

Strain effects on oxygen vacancy energetics in KTaO_3

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1. The determination of oxygen chemical potential

The oxygen chemical potential is considered as a function of temperature and pressure, and it can be shown that expression:^{1,2}

$$\mu_{\text{O}}(T,p) = \mu_{\text{O}}(T,p^0) + \frac{1}{2}k_{\text{B}}T\ln\left(\frac{p}{p^0}\right) \quad (\text{S1})$$

Here p^0 is the standard pressure, k_{B} is the Boltzmann constant, and $\mu_{\text{O}}(T,p^0)$ is the temperature-dependent function, which is described as:

$$\begin{aligned} \mu_{\text{O}}(T,p^0) &= \mu_{\text{O}}(0\text{ K}, p^0) + \frac{1}{2}\Delta G(\Delta T, p^0, \text{O}_2) = \mu_{\text{O}}(0\text{ K}, p^0) + \frac{1}{2}[H(T, p^0, \text{O}_2) - H(0\text{ K}, p^0, \text{O}_2)] \\ &\quad - \frac{1}{2}[S(T, p^0, \text{O}_2) - S(0\text{ K}, p^0, \text{O}_2)] \end{aligned} \quad (\text{S2})$$

We choose the reference state of $\mu_{\text{O}}(0\text{ K}, p)$ to be the total energy of oxygen in an isolated molecule, i.e., $\mu_{\text{O}}(0\text{ K}, p) = \frac{1}{2}\mu_{\text{O}_2}(\text{molecular}) = -4.25\text{ eV}$, with a correction of 1.36 eV for the known errors in the O_2 energy.³ H and S are the enthalpy and entropy at standard pressure, respectively, which is experimentally determined and tabulated in thermochemical tables.⁴ Based on Eq.(S1) and (S2), the oxygen chemical potential $\mu_{\text{O}}(T,p)$ is determined and shown in Fig. S1.

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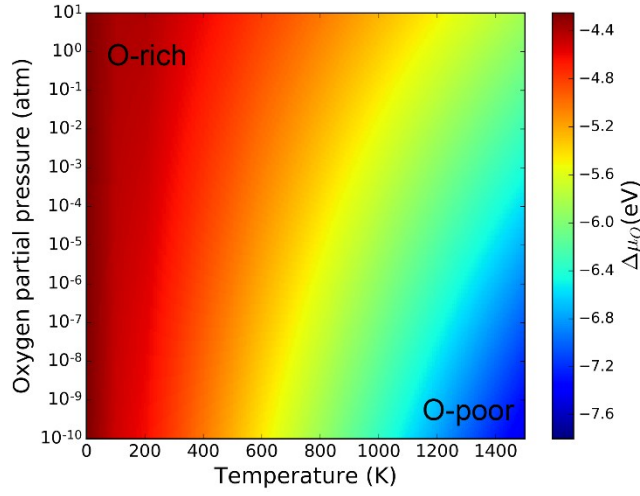


Fig. S1. Oxygen chemical potential as a function of temperature and pressure.

2. The determination of valence band maximum in perfect KTaO_3 supercell

The variation of valence band maximum in perfect KTaO_3 . The value is calculated as the following equation:

$$E_{VBM}^{perfect} = E_T(0) - E_T(+1) \quad (S3)$$

Here $E_T(0)$ and $E_T(+1)$ are the total energy of perfect supercell at 0 and +1 charge state, respectively. We find that the valence band maximum in KTaO_3 decreases as the in-plane strain decreases from -2.5% compressive to 2.5% tensile, which is due to the orbital splitting resulting from the variation of point group symmetry. Similar results have also been reported for SrTiO_3 .⁵

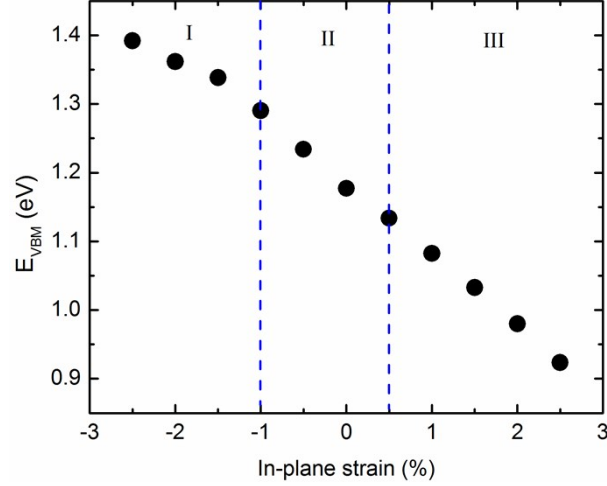


Fig. S2. The variation of $E_{VBM}^{perfect}$ in different in-plane strain states.

3. The detail information about the relaxation energy calculation

The relaxation energy is measured by subtracting the total energy of the defect system without relaxation from the total energy of the fully relaxed system:

$$E_r(V_O^q) = E_T(V_O^q, fully\ relaxed) - E_T(V_O^q, without\ relaxation) \quad (S4)$$

Table SI. The total energy of defect systems for the IP- and OP- V_O^{2+} with and without relaxation.

Strain (%)	Without relaxation (eV)		With relaxation (eV)	
	IP- V_O^{2+}	OP- V_O^{2+}	IP- V_O^{2+}	OP- V_O^{2+}
-2.5	-921.794	-921.517	-924.142	-924.637
-2	-922.992	-922.793	-925.328	-925.707
-1.5	-923.916	-923.789	-926.263	-926.524
-1	-924.526	-924.453	-926.896	-927.067
-0.5	-924.808	-924.773	-927.225	-927.314
0	-924.777	-924.777	-927.261	-927.261
0.5	-924.527	-924.527	-927.079	-926.983
1	-923.999	-924.051	-926.640	-926.437
1.5	-923.260	-923.337	-926.033	-925.707
2	-922.407	-922.501	-925.314	-924.859
2.5	-921.473	-921.581	-924.515	-923.927

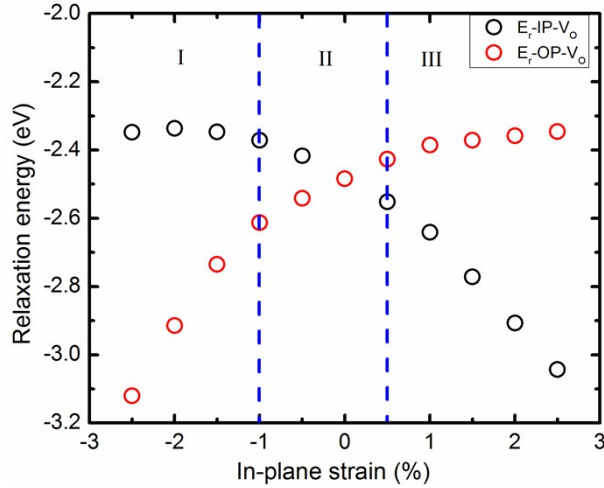


Fig. S3. The relaxation energy of IP- and OP- $V_{O^{2+}}$ for strained $KTaO_3$.

4. The vibration contributions to the free energy

In order to confirm our simplification of $\Delta G_f \approx \Delta E_f$ at high temperatures, we calculated the phonon vibration contributions for the free energy under volume constant condition.^{6,7} By considering the vibrational free energy in compressive -2.5% and unstrained $KTaO_3$, we find that the phonon contributions to the free energy are less than ~ 0.15 eV, as shown in Fig. S4 (here we didn't show the compressive -2.5% case for clarification, since they have the similar value with unstrained case), which will not alter our main conclusions. Thus we can confirm that this simplification is reasonable.

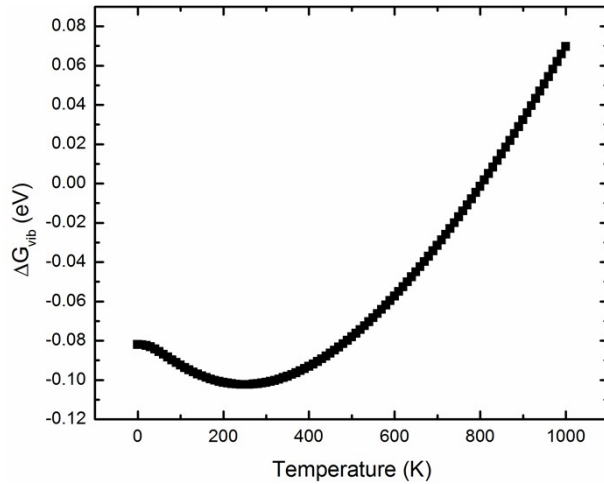


Fig. S4. Vibrational contributions to the free energy of $V_{O^{2+}}$ in unstrained $KTaO_3$ calculated using VASP/PBE in a $3 \times 3 \times 3$ supercell at constant volume condition. The compressive -2.5% case with the similar value is not shown here for clarification.

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