Research Article

Electronic Origin of Defect States in Fe-Doped LiNbO_3 Ferroelectrics

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We investigate the role of Fe in the electronic structure of ferroelectric LiNbO_3 by density-functional theory calculations. We show that Fe^{2+} on the Li site ($\text{Fe}^{2+}_{\text{Li}}$) features a displacement opposite to the direction of spontaneous polarization and acts as a trigger for the bulk photovoltaic (PV) effect. In contrast to Fe^{3+} on the Li site that forms the defect states (1e, a, and 2e) below the conduction band minimum, the reduction from Fe^{3+} to Fe^{2+} accompanied by a lattice relaxation markedly lowers only the a state (d_{z^2}) owing to a strong orbital hybridization with Nb-4d. The a state of $\text{Fe}^{2+}_{\text{Li}}$ provides the highest electron-occupied defect state in the middle of the band gap. A reduction treatment of Fe-LN is expected to increase the concentration of Fe^{2+} and therefore to enhance the PV effect under visible light illumination.

1. Introduction

Spatial symmetry breaking in polar materials offers various functions including piezoelectricity, ferroelectricity, multiferroelectricity, and bulk photovoltaic (PV) effect. Because ferroelectric lithium niobate (LiNbO_3 ; LN) has a strong polar lattice arising from cooperative displacements of the constituent atoms, LN has been used in many applications including acousto-optic [1–3], electro-optic [1, 4–6], and optical-frequency conversion [1, 7–10] devices. Historically, the photorefractive effect was first discovered in LN [11, 12] and was found to be enhanced in iron-doped lithium niobate (Fe-LN) [13]. The photorefractive effect is recognized as the cause of an optical damage in the nonlinear optics, whereas it is utilized for holographic memory storages [14, 15].

Recently, the PV effect in ferroelectrics has attracted renewed interests, because the working principle can be applied to the devices that generate a high voltage beyond the limitation of present semiconductor-based solar cells [16–19]. The bulk PV effect in ferroelectrics arises from asymmetric carrier dynamics because of spatial symmetry breaking [20]. The photoinduced feature of the generation and dissociation

of charge carriers in Fe-LN under visible light make it a promising candidate for the ferroelectric material used in the PV devices. Although a large number of experimental studies on Fe-LN have been conducted for several decades [21, 22], first-principles calculations of the electronic structures have been reported very recently [23–26].

Sanson et al. [25] have performed density-functional theory (DFT) calculations for Fe-LN in addition to local structure studies by an extended X-ray absorption fine structure spectroscopy. They reveal that Fe^{2+} on the Li site ($\text{Fe}^{2+}_{\text{Li}}$) produces defect states inside the band gap and that the a state in the minority spin band forms the Fermi energy (E_F). According to Inoue et al. [26], a tensile strain from substrates markedly enhances the PV effect in Fe-LN epitaxial thin films whereas their DFT calculations show that neither tensile nor compressive strain plays a minor role in the electronic structure of $\text{Fe}^{2+}_{\text{Li}}$ -LN. However, the following question remains unresolved: why the d-wave states of $\text{Fe}^{2+}_{\text{Li}}$ differ in the majority and minority spin bands. In addition, the orbital interaction between $\text{Fe}^{2+}_{\text{Li}}$ and its neighbors should play an important role, but the bonding and antibonding interactions related to the Fe^{2+} -d states have not been understood yet.

To establish the materials design for enhanced PV effect in the LN system, the electronic origin of the defect states originating from $\text{Fe}^{2+}_{\text{Li}}$ needs to be clarified.

In this paper, we report the electronic structure of $\text{Fe}^{2+}_{\text{Li}}$ -LN obtained by DFT calculations and discuss the orbital interactions of $\text{Fe}^{2+}_{\text{Li}}$ with its neighbors. We demonstrate that the mixing between Fe-3d and Nb-4d plays a crucial role in the electronic structure. Our calculations show that the a state of $\text{Fe}^{2+}_{\text{Li}}$ resulting from the hybridization of Fe- d_{z^2} and Nb-4d is the highest electron-occupied defect state in the middle of the band gap and acts as a trigger for the PV effect under visible light.

2. Method of DFT Calculations

We performed DFT calculations within the local density approximation (LDA) [27] by the PAW (projector-augmented wave) method [28] using a plane wave basis set as implemented in the Vienna *ab initio* simulation package (VASP) [29]. A plane wave cut-off energy was set to be 520 eV, and an electronic energy was converged to less than 10^{-5} eV in all calculations. First, the hexagonal unit cell of LN in space group $R3c$ was structurally optimized until the Hellmann-Feynman force on each atom was less than 0.1 eV/nm. A k -mesh of $3 \times 3 \times 3$ centered on the Γ point was used in the geometrical optimization for lattice parameters and fractional coordinates. The lattice parameters of the optimized LN cell agree well with the experimental values [30] within 0.7%.

We employed a simplified local spin density approximation (LSDA + U approach) [31] as a correction for localized and strongly correlated electrons within on-site Coulomb terms of $U - J = 3$ eV for Nb-4d [32] and $U - J = 4$ eV for Fe-3d [23, 30]. The details of the influence of the $U - J$ terms on the electronic structures are discussed later. The occupation sites of Fe in LN have been reported as Fe on the Li site (Fe_{Li}) [33–40] and Fe on the Nb site (Fe_{Nb}) [38, 39]. Here, we adopt the model of Fe^{2+} on the Li site ($\text{Fe}^{2+}_{\text{Li}}$), according to the reports [23, 41], because we focus our attention on the defect states arising from $\text{Fe}^{2+}_{\text{Li}}$ that absorbs visible light. To make a supercell of Fe-LN, the setting of the optimized LN cell (hexagonal) was transformed to the rhombohedral cell ($\text{Li}_{16}\text{Nb}_{16}\text{O}_{48}$) in space group $P1$. In this cell one Li atom was replaced by one Fe atom, leading to $\text{Li}_{15}\text{FeNb}_{16}\text{O}_{48}$. This rhombohedral setting was changed again to the hexagonal one in space group $R3$. This Fe-LN cell [$\text{Li}_{15}\text{FeNb}_{16}\text{O}_{48}$ ($Z = 3$)] was geometrically optimized (with a k -mesh of $3 \times 3 \times 3$ centered on the Γ point).

In the model of $\text{Fe}^{2+}_{\text{Li}}$, the charge neutrality is supposed to be satisfied by the following two possible compensations: one is the formation of the small polaron, $\text{Fe}^{2+}_{\text{Li}}\text{-Nb}^{4+}_{\text{Nb}}$, [41, 42] and the other is the creation of Li vacancy (V'_{Li}) [23], where the prime denotes one negative charge. First, we tested the small polaron model of $\text{Fe}^{2+}_{\text{Li}}\text{-Nb}^{4+}_{\text{Nb}}$. In the Fe-LN cell, there are eight different kinds of the Nb sites in view of the symmetry. Prior to the geometrical optimizations, magnetic moment of $+1 \mu_B$ (where μ_B denotes Bohr magneton) or $-1 \mu_B$ was put to each of the Nb atom, and that of Fe was set to be $+4 \mu_B$ assuming the high spin configuration. After the

geometrical optimizations for all of the supercells, the total magnetic moment was converged to be $+4 \mu_B$ and the E_F was located inside the conduction band (the Nb-4d band). This implies that Fe-LN crystals with the $\text{Fe}^{2+}_{\text{Li}}\text{-Nb}^{4+}_{\text{Nb}}$ polaron exhibit a metallic behavior having a low resistivity, which cannot explain the experimental result of the high resistivity of Fe-LN crystals [43]. These results force us to consider that the small polaron model of $\text{Fe}^{2+}_{\text{Li}}\text{-Nb}^{4+}_{\text{Nb}}$ is not suitable for the charge compensation in the ground state.

Next we examined the V'_{Li} model [23] by using the supercell containing V'_{Li} and $\text{Fe}^{2+}_{\text{Li}}$, that is, $\text{Li}_{14}\text{FeNb}_{16}\text{O}_{48}$ (the V'_{Li} cell) in space group $P1$. The Fe-LN cell has seven different kinds of Li sites. We performed the geometrical optimizations for all of the supercells with V'_{Li} on each of the Li sites. The cells with V'_{Li} on the first nearest neighbor (NN) and seventh NN sites with respect to $\text{Fe}^{2+}_{\text{Li}}$ exhibited a small total energy by 30–90 meV compared with the other cells. These results suggest that V'_{Li} is not necessarily stabilized adjacent to $\text{Fe}^{2+}_{\text{Li}}$ and lead to a structural picture of the $\text{Fe}^{2+}_{\text{Li}}$ -LN lattice with a random distribution of V'_{Li} .

In reality, $\text{Fe}^{2+}_{\text{Li}}$ -LN should have an averaged structure similar to the LN host in $R3c$ space group. This symmetry is, however, completely lost in the V'_{Li} model owing to the presence of V'_{Li} on the specific site. In order to take into account the threefold rotation axis along the c axis, we adopted the $\text{Fe}^{2+}_{\text{Li}}$ -LN cell without V'_{Li} [$\text{Li}_{15}\text{FeNb}_{16}\text{O}_{48}$ ($Z = 3$) in space group $R3$], where the valence state of Fe was controlled to be Fe^{2+} . This structural model is the same as that reported by Sanson et al. [25]. The calculations of the $\text{Fe}^{3+}_{\text{Li}}$ -LN cell were also conducted in a similar manner for comparison. The electronic band structures and density of states (DOS) of the geometrically optimized cells were calculated with a k -mesh of $3 \times 3 \times 3$ centered on the Γ point. While the calculations with a denser k -mesh were tested, we confirmed that the results of the electronic structures are essentially the same, as reported in [25].

3. Results and Discussion

Figure 1(a) displays the crystal structure around iron in the $\text{Fe}^{2+}_{\text{Li}}$ -LN cell after the geometrical optimization. In the LN cell, Nb atoms are displaced along the c axis by approximately 0.02 nm, and this cooperative displacement yields a spontaneous polarization (P_s). In the $\text{Fe}^{2+}_{\text{Li}}$ -LN cell the bond length of Fe-O1 ($l_b = 0.200$ nm) is shorter by 0.02 nm than that of Fe-O2 ($l_b = 0.221$ nm), showing that Fe^{2+} is displaced in the direction opposite to P_s . The bond valence sum (BVS) of $\text{Fe}^{2+}_{\text{Li}}$ is estimated to be +2.3, which is slightly larger than the nominal valence (+2). Figures 1(b)–1(d) display the electronic band structures. The total density of states (DOS) and their partial DOS (PDOS) are also shown in Figures 2(a)–2(c). For the LN ($R3c$) cell (Figures 1(b) and 2(a)), the E_F is set to be 0 eV. In these figures, the valence band maximum (VBM) mainly composed of the O-2p band is aligned to the same level. Our calculations show that the band gap is indirect: the VBM is located at the Λ point (1/2 1/2 1/2) and the conduction band minimum (CBM) is positioned at the Γ point. Because the maximum of the valence band at the Γ point is very

FIGURE 1: (a) Crystal structure around Fe²⁺ in the Fe²⁺_{Li}-LN cell after the geometrical optimization obtained by the DFT calculations and the electronic band structures of the (b) LN, (c) Fe²⁺_{Li}-LN, and (d) Fe³⁺_{Li}-LN cells.

close in energy to the VBM and the difference is as small as 0.02 eV, we regard the maximum of the valence band at the Γ point as the VBM. The band gap (E_g) estimated from the CBM and the VBM is 3.5 eV. This E_g value is quantitatively in good agreement with the experimental gap of 3.8 eV [44]. In general, band gap is usually underestimated due to the well-known problem of LDA [45] while the appropriate choice of the $U-J$ term for Nb-4d with the LSDA + U approach enables us to obtain a reasonable E_g comparable to the experimental gap; the influences of the $U-J$ terms are described later. The valence band (VB) in the energy of -5-0 eV is the O-2p dominant band while the conduction band (CB) in 3.4-5.5 eV consists mainly of the Nb-4d band (Figure 3(a)). The orbital hybridization between Nb-4d and O-2p results in the small

but apparent portion of PDOS of Nb-4d in the VB and that of O-2p in the CB. The PDOS of Li is not significant in both the VB and CB, which presents the ionic character of Li⁺ in the LN lattice.

In point group 3, the d states are divided into $1e$, a , and $2e$ (Figure 3(b)). Fe²⁺ has a $3d^6$ electron configuration, which is described as $1e^2 a^1 2e^2$ in the majority spin ($\uparrow$) band and $a^1 1e^0 2e^0$ in the minority spin ($\downarrow$) band [41, 46]. The detailed analysis of the Fe²⁺-3d states leads to the order of $1e$, a , and $2e$ with increasing energy in the $\uparrow$ band, as is illustrated in the energy diagram of the d states in the Fe²⁺_{Li}-LN cell (Figure 3(b)). The hybridization of Fe²⁺-3d and O-2p provides the bonding states ($1e$, a , and $2e$) and the antibonding states ($1e^*$, a^* , and $2e^*$), where (*) denotes

FIGURE 2: Total and partial density of states (DOS) of the (a) LN, (b) $\text{Fe}^{2+}_{\text{Li-LN}}$, and (c) $\text{Fe}^{3+}_{\text{Li-LN}}$ cells.

FIGURE 3: Proposed energy diagram resulting from the orbital interactions among Fe-3d, Nb-4d, and O-2p: (a) the schematic band structure of LN and (b) the Fe-3d states in point group 3. (c) The orbital hybridization between Fe-3d and O-2p yielding the defect states in the majority spin ($\uparrow$) band. (d) The Nb-4d and O-2p interaction leading to the O(2p)-dominant states O(2p)[Nb(4d)] in the VB and the Nb(4d)-dominant states Nb(4d)[O(2p)] in the CB. (e) The orbital interactions between Fe-3d_{z²} and the adjacent orbitals (Nb-4d and O-2p) leading to the defect states in the minority spin ($\downarrow$) band. (f) The energy levels with an electronic configuration of the Fe²⁺(3d⁶)-related defect states: $1e^2a^12e^21e^{*2}a^{*1}2e^{*2}$ in the $\uparrow$ band and $a^11e^02e^0a^{*0}1e^{*0}2e^{*0}$ in the $\downarrow$ band.

the antibonding state. In the $\uparrow$ band, all of these states are occupied by electrons and the a^* and $2e^*$ states form defect states above the VBM (Figure 1(c)).

In the $\downarrow$ band, we note that the a state is markedly lowered in energy whereas the $1e$ and $2e$ are located above the CBM, as can be seen in Figures 1(c), 2(b), and 3(f). The detailed analysis reveals that the lowering in energy of the a state ($\downarrow$) stems from the two orbital interactions as depicted in Figure 3: one is the direct hybridization with Nb1-4d (the line I) and the other is the mixing with the antibonding state of the Nb2-4d (O-2p) states (the line II). As a result, Fe²⁺ possesses three localized defect states inside the band gap, so-called gap states: a^* and $2e^*$ in the $\uparrow$ band and a in the $\downarrow$ band. The gap states of a^* and $2e^*$ exist near the VBM, and the a state ($\downarrow$) forms the E_F in the middle of the band gap. Due to Fe²⁺_{Li} with the a state ($\downarrow$), the apparent gap between the occupied state and the CBM narrows to 1.6 eV, which agrees well with the onset of the optical absorption of Fe-LN crystals [42]. This result shows that visible light with $\hbar\omega \geq 1.6$ eV leads to the electron excitation from Fe²⁺ to Nb⁵⁺. This intervalence transfer transition oxidizes Fe²⁺ to Fe³⁺ and reduces Nb⁵⁺ to Nb⁴⁺, which forms the Fe-Nb

dipole. The total optical absorption essentially results from a superposition of the electron transfers from the a state ($\downarrow$) to the CB [41].

Next, we discuss the results of the Fe³⁺_{Li}-LN cell shown in Figures 1(d) and 2(c). Fe³⁺ has a 3d⁵ electron configuration with $1e^2a^12e^2$ in the $\uparrow$ band and $1e^0a^02e^0$ in the $\downarrow$ band. The analysis of the Fe³⁺-d states shows the orders of $1e$, a , and $2e$ in the $\uparrow$ band and a , $1e$, and $2e$ in the $\downarrow$ band with increasing energy. Compared with the Fe²⁺_{Li}-LN cell, the Fe³⁺-3d states are lowered in energy regardless of the $\uparrow$ and $\downarrow$ bands. Only the $2e^*$ state ($\uparrow$) constitutes the occupied gap state and forms the E_F . The unoccupied states of a , $1e$, and $2e$ in the $\downarrow$ band are present below the CBM. The energy gap between the occupied $2e^*$ state and the CBM on the Γ point is as large as 3 eV, indicating that visible light with a photon energy less than 3 eV ($\hbar\omega < 3$ eV) cannot cause a charge transfer from Fe³⁺ to Nb⁵⁺. Thus, Fe³⁺_{Li} in the ground state plays a minor role in the PV effect under visible light.

For the bulk PV effect in Fe-LN under visible light, the defect states inside the band gap are of particular importance. We depict the wave function of the occupied a state ($\downarrow$) of the Fe²⁺_{Li}-LN cell in Figure 4(a) and its two-dimensional

FIGURE 4: Wave functions of the occupied a state in the minority spin ($\downarrow$) band of the Fe^{2+} -LN cell (a) in a three-dimensional view and its two-dimensional projections on the (b) Nb1-Fe-Nb3 (c) Nb1-Fe-O2 and (d) O2-Fe-O1 planes.

projections in Figures 4(b)–4(d). This a state is composed mainly of the d_{z^2} orbital of Fe^{2+} and has a small contribution of O-2p. In Figures 4(b) and 4(d) we display the above-described two orbital interactions, that is, the direct hybridization of Fe- d_{z^2} with Nb1-4d and the mixing with the Nb2-4d (O-2p) antibonding state, respectively. It is interesting to note that the a state ($\downarrow$) is indeed localized around $\text{Fe}^{2+}_{\text{Li}}$. In contrast, the wave function of the CBM on the Γ point exhibits the Nb-4d character and is delocalized throughout the crystal, as shown in Figure 5.

Here, we discuss the generation and recombination of carriers photoexcited by visible light illumination. Figure 6 exhibits the schematic illustration of the configuration coordinate diagram representing the optical absorption (E_{opt}), Frank-Condon relaxations (E_{relax1} and E_{relax2}), and

photoluminescence (E_{PL}). The energy curve of $\text{Fe}^{2+}_{\text{Li}}$ -LN varies with respect to the configuration coordinate (q) where the energy minimum (E_A) achieved at q^- represents a thermal ionization energy of acceptor (1.8 eV for Fe^{2+} in LN) [23, 47]. The curve of $\text{Fe}^{3+}_{\text{Li}}$ -LN exhibits an excited state caused by light illumination. We adopt the experimental value of the E_g of 3.8 eV. The optical absorption in $\text{Fe}^{2+}_{\text{Li}}$ -LN (E_{opt}) has been reported to show a peak at around 2.5 eV, which changes the valence state from Fe^{2+} to Fe^{3+} [42]. During the photoinduced electron excitation with a time scale of ~ 0.1 ps [48, 49], the valence state of Fe changes at a fixed coordinate of q^- while the $\text{Fe}^{2+}_{\text{Li}}$ -LN lattice remains unchanged. This excited state loses its surplus energy by displacing the neighboring ions (thermalization) and is relaxed to the coordinate of q^0 along the $\text{Fe}^{3+}_{\text{Li}}$ -LN curve,

FIGURE 5: Wave function of the conduction band minimum (CBM) on the Γ point representing the Nb-4d character, which is delocalized throughout the crystal.

FIGURE 6: Schematic illustration of the configuration coordinate (q) diagram showing the optical absorption (E_{opt}), Frank-Condon relaxations (E_{relax1} and E_{relax2}), and photoluminescence (E_{PL}) accompanied by the valence and conduction bands with an E_g of 3.8 eV.

leading to the formation of free small polaron composed of an electron (e^-) and Nb^{5+} [41, 42]. The recombination time of the small polaron has been reported as ~ 40 ns in $\text{MgO}(5\%)$ -doped LN [49]. The Fe valence state returns to Fe^{2+} at the coordinate of q^0 accompanied by a photoluminescence with an energy of $E_{\text{PL}} \sim 1.6$ eV [50]. Then, the ground state coordinate q^- is reached by a relaxation along the curve of $\text{Fe}^{2+}_{\text{Li-LN}}$. From our DFT calculations, we estimate the two Frank-Condon relaxations (E_{relax1} and E_{relax2}) as 0.5 eV

TABLE 1: Parameters of the electronic band structures at the Γ point calculated for the $\text{Fe}^{2+}_{\text{Li-LN}}$ cell within the LSDA + U approach with various $U - J$ terms of Fe-3d (the $U - J$ value of Nb-4d is fixed to be 3 eV). The value of band gap (E_g) accords with the energy difference between the CBM and the VBM.

$U - J$ (eV)	E_g (eV)	CBM ^a - $a\downarrow$ (eV)	$a\downarrow$ - VBM ^b (eV)
[Fe-3d]			
2	3.46	1.04	2.42
4	3.51	1.60	1.91
6	3.52	2.30	1.22
8	3.52	2.99	0.53
Experiment	3.8 ^c	1.6 ^d	—

^aConduction band maximum.

^bValence band maximum.

^cReference [44].

^dThe onset energy of the optical absorption in $\text{Fe}^{2+}_{\text{Li-LN}}$ [42].

and 0.4 eV, respectively, which satisfy the following energy relations:

$$E_{\text{opt}} = E_{\text{relax1}} + E_{\text{relax2}} + E_{\text{PL}}, \quad (1)$$

$$E_g = E_{\text{PL}} + E_{\text{relax2}} + E_A.$$

Finally, we consider the influences of the $U - J$ terms on the electronic structures and the gap state of Fe-3d in the $\text{Fe}^{2+}_{\text{Li-LN}}$ cell. In the simplified LSDA + U approach, the $U - J$ term is treated as an empirical parameter for representing localized, strongly correlated electrons. Nahm and Park [32] have investigated the crystal and electronic structures of LiNbO_3 with an antisite defect of Nb on the Li site in the range of $U - J = 3 - 5$ eV and reported that the electronic structure is well described with $U - J = 4$ eV for Nb-4d. Sanson et al. [25] have studied the structural distortion and electronic states of $\text{Fe}^{2+}_{\text{Li-LN}}$ in the range of $U - J = 3 - 5$ eV for the d orbitals and concluded that the $U - J$ value of 4 eV is suitable for both Nb-4d and Fe-3d for describing the local structure around Fe and the gap state of Fe-3d. Here, we investigate the influence of the $U - J$ terms (2–8 eV) on the E_g and the $a\downarrow$ gap state, the details of which are summarized in Tables 1 and 2. In Figure 7, we plot the CBM and the $a\downarrow$ state with respect to the VBM as a function of $U - J$. Because the VBM is set to be 0 eV, the value of the CBM is equal to E_g and the energy of the $a\downarrow$ state indicates the energy gap from the VBM. With the fixed $U - J$ of 3 eV for Nb-4d (Figure 7(a)), the E_g does not depend on $U - J$ of Fe-3d and remains unchanged at 3.5 eV. This result shows that the E_g is essentially independent of the character of Fe-3d. The energy level of the $a\downarrow$ state is lowered with increasing $U - J$ of Fe-3d. As for the results with the fixed $U - J$ of 4 eV for Fe-3d (Figure 7(b)), the E_g widens with increasing $U - J$ of Nb-4d while the $a\downarrow$ level remains constant, revealing that the $U - J$ term of Nb-4d does not lead to a marked change in the character and depth of the gap states of Fe-3d in LN.

To verify the calculation results, we need to take account of the two experimental types of data: one is the E_g of 3.8 eV [44] and the other is the onset energy of the optical absorption in $\text{Fe}^{2+}_{\text{Li-LN}}$ of 1.6 eV [42]. Because the highest occupied electron is located at the $a\downarrow$ state, the difference of

FIGURE 7: Energy levels at the Γ point of the $a\downarrow$ gap state of Fe-3d and the CBM with respect to the VBM in the $\text{Fe}^{2+}_{\text{Li}}\text{-LiNbO}_3$ cell calculated by the LSDA + U approach with various $U - J$ terms: (a) the $U - J$ value of Nb-4d is fixed to be 3 eV and that of Fe-3d varies and (b) the $U - J$ value of Fe-3d is fixed to be 4 eV and that of Nb-4d varies. The value of band gap (E_g) accords with the energy difference between the CBM and the VBM.

TABLE 2: Parameters of the electronic band structures at the Γ point calculated for the $\text{Fe}^{2+}_{\text{Li}}\text{-LiNbO}_3$ cell within the LSDA + U approach with various $U - J$ terms of Nb-4d (the $U - J$ value of Fe-3d is fixed to be 4 eV). The value of band gap (E_g) accords with the energy difference between the CBM and the VBM.

$U - J$ (eV) [Nb-4d]	E_g (eV)	CBM ^a - $a\downarrow$ (eV)	$a\downarrow$ - VBM ^b (eV)
2	3.39	1.49	1.90
3	3.51	1.60	1.91
4	3.65	1.72	1.93
6	3.91	1.97	1.95
8	4.19	2.23	1.96
Experiment	3.8 ^c	1.6 ^d	—

^aConduction band maximum.

^bValence band maximum.

^cReference [44].

^dThe onset energy of the optical absorption in $\text{Fe}^{2+}_{\text{Li}}\text{-LiNbO}_3$ [42].

the CBM and the $a\downarrow$ state (CBM - $a\downarrow$) can be considered to indicate the onset energy of the optical absorption. The CBM - $a\downarrow$ is overestimated for the $U - J$ values larger than 6 eV and underestimated for those smaller than 2 eV. We conclude that the $U - J$ terms of 4 eV (Fe-3d) and 3 eV (Nb-4d) are appropriate for representing the electronic feature of the gap state originating from Fe-3d in $\text{Fe}^{2+}_{\text{Li}}\text{-LN}$, which is consistent with [23, 25, 30, 32]. We confirmed that the orbital interactions shown in Figures 3–5 play an essential role in the calculation results regardless of the $U - J$ values.

One straightforward way to enhance the bulk PV effect in $\text{Fe}^{2+}_{\text{Li}}\text{-LN}$ is to increase the concentration of Fe^{2+} . Investigations with Mössbauer spectroscopy have shown that the dominant valence state of Fe in LN sintered in air is Fe^{3+} and that the concentration of Fe^{2+} [Fe^{2+}] is lower than the detection limit [51]. This result suggests that [Fe^{2+}] is much

lower than that of [Fe^{3+}] in Fe-LN sintered or annealed in air. A reduction treatment of Fe-LN is expected to increase [Fe^{2+}] and therefore to enhance the bulk PV effect in either bulk or thin-film form.

4. Conclusion

We have investigated the electronic structures of $\text{Fe}^{2+}_{\text{Li}}\text{-LN}$ and $\text{Fe}^{3+}_{\text{Li}}\text{-LN}$ by DFT calculations and discussed the electronic origin of the defect states inside the band gap. Our calculations show that $\text{Fe}^{2+}_{\text{Li}}$ is displaced in the direction opposite to spontaneous polarization and acts as a trigger for the bulk PV effect under visible light. The a state, which is mainly composed of the $\text{Fe}^{2+}_{\text{Li}}\text{-}d_{z^2}$ orbital, forms a localized defect state in the middle of the band gap. The following two orbital interactions lead to a noticeable lowering in energy of the a state in the minority spin band that forms the E_F inside the band gap: the direct hybridization of $\text{Fe-}d_{z^2}$ with Nb-4d and the orbital mixing of $\text{Fe}^{2+}_{\text{Li}}\text{-}d_{z^2}$ with the antibonding state of Nb-4d (O-2p). It is proposed that a reduction treatment of Fe-LN increases the concentration of Fe^{2+} and therefore enhances the PV effect in either bulk or thin-film form.

Competing Interests

The authors declare that they have no competing interests.

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