-a)$ direction. This rotation requires that the $\Gamma_5^-$ order parameter pass through the $(0,a)$ or $(a,0)$ direction. Table II reveals that the $Cm2a$, $Cm2m$, $C2$, and $Cm$ structures satisfy this requirement. Interestingly, the energies of $Cm2a$, $C2$, and $Cm$ are all near 100 meV/f.u. (within 10 meV/f.u. of each other), whereas $Cm2m$ is somewhat higher (133.20 meV/f.u.). Due to its higher barrier, we do not consider the $Cm2m$ pathway further in this work.

Using these identified structures, we construct the two lowest energy two-step ferroelectric switching pathways in Figure 2(b-c). Figure 2(b) shows a pathway that...
passes through $Cm2a$ twice as the polarization rotates in two 90° steps. At the midpoint of the switching path, the structure passes through an orthorhombic twin domain of $P2_1ab$. Note that the structure passes through different domains of $Cm2a$ in the first and second steps. As the polarization rotates counterclockwise, the $X^+_3$ order parameter rotates clockwise by 90° in the first step, and then rotates back to its original orientation in the second step. In each step, the $X^+_2$ order parameter turns off so that it reaches zero at the $Cm2a$ structure, and then turns on again reoriented by 90°. The $Cm2a$ structure is shown in Figure 3(b). Here the $(a,a)$ direction of $X^+_3$ establishes an octahedral tilt pattern where the tilt axes of adjacent perovskite layers are perpendicular to each other, so that there are $a^−b^0b^0$ and $b^0a^−b^0$ rotations in the dark and light grey perovskite layers in Figure 3(b), respectively. Note that the higher energy $Cm2m$ pathway follows a similar evolution of structural order parameters as the $Cm2a$ path, except the $X^+_2$ rather than the $X^+_3$ order parameter rotates during the switching process.

The second two-step switching path that we investigate is shown in Figure 2(c). The $Γ^-_5$ and $X^-_3$ order parameters follow the same sequence as in Figure 2(b), except now the $X^-_2$ order parameter makes two 90° rotations while maintaining finite amplitude, rather than turning off/on. The barrier structure in the first step has symmetry $C2$, whereas in the second step it has symmetry $Cm$. The $C2$ and $Cm$ structures are shown in Figure 3(c) and (d), respectively. These structures have the same $a^−b^0b^0/b^0a^−b^0$ octahedral tilt pattern as $Cm2a$. The $C2$ and $Cm$ structures share the same $X^+_2$ rotation pattern, where every other perovskite layer (the colored green in Figure 3(c-d)) exhibits finite amplitude rotations about [0 0 1], and the other (grey) layers have no $X^+_2$ rotation amplitude. The difference between the $C2$ and $Cm$ structures is the orientation of the polarization with respect to the $X^+_3$ and $X^-_2$ order parameters: in $C2$ the polarization lies along the $X^+_3$ tilt axis of the green octahedra which have finite $X^+_2$ rotations, whereas in $Cm$ the polarization lies along the $X^-_2$ tilt axis of the grey octahedra which have no $X^+_2$ rotation.

In order to investigate how the energy changes during switching, Figure 2(d) shows nudged elastic band (NEB) calculations of the energy as a function of switching coordinate for the paths in Figure 2(a-c). Both two-step paths have a significantly lower energy barrier than the one-step $Pc$ path, with the energy barriers for the $C2/Cm$ path (96.68 and 99.06 meV/f.u. in the first and second steps, taken from Table II) being slightly lower than the $Cm2a$ path (103.46 meV/f.u.).

Figure 4 shows how the amplitudes of the $X^+_3$, $X^-_3$, and polar $Γ^-_5$ distortions evolve along each ferroelectric switching path, obtained from NEB calculations. In the one-step switching path shown in Figure 4(a), the polar distortion amplitude goes to zero at the barrier structure $Pc$, whereas the $X^+_2$ and $X^-_2$ distortion amplitudes remain almost unchanged throughout the switching process. In the two-step switching path via $Cm2a$ shown in Figure 4(b), at the $Cm2a$ barrier the polar distortion amplitude decreases by about half and that of $X^+_2$ amplitude goes to zero, whereas the $X^-_3$ amplitude again changes very little throughout the switching process. Finally, for the two-step $C2/Cm$ path shown in Figure 4(c), all three distortion amplitudes remain finite throughout the switching process, although the polar and $X^-_2$ amplitudes are suppressed upon approaching the $C2/Cm$ barriers.

To summarize, we find that the two-step switching paths have lower energy barriers than the one-step switching path in Bi$_2$WO$_6$. This implies that switching proceeds via two 90° steps, in agreement with the experimental observations of Ref. 29. We find that the two-step paths that pass through $Cm/C2$ and $Cm2a$ have almost the same energy barrier (≈100 meV/f.u.), with the barrier for the $Cm/C2$ path being slightly lower. We also investigate the epitaxial strain dependence of these energy barriers (Appendix B), and find that the two-step barriers remain the lowest energy except possibly under highly compressive strains. The two-dimensional structural order parameters facilitate the lower energy two-step switching, which involves order parameter rotation rather than completely turning the polarization off/on. We make use of these ferroelectric switching paths in the next section to guide us to the relevant structural

![Figure 2](image_url)

**FIG. 2.** Ferroelectric switching pathways in Bi$_2$WO$_6$. (a)-(c) show how the $X^+_3$, $X^-_3$, and $Γ^-_5$ ($P$) order parameters, denoted by blue, red, and black arrows, respectively, evolve along the switching path. Path (a) is a one-step path, whereas paths (b)-(c) are two-step paths which pass through an orthorhombic twin of $P2_1ab$ at the midpoint of the switching path. (d) Energy as a function of switching coordinate for the paths shown in (a)-(c).
Amplitude [Å]

The distinct W Wyckoff positions, indicated by grey (2a) and dark grey (4c) octahedra, and two symmetrically inequivalent W-sites on the 2b position indicated in light and dark grey, respectively. Similarly, the Cm structure (d) has two distinct W Wyckoff positions, indicated by grey (2a) and green (4b) octahedra, and two symmetrically inequivalent W-sites on the 2a position indicated in light and dark grey, respectively.

**C. Spin directionality of magnetic dopants**

We next investigate the impact of polarization reversal on the spin orientation of magnetic dopants in Bi₂WO₆. Magnetic dopants in Bi₂WO₆ exhibit magnetocrystalline anisotropy—a preferred directionality of the unpaired electron spins—that arises due to the crystal field at the dopant site and spin-orbit coupling. Here, we consider Fe³⁺ substitutional defects on W-sites, which is one of the potential defect species in Bi₂WO₆. Although the P2₁ab structure only contains one distinct W site, the barrier structures encountered in the two-step switching processes contain multiple symmetry-distinct W sites (and hence dopant positions), which are shown in Figure 3(b-d). The energetics of this defect and alternative phases in which to explore the spin orientation of magnetic dopants in Bi₂WO₆.

**FIG. 3.** Barrier structures of Bi₂WO₆ realized along the ferroelectric switching paths. The Cm2a structure (b) has two distinct W Wyckoff positions, indicated by the light grey (4b) and dark grey (4c) octahedra. The C2 structure (c) also has two distinct W Wyckoff positions, indicated by grey (2b) and green (4c) octahedra, and two symmetrically inequivalent W-sites on the 2b position indicated in light and dark grey, respectively. Similarly, the Cm structure (d) has two distinct W Wyckoff positions, indicated by grey (2a) and green (4b) octahedra, and two symmetrically inequivalent W-sites on the 2a position indicated in light and dark grey, respectively.

**FIG. 4.** Amplitudes of the X₁⁺, X₂⁺, and Γ₅⁻ (P) structural distortions as a function of switching coordinate for each of the switching paths shown in Figure 2: (a) one-step switching with barrier Pcab, (b) two-step switching with barrier Cm2a, and (c) two-step switching with barriers C2/Cm. The amplitudes are obtained from NEB calculations and are reported for a 36-atom computational cell.

Fe-sites will be fully considered in a forthcoming work.

Figure 5 tracks the change in the MCAE surface along the two lowest energy switching pathways, P2₁ab → C2 → P2₁ab → Cm → P2₁ab and P2₁ab → Cm2a → P2₁ab, revealing the change in directionality of the Fe-dopant spins during switching. Beginning in the P2₁ab phase with the polarization P oriented along [1 0 0], we identify a spin easy axis that lies in the crystallographic ab-plane at 11° with respect to P. In the octahedral orientation indicated in the first step, the spin easy axis is along ⟨1 0 0⟩. The calculated magnitude of the MCAE is 530 µeV, which is the energy difference between the x and z principal axes of the MCAE surface. In addition, we calculate an in-plane anisotropy between the x and y principal axes of 130 µeV. The principal axes of the MCAE surface for each of the switching steps are given in Appendix C.

Taking the Cm2a path (Figure 5a), the Fe-dopant (along with all the octahedra in the top layer) first passes through the 4c Wyckoff position in Cm2a, which has site symmetry m. On this site the MCAE is significantly increased to 940 µeV and the spin easy axis is (−0.7, 0.7, 0.0). At 90° switching, the structure re-
FIG. 5. Change in spin directionality on an Fe-dopant during switching (a) via the Cm2a intermediate phase and (b) via the C2 and Cm phases. Magnetocrystalline anisotropy energy surfaces are plotted with red arrows indicating the spin easy directions and black arrows showing the polar axis in the P21ab phases. In the crystal structures, purple, red and gold spheres are W, O and Fe respectively, and only WO₆ octahedra are shown; the Fe-dopant sits in the upper layer with the dark grey octahedra and the lower layer is light grey.

turns to the P21ab phase with spin easy axis now along (−0.2, 1.0, 0.0), a rotation of 112° around the c-axis from the original spin easy axis. Passing through the Cm2a structure a second time, the dopant (and all octahedra in the top layer) is in the 4b Wyckoff position with site symmetry 2, resulting in a slightly lower MCAE of 730 µeV compared to the 4c site, although the spin easy axis remains the same. This can be understood by the variation in off-centering of Fe, making a 170° O–Fe–O bond angle in the 4c position compared to 180° in the 4b position (taking the bonds aligned parallel to the spin axis). In the last step, the structure returns to P21ab with P switched by 180° and the spin easy axis returned to (1.0, −0.2, 0.0). (Beginning in one of the orientations in the lower layer, the Fe-dopant would pass through the 4b Wyckoff position first and the 4c position second.)

Alternatively, taking the C2/Cm path (Figure 5b), the Fe-dopant first passes through the C2 phase in Wyckoff position 2b (site symmetry 2) and secondly through the Cm phase in Wyckoff position 2a (site symmetry m). The MCAE values are 750 µeV and 970 µeV respectively, and the spin easy axis is along (−0.7, 0.7, 0.0) in both
cases. As in the $Cm\bar{2}a$ path, a $90^\circ$ switch in the polarization direction results in a rotation of the spin easy axis by $112^\circ$ about the c-axis. The similarity in crystal field environment in the two switching pathways accounts for the resemblance between the MCAE surfaces in Figure 5a-b. Details of the site symmetries and in-plane and out-of-plane MCAE are listed in Table III, including alternative dopant positions. There are symmetrically inequivalent W-sites on the 2a Wyckoff position in $Cm\bar{2}$ and the 2b position in $C2$, which have a slightly different crystal field environment from the sites considered above, resulting in small differences in the MCAE values. In addition, an alternative domain choice for the switching pathways could have taken the Fe-dopant through the 4b position in $Cm\bar{2}$ and the 4c position in $C2$. MCAE data is not available for the latter as the structural optimization on this site did not converge the forces on the ions below a reasonable number.

The MCAEs reported here are typical of 3d transition metal atoms, and their low magnitudes indicate that thermally induced switching could occur if not kept at very low temperatures. This could be sufficient for devices operating at cryogenic temperatures (e.g. quantum computing); an MCAE of 0.5 meV corresponds to an energy barrier of ~6 K, three orders of magnitude greater than the typical mK operating temperatures of many quantum devices. However, strategies to increase the MCAE should be explored to exclude thermally induced switching in higher temperature applications. These could include systems with reduced dimensionalities and 4d or 5d transition metal and rare earth atoms which have been shown to exhibit giant MCAE values.

**CONCLUSION**

We use a combination of group theoretic analysis and DFT calculations to determine the intrinsic ferroelectric switching pathways of Bi$_2$WO$_6$. We identify several pathways: a one-step pathway, via $P \bar{a} 2b$, and three two-step pathways, via $C2/Cm$, $Cm\bar{2}a$ and $Cm\bar{2}m$. By comparing energies of the barrier structures we find that the two-step paths are lower energy than the one-step path, in agreement with experiment. In particular, the $C2/Cm$ path provides the lowest energy barrier of 97-99 meV/f.u. and the $Cm\bar{2}a$ barrier is only slightly higher at 103 meV/f.u.. These intrinsic switching barrier energies are comparable to those of other structurally complex ferroelectrics such as LiNbO$_3$ and Ca$_3$Ti$_2$O$_7$, which have barriers of 130 meV/f.u. and 64 meV/f.u. respectively.

Magnetic defects experience a change in crystal field environment during switching, resulting in a change in magnetic anisotropy at each switching step. Contrasting with Fe$^{3+}$ dopants in PbTiO$_3$ which exhibit a spin easy plane, the lower crystallographic symmetry of Bi$_2$WO$_6$ results in a spin easy axis. By calculating MCAE surfaces, we find how the spin orientation of a Fe$^{3+}$ substitutional defect on W-sites changes during polarization switching. In the $P \bar{2}a1b$ structure, the spin easy axis is in the $ab$-plane at 11° with respect to the polar axis and has an out-of-plane MCAE of 530 µeV and an in-plane MCAE of 130 µeV. During ferroelectric switching via intermediate phases, the spin easy axis rotates within the $ab$-plane and the MCAE is considerably increased (650-980 µeV out-of-plane, 130-530 µeV in-plane) due to changes in the local crystal environment of the dopant. We find that switching the polarization by $90^\circ$ in Bi$_2$WO$_6$ results in a $112^\circ$ rotation of the spin easy axis. However, a full $180^\circ$ reversal of the polarization returns the spin easy axis to its original orientation.

Based on these results, we suggest that a possible pathway to achieve full spin control with $180^\circ$ polarization switching is to consider ferroelectrics where an additional structural distortion that couples to the polarization must change during $180^\circ$ switching. If this structural distortion also impacts the magnetic anisotropy, then the change to the distortion due to polarization switching may result in a different spin easy axis in the $+P$ and $-P$ states. For example, changes to octahedral rotation distortions, which are extremely common in (layered) perovskite oxides, can modify spin easy planes and axes. Although the $X_3^+$ and $X_2^+$ octahedral rotation patterns in Bi$_2$WO$_6$ change along the two-step switching paths, the octahedral rotation amplitudes and pattern in the starting ($+P$) and final ($-P$) structures are the same. However, there are other layered perovskite ferroelectrics, such as the Aurivillius compound SrBi$_2$Ta$_2$O$_9$ and several $n=2$ Ruddlesden-Popper ferroelectric oxides, where reversal of the polarization requires by symmetry that the sense of an octahedral rotation also reverse. Compounds such as these may provide the necessary ingredients to create distinct low symmetry environments and hence different MCAE surfaces in polarization reversed states.
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AUTHOR CONTRIBUTIONS

K.I. and N.P. contributed equally to this work.

Appendix A: Additional subgroups of $I\bar{4}/mmm$

Table A1 reports the subgroups of $I\bar{4}/mmm$ generated by distinct directions of the $\Gamma_5^-, X_2^+, \text{ and } X_3^+$ order parameters, along with the distortion amplitudes, lattice parameters, and total energies of Bi$_2$WO$_6$ after DFT structural relaxations in each space group.

FIG. A1. Energy of the ferroelectric switching barrier structures $B$ above $P2_1ab$ as a function of epitaxial strain. The strain is applied biaxially in the $ab$ plane, and 0% strain is defined with respect to the $P2_1ab$ lattice parameters.

Appendix B: Epitaxial strain

Figure A1 presents the energies of the ferroelectric switching barrier structures discussed in the main text as a function of epitaxial strain. In these calculations, biaxial strain is applied in the $ab$-plane, and the lattice parameter $c$ and all atomic positions are allowed to relax. We find that all energy barriers increase upon going from compressive to tensile strain. The $Pocab$ energy barrier changes the most dramatically with strain. The $C2/Cm$ structures provide the lowest energy barriers at all strains that we consider, although under highly compressive strains (larger than 2%) the $Pcab$ barrier may become lowest, which would suggest a crossover from two- to one-step switching being the lowest energy path.

Table A2 reports the principal axes of the MCAE surfaces shown in Figure 5. These axes are orthonormal vectors which describe the three principal axes of rotation of the MCAE surface. The spin easy axis lies along the $x$ principal axis.

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TABLE A1. Subgroups of $I4/mmm$ established by distinct directions of the $\Gamma_5^-, X_2^+$, and $X_3^+$ order parameters. Total energies, distortion amplitudes, and lattice parameters obtained from DFT structural relaxations of $\text{Bi}_2\text{WO}_6$ in each space group are given. The energies are reported relative to the energy of $P2_1$ $ab$, which is set to 0 meV/f.u., and the distortion amplitudes are obtained by decomposing the distorted structures with respect to $I4/mmm$ and are reported for a 36-atom computational cell.

| Irrep | Direction Space group (N$^o$) | Amplitude (Å) | Lattice parameters (Å) | Energy (meV/f.u.) |
|-------|--------------------------------|---------------|-------------------------|-----------------|
|      |                                | $a$           | $b$                     | $c$             |
| $\Gamma_5^-$ | $\text{Imm}2$ (44) | 1.47          | 5.472 5.472             | 16.575 154.54   |
| (a, a) | $\text{Fmm}2$ (42)           | 1.25          | 5.504 5.461             | 16.436 133.91   |
| $X_2^+$  | (a, a) $\text{Bbcm}$ (64)   | 1.31          | 5.290 5.290             | 16.646 231.32   |
| (a, a) | $\text{P}4/\text{mbm}$ (127)| 0.80          | 5.349 5.349             | 16.524 310.16   |
| $X_3^+$  | (a, a) $\text{Bbcm}$ (64)   | 1.48          | 5.368 5.395             | 16.663 178.40   |
| (a, a) | $\text{P}4_2/\text{ncm}$ (138)| 1.51          | 5.393 5.393             | 16.576 161.40   |

TABLE A2. Principal axes of the magnetocrystalline anisotropy energy surfaces for each of the switching steps shown in Figure 5.

| Switching Phase Wyckoff figure | x       | y       | z       |
|--------------------------------|---------|---------|---------|
| 5(a) $P2_1$ $ab$ 4a            | 1.0 -0.2 0.0 | 0.2 0.9 0.3 | -0.1 -0.3 -0.9 |
| $Cn(2a)$ 4c                   | 0.7 -0.7 0.0 | 0.6 0.6 -0.5 | -0.3 -0.3 -0.9 |
| $P2_1$ $ab$ 4a                | -0.2 1.0 0.0 | -0.9 -0.2 -0.3 | -0.3 -0.1 -0.9 |
| $Cn(2a)$ 4b                   | 0.7 -0.7 0.0 | -0.7 -0.7 -0.3 | 0.2 0.2 -0.9 |
| $P2_1$ $ab$ 4a                | -1.0 0.2 0.0 | 0.2 0.9 0.3 | 0.1 0.3 -0.9 |
| 5(b) $P2_1$ $ab$ 4a            | 1.0 -0.2 0.0 | 0.2 0.9 0.3 | -0.1 -0.3 -0.9 |
| $C2$ 2b                       | 0.7 -0.7 0.0 | -0.7 -0.7 -0.3 | 0.2 0.2 -1.0 |
| $P2_1$ $ab$ 4a                | -0.2 1.0 0.0 | -0.9 -0.2 -0.3 | -0.3 -0.1 -0.9 |
| $Cm$ 2a                       | 0.7 -0.7 0.0 | -0.6 -0.6 -0.4 | -0.3 -0.3 -0.9 |
| $P2_1$ $ab$ 4a                | -1.0 0.2 0.0 | 0.2 0.9 0.3 | 0.1 0.3 -0.9 |

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