Strain effects on oxygen vacancy energetics in KTaO$_3$†

Jianqi Xi,$^a$ Haixuan Xu,$^a$ Yanwen Zhang$^{ab}$ and William J. Weber$^{ab}$

Due to lattice mismatch between epitaxial films and substrates, in-plane strain fields are produced in the thin films, with accompanying structural distortions, and ion implantation can be used to controllably engineer the strain throughout the film. Because of the strain profile, local defect energetics are changed. In this study, the effects of in-plane strain fields on the formation and migration of oxygen vacancies in KTaO$_3$ are investigated using first-principles calculations. In particular, the doubly positive charged oxygen vacancy ($V_{O}^{2+}$) is studied, which is considered to be the main charge state of the oxygen vacancy in KTaO$_3$. We find that the formation energies for oxygen vacancies are sensitive to in-plane strain and oxygen position. The local atomic configuration is identified, and strong relaxation of local defect structure is mainly responsible for the formation characteristics of these oxygen vacancies. Based on the computational results, formation-dependent site preferences for oxygen vacancies are expected to occur under epitaxial strain, which can result in orders of magnitude differences in equilibrium vacancy concentrations on different oxygen sites. In addition, all possible migration pathways, including intra- and inter-plane diffusions, are considered. In contrast to the strain-enhanced intra-plane diffusion, the diffusion in the direction normal to the strained plane is impeded under the epitaxial strain field. These anisotropic diffusion processes can further enhance site preferences.

1 Introduction

ABO$_3$ perovskites are a family of materials that possess a wide range of physical properties, such as ferroelectricity, ferromagnetism, multiferroicity, superconductivity, and photo-electrochemical sensitivity.$^1$ Among these materials, KTaO$_3$ has received much attention both experimentally and theoretically due to its interesting physical properties.$^2$–$^5$ For example, due to the high permittivity and low dielectric loss, it is a promising candidate for applications in microwave devices.$^2$ A recent investigation on the interface between doped KTaO$_3$ and an ionic liquid has shown the occurrence of superconductivity,$^3$ and the strongly polarized surface in KTaO$_3$ can create a two-dimensional electron gas (2DEG) near the surface region.$^4$–$^5$ In addition, as an incipient ferroelectric, KTaO$_3$ exhibits increasing dielectric permittivity with decreasing temperature. In bulk form, KTaO$_3$ possesses a perovskite-type cubic crystal structure and exhibits paraelectric behavior at the lowest temperature (0 K).$^6$–$^8$ However, in recent years, biaxial strains induced by epitaxy have been used to tune ferroelectric properties.$^9$–$^{11}$ By using thermal non-equilibrium techniques, such as molecular beam epitaxy (MBE) or pulsed laser deposition (PLD), KTaO$_3$ thin films grown on a single-crystal SrTiO$_3$ substrate$^9$–$^{10}$ can induce a biaxial strain on the order of 1.8%. The temperature dependence of the in-plane dielectric constant indicates that the nonpolar ground state of KTaO$_3$ can be markedly transformed, to a polar state, by applying small strains. Similar results have also been found in SrTiO$_3$ thin films, where epitaxial strains can dramatically induce ferroelectricity at room temperature.$^{11}$ Recent studies have also demonstrated that ion implantation can be used to controllable strain engineer perovskite films to create new functionalities and properties.$^{12}$–$^{15}$

Experimental and theoretical results indicate that the oxygen vacancy is easily formed in perovskites, since the formation energy is relatively low. Oxygen vacancy defects are expected to significantly influence the properties and functionality of perovskite thin films. For example, the formation and distribution of oxygen vacancies have been proposed as the source for the insulator-to-metal transition in SrTiO$_{3-x}$ thin films.$^{16}$ The local structural relaxations, due to the existence of oxygen vacancies, is also proposed to affect the ferroelectric properties in KTaO$_3$ thin films.$^{17}$–$^{18}$ In addition, the migration and redistribution of oxygen vacancies have been reported to play an important role in the degradation of ferroelectric devices.$^{19}$–$^{20}$ Due to the important impact of oxygen vacancies on the properties of perovskite films, clarifying the energetics of oxygen vacancy formation and migration in perovskite thin films is crucial.

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In KTaO$_3$ thin films, biaxial strain from the lattice mismatch between KTaO$_3$ and substrate changes the symmetry of the oxygen octahedral, which modifies the energetics of oxygen vacancies that in turn affects the properties of the thin films. Therefore, better understanding of the properties of oxygen vacancies under biaxial strain field is important. To date, only a few studies have reported on oxygen vacancy energetics in perovskite thin films under an epitaxial strain field. Yang et al. have investigated the distribution and migration of neutral oxygen vacancies ($V^0_\text{O}$) in thin film BaTiO$_3$ through first principles. Under a compressive in-plane strain field, the formation energies and inter-plane migration barriers of oxygen vacancies are increased, suggesting that degradation of ferroelectricity induced by oxygen vacancies can be effectively mitigated by applying compressive strain. Similar results have also been reported for LaMnO$_3$ epitaxial thin film. The increase in formation energy under compressive strains can be understood from the chemical expansion concept, where it is generally observed that neutral oxygen vacancies induce larger lattice volume compared to the oxygen ion, which destabilizes the vacancy in the smaller volume provided by compressive strain. However, by using the same method, Aschauer et al. have found that the formation energy of neutral oxygen vacancies seems to be unresponsive to compressive strain in biaxially strained CaMnO$_3$. These results suggest that oxygen vacancy energetics may be rather complex and material dependent. In order to understand the properties of oxygen vacancies in thin film of KTaO$_3$, it is crucial to investigate the mechanic and quantitative impact of biaxial strain on the defect formation and migration.

In this study, the formation and migration energies of oxygen vacancies in biaxially strained KTaO$_3$ are investigated using first-principles calculations. In particular, the doubly positive charged oxygen vacancy is studied as a function of oxygen partial pressure and strain, and the site preference for these oxygen vacancies is discussed. Finally, the possible migration pathways, including intra- and inter-plane diffusions, of oxygen vacancies are investigated.

2 Computational methods

Density functional theory (DFT) calculations are performed using the VASP code with the projector augmented wave method (PAW). The PAW potentials for K, Ta, and O contain 9, 5, and 6 valence electrons, respectively, i.e., K: 3s$^2$3p$^6$4s$^1$, Ta: 5d$^1$6s$^2$, and O: 2s$^2$2p$^4$. The exchange correlation functional of Perdew–Burke–Ernzerhof revised for solids (PBEsol) is chosen, which improves equilibrium properties of solid. The defects are simulated using a supercell of 135 atoms, which is a $3 \times 3 \times 3$ repetition of the cubic KTaO$_3$ with $Pm\bar{3}m$ space group. All the calculations are performed with a cutoff energy of 500 eV for the plane-wave basis set and with spin-polarized conditions. A $2 \times 2 \times 2$ k-point mesh is used for integrations over the Brillouin zone. Both errors from the cutoff energy and the k-point convergence are less than 1 meV per atom. Structures and atomic coordinates are fully relaxed until forces on the ions converged to below $1 \times 10^{-2}$ eV Å$^{-1}$. The calculated lattice parameter of 3.996 Å for the cubic phase of KTaO$_3$ is in good agreement with the experimental value of 3.988 Å. To simulate the biaxial strain condition imposed by the misfit substrate, the in-plane epitaxial strains are applied on the $a$-$b$ plane, and lattice constant along the $c$-axis and the inner ion positions are fully relaxed. For simplification, we assume an isotropic in-plane strain so that the strained unit cell geometry of the KTaO$_3$ is tetragonal, $|a| = |b| = a$ and $|c| = c_0$, and the in-plane strain value is defined as $s = (a - a_0)/a_0$, where $a_0$ is the lattice constant of unstrained cubic KTaO$_3$, and $a$ is the in-plane lattice parameter of biaxially strained KTaO$_3$ film. Negative means compressive in-plane strain and positive is tensile in-plane strain, reference to the unstrained cubic case. By using this method, we can isolate the pure strain effects from other effects present in actual thin film samples, such as structural defects, chemical inhomogeneities, and interfaces. The possible symmetry groups are obtained as the polar $P4mm$ and $Am\bar{m}2$, as well as the nonpolar $P4/mmm$, as discussed below. Our system under biaxial in-plane strain is different from the slab model where the slab with vacuum or surface is periodically repeated to produce a supercell.

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Fig. 1 The schematic illustration of strained KTaO$_3$ in different in-plane strain fields. There are two oxygen vacancy positions in strained KTaO$_3$: in the biaxial strain $a$-$b$ plane (IP-$V^0_\text{O}$) and out of the $a$-$b$ plane (OP-$V^0_\text{O}$).
The oxygen vacancies in KTaO$_3$ are created by removing oxygen atoms from the perfect lattice. The formation energy of oxygen vacancy is determined by the expression:

$$\Delta E_f (V_{O}^{q}) = E_f (V_{O}^{q}) - E_f (\text{perfect}) + \mu_O$$

$$+ q\left(E_f^\text{perfect} + \frac{V_{\text{VBM}}^q - V_{\text{VBM}}^\text{perfect}}{C_0}\right)$$

(1)

where $E_f (V_{O}^{q})$ is the total energy of a KTaO$_3$ supercell with one oxygen vacancy in charge state $q$ (here $q$ is 2+) and $E_f (\text{perfect})$ is the total energy of the host supercell. $\mu_O$ is the oxygen chemical potential, which is a function of temperature and pressure, as shown in Fig. S1 (ESI†). According to previous experimental reports,$^9,10,36$ the typical growth temperature for KTaO$_3$ thin film is about 1000 K, and the oxygen partial pressures can lie in the range from 10$^{-10}$ to 1 atm, in which the oxygen chemical potential changes from $-5.35$ eV to $-6.34$ eV. In this study, we use the chemical potential, $\mu_O = -6.34$ eV, corresponding to conditions at 10$^{-10}$ atm and 1000 K. $E_f^\text{perfect}$ is the Fermi level measured from the valence band maximum (VBM), which changes within the band gap, $E_g$. In this work, we choose the same value of the Fermi level in each strained case in order to compare formation energies under different strain fields. The calculated $E_g = 2.2$ eV in the cubic KTaO$_3$ is smaller than the experimental value, about 3.6 eV,$^{37}$ which is a typical issue for GGA functionals. 14,38 The band-gap corrections are performed within the band gap. As expected, this correction term for V$^{2+}_O$ based on the characteristics of defect-induced electronic states. In the case of IP-V$^{2+}_O$, the formation energies of IP- and OP-V$^2_O$ are also calculated with the in-plane strain. The change in formation energy of V$^2_O$ as a function of system size and in-plane strain state at 1000 K and 10$^{-10}$ atm, with the Fermi level chosen at the middle of band gap, $\sim 1.8$ eV.

3 Results and discussion

3.1 Atomic structure of defect-free KTaO$_3$

The influence of in-plane strain on the atomic structure of KTaO$_3$ is characterized by the relative ionic displacement and the changes in bond lengths, optimized cell volume and lattice parameters, as shown in Fig. 3. Similar to SrTiO$_3$,$^{46}$ we find three distinct regions (I, II, and III) in the strained of KTaO$_3$, corresponding to different space groups, in Fig. 3(a) (here we do not show the $Pm\bar{3}m$ space group for the unstrained KTaO$_3$ for clarity). For small tensile or compressive in-plane strains ($-1\% < s < 0.5\%$, II), the structure of KTaO$_3$ remains centrosymmetric, while the phase becomes $P4/mmm$. For large enough compressive epitaxial strains ($s < -1\%$, I), the Ta atom shifts up from the body-center position; at the same time, the oxygen atoms move down from the face-center position in order to stabilize the octahedral structure. The space group of the tetragonal phase is transformed into the non-centrosymmetric $P4/mmm$, with polarization along the [001] direction. This process is different from that in SrTiO$_3$, where rotation of the oxygen octahedral to a $P4/mcm$ phase transition has been found for large compressive strain fields.$^{47-49}$ In KTaO$_3$, however, we do not observe the transition to the $P4/mcm$ phase even for large compressive in-plane strains on the order of $-5\%$. Above a critical value of tensile strain ($s > 0.5\%$, III), KTaO$_3$ becomes ferroelectric and transforms to an orthorhombic $Amnm$ structure. This is also a non-centrosymmetric structure with polarization along [110]. These results are consistent with a previous study.$^9$

The Ta–O bond lengths are also examined in strained KTaO$_3$, as shown in Fig. 3(b). Considering the above phase transitions, the Ta–O octahedral structure will not maintain the $O_h$ symmetry, and the corresponding Ta–O bond lengths become distinctive. In phase II, the symmetry of the octahedral structure lowers to $D_{4h}$, and the in-plane Ta–O bond lengths (Ta–O1/2 or Ta–O3/4) are different from the out-of-plane Ta–O bond lengths (Ta–O5/6). In phase I, the symmetry further lowers into $C_{4v}$. The notable lift of Ta atom along [001] causes the Ta–O5 bond length to be significantly larger than that of Ta–O6, while the in-plane Ta–O bond lengths...
bonds remain equivalent. Similarly, the Ta atom displaces, in phase III, along [110], which lowers the symmetry to $C_{2v}$. In this case, the Ta–O1/2 and Ta–O3/4 bond lengths become different, while the Ta–O5/6 bond lengths become similar.

The strain dependence of the optimized cell volume is shown in Fig. 3. It is found that in-plane strain leads to net changes in volume, which is similar to CaMnO₃.²⁴ In addition, it should be noted that the variation of volume is non-linear with in-plane strain, i.e., the slopes in phase I and III are smaller than that in phase II. This behavior is also reflected in the lattice parameters in Fig. 3(d), where the variation of out-of-plane lattice parameter, $c$, is more rapid in phase I and III than in phase II; and compared with the variation in phase III, the change is steeper in phase I. These changes in slopes in the $c$-axis lattice parameter and supercell volume are associated with the ferroelectric phase transitions, which can be demonstrated by calculating the volume and the $c$-lattice parameter of the biaxial strained KTaO₃, without polarized phase transitions, as shown by the dash line in Fig. 3(c) and (d). Similar phenomena have been reported in other perovskites, e.g. SrTiO₃, BaTiO₃ and CaTiO₃, as well as some fluoride, rock-salt and pyrochlore materials.⁵² Based on the above argument, a large contraction of the in-plane lattice parameter, with a corresponding net reduction of volume, that occurs under compressive strain, as shown in Fig. 3(c) and (d), could be expected to lower the formation energy of the IP-V$_{2+}^O$ more than that of the OP-V$_{2+}^O$. However, it should point out that the decrease in formation energy for the OP-V$_{2+}^O$ is more dramatic than that for the IP-V$_{2+}^O$, when the in-plane lattice parameter decreases, as shown in Fig. 4(a). This unusual behavior is also demonstrated by the decrease in formation energy of the IP-V$_{2+}^O$ with increasing in-plane tensile strain, as shown in Fig. 4(a), and corresponding increase of the in-plane lattice parameter shown in Fig. 3(d). Therefore, an argument based solely on chemical expansion cannot entirely explain these results.

3.2 Defect formation behavior in strained KTaO₃

The formation energies of two different oxygen vacancies (IP- and OP-V$_{2+}^O$) in KTaO₃ are illustrated in Fig. 4(a) as a function of the applied in-plane strain. The results reveal that the formation energies of IP-V$_{2+}^O$ and OP-V$_{2+}^O$ have different responses to in-plane strains. When the in-plane lattice constant decreases, both vacancies lower their formation energies; this is in contrast to the variation of V$_O^0$ in BaTiO₃,²¹ and LaMnO₃,²² where both vacancies increase their formation energies. This discrepancy is not surprising in light of the different chemical expansion behavior for neutral and charged oxygen vacancies.²⁶,²⁷ As shown in Fig. 4(b), the 2+ charged oxygen vacancy, i.e. V$_{2+}^O$, in KTaO₃ leads to lattice contraction, which is associated with lowering of the formation energy for V$_O^0$ in a compressive field; on the other hand, V$_O^0$ causes lattice expansion, which may increase the formation energy of V$_O^0$ in a compressive field. Similar phenomena have been reported in other perovskites, e.g. SrTiO₃, BaTiO₃ and CaTiO₃, as well as some fluoride, rock-salt and pyrochlore materials.⁵² Based on the above argument, a large contraction of the in-plane lattice parameter, with a corresponding net reduction of volume, that occurs under compressive strain, as shown in Fig. 3(c) and (d), could be expected to lower the formation energy of the IP-V$_{2+}^O$ more than that of the OP-V$_{2+}^O$.

Fig. 3 Structural properties as a function of in-plane strain, $s$, in perfect KTaO₃: (a) relative ionic displacements (reference to K ions, in fractional coordinates); (b) Ta–O bond lengths; (c) changes in the optimized supercell volume; (d) lattice parameters. The dash line in (c) and (d) are the changes of structure in phases without polarization.
Indeed, the above trends with regard to the strain-dependent formation energy can be readily understood through an analysis of the local structure upon creation of an $V^{2+}_{2O}$. The atomic configurations of the oxygen vacancy before and after relaxation are systematically explored. Our calculations indicate that the presence of an $V^{2+}_{2O}$ leads to an outward relaxation of the nearest-neighboring Ta atoms from their ideal positions, which is consistent with previous studies.\textsuperscript{17} Table 1 summarizes the calculated interatomic distance between $V^{2+}_{2O}$ and its nearest-neighboring Ta atoms before and after relaxation in different strain fields. It is found that in a compressive field, the existence of the OP-$V^{2+}_{2O}$ tends to counterbalance the distances between the nearest two Ta atoms and the $V^{2+}_{2O}$ along the polarization axis, which gives rise to a significant structural relaxation, stabilizing the defect structures and lowering the total energy. Compared with the OP-$V^{2+}_{2O}$, the magnitude of the atomic displacements in the IP-$V^{2+}_{2O}$ system is relatively small because of the clamped in-plane lattice parameter, which prevents the local structure from fully relaxing. Similar results are found in PbTiO$_3$.\textsuperscript{53} A comparison of the total energies for the systems of IP-$V^{2+}_{2O}$ and OP-$V^{2+}_{2O}$ indicates that the oxygen vacancy in an OP site is nearly 0.5 eV more stable when the in-plane strain decreases to $-2.5\%$ of the unstrained lattice constant, the total energy for the IP-$V^{2+}_{2O}$ system is 0.6 eV lower than that for the OP-$V^{2+}_{2O}$ system. The large relaxation of local structures around the IP-$V^{2+}_{2O}$ system is 0.488 Å, which is significantly larger than that around the OP-$V^{2+}_{2O}$. The large relaxation of local structures around the IP-$V^{2+}_{2O}$ system is 0.488 Å, which is significantly larger than that around the OP-$V^{2+}_{2O}$, causing the local defect structure in the IP-$V^{2+}_{2O}$ system to fully relax. At the same time, the stretched in-plane strain enhances the displacement of the nearest Ta atoms in the IP-$V^{2+}_{2O}$ system compared with the OP-$V^{2+}_{2O}$ system, causing the local defect structure in the IP-$V^{2+}_{2O}$ system to fully relax. For example, when the in-plane lattice constant increases to $2.5\%$ of the unstrained lattice constant, the total displacement of Ta atoms around the IP-$V^{2+}_{2O}$ is 0.488 Å, which is significantly larger than that around the OP-$V^{2+}_{2O}$, and the total energy for the IP-$V^{2+}_{2O}$ system is 0.6 eV lower than that for the OP-$V^{2+}_{2O}$ system. The large relaxation of local structures around the IP-$V^{2+}_{2O}$ stabilizes the system and lowers the formation energy. These results suggest that the characteristic relaxations are mainly responsible for the formation behavior of doubly charged oxygen vacancies.\[ESI\textsuperscript{†} give more detailed information about how to determine the relaxation energy].

### Table 1

<table>
<thead>
<tr>
<th>Strain (%)</th>
<th>IP-$V^{2+}_{2O}$</th>
<th>OP-$V^{2+}_{2O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before (Å)</td>
<td>After (Å)</td>
</tr>
<tr>
<td>$-2.5$</td>
<td>1.952</td>
<td>2.054</td>
</tr>
<tr>
<td>$-2$</td>
<td>1.960</td>
<td>2.077</td>
</tr>
<tr>
<td>$-1.5$</td>
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</tr>
<tr>
<td>$-1$</td>
<td>1.978</td>
<td>2.123</td>
</tr>
<tr>
<td>$-0.5$</td>
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<tr>
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<td>2.173</td>
</tr>
<tr>
<td>0.5</td>
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<td>2.197</td>
</tr>
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<td>1</td>
<td>2.045 (1.991)</td>
<td>2.226 (2.215)</td>
</tr>
<tr>
<td>1.5</td>
<td>2.091 (1.966)</td>
<td>2.259 (2.231)</td>
</tr>
<tr>
<td>2</td>
<td>2.129 (1.949)</td>
<td>2.290 (2.248)</td>
</tr>
<tr>
<td>2.5</td>
<td>2.162 (1.937)</td>
<td>2.322 (2.265)</td>
</tr>
</tbody>
</table>

Fig. 4  (a) The formation energy of IP-$V^{2+}_{2O}$ and OP-$V^{2+}_{2O}$ in strained KTaO$_3$ as a function of the applied in-plane strain at 1000 K and 10$^{-10}$ atm condition, and the Fermi level is chosen in the middle of band-gap of the unstained case; (b) the stability of a neutral (red circle) and positively doubly charged oxygen vacancy (black circle) in unstrained KTaO$_3$. |
[X'] under equilibrium conditions can be estimated from the following equation:

\[ [X'] = N(X) \exp\left( \frac{-\Delta G_t(X')}{k_BT} \right) \]  

where the pre-exponential factor \( N(X) \) denotes the concentration of possible lattice sites for the defect X (IP- and OP-V\(_{2}\)), \( \Delta G_t \) is the free energy for defect formation (since our calculation is under constant volume conditions, the free energy should be the Helmholtz free energy), and we assume that \( \Delta G_t \approx \Delta E_t \), \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature. The calculated equilibrium defect concentration at a typical thin-film growth temperature of 1000 K\(^9,10,36\) is shown in Fig. 5, as a function of oxygen partial pressure and in-plane strain. The results reveal that at extremely low partial pressure conditions, \( 10^{-10} \text{ atm} \), the oxygen vacancy concentration is very high, corresponding to the oxygen deficient region, which is consistent with previous experimental results.\(^{36}\)

As the partial pressure increases, the concentration of oxygen vacancies decreases, but still around \( 10^{15} \text{ cm}^{-3} \), even at 0.21 atm. These results suggest that oxygen vacancies should exist in KTaO\(_3\) thin films under typical growth conditions, such as partial pressures of \( 10^{-10} \text{ atm} \) and \( 10^{-4} \text{ atm} \), which may be associated to the relaxor-like behavior between the paraelectric and long-range ordered ferroelectric.\(^8\) In fact, Mota et al. have reported that charged oxygen vacancies are responsible for the Cole–Cole dipolar relaxation, which would be suppressed with decreasing vacancy concentration.\(^{36}\)

Similar results can also be found for SrTiO\(_3\) thin films.\(^{54}\) Besides the partial pressure, strain is another degree of freedom to control the defect concentration in KTaO\(_3\). The variation of equilibrium oxygen vacancy concentrations in different strain fields results from the strain-modified vacancy formation energies. For example, in Fig. 5(b), the out-of-plane oxygen vacancy concentration at 0.21 atm increases from \( \sim 10^{15} \text{ cm}^{-3} \) to \( \sim 10^{19} \text{ cm}^{-3} \) as the in-plane strain decreases from 2.5% tensile to \(-2.5%\) compressive.

In the present work, we assume that \( \Delta G_t \approx \Delta E_t \) and neglect the contribution of phonons to the free energy, \( \text{i.e., the lattice vibrational free energy, } \Delta G_{\text{vib}}, \) which may have a significant impact at higher temperatures. For example, previous first principles phonon calculations in BaZrO\(_3\) under constant pressure conditions have shown that the magnitude of \( \Delta G_{\text{vib}} \) is comparable in both the bulk and thin films with different thicknesses, especially at high temperature, \( e.g., \sim 1 \text{ eV at } 1000 \text{ K} \), because of local relaxation and the large negative formation volume of \( V_{2^+}. \)\(^{55-57}\) However, in the present work, we are simulating the dilute limit system, where the change of the supercell volume during a defect formation process in a crystal is negligible, \( \text{i.e., the fixed volume}.\(^{57,58}\)

In this case, the contribution from the phonons under constant volume condition will be smaller than that under constant pressure condition. Previous studies have shown that this contribution to the free energy under constant volume condition is very small, even at 1000 K, about 0.2 eV in ZnO\(^{58}\) and 0.4 eV in BaZrO\(_3\).\(^{57}\) By calculating the vibrational free energy in strained \(-2.5%\) and unstrained KTaO\(_3\), we find that the phonon contributions to the free energy from 0 K to 1000 K are less than \( \sim 0.15 \text{ eV} \), as shown in Fig. S4 (ESI\(^+\)), which will not alter our conclusions and confirms that our assumption regarding free energy is reasonable.

From Fig. 5, we can clearly see that the concentrations of IP- and OP-V\(_{2}^+\) are different due to the distinctive formation behavior in strain fields. For example, the formation energy of IP-V\(_{2}^0\) for 2.5% tensile strain is about 0.6 eV lower than that of the OP-V\(_{2}^+\), causing a larger concentration of the single IP-V\(_{2}^0\), compared with the OP-V\(_{2}^0\). These results suggest that epitaxial strain cannot only tune the vacancy concentration in thin films, but can also affect the vacancy site preference. In Fig. 6, we show that the equilibrium V\(_{2}^0\) ratio of IP/OP and OP/IP as a function of temperature for compressive \((-2.5%)\) and tensile \((2.5%)\) strain, respectively. At the typical growth temperature of 1000 K\(^9,10,36\), it can be seen that the ratio of OP/IP for \(-2.5%\) strain is \( \sim 262 \), and the ratio of IP/OP for 2.5% strain is \( \sim 1496 \). In addition, as temperature decreases, the ratio of OP/IP in a compressive field or IP/OP in a tensile field is increased; at the same time, isotropically dynamic processes become insignificant, which may enhance the site preference of oxygen vacancies. These results demonstrate the oxygen vacancy site preference is controlled by epitaxial strain and temperature.

Based on the present theoretical results, the control of oxygen vacancies in KTaO\(_3\) thin film could be achieved by tuning the processing conditions, such as oxygen partial pressure, temperature.

![Fig. 5](https://example.com/filename.png)

**Fig. 5** The concentration of oxygen vacancy in KTaO\(_3\) at the typical growth temperature of 1000 K as a function of partial pressure and in-plane strain, (a) for IP-V\(_{2}^0\) and (b) for OP-V\(_{2}^+\).
and strain field, thereby providing a route by which the ferroelectric properties of KTaO₃ thin film can be optimized. However, in the present study, the formation energy calculation is only focused on the homogeneously isolated single vacancies. Defect complexes and vacancy ordering induced by the accumulation of single vacancies have not been included in calculations. We expect that the interaction energy between defects, although not treated in this work, is also dependent on the external strain. Besides the defect interaction, the mobility of oxygen vacancies is another key factor that determines the degree of defect agglomeration. Therefore, in the next section, we further examine the influence of strain on the migration barrier of oxygen vacancies.

3.4 Defect diffusion behavior in strained KTaO₃

For the diffusion of oxygen vacancies in strained KTaO₃, two different migration processes are considered, first within the ab-plane (intra-plane), and then between the ab-planes (inter-plane), as shown in Fig. 7. We know that there are two ab-planes in KTaO₃, identifiable as TaO₂ and KO planes. The distance between oxygen sites within a KO plane is much larger than that in a TaO₂ plane, even in the strained systems, which indicates that the activation energy for diffusion within the KO plane should be higher than that in the TaO₂ plane. Therefore, it is reasonable to assume that the diffusion mechanisms within the KO plane are unlikely to play an important role in V²⁺O diffusion, and we will restrict the intra-plane migration within the TaO₂ plane.

3.4.1 Intra-plane migration of oxygen vacancy. Based on the characteristics of the crystal structure for strained KTaO₃ in Section 3.1, the diffusion pathways within the ab-plane are determined: for the compressive in-plane strain field, only one diffusion pathway (1 2 2) is described, while for the tensile in-plane strain field, at least two pathways (1 2 2 and 3 2 4, corresponding to the minimum and maximum distances, respectively) have to be considered as the in-plane lattice parameter increases. The intra-plane migration barriers for these pathways are plotted in Fig. 8. We find that, in phase I, the energy barrier decreases as the in-plane compressive strain increases from 1% to 2.5%, which may be related to the strong polarization field. In phase I, the polarization field along the [001] direction separates the diffusing oxygen atom and its nearest-neighboring Ta atom in the diffusion process, which weakens the Ta–O interaction, especially at the saddle point, and thus decreases the barrier. In phase II and III, the general reduction in migration barrier with increasing in-plane compressive strain from −1% to 2.5% can be understood as a dilation of the supercell, as shown in Fig. 3(c), providing more space for oxygen diffusion.
atom diffusion, and thus decreasing the diffusion barrier of oxygen vacancies. In phase III, the barriers for pathways 1 → 2 and 3 → 4 are distinctive due to the different intermediate states, as shown in Fig. 8, where along both pathways the transition O atom pushes the nearest-neighboring Ta atom to move outward. For the case of the Ta atom displaced by tensile strain towards the O1 and O2 atom, the additional relaxation of this Ta atom by the transition O atom moving along pathway 3 → 4 is constrained, which induces a higher energy at the saddle point, compared with that in pathway 1 → 2, where relaxation of the same Ta atom along [110] is possible. The above results show that the migration barrier of the oxygen vacancy within the TaO2 plane can be decreased by the strain field, especially in the cases of tensile fields, which may promote the possibility of V2+O agglomeration within the TaO2 plane.

### 3.4.2 Inter-plane migration of oxygen vacancy.

For inter-plane diffusion, all possible diffusion pathways (1 → 5, 1 → 6, and 3 → 5) are considered, as shown in Fig. 7. The migration barriers of these pathways are summarized in Table 2. As the in-plane lattice parameter decreases, the migration barrier of the oxygen vacancy from the TaO2-plane to the KO-plane (from the IP-V2+O to the OP-V2+O) decreases, while the barrier from the KO-plane to the TaO2-plane (from the OP-V2+O to the IP-V2+O) increases. The distinction of the two barriers originates from the different formation energies for the IP-V2+O and the OP-V2+O as discussed in Section 3.2. When the in-plane lattice parameter increases, oxygen vacancy migration from the TaO2-plane to the KO-plane becomes more difficult, while the barrier in the opposite direction is dramatically decreased. These results indicate that under compressive strains, the oxygen vacancy in the TaO2-plane migrates more easily onto the KO-plane, as compared with the opposite direction, especially for large compressive in-plane strain, and vice versa for tensile strains. Therefore, in contrast to the strain-enhanced intra-plane diffusion, diffusion in the direction normal to the plane of strain is impeded under an epitaxial strain field. Based on these results, we can expect that this anisotropic

### Table 2

Migration of oxygen vacancy in strained KTaO3. The values in the parentheses are the migration barriers in the opposite direction. The energy barrier of pathway 1 → 3 is estimated within the barriers of pathway 1 → 2 and 3 → 4.

<table>
<thead>
<tr>
<th>Compressive Strain (%)</th>
<th>Inter-plane diffusion barrier (eV)</th>
<th>Intra-plane diffusion barrier (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 → 5</td>
<td>1 → 6</td>
</tr>
<tr>
<td></td>
<td>0.734 (1.229)</td>
<td>0.835 (1.329)</td>
</tr>
<tr>
<td></td>
<td>0.800 (1.179)</td>
<td>0.858 (1.237)</td>
</tr>
<tr>
<td></td>
<td>0.858 (1.119)</td>
<td>0.862 (1.123)</td>
</tr>
<tr>
<td></td>
<td>0.888 (1.059)</td>
<td>0.888 (1.059)</td>
</tr>
<tr>
<td></td>
<td>0.903 (0.992)</td>
<td>0.903 (0.992)</td>
</tr>
<tr>
<td>Unstrained</td>
<td>0.915 (0.915)</td>
<td></td>
</tr>
<tr>
<td>Tensile Strain (%)</td>
<td>Inter-plane diffusion barrier (eV)</td>
<td>Intra-plane diffusion barrier (eV)</td>
</tr>
<tr>
<td></td>
<td>1 → 5</td>
<td>1 → 6</td>
</tr>
<tr>
<td></td>
<td>0.929 (0.833)</td>
<td>0.929 (0.833)</td>
</tr>
<tr>
<td></td>
<td>0.949 (0.747)</td>
<td>0.946 (0.743)</td>
</tr>
<tr>
<td></td>
<td>0.827 (0.827)</td>
<td>0.827–0.828</td>
</tr>
<tr>
<td></td>
<td>0.775 (0.775)</td>
<td>0.775–0.778</td>
</tr>
<tr>
<td></td>
<td>0.760 (0.760)</td>
<td>0.760–0.823</td>
</tr>
<tr>
<td></td>
<td>0.651 (0.651)</td>
<td>0.651–0.807</td>
</tr>
<tr>
<td></td>
<td>0.880 (0.880)</td>
<td>0.880 (0.880)</td>
</tr>
<tr>
<td></td>
<td>0.880 (0.880)</td>
<td>0.880 (0.880)</td>
</tr>
<tr>
<td></td>
<td>0.827 (0.827)</td>
<td>0.827–0.828</td>
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<td>0.775 (0.775)</td>
<td>0.775–0.778</td>
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<td></td>
<td>0.760 (0.760)</td>
<td>0.760–0.823</td>
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<tr>
<td></td>
<td>0.715 (0.715)</td>
<td>0.715 (0.715)</td>
</tr>
<tr>
<td></td>
<td>0.807 (0.807)</td>
<td></td>
</tr>
</tbody>
</table>
diffusion property further enhances site preferences, especially at low temperature.

4 Conclusions

In this work, the defect formation energies and migration energies of V$_{O}^{2-}$ in biaxial strained KTaO$_3$ have been systematically studied. Our results show that formation energies for oxygen vacancies are sensitive to in-plane strain and oxygen positions. The formation energies of the oxygen vacancies in different positions (the IP-V$_{O}^{2-}$ and the OP-V$_{O}^{2-}$) are found to decrease as the in-plane lattice parameter decreases. Compared with the IP-V$_{O}^{2-}$, the variation of formation energy for the OP-V$_{O}^{2-}$ is more sensitive to in-plane strain. For instance, compared to unstrained cubic KTaO$_3$, the formation energies of IP-V$_{O}^{2-}$ and OP-V$_{O}^{2-}$ are reduced by 0.12 eV and 0.6 eV under -2.5% in-plane strain, respectively. When the in-plane lattice parameter increases under tensile strain, however, the response is reversed: the formation energy decreases for the IP-V$_{O}^{2-}$ but increases for the OP-V$_{O}^{2-}$. These findings suggest that epitaxial strain can also induce apparent site preferences for the oxygen vacancy, which results in orders of magnitude differences in vacancy concentrations on the two sites at typical growth temperature for epitaxial thin films. The reason for the influence of epitaxial strain on the formation of oxygen vacancies has been analyzed. It is found that strong relaxation of the local defect structures is mainly responsible for the formation behavior of these oxygen vacancies. The calculated equilibrium vacancy concentration at typical growth temperatures shows that in-plane strain is another degree of freedom that affects defect concentration. These results will provide guidelines for controlling processing conditions in order to optimize functionalities based on oxygen vacancies.

Besides the thermodynamics, the kinetic behavior of oxygen vacancies has been investigated. All possible migration pathways have been considered, and it is observed that the V$_{O}^{2-}$ migration barrier can also be tuned by epitaxial strain. For in-plane diffusions, the migration barriers for the oxygen vacancy within the TaO$_2$ plane can be decreased, especially as the in-plane lattice parameter increases, which would increase the mobility of oxygen vacancies and promote the possibility of V$_{O}^{2-}$ agglomeration within the TaO$_2$ plane. For inter-plane diffusions, the migration barrier of the oxygen vacancy from the TaO$_2$-plane to KO-plane (from the IP-V$_{O}^{2-}$ to the OP-V$_{O}^{2-}$) increases with increasing strain (from compressive to tensile), while the migration barrier from the KO-plane to the TaO$_2$-plane (from the OP-V$_{O}^{2-}$ to the IP-V$_{O}^{2-}$) decreases as in-plane strain increases. These results suggest that fully successive diffusion in the direction normal to the biaxial strain plane is obstructed under the strain field.

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References
