Band gap narrowing in nitrogen-doped La$_2$Ti$_2$O$_7$
predicated by density-functional theory calculations

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Fig.S1 DOS (a) and band structure (b) of La$_2$Ti$_2$O$_7$ with the N$_s$ defect calculated using the conventional DFT. The dash line annotates the Fermi level.
Fig. S2 Defect formation energy (E(eV)) when Ns co-exists with Ti. A plot as a function of chemical potentials of Ti($\mu_{Ti}$ - $\mu_{Ti}$(bulk)) and O($\mu_{O}$ - $\mu_{O}$(gas)). The colored lines show how the defect formation energy varies with the chemical potentials.

The heat of formation of La$_2$Ti$_2$O$_7$ is expressed as follows:

$$\Delta = E_H - 2\mu_{La(bulk)} - 2\mu_{Ti(bulk)} - 7\mu_{O(gas)} \quad (s1)$$

$\mu_{O(gas)}$ is determined by the energy of one oxygen molecule, i.e., $\mu_{O} = \mu_{O(gas)} = 1/2\mu_{O_2}$. $\mu_{La}$ and $\mu_{Ti}$ were obtained by the energy of the bulk metal. In a non-equilibrium process, the atomic chemical potential should be smaller than that of the corresponding elements in their most stable forms. In addition, the $\Delta$ value is negative for stable materials. Therefore, $\mu_{O}$, $\mu_{Ti}$, $\mu_{La}$ satisfy:

$$\Delta + 7\mu_{O(gas)} \leq 7\mu_{O} \leq 7\mu_{O(gas)} \quad (s2a)$$
$$\Delta + 2\mu_{Ti(bulk)} \leq 2\mu_{Ti} \leq 2\mu_{Ti(bulk)} \quad (s2b)$$
$$\Delta + 2\mu_{La(bulk)} \leq 2\mu_{La} \leq 2\mu_{La(bulk)} \quad (s2c)$$

According to formulas (s2a) and (1) in the main text, we can get the relation between $\mu_{O}$, $\mu_{Ti}$ and $E_{form}$, plotted as a function of $\mu_{Ti} - \mu_{Ti(bulk)}$ and $\mu_{O} - \mu_{O(gas)}$ as shown in Fig. S2 and Fig. S3.
Fig. S3 Formation energy of point-defects in La$_2$Ti$_2$O$_7$: (a) Ns, (b) Ns+Ti$_i$, (c) 2Ns, (d) 2Ns+Vo. \( \mu_O \) is determined by the energy of one nitrogen molecule, i.e., \( \mu_N = \mu_{N(gas)} = \frac{1}{2}\mu_{N_2} \).

Fig. S4 DOS (a) and band structure (b) of La$_2$Ti$_2$O$_7$ with the N$_s$ and the Ti$_i$ defects in a supercell calculated using the conventional DFT. The dash line annotates the Fermi level.
Fig. S5 DOS (a) and band structure (b) of La$_2$Ti$_2$O$_7$ with two N$_s$ and one V$_o$ defects in a supercell calculated using the conventional DFT. The dash line annotates the Fermi level.

Fig. S6 DOS (a) and band structure (b) of La$_2$Ti$_2$O$_7$ with two N$_s$ defects in a supercell calculated using the conventional DFT. The dash line annotates the Fermi level.