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Electronic properties of *A*-site substituted lead zirconate titanate: Density functional calculations

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First-principles density functional theory calculations have been applied to study the electronic and optical properties of *A*-site substituted lead zirconate titanate (PZT), where group IIIA and group VB elements partially substitute Pb sites. The conduction band minima in the group IIIA element substituted PZT systems are found to be shared by Ti 3*d* and dopant states, which reduce the occupation on Ti 3*d* states by the electrons. Moreover, correlations between dopant electrons introduce the Mott-Hubbard band gap into PZT, which is intrinsically a charge-transfer insulator. This leads to a systematic reduction of energy and optical band gaps with increased atomic number of group IIIA substitutes. Similar chemical trend was found for group VB substitutes, which is, however, closely related to the electron bandwidth of Ti 3*d* states in the charge-transfer band gaps. All the trivalent substitutes are confirmed to effectively dilute the concentration of the oxygen vacancies under Pb-deficient conditions by our theoretical calculations.

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I. INTRODUCTION

Ferroelectric perovskite-structure crystals have a general formula ABO_3, where A is a monovalent or divalent cation with large radius, B is a pentavalent or tetravalent metal with small radius, and O is oxygen. Lead zirconate titanate [$\mathrm{Pb(Zr}_x\mathrm{Ti}_{1-x})\mathrm{O}_3$ or PZT] is one of the most important members in the ferroelectric perovskite family due to its remarkable ferroelectric and piezoelectric features in polycrystalline form.[1] PZT is a solid solution of two simple perovskites, lead titanate ($PbTiO_3$) and lead zirconate ($PbZrO_3$), with a broad range of Curie temperatures, which increases from 230 to 490 °C as the Ti content increases from 0% to 100%. PZT has two different ferroelectric structures below the Curie temperature, depending on the Zr/Ti composition ratio (tetragonal and rhombohedral at Ti and Zr rich, respectively). There is also a morphotropic phase boundary region (Zr/Ti=48/52) in which the tetragonal and rhombohedral structures coexisted.[2]

PZT-based ceramics have been broadly used in a large range of applications in the past decades, such as actuators, ultrasonic transducers, sensors, resonators, and piezoelectric transformers.[3,4] In recent years, PZT thin films are recognized as the most promising capacitor materials in nonvolatile ferroelectric random access memory (FeRAM) applications,[5] which offer a number of advantages, including notably lower power consumption, faster write speed, good nonvolatility, and radiation hardness.

However, PZT suffers a severe degradation of remnant polarization after a number of writing and reading cycles, namely, fatigue.[6] Intensive attention has been attracted for an understanding of the origin of fatigue, and it has now been widely accepted that many crucial mechanisms leading to fatigue are associated with the formation and redistribution of oxygen vacancies in the PZT thin films, through domain pinning[7] and space charge effect.[8] In addition, theoretical studies have shown that the possible origin of the fatigue is associated with the reduced π bonds between Ti 3*d* and O 2*p* states caused by electrons released from oxygen vacancies.[9]

Doping has been proved to be an effective way in controlling the ferroelectric behaviors of PZT.[10–12] The doping substitutes can either occupy *A* site, *B* site, or both, as donor or acceptor based on their chemical valences with respect to the original ions. Generally, donor substitutes soften the ferroelectric properties of PZT. For example, they enhance the dielectric constants, bulk resistivity, and remnant polarization, as well as reduce the coercive field, which are particularly favored in FeRAM applications. Moreover, donor substitutes are expected to improve the fatigue behavior of PZT, which is ascribable to the diluted oxygen vacancy concentrations by the donors.

While many donor-substituted PZT systems have been experimentally developed,[10–14] a systematic study on the variation of doping effects of different substitutes is still lacking. This systematic study is of great importance because it not only offers a better understanding of the doping effects but also provides guidance for materials selection. Our previous work has thoroughly investigated the electronic properties of *B*-site donor doped PZT and their effects on the fatigue behavior.[15] In this work, we extend our research to the effects of *A*-site donor substitutes in lead zirconate titanate. Electronic structures, optical properties, vacancy formations, and fatigue behaviors of PZT systematically doped with *A*-site substitutes were investigated, using first-principles density functional theory.

II. THEORY AND COMPUTATIONAL DETAILS

$2\times2\times4$ supercells were adopted for all theoretical calculations in this study. It is assumed that in the doped system, a Pb atom at the spatial center of the supercell is missing and other two Pb atoms are replaced by the substitutes in order to maintain the electroneutrality. The plane-wave calculations were based on density functional theory (DFT) with generalized gradient approximations (GGAs). Perdew-Burke-Ernzerhof exchange-correlation parametrization was employed in determining ionic and electronic ground states. The pseudopotential approach was used, where the Pb $5d,6s,6p$, O $2s,2p$, Ti $3d,4s$, and Zr $4s,4p,4d,5s$ orbitals were regarded as valence orbitals. For the substitutes, the outmost d and s orbitals of the group IIIA elements and outmost s and p orbitals of group VB elements were considered as valence electrons in the calculations. The atomic positions in each supercell were fully optimized without any symmetry restrictions except that the lattice parameters of the supercells, $a=b=7.892$ Å and $c/a=2.094$, were used based on experimental values of the undoped PZT (Zr/Ti=25/75).[16] For calculations on density of states (DOS), energy gaps, and optical properties, the meta-GGA method was applied due to its better prediction of the electronic structures of the systems, where the second derivative of the density or the kinetic energy density is included in addition to the density and the magnitude of the gradient of the density.[17] The convergence tests were taken before any geometry optimization, from which a $2\times2\times1$ K mesh and the cutoff energy at 400 eV were determined. The calculations of the DOS and band structures were conducted with a $6\times6\times3$ K mesh and a cutoff energy at 400 eV. The code we employed in our density functional theory calculations is the Vienna *ab initio* simulation package (VASP).

We screened all group IIIA and group VB elements (A^{3+}) as a substitution dopant to the Pb site in $PbTiO_3$. The ionic radii of group IIIA elements Sc, Y, and La and group VB elements Sb and Bi are 0.73, 0.89, 1.06, 0.76, and 0.96 Å, respectively, with a valency of +3, which are compatible with that of the Pb^{2+} ion (1.20 Å). The tolerance factor, which was introduced by Goldschmidt,[18] was calculated for each ATiO$_3$ system with a full A-site substitution by the dopants and is in the relatively stable range (0.89–0.92) of perovskites. On the contrary, the calculated factors for all other group VB elements N^{5+}(0.16 Å), P^{5+}(0.44 Å), and As^{5+}(0.58 Å) were below 0.65. These substitutes may lead to the instability of the perovskite structure and therefore are of no interest in this study.

III. RESULTS AND DISCUSSION

A. Pure lead zirconate titanate

The DOS study of undoped PZT is given in Fig. 1 and our result is consistent with other first-principles calculation results reported previously.[19] According to the description of the Zaanen-Sawatzky-Allen (ZSA) framework, an insulating transition-metal system whose band gap is an energy difference between filled p bands of ligand anions and unoccupied upper Hubbard $3d$ bands (Δ) is the so-called charge-transfer (CT) insulator.[20] As the band gap of undoped PZT is typically the energy difference between occupied O $3p$ states at the valence band maximum (VBM) and unoccupied Ti $3d$ and Zr $4d$ states in the conduction band minimum (CBM), lead zirconate titanate belongs to the category of charge-transfer insulators.

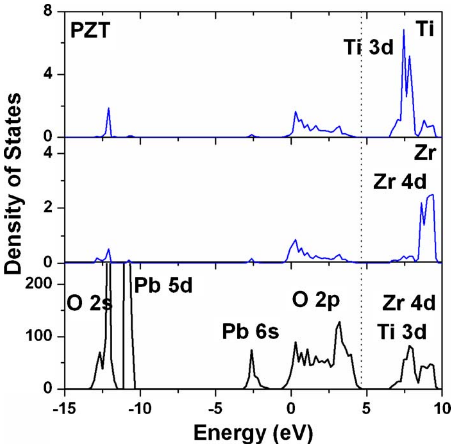

FIG. 1. (Color online) Calculated density of states (DOS) of undoped PZT and partial density of states (PDOS) of Ti and Zr ions.

Optical property calculations were carried out for the absorption spectra of PZT systems. The optical band gap E_g was determined from Tauc's formula,[21]

$$(\alpha E)^2 = A(E - E_g), \tag{1}$$

where $\alpha=4\pi\kappa/\lambda$ is the absorption coefficient, E is the photon energy, and A is a constant. Thus, the E_g values are therefore determined by extrapolating the linear portion of the plot relating $(\alpha h\nu)^2$ versus $h\nu$ to $(\alpha h\nu)^2=0$.

The calculated band gap of the absorption spectrum of PZT is shown in Fig. 2. The energy band gaps (1.75 eV) calculated in meta-GGA scheme are greatly underestimated with respect to the experimental energy gaps due to the fact that density functional theory fails to take account of orbital dependence of the Coulomb and exchange interactions.

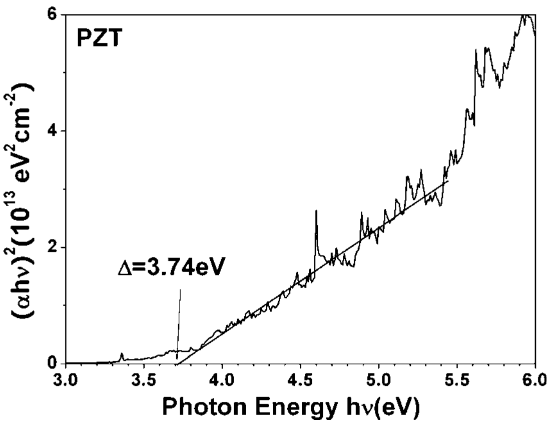

FIG. 2. The calculated absorption spectra of the undoped PZT. The optical band gap E_g was determined from Tauc's formula.

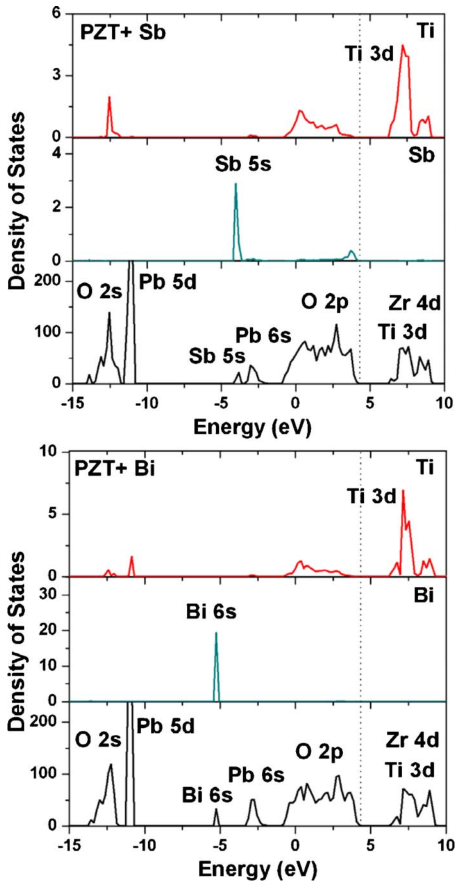

FIG. 3. (Color online) Calculated density of states (DOS) and partial density of states (PDOS) of the PZT systems with (a) Sb substitutes and (b) Bi substitutes.

However, our calculated optical band gap of PZT (3.74 eV) is quite close to the experimental values (3.66 eV) (Ref. 22) and theoretical results.[23]

B. *B*-site substituted lead zirconate titanate

Electronic properties of lead zirconate titanate with *B*-site substitutional group VA (V^{5+},Nb^{5+},Ta^{5+}), group VIA (W^{6+},Mo^{6+}), and group VB (Sb^{5+},Bi^{5+}) elements have been investigated in our previous study.[15] It is found that when group VB (Sb^{5+},Bi^{5+}) elements act as *B*-site substitutes, the doped PZT systems have similar conduction band structures as those of undoped PZT. The energy states of Sb and Bi ions are mainly located below the Fermi level. Group VA (V^{5+},Nb^{5+},Ta^{5+}) and group VIA (W^{6+},Mo^{6+}) *B*-site substitutes, however, contribute their *d* electron states to the conduction band minima of the PZT.

C. *A*-site substituted lead zirconate titanate with group VB elements (Sb^{3+},Bi^{3+})

The DOSs of the PZT systems substituted by the group VB elements at *A* site are shown in Fig. 3. Bi-doped PZT and Sb-doped PZT have similar conduction band structure to that of undoped PZT. Moreover, the DOS results are even identical to those of PZT systems substituted by group VB elements (Bi, Sb) at *B* site. The energy states of Bi ions (Bi 6*s*) are mainly located at 10 eV below the Fermi level, and those of Sb ions (Sb 5*s*) at around 8 eV below Fermi level. As doping of Bi and Sb has little effect on the electronic structure of the CBMs of the PZT system, these two systems remain as charge-transfer insulators.

Theoretical studies have shown that the possible origin of the fatigue is associated with the reduced π bonds between Ti 3*d* and O 2*p* states caused by remaining electrons released from oxygen vacancies.[9] While the stability of ferroelectricity is closely related to the magnitude of these bonds, occupation of Ti 3*d* states by electrons is detrimental to the bonding. As the CBMs of the Bi-doped and the Sb-doped PZT are still dominated by the Ti 3*d* states, the electrons released from oxygen vacancies could accordingly occupy the Ti 3*d* states and reduce the π bonds between Ti 3*d* and O 2*p* as in the undoped PZT. Considering our previous results for *B*-site substitutes, we conclude that the group VB substitutions (Bi, Sb) do not relieve the fatigue problems of PZT, regardless of their site occupancy.

Reduced energy and optical band gap of the doped systems with increased atomic number of the dopants were observed for group VB trivalent *A*-site substitutes. For these systems, the band gaps remain as charge-transfer gaps between occupied O 2*p* valence band and unoccupied Ti 3*d* conduction band, as shown in Fig. 4 (bottom). The Ti 3*d* bandwidth (W) is closely related to the ionic size of the *A*-site cation, in view that the ionic size of the *A*-site cation mediates the Ti–O–Ti bond angle. As the size of *A*-site cation decreases, the Ti–O–Ti bond angle bends and deviated from 180° (the angle is calculated to be 164.5° in pure PZT system, 157.4° in Bi-doped PZT system, and 155.7° in Sb-doped PZT system), giving rise to narrower electronic bandwidth (W) and accordingly broader band gaps.

D. *A*-site substituted lead zirconate titanate with group IIIA elements (Sc^{3+},Y^{3+},La^{3+})

For the group IIIA element substituted systems, the CBMs are consisted of both dopant states and Ti 3*d* states; La 4*f* states, Sc 3*d* states, and Y 4*d* states also contribute to the CBM in the respective system (Fig. 5). These donor states share the remaining electrons at the CBMs released by oxygen vacancies with the Ti 3*d* orbitals. With less occupied Ti 3*d* states and therefore less reduced π bonding, the La-, Sc-, and Y-doped systems are less susceptible to ferroelectric fatigue.[24]

Moreover, the correlation between electrons introduced into PZT by the group IIIA trivalent cations introduces an impurity electron band with intensive Ti 3*d* states in the band gap, consistent with the Mott-Hubbard description of the transition-metal compound in the ZSA framework (Fig. 6 top). The substituted PZT systems are no longer rigidly CT insulators; the character of the Mott-Hubbard band gap appears more dominant with increased doping level, until a pure Mott-Hubbard insulator is achieved as full substitution of *A*-site cations by the substitutes. This effect of substitution in PZT is similar to the picture described in La- or Y-doped $BaTiO_3$ and $SrTiO_3$ systems.[25,26]

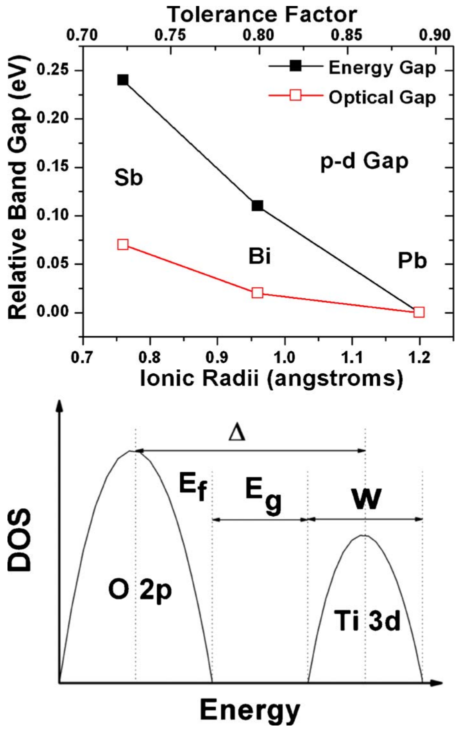

FIG. 4. (Color online) (Top) Calculated variations of energy band gaps and optical band gaps of PZT with group VB substitutes. (Bottom) Schematic density of states of PZT systems with group VB substitutes. E_f denotes the Fermi energy. Δ is the energy difference between filled O $2p$ bands and unoccupied Ti $3d$ band. W is the one-electron bandwidth of Ti $3d$ states.

The calculated shifts of energy and optical band gaps of the doped PZT systems are summarized in Fig. 6. The chemical trend of the optical band gaps by the substitution is consistent with that of energy band gaps, which also agrees well with available experiments.[27] Similar to the chemical trends of group VB trivalent substitutes, a reduction of both energy and optical band gaps of the doped systems with increased atomic number of the group IIIA trivalent substitutes was observed.

As mentioned earlier, substitution of group IIIA dopants Sc^{3+}, Y^{3+}, and La^{3+} for Pb^{2+} introduces an impurity band in the PZT band gap, leading to the reduction of the band gap with respect to pure PZT. This mid-band-gap impurity band was ascribed to a lower Hubbard band (LHB) associated with Ti $3d$ electrons. The splitting of the lower Hubbard band from the upper Hubbard band (UHB) is due to the correlation between electrons introduced into PZT by the group IIIA trivalent cations. On the other hand, the systematic reduction of band gaps with the increased atomic number of group IIIA substitutes is associated with the Ti $3d$ t_{2g} electron bandwidth (W). Ti $3d$ electron transfer in titanium oxides is governed by the supertransfer process mediated by the O $2p$ states rather than the direct transfer between the $3d$ states.[28] The Ti–O–Ti bonding angle deviates more and more from 180°, as the ionic size decreases with the atomic number of group IIIA dopants (161.4°, 157.5°, and 156.1° for La-, Y-, and Sc-doped PZT systems, respectively, from our calculations). Accordingly, the electron bandwidth (W) be-

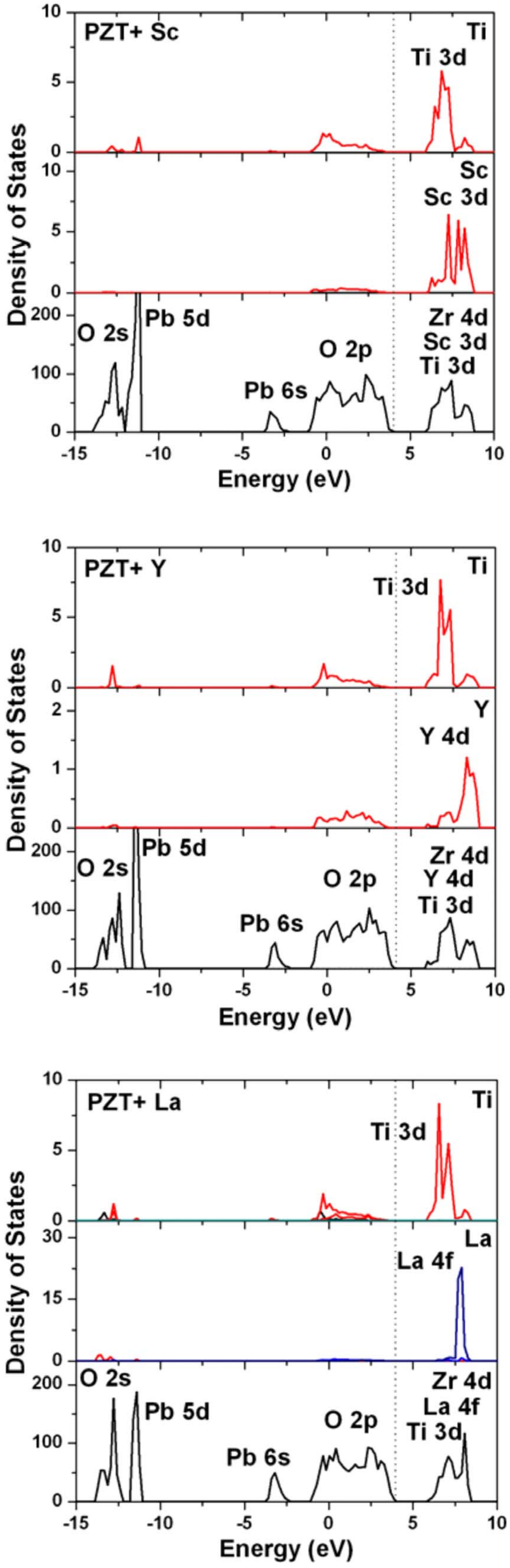

FIG. 5. (Color online) Calculated density of states (DOS) and partial density of states (PDOS) of the PZT systems with (a) Sc substitutes, (b) Y substitutes, and (c) La substitutes.

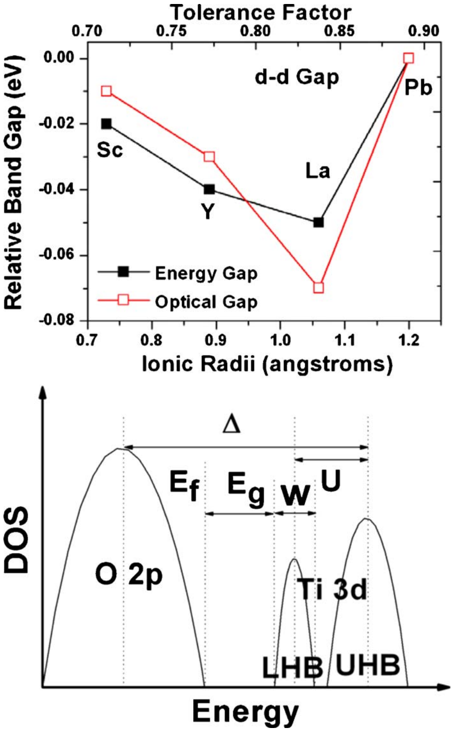

FIG. 6. (Color online) (Top) Calculated shift of energy band gaps and optical band gaps of PZT with group IIIA substitutes. (Bottom) Schematic density of states of PZT systems with group IIIA substitutes. LHB is the lower Hubbard band and UHB is the upper Hubbard band. E_f denotes the Fermi energy. Δ is the energy difference between filled O 2*p* bands and unoccupied Ti 3*d* band. *W* is the one-electron bandwidth of the Ti 3*d* lower Hubbard band.

comes smaller and the band gap energy increases, while the atomic number of group IIIA substitutes decreases.

E. Formation energy of oxygen vacancies

The formation energies (E_f) of the neutral oxygen vacancies in the substituted and pure PZT systems were also calculated (Table I) based on

$$E_f = E_{\text{defect}} - E_{\text{perfect}} + \mu, \tag{2}$$

where E_{defect} and E_{perfect} are the total energy of the defected supercell and of the perfect supercell, respectively, and μ denotes the chemical potential of oxygen determined under oxygen-rich conditions, which is in consistence with the experiment atmosphere.

It is noteworthy that the spontaneous formation of Pb vacancies may create oxygen vacancies through the Schottky equilibria in order to keep local electroneutrality, as shown in

$$\text{null} \rightarrow V''_{\text{Pb}} + V_{\text{O}}^{**}. \tag{3}$$

The formation energy of oxygen vacancies in Pb-deficient PZT could be as low as −3.80 eV, as revealed in Table I. Accordingly, a large number of Pb-O Schottky vacancy pairs exist in the PZT lattice. Poykko and Chadi[29] found that these Schottky vacancy pairs are not closely bounded. As oxygen vacancies have a strong mobility, they could easily migrate to the electrode interfaces or form oxygen vacancy planes to pin the domain walls.

Donor substitutes could prevent the formation of oxygen vacancies, while still allowing the Pb vacancy to exist. Taking the dopant La^{3+}, for example, as shown in Eq. (4), the two holes caused by the evaporation of Pb can be compensated by two electrons from the donor substitutes instead of by the formation of oxygen vacancies,

$$\text{La}_2\text{O}_3 + \frac{7}{2}\text{O}_2 \underset{3\text{PbTiO}_3}{\rightarrow} V''_{\text{Pb}} + 2\text{La}^{*}_{\text{Pb}} + 9\text{O}^{x}_{\text{O}} + \text{PbO}. \tag{4}$$

Our calculated results also confirm that all the *A*-site donor-substituted systems have relatively higher formation energy of oxygen vacancy. This effective reduction of oxygen vacancy concentration by substitution of Pb^{2+} ions results in the softening of a large number of ferroelectric properties in PZT, including relieved fatigue, enhanced dielectric constant, reduced coercive field, and increased remnant polarization.

IV. CONCLUSIONS

First-principles density functional theory study of the electronic structures, optical behaviors, vacancy formations, and fatigue behaviors in *A*-site donor-substituted lead zirconate titanate was conducted. The role of the substitutes is discussed and the mechanisms of the doping behaviors are offered.

(1) It is found that the conduction bands in the group IIIA element (Sc^{3+}, Y^{3+}, La^{3+}) substituted PZT systems are shared by Ti 3*d* and dopant states. These unique band structures lead to a reduced occupation on Ti 3*d* by the electrons released from oxygen vacancies, which makes them less susceptible to fatigue. On the other hand, group VB elements substituted (Bi, Sb) either as trivalent *A*-site donors or as pentavalent *B*-site donors fail to relieve the fatigue of PZT

TABLE I. Calculated formation energy of oxygen vacancies in pure PZT, Pb-deficient PZT, and *A*-site substituted PZT systems under oxygen-rich conditions, where the chemical potential of oxygen in the oxygen-rich condition was determined by considering the isolated oxygen molecule with a bonding length of 1.21 Å.

	Undoped		Group IIIA			Group VB	
Dopants	Pure	Pb-deficient	Sc	Y	La	Sb	Bi
Formation energy (eV)	0.37	−3.80	0.39	0.45	0.41	0.54	0.40

systems due to the lack of substitute states at the CMB of respective system.

(2) The systematical shift of both energy and optical band gap with atomic number of substitutes is closely related to the character of the band gaps and the electron bandwidth of Ti 3*d* states. Group VB trivalent substitutes do not change the character of the band gap of the charge-transfer insulator PZT, and their ionic sizes determine the electron bandwidth of Ti 3*d* states and the band gap. Group IIIA trivalent substitutes, however, introduce impurity band with Mott-Hubbard character into the PZT band gap, leading to a reduction of band gap compared with that of pure PZT. The systematic shift of the band gap can be explained by the changes of LHB mediated by the ionic size of group IIIA substitutes.

(3) All the substitutes are found to effectively dilute the concentration of the oxygen vacancies by releasing two electrons to compensate the holes in Pb-deficient lattice, leading to the softening of the ferroelectric properties of PZT.

This study provided new knowledge for the effects of systematic foreign donor substitution on the electronic structure of PZT, which may aid in the design of new materials.

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