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Kyoto University
First-principles study of native defects and lanthanum impurities in NaTaO$_3$

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The formation energies and electronic structure of lattice vacancies, antisite defects, and lanthanum impurities in NaTaO$_3$ are investigated using first-principles calculations based on density-functional theory. The Na antisite and the Ta vacancy, which are both multiple acceptors, are energetically favorable under O-rich conditions, whereas the O vacancy, which is a double donor, is preferred under O-poor conditions. The Ta antisite is a quadruple donor but its high formation energy renders it unlikely to be stable under the thermal equilibrium other than p-type and O-poor conditions. In La-doped NaTaO$_3$, substitutional La at the Na site is likely to form as a double donor under O-poor conditions. It is expected to generate carrier electrons except for heavily doped cases where compensation by acceptorlike La at the Ta site, as well as the native acceptors, is significant. For all the native defects and La impurities, no localized one-electron states are found in the band gap, which is consistent with the shallow donor/acceptor behavior determined using the formation energies.

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I. INTRODUCTION

In recent years, the photocatalytic water splitting into H$_2$ and O$_2$ has been extensively studied because of its great possibility as a source of clean and renewable hydrogen energy. To date, numerous photocatalytic materials have been found, e.g., TiO$_2$ (Refs. 2–4), SrTiO$_3$ (Refs. 5 and 6), K$_2$Nb$_6$O$_{17}$ (Ref. 7), Sr$_2$Nb$_4$O$_{12}$ (Refs. 8 and 9), Ta$_2$O$_5$ (Ref. 10), and NaTaO$_3$ (Refs. 11–14). Among them, perovskite-type NaTaO$_3$ is a candidate for a high-efficiency photocatalyst. This material shows promising stability and high photocatalytic activity under ultraviolet light irradiation ($\lambda < 300$ nm) (Refs. 11–14). In particular, La-doped NaTaO$_3$ with loaded NiO has been reported to show very high photocatalytic efficiency for water splitting giving a 56% quantum yield at $\lambda = 270$ nm (Ref. 11).

For high photocatalytic activity, certain physical and chemical properties are required: (i) a high concentration of charge carriers—a large number of photogenerated electrons and holes and their separation are important for improving the catalytic activity; (ii) large surface area—this can affect the number of sites where photocatalytic activation takes place; and (iii) good crystallinity and purity—since native point defects and impurities, as well as line and planar defects, can act as recombination centers of the photogenerated electrons and holes, their concentrations should be reduced. For further development of highly efficient photocatalysts, therefore, a systematic study of the defect properties of candidate materials is necessary. In the case of TiO$_2$, a prototypical photocatalyst that is commercially used, the behavior of native defects and various impurities in the bulk and on the surface has been intensively studied both theoretically and experimentally. On the other hand, the defect properties in NaTaO$_3$ are not well explored theoretically in particular. The understanding in the mechanism of how La doping leads to the observed photocatalytic efficiency, which can be related to the change in carrier concentration, is also limited.

In this work, we present a comprehensive study on the native defects and lanthanum impurities in NaTaO$_3$. Our aim is to elucidate: (i) which native defects are likely to form; (ii) which atomic site is preferable for doped La; and (iii) how native defects and doped La affect the carrier concentration in NaTaO$_3$:La. Through the first-principles calculations of the defect formation energies and electronic structure, we address these issues here.

II. METHODOLOGY

A. Formation energy and transition level

The formation energy of a defect or impurity is estimated as

$$E^i(D,q) = E_f(D,q) - E_f(\text{perfect}) = \sum_i n_i \mu_i + q(E_{\text{VBM}} + E_F),$$

(1)

where $E_f(D,q)$ is the total energy of a supercell with one defect or impurity $D$ in charge state $q$ and $E_f(\text{perfect})$ is the total energy of the perfect-crystal supercell. $n_i$ is the number of atoms of type $i$ being added to ($n_i > 0$) or removed from ($n_i < 0$) in the perfect-crystal supercell and $\mu_i$ is the atomic chemical potential. $E_{\text{VBM}}$ is the energy of the valence-band maximum (VBM) and $E_F$ is the Fermi level measured from the VBM, varying in the range of the band gap $E_s$. The defect transition level $\varepsilon(q'/q)$ is described by the Fermi level where the formation energy for charge state $q$ equals that for another charge state $q'$,

$$\varepsilon(q'/q) = [E_{\text{VBM}}(D,q') - E_{\text{VBM}}(D,q)]/(q' - q),$$

(2)

where $E_{\text{VBM}}(D,q)$ is the defect formation energy for charge state $q$ when $E_F$ is at the VBM.

In compound systems, the defect formation energy depends on the atomic chemical potential $\mu_i$. For ternary NaTaO$_3$, the limit of $\mu_i$ ($i = \text{Na, Ta, and O}$) is determined from the equilibrium conditions with various phases containing Na, Ta, and O. The chemical potentials of the three elements should be correlated as.
The calculated formation energy can include some systematic errors due to the approximation to the density-functional theory and the limitation in the simulation cell for defects. Therefore, we should consider some reasonable corrections:

(i) \textit{VBM alignment}—$E_{\text{VBM}}$ in defective supercells is generally different from $E_{\text{VBM}}$ in a perfect-crystal supercell, and this difference becomes large when supercells contain highly charged defects.\cite{18} Thus, it is necessary to line up $E_{\text{VBM}}$ between the perfect and defective supercells. For this purpose, average potentials in a perfect-crystal supercell and those in a bulklike environment far from the defects in defective supercells were used as references.\cite{19–23}

(ii) \textit{Band-gap correction}—the underestimation of $E_g$ caused by the generalized gradient approximation (GGA) employed in the present calculations can be reflected in the defect formation energies. To correct such GGA band-gap error, the energy of the conduction-band minimum (CBM) $E_{\text{CBM}}$ was simply increased to agree with the experimental band gap. Following the shift of $E_{\text{CBM}}$, the formation energies of defects with electronic states showing conduction-bandlike characteristics were raised by adding $m\Delta E_g$, where $m$ is the number of electrons at the defect state and $\Delta E_g$ is the difference between the experimental and calculated band gaps.\cite{24}

(iii) \textit{Image charge interaction correction}—the Makov-Payne method is often employed for the correction of electrostatic interactions between the image charges generated by charged defects in semiconductors and insulators. It models the interactions with a multipole expansion leading to $L^{-1}$, $L^{-3}$, and $L^{-5}$-dependent terms where $L$ denotes interdefect distance. The formal charges of defects are used for the $L^{-1}$ term describing the monopole-monopole interactions, i.e., Madelung energies.\cite{26} However, the use of formal charges can overestimate or underestimate the correction of the Madelung energies depending on the spatial distribution of the defect-induced charge density.\cite{18,27–29} In addition, for systems where elastic interactions are significant, the corrections in higher orders are not straightforward because of the complex cell-size dependences of formation energies.\cite{29,30} We tested the Makov-Payne method for selected native defects in NaTaO$_3$ and will discuss the results in Sec. II C.

\section*{B. Computational details}

The first-principles calculations were performed by the projector augmented-wave (PAW) (Ref. 31) method as implemented in the Vienna \textit{ab initio} simulation package (VASP) (Refs. 32–34). The exchange-correlation functional is constructed by the GGA proposed by Perdew, Burke, and Ernzerhof.\cite{35} PAW data sets with radial cutoffs of 1.2, 1.5, 0.8, and 1.5 Å were used for Na, Ta, O, and La, respectively. To describe the electronic wave functions with a plane-wave basis set, an energy cutoff of 400 eV was employed.

In order to investigate the structural and electronic properties of the NaTaO$_3$ perfect crystal, we performed geometry optimization for the unit cell. The Brillouin zone was sampled using a $6 \times 6 \times 6$ $k$-point mesh generated on the

\begin{align}
\mu_{\text{Na}} + \mu_{\text{Ta}} + 3\mu_{\text{O}} &= \mu_{\text{NaTaO}_3(\text{bulk})}, \\
\mu_{\text{Na}} + \mu_{\text{O}} &= \mu_{\text{Na}_2\text{O}(\text{bulk})}, \\
\mu_{\text{O}} &= \frac{1}{2}\mu_{\text{O}_2(\text{molecule})}, \\
2\mu_{\text{Ta}} + 5\mu_{\text{O}} &= \mu_{\text{Ta}_2\text{O}_5(\text{bulk})}, \\
2\mu_{\text{Ta}} + 2\mu_{\text{O}} &= \mu_{\text{TaO}_2(\text{bulk})}, \\
\mu_{\text{Ta}} &= \mu_{\text{Ta}(\text{bulk})}, \\
\mu_{\text{Na}} &= \mu_{\text{Na}(\text{bulk})}, \\
\mu_{\text{O}} &= \mu_{\text{O}(\text{bulk})}.
\end{align}
basis of the Monkhorst-Pack scheme with the $\Gamma$ point centered. The cubic phase ($Pm\bar{3}m$ with $a=b=c=3.929$ Å and $\alpha=\beta=\gamma=90^\circ$) (Ref. 37) was considered in the present study; it is very close to the monoclinic phase ($P2_1/m$ with $a=3.8995$ Å, $b=3.8965$ Å, and $c=3.8995$ Å, $\alpha=\gamma=90^\circ$, and $\beta=90.15^\circ$) (Ref. 38) that shows, according to recent reports, 39,40 the highest photocatalytic efficiency among various structures of NaTaO$_3$. As expected from the similarity in the lattice structures, the electronic structures of the cubic and monoclinic phases have been reported to be very similar. 39–42 The lattice constant of the cubic structure was computed to be 3.975 Å in the present work and is in good agreement with the experimental value of 3.929 Å (Ref. 37). The calculated electronic structure will be detailed in Sec. III A.

For the simulation of native defects and La impurities, we used a $3 \times 3 \times 3$ supercell containing 135 atoms. The Brillouin zone was sampled using a $2 \times 2 \times 2$ mesh with the $\Gamma$ point centered. The atomic positions were relaxed until the Hellmann-Feynman force on each atom was reduced to a point centered. The atomic positions were relaxed until the electronic relaxation concomitant with the atomic relaxation is not applied, the range of the Fermi level is truncated, and the correction for image-charge interactions using the formal defect charges and an experimental static dielectric constant indicating the dominance of the Madelung energy contributions. For $V_O$, which exhibits an exceptional behavior as described below, the neutral and + charge states were also investigated. The results are presented in Fig. 2 as a function of $L^{-1}$, where $L$ denotes interdefect distance equivalent to the cell constant.

Concerning the VBM correction, we obtained the average potential differences of up to 0.1 eV for all the defects in the relevant charge states. The resultant correction term, i.e., the average potential difference multiplied by the defect charge ranged only up to 0.5 eV for $V_{Ta}$ and 0.2 eV for the other defects. The uncertainty of the VBM correction is not expected to affect the discussion given in Secs. II C and III C.

The band gap of the $3 \times 3 \times 3$ perfect-crystal supercell was calculated to be 2.27 eV using the total-energy differences (2.23 eV in one-electron structure). Therefore, we employed $\Delta E_F = 1.83$ eV for the correction of the band gap and defect formation energies, which results in the corrected band gap being equal to an experimental value of 4.1 eV (Ref. 43). The correction of formation energies was applied to $V_O$ and $LaNa$ whose donor states are close to the CBM and the wave-function characteristics are similar to those of the CBM. For $TaNa$, a localized donor state was found to be induced slightly above the CBM, which will be described in Sec. III B. This state is mainly characterized by Ta 5$d$ as well as the conduction band of perfect NaTaO$_3$. Therefore, we also applied the correction for $TaNa$. It is noted that the results before the band-gap correction can be readily recovered from Figs. 5 and 7 showing the Fermi-level dependence of the formation energies (presented later). When the correction is not applied, the range of the Fermi level is truncated at the calculated CBM ($E_F = 2.27$ eV). Because all the donor-like defects exhibit the highest charge states without occupied in-gap states in the whole range of the Fermi level, the positions of the lines representing formation energies are preserved for all the defects.

C. Image charge interaction

The correction for image charge interactions using the Makov-Payne method was tested for the native defects in the highest charge state, i.e., $V_{Na^+}$, $V_{Ta^{4+}}$, $NaTa^{4+}$, $TaNa^{4+}$, and $V_{O^-}$. The formation energies of these defects before and after the atomic relaxation were obtained using four kinds of supercells containing 40, 135, 320, and 625 atoms, respectively. For $V_O$, which exhibits an exceptional behavior as described below, the neutral and + charge states were also investigated. The results are presented in Fig. 2 as a function of $L^{-1}$, where $L$ denotes interdefect distance equivalent to the cell constant. The values without the VBM alignment are shown because it can lead to the double count of the correction. In addition, the band-gap correction, which is to be applied to $V_O^0$ and $V_O^+$, has not been considered to compare raw values.

In the case of $V_{Na^+}$, $V_{Ta^{4+}}$, and $NaTa^{4+}$, nearly linear $L^{-1}$ dependences with negative slopes are recognized for the values before atomic relaxation. The slopes are close to those estimated using the formal defect charges and an experimental static dielectric constant indicating the dominance of the Madelung energy contributions. For $TaNa^{4+}$, the deviation from the linear dependence implies an overlap of higher-order terms. After relaxation, the cell-size dependences are markedly reduced for all of these defects as a result of an electronic relaxation concomitant with the atomic relaxation and/or the overlap of elastic effects.

The formation energies of $V_O$ before atomic relaxation also show nearly linear dependences for all the charge states. As expected from the Madelung energy contribution, the neutral charge state has almost no cell-size dependence and the slope increases toward the negative side with the increase in the defect charge. The formation energies after relaxation significantly decrease as the cell size increases ($L^{-1}$ decreases) and the cell-size dependences are similar to each other. This behavior of $V_O$ after relaxation may be attributed to elastic effects, which was also found in the previous first-
principles of $V_O$ in perovskite SrTiO$_3$ (Refs. 44 and 45).

Summarizing these results, the cell-size dependences are small for the defects other than $V_O$ after relaxation. When the 135-atom supercells are used, the formation energies are different by only up to 0.7 eV from those extrapolated to the dilute limit ($L^{-1} \rightarrow 0$) by assuming the $L^{-1}$ and $L^{-3}$ dependences. In other words, the corrections based on the Makov-Payne method (and the corrections for elastic contributions) cause changes of this amount. Thus, we estimate the errors of the formation energies to be less than 0.7 eV, which do not affect the relative defect energetics discussed later. For $V_O$, the strong elastic contribution after relaxation makes the extrapolation to the dilute limit difficult; whereas the dependence of the elastic contribution has been reported to be linear against $L^{-1}$ (Ref. 29), the present results seem to deviate from it. A crude estimate assuming the $L^{-1}$ dependence yielded values that are 2–3 eV lower than those for the 135-atom cells. However, even such 2–3 eV changes do not alter our discussion as shown later. In addition, similar dependences for the three charge states suggest that the transition levels are not significantly affected. In Sec. III we present the results without the corrections for electrostatic and elastic interactions, i.e., those from 135-atom cells with the VBM and band-gap corrections only for consistency.

III. RESULTS AND DISCUSSION

A. Electronic structure of perfect NaTaO$_3$

The electronic structure of the NaTaO$_3$ perfect crystal was studied as basic work for the investigation of native defects and impurities in this material. Figure 3 shows the calculated band structure and the total and partial density of states (DOS) of the perfect crystal with a five-atom unit cell. For the DOS, a $\Gamma$-centered $24 \times 24 \times 24$ $k$-point mesh was used for the Brillouin-zone integration and the eigenvalues were interpolated using a corrected tetrahedron method.

As shown in Fig. 3, the band structure of perovskite-type cubic NaTaO$_3$ is calculated to be the indirect-gap type. The calculated gap is 2.23 eV, which is much smaller than the experimental value of $\sim$4.1 eV (Ref. 43) owing to the well-known GGA shortcoming. The CBM is located at the $\Gamma$ (0,0,0) point, while the VBM is located at the $R$ (1/2,1/2,1/2) point. The state of the conduction-band edge at $X$ (1/2,0,0) and that of the valence-band edge at $M$ (1/2,0,1/2) have very similar energies to the CBM and VBM, respectively.

The valence-band ranges from $-5.7$ to 0 eV and is mainly characterized by O 2$p$. The conduction band mainly consists of Ta 5$d$. There is also a large component of O 2$p$ in the conduction band mixed with Ta 5$d$. Ta 6$s$ and Ta 6$p$ constitute the deep states in the valence band hybridizing with O 2$p$. The states associated with Na 3$s$ and 3$p$ are found in a high-energy region in the conduction band and do not appear near the band gap. The overall features of our results are similar to those of previously reported computational results obtained by the full-potential-linearized-augmented-plane-wave (LAPW) (Ref. 41) and full-potential-linear muffin-tin-orbitals (LMTO) (Ref. 42) methods.

B. Vacancy and antisite defect in NaTaO$_3$

Figure 4 shows the formation energies of neutral defects $V_O$, $V_{Na}$, $V_{Ta}$, $Na_{Ta}$, and $Ta_{Na}$ under each equilibrium condition. The formation energy of $V_{Na}$ is relatively low, in particular, between conditions 1 and 3 (Na-poor and O-rich conditions). Under these conditions, the formation energy of $V_O$ is relatively high and decreases toward O-poor conditions (conditions 4–6), while that of $V_{Ta}$ is relatively low and increases toward the O-poor conditions. For antisite defects, namely, Na$_{Ta}$ and Ta$_{Na}$, the formation energies are high under most equilibrium conditions. However, they are very sensitive to the equilibrium condition. The formation energy of Na$_{Ta}$ under condition 1, for instance, is as low as that of V$_{Na}$. The formation energies of V$_{Na}$ and V$_{Ta}$ calculated here are similar to the reported values for cation vacancies in isostructural systems NaNbO$_3$ (Ref. 47) and KTaO$_3$ (Ref. 48).

To discuss the stability of defects, the Fermi-level dependence of the formation energies was investigated because the energetically favorable charge state of defects can vary with the Fermi level. Figure 5 shows the defect formation energies against the Fermi level in two extreme cases: condition 1 (O-rich limit) and condition 5 (O-poor limit). Under condi-
FIRST-PRINCIPLES STUDY OF NATIVE DEFECTS AND La IMPURITY IN NaTaO$_3$

FIG. 5. (Color online) Formation energies of native defects as a function of the Fermi level under condition 1 (O-rich limit) and condition 5 (O-poor limit).

FIG. 6. (Color online) Site-decomposed electron DOS in the vicinity of $V_{\text{Na}}, V_{\text{Ta}}, V_{\text{O}}$, $\text{NaTa}^4+$, and $\text{TaNa}^{6+}$ (per atom) along with the total DOS of the perfect crystal (per unit cell). The solid curve denotes the DOS of the defect-related atoms. The DOS of the Na component of $\text{NaTa}^4+$ and the Ta component of $\text{TaNa}^{6+}$ are, respectively, multiplied and divided by five for easy visualization. The dashed lines indicate the positions of the CBM and VBM.

Both defects are very similar, which means that Na of $\text{NaTa}^4+$ does not strongly couple to the nearby two O atoms. For $\text{TaNa}^{6+}$, the calculated electronic structure is quite different from that of $V_{\text{Na}}$. Slightly above the CBM, an unoccupied localized state is induced by the antisite Ta 5$d$ hybridized with nearly twelve O 2$p$. For the other charge states, we found that the localized state is partially occupied by electrons. However, this does not produce any in-gap state.

The distances between the native defects and their nearest neighboring atoms are summarized in Table I. The neighboring atoms of $V_{\text{Na}}, V_{\text{Ta}}, V_{\text{O}}$, and $\text{NaTa}$ are displaced outward, whereas those of $\text{TaNa}$ are displaced inward. Except for $\text{TaNa}^{6+}$, there is almost no dependence on the charge state—indicating a weak dependence of the electronic structure on the charge state. This is consistent with the behavior of these defects as shallow donors or shallow acceptors suggested from the transition levels and the one-electron structures. For $\text{TaNa}^{6+}$, the occupancy of the localized state changes the interaction with the neighboring atoms.

C. Lanthanum Impurity in NaTaO$_3$

In order to elucidate the role of La impurities, we examined the formation energy of substitutional La as a function of the atomic chemical potentials and the Fermi level. As
TABLE I. Distances between defects and their nearest neighboring atoms after atomic relaxation. X (perfect) (X=Na, Ta, and O) denotes the distance between atom X and its neighbors in the perfect crystal. The neighboring atomic species and their coordination numbers are shown in parentheses.

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<th>Distance (Å)</th>
<th>Defect</th>
<th>Distance (Å)</th>
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</thead>
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<tr>
<td>Na (perfect)</td>
<td>2.811 (O × 12)</td>
<td>Na (perfect)</td>
<td>2.811 (O × 12)</td>
</tr>
<tr>
<td>Vₐ¹ Na</td>
<td>2.867</td>
<td>TaO⁰ Na</td>
<td>2.606</td>
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<tr>
<td>Vₐ⁻ Na</td>
<td>2.872</td>
<td>TaO⁺ Na</td>
<td>2.594</td>
</tr>
<tr>
<td>Ta (perfect)</td>
<td>1.988 (O × 6)</td>
<td>TaO²⁺ Na</td>
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<td>2.540</td>
</tr>
<tr>
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<td>TaO⁴⁺ Na⁺</td>
<td>2.519</td>
</tr>
<tr>
<td>Vₐ²⁻ Ta</td>
<td>2.101</td>
<td>Ta (perfect)</td>
<td>1.988 (O × 6)</td>
</tr>
<tr>
<td>Vₐ³⁻ Ta</td>
<td>2.101</td>
<td>NaO⁰ Ta</td>
<td>2.111</td>
</tr>
<tr>
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<td>2.105</td>
<td>NaO⁺ Ta</td>
<td>2.111</td>
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<td>Vₐ³⁻ Ta</td>
<td>2.111</td>
<td>NaO²⁺ Ta</td>
<td>2.111</td>
</tr>
<tr>
<td>O (perfect)</td>
<td>1.988 (Ta × 2)</td>
<td>NaO³⁻ Ta</td>
<td>2.111</td>
</tr>
<tr>
<td>Vₐ¹ O</td>
<td>2.082</td>
<td>NaO⁴⁺ Ta⁺</td>
<td>2.112</td>
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<tr>
<td>Vₐ²⁺ O</td>
<td>2.085</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vₐ³⁻ O</td>
<td>2.087</td>
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</table>

positions of the doped La, we considered two substitutional sites, LaNa and LaTa. Because the ionic radius of La³⁺ (1.34 Å) (Ref. 49) is as large as that of Na⁺ (1.39 Å) (Ref. 49), the location of La at the interstitial site is also unlikely because of the close-packed structure.

Figure 7 shows the calculated formation energies of LaNa and LaTa. For the neutral charge state, both LaNa and LaTa have high formation energies under O-rich conditions (1 and 2). Going toward O-poorer conditions (3–6), the formation energy of LaNa is significantly lowered, whereas the formation energy of LaTa increases and becomes much higher than that of LaNa. Only under condition 1, namely, at the O-rich limit, LaTa is more stable than LaNa. However, the formation energy of LaTa is still too high to form in a substantial concentration.

The formation energies of LaNa and LaTa against the Fermi level are shown in Fig. 7(b) for the two extreme cases, namely, conditions 1 and 5 corresponding to the O-rich and O-poor limits, respectively. For LaNa, no transition level is found and the 2+ charge state is energetically favorable for the whole range of the Fermi level. On the other hand, LaTa shows two transition levels near the VBM: ε(0/−) = 0.1 eV and ε(−/2−) = 0.2 eV. Therefore, LaNa and LaTa are a shallow donor and shallow acceptor, respectively. Under O-rich conditions such as condition 1, it is expected that the growth of n-type NaTaO₃:La is difficult since LaTa as well as native multiple acceptors (NaTa and VTa) are expected to form spontaneously and then compensate carrier electrons. Under O-poor conditions, LaTa is more stable than LaNa only in a highly n-type region and has a positive formation energy throughout the whole range of the Fermi level. Thus, LaNa can induce a high electron concentration in NaTaO₃:La.

From the analysis of the one-electron structure, we found that both LaNa and LaTa introduce no localized states in the calculated band gap. The site-decomposed electron DOS in the vicinity of LaNa²⁺ and LaTa²− is shown in Fig. 8. A notable feature of these DOS is the deep defect state of LaTa located at −11 eV below the VBM. This state results from the coupling of La 5p, O 2s, and O 2p. Unlike the LaTa²−, no high DOS peak of La is found for LaNa²⁺. The one-electron structures without localized states in the band gap for LaNa and LaTa are consistent with the shallow donor/acceptor characteristics suggested from the transition levels shown in Fig. 7(b).

The atomic structures around LaNa and LaTa are slightly relaxed, which are recognized in Table II. The neighboring O atoms of LaNa are displaced inward by 0.1 Å from their positions in perfect NaTaO₃, whereas the neighboring O atoms of LaTa are displaced outward by 0.2 Å. The charge state dependence is very weak for both LaNa and LaTa. Such different atomic displacements can be related to the difference in ionic radii. The ionic radii of 12-fold coordinated La³⁺ (1.36 Å) and Na⁺ (1.39 Å) (Ref. 49) are nearly the same, whereas those of sixfold-coordinated La³⁺ (1.03 Å) and Ta⁵⁺ (0.64 Å) (Ref. 49) are considerably different. The larger relaxation and high formation energy of LaTa can be partly attributed to the large size mismatch.

On the basis of the experiments, the photocatalytic efficiency of NaTaO₃:La has been reported to become higher as...
as a possible reason behind this high efficiency, which was expected to induce $n$-type conductivity, high crystallinity, and small crystal size. However, the photocatalytic activity decreased above some doping level and the suggested role of LaNa could not explain this opposite phenomenon. Our results can be a guide for understanding this observed behavior of NaTaO$_3$:La. Under O-poor conditions (for instance, conditions 3–6), the intersection between the lines representing the formation energies of LaNa and LaTa is located in an $n$-type region as recognized for condition 5 in Fig. 7(b). With a low La concentration, La should favor LaNa as a double donor, which is consistent with the suggestion in Ref. 11. However, such a formation of LaNa leads to the shift of $E_F$ toward the CBM. As a result, after a certain La-doping level, LaTa becomes more stable than LaNa and native multiple acceptors (V$_{Ta}$ and Na$_{Ta}$) can also form, leading to the saturation in carrier concentration. The decrease in the photocatalytic activity experimentally observed for heavily La-doped NaTaO$_3$ might be attributed to the saturation in carrier concentration and the increase in the concentration of La and the native acceptorlike defects that can act as recombination centers.

IV. SUMMARY

Using first-principles calculations, we investigated the formation energies and electronic structure of native defects and lanthanum impurities in NaTaO$_3$. Under O-rich conditions, the formation energies of Na$_{Ta}$ and V$_{Ta}$ are the lowest and negative throughout a wide range of the Fermi level. Under O-poor conditions, V$_{O}$ is a dominant defect and acts as a double donor. Ta$_{Na}$ has a high formation energy under most equilibrium conditions and it is expected to form only in a $p$-type region under O-poor conditions. In La-doped NaTaO$_3$, LaTa is likely to form as a shallow acceptor under O-rich conditions whereas LaNa forms as a double donor under O-poor conditions. The site preference of La, however, also depends on the Fermi level, leading to self-compensation in heavily doped cases. In the one-electron structure, no localized defect state is found in the calculated band gap for all the considered defects. These electronic structures are consistent with the shallow donor or acceptor behavior suggested from the transition levels.

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43 An experimental value of the monoclinic phase whose electronic structure is reported to be very close to that of the cubic phase in Ref. 39.