Figure S1. Side (left panels) and perspective (right panels) views of the initial structures of Li$_4$Ti$_5$O$_{12}$ and their $S$ values of the selected 58 models. Spheres in green, blue, and red represent Li, Ti, and O atoms, respectively; spheres in dark and light green represent Li atoms at the 16d and 8a sites, respectively. Numbers in blue and red represent the ten least and most stable structures, respectively.
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Figure S2 Side (left panels) and perspective (right panels) views of the optimized structures of Li$_4$Ti$_5$O$_{12}$ and total energy of the selected 58 models. Spheres in yellow, green, blue, and red represent Na, Li, Ti, and O atoms, respectively. Numbers in blue and red represent the 10 least and 10 most stable structures, respectively.
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Figure S3 Side (left panels) and perspective (right panels) views of the initial structures of Na$_3$LiTi$_5$O$_{12}$ and S values of the selected 58 models. Spheres in yellow, green, blue, and red represent Na, Li, Ti, and O atoms, respectively. Numbers in blue and red represent the ten least and most stable structures, respectively.
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**Figure S4** Side (left panels) and perspective (right panels) views of the optimized structures of Na$_3$LiTi$_5$O$_{12}$ and total energy of selected 58 models. Spheres in yellow, green, blue, and red represent Na, Li, Ti, and O atoms, respectively. Numbers in blue and red represent the ten least and most stable structures, respectively.
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Figure S5 DOS of Li$_4$Ti$_5$O$_{12}$ of the ten least stable structures from the 58 selected models. The ordinate is $DOS$ [eV$^{-1}$] and the abscissa is $E - E_F$ (the Fermi energy) [eV].
Figure S6 DOS of Li$_4$Ti$_5$O$_{12}$ for which $S$ is around 5.7 selected from the 58 models. The ordinate is $DOS$ [eV$^{-1}$] and the abscissa is $E - E_F$ (the Fermi energy) [eV].

Figure S7 DOS of Li$_4$Ti$_5$O$_{12}$ for which $S$ is around 5.5 selected from the 58 models. The ordinate is $DOS$ [eV$^{-1}$] and the abscissa is $E - E_F$ (the Fermi energy) [eV].
**Figure S8** DOS of Li₄Ti₅O₁₂ for which $S$ is around 5.3 selected from the 58 models. The ordinate is $DOS$ [eV⁻¹] and the abscissa is $E - E_F$ (the Fermi energy) [eV].

**Figure S9** DOS of Li₄Ti₅O₁₂ for which $S$ is around 5.0 selected from the 58 models. The ordinate is $DOS$ [eV⁻¹] and the abscissa is $E - E_F$ (the Fermi energy) [eV].
Figure S10 DOS of Li₄Ti₅O₁₂ for which S is around 4.9 selected from the 58 models. The ordinate is $DOS \ [eV^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) [eV].

Figure S11 DOS of Li₄Ti₅O₁₂ for which S is around 4.6 selected from the 58 models. The ordinate is $DOS \ [eV^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) [eV].
Figure S12 DOS of Li$_4$Ti$_5$O$_{12}$ for which $S$ is around 4.4 selected from the 58 models. The ordinate is $DOS$ [eV$^{-1}$] and the abscissa is $E - E_F$ (the Fermi energy) [eV].

Figure S13 DOS of Li$_4$Ti$_5$O$_{12}$ for which $S$ is around 4.2 selected from the 58 models. The ordinate is $DOS$ [eV$^{-1}$] and the abscissa is $E - E_F$ (the Fermi energy) [eV].
Figure S14 DOS of Li$_4$Ti$_5$O$_{12}$ for which $S$ is around 4.0 selected from the 58 models. The ordinate is $DOS [eV^{-1}]$, and the abscissa is $E - E_F$ (the Fermi energy) [eV].

Figure S15 DOS of Li$_4$Ti$_5$O$_{12}$ for which $S$ is around 3.9 selected from the 58 models. The ordinate is $DOS [eV^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) [eV].
Figure S16 DOS of Li$_4$Ti$_5$O$_{12}$ for which $S$ is around 3.7 selected from the 58 models. The ordinate is $DOS$ [eV$^{-1}$] and the abscissa is $E - E_F$ (the Fermi energy) [eV].
**Figure S17** DOS of the ten most stable Li$_4$Ti$_5$O$_{12}$ selected from the 58 models. The ordinate is $DOS$ [eV$^{-1}$] and the abscissa is $E - E_F$ (the Fermi energy) [eV]. $\Delta E$ is the energy difference in the total energy from the most stable structure.

\[
\begin{align*}
\Delta E &= 0.31 \text{ eV} \\
\Delta E &= 1.12 \text{ eV} \\
\Delta E &= 0.12 \text{ eV} \\
\Delta E &= 0.75 \text{ eV} \\
\Delta E &= 0.00 \text{ eV} \\
\Delta E &= 1.54 \text{ eV} \\
\Delta E &= 0.19 \text{ eV} \\
\Delta E &= 0.94 \text{ eV} \\
\Delta E &= 0.20 \text{ eV} \\
\Delta E &= 0.53 \text{ eV}
\end{align*}
\]
**Figure S18** DOS of the ten least stable Na$_3$LiTi$_5$O$_{12}$ selected from the 58 models. The ordinate is $DOS$ [eV$^{-1}$] and the abscissa is $E - E_F$ (the Fermi energy) [eV].
Figure S19 DOS of Na$_3$LiTi$_5$O$_{12}$ for which $S$ is around 5.3 selected from the 58 models. The ordinate is $DOS$ [eV$^{-1}$] and the abscissa is $E - E_F$ (the Fermi energy) [eV].

Figure S20 DOS of Na$_3$LiTi$_5$O$_{12}$ for which $S$ is around 5.2 selected from the 58 models. The ordinate is $DOS$ [eV$^{-1}$] and the abscissa is $E - E_F$ (the Fermi energy) [eV].
**Figure S21** DOS of Na$_3$LiTi$_5$O$_{12}$ for which $S$ is around 5.0 selected from the 58 models. The ordinate is $DOS$ [eV$^{-1}$] and the abscissa is $E - E_F$ (the Fermi energy) [eV].

**Figure S22** DOS of Na$_3$LiTi$_5$O$_{12}$ for which $S$ is around 4.8 selected from the 58 models. The ordinate is $DOS$ [eV$^{-1}$] and the abscissa is $E - E_F$ (the Fermi energy) [eV].
Figure S23 DOS of Na$_3$LiTi$_5$O$_{12}$ for which $S$ is around 4.7 selected from the 58 models. The ordinate is $DOS$ [eV$^{-1}$] and the abscissa is $E - E_F$ (the Fermi energy) [eV].

Figure S24 DOS of Na$_3$LiTi$_5$O$_{12}$ for which $S$ is around 4.5 selected from the 58 models. The ordinate is $DOS$ [eV$^{-1}$] and the abscissa is $E - E_F$ (the Fermi energy) [eV].
Figure S25 DOS of Na₃LiTi₅O₁₂ for which $S$ is around 4.3 selected from the 58 models. The ordinate is $DOS \ [eV^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) [eV].

Figure S26 DOS of Na₃LiTi₅O₁₂ for which $S$ is around 4.0 selected from the 58 models. The ordinate is $DOS \ [eV^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) [eV].
Figure S27 DOS of Na$_3$LiTi$_5$O$_{12}$ for which $S$ is around 3.9 selected from the 58 models. The ordinate is $DOS$ [eV$^{-1}$] and the abscissa is $E - E_F$ (the Fermi energy) [eV].

Figure S28 DOS of Na$_3$LiTi$_5$O$_{12}$ for which $S$ is around 3.7 selected from the 58 models. The ordinate is $DOS$ [eV$^{-1}$] and the abscissa is $E - E_F$ (the Fermi energy) [eV].
Figure S29 DOS of Na$_3$LiTi$_5$O$_{12}$ for which $S$ is around 3.6 selected from the 58 models. The ordinate is $DOS \ [eV^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) $[eV]$. 
Figure S30 DOS of the ten most stable Na$_3$LiTi$_5$O$_{12}$ selected from the 58 models. The ordinate is $DOS \ [eV^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) [eV]. $\Delta E$ is the energy difference in the total energy from the most stable structure.
Figure S31 Side (upper panels) and top (lower panels) views of the optimized structures of (a) Li$_4$Ti$_5$O$_{12}$, (b) Na$_3$LiTi$_5$O$_{12}$, (c) Na$_4$Ti$_5$O$_{12}$, (d) Cu$_3$LiTi$_5$O$_{12}$, (e) Ag$_3$LiTi$_5$O$_{12}$, and (f) K$_3$LiTi$_5$O$_{12}$, among which the former five (a-e) retains the spinel structure while the last (f) does not. Spheres in light blue, red, green, yellow, dark blue, gray, and purple represent Ti, O, Li, Na, Cu, Ag, and K atoms, respectively. The structures were optimized for both atomic positions and lattice parameters.
Figure S32 Displacement of O atoms from the Wyckoff positions (32e) of the Fd$\overline{3}$m symmetry (spinel). (a) Li$_4$Ti$_5$O$_{12}$, and (b) Na$_3$LiTi$_5$O$_{12}$. LTO-1 and NTO-1 (LTO-10 and NTO-10) indicate the most stable (the 10-th stable) models.
Figure S33 Comparison of the results (optimized structures, \( S \) values, and \( \Delta E \) values) of spinel-titanates ((a) LTO, and (b) NTO) with the predicted configurations by previous works \([30, 31]\) (left panels) and the most stable configurations among the 13,444 (LTO) and 8,444 (NTO) models (right panels). The figures are perspective views of the optimized structures; spheres in yellow, light green, dark green, blue, and red represent Na, Li in the 8a sites, Li in the 16d sites, Ti, and O atoms, respectively. \( \Delta E \) is the energy difference from the most stable structures in our calculated models. The values in parenthesis are the values before the optimization.