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ARTICLE *in* NANO LETTERS · DECEMBER 2014

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# Multiferroic Grain Boundaries in Oxygen-Deficient Ferroelectric Lead Titanate

Takahiro Shimada,<sup>\*,†,‡</sup> Jie Wang,<sup>†,§</sup> Taku Ueda,<sup>†</sup> Yoshitaka Uratani,<sup>†</sup> Kou Arisue,<sup>†</sup> Matous Mrovec,<sup>‡</sup> Christian Elsässer,<sup>‡</sup> and Takayuki Kitamura<sup>†</sup>

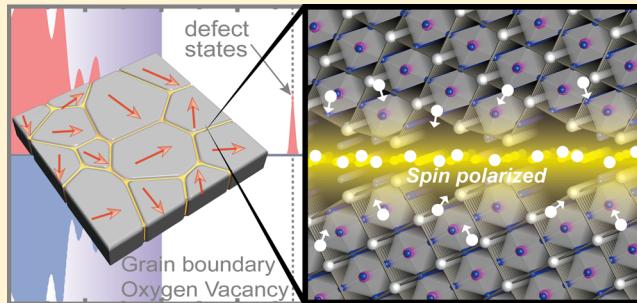
<sup>†</sup>Department of Mechanical Engineering and Science, Kyoto University, Nishikyo-ku, Kyoto 615-8540, Japan

<sup>‡</sup>Fraunhofer Institute for Mechanics of Materials IWM, Wöhlerstraße 11, 79108 Freiburg, Germany

<sup>§</sup>Department of Engineering Mechanics, School of Aeronautics and Astronautics, Zhejiang University, Hangzhou 310027, China

## S Supporting Information

**ABSTRACT:** Ultimately thin multiferroics arouse remarkable interest, motivated by the diverse utility of coexisting ferroelectric and (anti)ferromagnetic order parameters for novel functional device paradigms. However, the ferroic order is inevitably destroyed below a critical size of several nanometers. Here, we demonstrate a new path toward realization of atomically thin multiferroic monolayers while resolving a controversial origin for unexpected “dilute ferromagnetism” emerged in nanocrystals of nonmagnetic ferroelectrics  $\text{PbTiO}_3$ . The state-of-the-art hybrid functional of Hartree–Fock and density functional theories successfully identifies the origin and underlying physics; oxygen vacancies interacting with grain boundaries (GBs) bring about (anti)ferromagnetism with localized spin moments at the neighboring Ti atoms. This is due to spin-polarized defect states with broken orbital symmetries at GBs. In addition, the energetics of oxygen vacancies indicates their self-assembling nature at GBs resulting in considerably high concentration, which convert the oxygen-deficient GBs into multiferroic monolayers due to their atomically thin interfacial structure. This synthetic concept that realizes multiferroic and multifunctional oxides in a monolayered geometry through the self-assembly of atomic defects and grain boundary engineering opens a new avenue for promising paradigms of novel functional devices.



**KEYWORDS:** Dilute ferromagnetism, grain boundaries, vacancies, ferroelectrics, self-organization, multiferroics

Ferroelectric perovskite oxides, such as  $\text{PbTiO}_3$  or  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  solid solutions, are an important class of electroceramic materials that exhibit not only spontaneous polarization but also a variety of related properties including a large piezoelectric response and a high dielectric constant.<sup>1</sup> These multiple functionalities have been exploited for a long time for technological applications such as nonvolatile random access memory (FeRAM), transducers, and electromechanical devices.<sup>2,3</sup> These conventional ferroelectrics are intrinsically nonmagnetic due to a formal  $d^0$  electron configuration (e.g.,  $\text{Ti}^{4+}$ ) that drives cation off-centering for ferroelectricity, whereas a partially filled d state is required for a magnetic moment.<sup>4</sup> Nevertheless, recent experimental studies have unexpectedly discovered the dilute ferromagnetism in nanocrystalline samples of nonmagnetic ferroelectrics at room temperature.<sup>5–7</sup> The coexistence of two different ferroic order parameters, namely, ferroelectric and ferromagnetic/antiferromagnetic polarizations, is known as multiferroics, and the strong interaction of two ferroic orders, i.e., the magnetoelectric effect, will open a new door for realization of advanced applications beyond the conventional ferroelectrics, e.g., multiple-state memory elements, new functional sensors, and

spintronic devices.<sup>8,9</sup> However, the origin of the unexpected dilute ferromagnetism in ferroelectric nanocrystals and the physics behind the emergence of ferromagnetism has not yet been identified.

Oxygen vacancies are the most abundant and common point defects in oxide materials, and often they give rise to a variety of additional functionalities that the perfect host materials do not possess, such as eventual conductivity of intrinsic imperfections.<sup>10</sup> Magnetization is, however, not associated with oxygen vacancies in the ferroelectric  $\text{PbTiO}_3$  single crystals,<sup>11</sup> but recent experimental measurements<sup>7</sup> imply an abundance of oxygen vacancies, i.e., a significant off-stoichiometry, in nanocrystalline  $\text{PbTiO}_3$  samples and their nontrivial effect on the emergence of ferromagnetism. On the basis of these apparently contradictory facts, here we explore the possibility of oxygen vacancies in conjunction with the planar defects of grain boundaries, which form a large volume fraction of nanocrystals, as a possible key for this unexpected dilute ferromagnetism.

**Received:** July 1, 2014

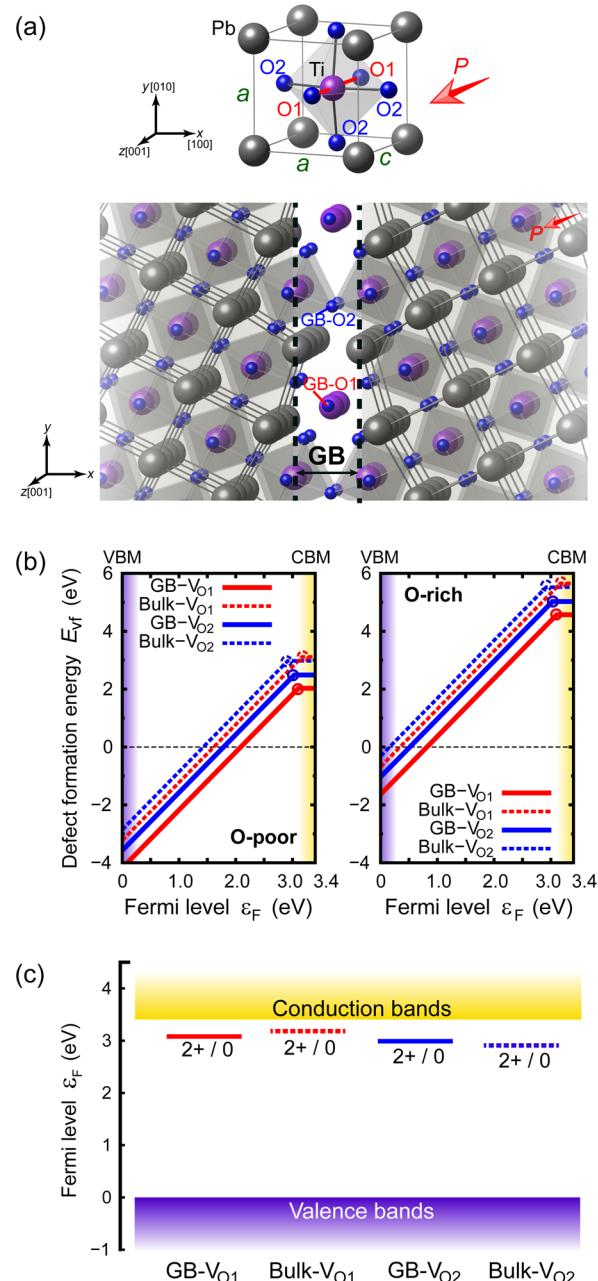
**Revised:** November 19, 2014

**Published:** December 8, 2014



The nature of vacancies is, in general, characterized by their unique electronic structure, i.e., the defect state in the band gap. This has mainly been studied from first-principles density functional theory (DFT) calculations for a long time. However, the results are rather scattered due to the use of different DFT approximations, such as the local density approximation (LDA) or the generalized gradient approximation (GGA), and some of these results apparently contradict the experimental observations.<sup>11–14</sup> This puzzling inconsistency was attributed very recently to the well-known underestimation error of the band gap,<sup>15</sup> which means that the DFT calculations for point defects incorrectly capture the edge of the conduction band instead of the true defect states that appear within the band gap.<sup>16,17</sup> This incorrect picture of defect electronic structures leads to a severe misprediction of the resulting energetic, structural, and electronic properties of vacancies. Therefore, to capture the true physics behind the emergence of ferromagnetism in PbTiO<sub>3</sub> is nontrivial and still remains a challenging issue.

The present letter explores an origin for and the underlying physics behind the “dilute ferromagnetism” in the nanocrystals of nonmagnetic PbTiO<sub>3</sub> using a hybrid functional of Hartree–Fock and density functional theories.<sup>18</sup> Hybrid functionals can capture better than LDA/GGA the band gaps and thus the electronic structures of defects in ferroelectrics, although the computations become much more demanding.<sup>11</sup> The hybrid functional calculations are performed using the projector augmented wave (PAW) method as implemented in the VASP code.<sup>19</sup> The Pb 5d, 6s, and 6p, the Ti 3s, 3p, 3d, and 4s, and the O 2s and 2p electrons are explicitly treated as valence states. We use the PAW pseudopotentials constructed based on the GGA of Perdew–Burke–Ernzerhof (PBE) functional.<sup>20</sup> The kinetic energy cutoff and *k*-point sampling were carefully chosen by preliminary convergence tests shown in Figures S1 and S2 in the Supporting Information, respectively. The electronic wave functions are expanded in plane waves up to a kinetic energy of 500 eV. Although the total energy and stresses converge at  $1 \times 2 \times 2$  *k*-point sampling, a finer  $1 \times 3 \times 3$  Monkhorst–Pack *k*-point sampling is used for the Brillouin zone integrations to obtain an accurate density of states. The exchange-correlation energies are described by the Heyd–Scuseria–Ernzerhof (HSE06) screened hybrid functional,<sup>18</sup> which contributes a part of exact nonlocal exchange of Hartree–Fock theory into a GGA.<sup>21</sup> The HSE06 hybrid functional successfully yields the tetragonal lattice constant  $a = 3.86 \text{ \AA}$  ( $c/a = 1.071$ ) (see Figure 1a) and the band gap  $E_{\text{gap}} = 3.4 \text{ eV}$  of ferroelectric PbTiO<sub>3</sub> in good agreement with the experimental values of  $a = 3.88 \text{ \AA}$  ( $c/a = 1.071$ ) and  $E_{\text{gap}} = 3.4 \text{ eV}$ , respectively.<sup>22,23</sup> Hence, the HSE06 hybrid functional calculations are free from the severe band gap error and are likely capable of describing the defect electronic structures beyond the commonly used LDA and GGA functionals.<sup>11</sup> In general, the hybrid functional yields better predictions about lattice constants, bulk moduli, and band gaps of various solids,<sup>18</sup> especially covalent materials,<sup>24</sup> compared with LDA and GGA, while it requires more computational costs and time<sup>18</sup> and sometimes mispredicts the phase stability of transition oxides.<sup>25</sup> In the present case, the hybrid functional correctly predicts the phase stability of PbTiO<sub>3</sub> that the tetragonal (ferroelectric) phase is energetically favorable over the cubic (paraelectric) phase with an energy difference of  $\Delta E = E_{\text{tetra}} - E_{\text{cubic}} = -0.09 \text{ eV/cell}$ , which is in good agreement with the values of  $\Delta E = -0.08$  and  $-0.06 \text{ eV/cell}$  obtained using GGA(PBEsol)<sup>21</sup> and LDA, respectively.



**Figure 1.** (a) Crystal structure of perovskite PbTiO<sub>3</sub> and atomic structure of a  $\Sigma 5$ (210) symmetrical tilt grain boundary (GB). The red arrow  $P$  indicates the direction of a spontaneous ferroelectric polarization. (b) Defect formation energies  $E_{\text{vf}}$  of oxygen vacancies at GBs (GB-V<sub>O1</sub> and -V<sub>O2</sub>) and inside the grain (Bulk-V<sub>O1</sub> and -V<sub>O2</sub>) as a function of the Fermi level  $\epsilon_{\text{F}}$  under the O-poor and O-rich conditions. The lines with nonzero slope correspond to the charge state 2+. (c) Charge transition levels of oxygen vacancies.

The interaction between vacancies and a grain boundary (GB) is studied by the commonly used periodic supercell approach.<sup>26</sup> The  $\Sigma 5$ (210) tilt GB is taken as a representative research sample of GBs in ferroelectric PbTiO<sub>3</sub> because this GB exhibits a low grain-boundary energy,<sup>26</sup> which makes its existence in polycrystals likely. The simulation supercell contains two grains as shown in the bottom panel of Figure 1a, where the crystal lattice of PbTiO<sub>3</sub> is rotated clockwise and counterclockwise by  $26.6^\circ$  around the [001] or *z* direction for the left-side and right-side grains, respectively. Thus, the *x* and *y*

directions of the left-side grain are [201] and [−102], respectively, while those of the right-side grain are [201] and [102], respectively. To avoid undesirable interaction from the neighboring GBs due to the periodic boundary conditions, the thickness of each grain is taken to be greater than 14 Å, which corresponds to more than three and half perovskite unit cells. The interfacial atomic configuration of the Σ5 GB used in this study was previously determined from detailed  $\gamma$ -surface calculations.<sup>26</sup> The spontaneous polarization is aligned along the  $z$  direction. An oxygen vacancy,  $V_{\alpha}^q$  ( $\alpha = O_1$  or  $O_2$ ), is introduced by removing one atom located at a position  $\alpha$  at the boundary or the bulk  $PbTiO_3$ . Here,  $O_1$  and  $O_2$  are the oxygen atoms located in the polar [001] direction and the nonpolar [100] or [010] directions relative to the Ti atom, respectively, and  $q$  (= 0, +, and 2+) denotes the charge state of the vacancy. The charged state is calculated by removing  $q$  electrons from the supercell with charge compensation of uniform background charges. The cell dimensions parallel the GB plane are greater than two unit cells by further doubling the supercell used in the previous study<sup>26</sup> to remove undesirable interaction from neighboring vacancies due to periodic boundary conditions.<sup>16,27</sup> In fact, a one unit cell length distance between neighboring oxygen vacancies causes about 0.1 eV uncertainty in defect formation energy while two or more unit cell length distances causes only 0.001–0.004 eV uncertainty, which does not affect the stability order of oxygen vacancies discussed below, and thus almost converges the formation energies. The simulation cell of the stoichiometric GB system thus contains 200 atoms. The positions of all atoms are relaxed by the conjugate gradient method until all the Hellmann–Feynman forces are less than 0.02 eV/Å.

The defect formation energy of oxygen vacancies is evaluated by

$$E_{vf}(V_O^q) = [E_{tot}(V_O^q) + \mu_O + q(E_{VBM} + \epsilon_F)] - E_{tot}(\text{perfect}) \quad (1)$$

where  $E_{tot}(V_O^q)$  and  $E_{tot}(\text{perfect})$  are the total energy of the supercell with and without an oxygen vacancy  $V_O^q$ , respectively.<sup>28</sup>  $E_{VBM}$  is the valence band maximum (VBM) (including a potential alignment correction<sup>11,30</sup>) and  $\epsilon_F$  is the Fermi level measured from the VBM, which varies from the VBM to the conduction band minimum (CBM).  $\mu_{\alpha}$  denotes the chemical potential of atom  $\alpha$ . According to the statistical thermodynamics theory, the chemical potential of an oxygen atom can be expressed as functions of oxygen partial pressure and temperature,<sup>29</sup> which enable us to discuss the formation of oxygen vacancies under oxygen-poor or rich conditions. In addition, the possible range of chemical potential of an oxygen atom  $\mu_O$  in  $PbTiO_3$  can be determined from the conditions of thermodynamic equilibrium and to preserve the formation of secondary phases,<sup>11</sup> and we showed that  $\mu_O$  can vary between the O-poor limit [ $\mu_{Pb} = \mu_{Pb(\text{bulk})}$ ,  $\mu_{Ti} + 2\mu_O = \mu_{TiO_2(\text{bulk})}$ , and  $\mu_{Pb} + \mu_{Ti} + 3\mu_O = \mu_{PbTiO_3(\text{bulk})}$ ] and the O-rich limit [ $\mu_O = (1/2)\mu_{O2(\text{molecule})}$ ].<sup>11</sup>

Figure 1b shows the calculated formation energy of oxygen vacancies at the GB (GB- $V_{O1}$  and - $V_{O2}$ ) and inside the grain (Bulk- $V_{O1}$  and - $V_{O2}$ ) as a function of the Fermi level  $\epsilon_F$ . Note that, at each Fermi level, we took the minimum formation energy among the charge states. Under the O-poor condition all oxygen vacancies have negative formation energies over a wide range of Fermi levels ( $0 < \epsilon_F < 2$  eV), which indicates that oxygen vacancies can form spontaneously during the crystal

growth or synthesis processes and thus have a high concentration. In contrast, the formation energies under the O-rich condition are higher, and thus, oxygen vacancy formation is less favorable, which results in a low concentration. These energetics of oxygen vacancies are consistent with the relevant experimental observations for bulk  $PbTiO_3$ ,<sup>31,32</sup> the concentration of oxygen vacancies decreases as the oxygen partial pressure increases (i.e., the condition changes from O-poor to O-rich). Considering the difference between the GB and the grain (bulk), the GB- $V_{O1}$  (or GB- $V_{O2}$ ) does exhibit a lower formation energy than the Bulk- $V_{O1}$  (or Bulk- $V_{O2}$ ) over all the Fermi levels. Therefore, oxygen vacancies are likely to form at GBs rather than inside grains and are preferentially trapped at GBs in the thermodynamic equilibrium. More specifically, GB- $V_{O1}$  is energetically favorable by 0.6 eV than GB- $V_{O2}$ . The trap energy of the most favorable  $V_{O1}$  at the GB is calculated to be  $E_{trap} \equiv E_{vf}(\text{Bulk-}V_{O1}) - E_{vf}(\text{GB-}V_{O1}) = 1.0 - 1.1$  eV, depending on the Fermi level, which is almost the same as the 1.0 eV reported for GBs in other perovskite oxides.<sup>33,34</sup> For comparison, as oxygen vacancies are also likely to be coupled with domain walls (DWs) (well-known as the pinning effect), the trap energy of DWs for  $PbTiO_3$  was reported to be 0.076–0.261 eV.<sup>35</sup> This trap energy is almost one-order smaller than that of GBs, and hence, oxygen vacancies are expected to predominantly concentrate at GBs in  $PbTiO_3$ . Indeed, transmission electron microscopy (TEM) observations used to directly measure the oxygen vacancies showed extremely high populations at GBs (more than 30% of O-sites are vacant) in perovskite oxide samples,<sup>36,37</sup> which indicates the self-assembling and concentrating nature of oxygen vacancies toward GBs. Note that the defect concentration as functions of oxygen partial pressure and temperature may be estimated by following the scheme in ref 38, which will be addressed in a future work.

The possible charge states of oxygen vacancies and the relevant transition levels are of importance to determine the electronic defect states. Since each charge state of oxygen vacancy shows each formation energy with a slope of  $q$  from eq 1 and Figure 1b showed the minimum formation energy among these charge states at each Fermi level, the change of slope in Figure 1b represents the point where the stable charge state of oxygen vacancies changes, i.e., charge transition level. The results are shown in Figure 1c. Oxygen vacancies both on the boundaries and inside the grains (bulk) show a change of slope from  $q = 2+$  to  $q = 0$  (i.e., 2+/0 transition) at the level slightly below the CBM, which indicates a double shallow donor nature of oxygen vacancies. This corresponds well with the *n*-type conductivity, which is experimentally observed in  $PbTiO_3$  under oxygen-poor conditions.<sup>10</sup> Thus, oxygen vacancies in  $PbTiO_3$  can be neutral or doubly ionized, as in other ferroelectric oxides.<sup>12</sup>

The magnetic spin moments and magnetic configurations of oxygen vacancies in the present  $PbTiO_3$  systems are summarized in Table 1. When oxygen vacancies are present inside grains (Bulk- $V_{O1}$  and - $V_{O2}$ ), no spin moment is observed, regardless of the possible charge states, and the system remains nonmagnetic as the intrinsic (defect-free)  $PbTiO_3$ . This result is consistent with our previous hybrid-functional study for oxygen vacancies in bulk ferroelectric oxides.<sup>11</sup> However, a nonzero and nontrivial magnetic spin moment of  $2.0\mu_B$  emerges when  $V_{O1}$  is trapped at the GB site (GB- $V_{O1}^0$ ). In addition, the magnetic moment induced by the GB- $V_{O1}^0$  favors the ferromagnetic (FM) configuration because the total energy

**Table 1. Magnetic Spin Moments  $M$  (in  $\mu_B$ /Vacancy) and Magnetic Configurations of Oxygen Vacancies at the Grain Boundary (GB) and Inside the Grain (Bulk) of Ferroelectric  $PbTiO_3$ ; the Oxygen Vacancies That Lead to Local Magnetic States Are Indicated in Boldface**

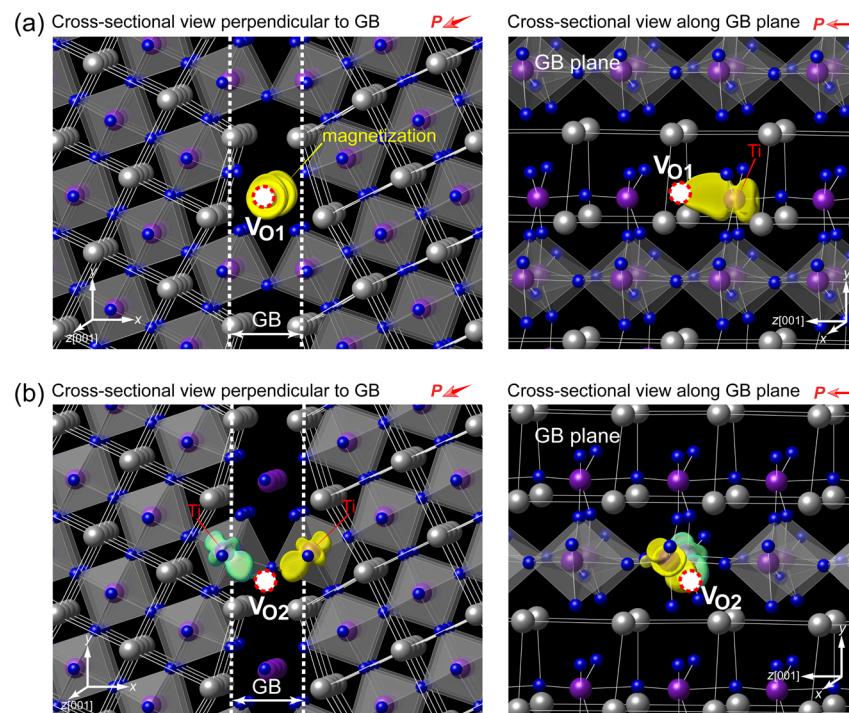
vacancy	grain boundary (GB)		inside grain (Bulk)	
	$V_{O1}^0/V_{O1}^{2+}$	$V_{O2}^0/V_{O2}^{2+}$	$V_{O1}^0/V_{O1}^{2+}$	$V_{O2}^0/V_{O2}^{2+}$
$M (\mu_B)$	2.0/0	0.0/0	0/0	0/0
magnetic phase	FM/NM	AFM/NM	NM/NM	NM/NM

difference between the FM and antiferromagnetic (AFM) configurations<sup>15,39</sup> is negative,  $E_{\text{tot}}^{\text{FM}}(\text{GB}-V_{O1}) - E_{\text{tot}}^{\text{AFM}}(\text{GB}-V_{O1}) = -82$  meV. This value is similar to that reported for oxygen-deficient CaO and thus is not exceptionally small or large but is probably common among deficient oxides.<sup>40</sup> Therefore, the interplay of oxygen vacancies and GBs indeed brings about ferromagnetism into the intrinsically nonmagnetic  $PbTiO_3$ . The detailed magnetization density distribution around the most favorable GB- $V_{O1}^0$  is visualized in Figure 2a. The magnetization is particularly localized at the Ti atom next to the GB- $V_{O1}$  site, which is strongly bonded with the GB-O1 atom in the perfect (defect-free)  $\Sigma 5$  GB through hybridization of the Ti 3d and the O 2p orbitals. This suggests that due to the formation of an oxygen vacancy the unbound Ti 3d electrons may contribute to the localized magnetization, as will be elaborated later. Similarly, oxygen vacancies  $V_{O2}$  formed at GBs also have nonzero spin moments, which are separately localized at the two Ti atoms adjacent to the  $V_{O2}$  site as shown in Figure 2b, although the formation of GB- $V_{O2}$  is less favorable than GB- $V_{O1}$ . The magnetic spin moments of the paired Ti atoms are, however, in an AFM configuration, which results in no net

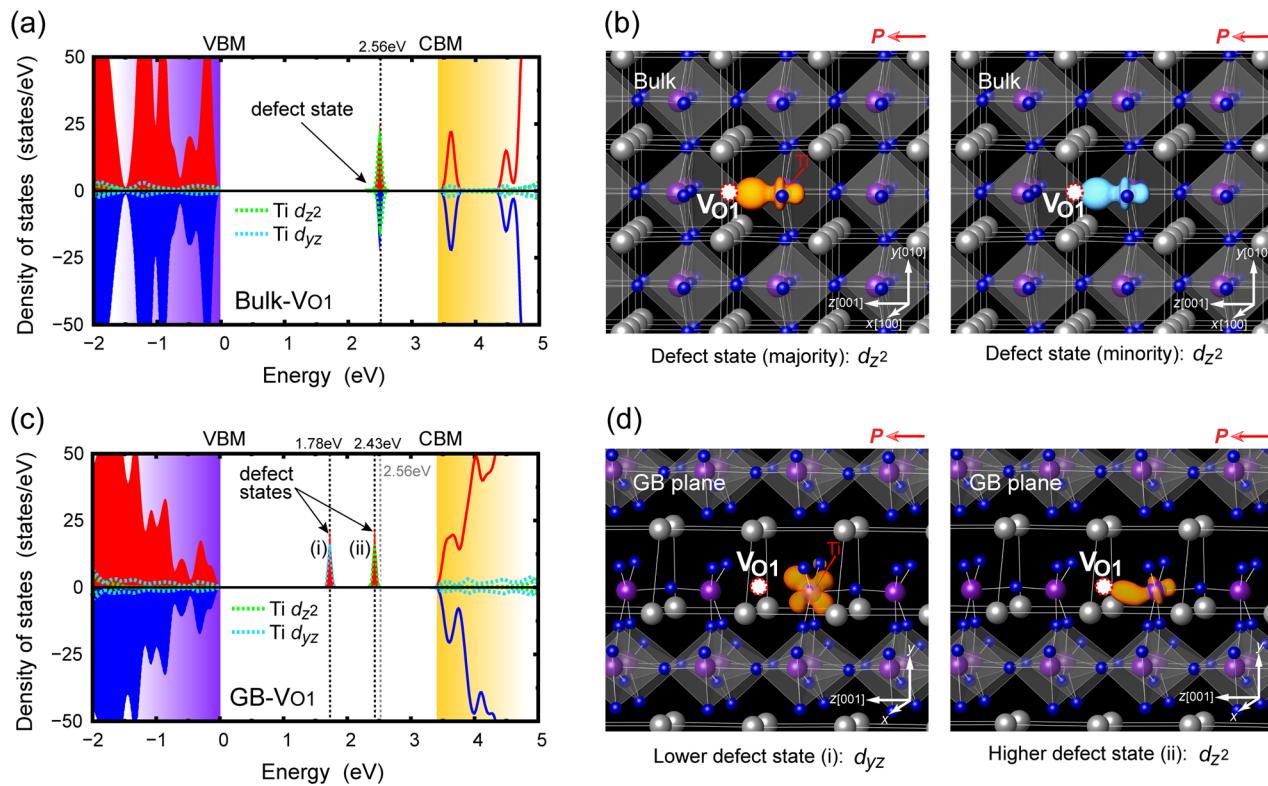
magnetic moment of the GB. Therefore, only  $V_{O1}$  coupled with GBs directly contributes to ferromagnetism although both oxygen vacancies at GBs have nonzero spin moments.

This result is well consistent with the relevant experimental observations and explains these reasonably: Zhang et al. reported that the magnetic moment in nanocrystalline  $PbTiO_3$  samples was considerably diminished by annealing in air rather than in a vacuum.<sup>7</sup> The oxygen-vacancy sites in the samples are filled with oxygen atoms by annealing in air; therefore, this experiment suggests oxygen vacancies as one of the possible key defects mediating dilute ferromagnetism. Another experiment reported by Wang et al. showed that, as the grain size of  $PbTiO_3$  samples increased from nanometers to micrometers, the remanent magnetic moment decreased and finally disappeared.<sup>6</sup> The larger grain size implies that there are fewer GBs included in the materials, so that the latter experiment suggests the GBs as another key ingredient. Both these experimental observations are consistent with our theoretical result that only the interaction of oxygen vacancies and GBs induces magnetism into  $PbTiO_3$ , whereas the vacancies and boundaries separately have no spin polarization. This provides strong evidence for the origin of dilute ferromagnetism in  $PbTiO_3$  nanocrystals.

To provide further electronic level insight into magnetism induced by oxygen vacancies at GBs, we analyze the electronic density of states (DOS). Figure 3a,c shows the DOS for the most favorable  $V_{O1}$  inside the grain (Bulk- $V_{O1}$ ) and at the boundary (GB- $V_{O1}$ ), respectively. Let us first focus on the DOS of Bulk- $V_{O1}$ ; there is a single electronic defect state between the VBM and CBM (see Figure 3a), which cannot be observed in the perfect (defect-free)  $PbTiO_3$  crystal. This state is therefore characteristic of the oxygen vacancy, i.e., the defect state of



**Figure 2.** Magnetic spin-density distribution around the (a) GB- $V_{O1}$  and (b) GB- $V_{O2}$ . The cross sections perpendicular to and along the grain boundary (GB) plane are shown in the left and right panels, respectively. The yellow and green areas indicate the iso-surfaces of spin densities of  $+0.04$  and  $-0.04 \mu_B/\text{\AA}^3$ , respectively. The iso-surface values are chosen to best show the nature of orbitals that contribute to emergent magnetizations. The red arrow  $P$  indicates the direction of the spontaneous ferroelectric polarization.



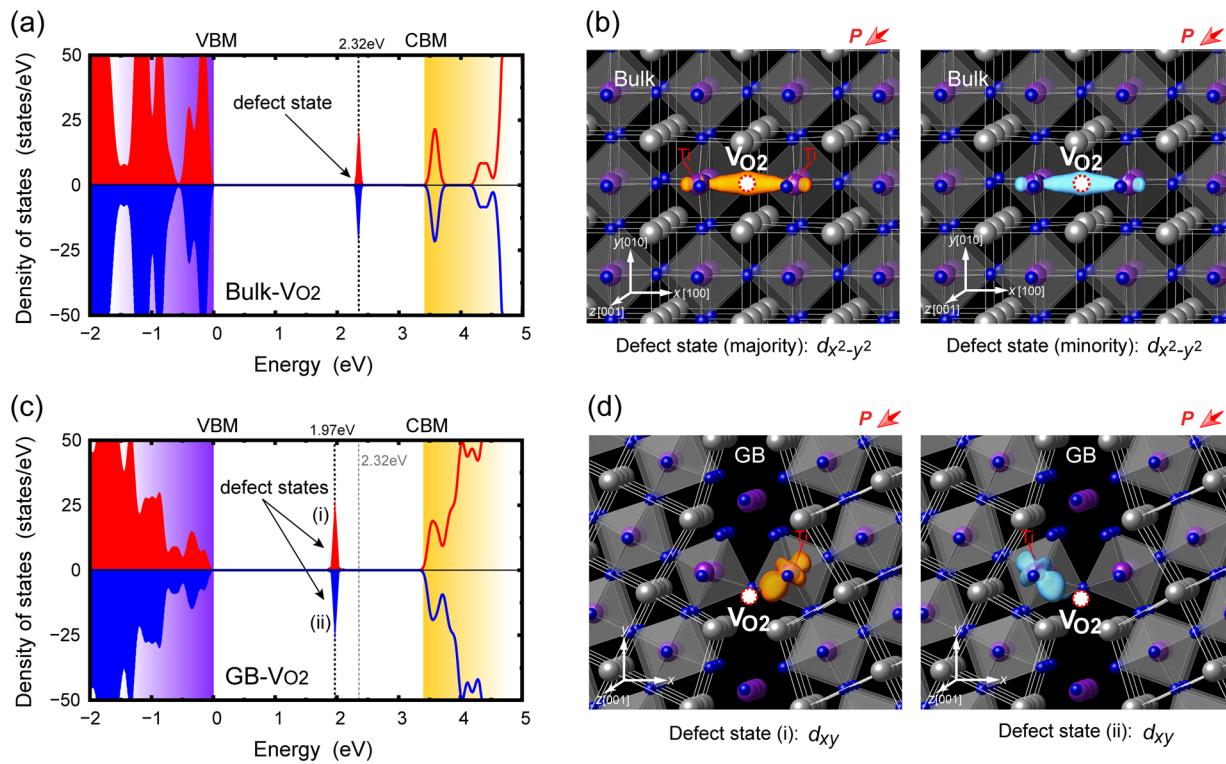
**Figure 3.** Electronic density of states (DOS) of (a) Bulk-V<sub>O1</sub> and (c) GB-V<sub>O1</sub>. The red and blue areas/lines show the DOS of the occupied/unoccupied states of majority and minority spins, respectively. The angle-resolved local DOS of the Ti atom adjacent to the vacancy site is simultaneously plotted. The squared wave functions of the defect states appearing within the band gap are visualized for (b) Bulk-V<sub>O1</sub> and (d) GB-V<sub>O1</sub>. The orange and light-blue iso-surfaces indicate the majority spin and minority spin densities of  $0.04 \text{ \AA}^{-3}$ , respectively. The red arrow P indicates the direction of the spontaneous ferroelectric polarization.

Bulk-V<sub>O1</sub>. The defect state is located at 2.56 eV above the VBM, and it is fully occupied by two electrons arising from the local nonstoichiometry. The state is therefore spin-unpolarized, which results in the nonmagnetic nature of Bulk-V<sub>O1</sub>. Note that the defect state level does not correspond to the charge transition level because they are different physical quantities. To illustrate further details, the squared wave function  $|\psi_e|^2$  of this defect state is also visualized in Figure 3b. The defect state is tightly localized between the Bulk-V<sub>O1</sub> and the adjacent Ti atom in [001]. As the shape of the wave function indicates, the main contribution to this defect state is from a  $d_z^2$  orbital of the neighboring Ti atom, which is hybridized with the O1 p<sub>z</sub> orbital in defect-free PbTiO<sub>3</sub> and forms a strong pdσ bond (see also Figure S3 in Supporting Information).<sup>41</sup> Thus, a partial loss of the O1–Ti bond due to the formation of Bulk-V<sub>O1</sub> should result in a  $d_z^2$ -dominant defect state localized at the Ti atom. This is consistent with the experimental observation that Ti<sup>4+</sup> is reduced to Ti<sup>3+</sup> or Ti<sup>2+</sup> in the O-deficient octahedra by charge compensation.<sup>42</sup>

In contrast to the Bulk-V<sub>O1</sub>, the oxygen vacancy at the GB (GB-V<sub>O1</sub>) is associated with two distinct defect states (i) and (ii) (see Figure 3c). The higher defect state (ii) of GB-V<sub>O1</sub> is located at 2.43 eV above the VBM, at almost the same position as that of Bulk-V<sub>O1</sub>, while the other defect state (i) appears below at 1.78 eV. Each defect state is partially occupied by a single majority spin electron, so that the defect states are spin-polarized and GB-V<sub>O1</sub> has a magnetic spin moment of  $2.0 \mu_B$ . The higher defect-state (ii) is localized at the neighboring Ti atom and is  $d_z^2$ -dominant (see Figure 3d), which is identical to that of Bulk-V<sub>O1</sub>. However, a distinctive  $d_{yz}$  orbital mainly

contributes to the lower defect state (i). The appearance of this lower  $d_{yz}$  state splits the fully occupied higher  $d_z^2$  state of Bulk-V<sub>O1</sub> into the two partially occupied defect states of GB-V<sub>O1</sub>, which results in the spin-polarization at the GB. This  $d_{yz}$ -dominant defect state may arise from the symmetry breaking at the GB: The Σ5 GB structure breaks the mirror symmetry in  $y$  but retains the symmetry in  $x$ , while both symmetries are maintained in the bulk interior (see also Figure 1a). The symmetry breaking at the GB induces atomic relaxation along  $y$ ; the O1 and neighboring Ti atoms on the GB shifts in + $y$  and - $y$ , respectively, while in the bulk interior the O1 and Ti atoms have the same  $y$  position (compare Figure 3d with b). This atomic distortion in  $y$  at GBs breaks the orbital symmetry of the  $d_z^2$ -dominant defect state and allows the additional  $d_{yz}$ -contribution. Such structural change and the resulting orbital symmetry break at GBs have been reported both experimentally and theoretically, and this feature is not a particularity of the Σ5 GB but is common among GBs.<sup>33–37,43,44</sup> Thus, a similar situation and resulting ferromagnetism can be expected in other GBs.

For GB-V<sub>O2</sub>, a similar electronic feature of defect states is observed. Figure 4a,c plots the DOS of Bulk-V<sub>O2</sub> and GB-V<sub>O2</sub>, respectively. For Bulk-V<sub>O2</sub>, a fully occupied defect state appears at 2.32 eV above the VBM and is localized between two adjacent Ti atoms (see Figure 4b). The defect state is  $d_x^2 - d_y^2$ -dominant, which may result from a loss of Ti–O2–Ti bond hybridizing the Ti  $d_x^2 - d_y^2$  and O2 p<sub>z</sub> orbitals.<sup>41</sup> Thus, the squared wave function of the defect state is distributed purely along the  $x$  axis parallel to the Ti–O2–Ti bonds. However, two defect states (i) and (ii) appear at a lower level of 1.97 eV



**Figure 4.** Electronic density of states (DOS) of (a) Bulk-V<sub>O2</sub> and (c) GB-V<sub>O2</sub>. The red and blue areas/lines show the DOS of the occupied/unoccupied states of the majority and minority spins, respectively. The squared wave functions of the defect states appearing within the band gap are visualized for (b) Bulk-V<sub>O2</sub> and (d) GB-V<sub>O2</sub>. The orange and light-blue iso-surfaces indicate the majority spin and minority spin densities of  $0.04 \text{ \AA}^{-3}$ , respectively. The red arrow P indicates the direction of the spontaneous ferroelectric polarization.

above the VBM. The defect states (i) and (ii) are not identical, as visualized in Figure 4d, because the defect state (i) is the majority spin localized at the right-side Ti atom, while the state (ii) is the minority spin localized at the left-side Ti atom. Since these defect states are  $d_{xy}$ -dominant in contrast to the bulk counterpart, which distributes purely along  $x$ , the split of defect state may also be due to the  $y$  symmetry break at GBs. This localized and separated feature of the two paired defect states results in spin polarizations split into two Ti atoms adjacent to GB-V<sub>O2</sub>. Note that the antiferromagnetic coupling of the split spin polarizations is probably due to the spin superexchange through indirect d–d hopping between the two equivalent Ti<sup>3+</sup> ions paired by V<sub>O2</sub>, as reported for oxygen vacancies in TiO<sub>2</sub>.<sup>45</sup>

Ferromagnetic or antiferromagnetic configurations of spin moments appear at locations where oxygen vacancies segregate at GBs. Considering the aforementioned observation that oxygen vacancies are highly concentrated at GBs and more than 30% of O-sites are vacant at least,<sup>36,37</sup> a large part of the GB planes should be almost entirely magnetized. The present results provide a novel concept for nanoscale materials design: high concentration of oxygen vacancies at the GB can add ferro- or antiferromagnetism to the material, changing it from simply ferroelectric to multiferroic. In addition, a GB can be regarded as a multiferroic monolayer due to its atomically thin interface structure. Such an extremely thin multiferroic cannot be expected by the direct scale-down of intrinsic multiferroics such as BiFeO<sub>3</sub> because the critical thickness should exist for the ferroelectric order, to be 2–6 unit cells,<sup>46–48</sup> due to insufficiency of screening by real electrodes or depolarizing field by materials surfaces. Recent developments in fabrication techniques have achieved precise control of both the density and arrangement of GBs.<sup>49</sup> Hence, it is becoming possible to

synthesize atomically thin multiferroics via self-assembly of defects and grain boundary engineering. The ultrahigh-density integration of multiferroic elements promises novel functional device paradigms such as multiferroic memory. This concept can be extended to other functional transition-metal oxides to bring about ferromagnetism in addition to the functionalities that the materials intrinsically possess. The proposal developed through the present results is thus promising, and it may stimulate future experimentation and simulation efforts on oxygen-deficient GBs in various functional oxides to explore novel functionalities in conjunction with the emerging dilute ferromagnetism.

In summary, a possible origin of dilute ferromagnetism in oxygen-deficient ferroelectric lead-titanate nanocrystals was explored using hybrid Hartree–Fock density functional calculations. No magnetic spin polarization is caused by an isolated oxygen vacancy in the bulk interior while an oxygen vacancy coupled with a grain boundary leads to the formation of magnetic moment localized at the adjacent Ti atom due to the spin-polarized defect states caused by the interfacial symmetry break at the GB. In addition, the energetics of oxygen vacancies indicates a self-assembly on GBs, which converts ferroelectric oxygen-deficient GBs into atomically thin multiferroic ones. The present results further indicate the potential for exploitation of a new avenue for the realization of monolayer interface-controlled multiferroics and multifunctional oxides through the self-assembly of atomic defects and grain boundary engineering. This may become a promising paradigm for novel functional devices.

## ■ ASSOCIATED CONTENT

### § Supporting Information

Total energies and stresses for the simulation supercell; total and atom-resolved angular-momentum-projected density of states (DOS) for ferroelectric PbTiO<sub>3</sub> bulk. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [shimada@me.kyoto-u.ac.jp](mailto:shimada@me.kyoto-u.ac.jp).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors acknowledge financial support for T.S. and T.K. from the Grant-in-Aid for Specially Promoted Research (Grant No. 25000012) and the Grant-in-Aid for Scientific Research (B) (Grant No. 26289006) from the JSPS and for J.W. from NSFC (Grants No. 11472242 and 11321202).

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