

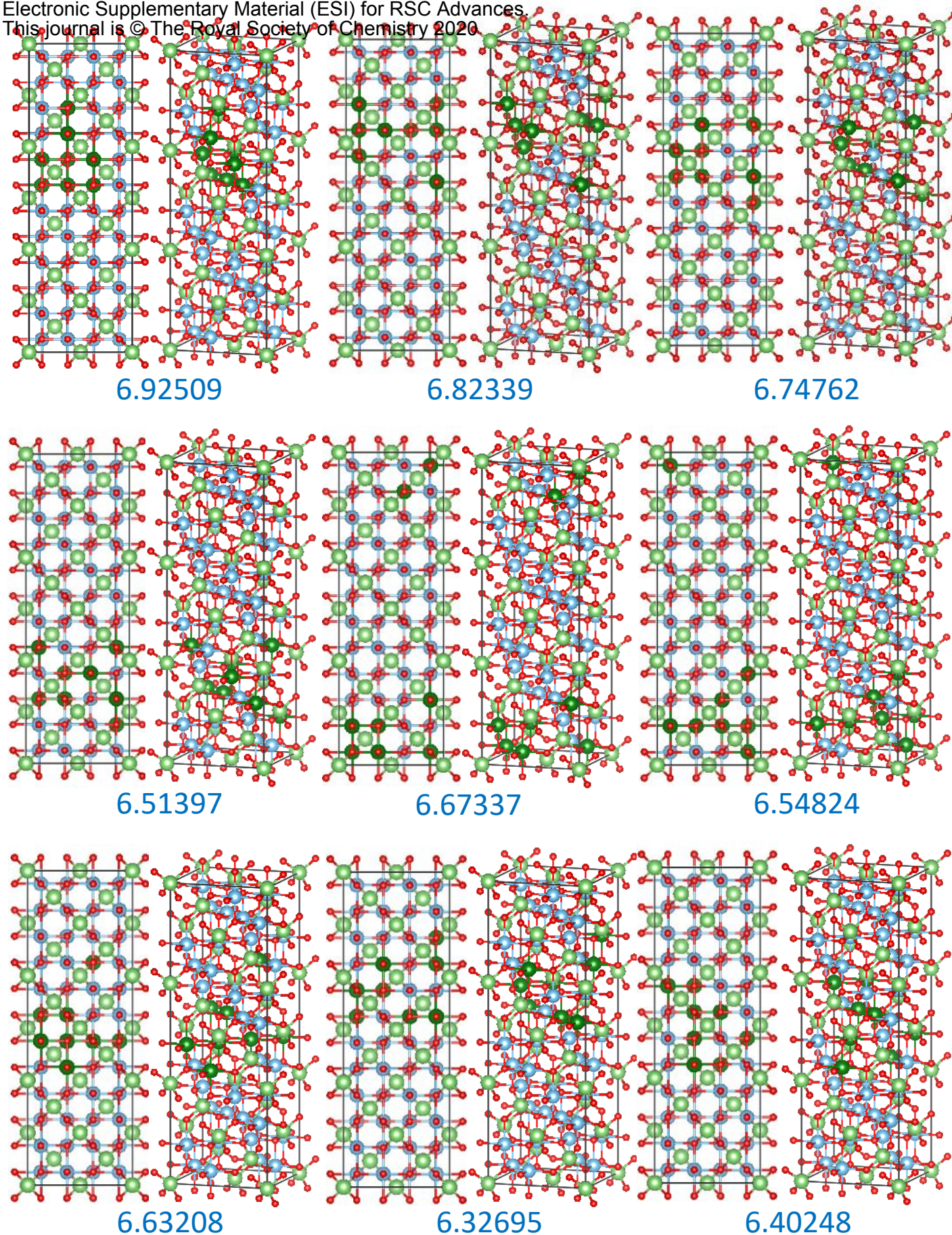


Figure S1. Side (left panels) and perspective (right panels) views of the initial structures of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and their S values of the selected 58 models. Spheres in green, blue, and red represent Li, Ti, and O atoms, respectively; spheres in dark and light green represent Li atoms at the 16d and 8a sites, respectively. Numbers in blue and red represent the ten least and most stable structures, respectively.

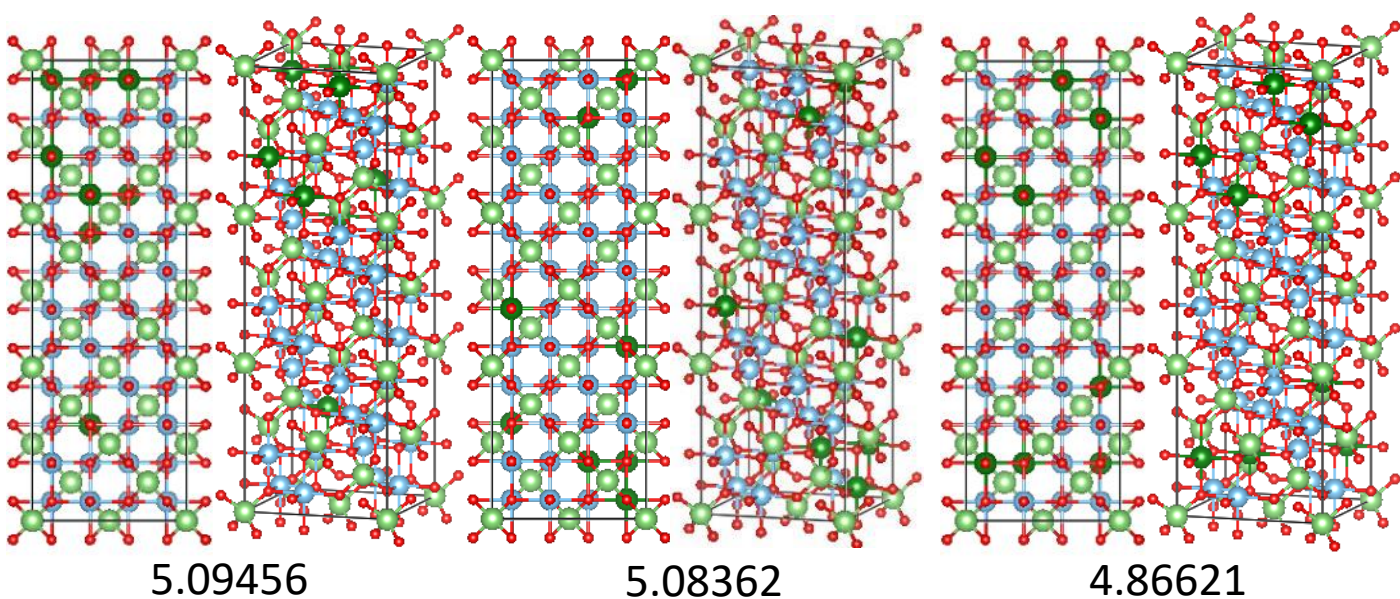
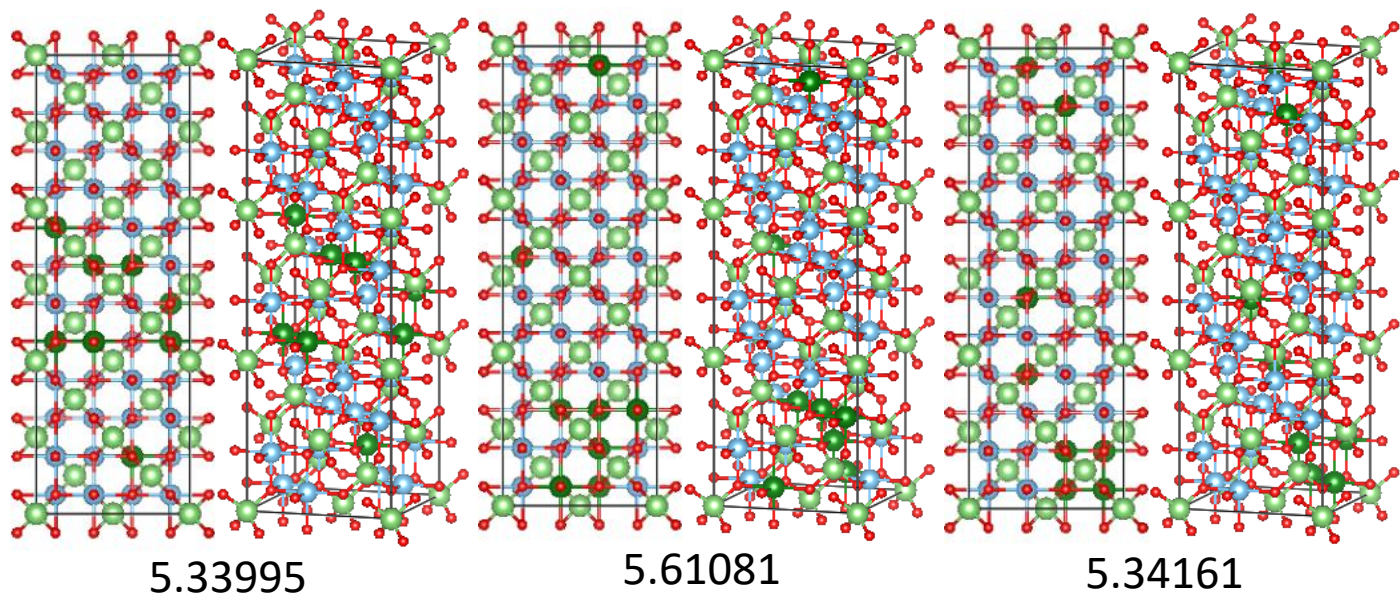
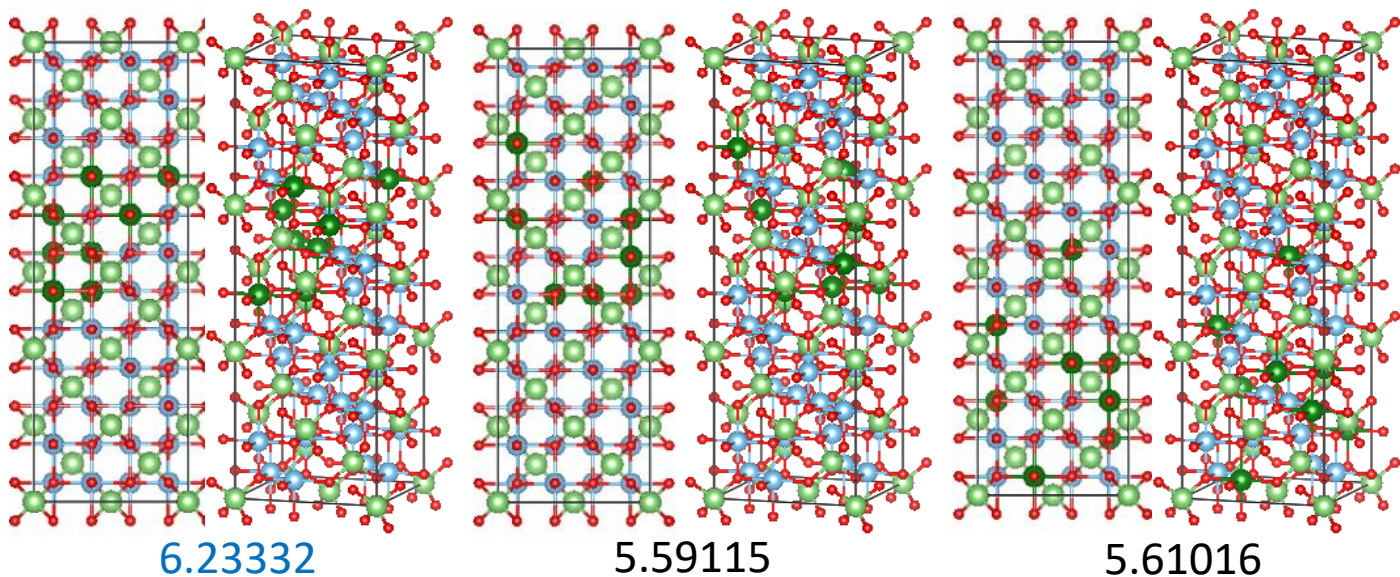


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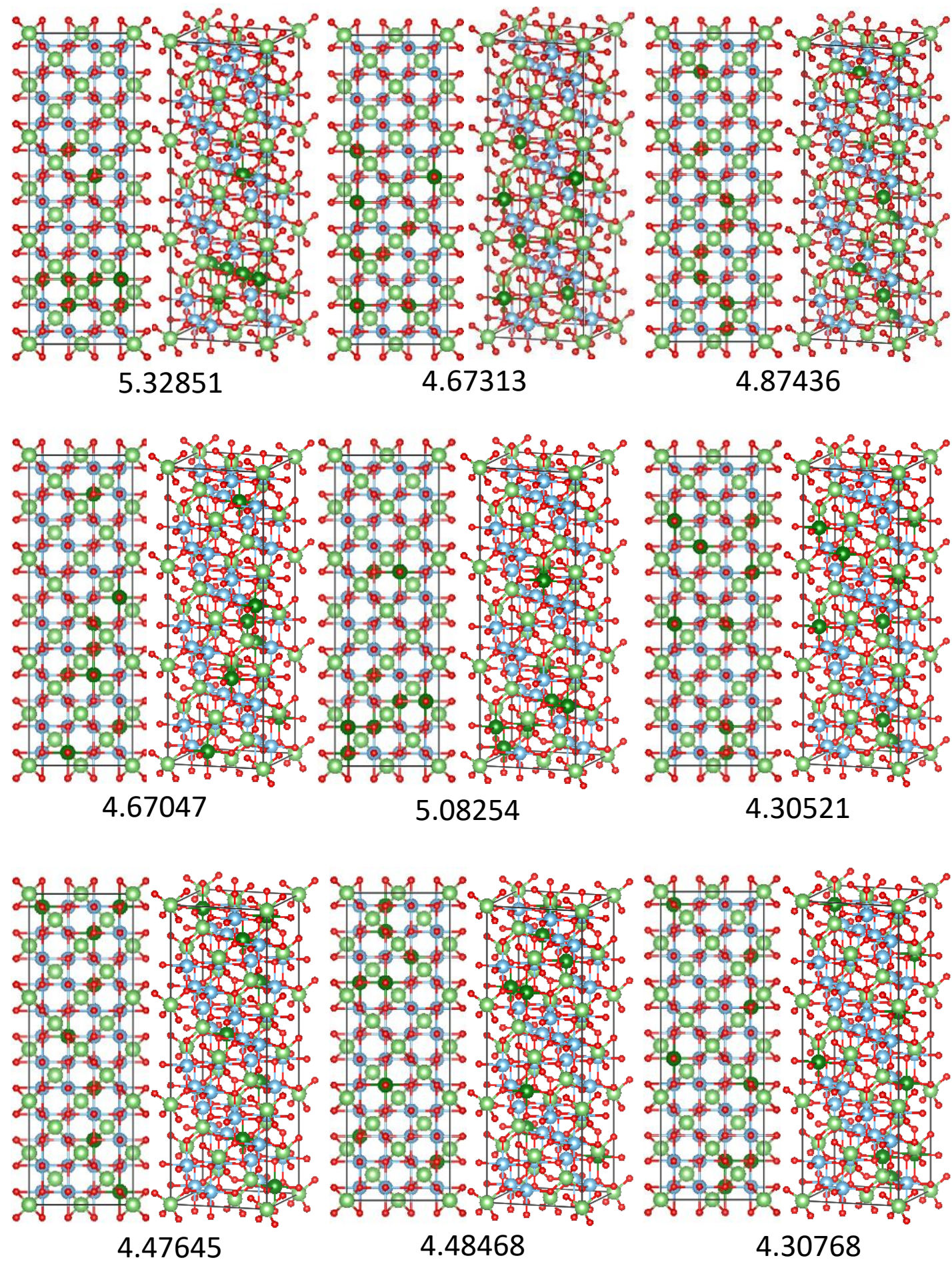


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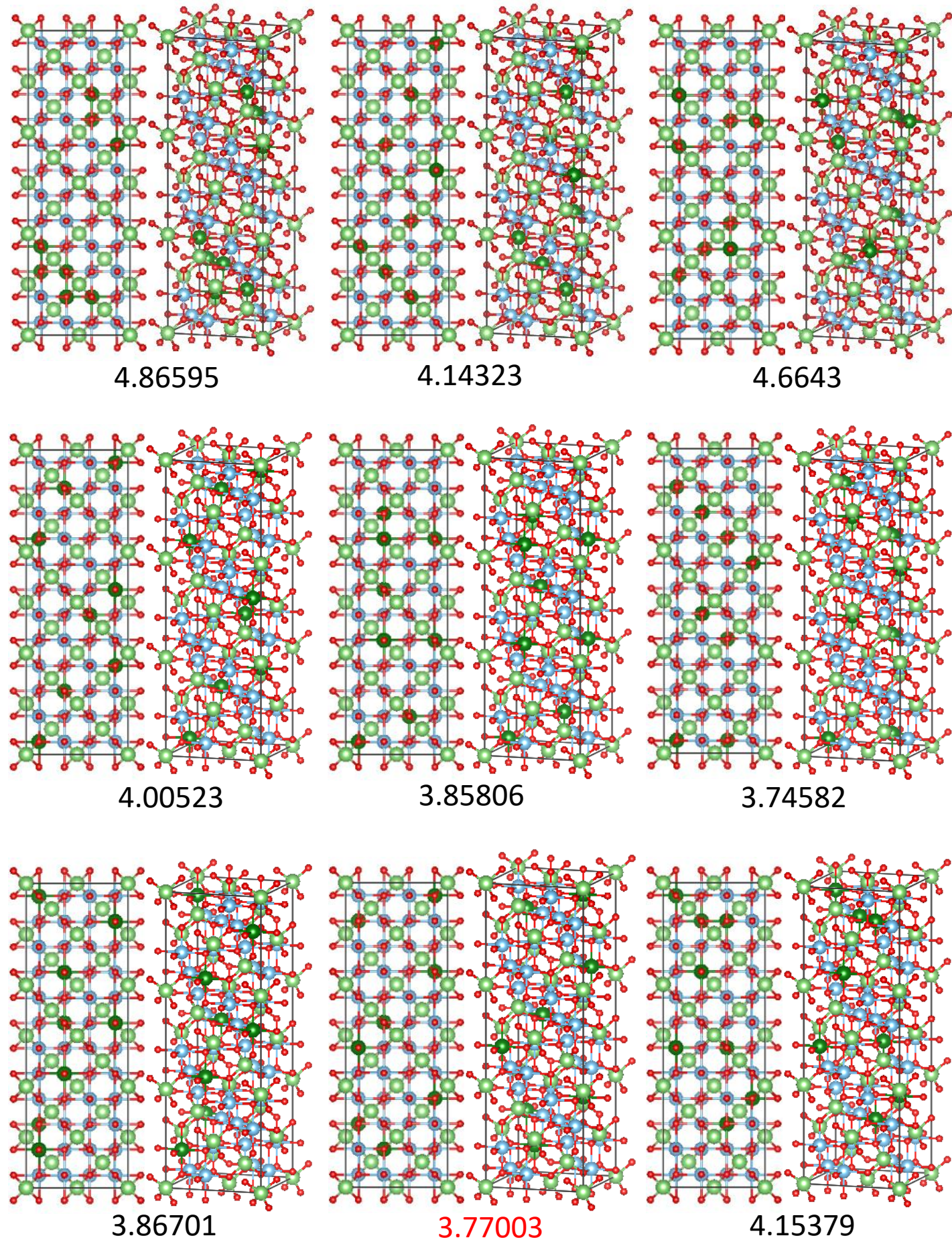


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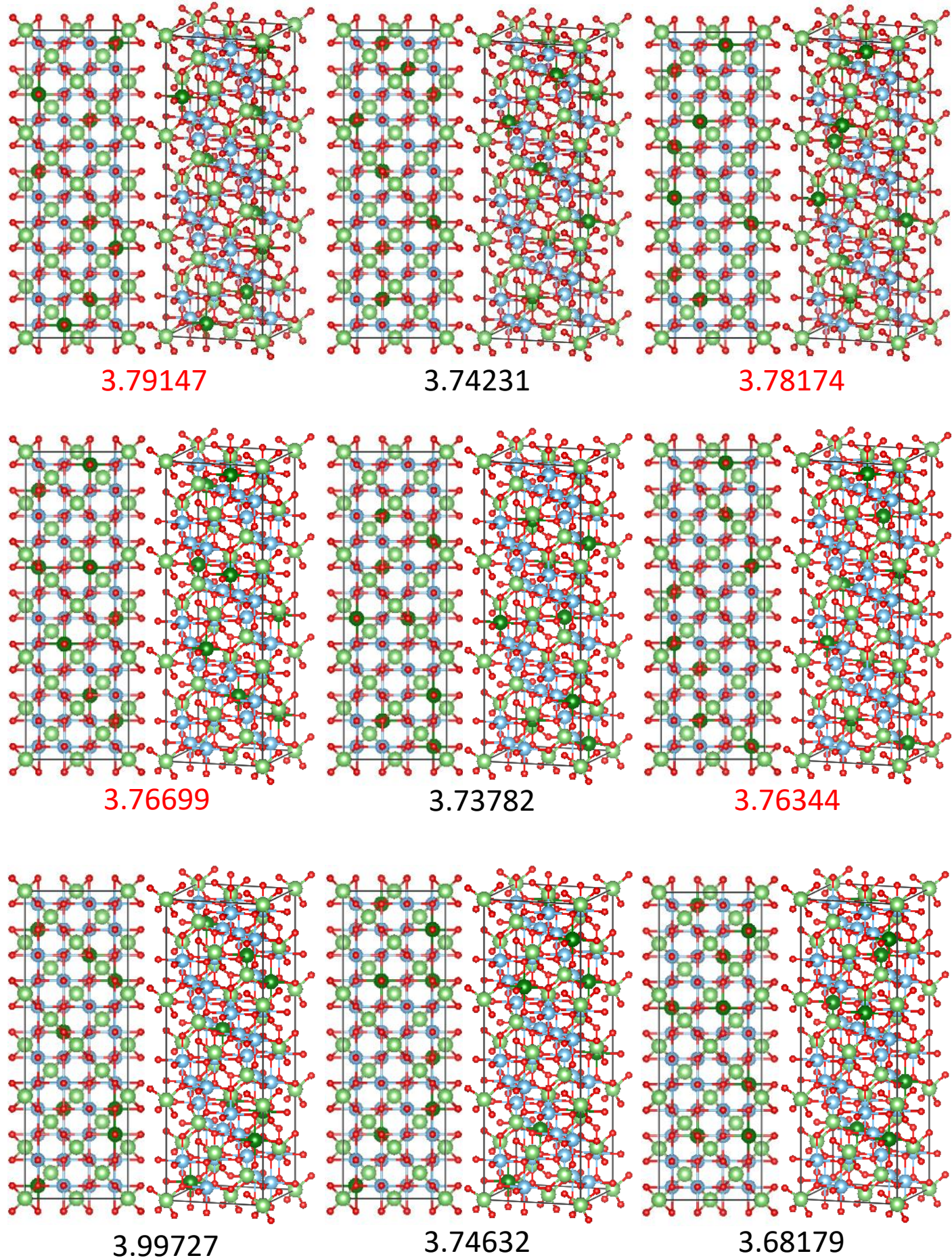


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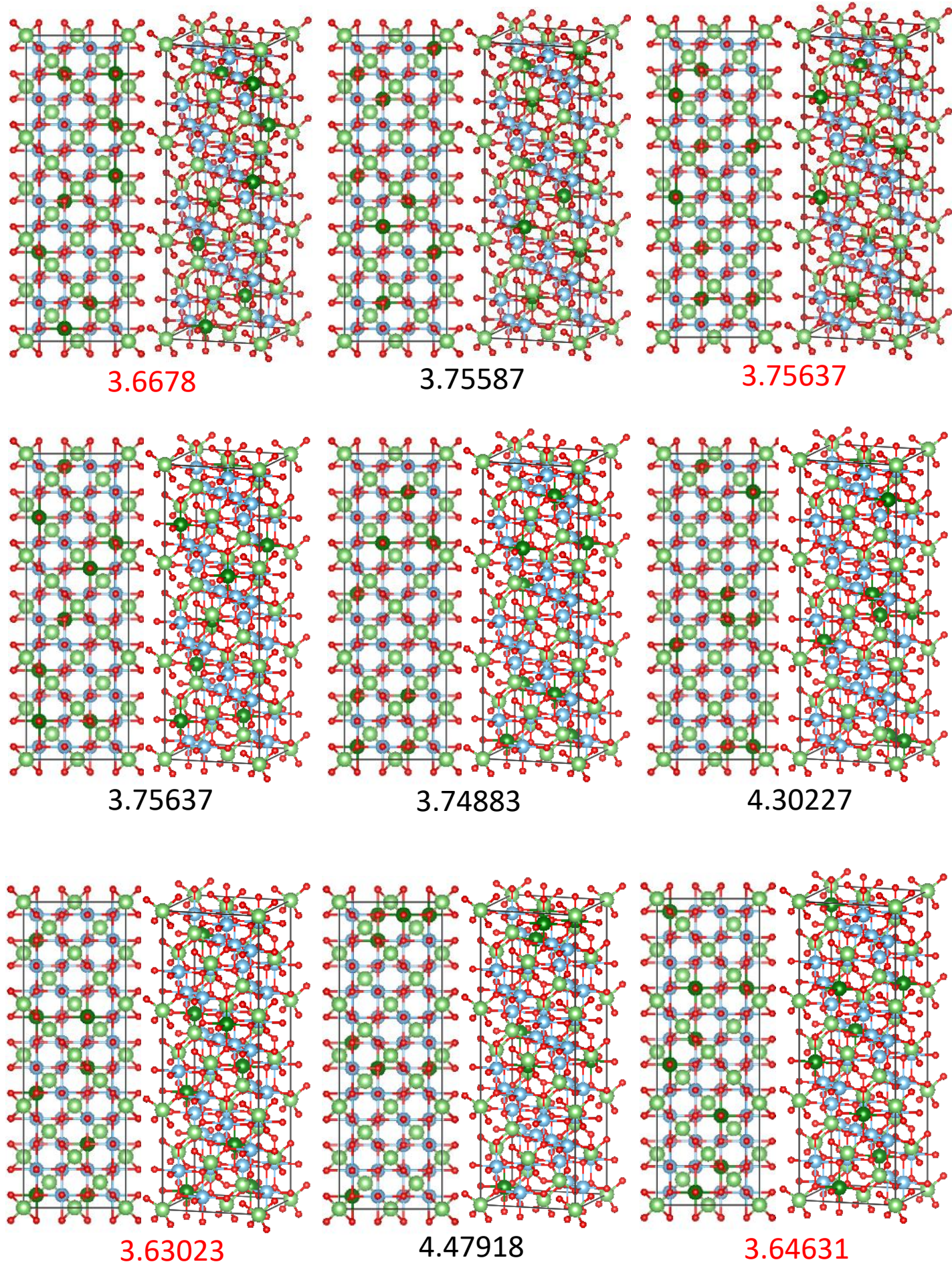


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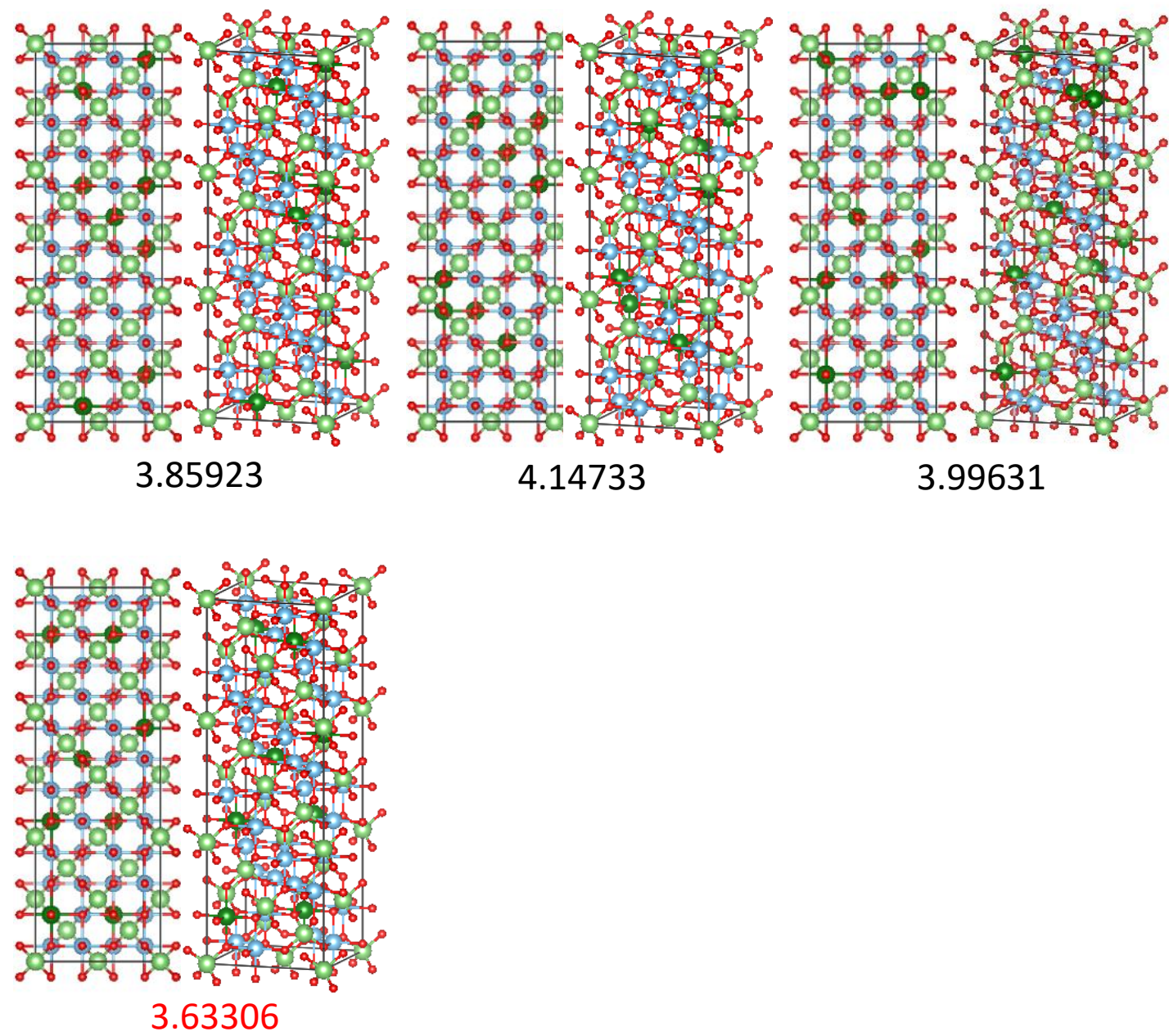


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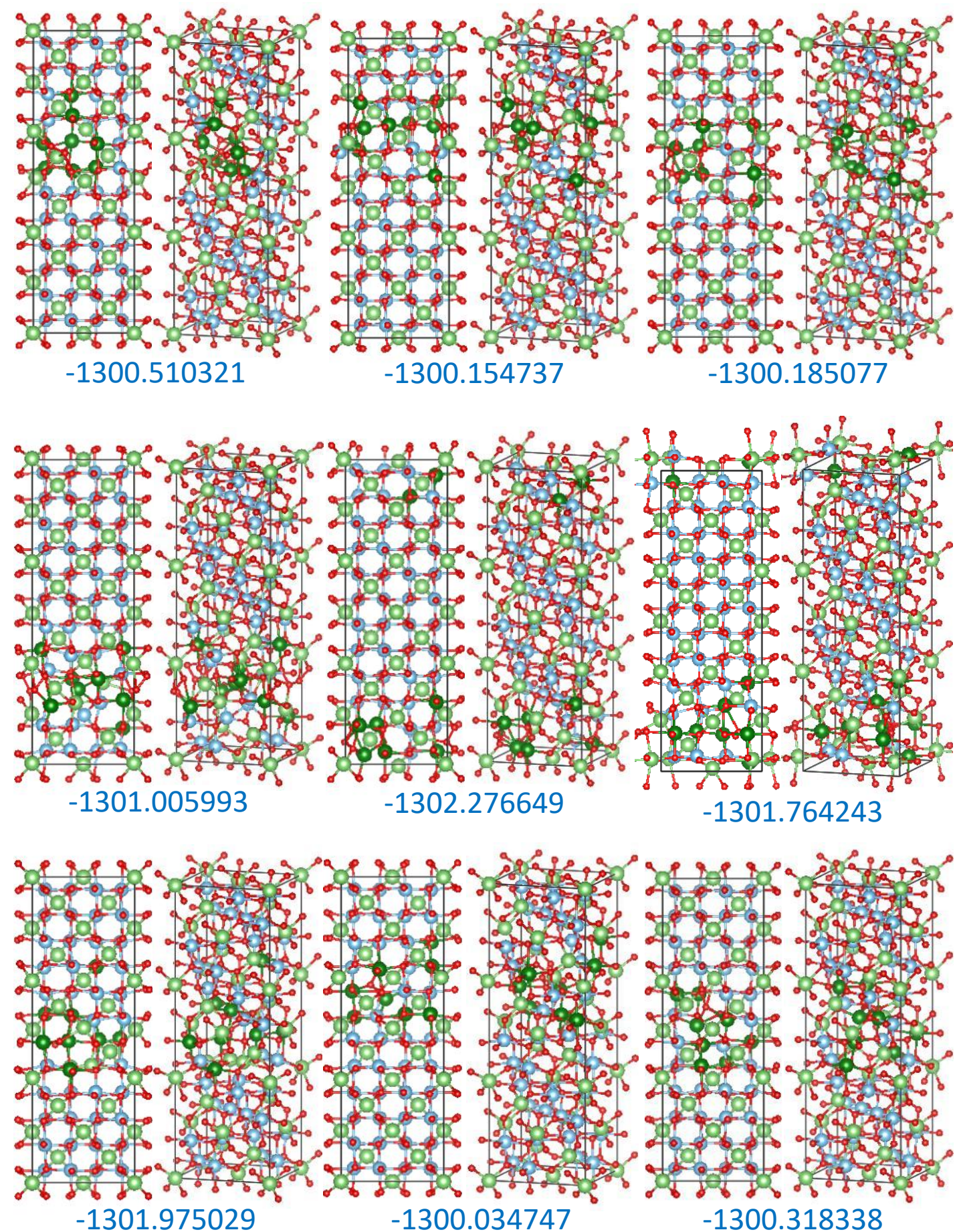


Figure S2 Side (left panels) and perspective (right panels) views of the optimized structures of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and total energy of the selected 58 models. Spheres in yellow, green, blue, and red represent Na, Li, Ti, and O atoms, respectively. Numbers in blue and red represent the 10 least and 10 most stable structures, respectively.

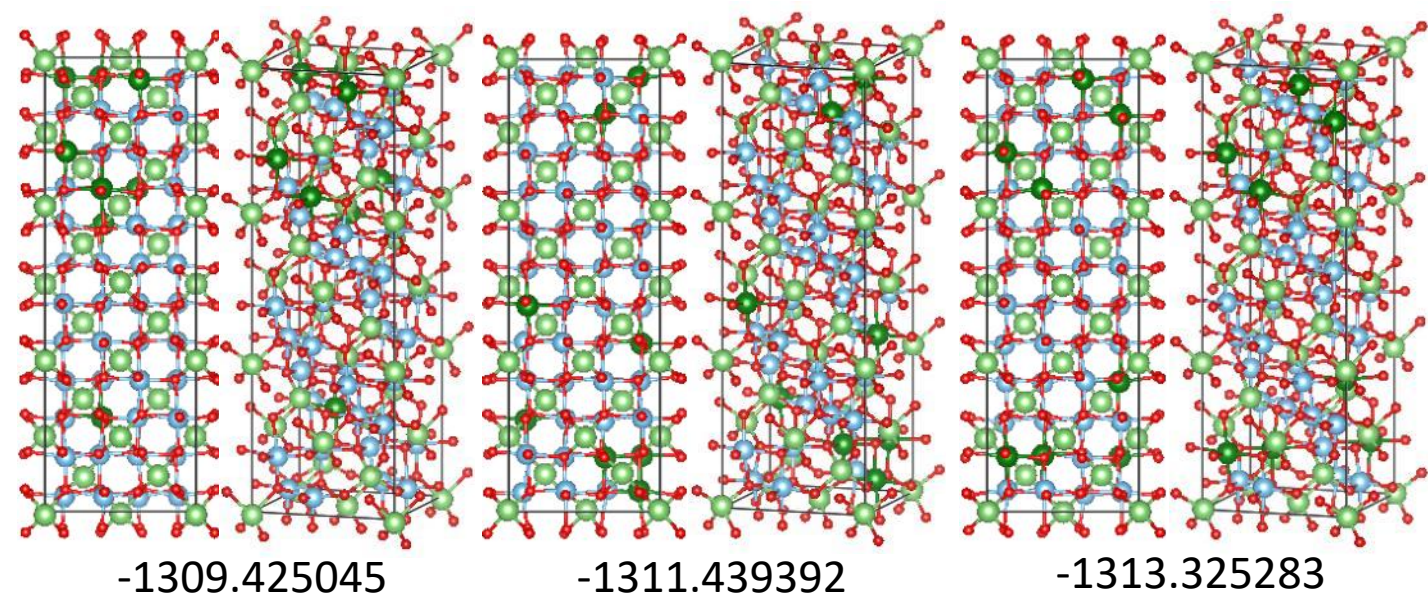
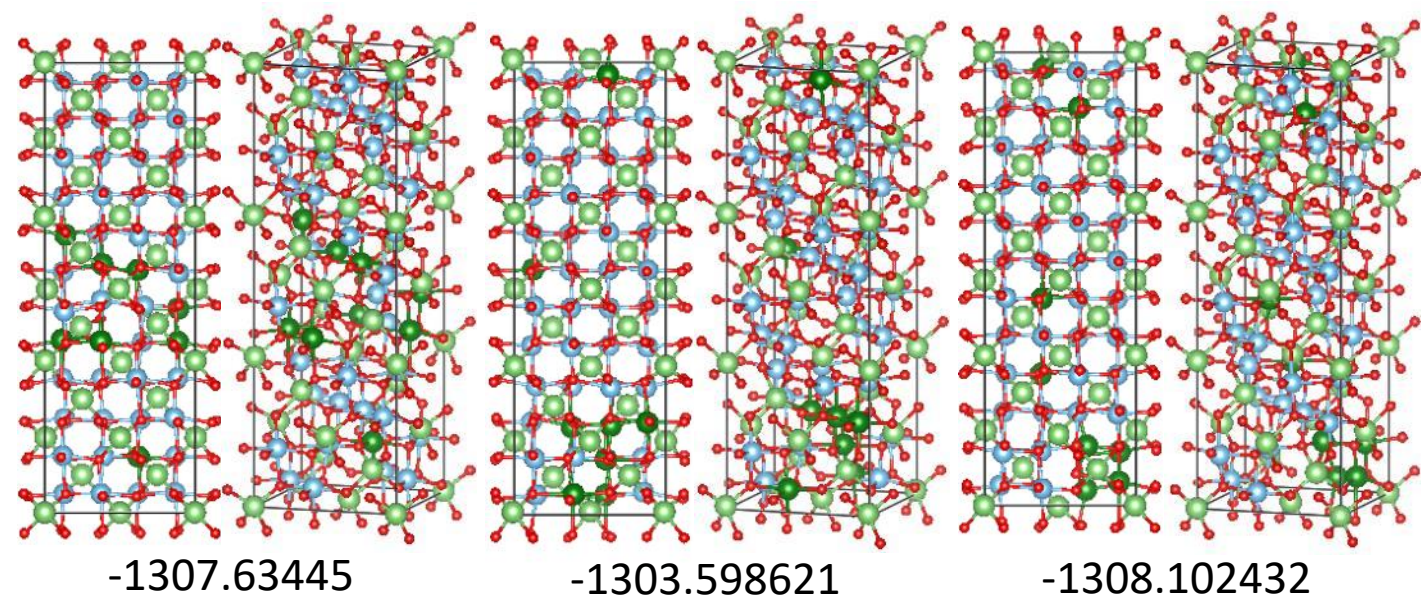
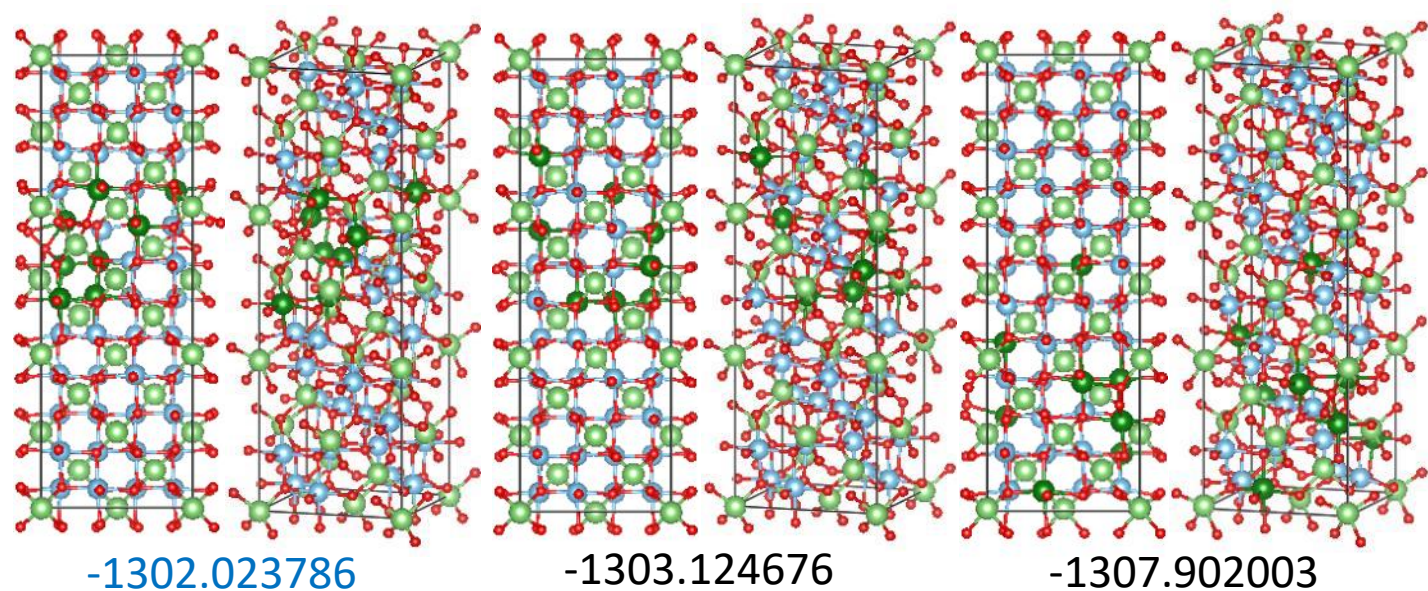


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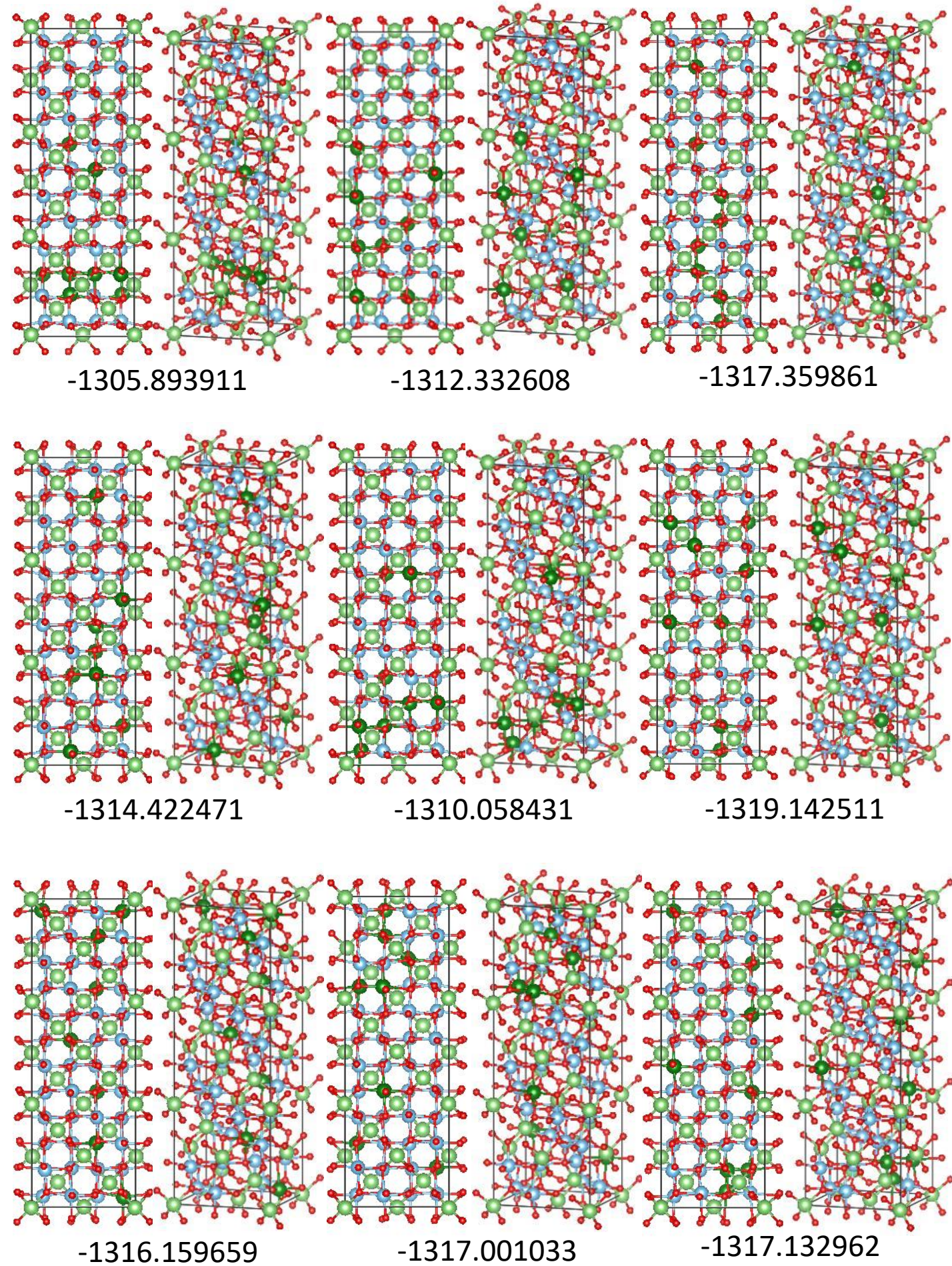


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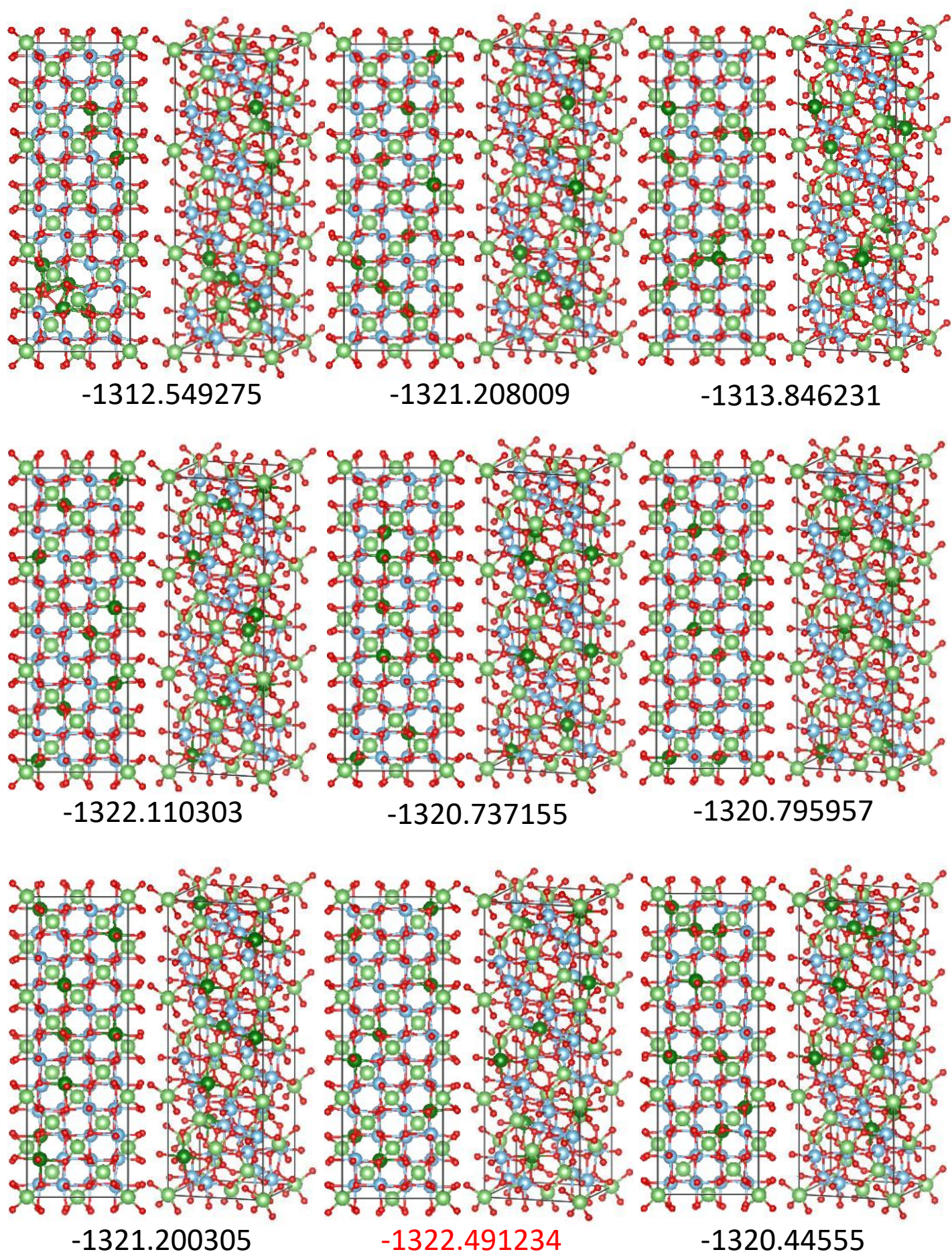
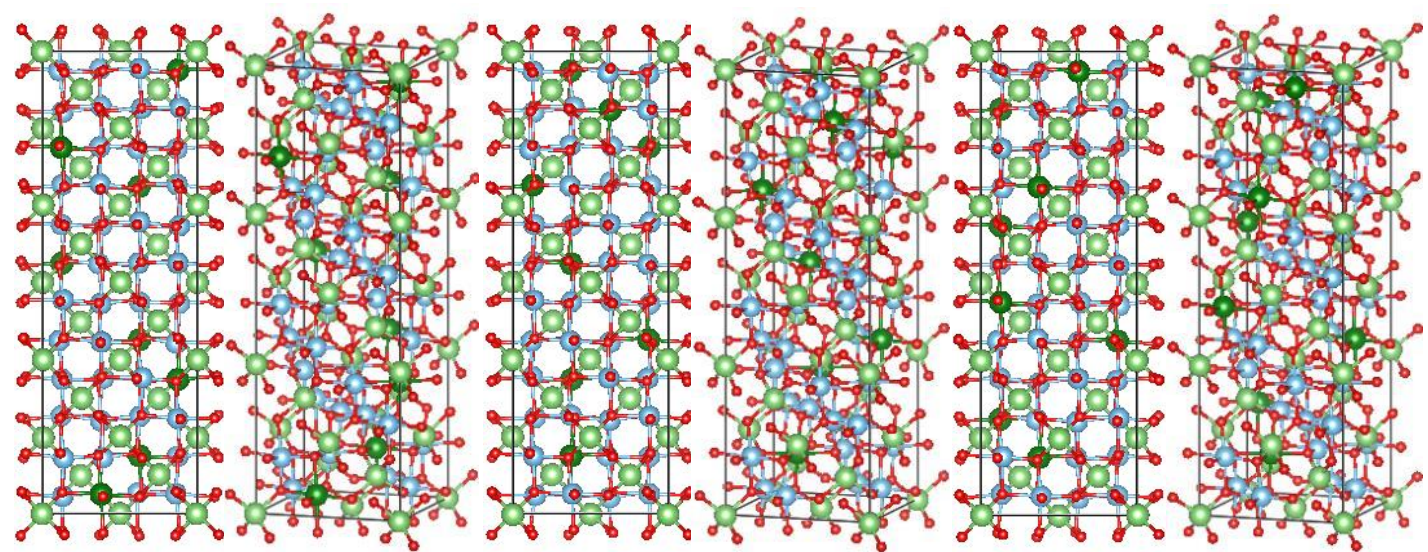


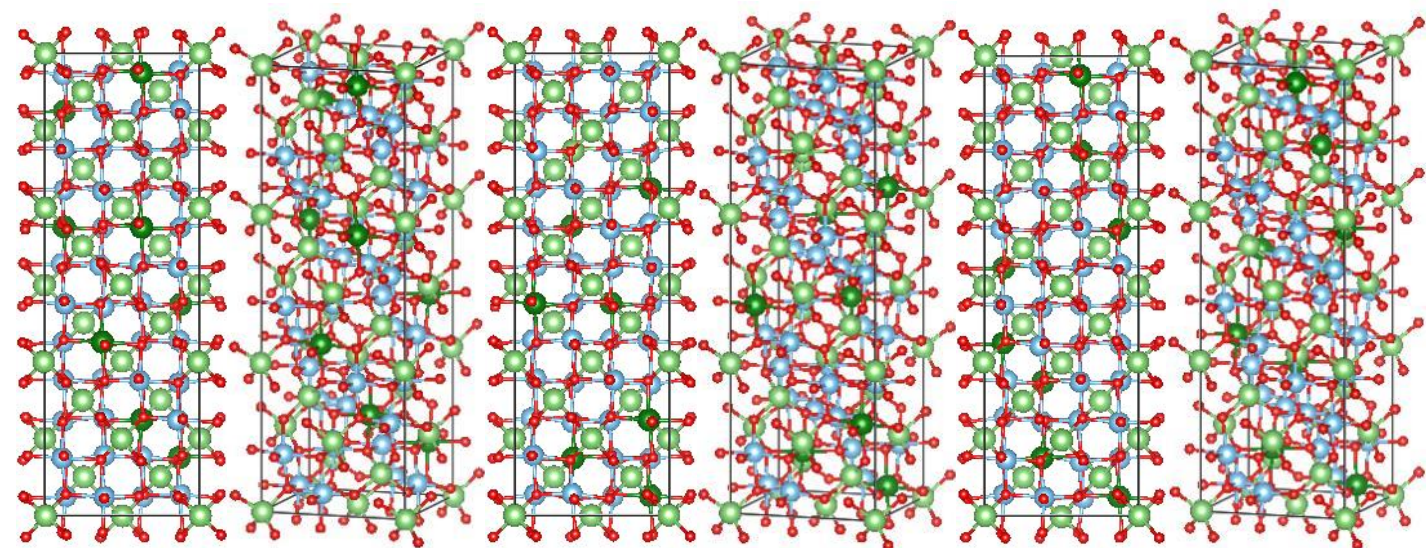
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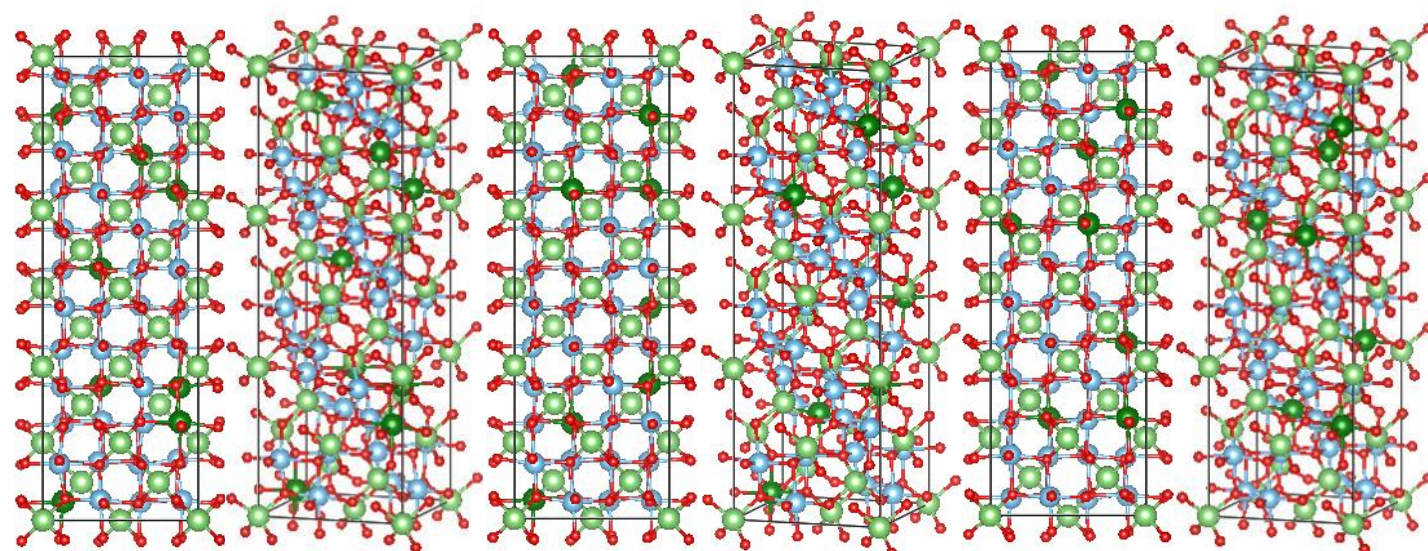
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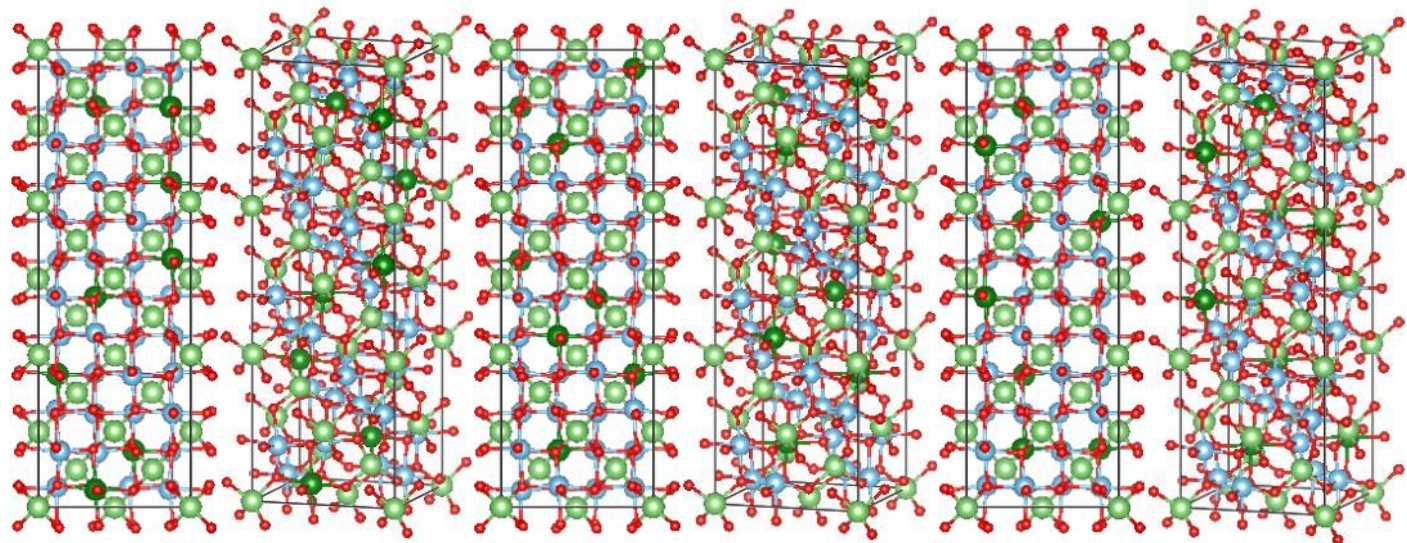


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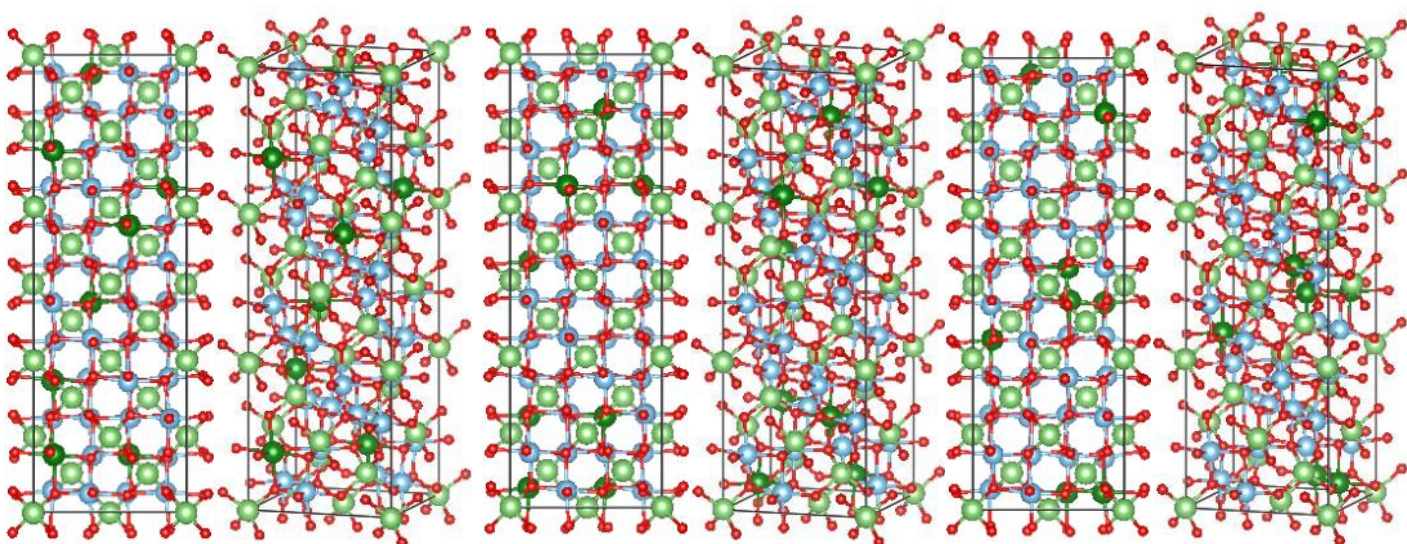
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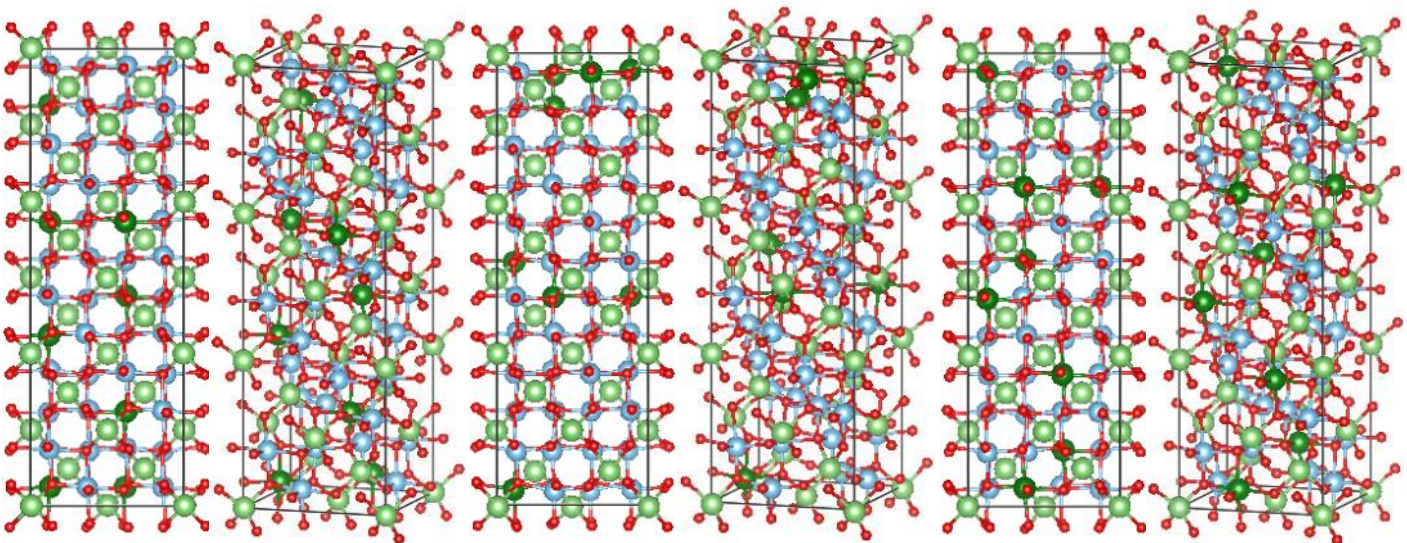
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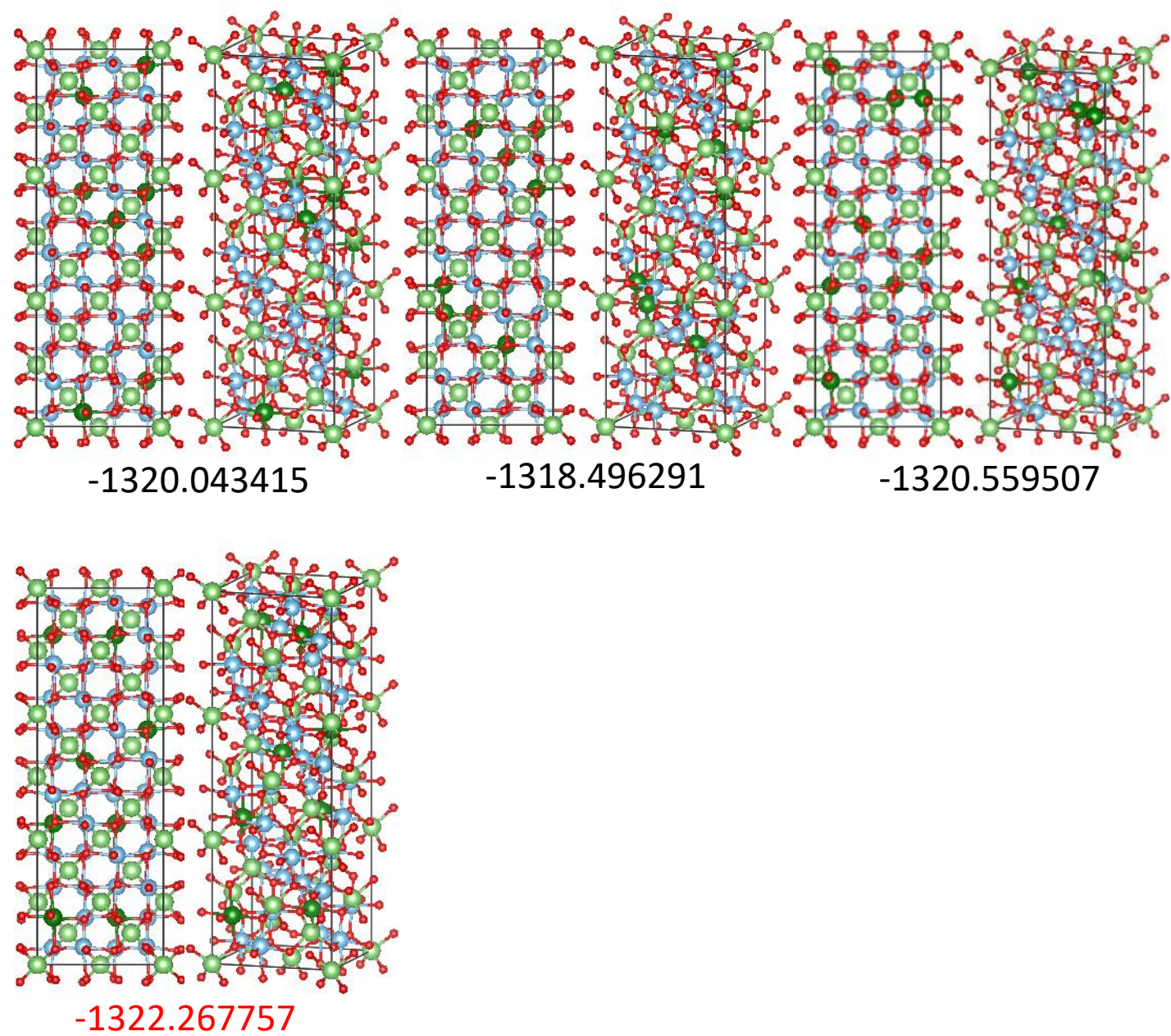


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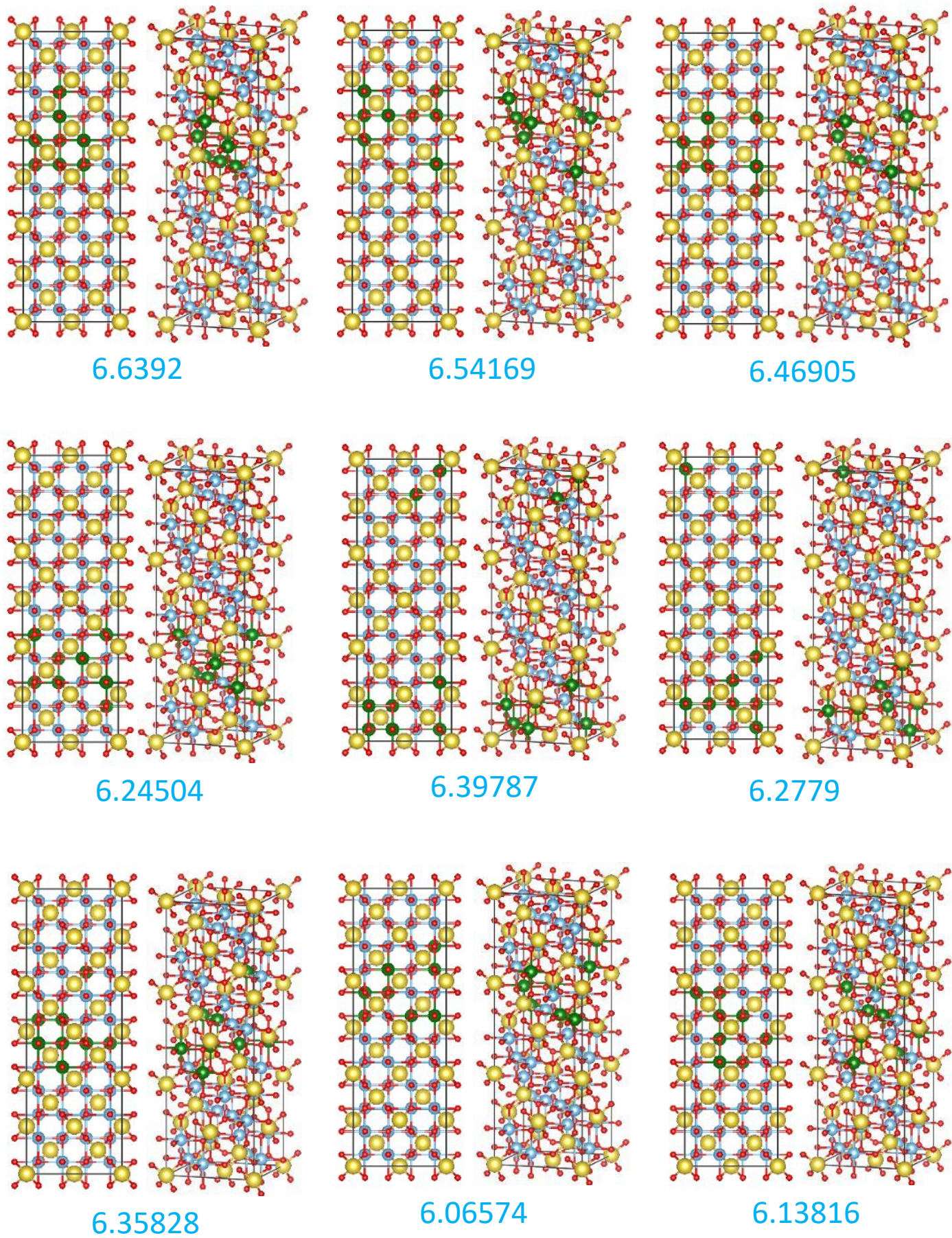
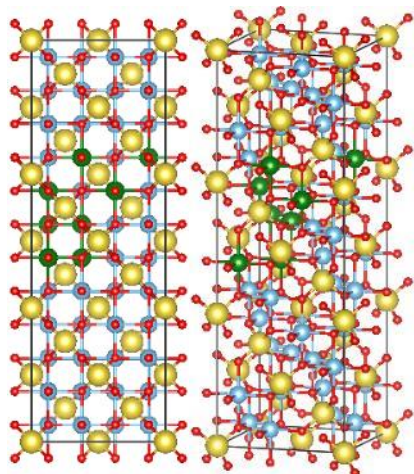
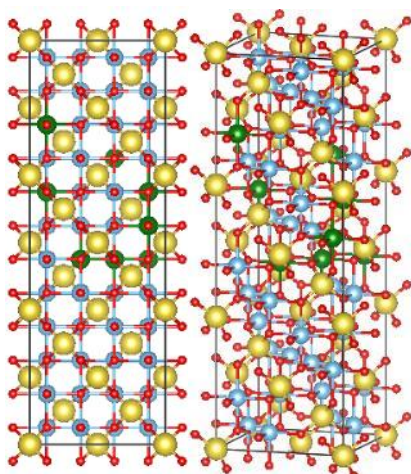


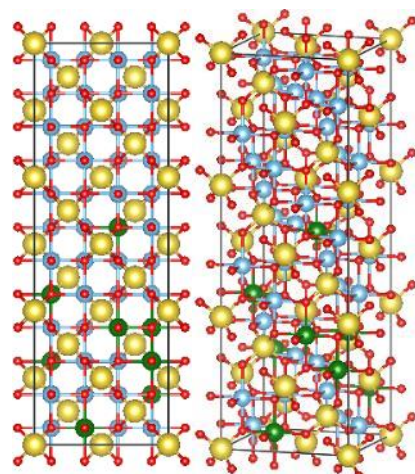
Figure S3 Side (left panels) and perspective (right panels) views of the initial structures of $\text{Na}_3\text{LiTi}_5\text{O}_{12}$ and S values of the selected 58 models. Spheres in yellow, green, blue, and red represent Na, Li, Ti, and O atoms, respectively. Numbers in blue and red represent the ten least and most stable structures, respectively.



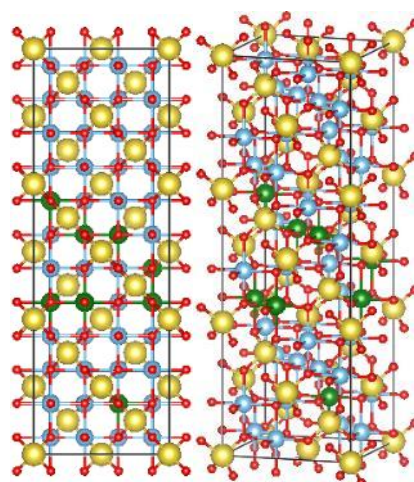
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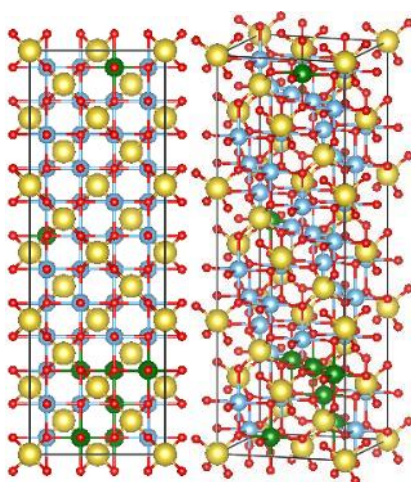
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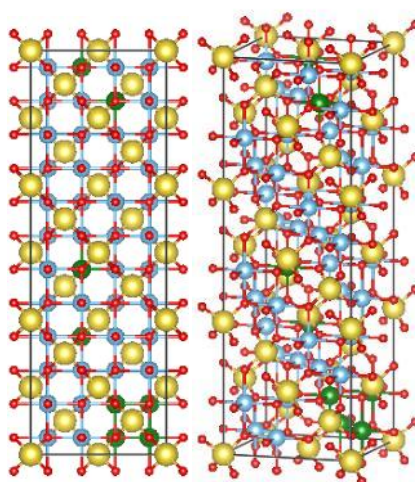
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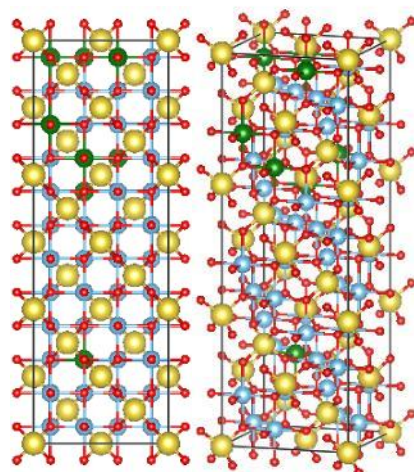
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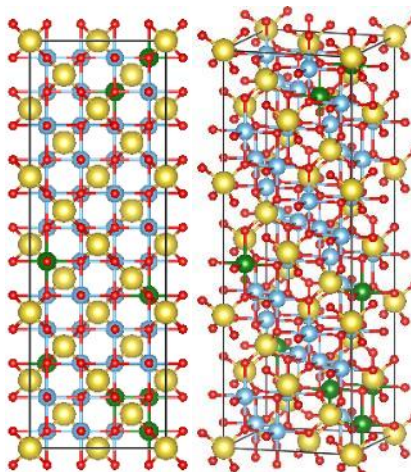
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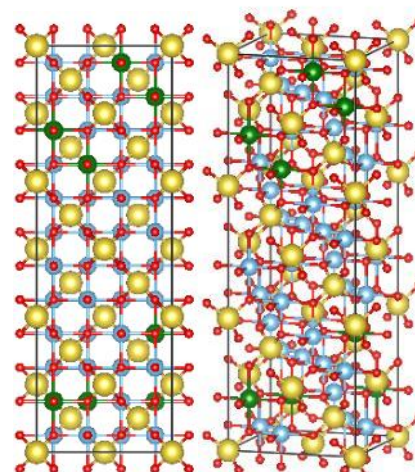
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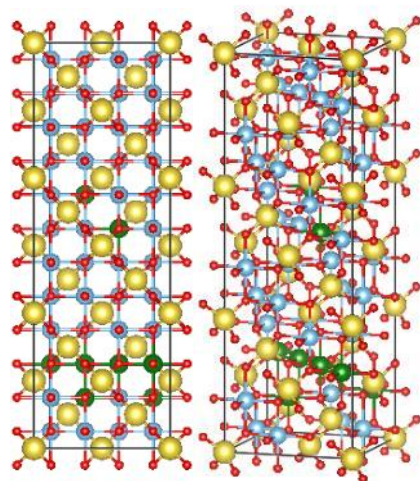


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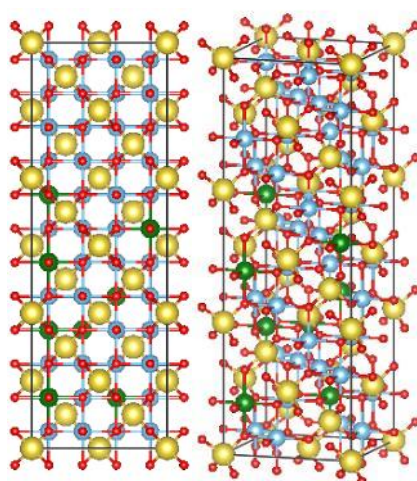


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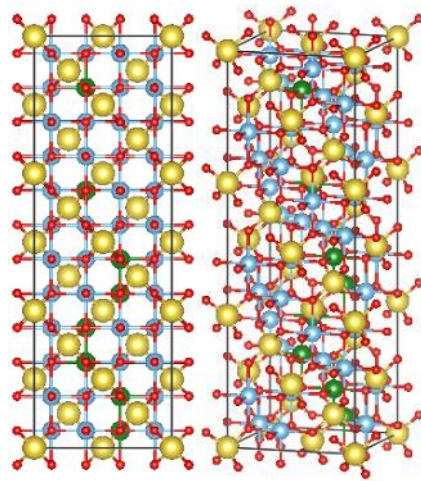
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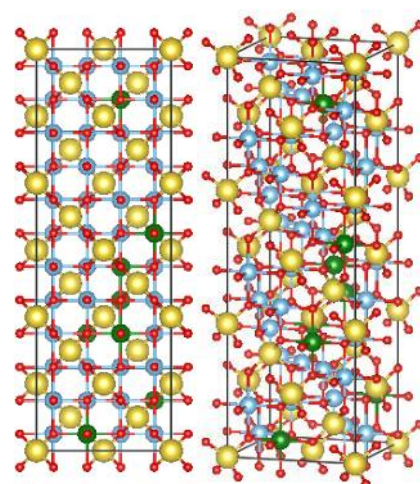
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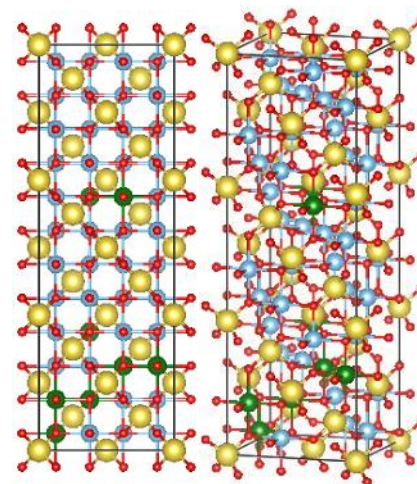
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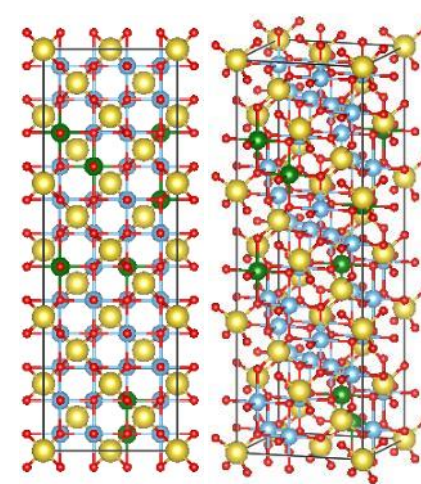
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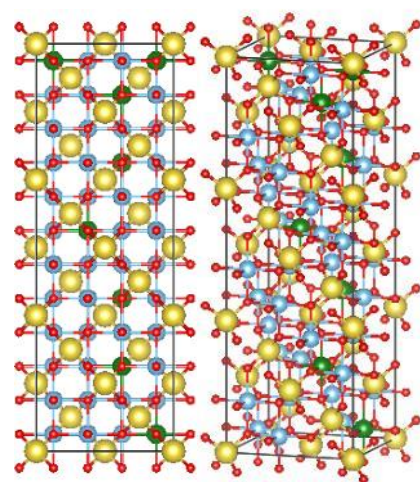
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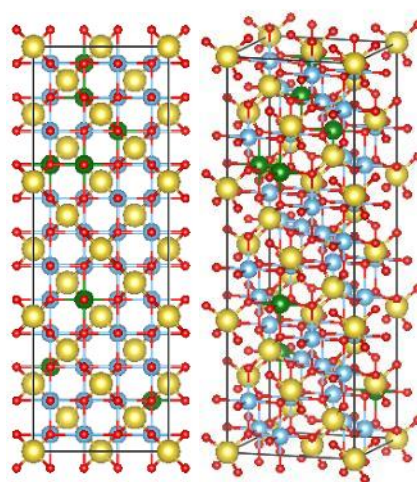
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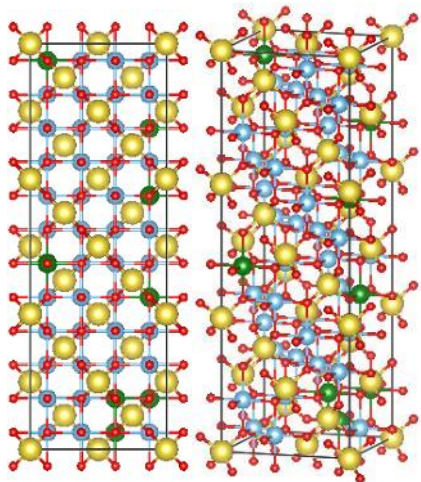
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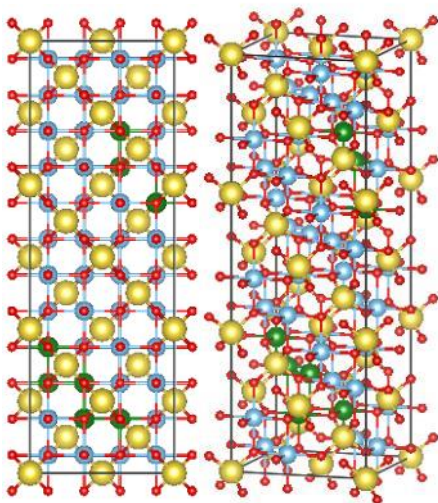


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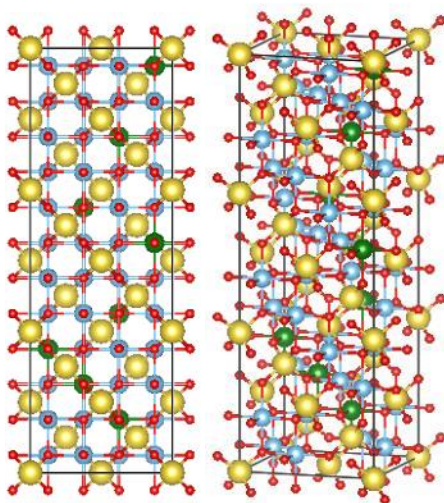


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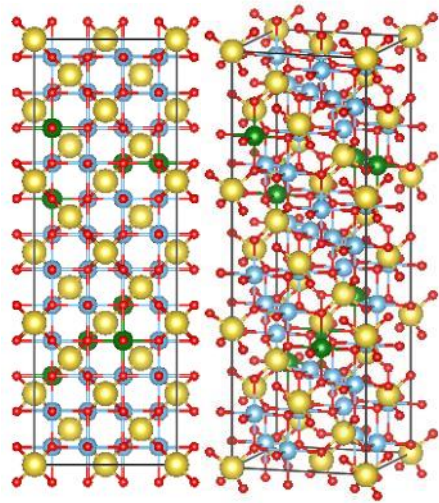
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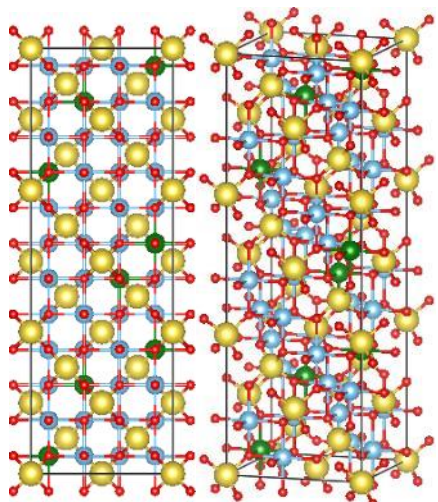
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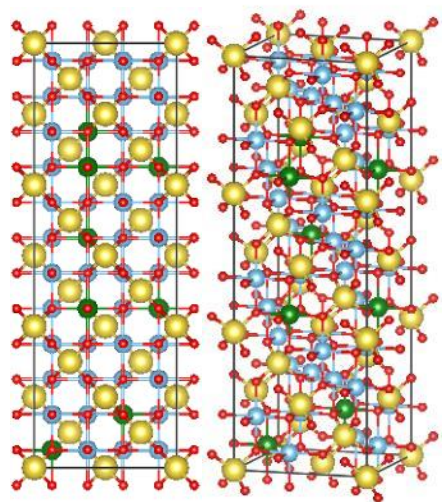
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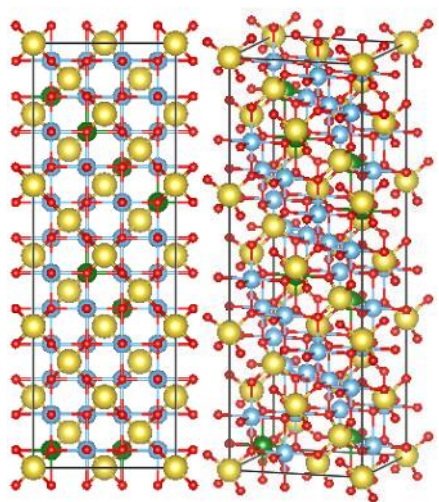
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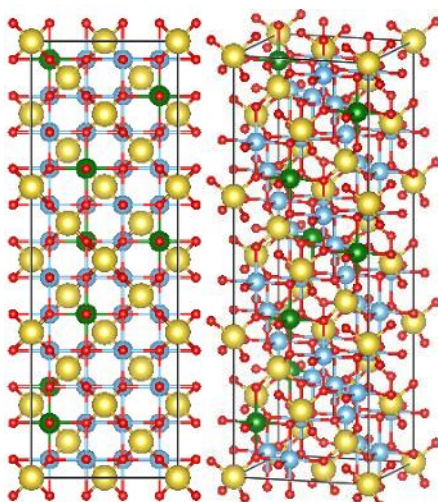
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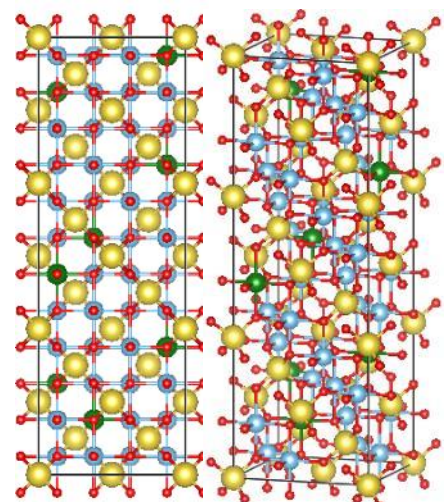
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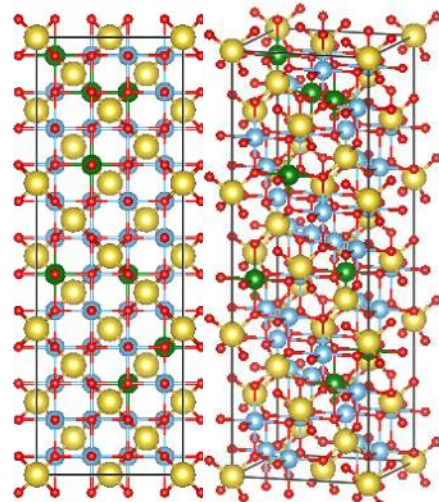
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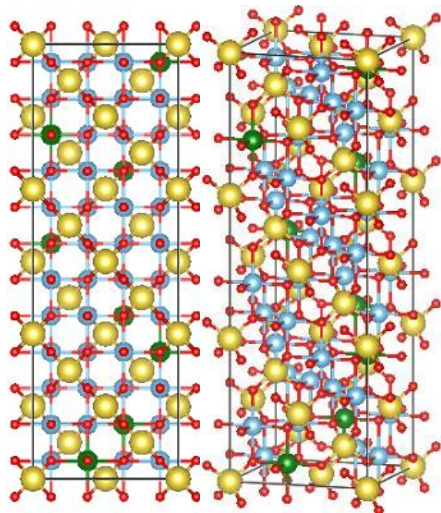


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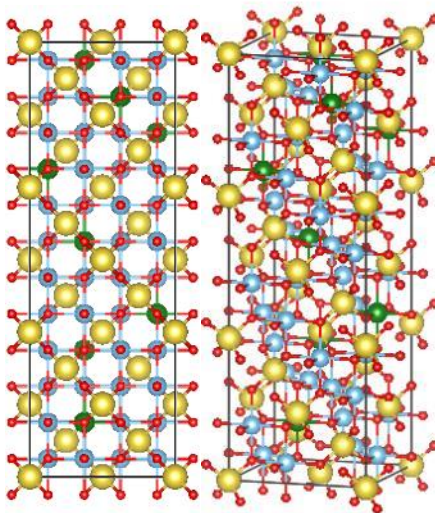


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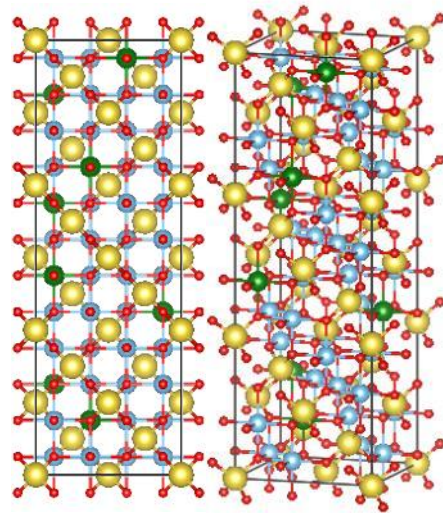
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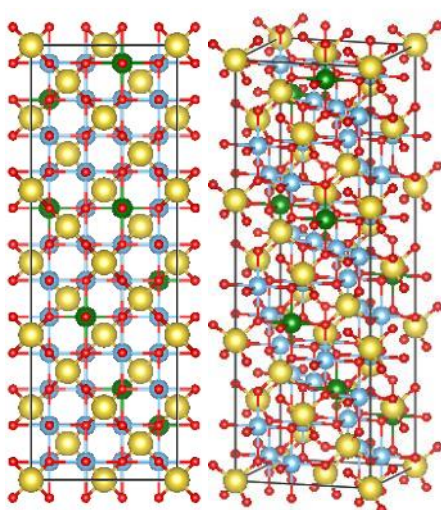
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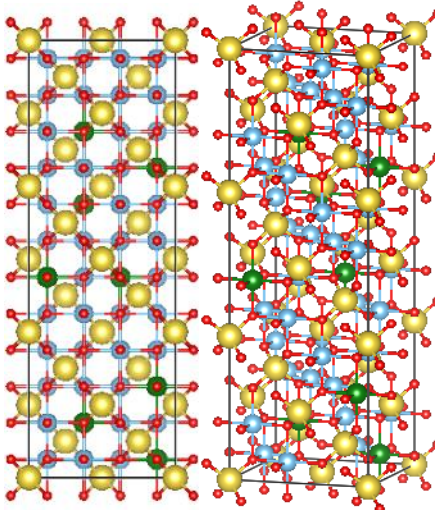
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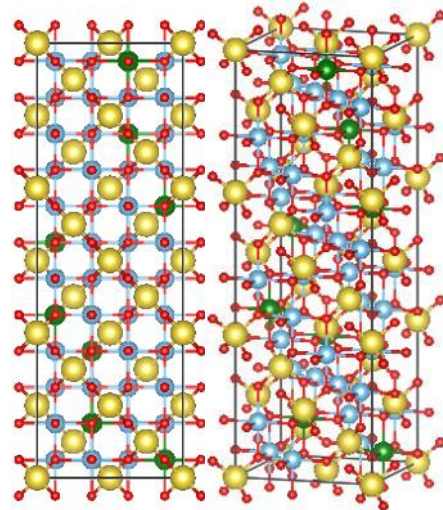
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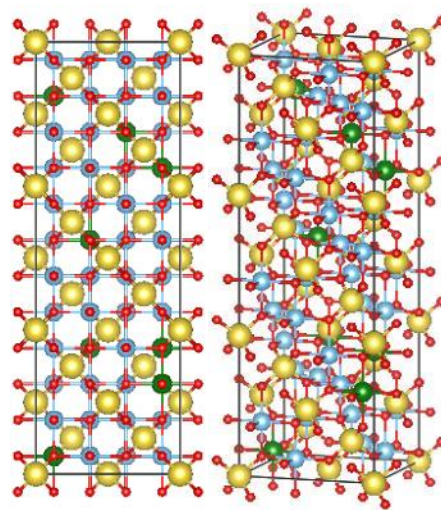
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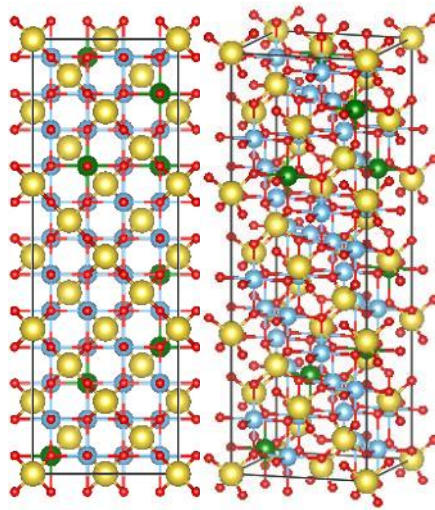
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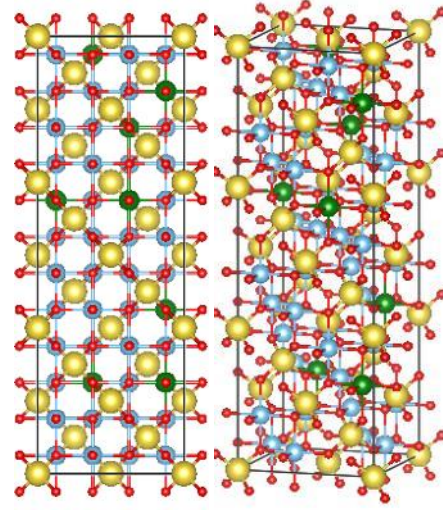
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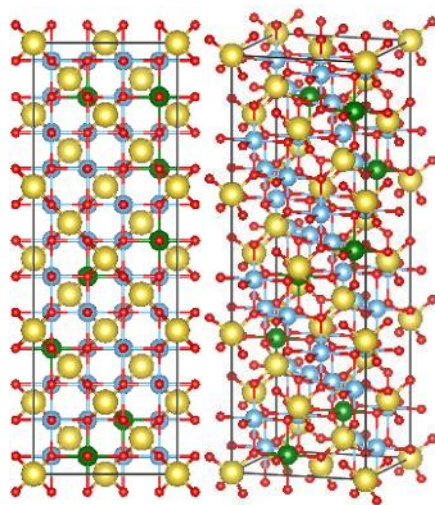


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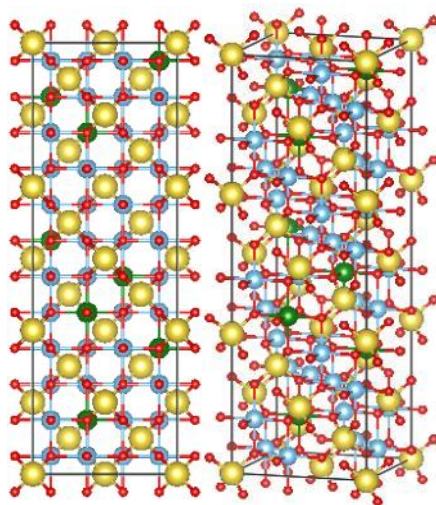


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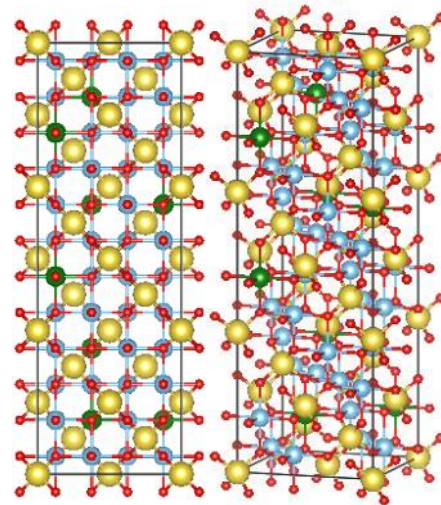
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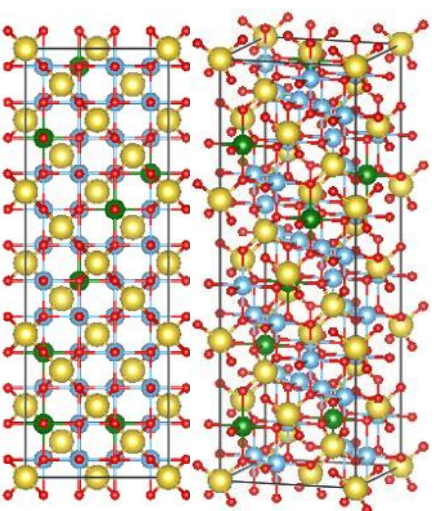
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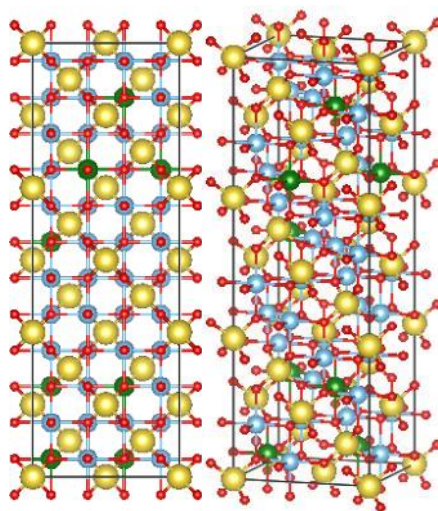
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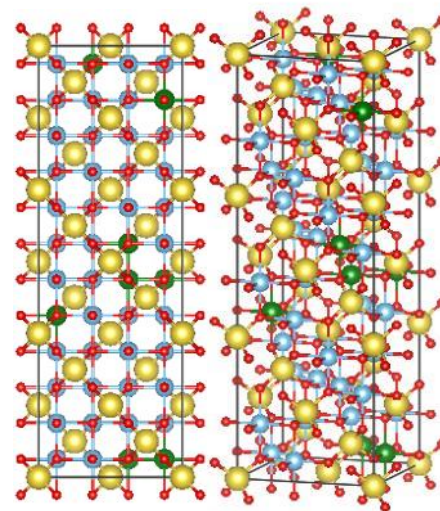
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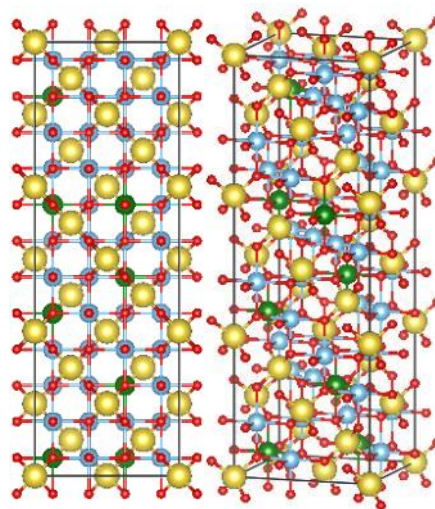
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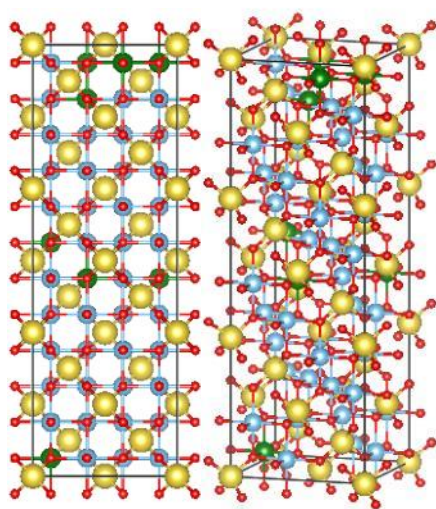
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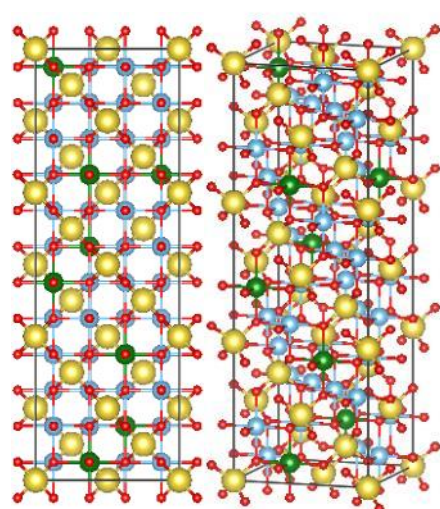
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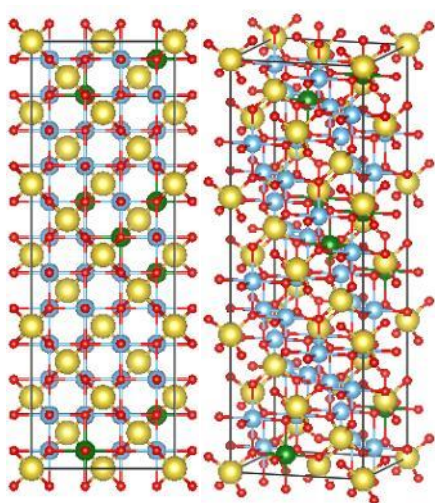


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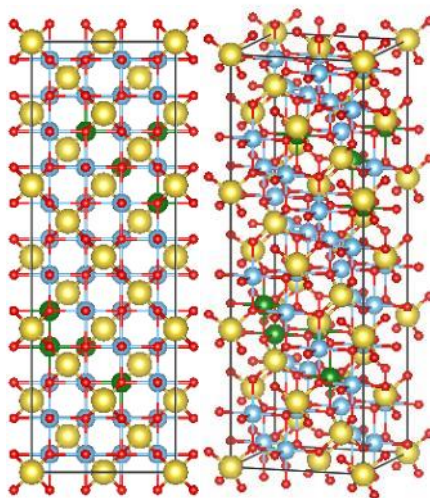


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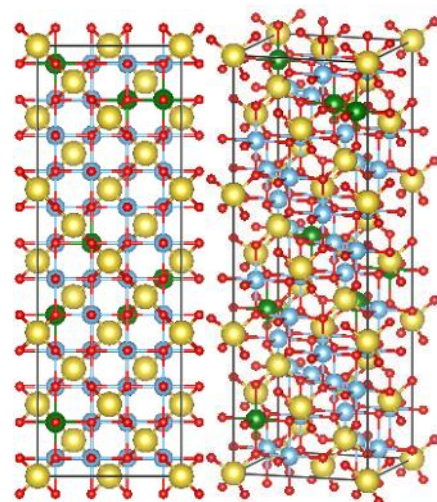
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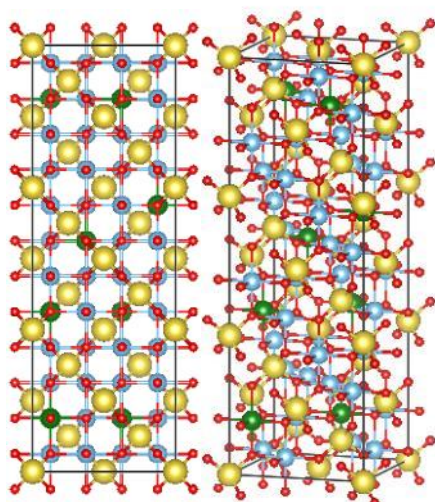
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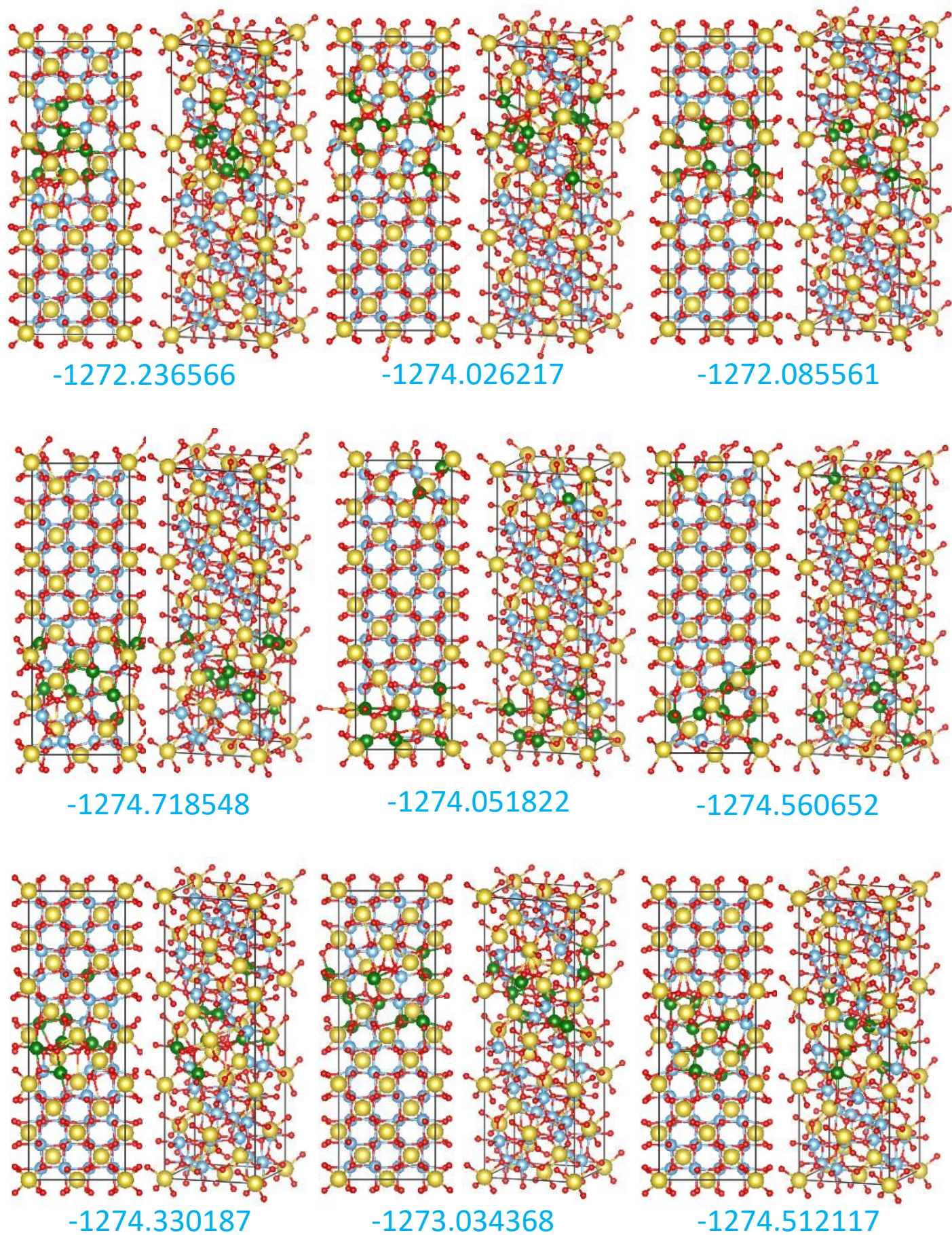
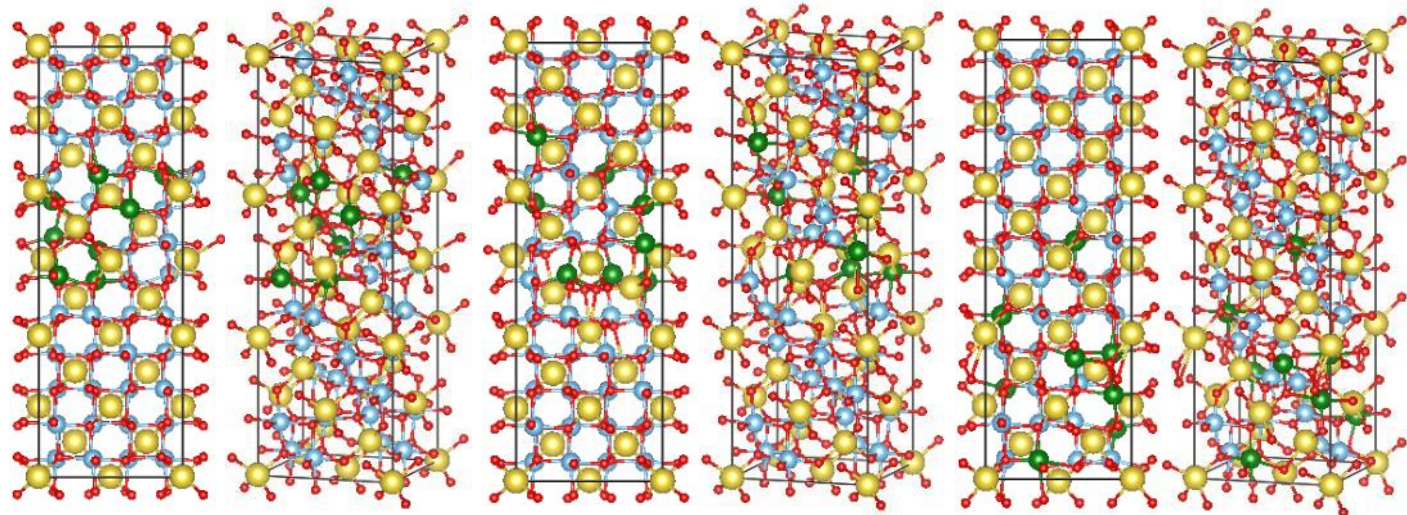


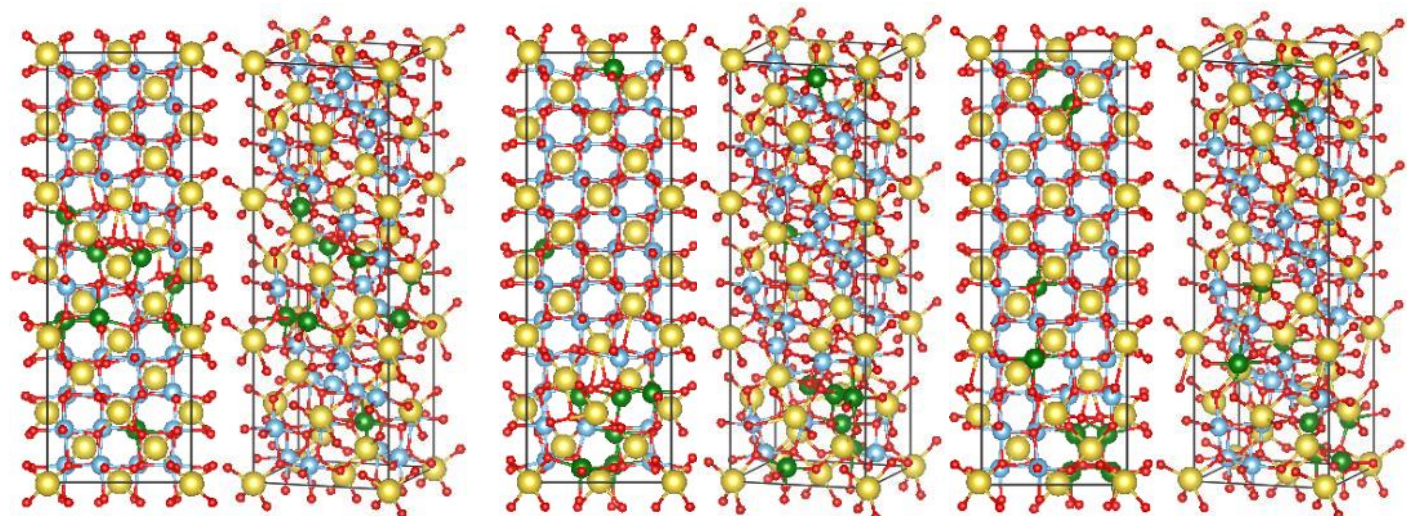
Figure S4 Side (left panels) and perspective (right panels) views of the optimized structures of $\text{Na}_3\text{LiTi}_5\text{O}_{12}$ and total energy of selected 58 models. Spheres in yellow, green, blue, and red represent Na, Li, Ti, and O atoms, respectively. Numbers in blue and red represent the ten least and most stable structures, respectively.



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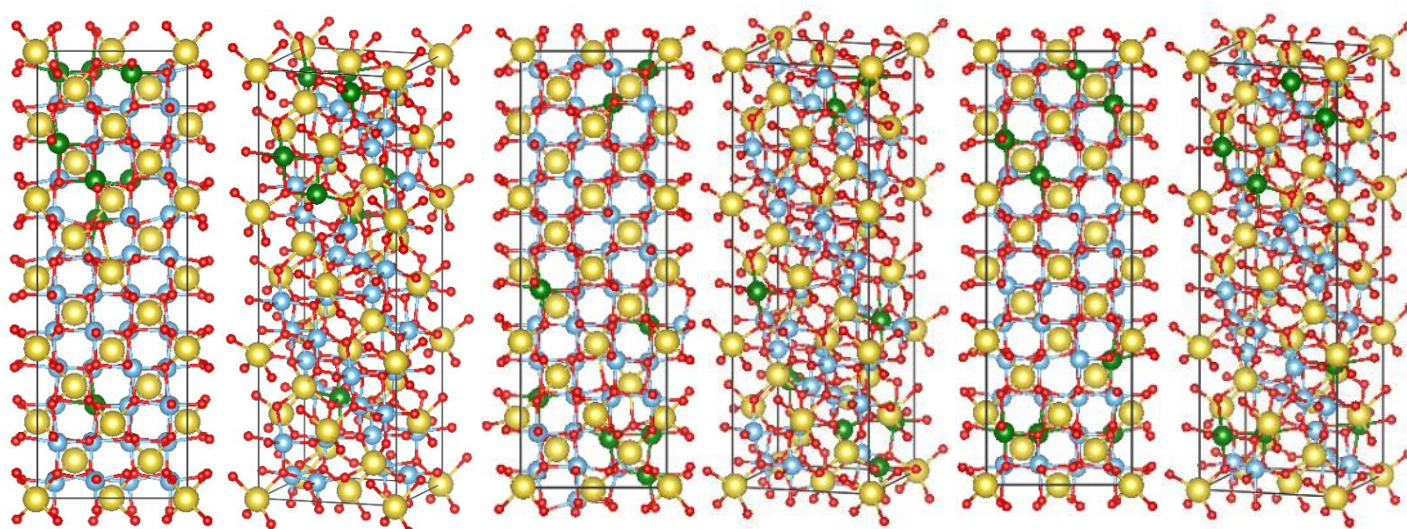
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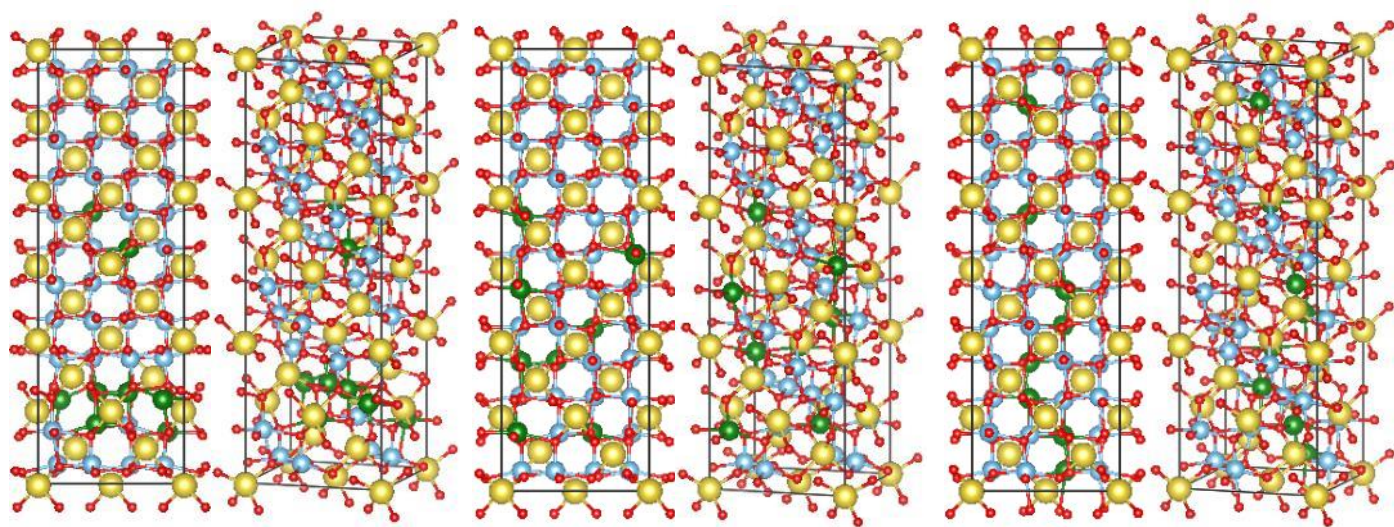


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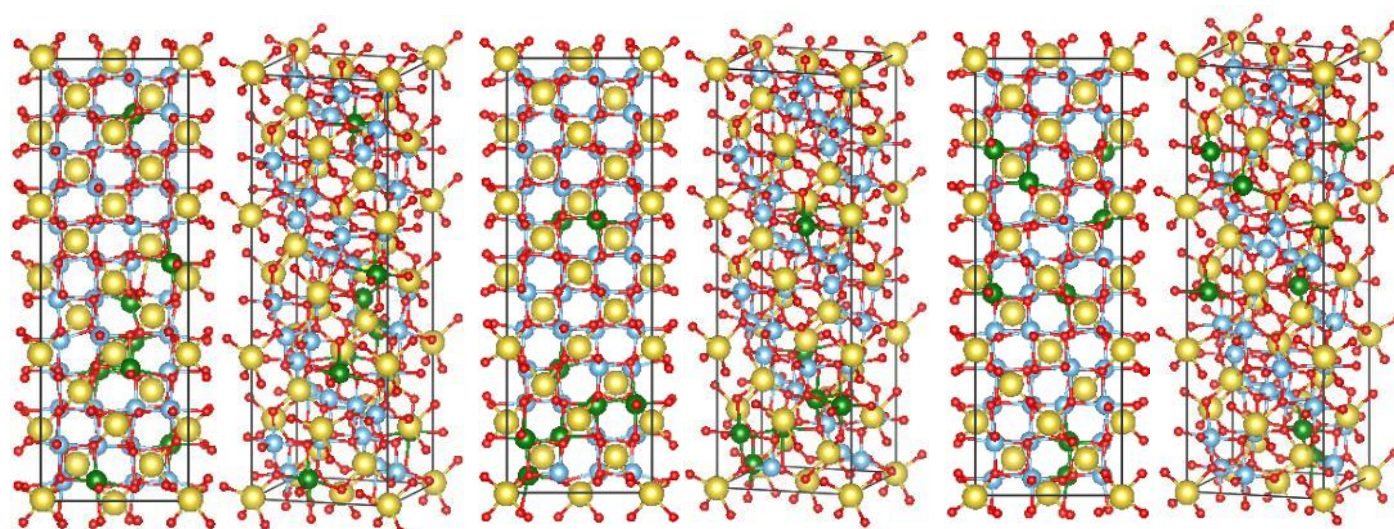
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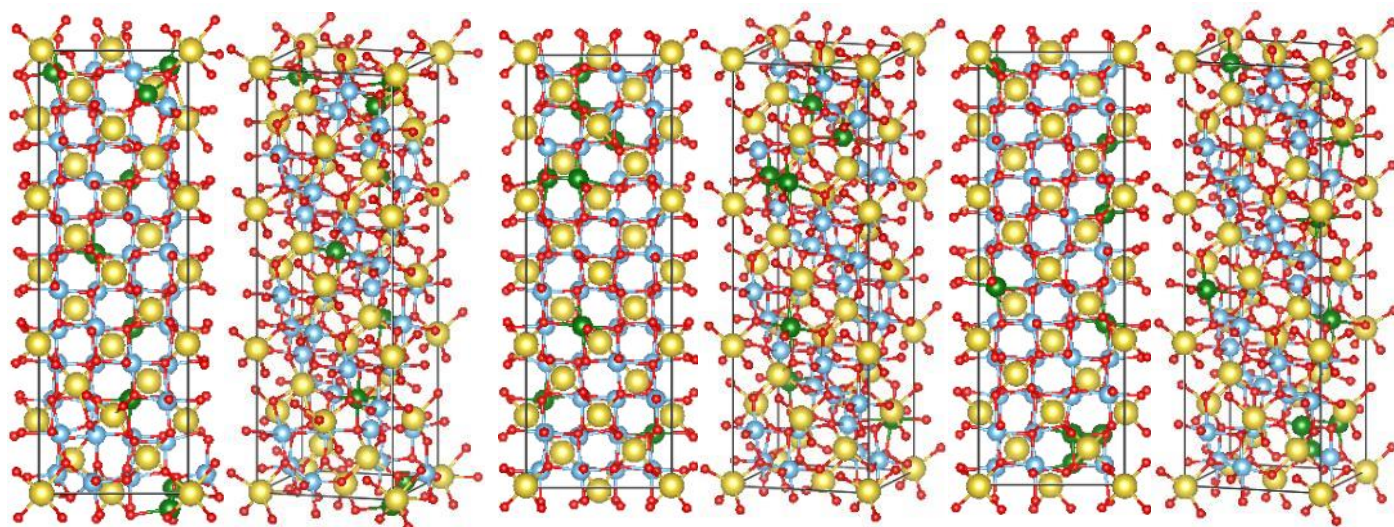
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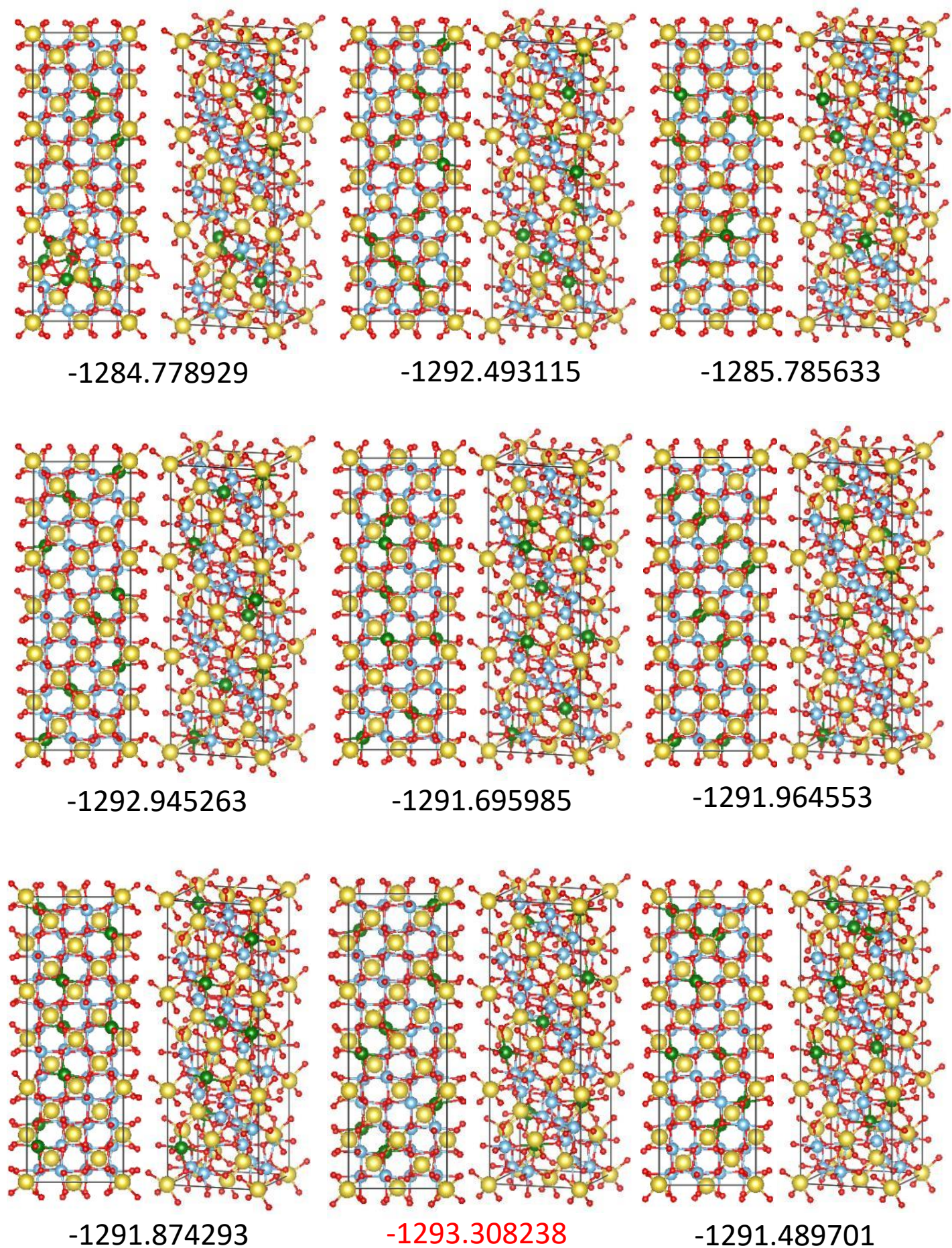
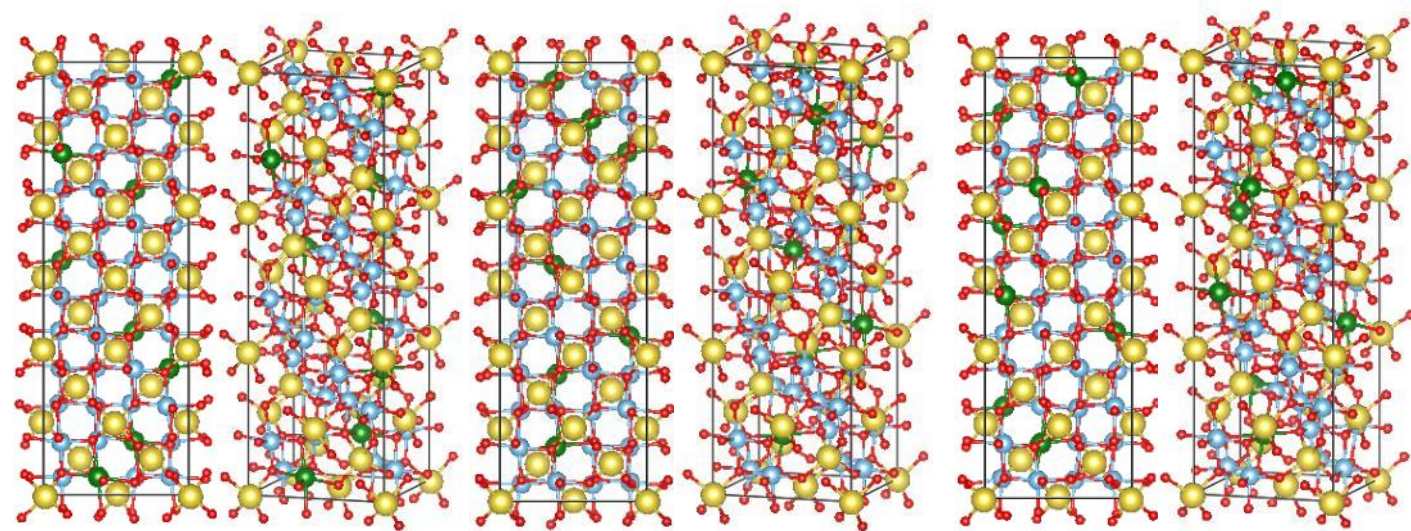


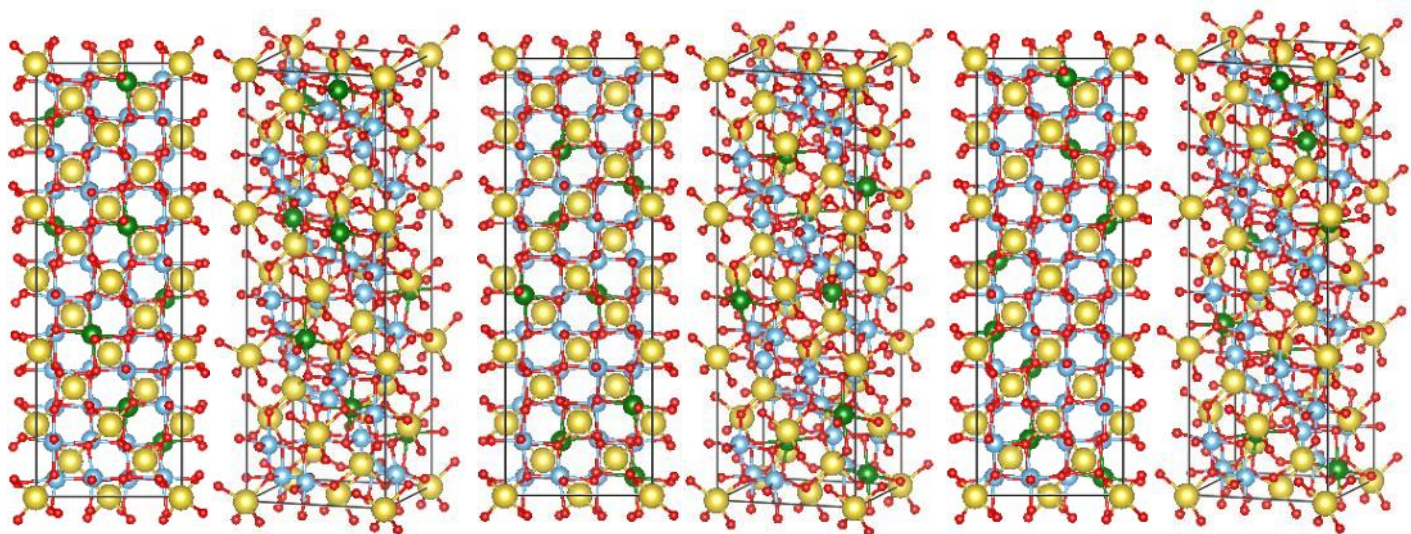
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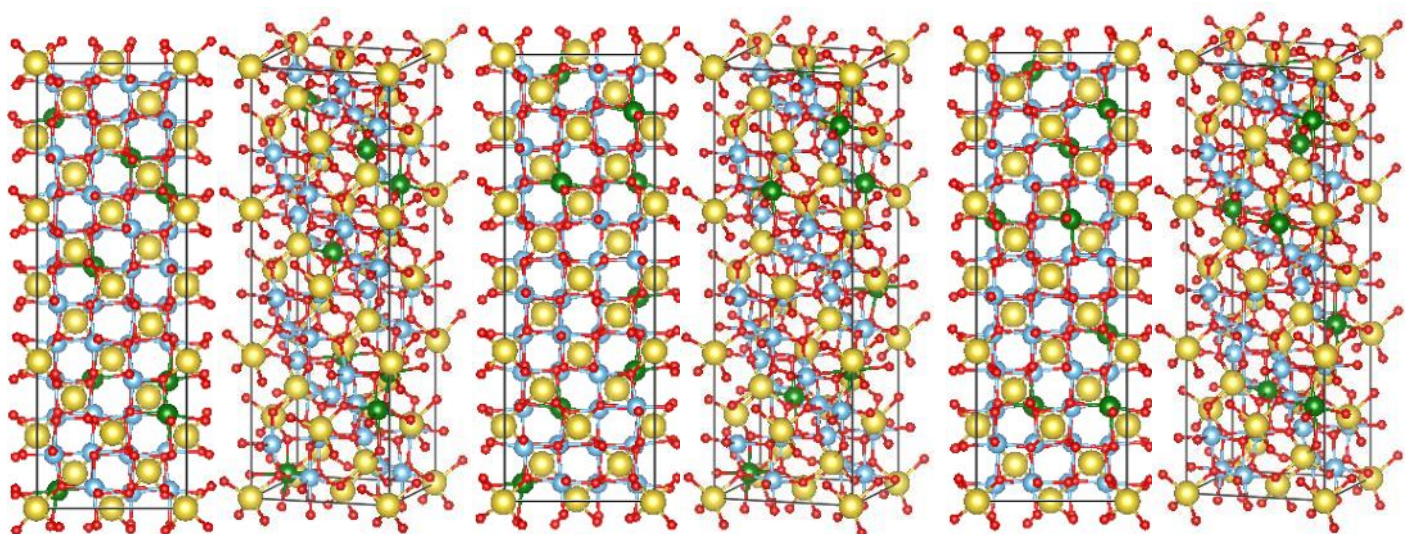
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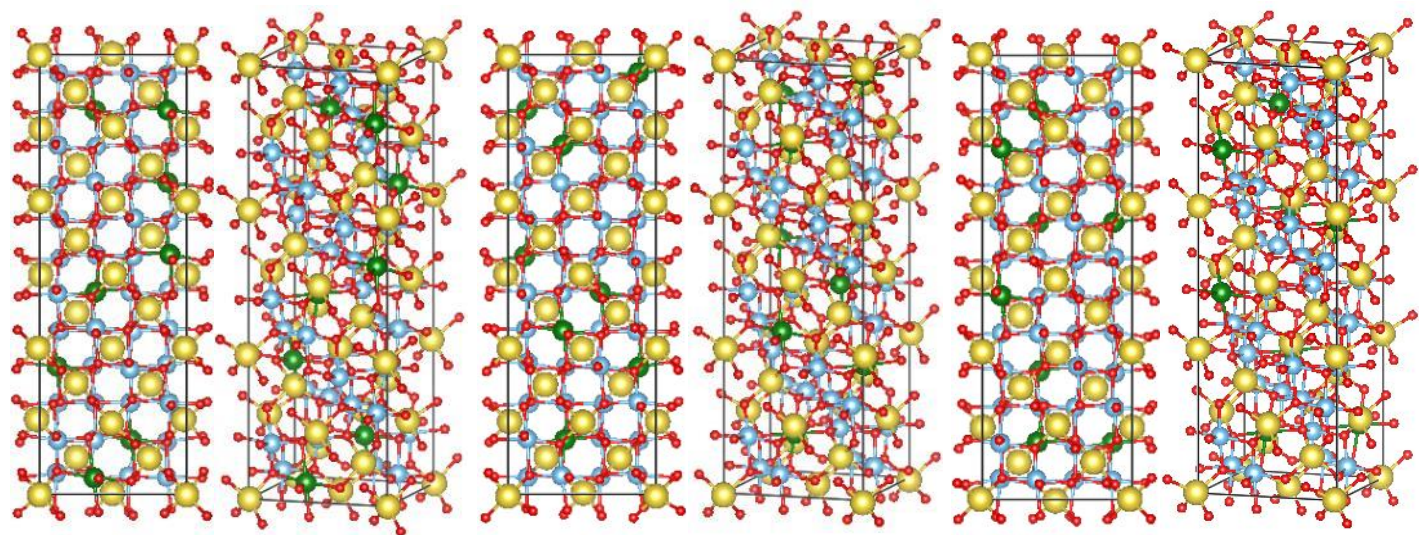


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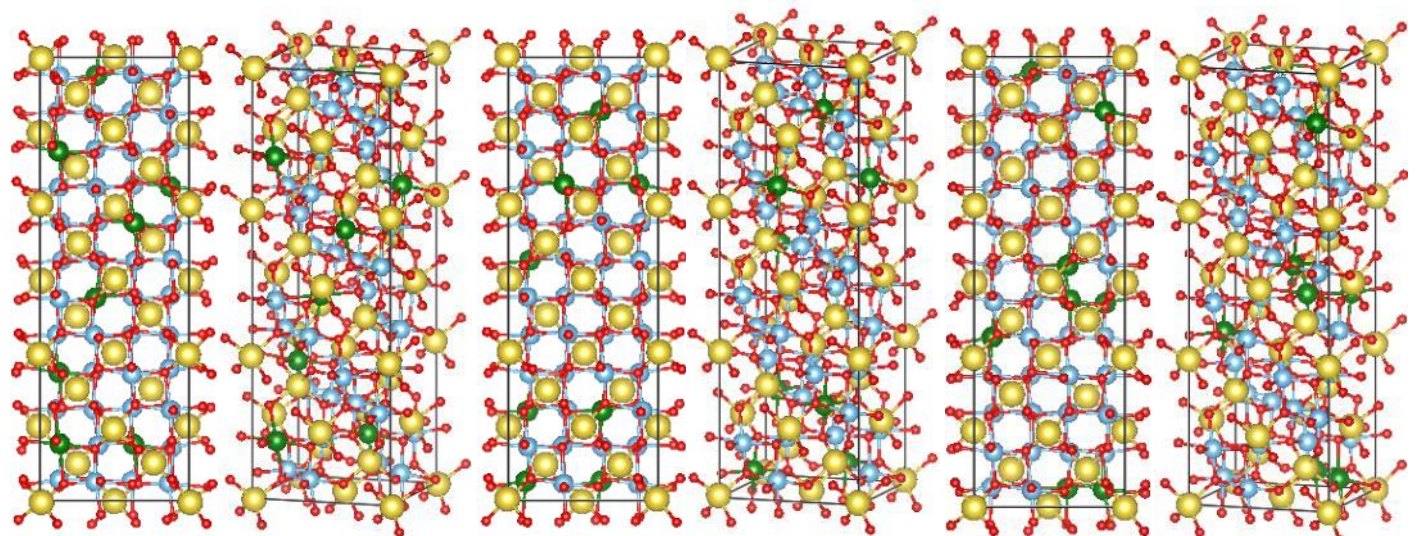
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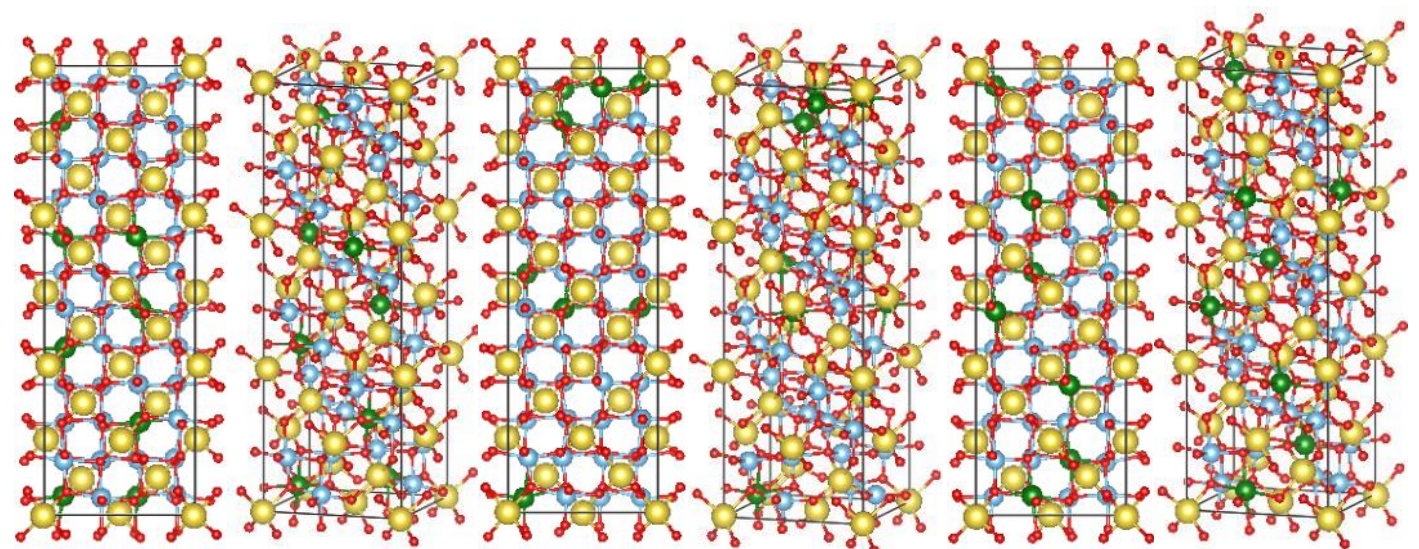
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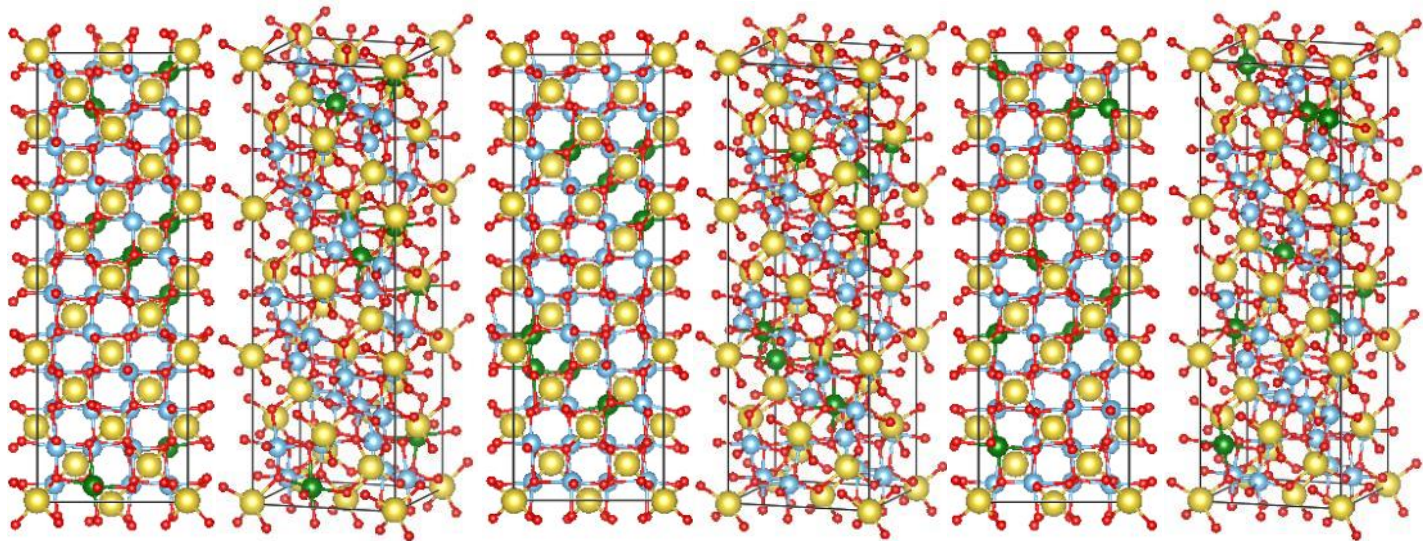


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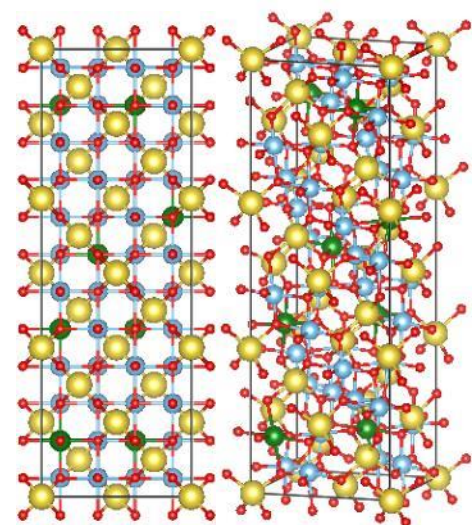
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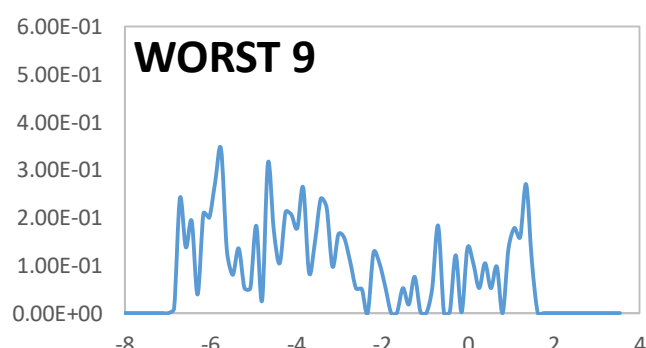
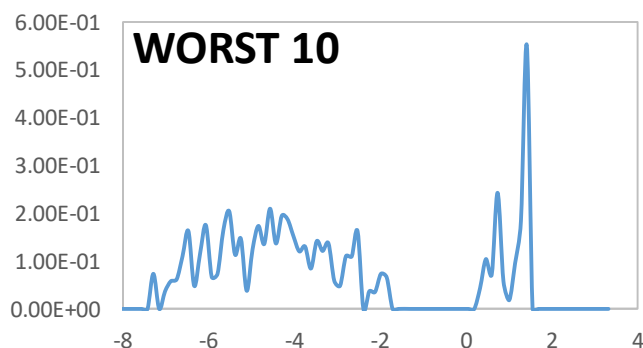
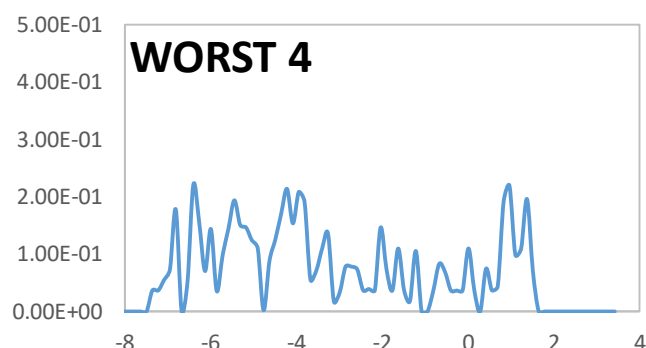
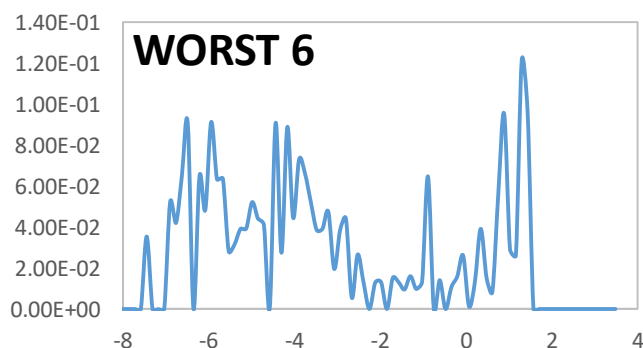
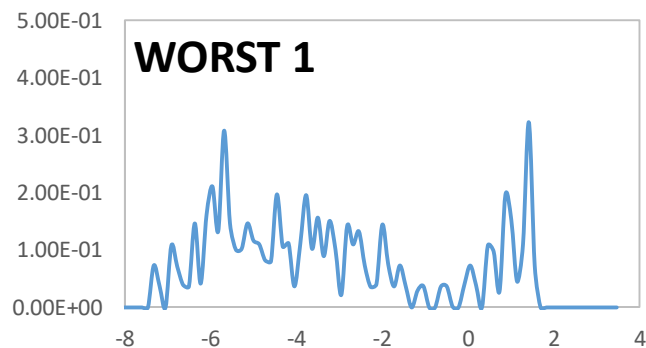
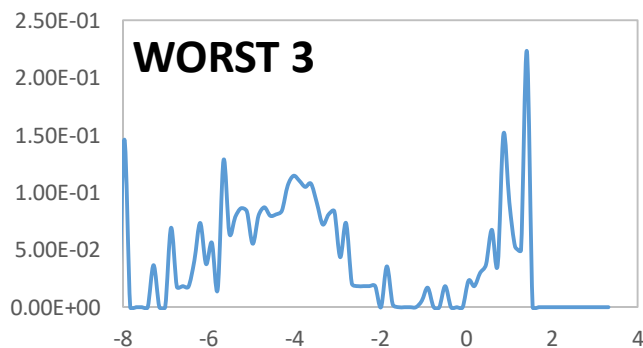
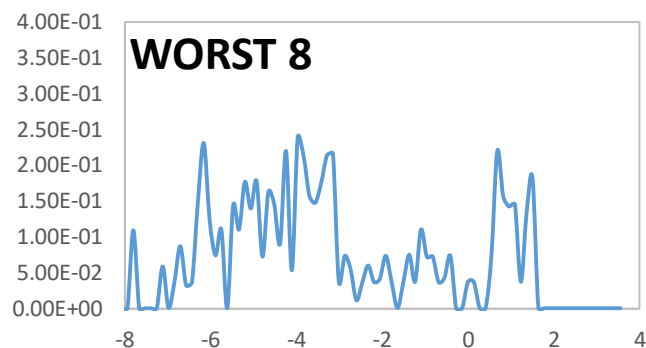
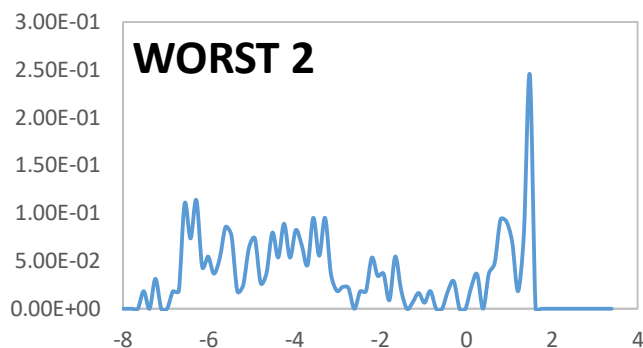
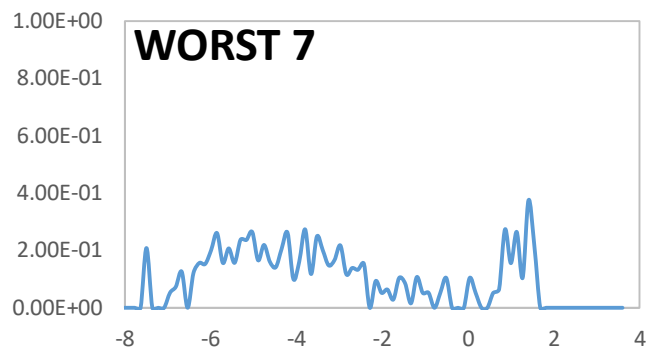
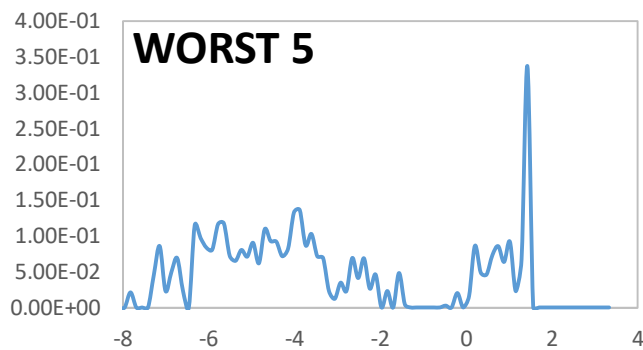


Figure S5 DOS of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ of the ten least stable structures from the 58 selected models. The ordinate is $\text{DOS} [\text{eV}^{-1}]$ and the abscissa is $E - E_{\text{F}}$ (the Fermi energy) $[\text{eV}]$.

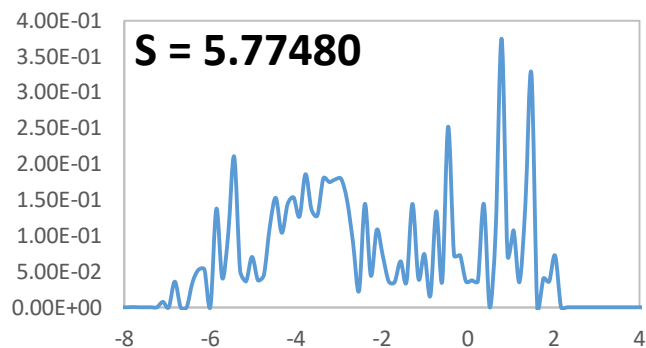
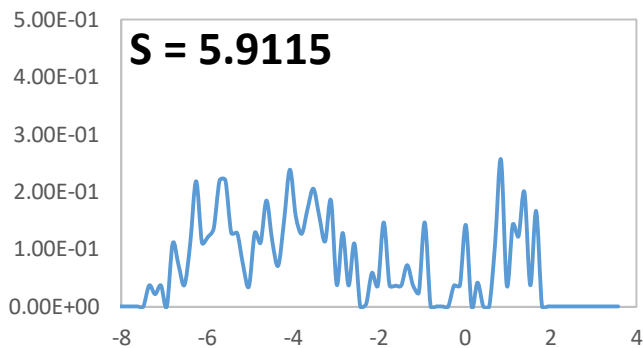
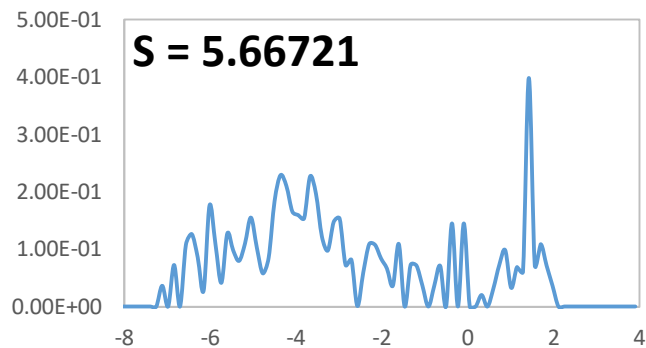


Figure S6 DOS of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for which S is around 5.7 selected from the 58 models. The ordinate is $\text{DOS} [\text{eV}^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) $[\text{eV}]$.

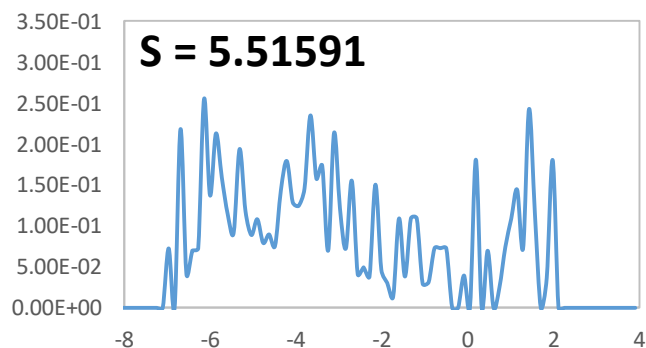
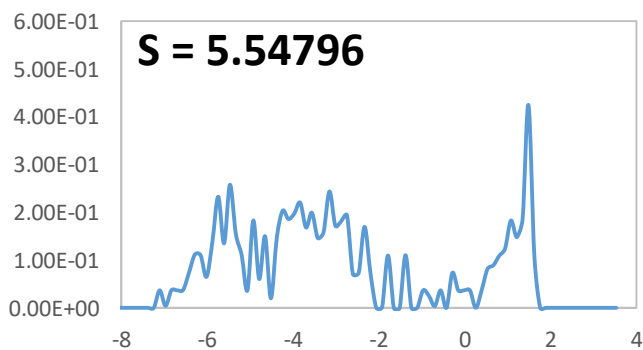
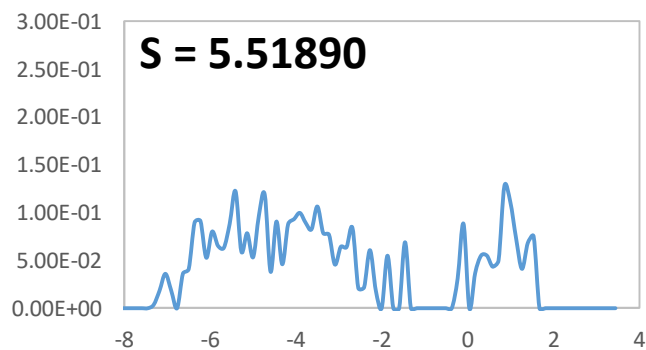


Figure S7 DOS of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for which S is around 5.5 selected from the 58 models. The ordinate is $\text{DOS} [\text{eV}^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) $[\text{eV}]$.

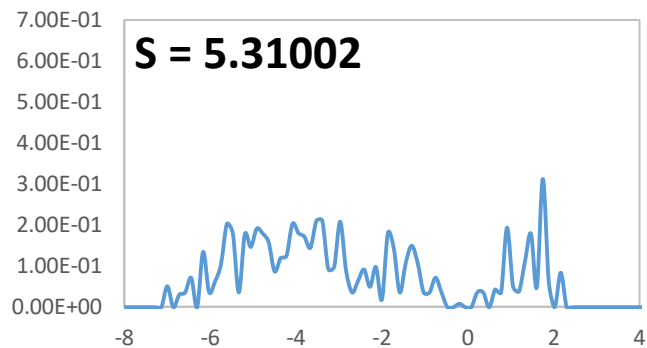
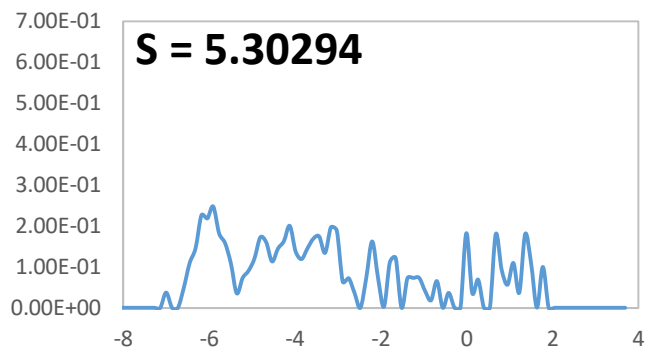
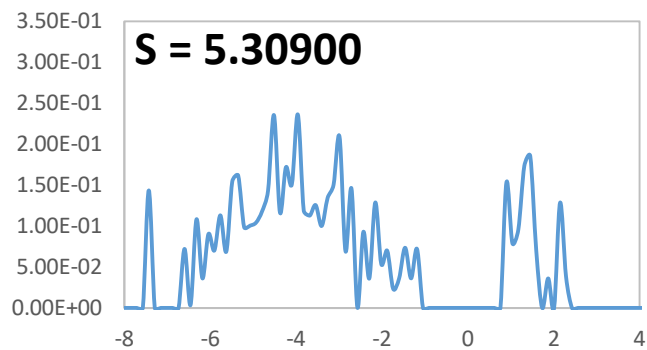


Figure S8 DOS of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for which S is around 5.3 selected from the 58 models. The ordinate is $\text{DOS} [\text{eV}^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) $[\text{eV}]$.

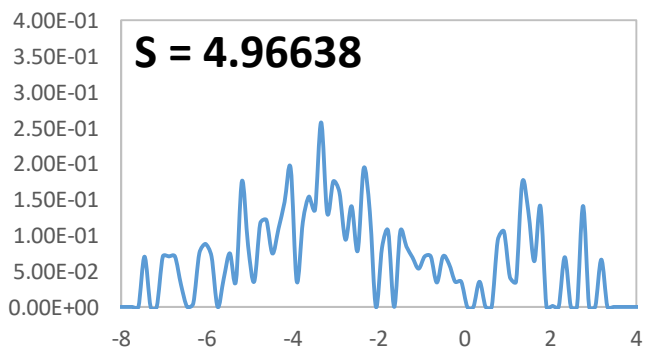
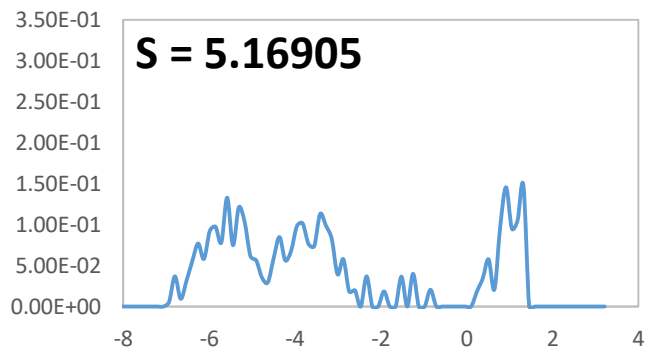
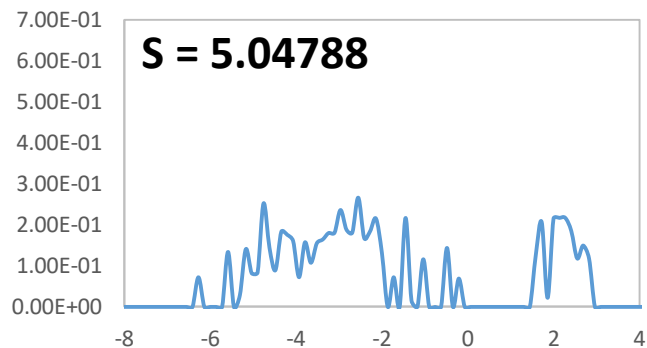


Figure S9 DOS of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for which S is around 5.0 selected from the 58 models. The ordinate is $\text{DOS} [\text{eV}^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) $[\text{eV}]$.

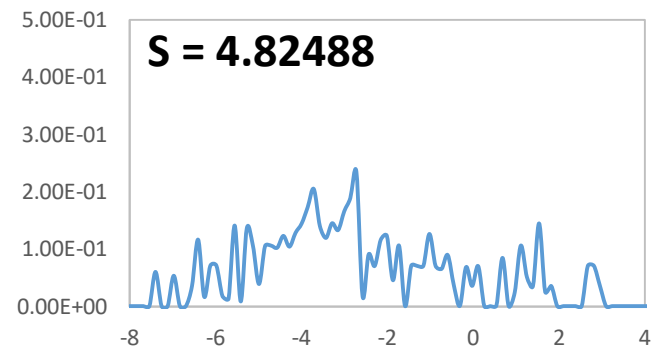
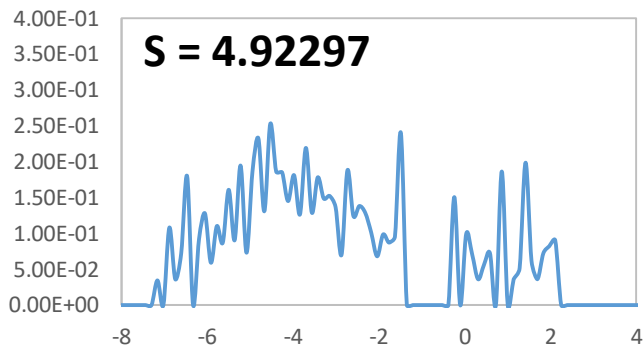
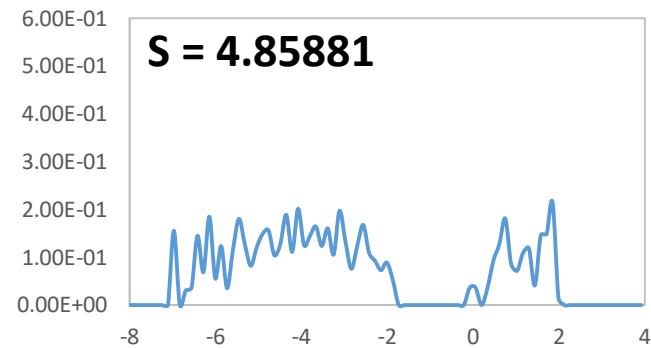


Figure S10 DOS of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for which S is around 4.9 selected from the 58 models. The ordinate is $\text{DOS} [\text{eV}^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) $[\text{eV}]$.

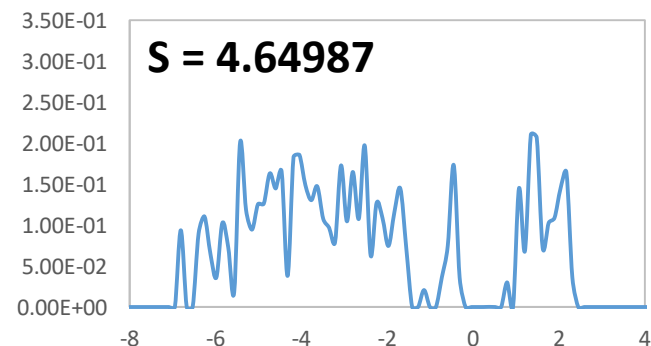
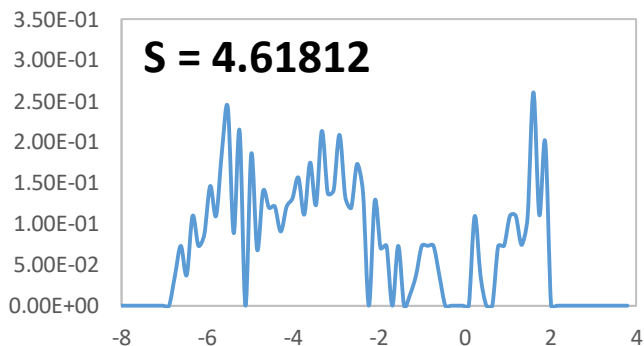
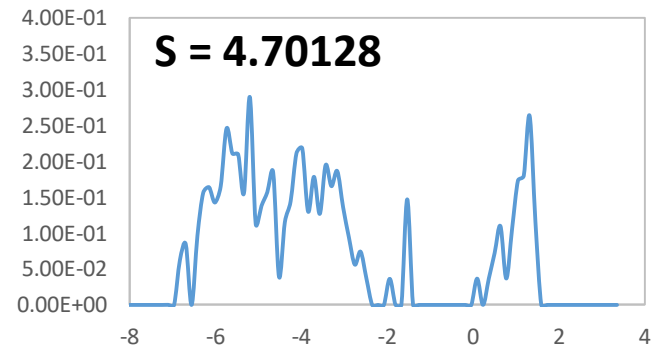


Figure S11 DOS of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for which S is around 4.6 selected from the 58 models. The ordinate is $\text{DOS} [\text{eV}^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) $[\text{eV}]$.

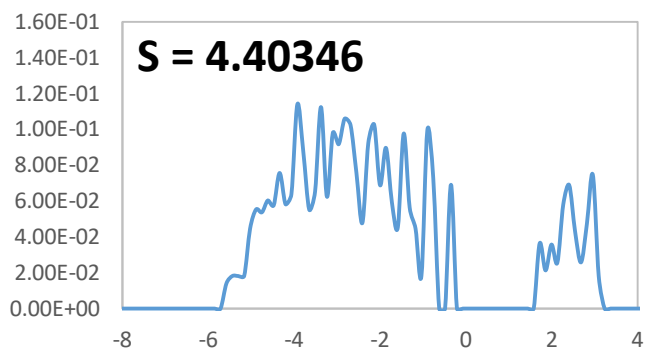
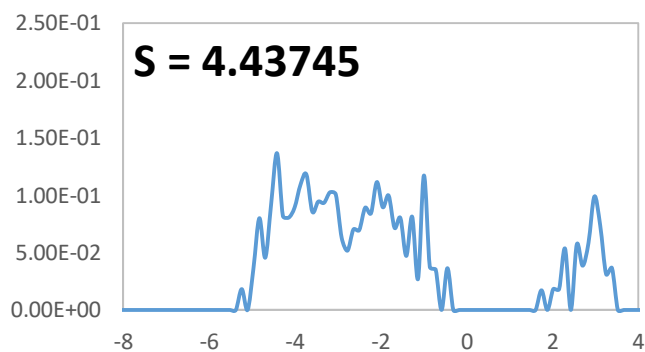
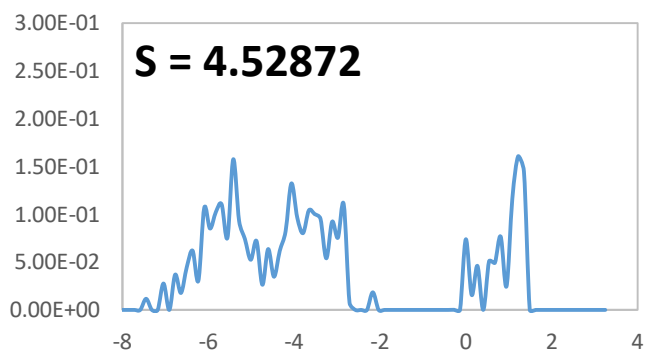


Figure S12 DOS of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for which S is around 4.4 selected from the 58 models. The ordinate is $\text{DOS} [\text{eV}^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) $[\text{eV}]$.

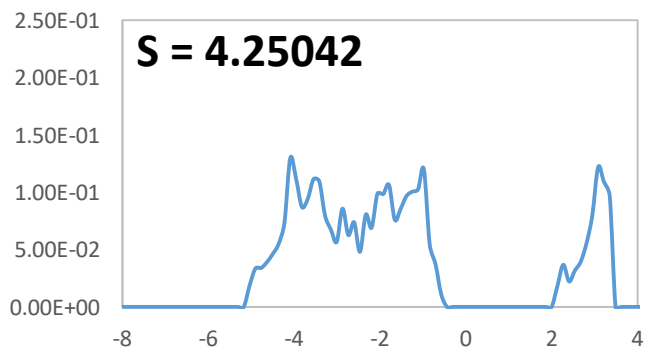
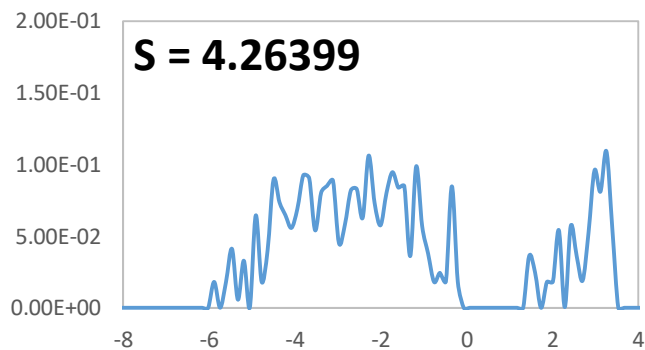
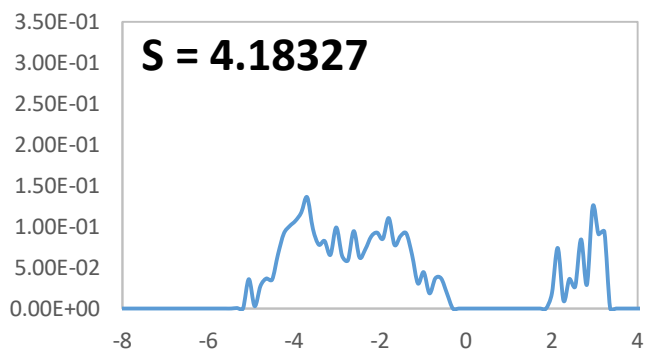


Figure S13 DOS of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for which S is around 4.2 selected from the 58 models. The ordinate is $\text{DOS} [\text{eV}^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) $[\text{eV}]$.

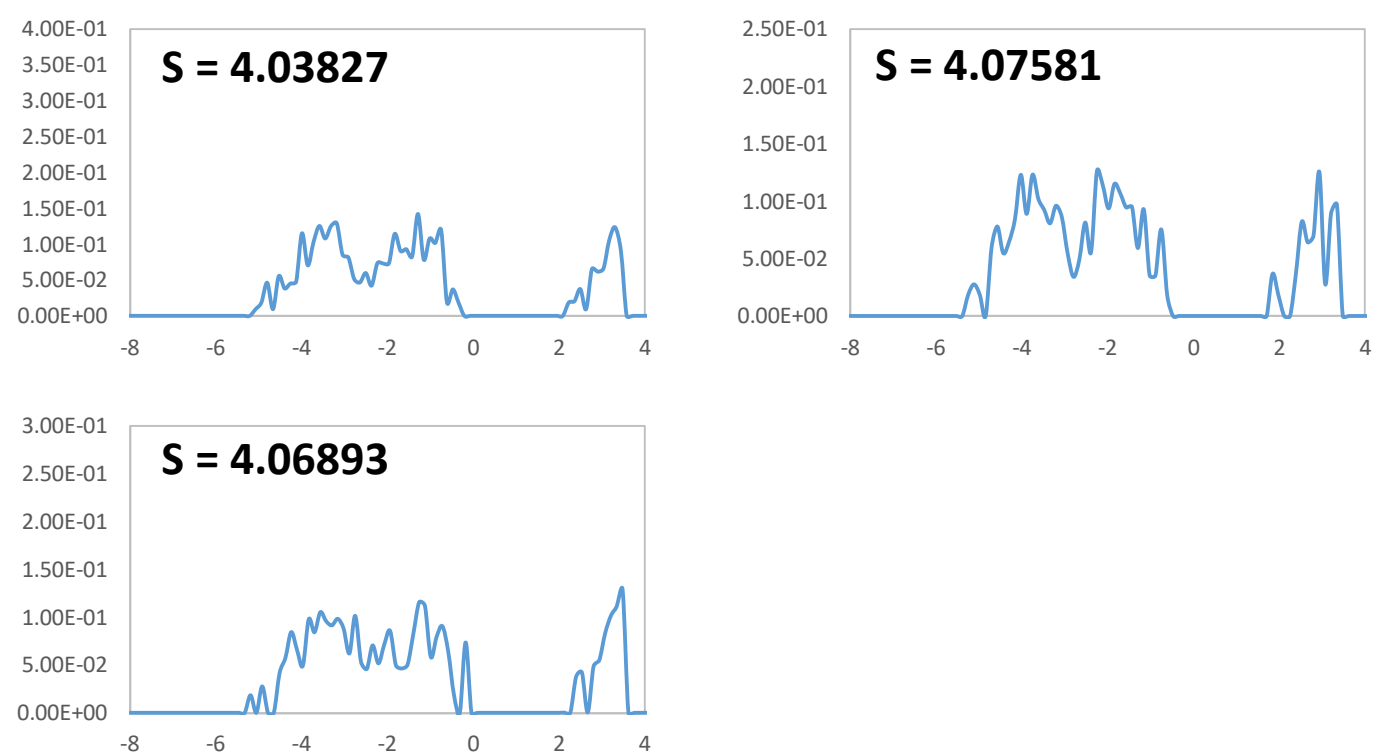


Figure S14 DOS of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for which S is around 4.0 selected from the 58 models. The ordinate is DOS [eV^{-1}], and the abscissa is $E - E_F$ (the Fermi energy) [eV].

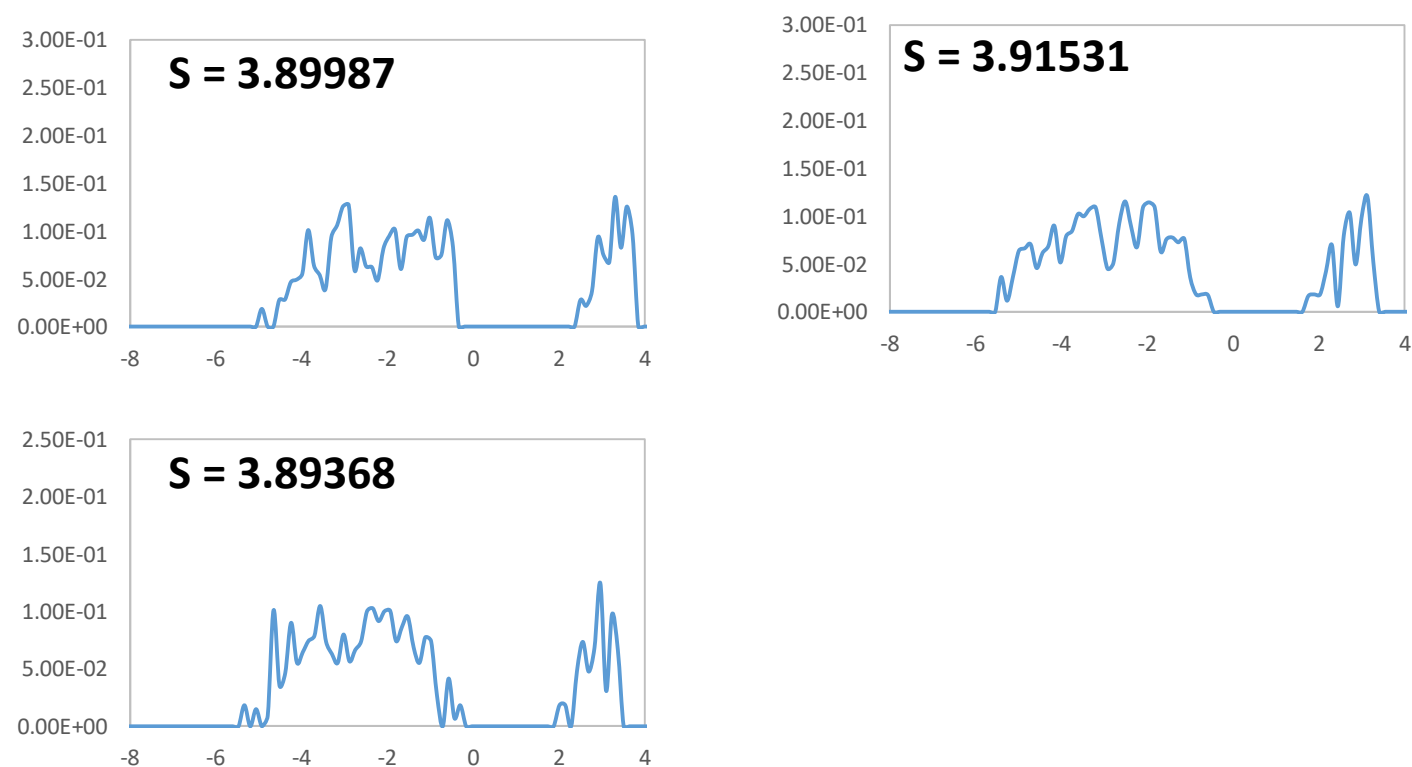


Figure S15 DOS of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for which S is around 3.9 selected from the 58 models. The ordinate is DOS [eV^{-1}] and the abscissa is $E - E_F$ (the Fermi energy) [eV].

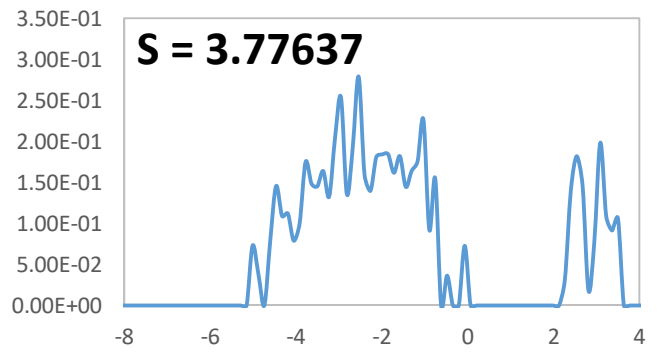
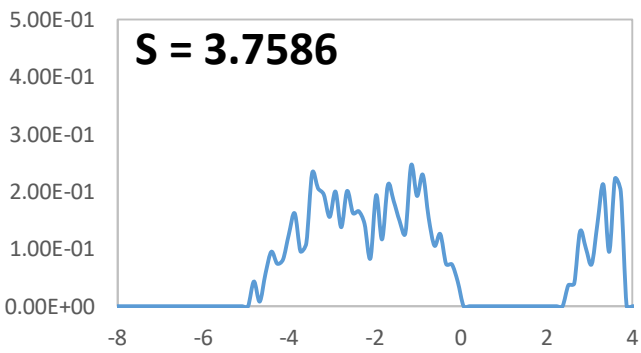
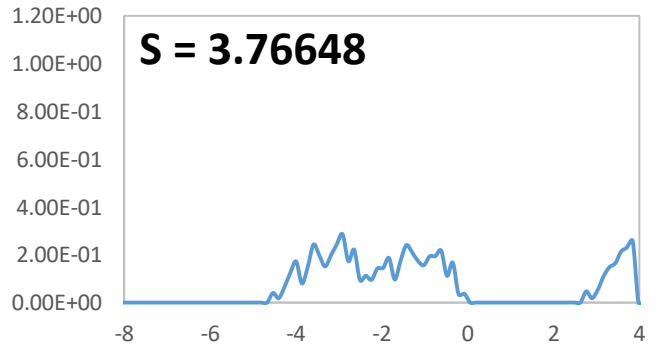
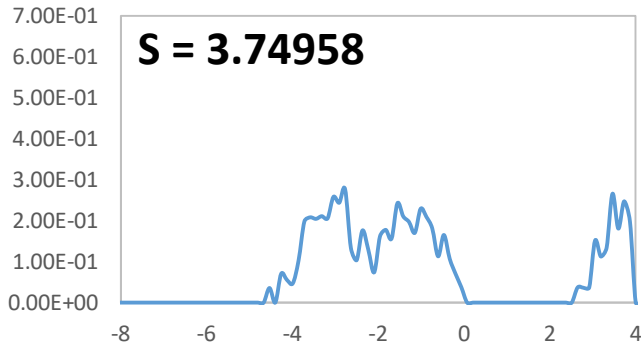
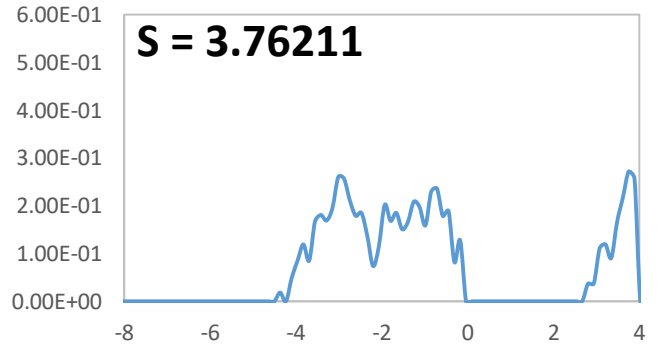
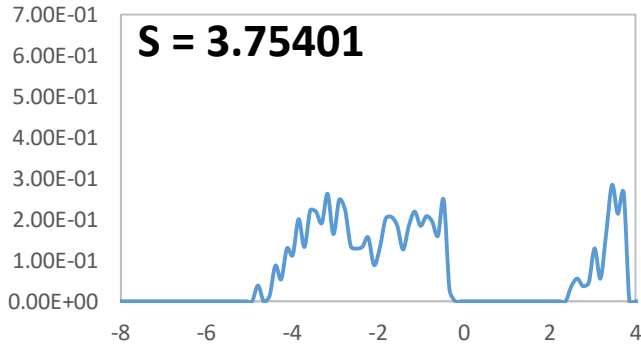
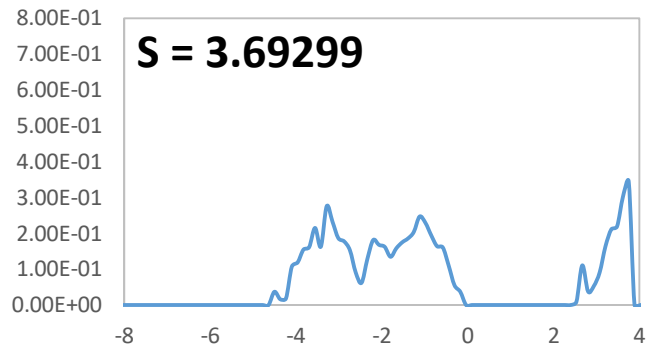
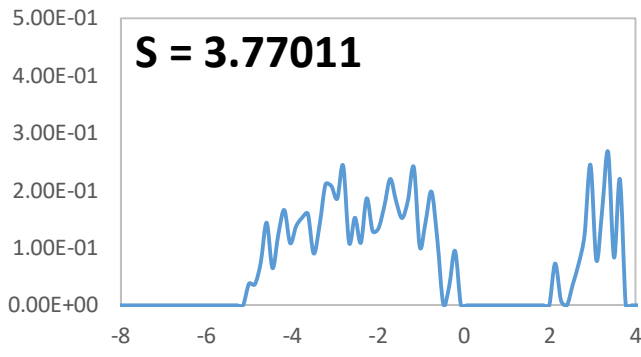


Figure S16 DOS of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for which S is around 3.7 selected from the 58 models. The ordinate is $\text{DOS} [\text{eV}^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) $[\text{eV}]$.

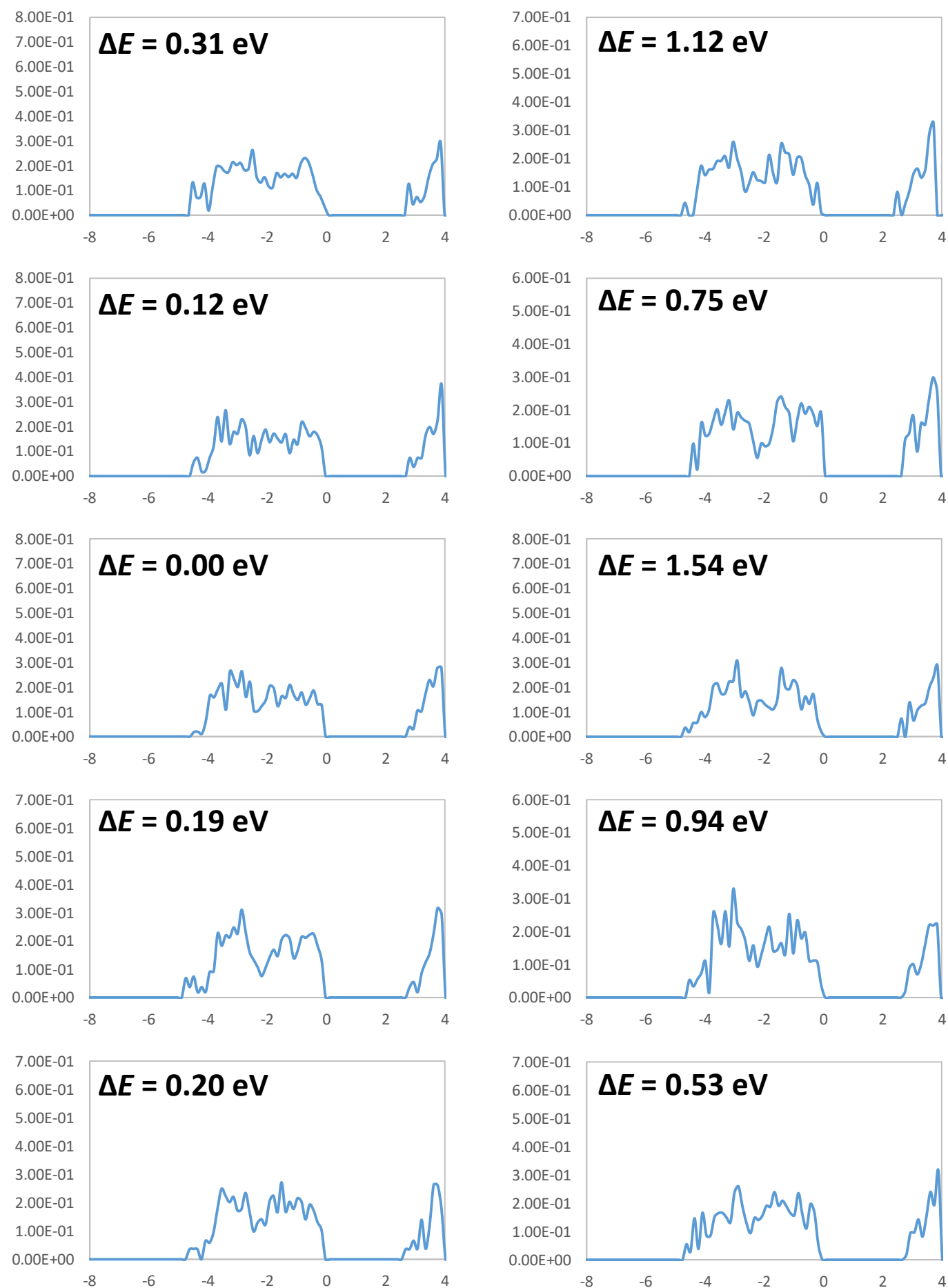


Figure S17 DOS of the ten most stable $\text{Li}_4\text{Ti}_5\text{O}_{12}$ selected from the 58 models. The ordinate is DOS [eV^{-1}] and the abscissa is $E - E_F$ (the Fermi energy) [eV]. ΔE is the energy difference in the total energy from the most stable structure.

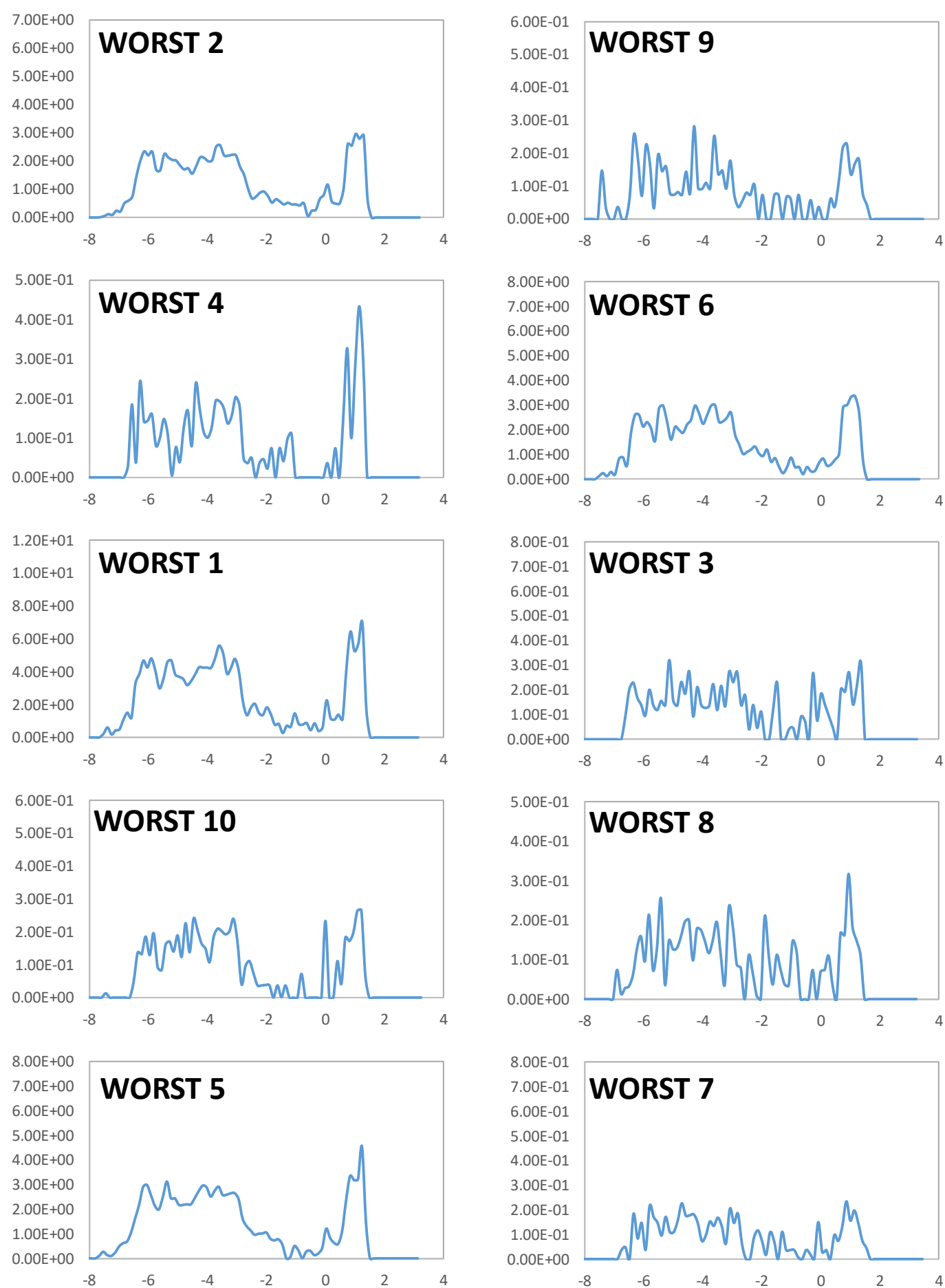


Figure S18 DOS of the ten least stable $\text{Na}_3\text{LiTi}_5\text{O}_{12}$ selected from the 58 models. The ordinate is DOS [eV⁻¹] and the abscissa is $E - E_F$ (the Fermi energy) [eV].

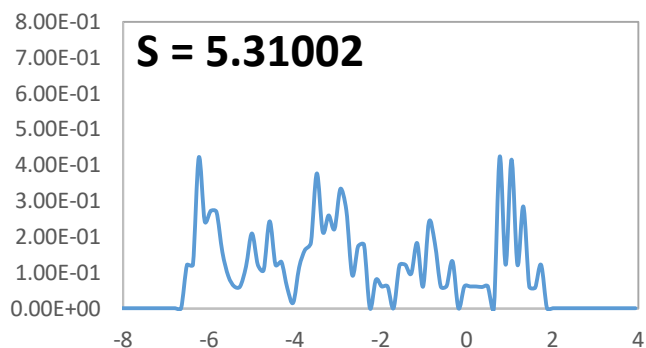
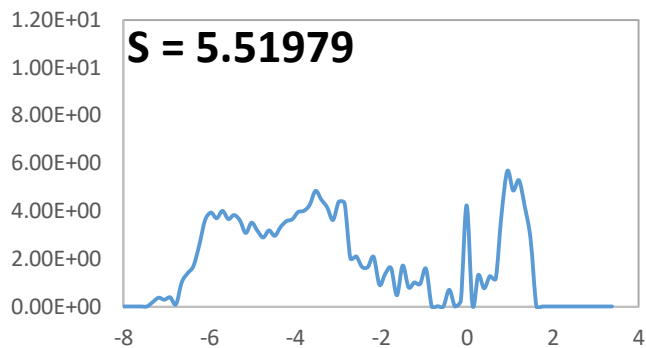
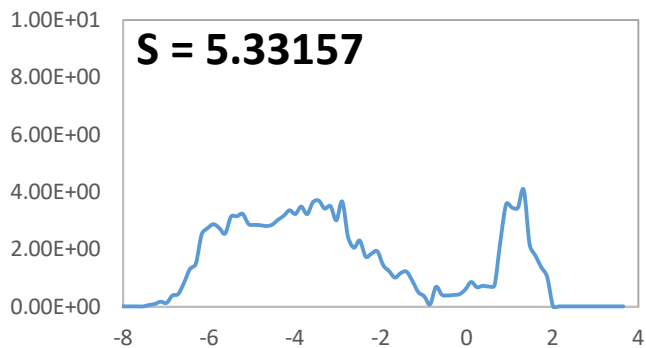


Figure S19 DOS of $\text{Na}_3\text{LiTi}_5\text{O}_{12}$ for which S is around 5.3 selected from the 58 models. The ordinate is $\text{DOS} [\text{eV}^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) $[\text{eV}]$.

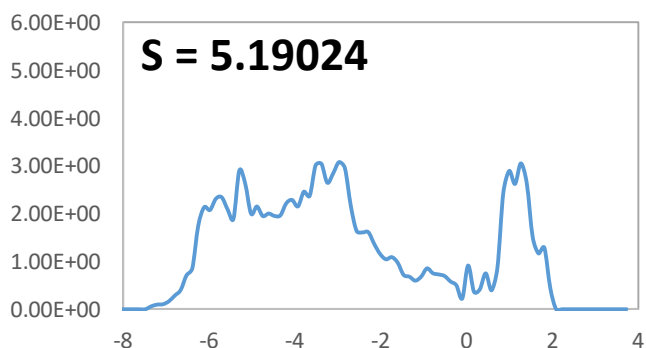
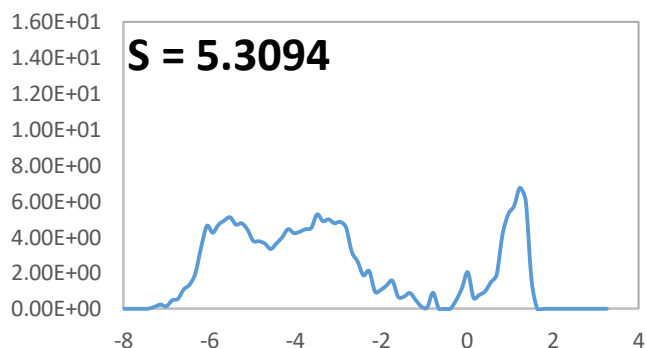
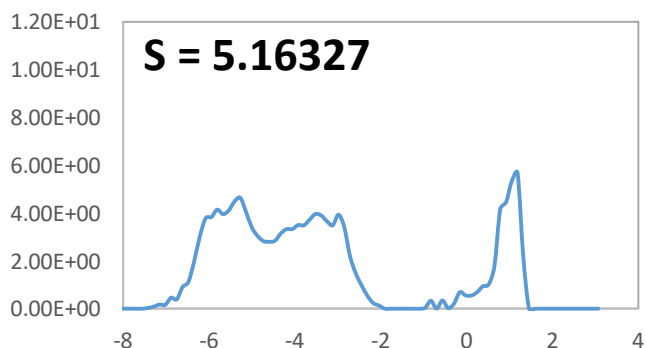


Figure S20 DOS of $\text{Na}_3\text{LiTi}_5\text{O}_{12}$ for which S is around 5.2 selected from the 58 models. The ordinate is $\text{DOS} [\text{eV}^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) $[\text{eV}]$.

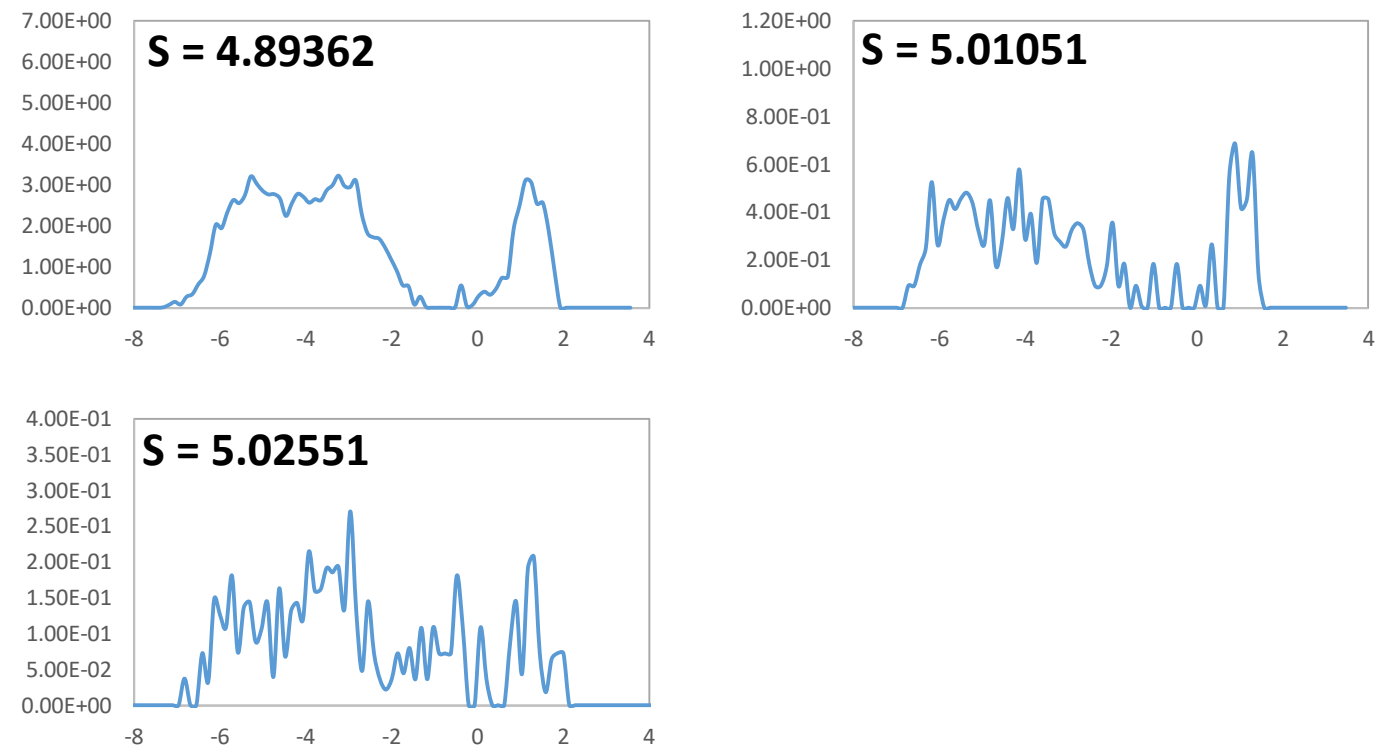


Figure S21 DOS of $\text{Na}_3\text{LiTi}_5\text{O}_{12}$ for which S is around 5.0 selected from the 58 models. The ordinate is $\text{DOS} [\text{eV}^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) $[\text{eV}]$.

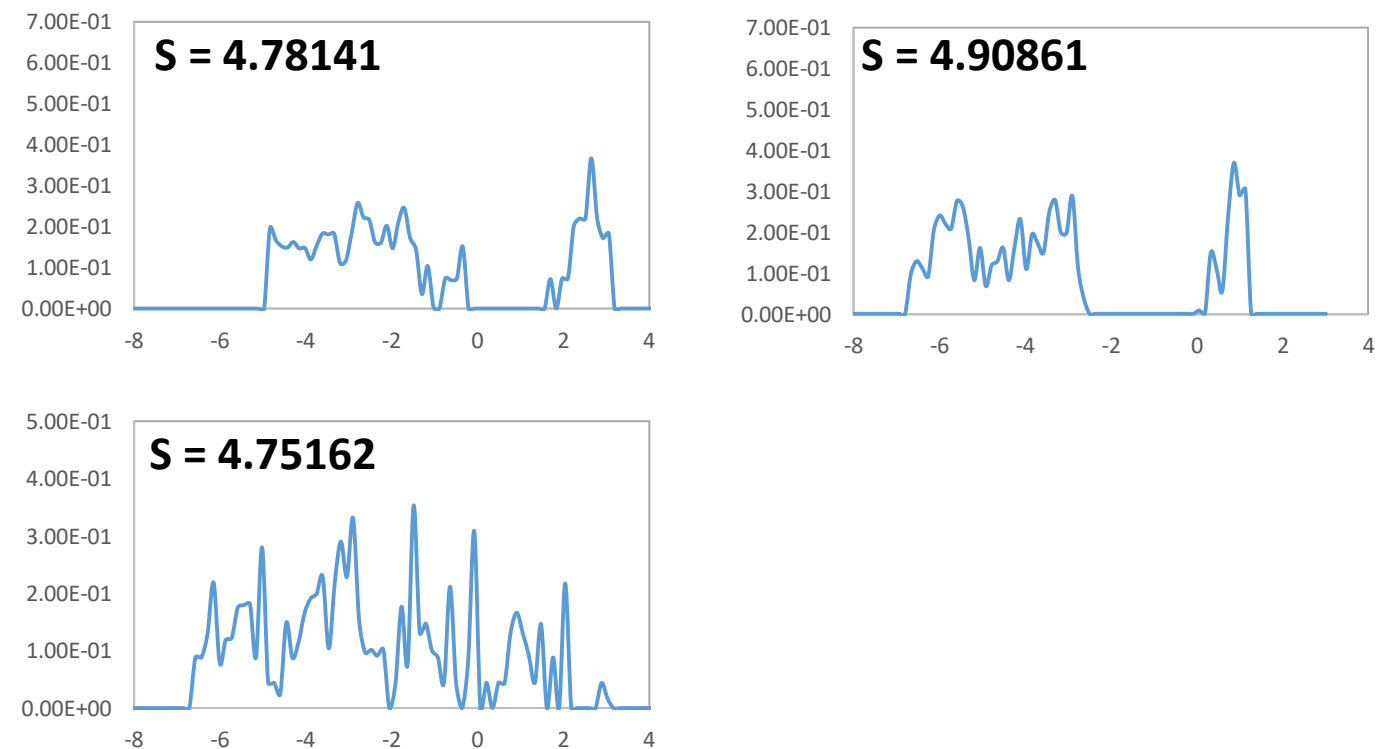


Figure S22 DOS of $\text{Na}_3\text{LiTi}_5\text{O}_{12}$ for which S is around 4.8 selected from the 58 models. The ordinate is $\text{DOS} [\text{eV}^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) $[\text{eV}]$.

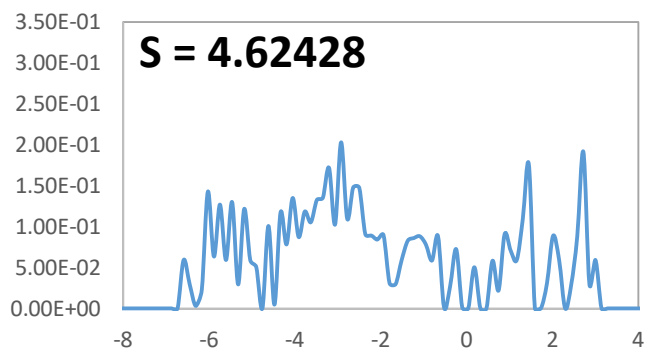
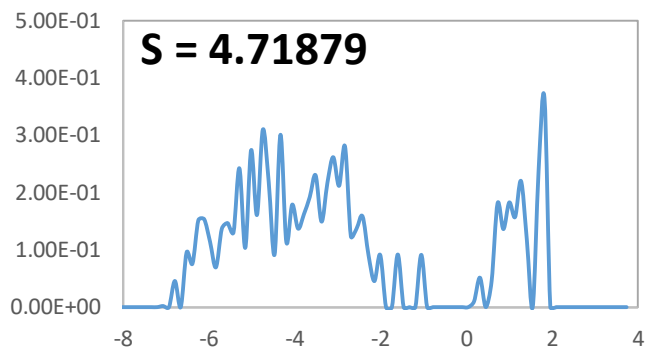
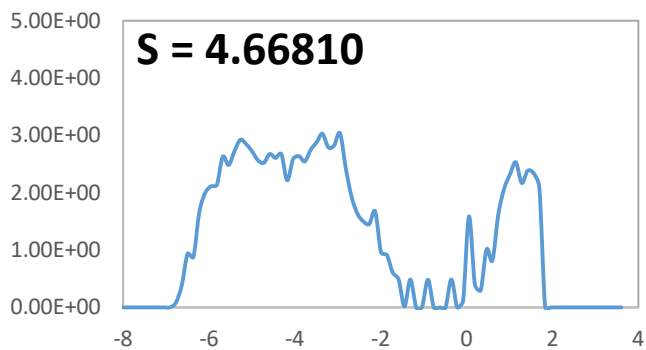


Figure S23 DOS of $\text{Na}_3\text{LiTi}_5\text{O}_{12}$ for which S is around 4.7 selected from the 58 models. The ordinate is $\text{DOS} [\text{eV}^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) $[\text{eV}]$.

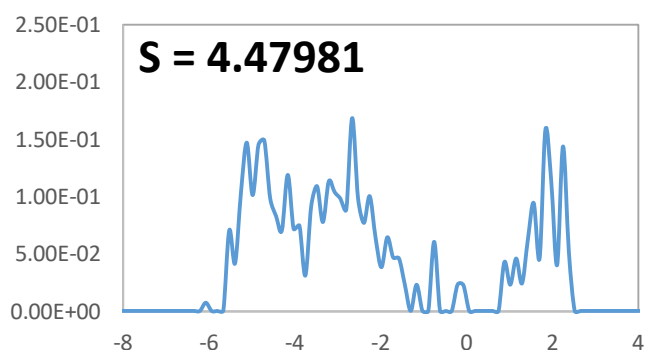
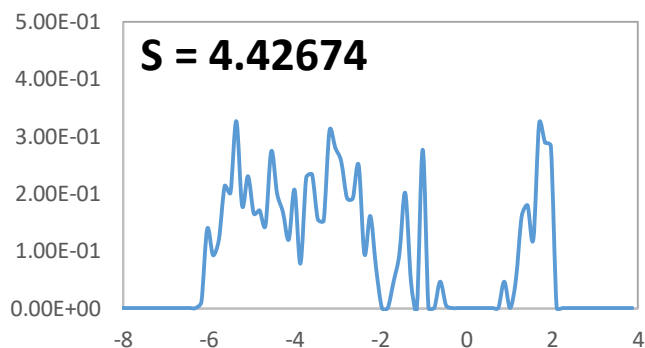
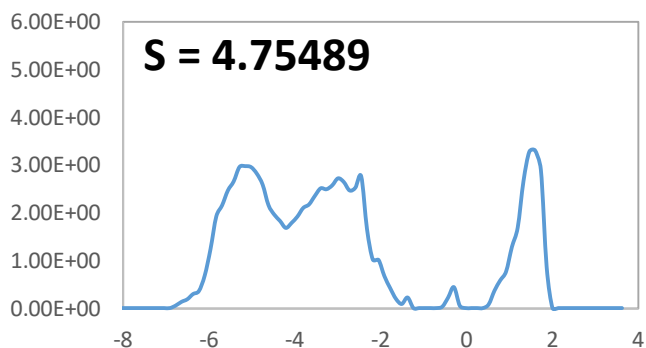


Figure S24 DOS of $\text{Na}_3\text{LiTi}_5\text{O}_{12}$ for which S is around 4.5 selected from the 58 models. The ordinate is $\text{DOS} [\text{eV}^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) $[\text{eV}]$.

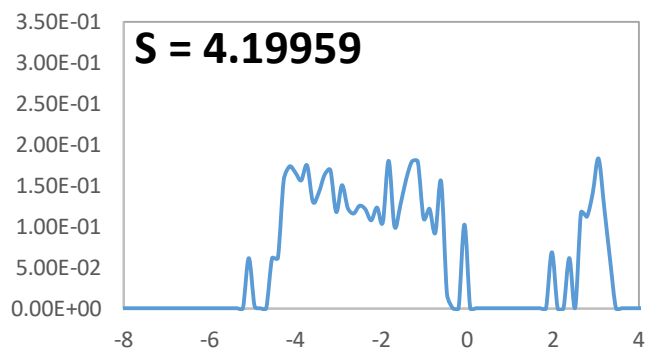
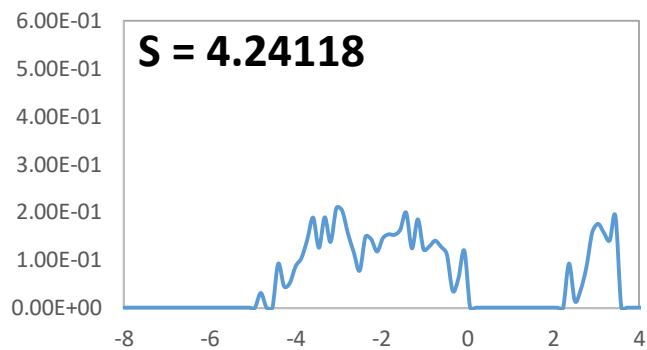
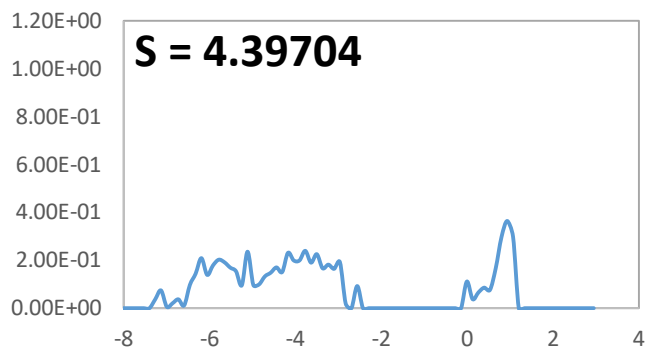


Figure S25 DOS of $\text{Na}_3\text{LiTi}_5\text{O}_{12}$ for which S is around 4.3 selected from the 58 models. The ordinate is DOS [eV^{-1}] and the abscissa is $E - E_F$ (the Fermi energy) [eV].

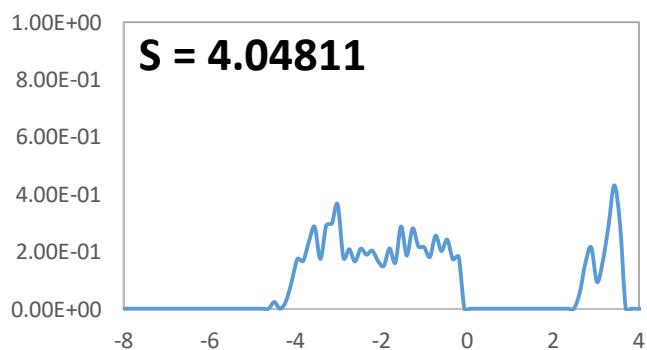
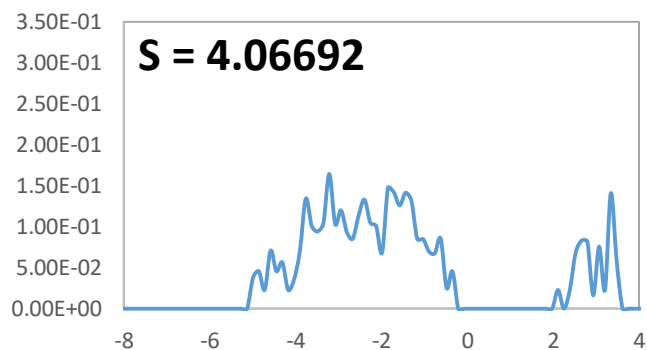
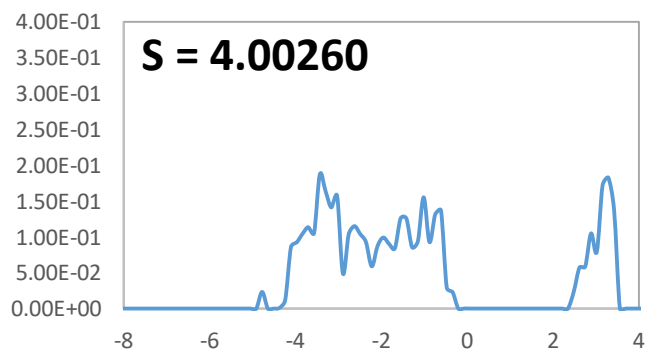


Figure S26 DOS of $\text{Na}_3\text{LiTi}_5\text{O}_{12}$ for which S is around 4.0 selected from the 58 models. The ordinate is DOS [eV^{-1}] and the abscissa is $E - E_F$ (the Fermi energy) [eV].

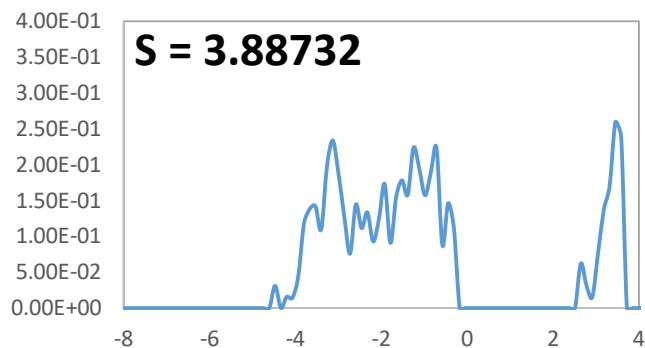
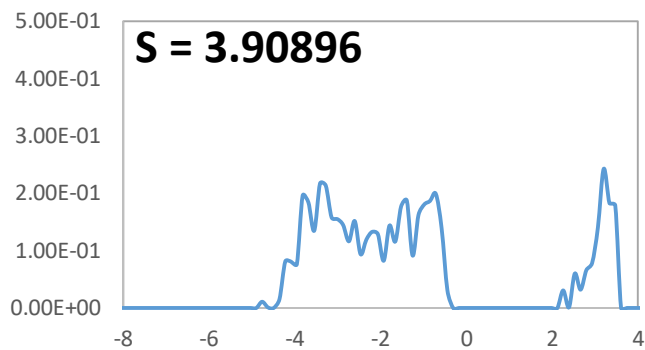
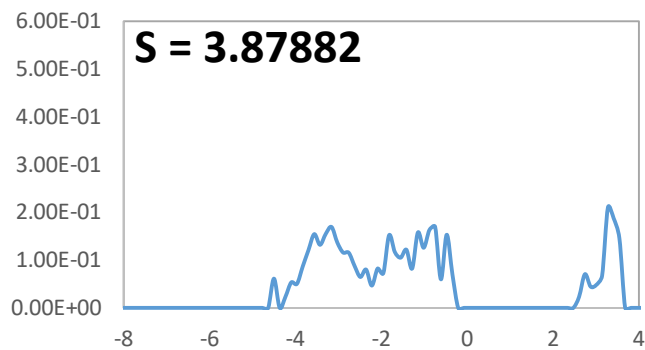


Figure S27 DOS of $\text{Na}_3\text{LiTi}_5\text{O}_{12}$ for which S is around 3.9 selected from the 58 models. The ordinate is $\text{DOS} [\text{eV}^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) $[\text{eV}]$.

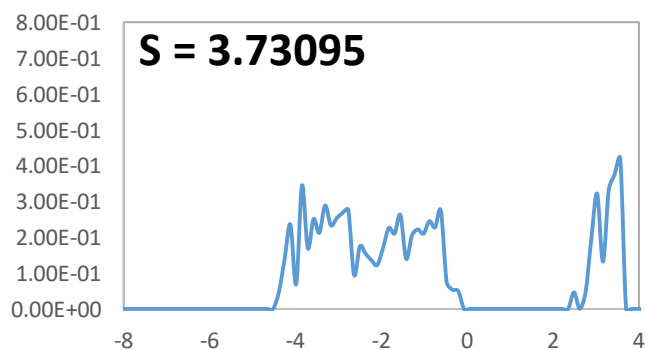
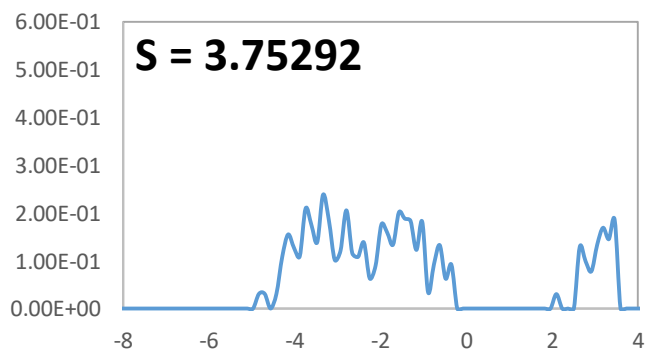
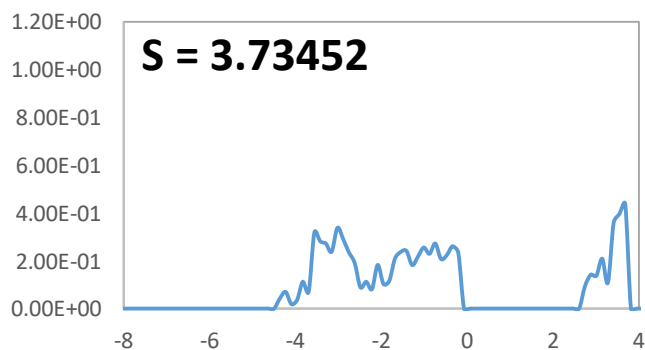


Figure S28 DOS of $\text{Na}_3\text{LiTi}_5\text{O}_{12}$ for which S is around 3.7 selected from the 58 models. The ordinate is $\text{DOS} [\text{eV}^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) $[\text{eV}]$.

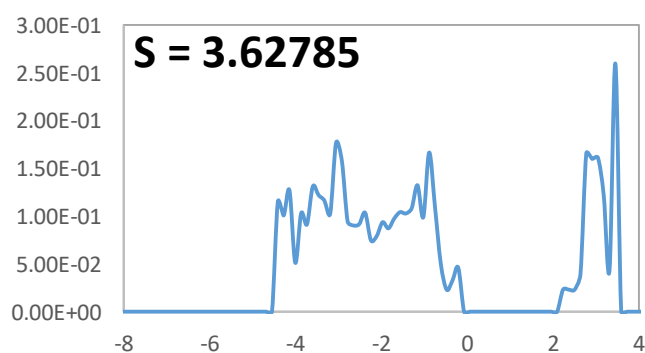
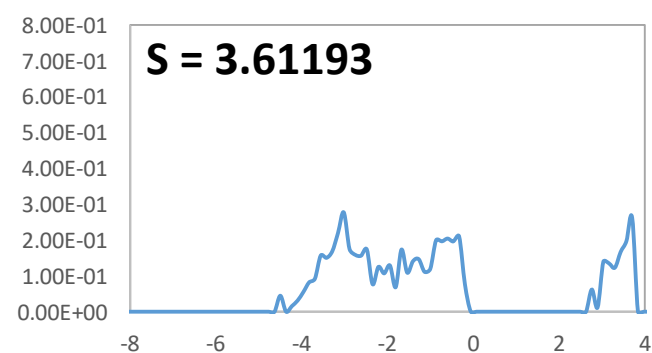
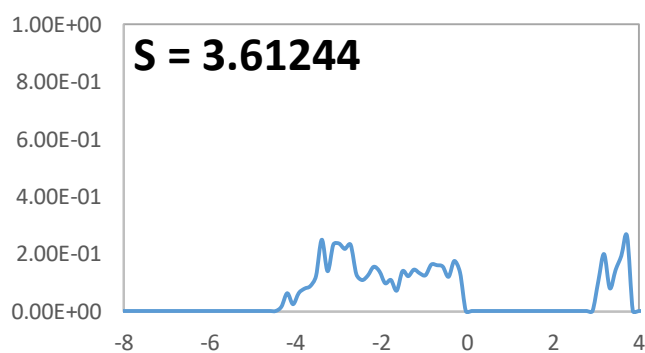
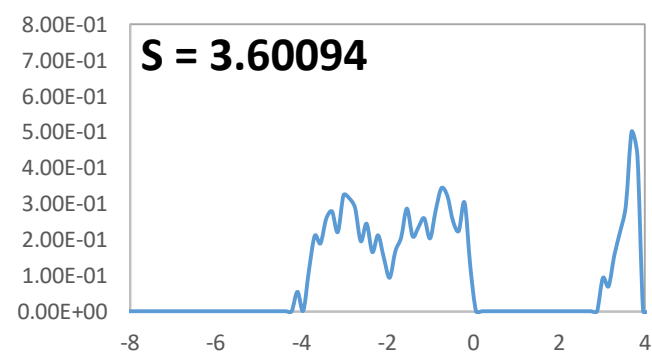
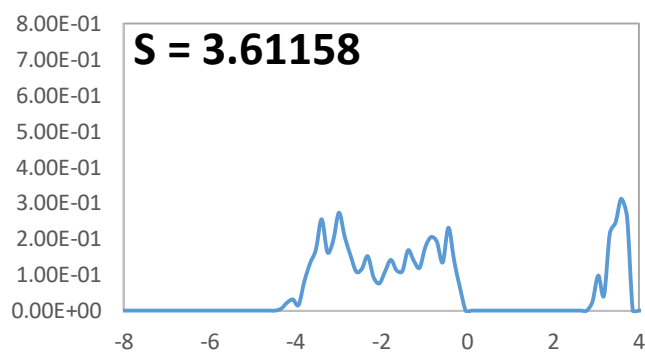
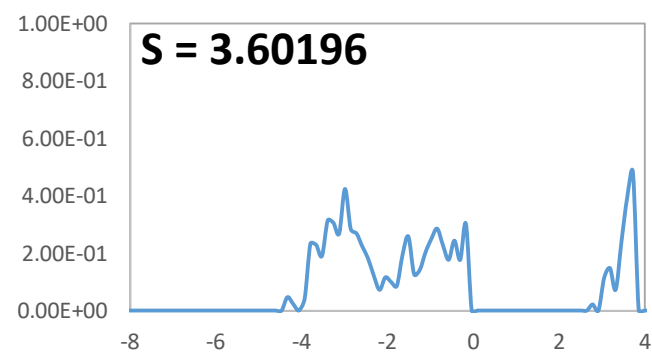
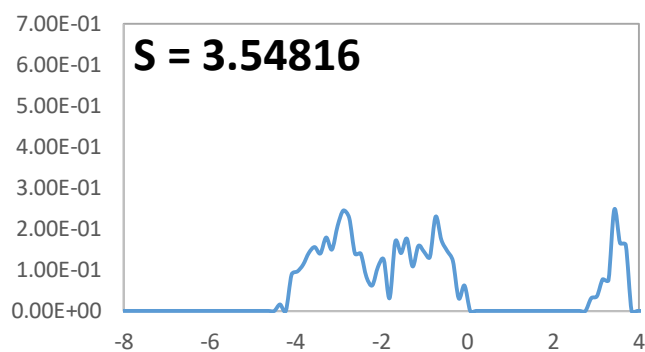
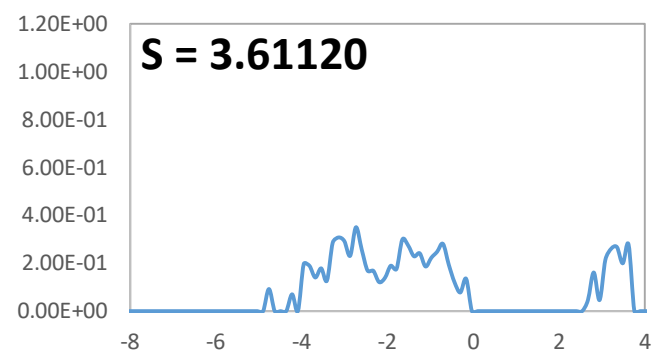


Figure S29 DOS of $\text{Na}_3\text{LiTi}_5\text{O}_{12}$ for which S is around 3.6 selected from the 58 models. The ordinate is $\text{DOS} [\text{eV}^{-1}]$ and the abscissa is $E - E_F$ (the Fermi energy) $[\text{eV}]$.

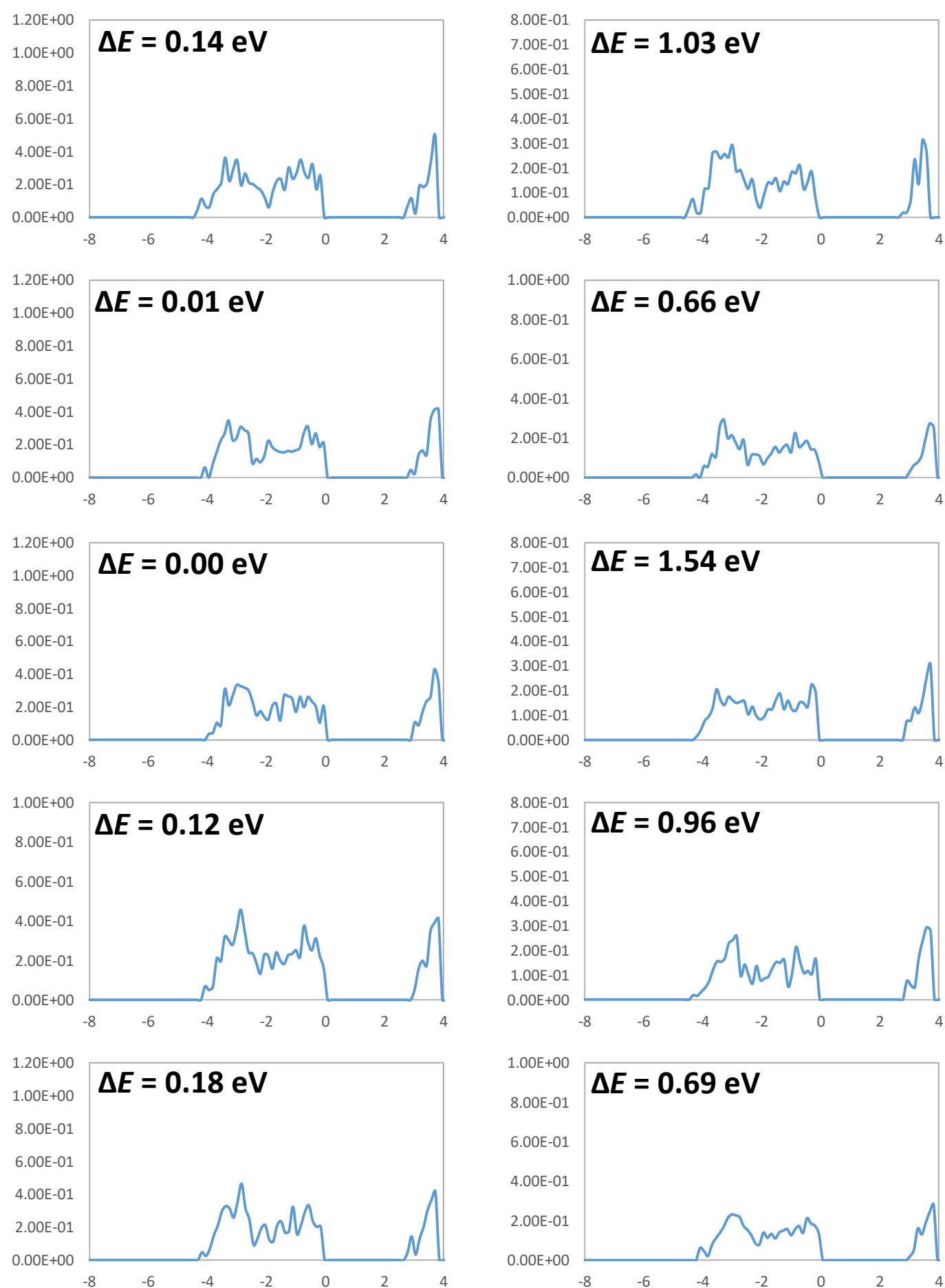


Figure S30 DOS of the ten most stable $\text{Na}_3\text{LiTi}_5\text{O}_{12}$ selected from the 58 models. The ordinate is DOS [eV^{-1}] and the abscissa is $E - E_F$ (the Fermi energy) [eV]. ΔE is the energy difference in the total energy from the most stable structure.

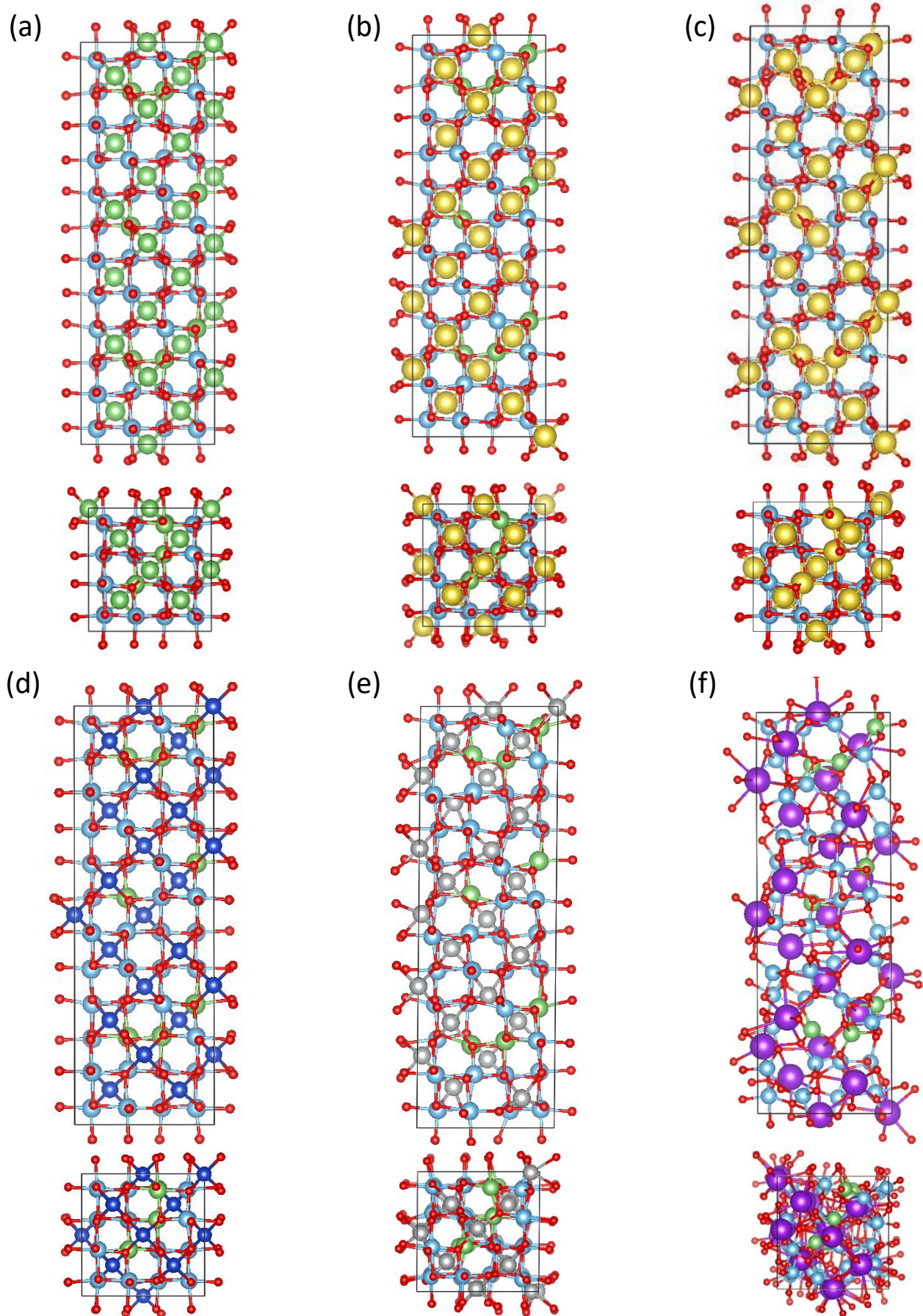


Figure S31 Side (upper panels) and top (lower panels) views of the optimized structures of (a) $\text{Li}_4\text{Ti}_5\text{O}_{12}$, (b) $\text{Na}_3\text{LiTi}_5\text{O}_{12}$, (c) $\text{Na}_4\text{Ti}_5\text{O}_{12}$, (d) $\text{Cu}_3\text{LiTi}_5\text{O}_{12}$, (e) $\text{Ag}_3\text{LiTi}_5\text{O}_{12}$, and (f) $\text{K}_3\text{LiTi}_5\text{O}_{12}$, 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.

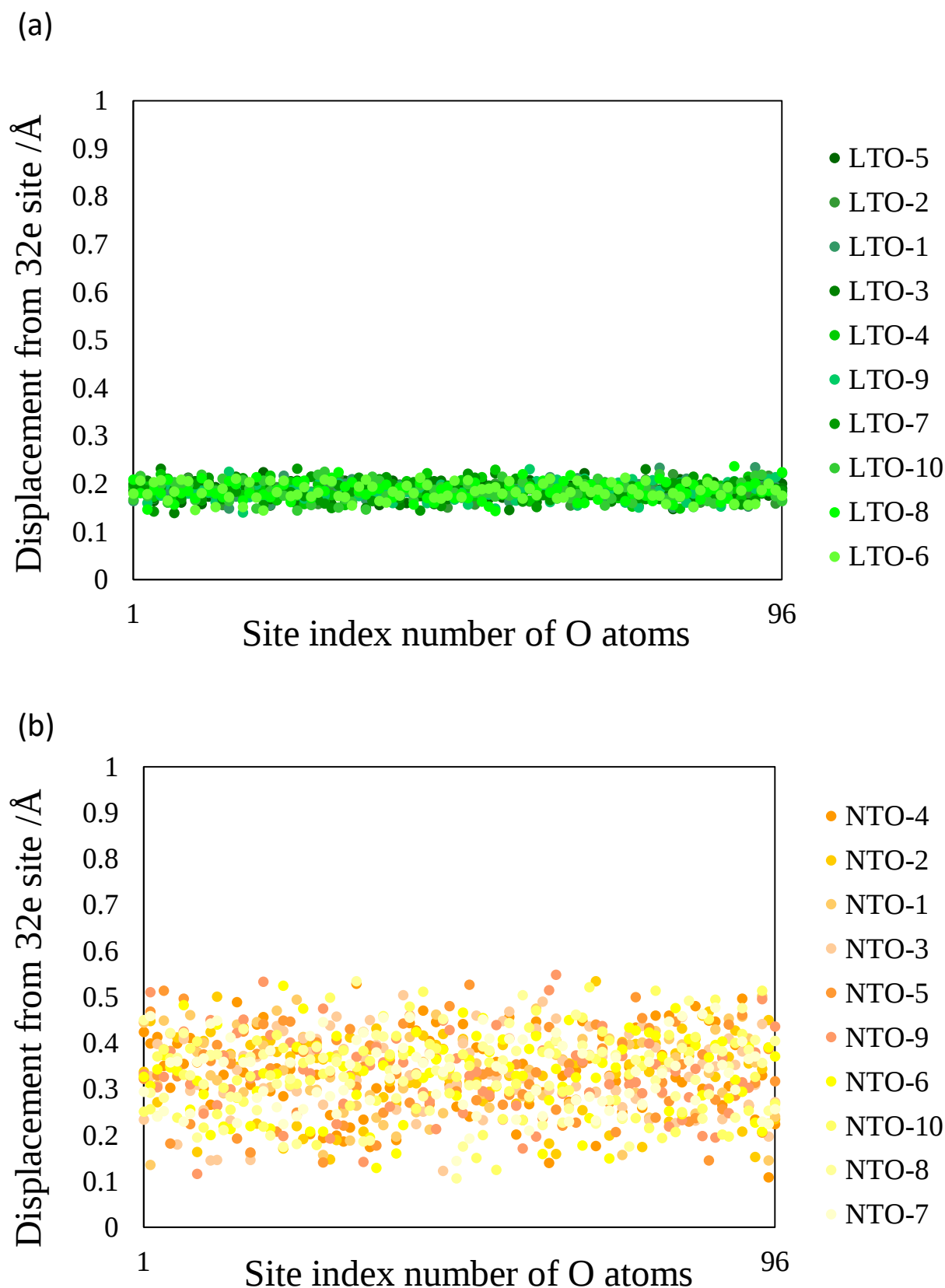


Figure S32 Displacement of O atoms from the Wyckoff positions (32e) of the $Fd\bar{3}m$ symmetry (spinel). (a) $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and (b) $\text{Na}_3\text{LiTi}_5\text{O}_{12}$. LTO-1 and NTO-1 (LTO-10 and NTO-10) indicate the most stable (the 10-th stable) models.

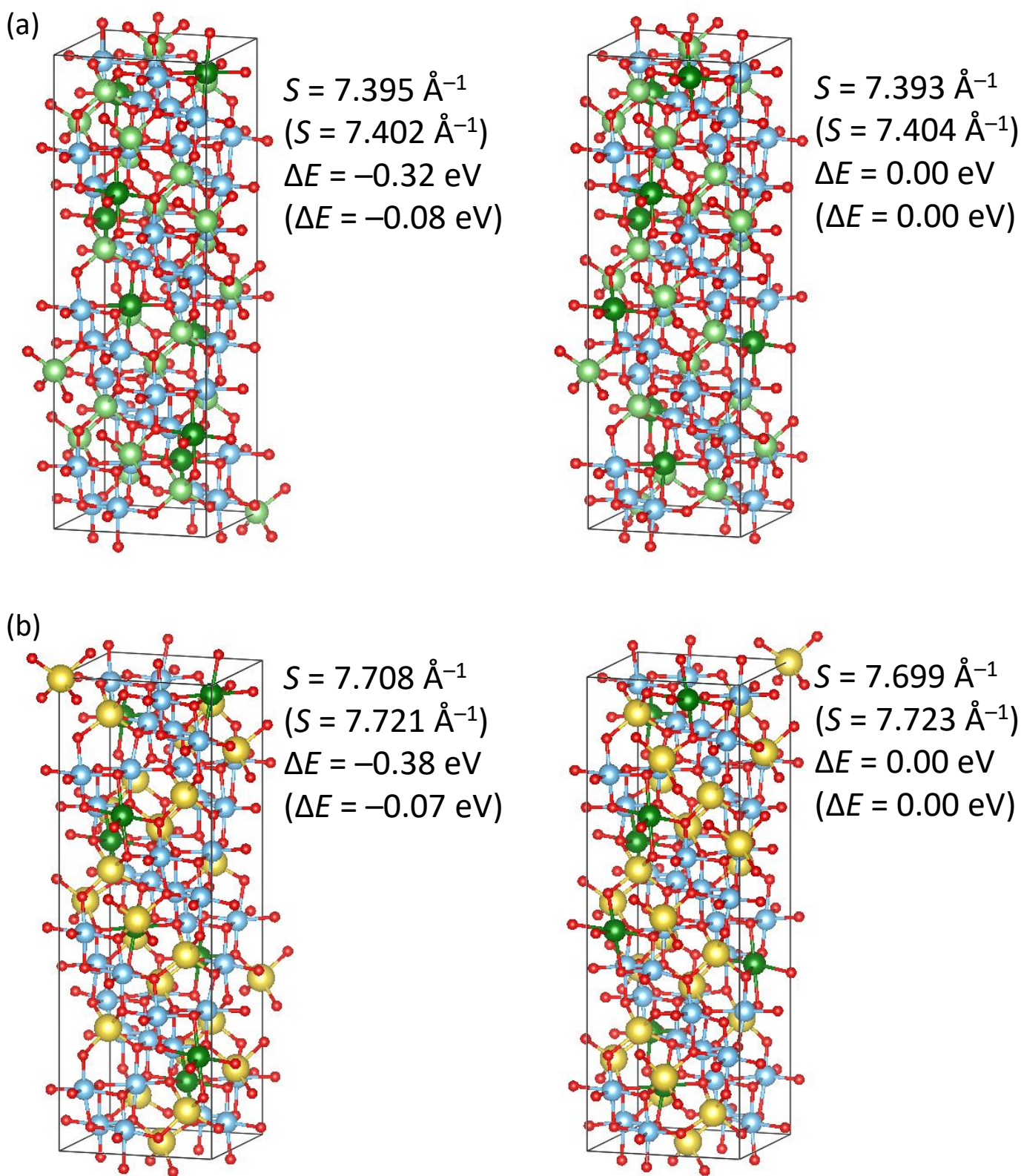


Figure S33 Comparison of the results (optimized structures, S values, and ΔE values) of spinel-titanates ((a) LTO, and (b) NTO) with the predicted configurations by previous works [30, 31] (left panels) and the most stable configurations among the 13,444 (LTO) and 8,444 (NTO) models (right panels). The 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. ΔE is the energy difference from the most stable structures in our calculated models. The values in parenthesis are the values before the optimization.