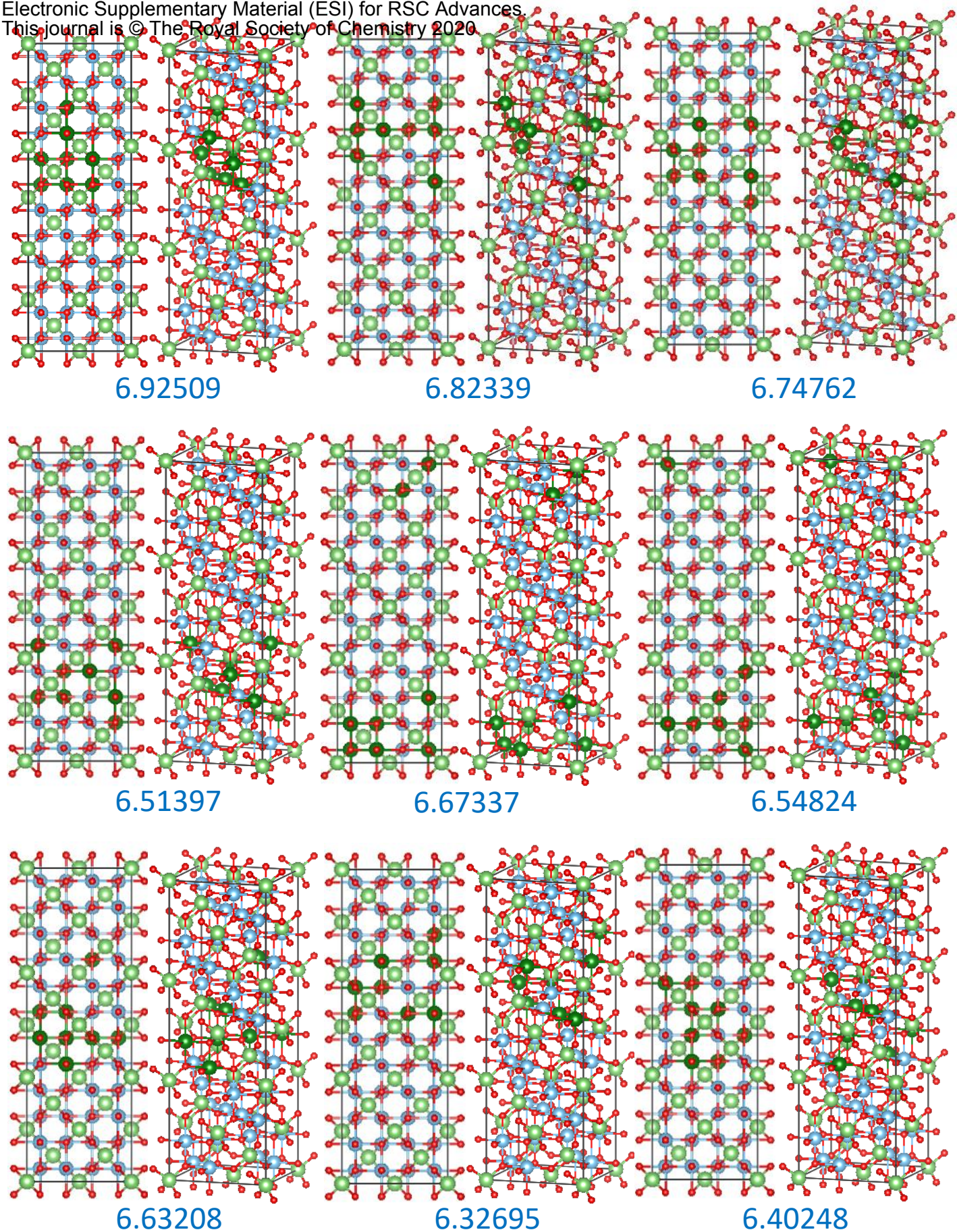
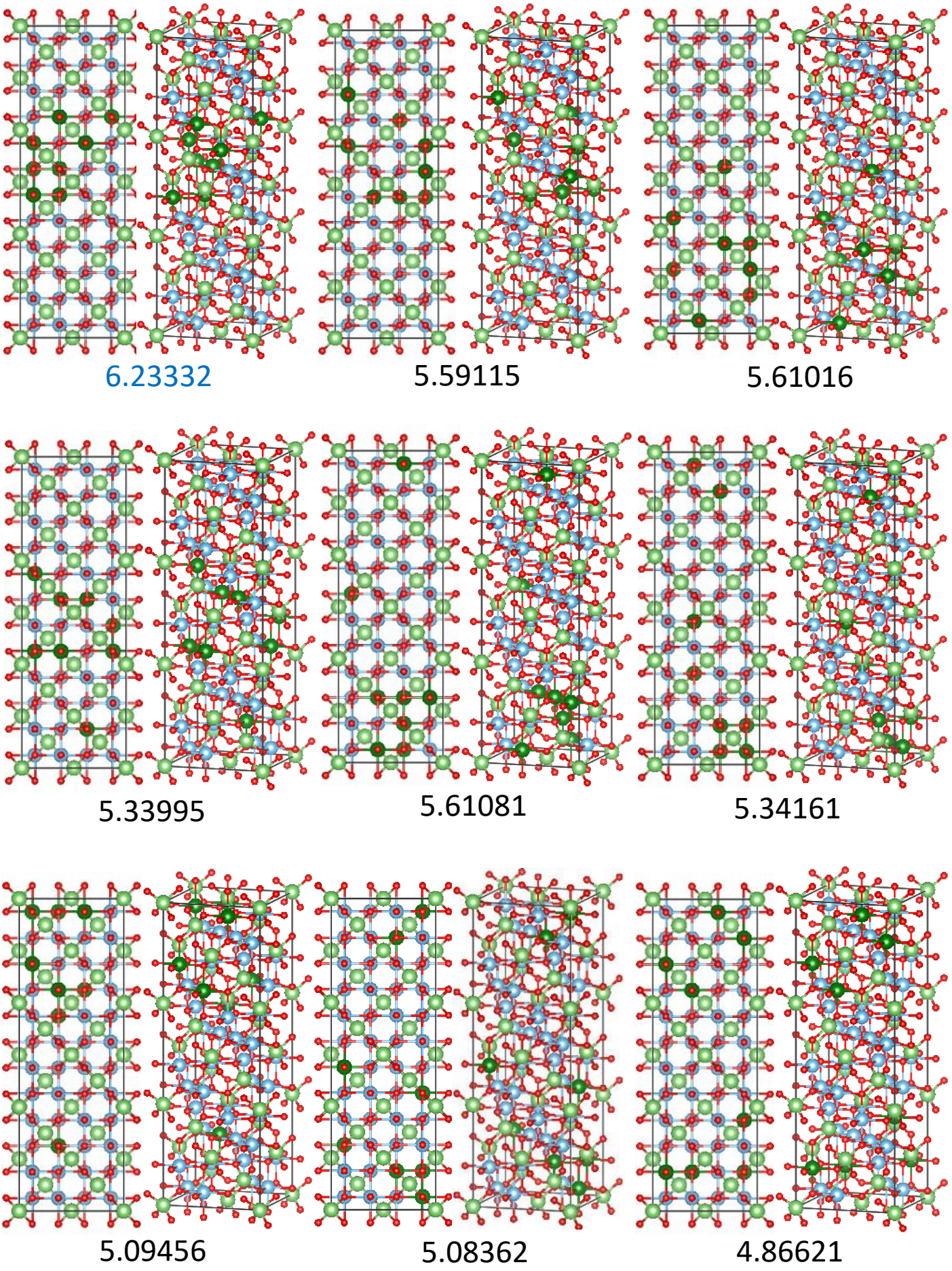


Figure S1. Side (left panels) and perspective (right panels) views of the initial structures of $Li_4Ti_5O_{12}$ and their *S* values of the selected 58 models. Spheres in green, blue, and red represent Li, Ti, and O atoms, respectively; spheres in dark and light green represent Li atoms at the 16d and 8a sites, respectively. Numbers in blue and red represent the ten least and most stable structures, respectively.



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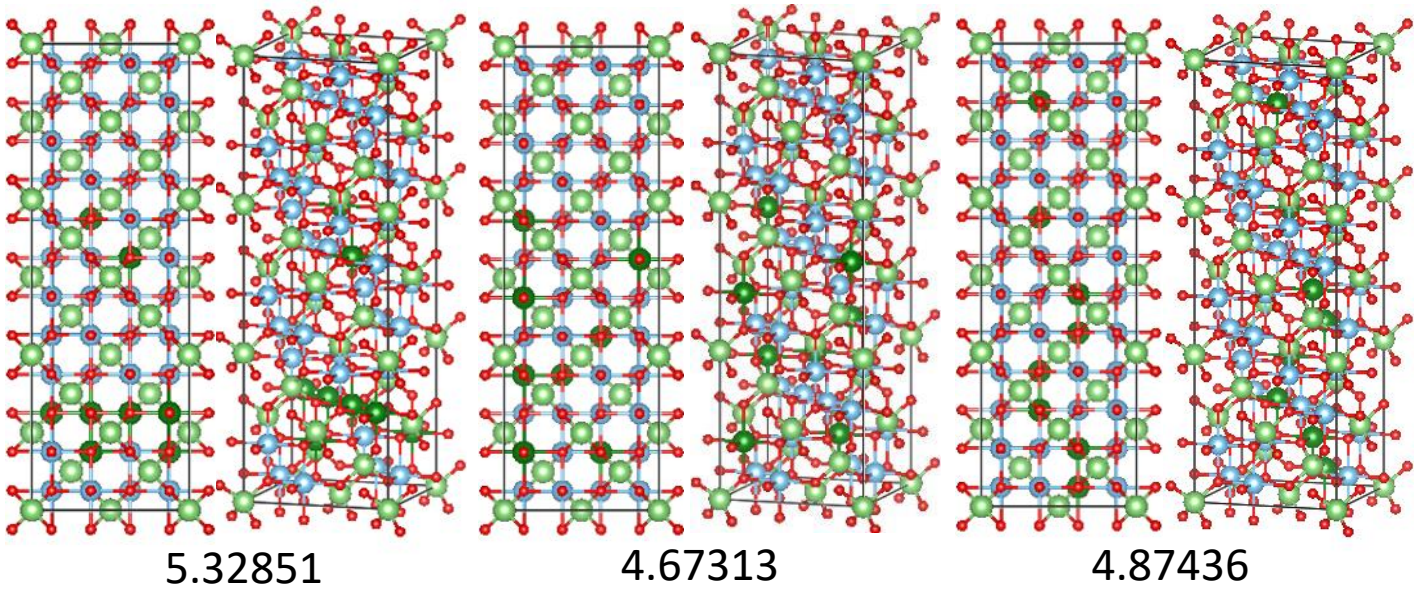

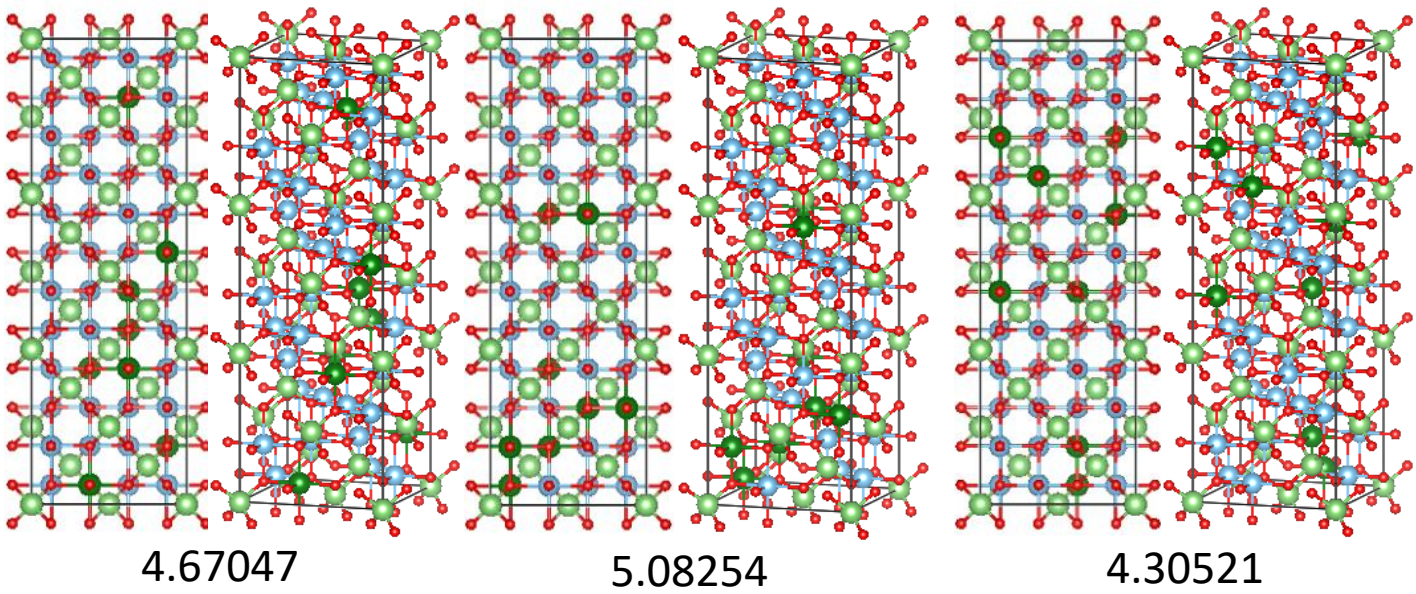

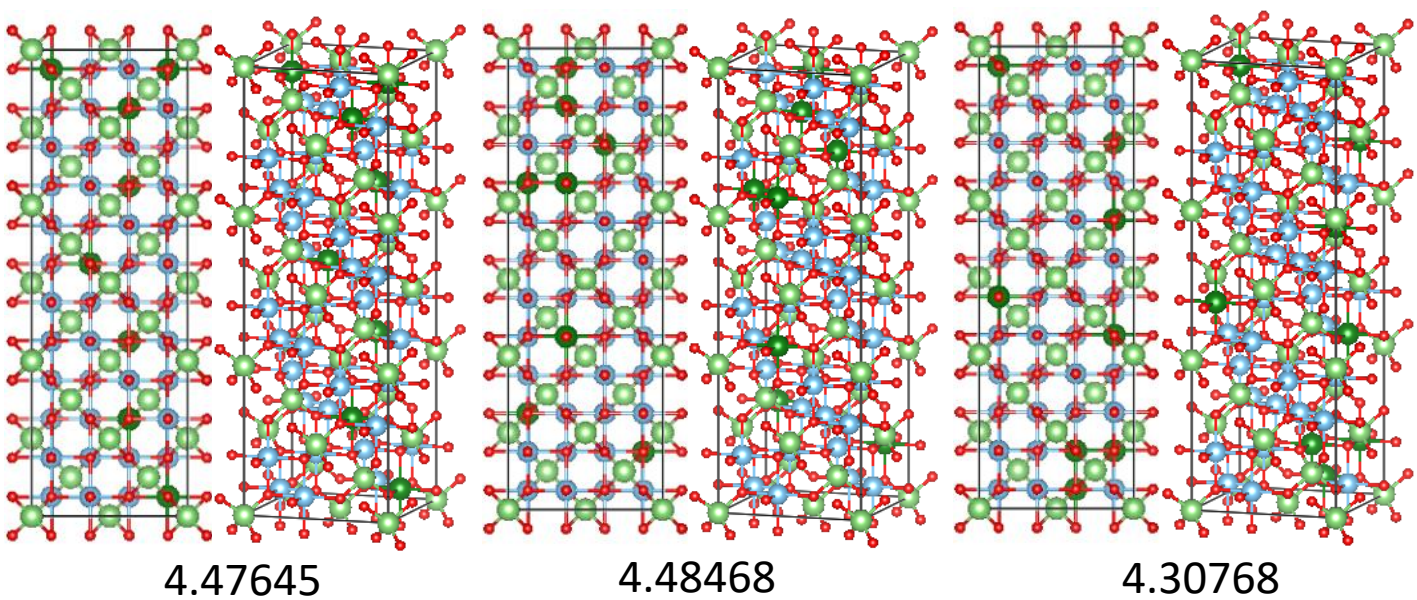

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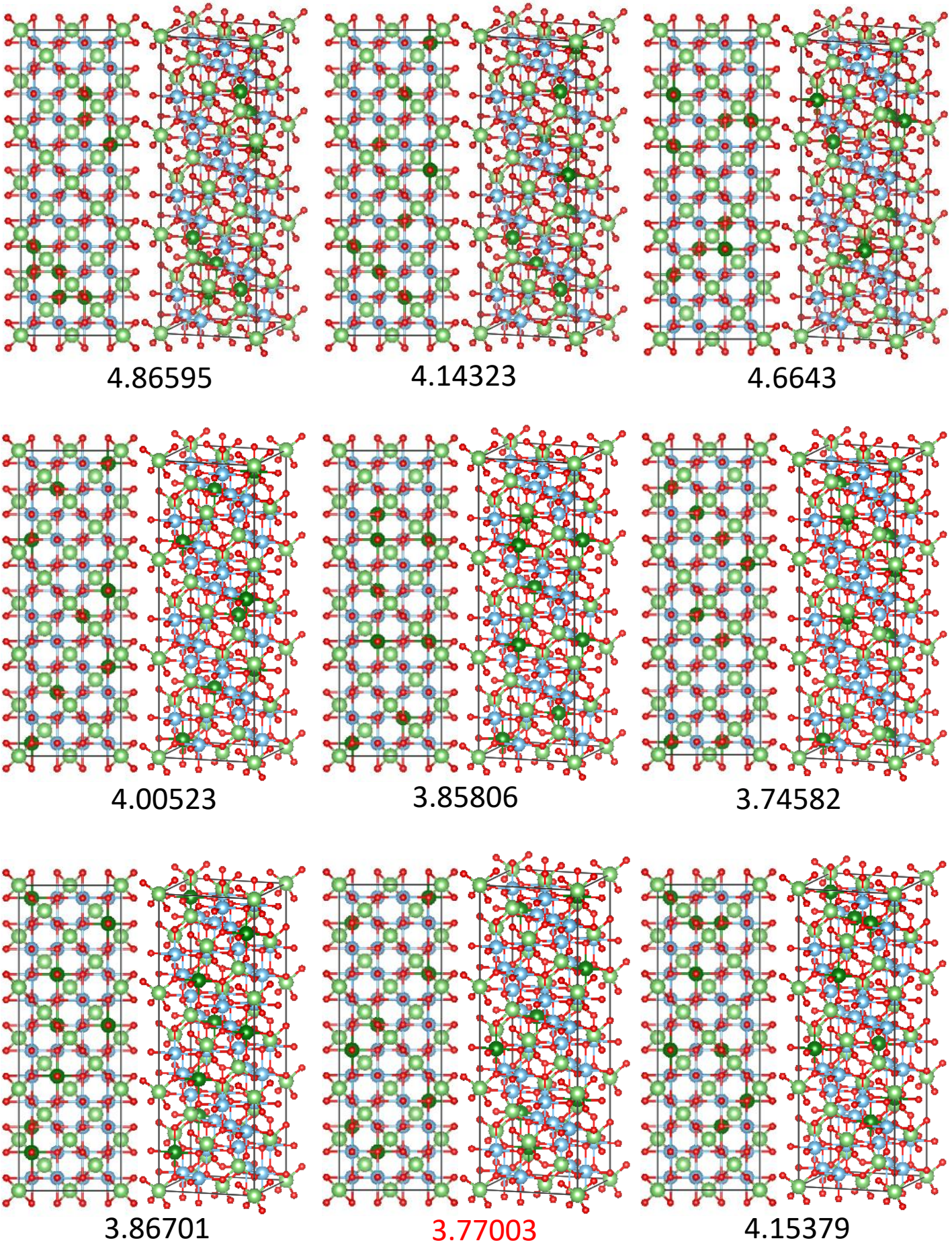

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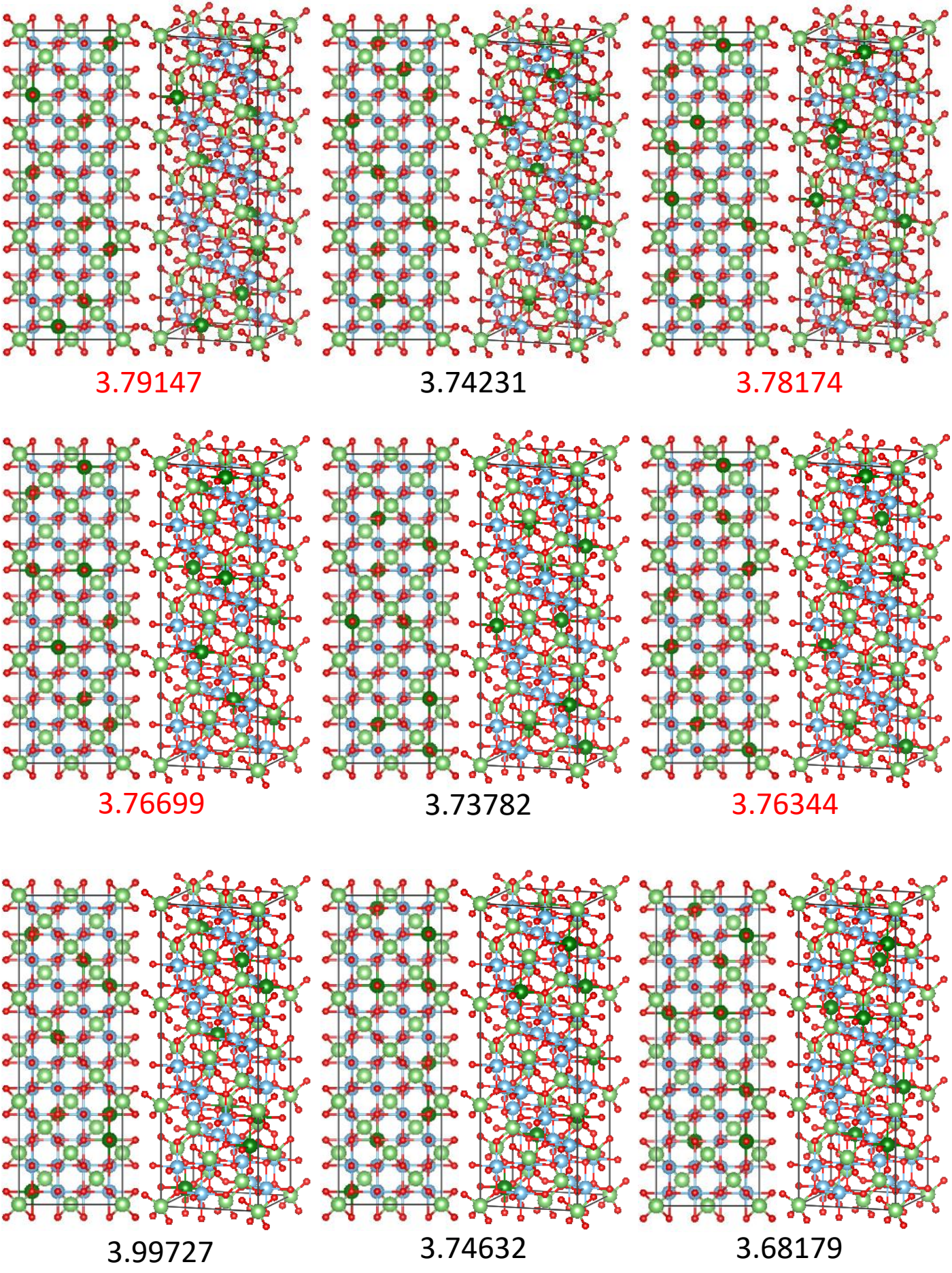

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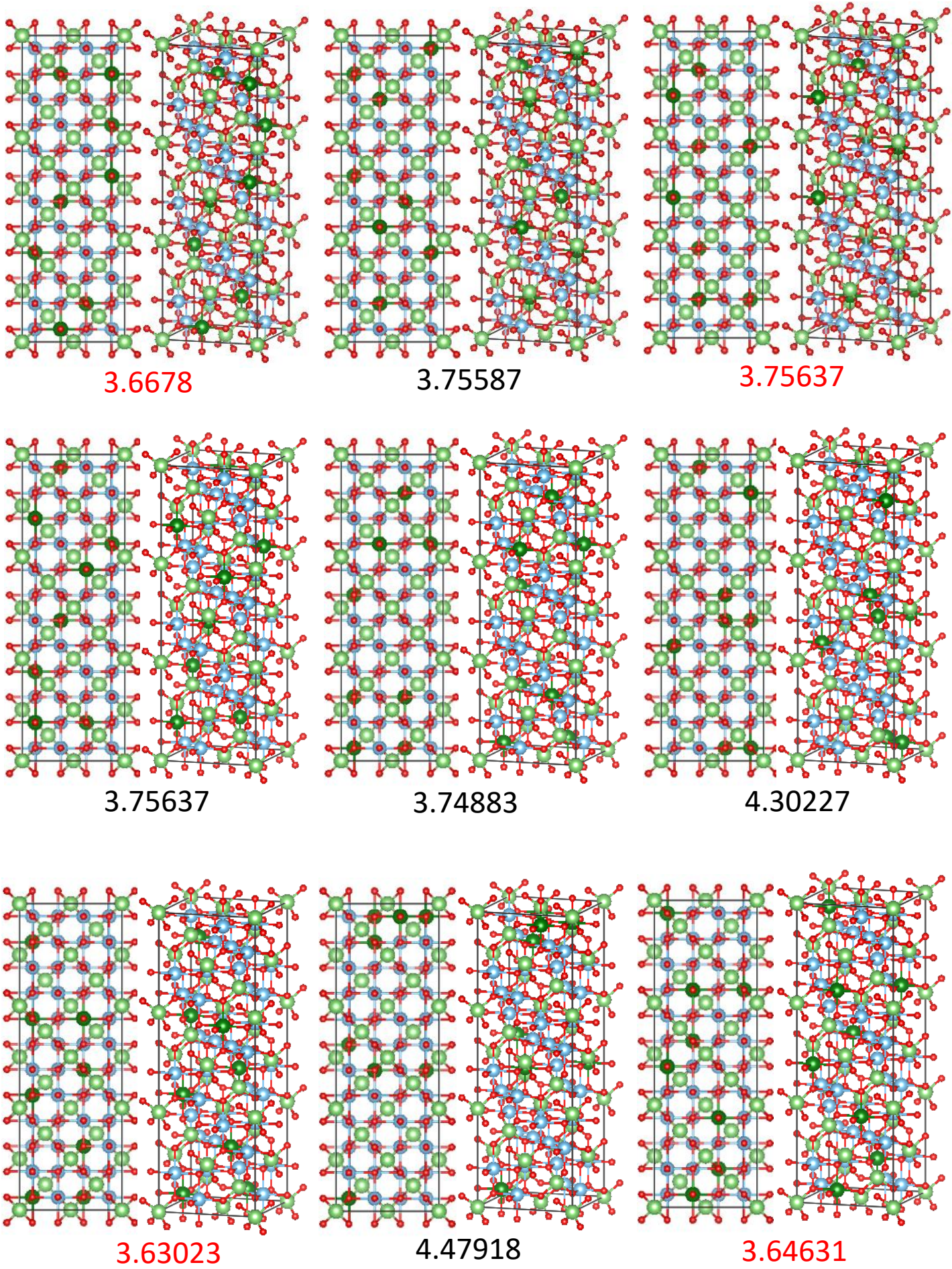

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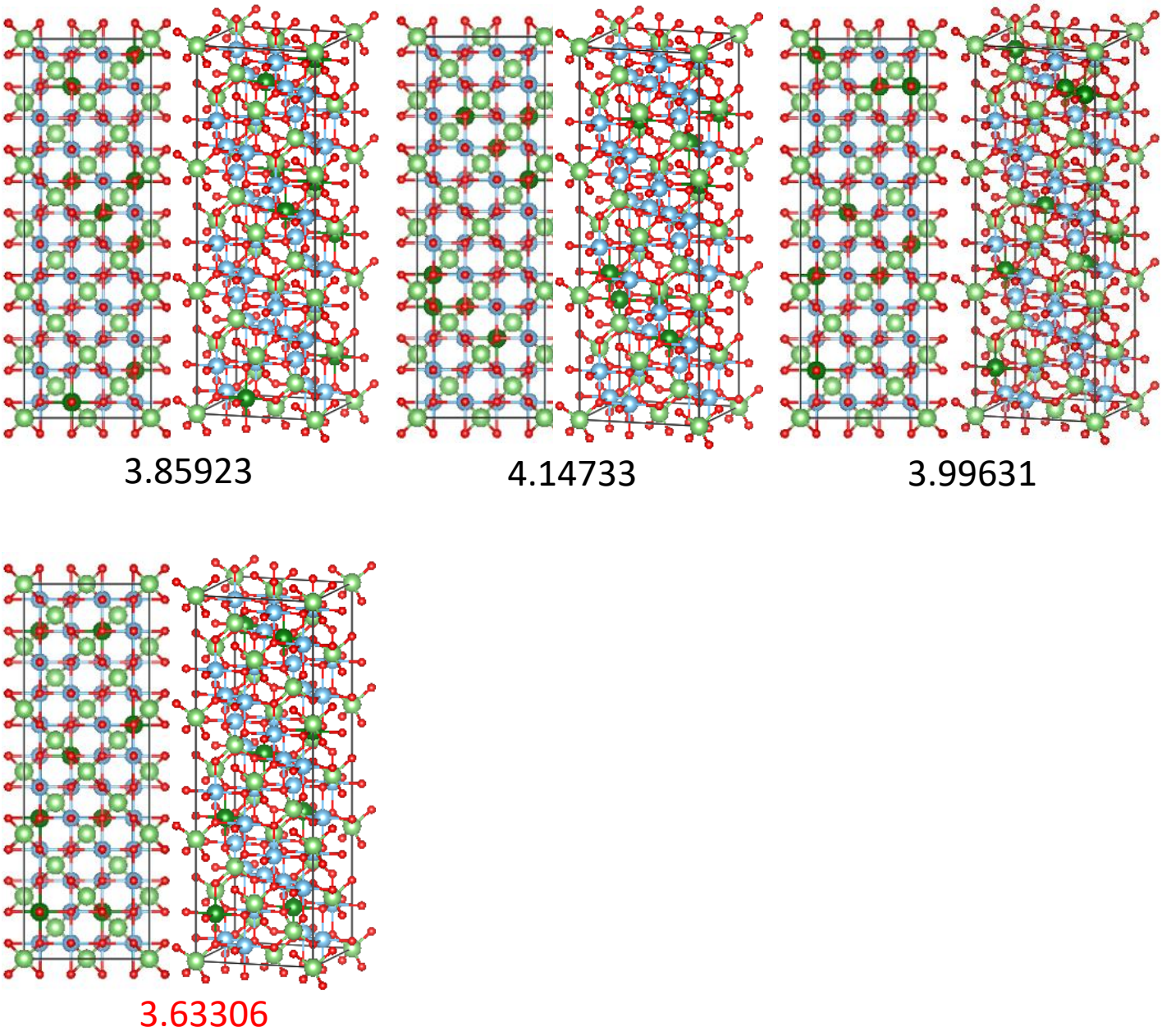

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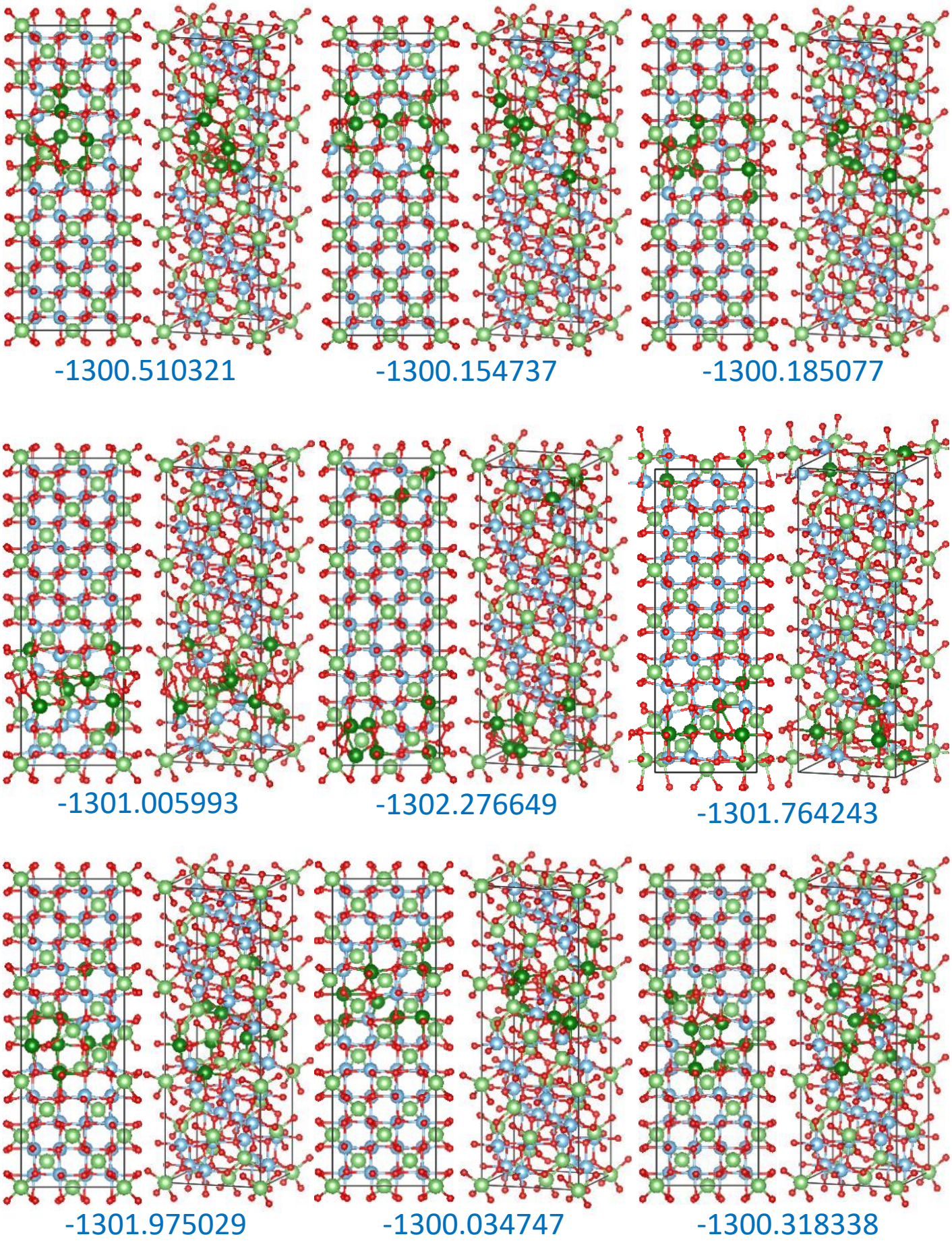
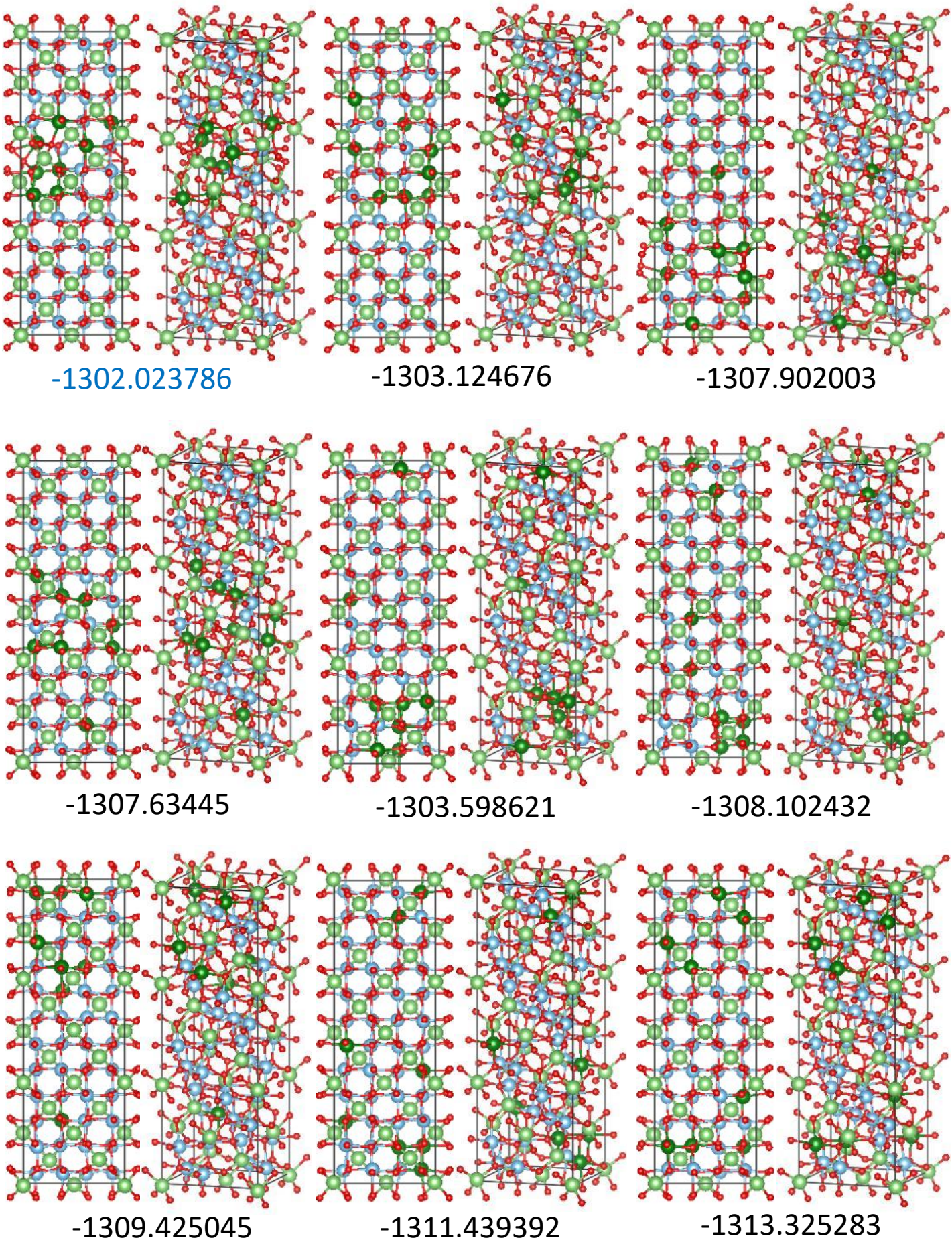


Figure S2 Side (left panels) and perspective (right panels) views of the optimized structures of $Li_4Ti_5O_{12}$ and total energy of the selected 58 models. Spheres in yellow, green, blue, and red represent Na, Li, Ti, and O atoms, respectively. Numbers in blue and red represent the 10 least and 10 most stable structures, respectively.



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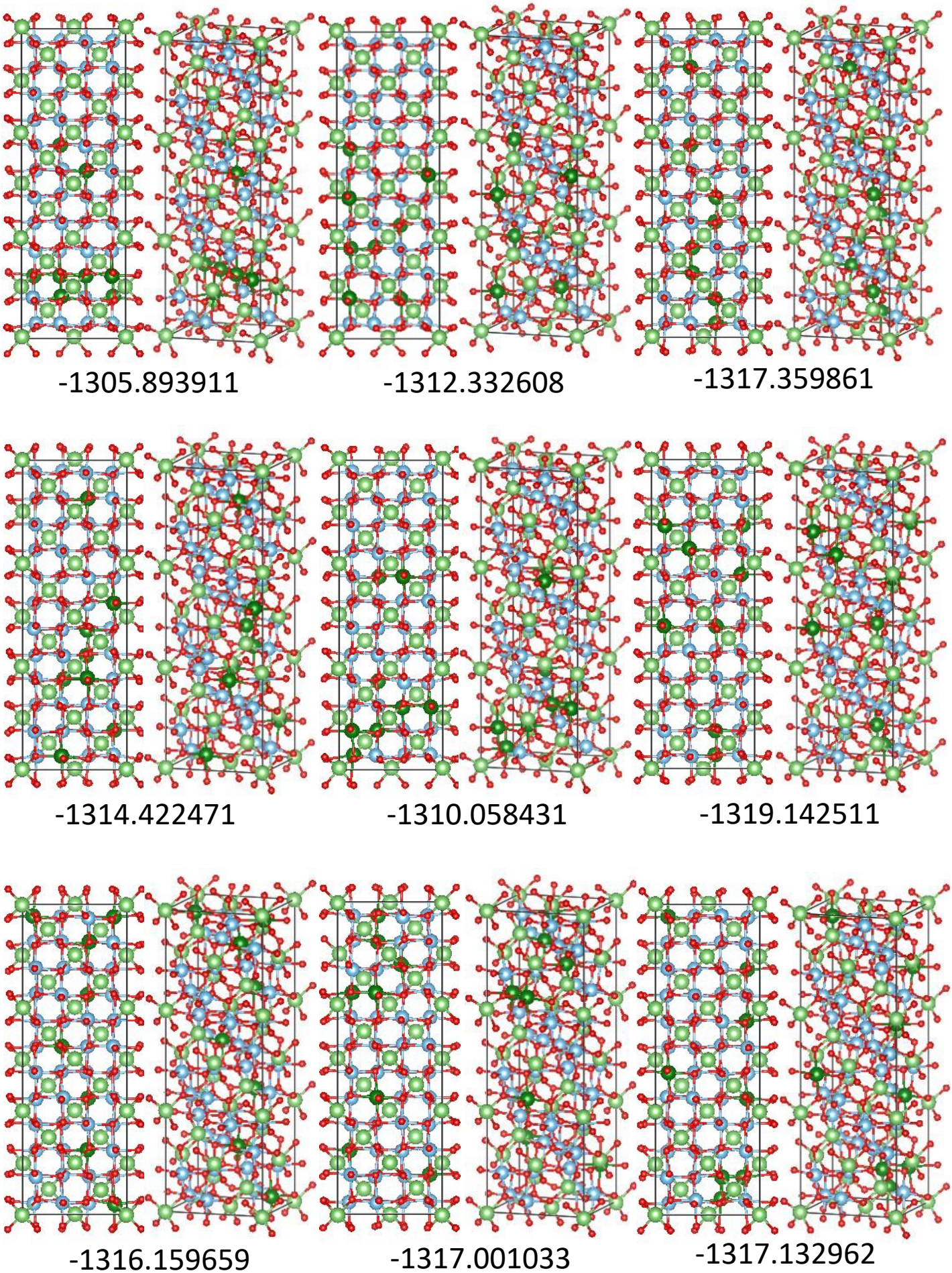

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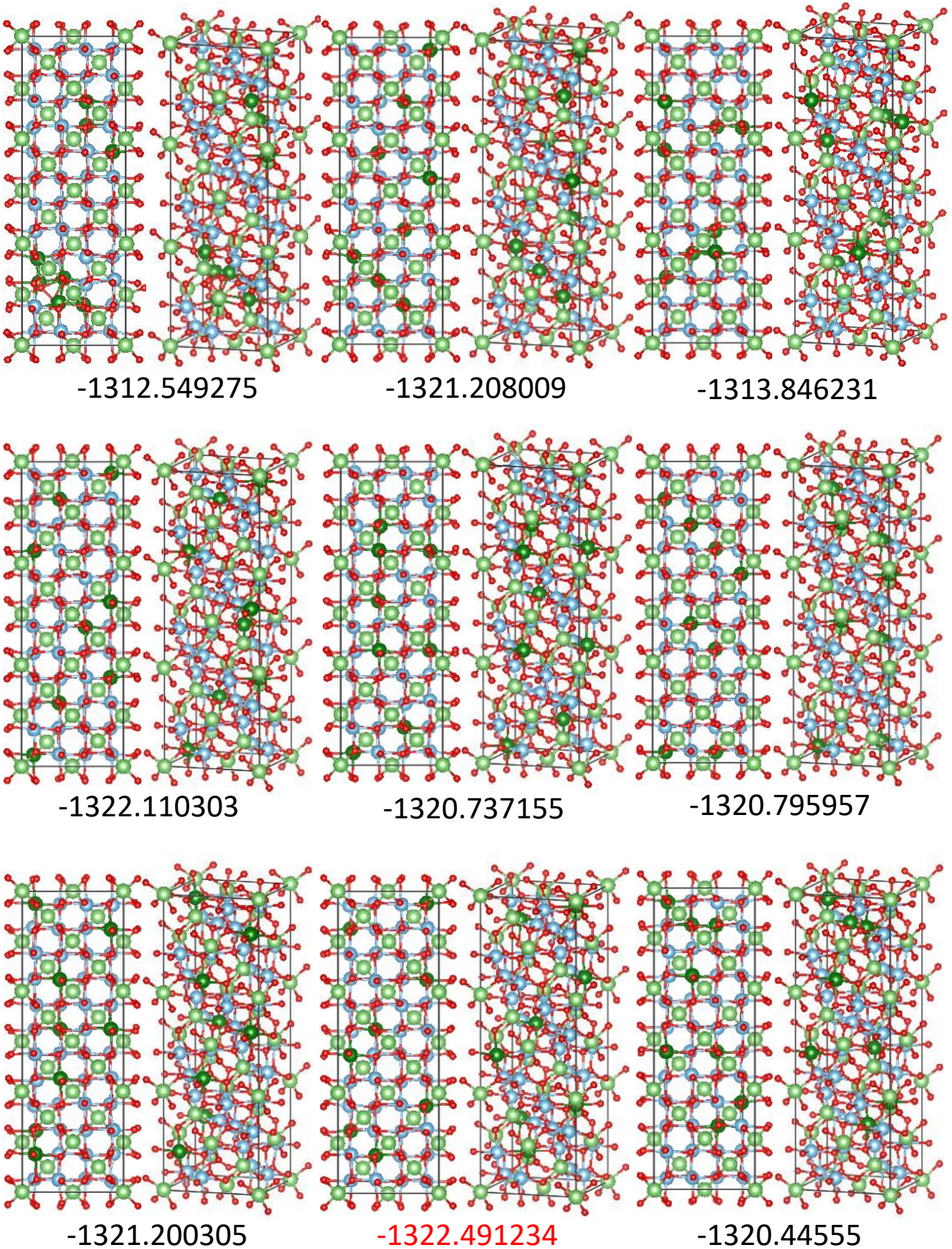

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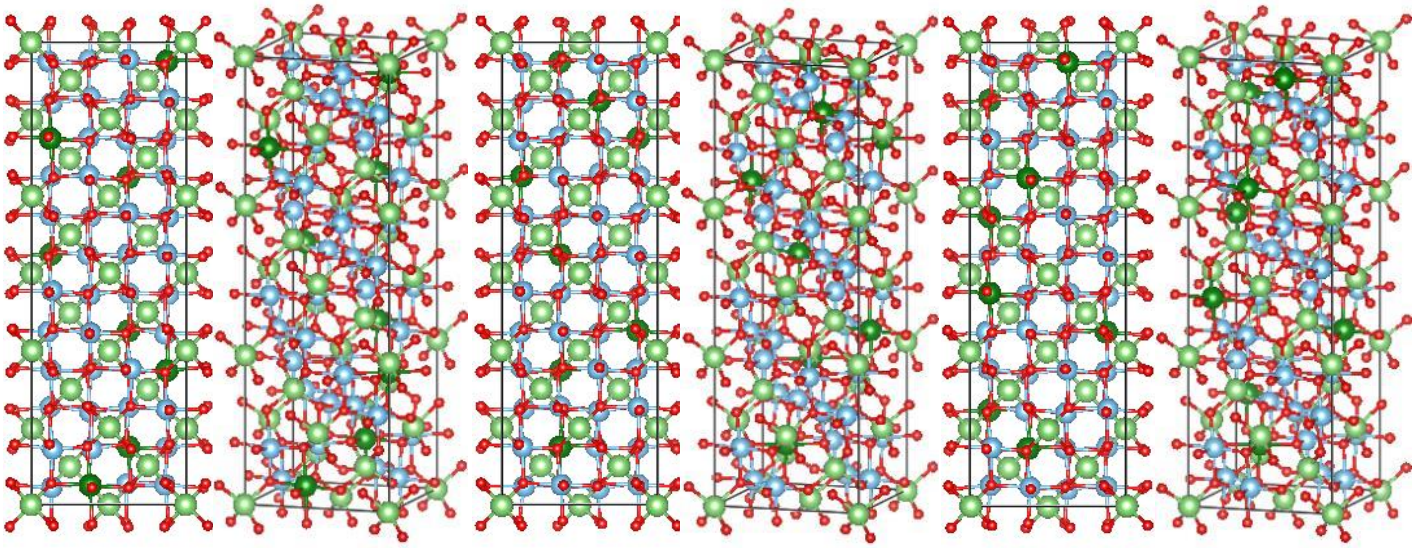

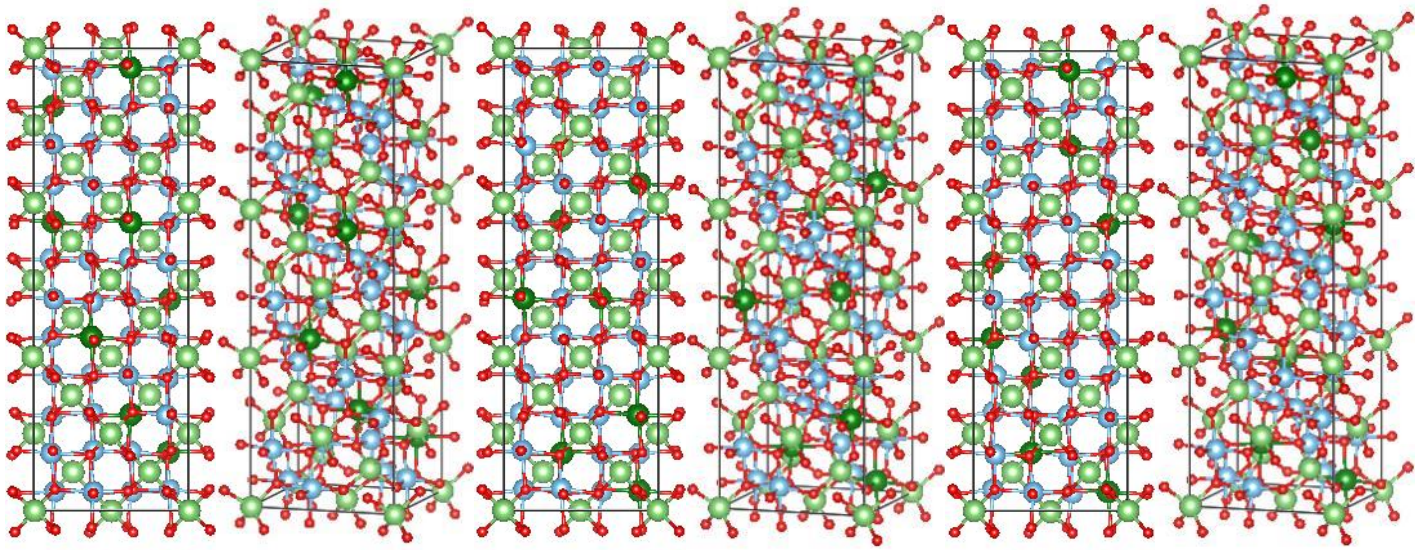

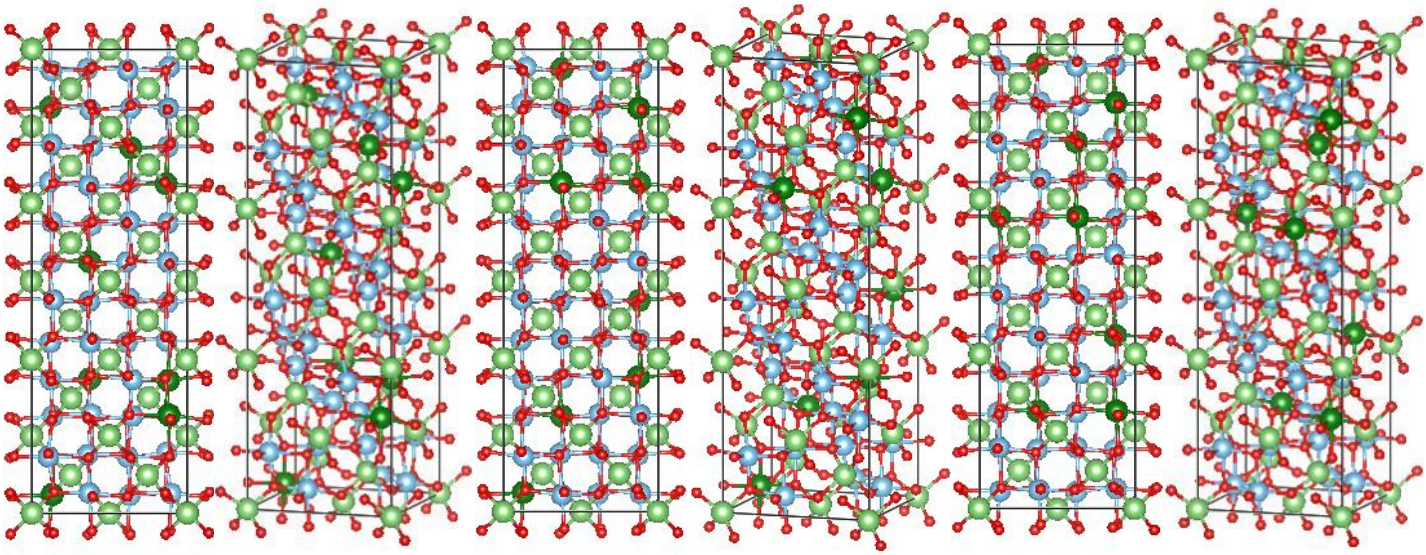

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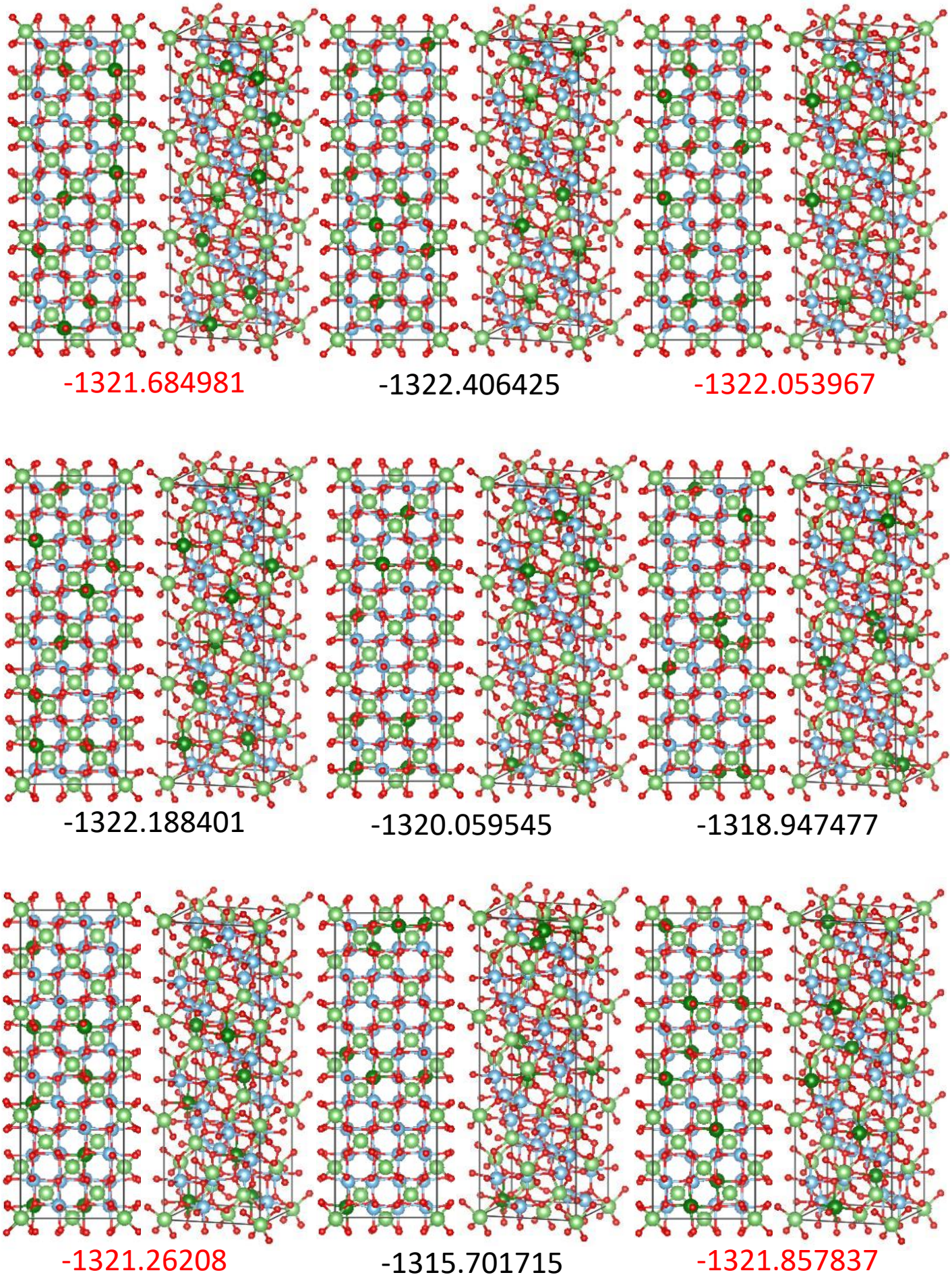

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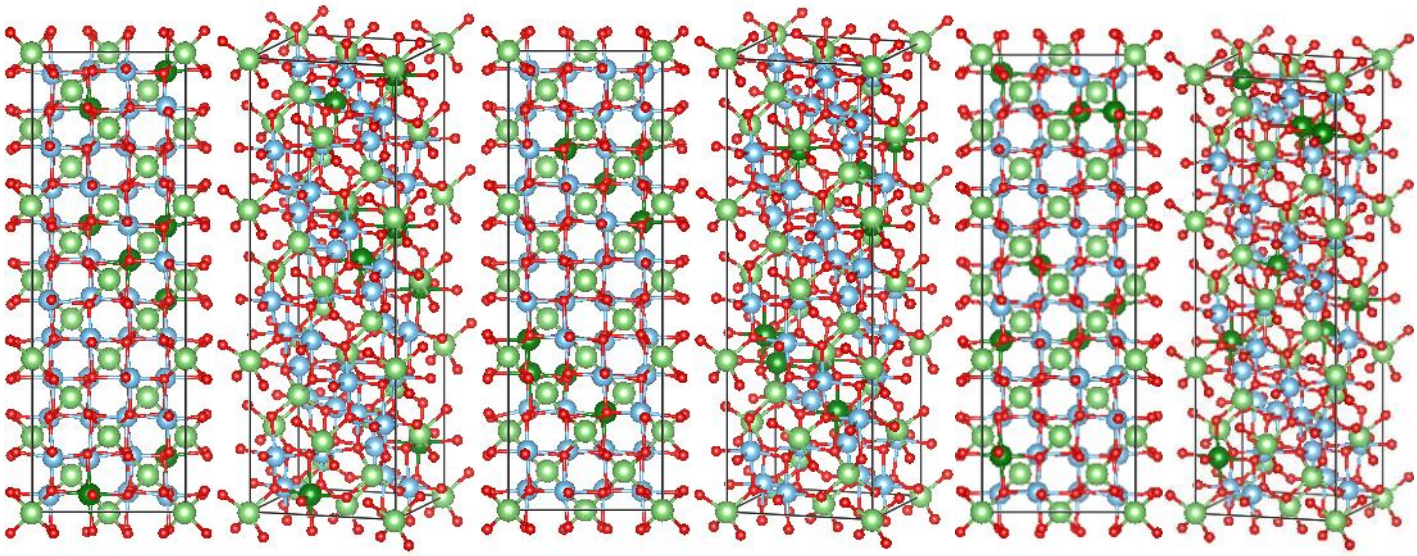

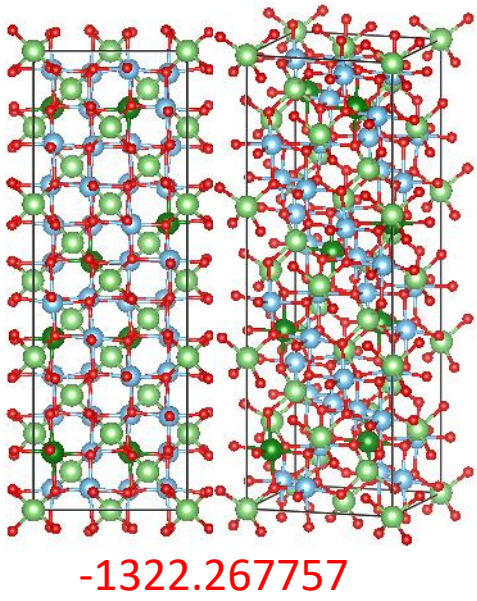

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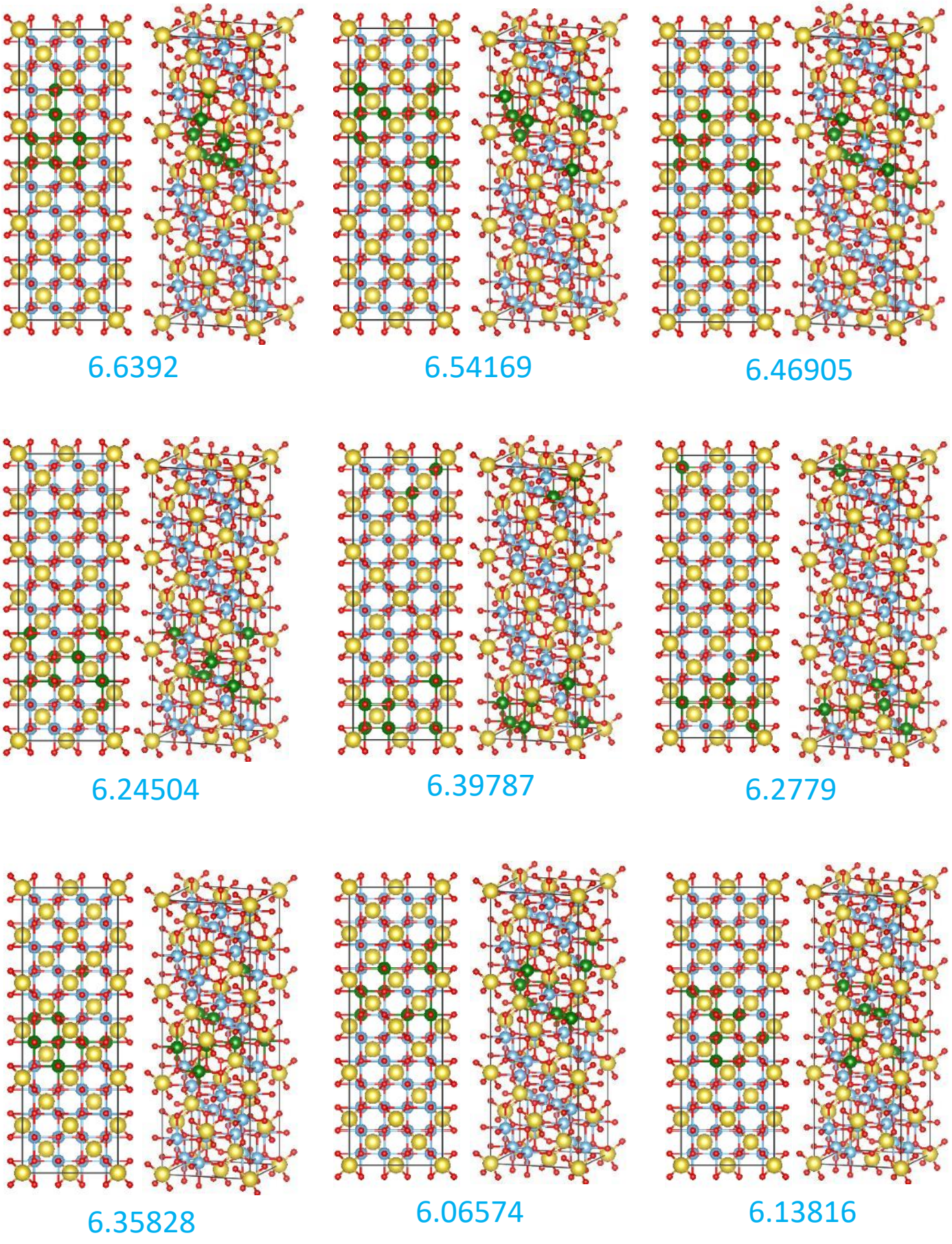
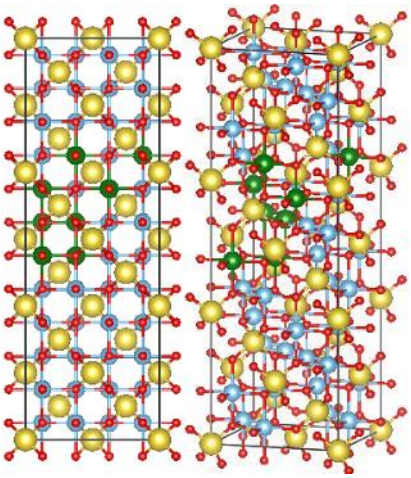


Figure S3 Side (left panels) and perspective (right panels) views of the initial structures of $Na_3LiTi_5O_{12}$ and *S* values of the selected 58 models. Spheres in yellow, green, blue, and red represent Na, Li, Ti, and O atoms, respectively. Numbers in blue and red represent the ten least and most stable structures, respectively.



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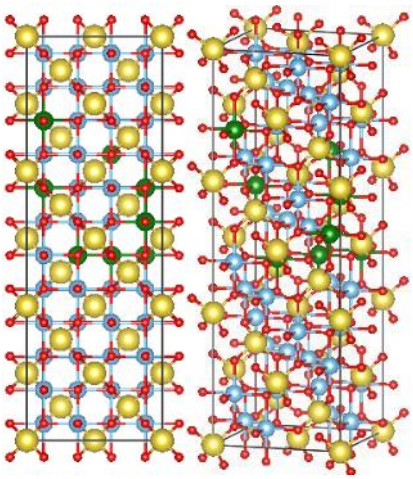

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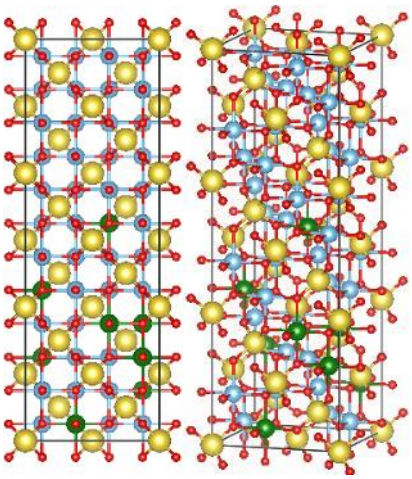

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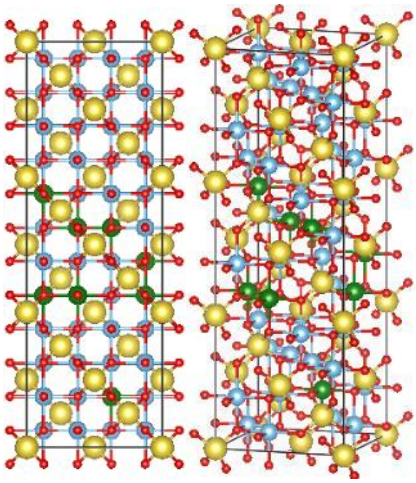

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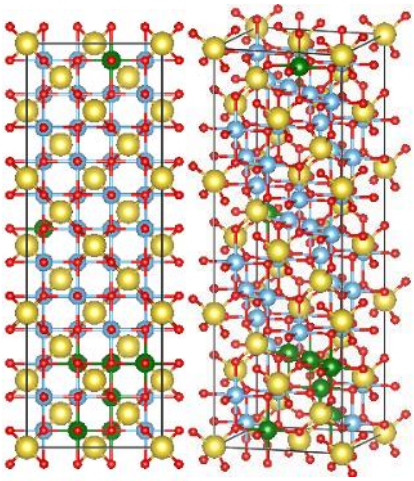

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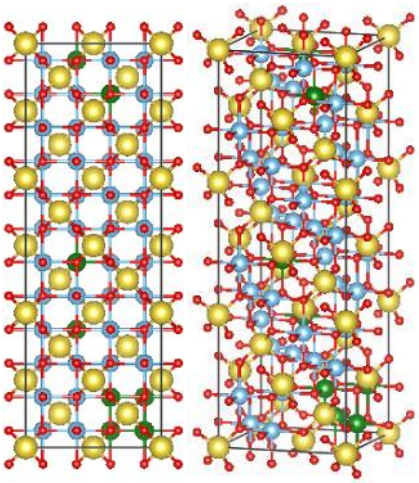

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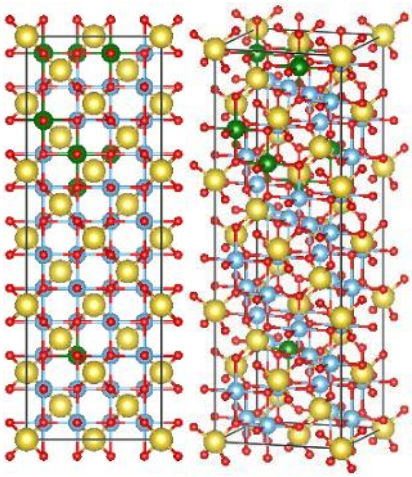

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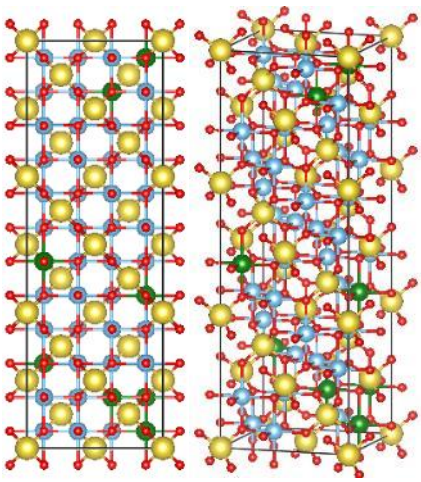

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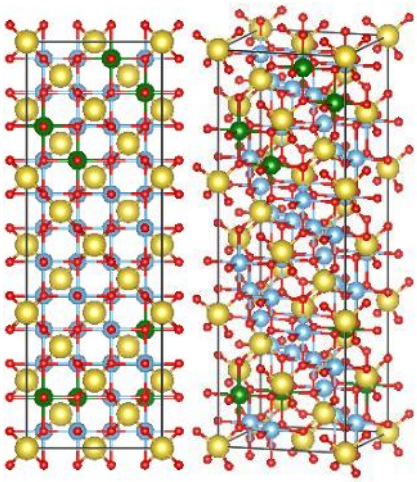

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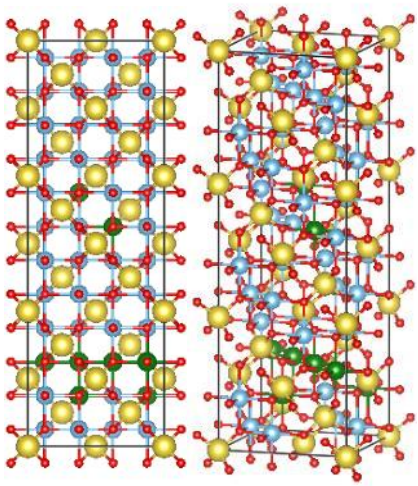

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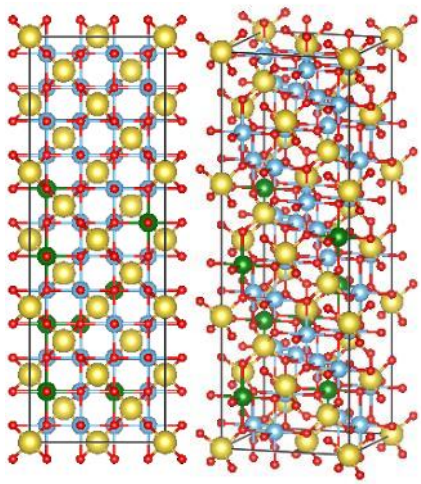

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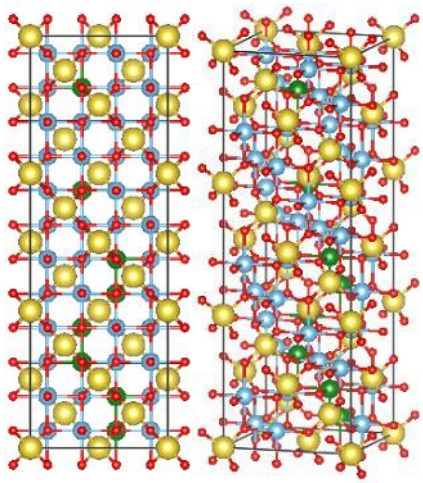

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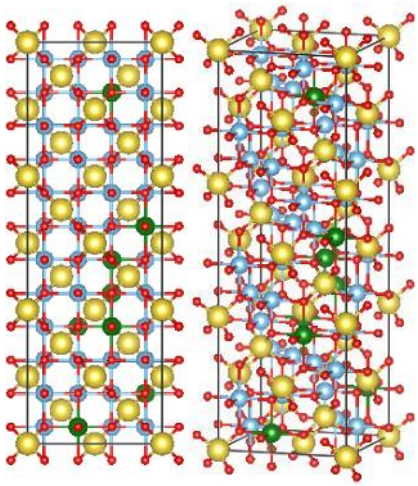

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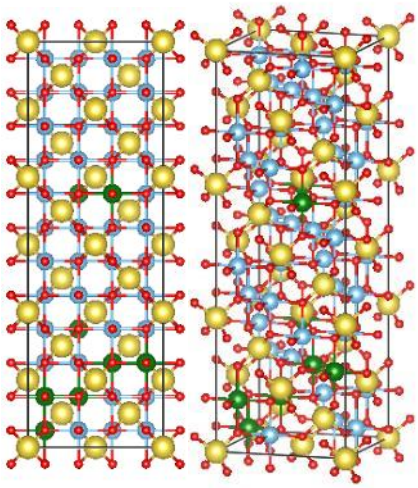

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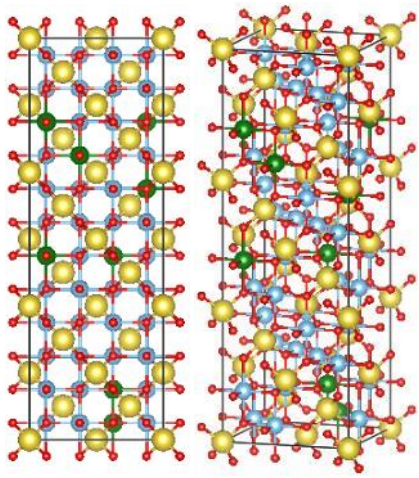

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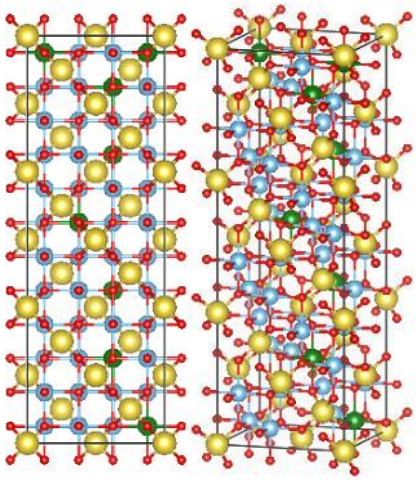

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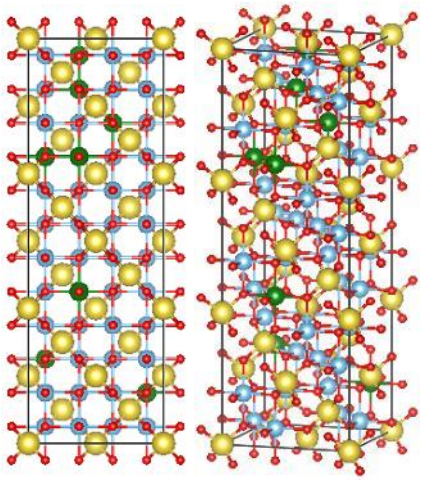

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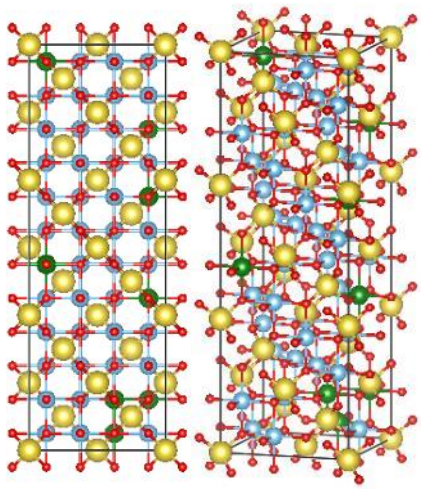

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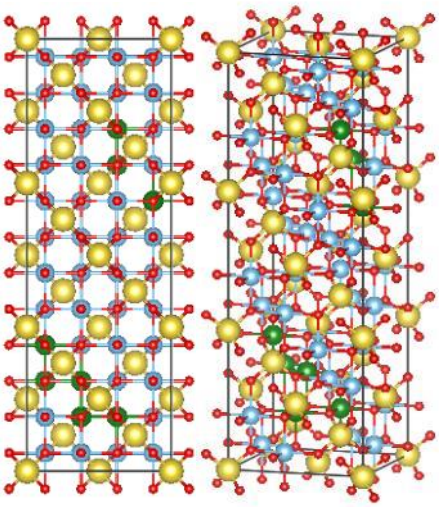

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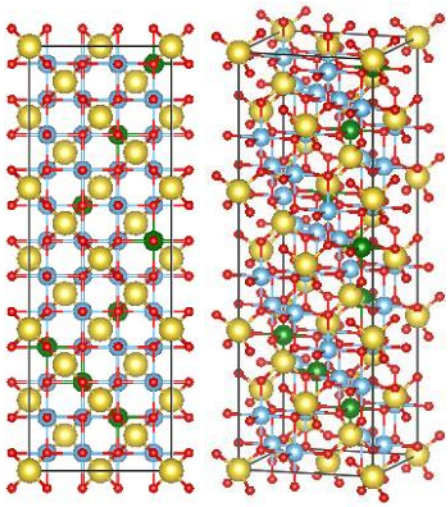

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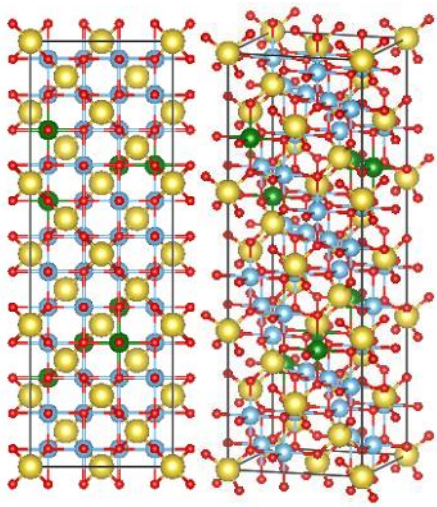

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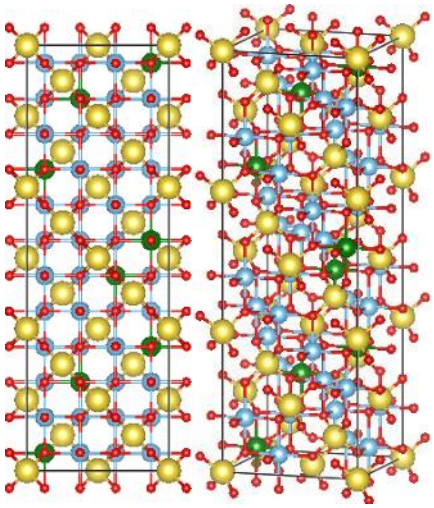

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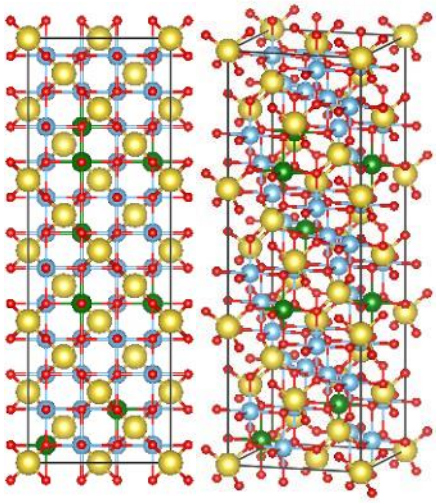

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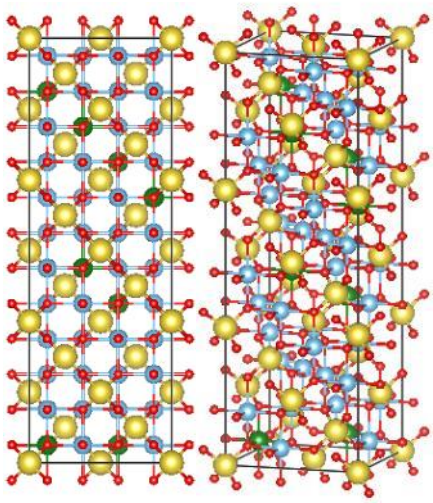

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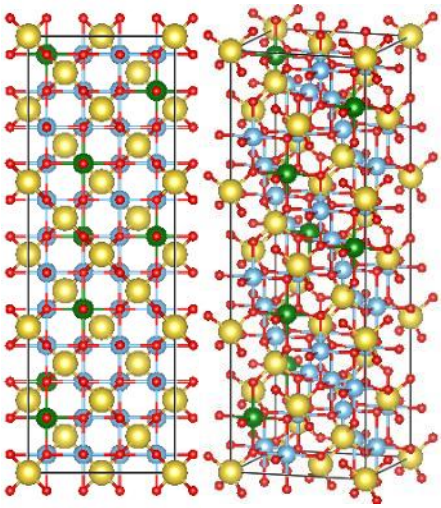

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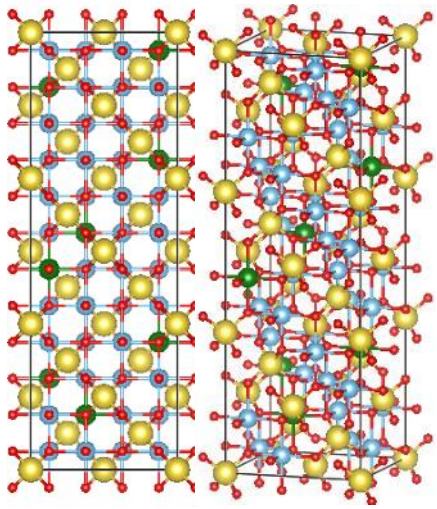

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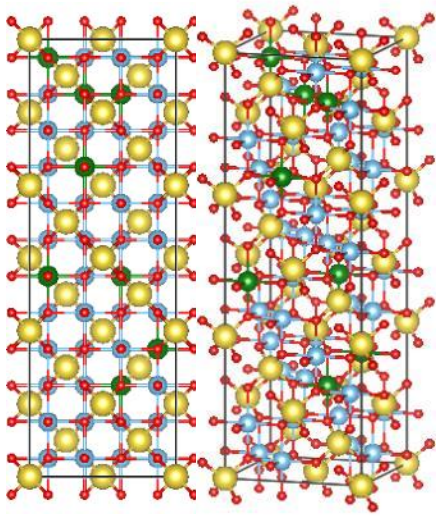

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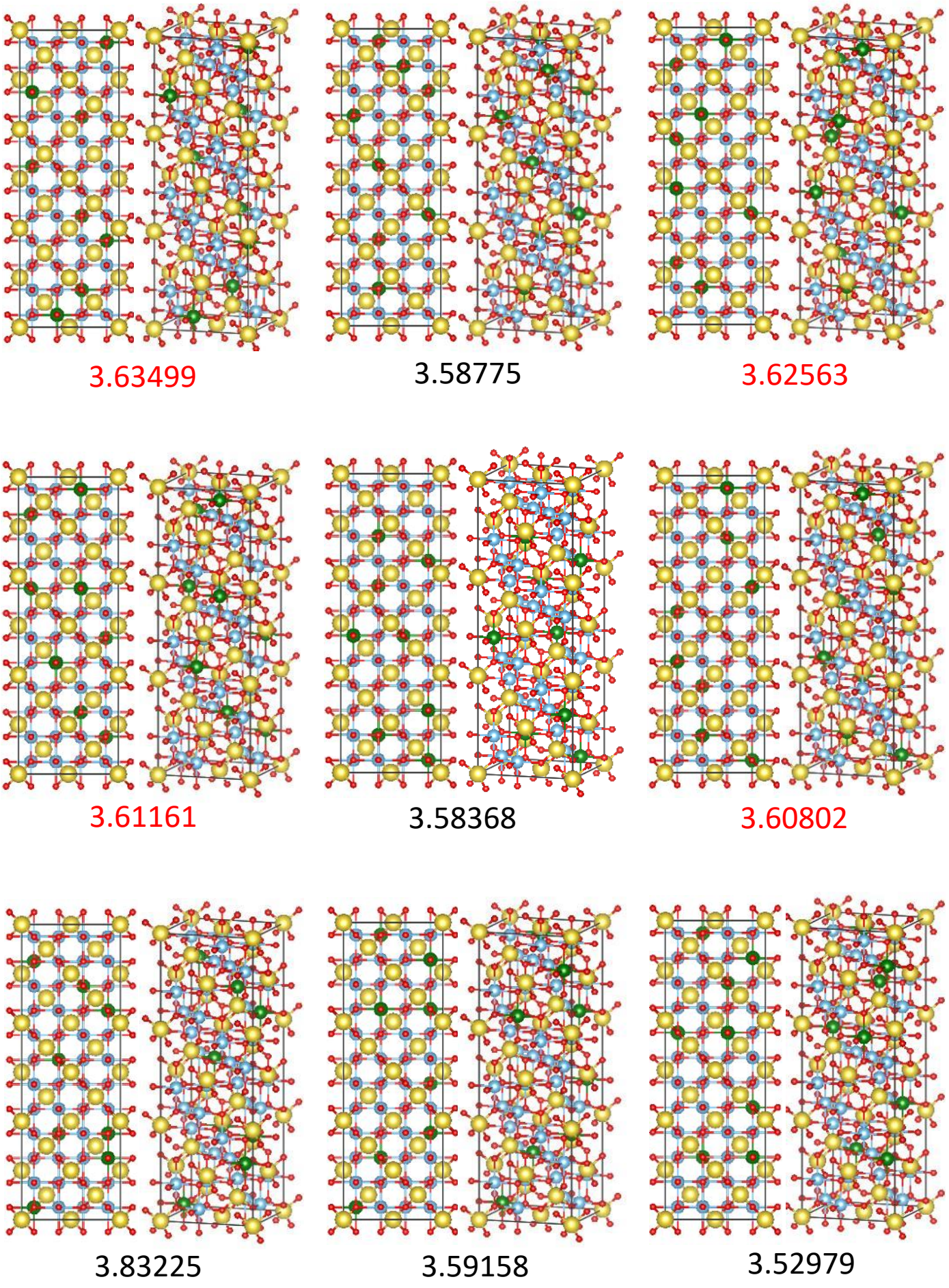

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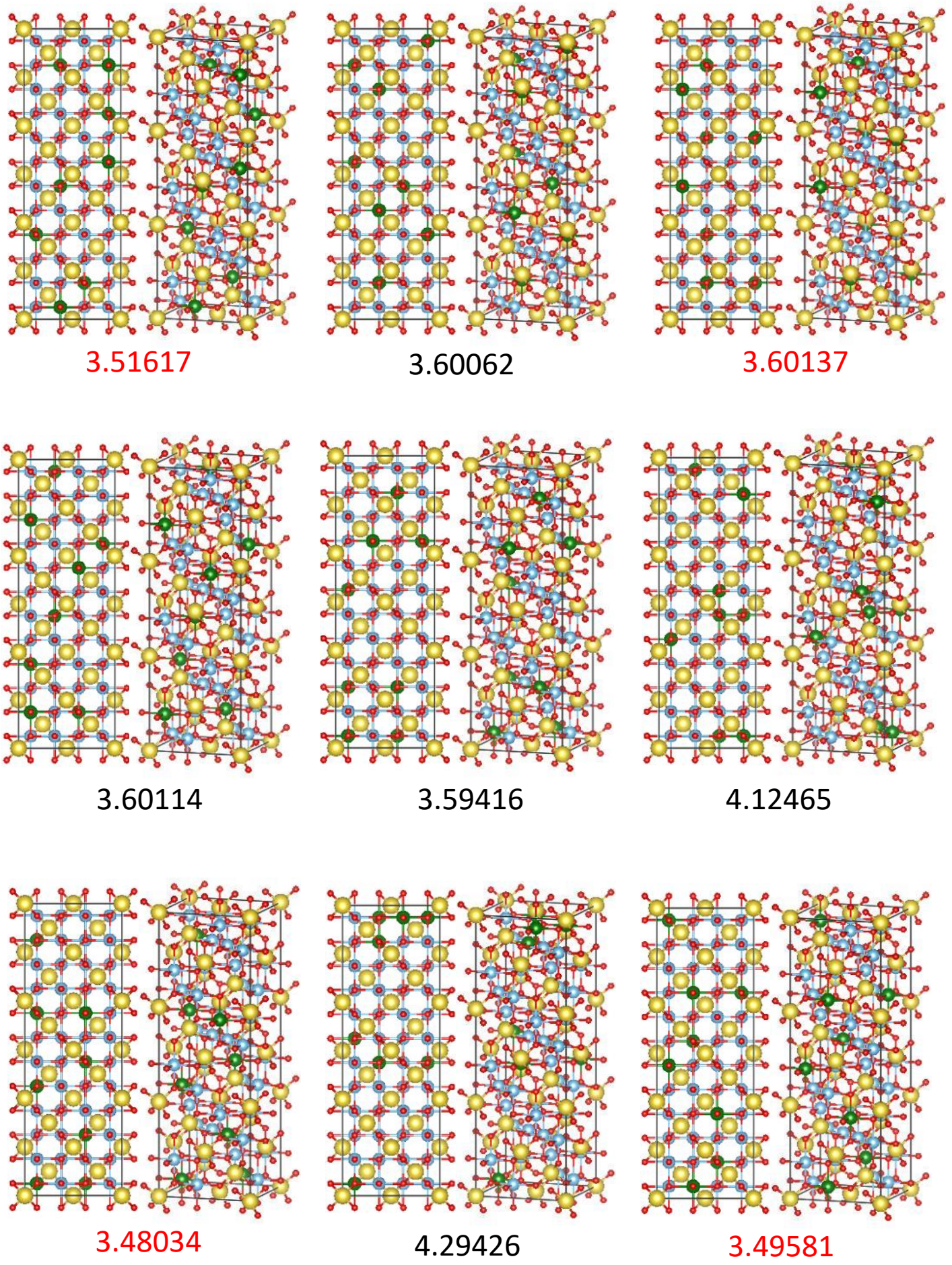

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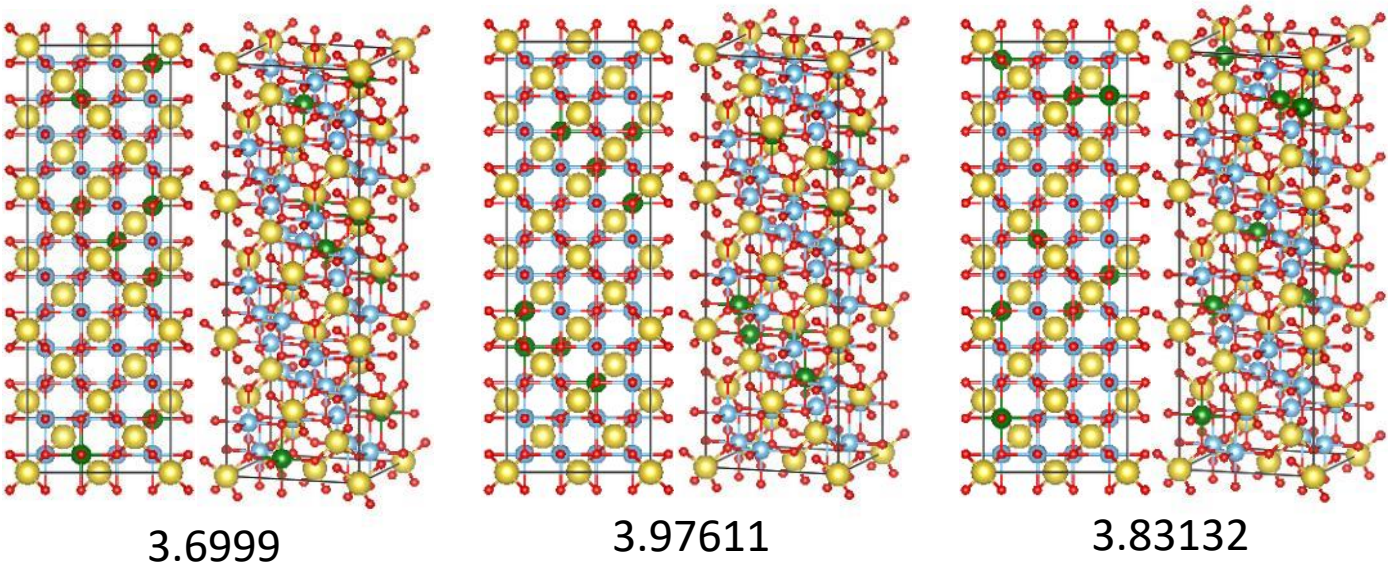

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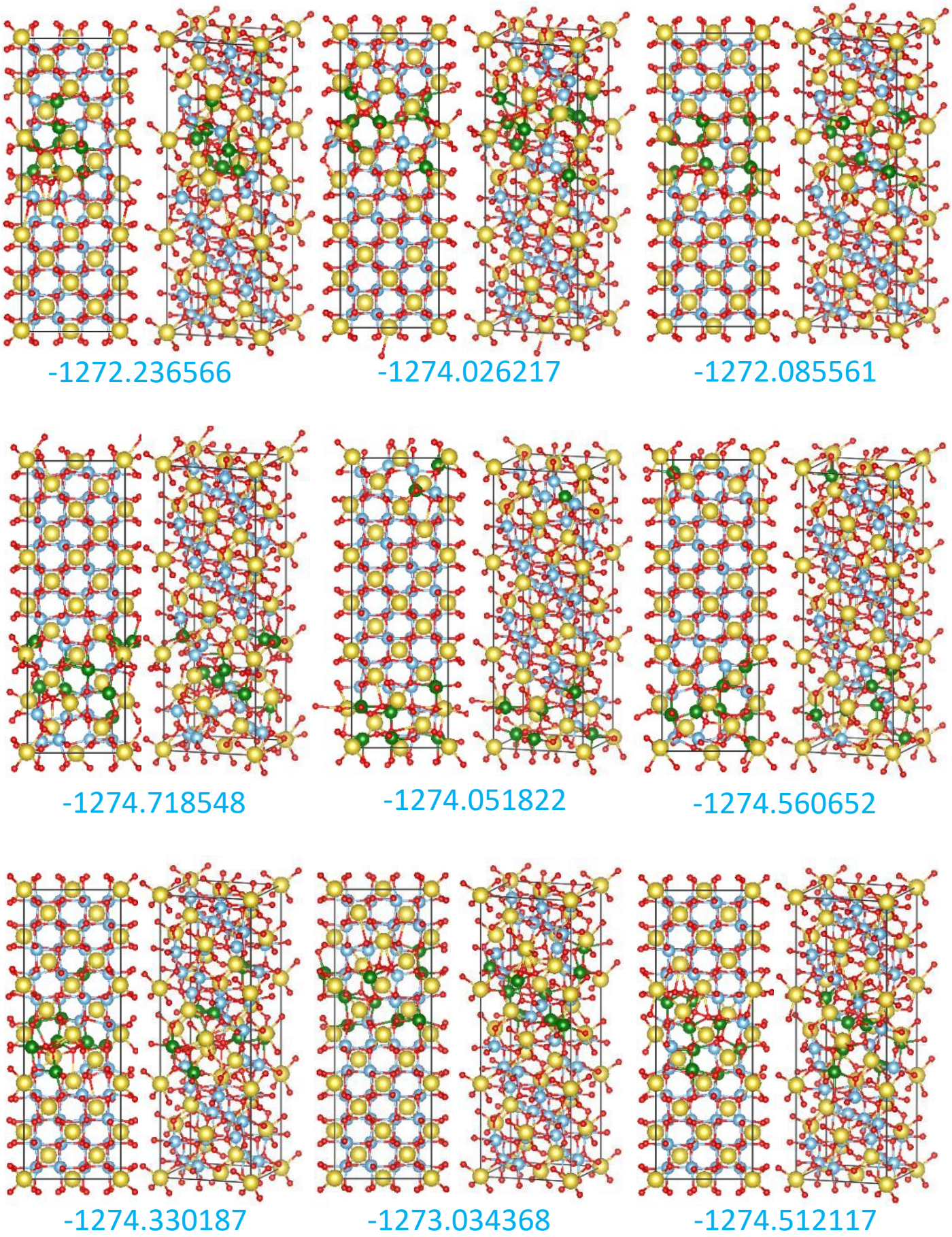
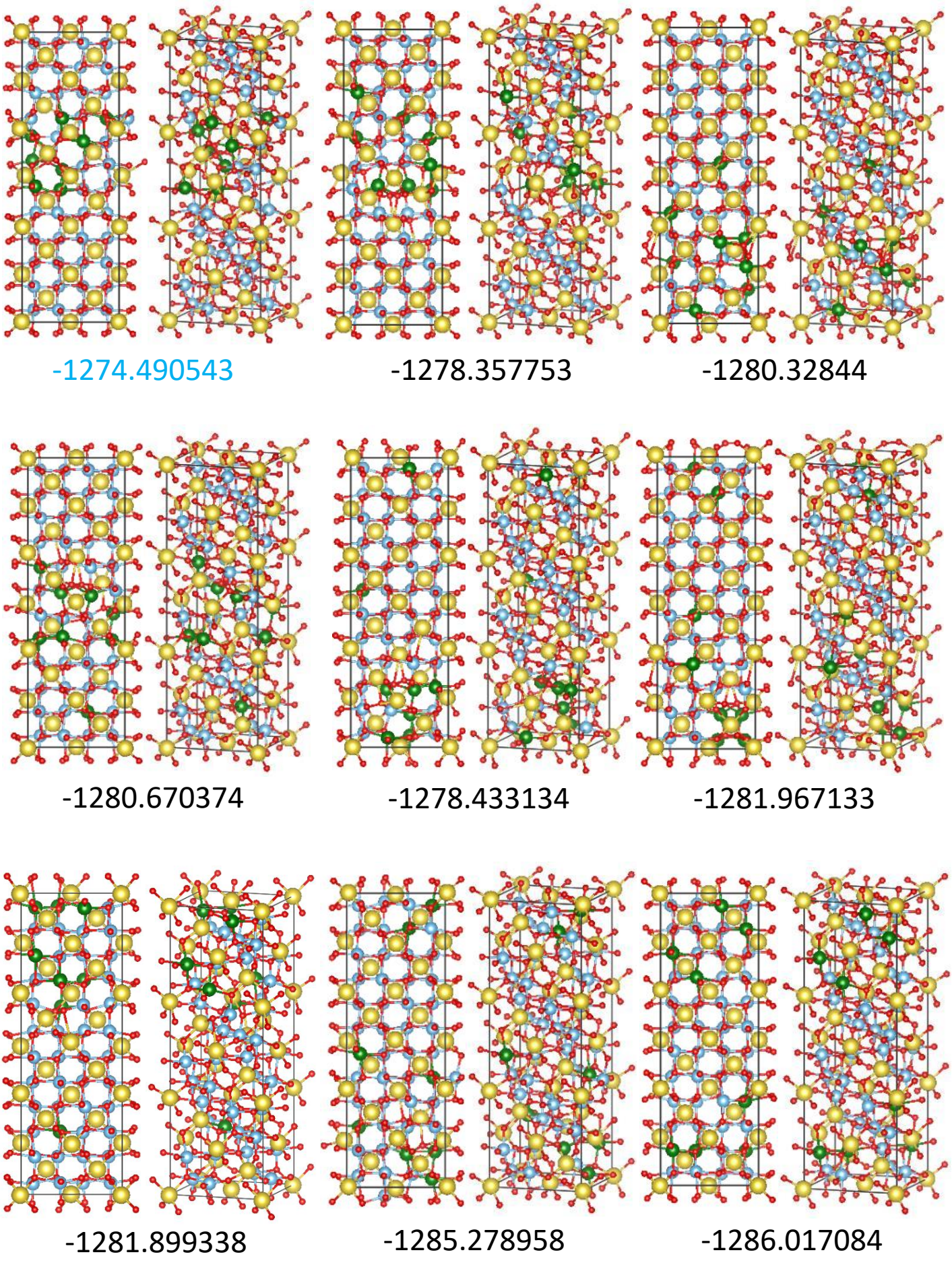


Figure S4 Side (left panels) and perspective (right panels) views of the optimized structures of $Na_3LiTi_5O_{12}$ and total energy of selected 58 models. Spheres in yellow, green, blue, and red represent Na, Li, Ti, and O atoms, respectively. Numbers in blue and red represent the ten least and most stable structures, respectively.



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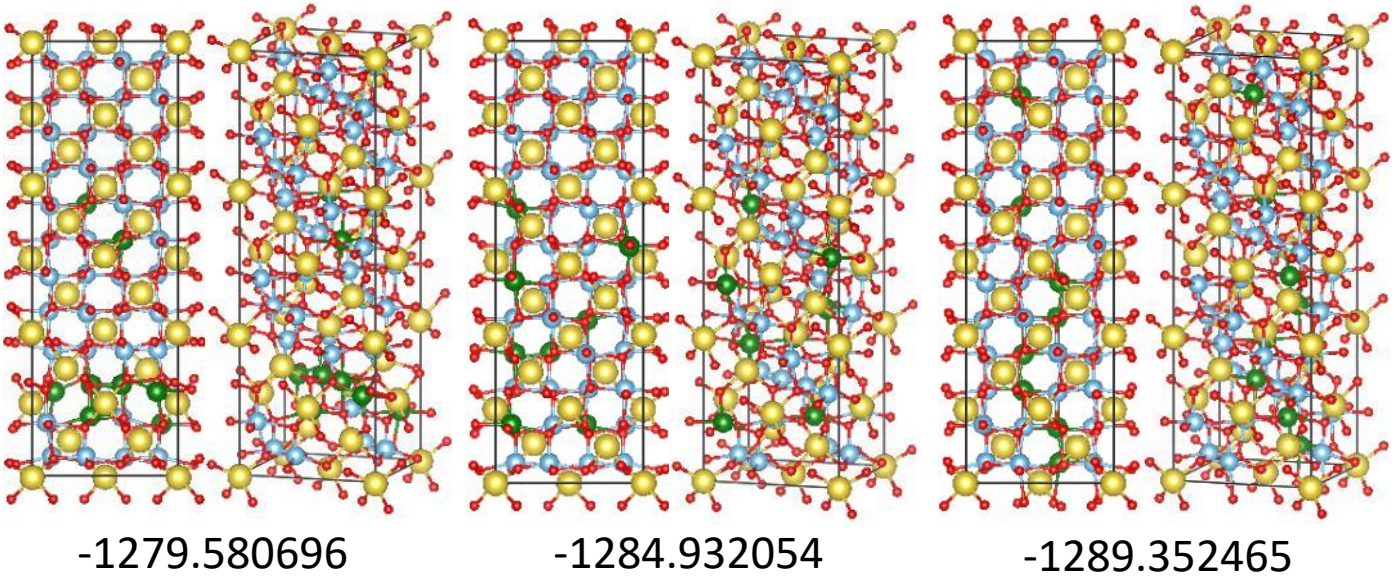

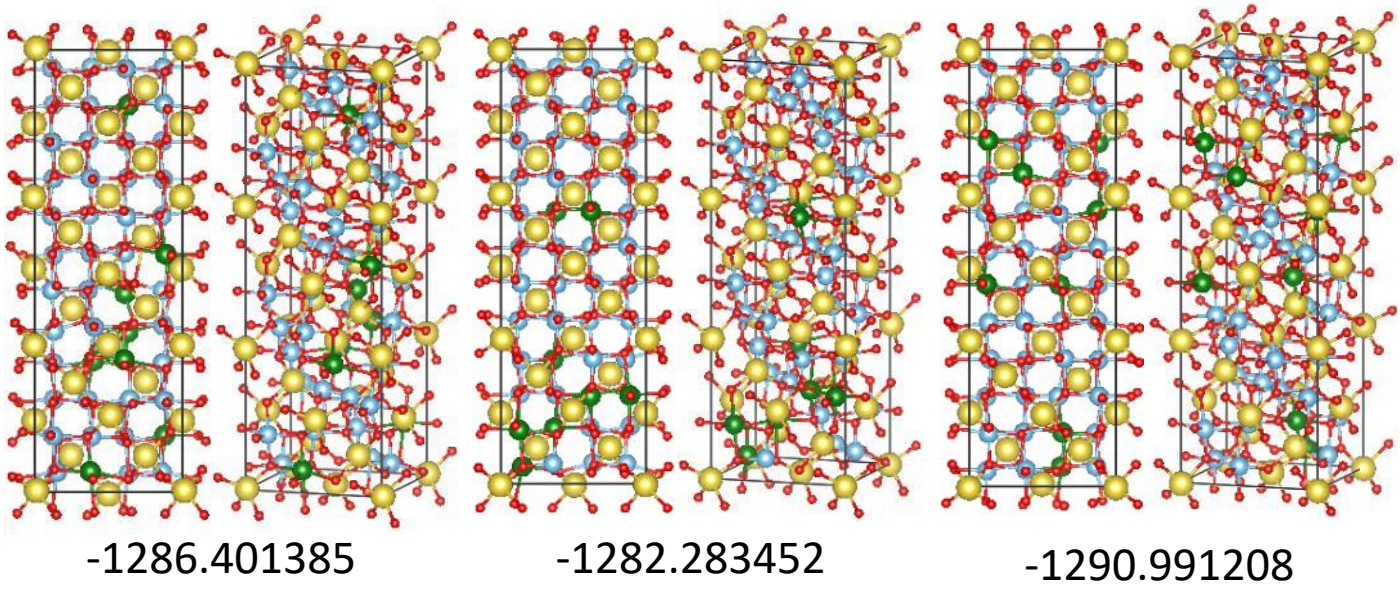

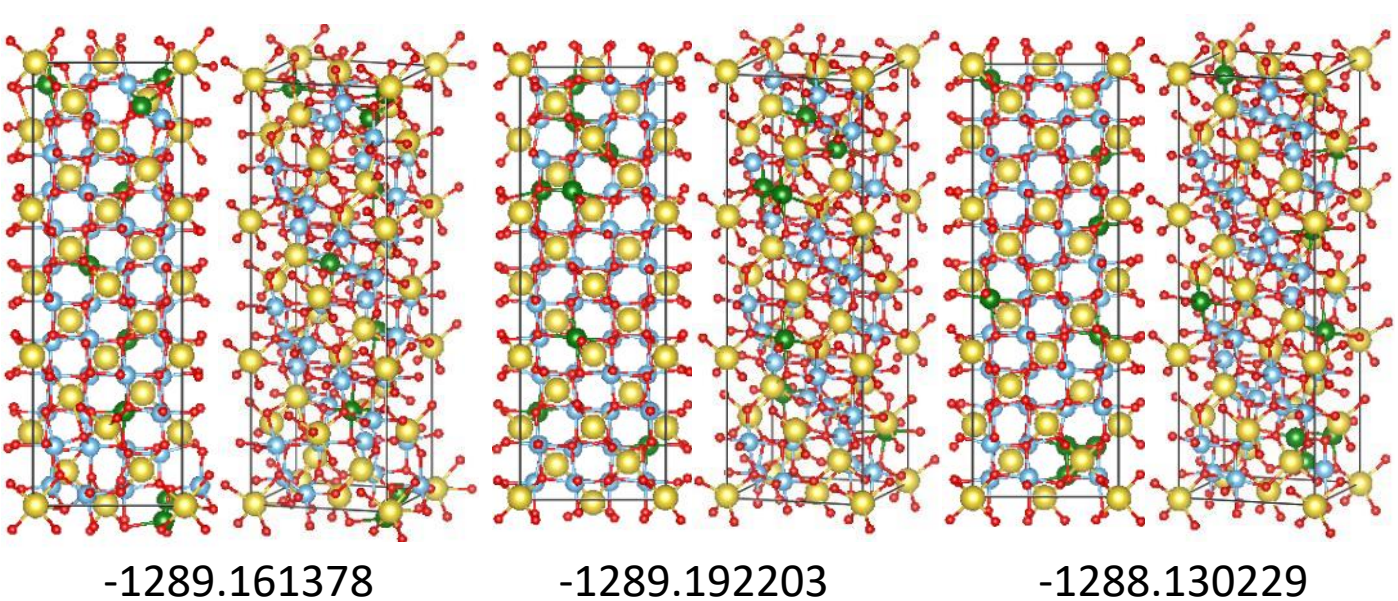

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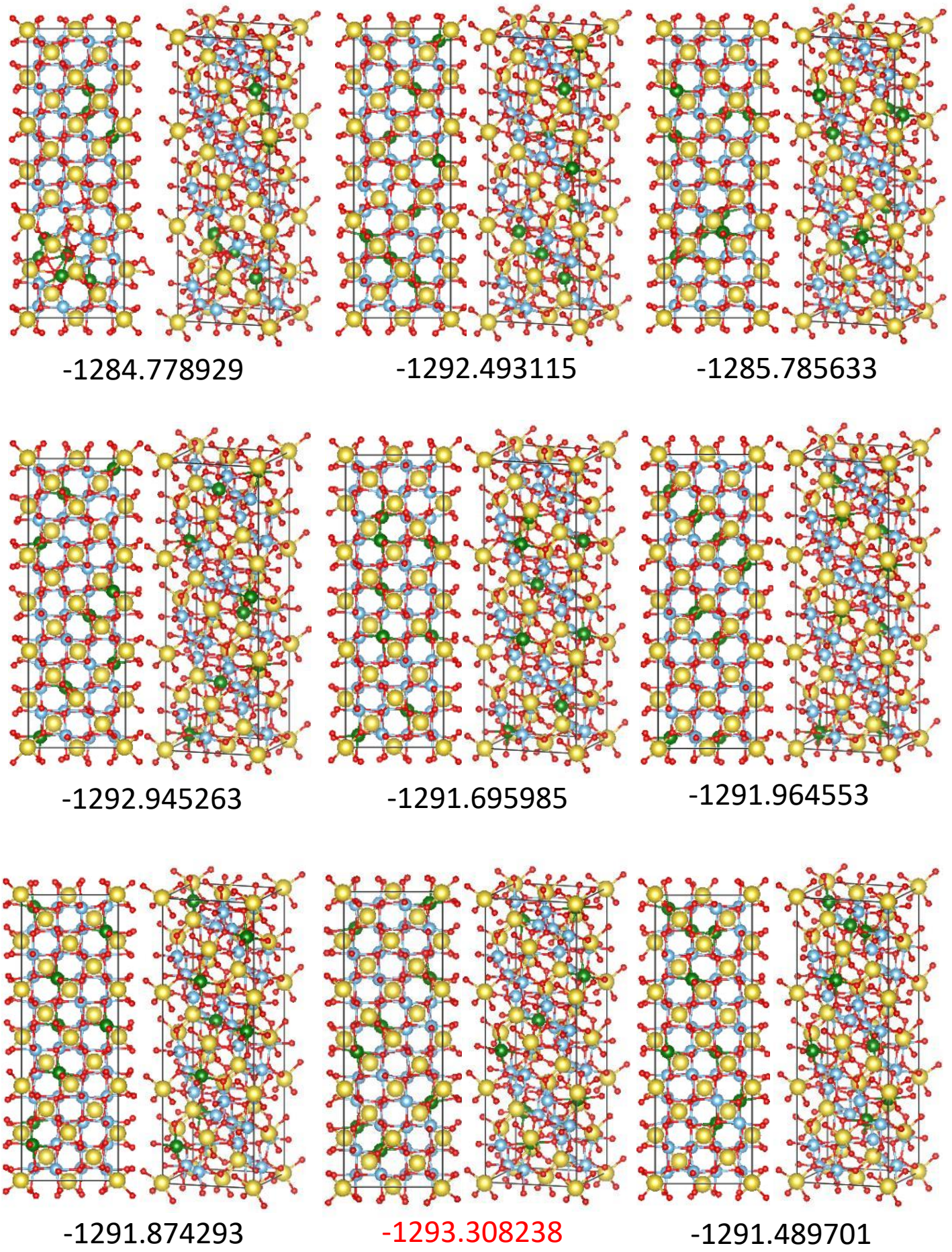

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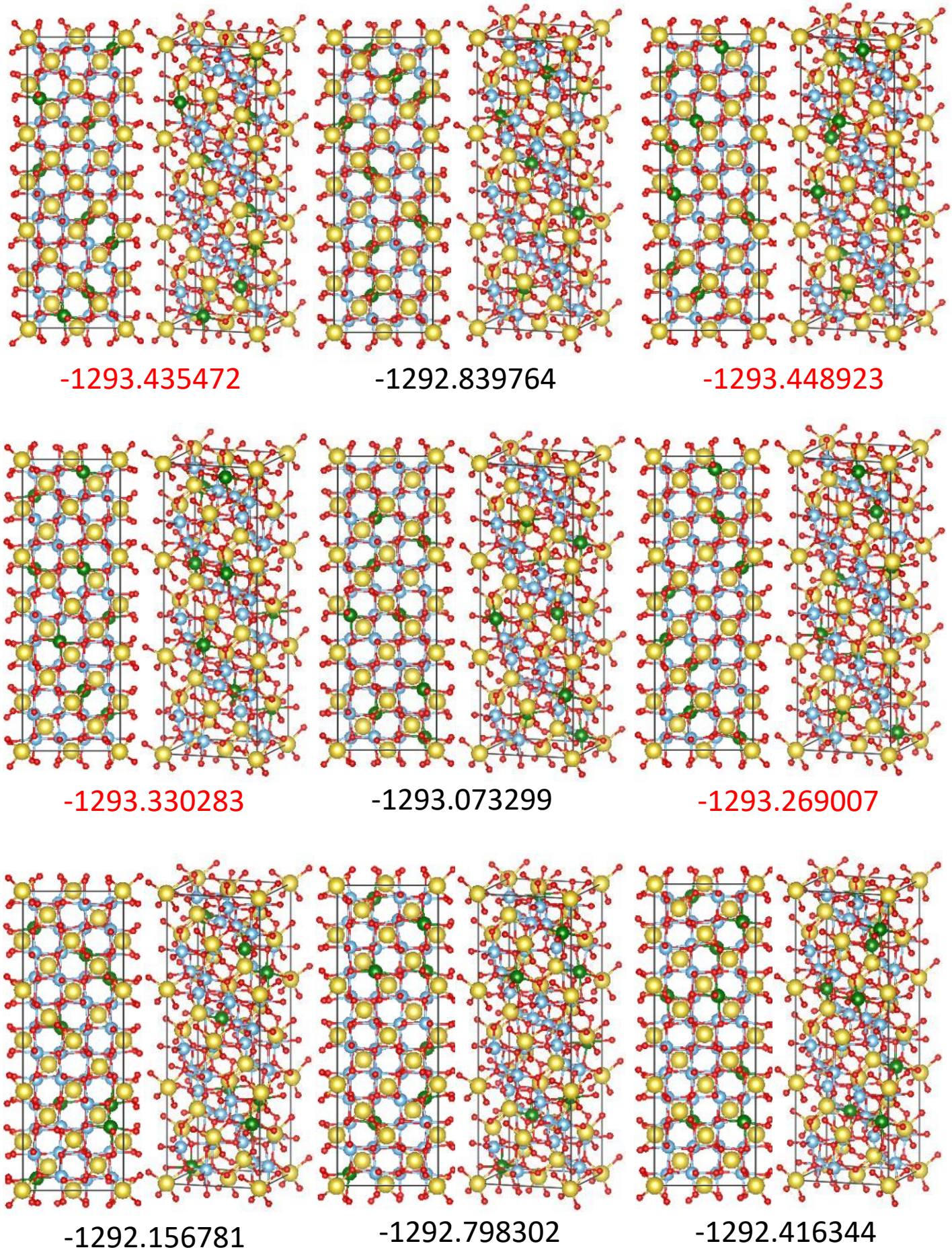

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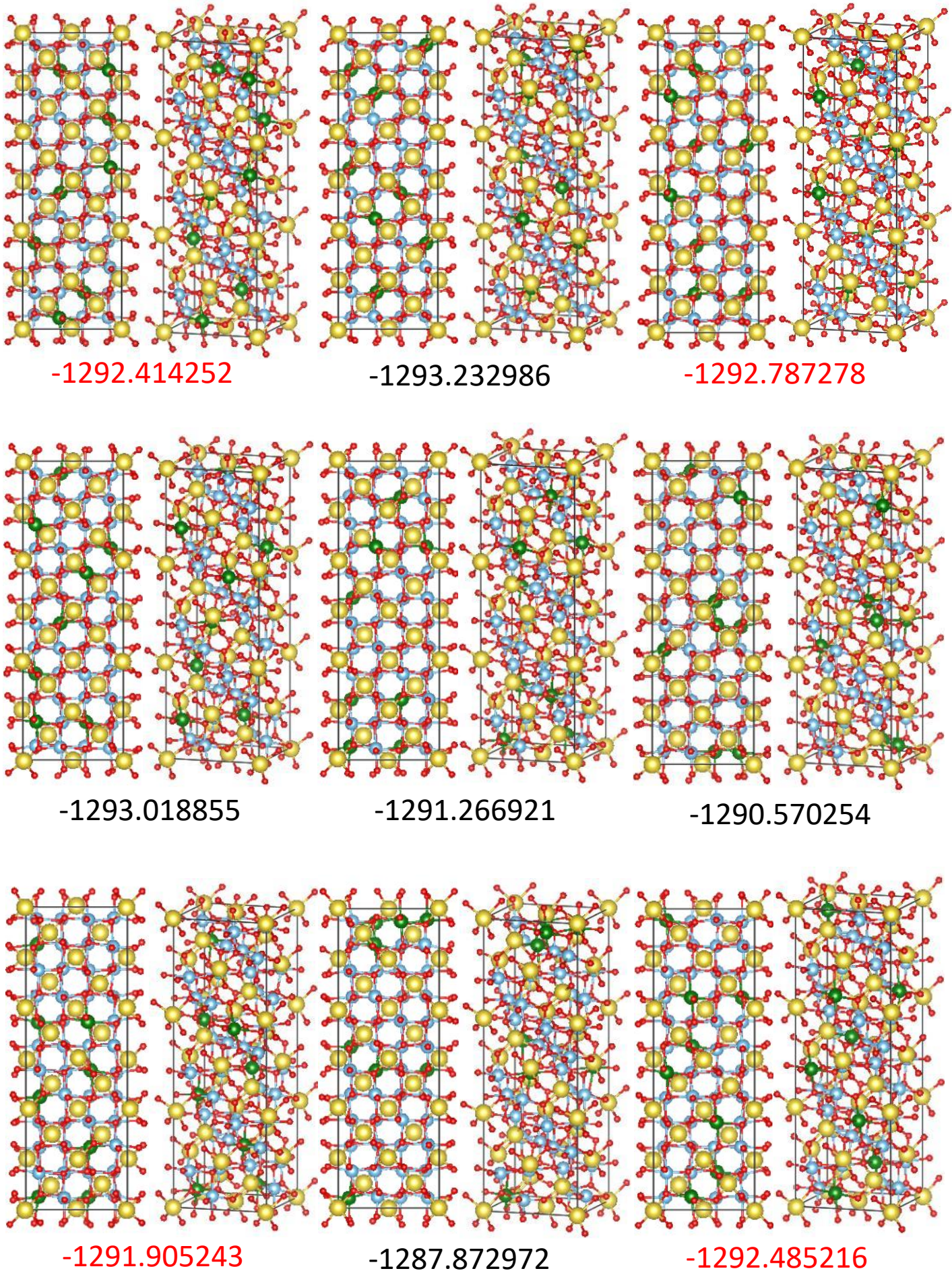

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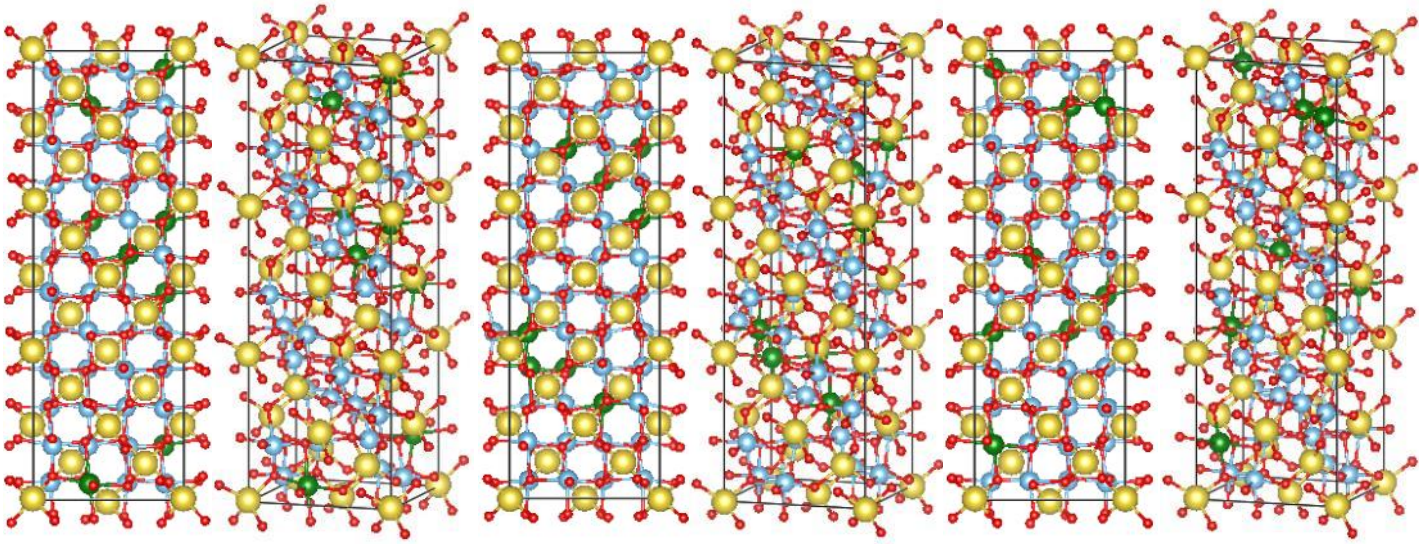


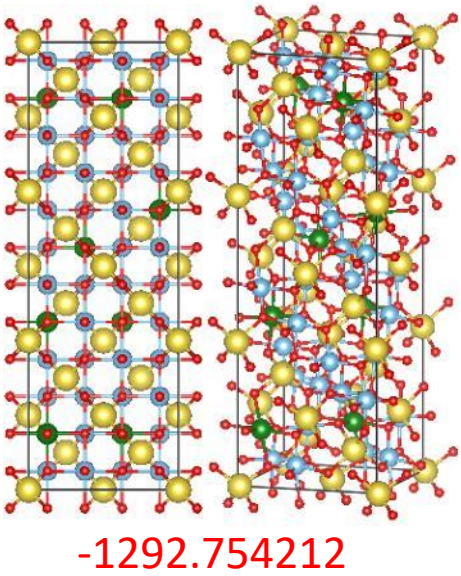


Figure S4 Continued from the previous page.

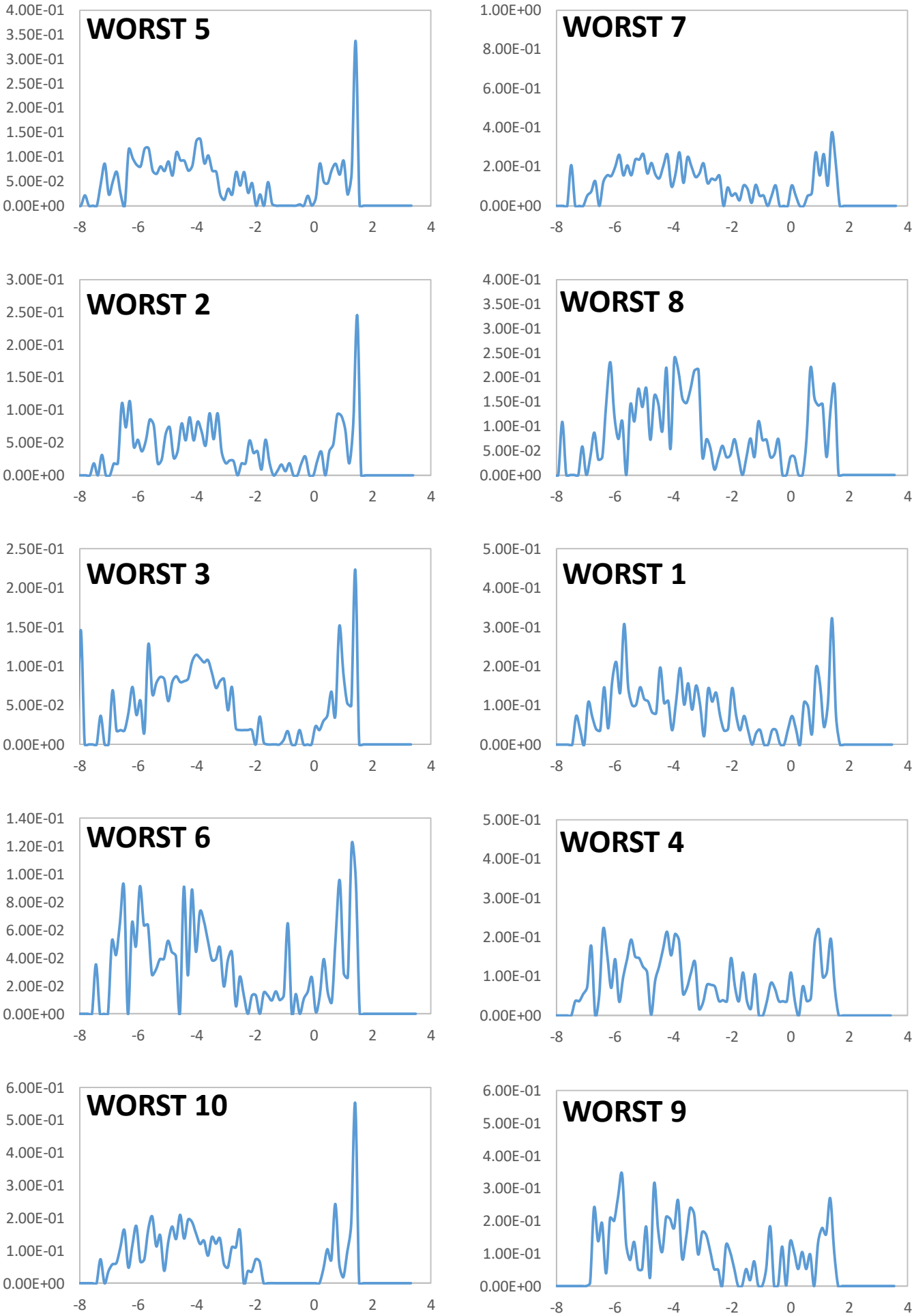
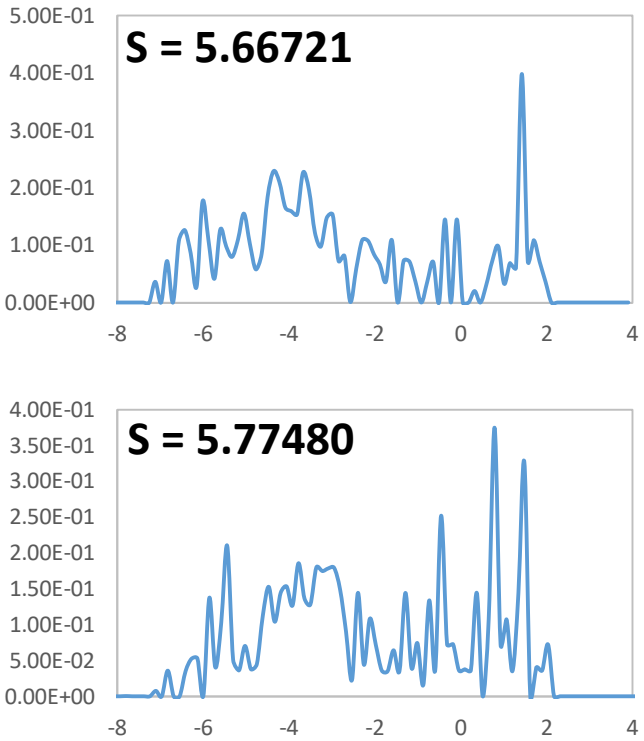


Figure S5 DOS of $Li_4Ti_5O_{12}$ of the ten least stable structures from the 58 selected models. The ordinate is *DOS* [eV^{-1}] and the abscissa is E - E_F (the Fermi energy) [eV].



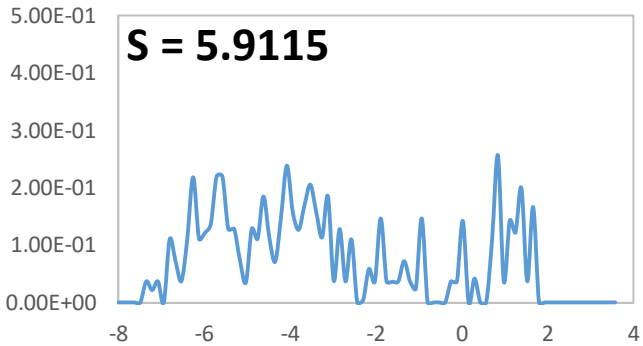
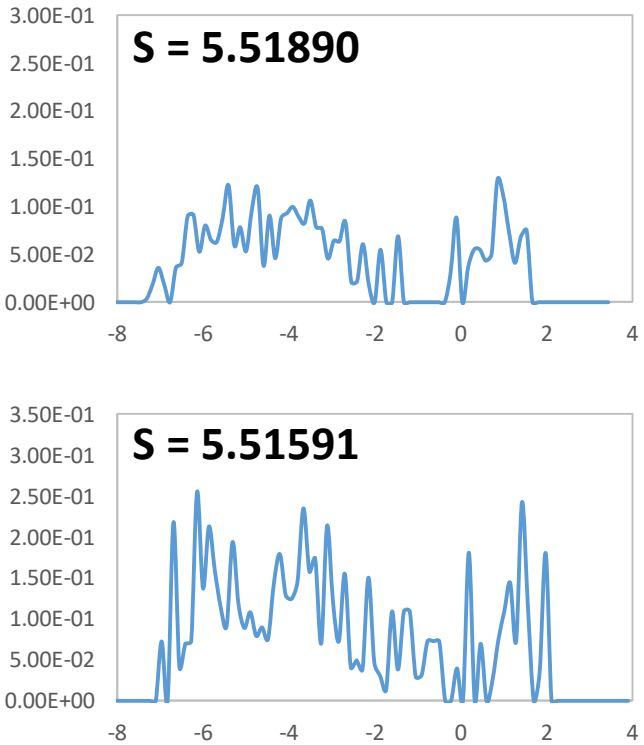


Figure S6 DOS of $Li_4Ti_5O_{12}$ for which *S* is around 5.7 selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is $E - E_F$ (the Fermi energy) [eV].



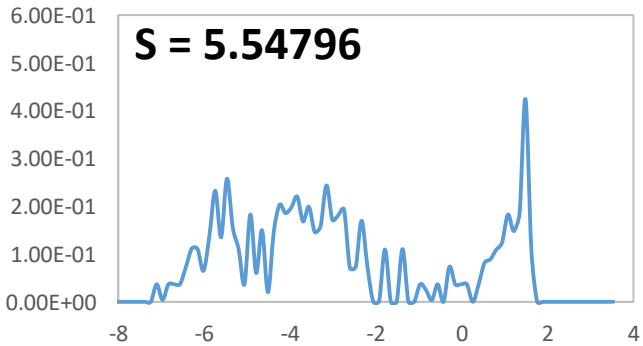
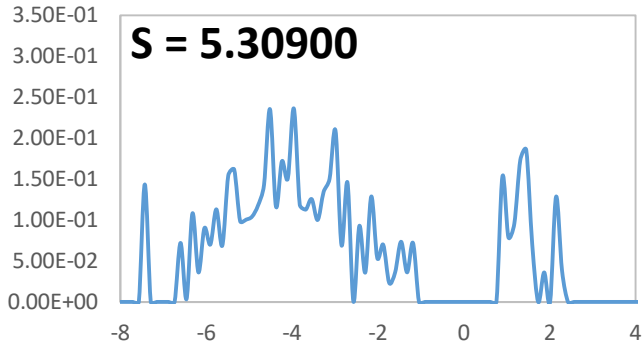
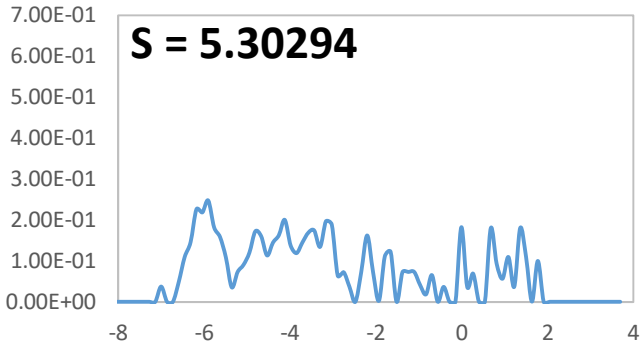


Figure S7 DOS of $Li_4Ti_5O_{12}$ for which *S* is around 5.5 selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is $E - E_F$ (the Fermi energy) [eV].





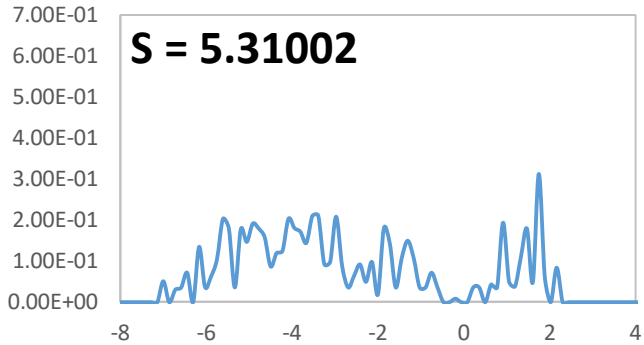
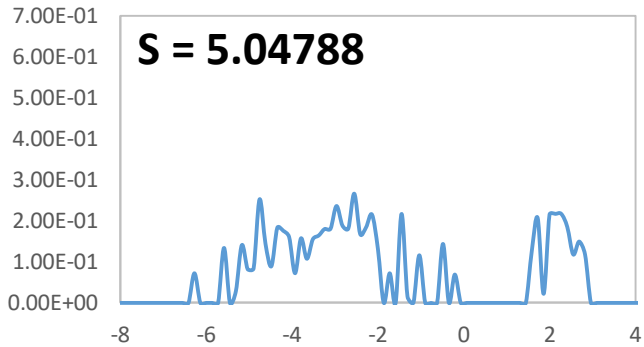
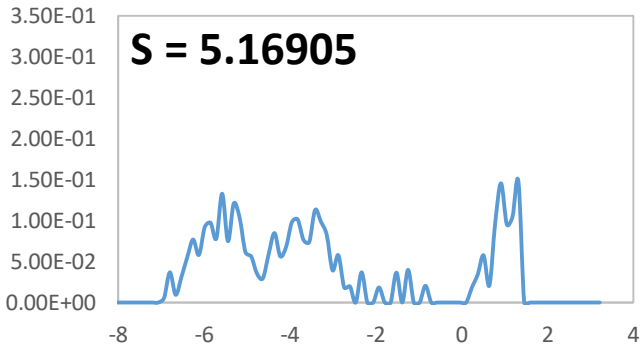


Figure S8 DOS of $Li_4Ti_5O_{12}$ for which *S* is around 5.3 selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is $E - E_F$ (the Fermi energy) [eV].





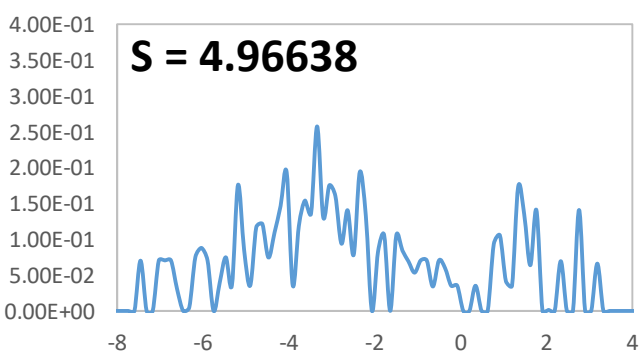
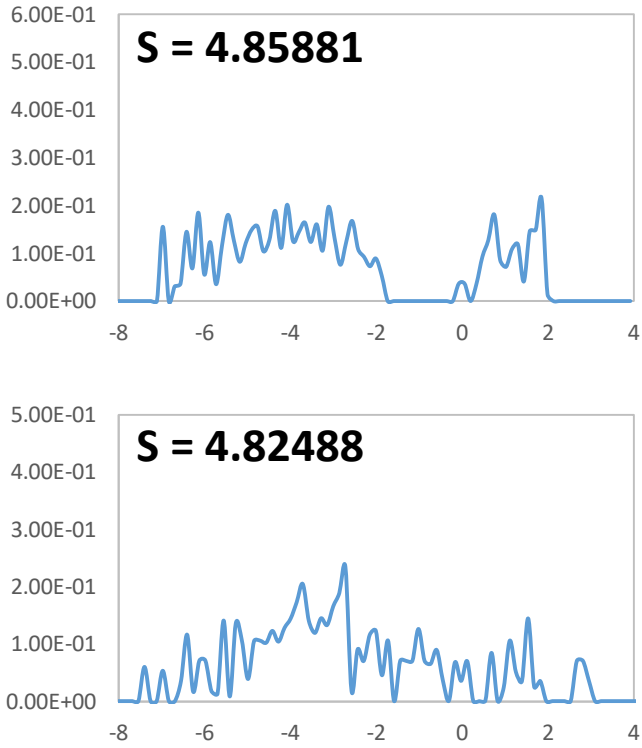


Figure S9 DOS of $Li_4Ti_5O_{12}$ for which *S* is around 5.0 selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is $E - E_F$ (the Fermi energy) [eV].



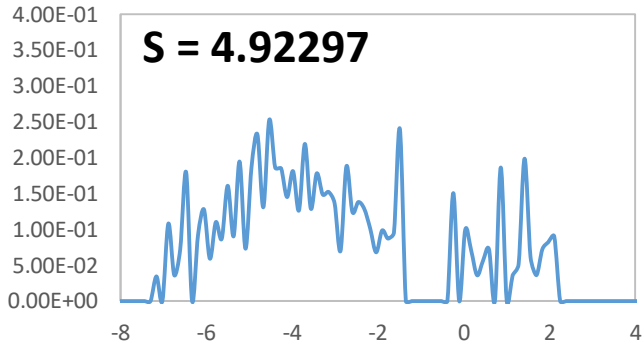
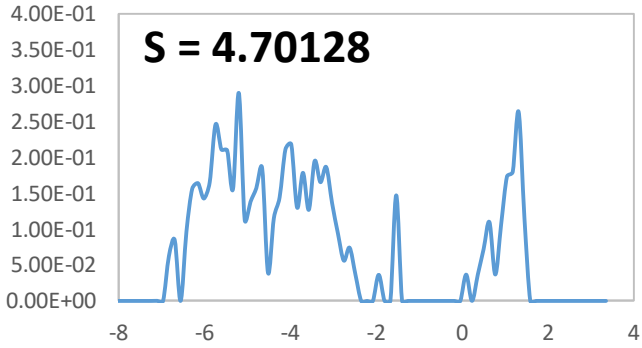
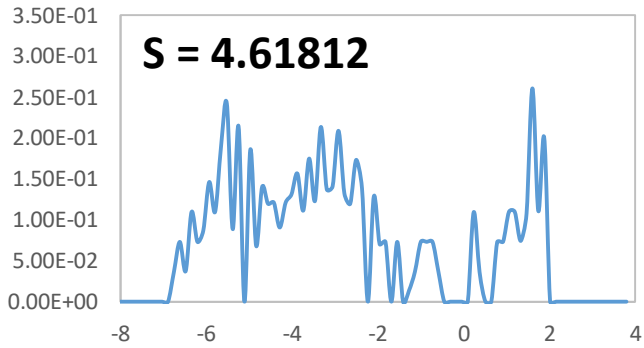


Figure S10 DOS of $Li_4Ti_5O_{12}$ for which *S* is around 4.9 selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is E - E_F (the Fermi energy) [eV].





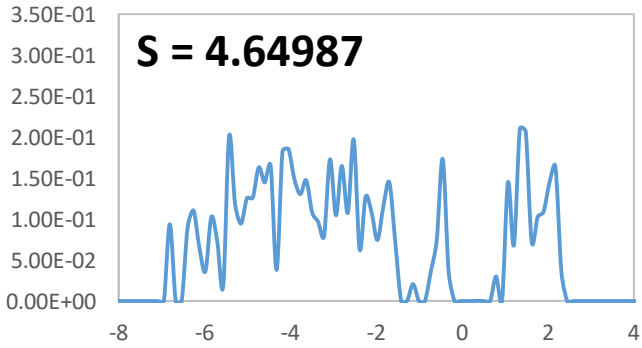
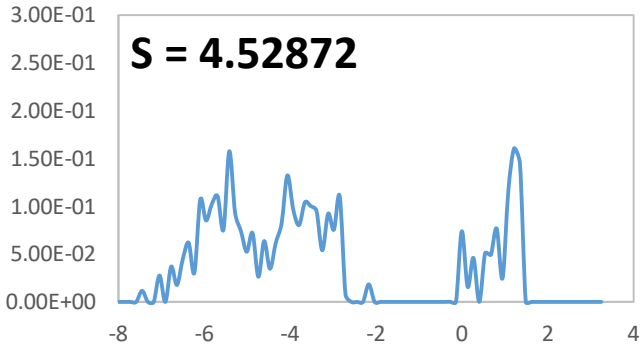
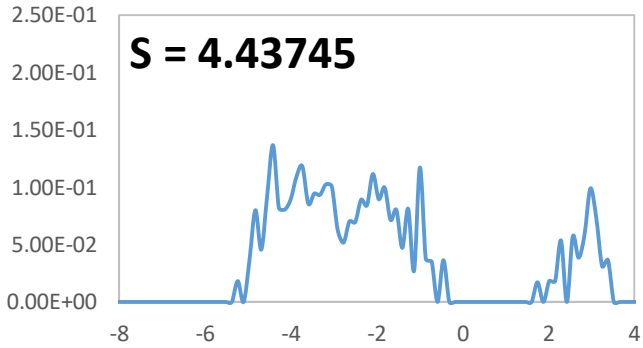


Figure S11 DOS of $Li_4Ti_5O_{12}$ for which *S* is around 4.6 selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is E - E_F (the Fermi energy) [eV].





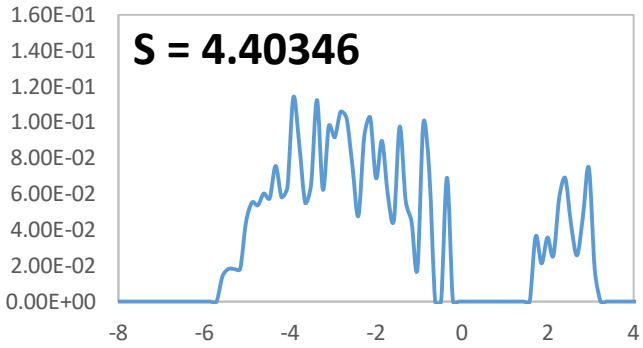
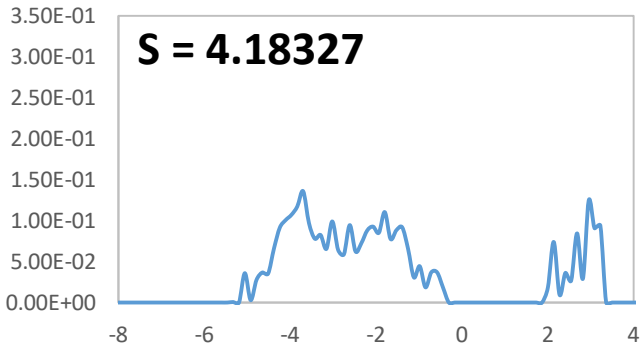
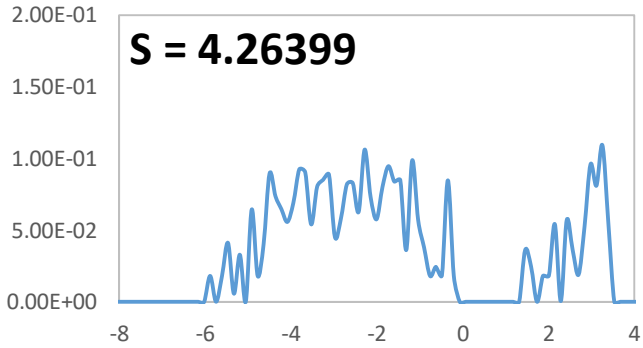


Figure S12 DOS of $Li_4Ti_5O_{12}$ for which *S* is around 4.4 selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is E - E_F (the Fermi energy) [eV].





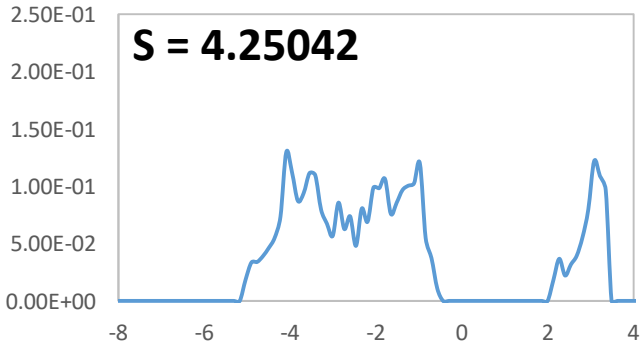
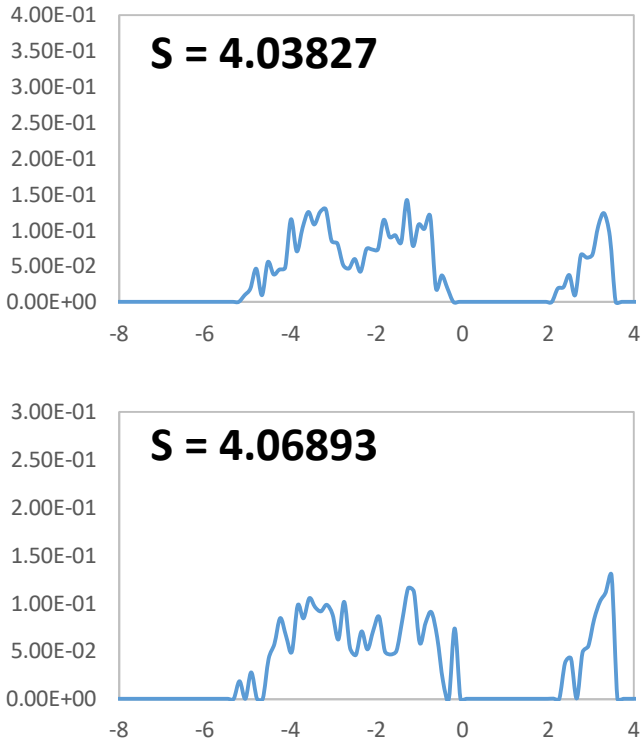


Figure S13 DOS of $Li_4Ti_5O_{12}$ for which *S* is around 4.2 selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is E - E_F (the Fermi energy) [eV].



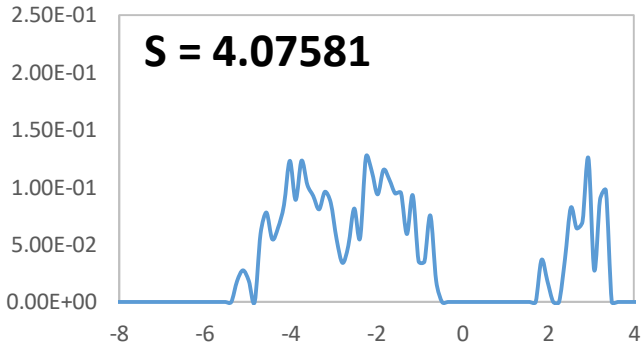
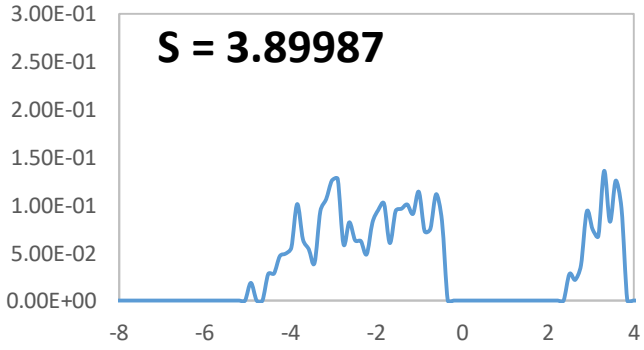
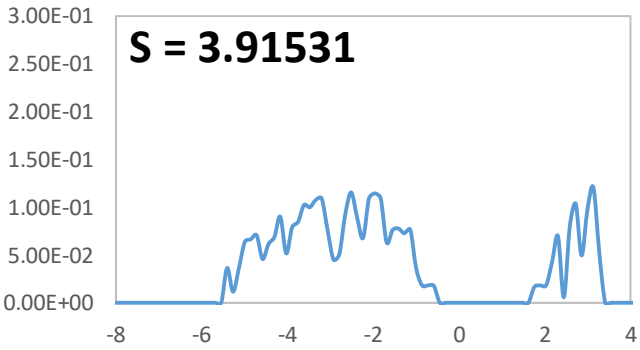


Figure S14 DOS of $Li_4Ti_5O_{12}$ for which *S* is around 4.0 selected from the 58 models. The ordinate is *DOS* [eV^{-1}], and the abscissa is E - E_F (the Fermi energy) [eV].





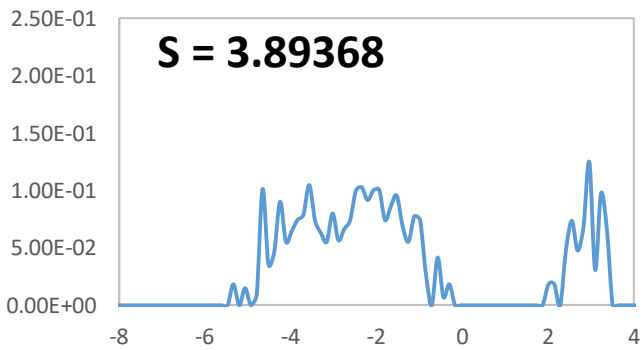


Figure S15 DOS of $Li_4Ti_5O_{12}$ for which *S* is around 3.9 selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is E - E_F (the Fermi energy) [eV].

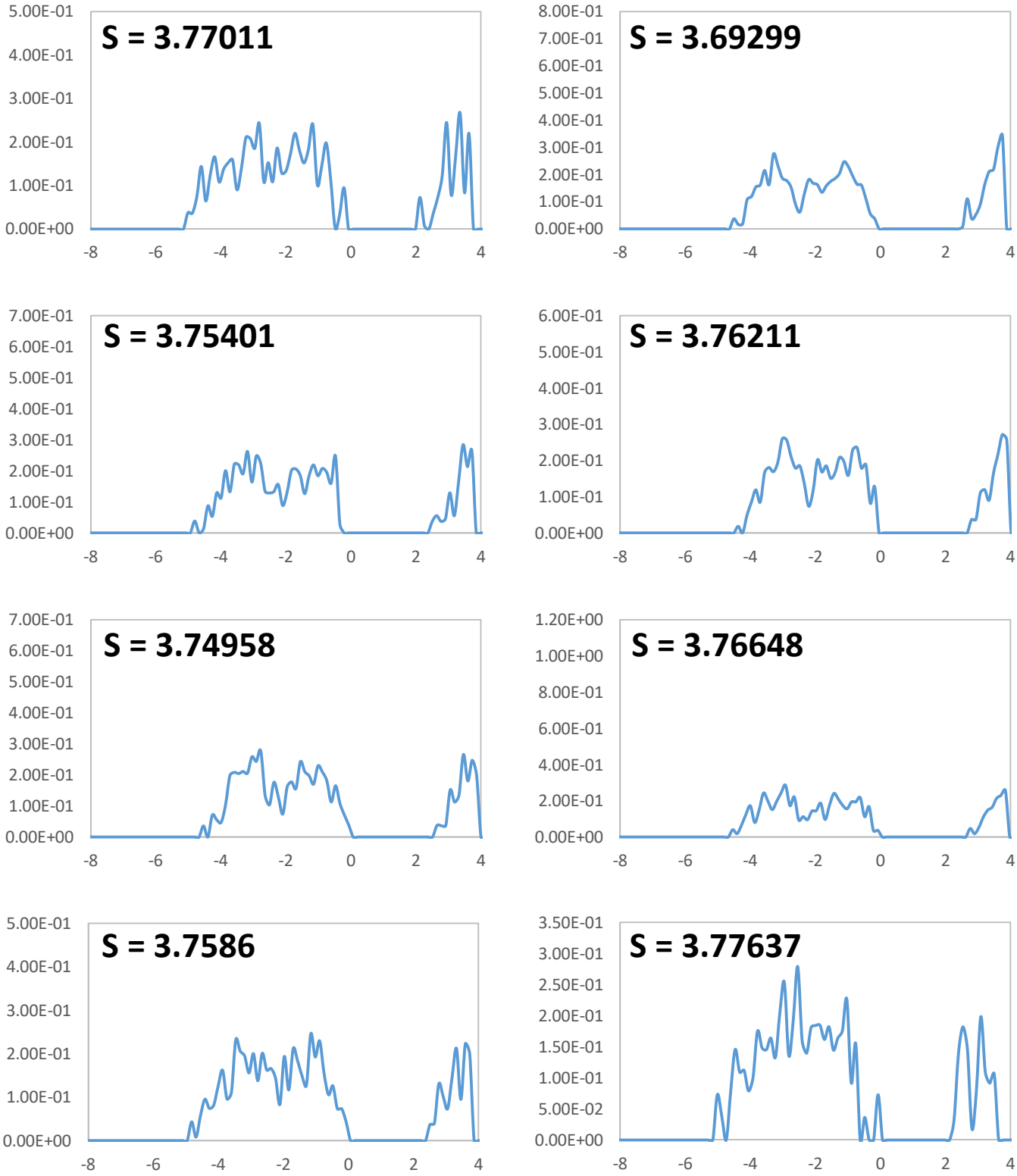


Figure S16 DOS of $Li_4Ti_5O_{12}$ for which *S* is around 3.7 selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is E - E_F (the Fermi energy) [eV].

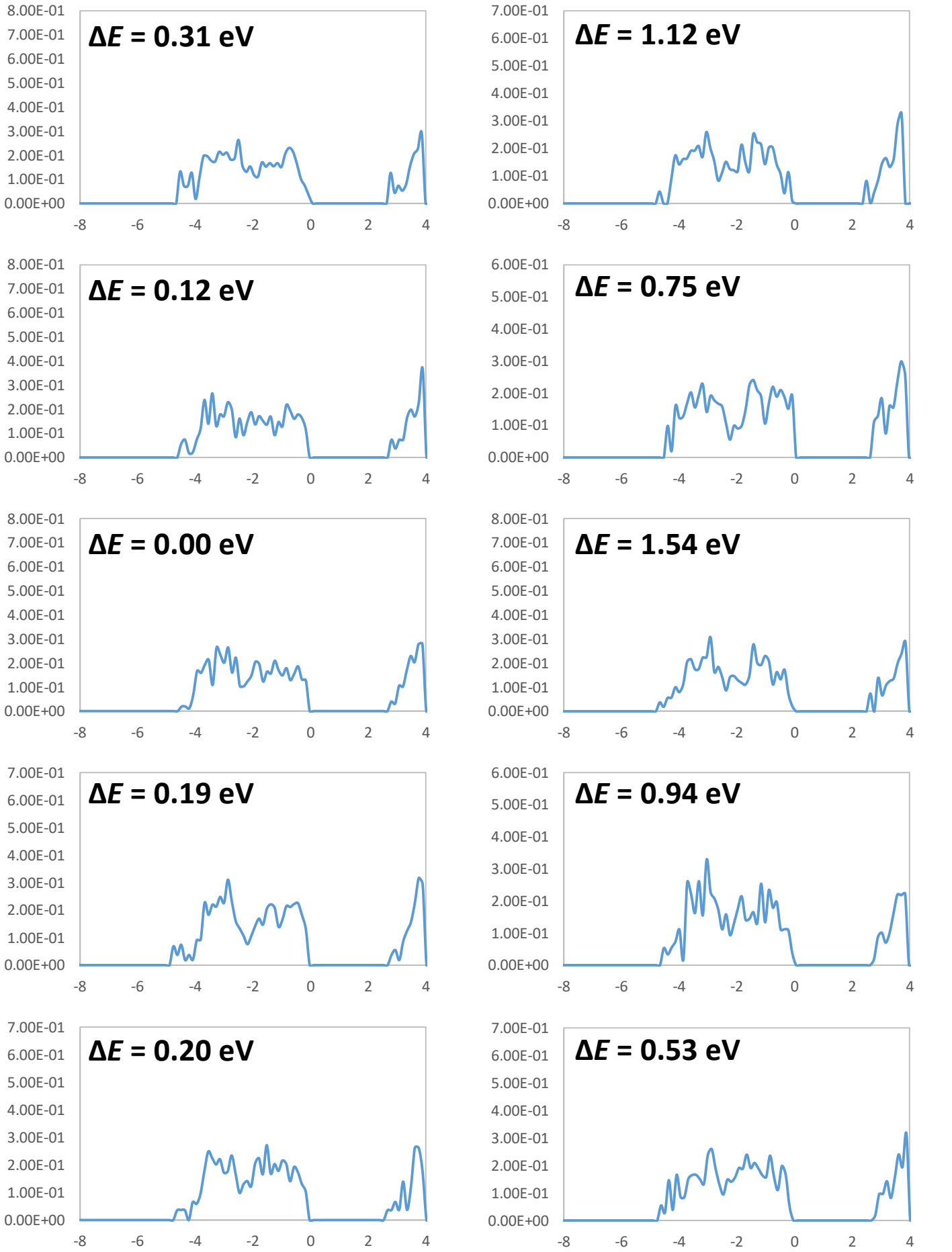


Figure S17 DOS of the ten most stable $Li_4Ti_5O_{12}$ selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is E - E_F (the Fermi energy) [eV]. ΔE is the energy difference in the total energy from the most stable structure.

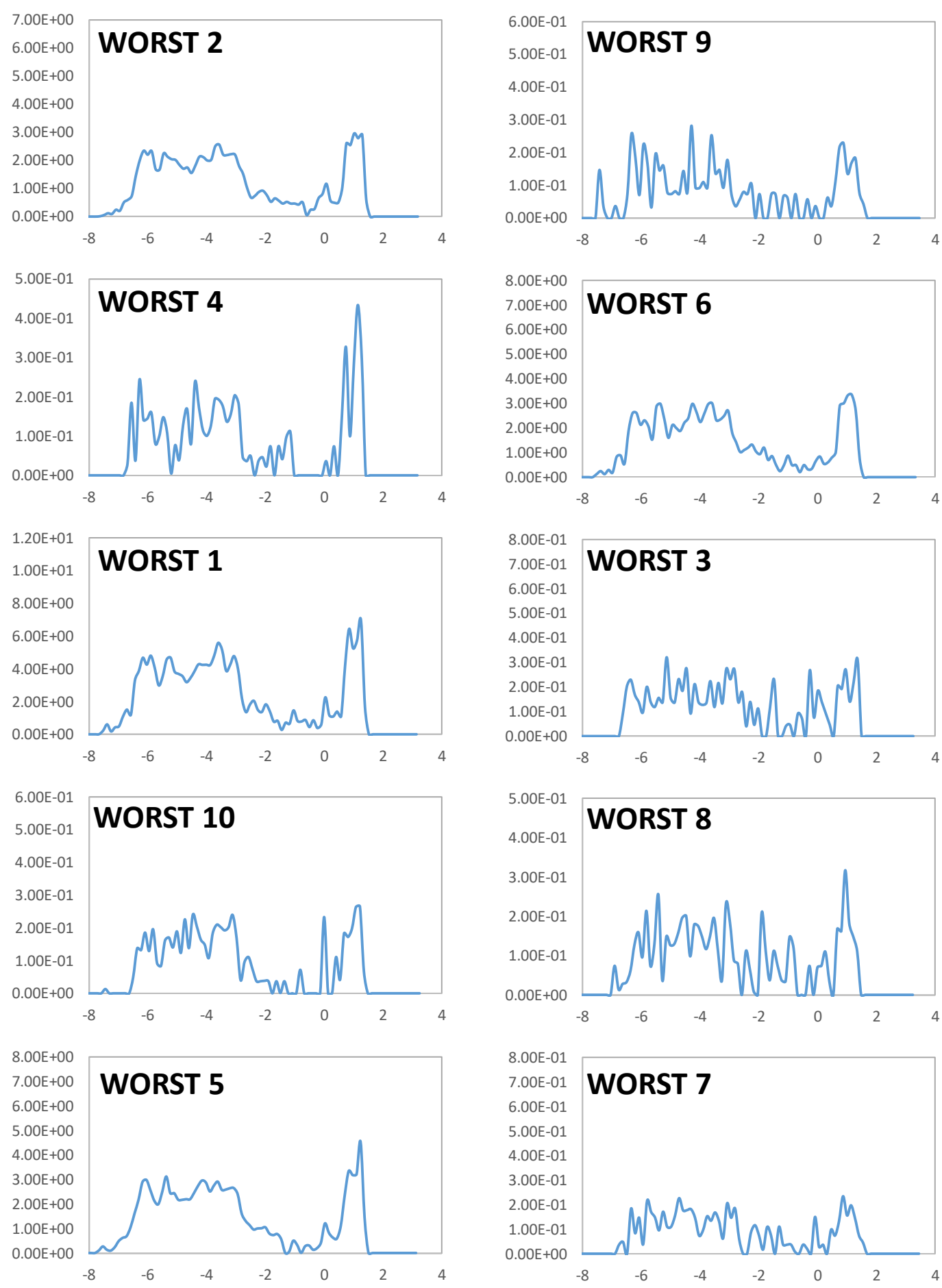
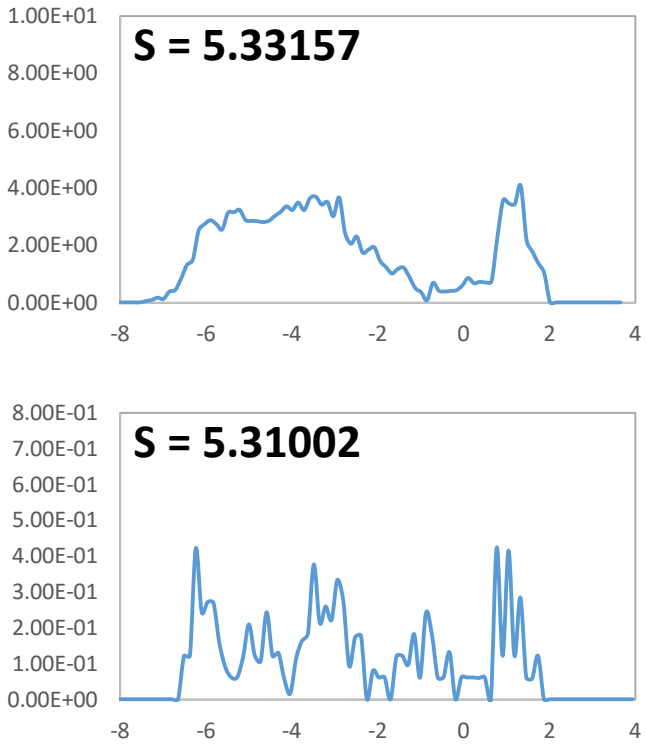


Figure S18 DOS of the ten least stable $Na_3LiTi_5O_{12}$ selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is E - E_F (the Fermi energy) [eV].



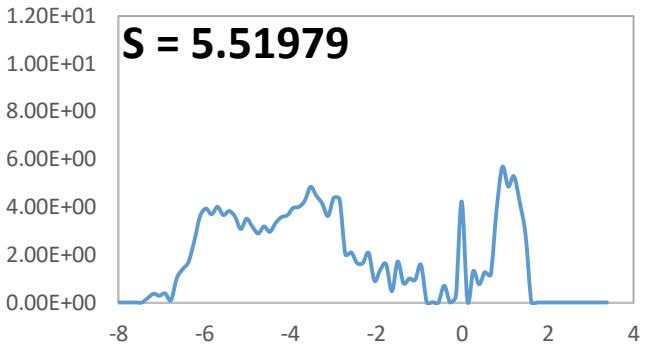
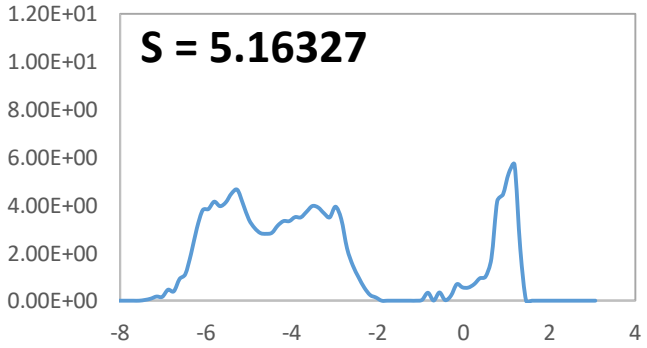
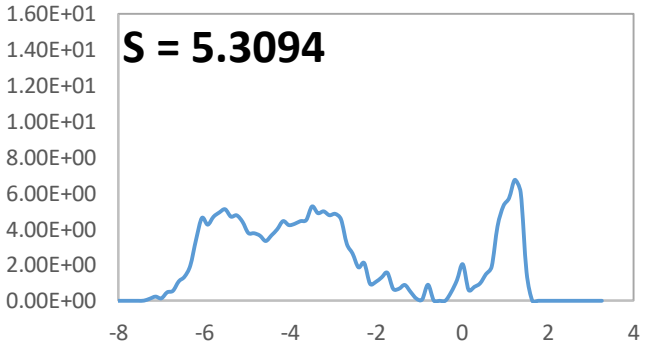


Figure S19 DOS of $Na_3LiTi_5O_{12}$ for which *S* is around 5.3 selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is $E - E_F$ (the Fermi energy) [eV].





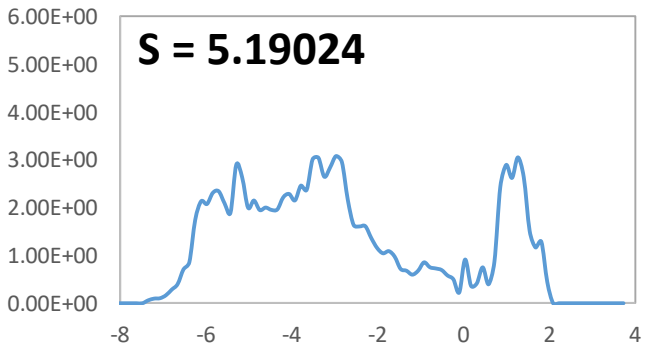
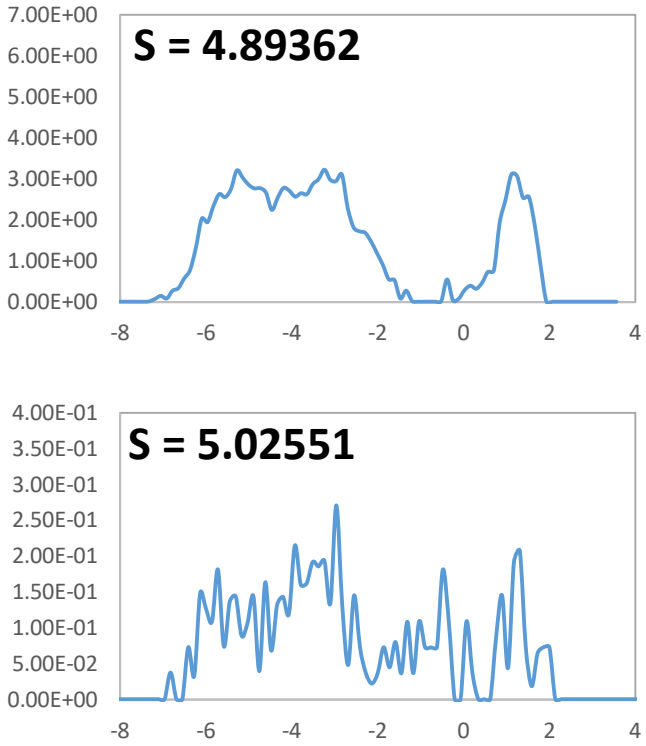


Figure S20 DOS of $Na_3LiTi_5O_{12}$ for which *S* is around 5.2 selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is $E - E_F$ (the Fermi energy) [eV].



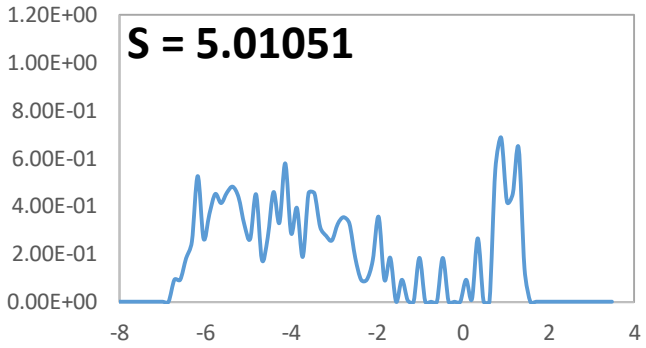
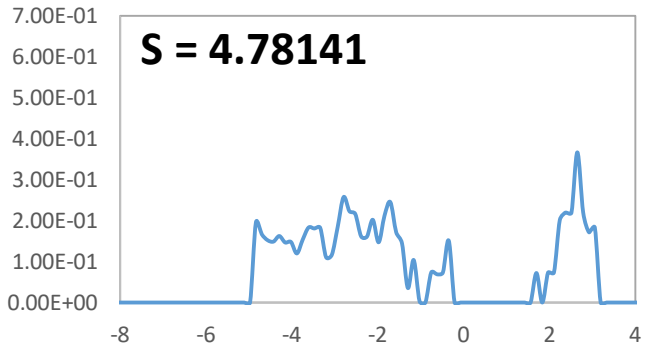
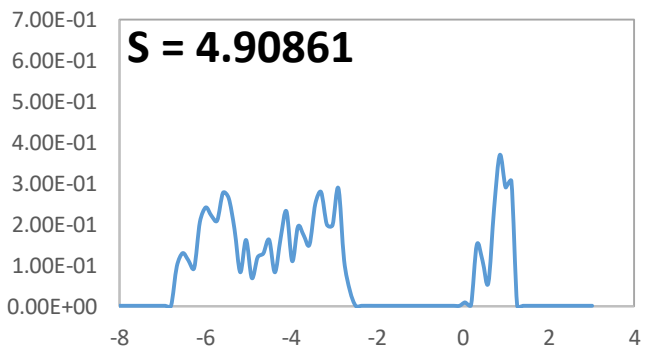


Figure S21 DOS of $Na_3LiTi_5O_{12}$ for which *S* is around 5.0 selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is $E - E_F$ (the Fermi energy) [eV].





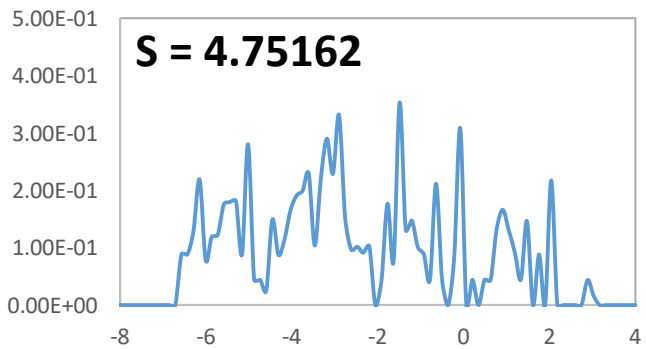
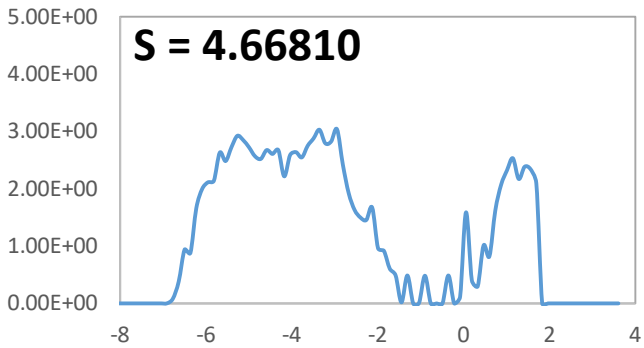
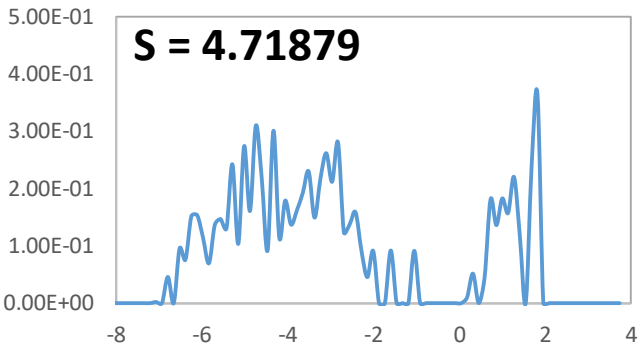


Figure S22 DOS of $Na_3LiTi_5O_{12}$ for which *S* is around 4.8 selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is $E - E_F$ (the Fermi energy) [eV].





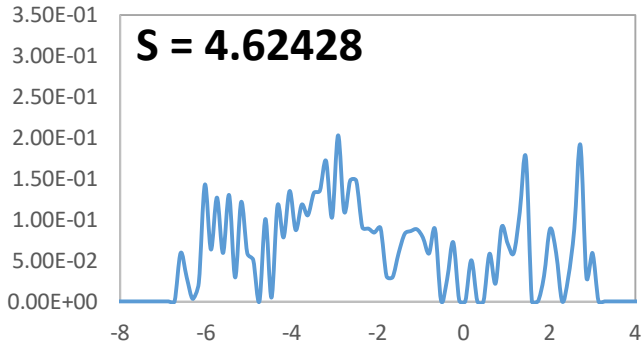
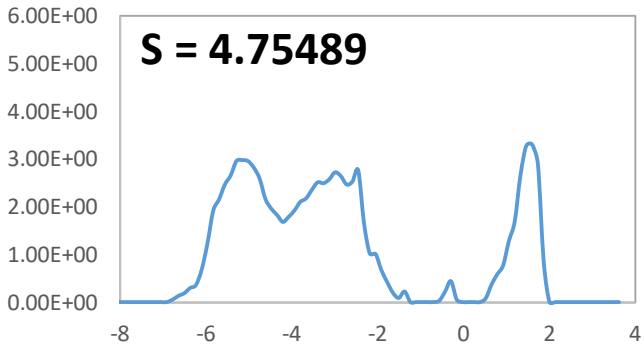
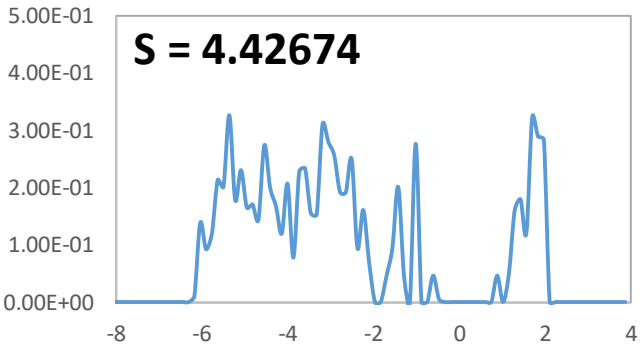


Figure S23 DOS of $Na_3LiTi_5O_{12}$ for which *S* is around 4.7 selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is $E - E_F$ (the Fermi energy) [eV].





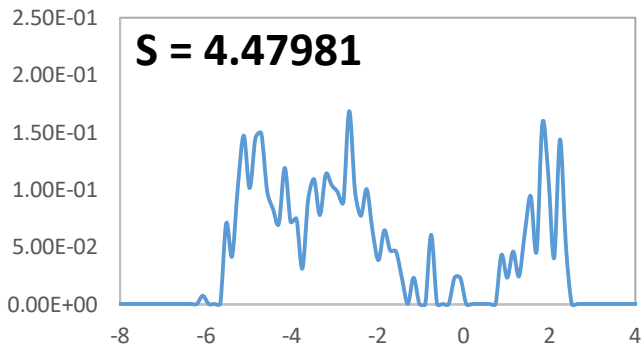
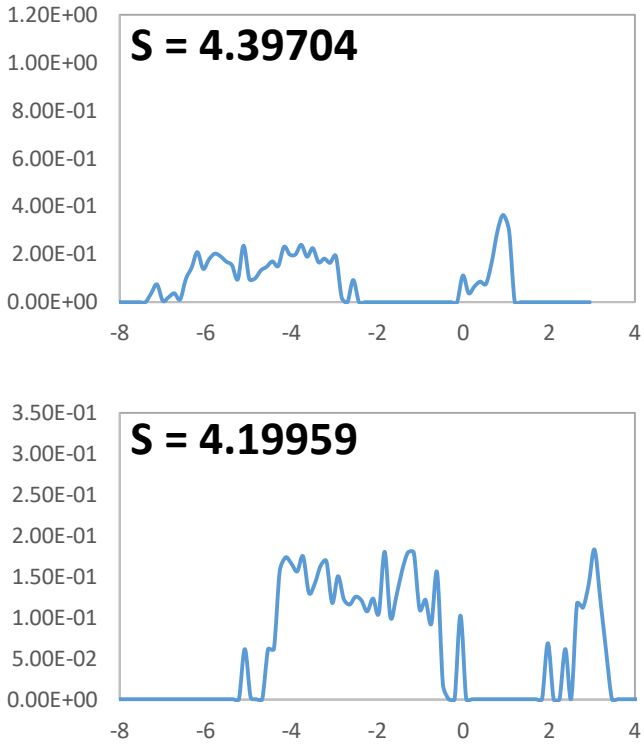


Figure S24 DOS of $Na_3LiTi_5O_{12}$ for which *S* is around 4.5 selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is $E - E_F$ (the Fermi energy) [eV].



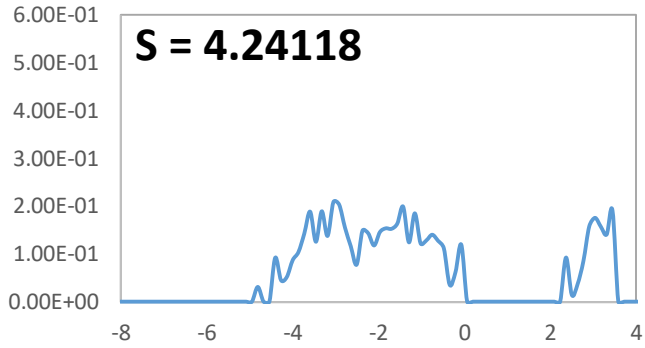
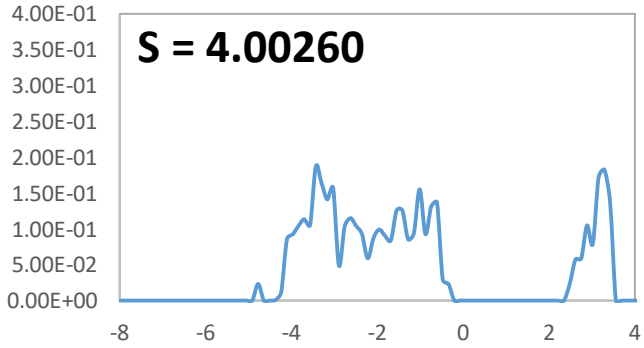
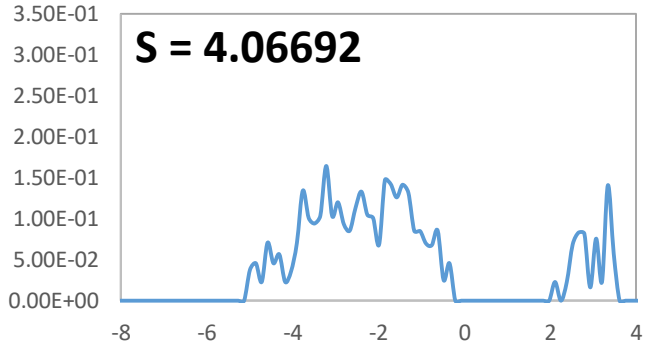


Figure S25 DOS of $Na_3LiTi_5O_{12}$ for which *S* is around 4.3 selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is E - E_F (the Fermi energy) [eV].





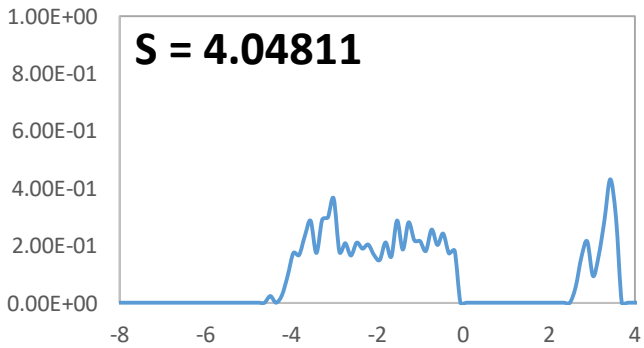
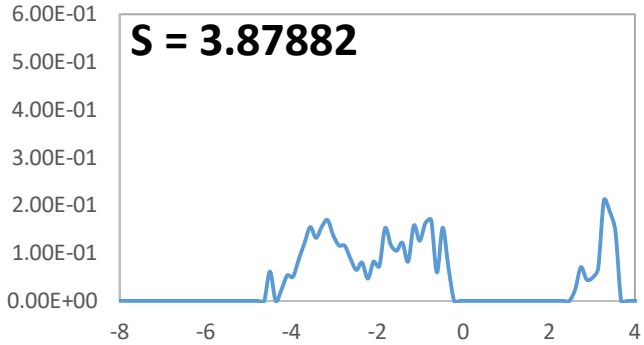
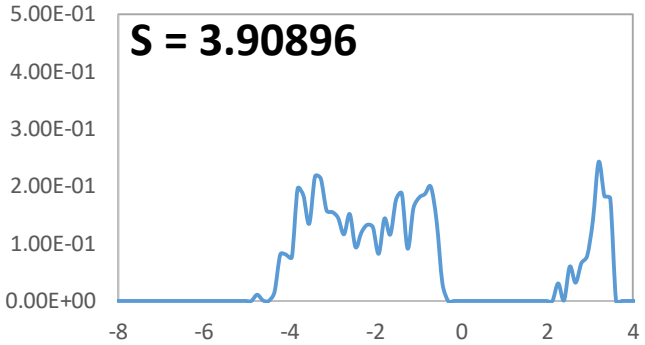


Figure S26 DOS of $Na_3LiTi_5O_{12}$ for which *S* is around 4.0 selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is E - E_F (the Fermi energy) [eV].





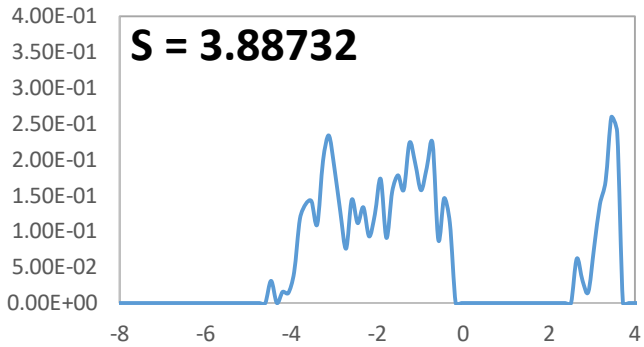
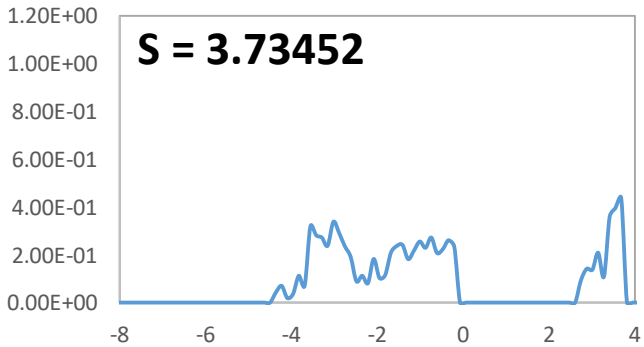
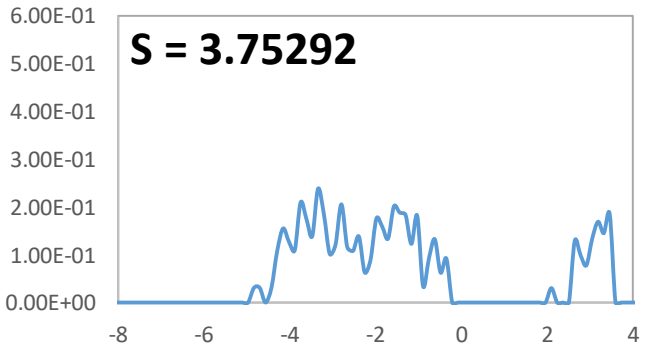


Figure S27 DOS of $Na_3LiTi_5O_{12}$ for which *S* is around 3.9 selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is $E - E_F$ (the Fermi energy) [eV].





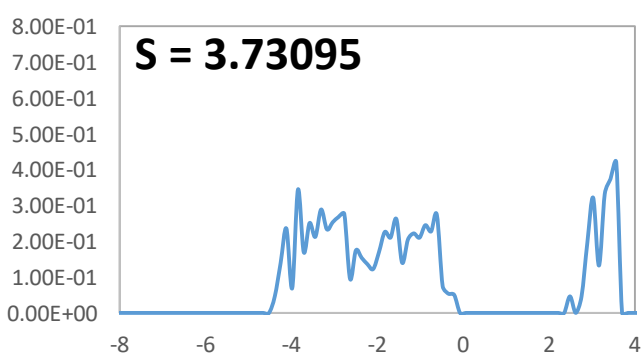


Figure S28 DOS of $Na_3LiTi_5O_{12}$ for which *S* is around 3.7 selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is $E - E_F$ (the Fermi energy) [eV].

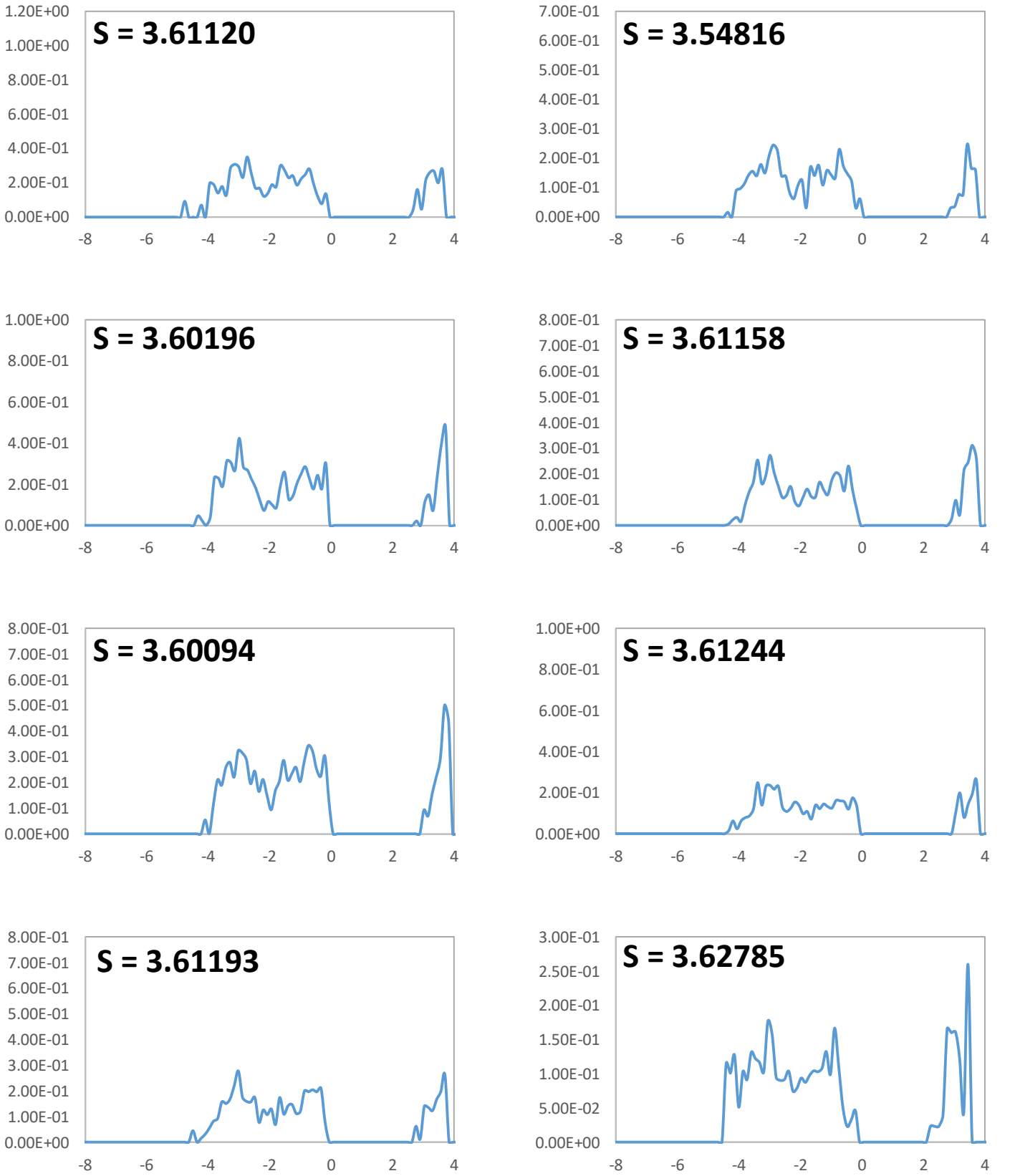


Figure S29 DOS of $Na_3LiTi_5O_{12}$ for which *S* is around 3.6 selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is E - E_F (the Fermi energy) [eV].

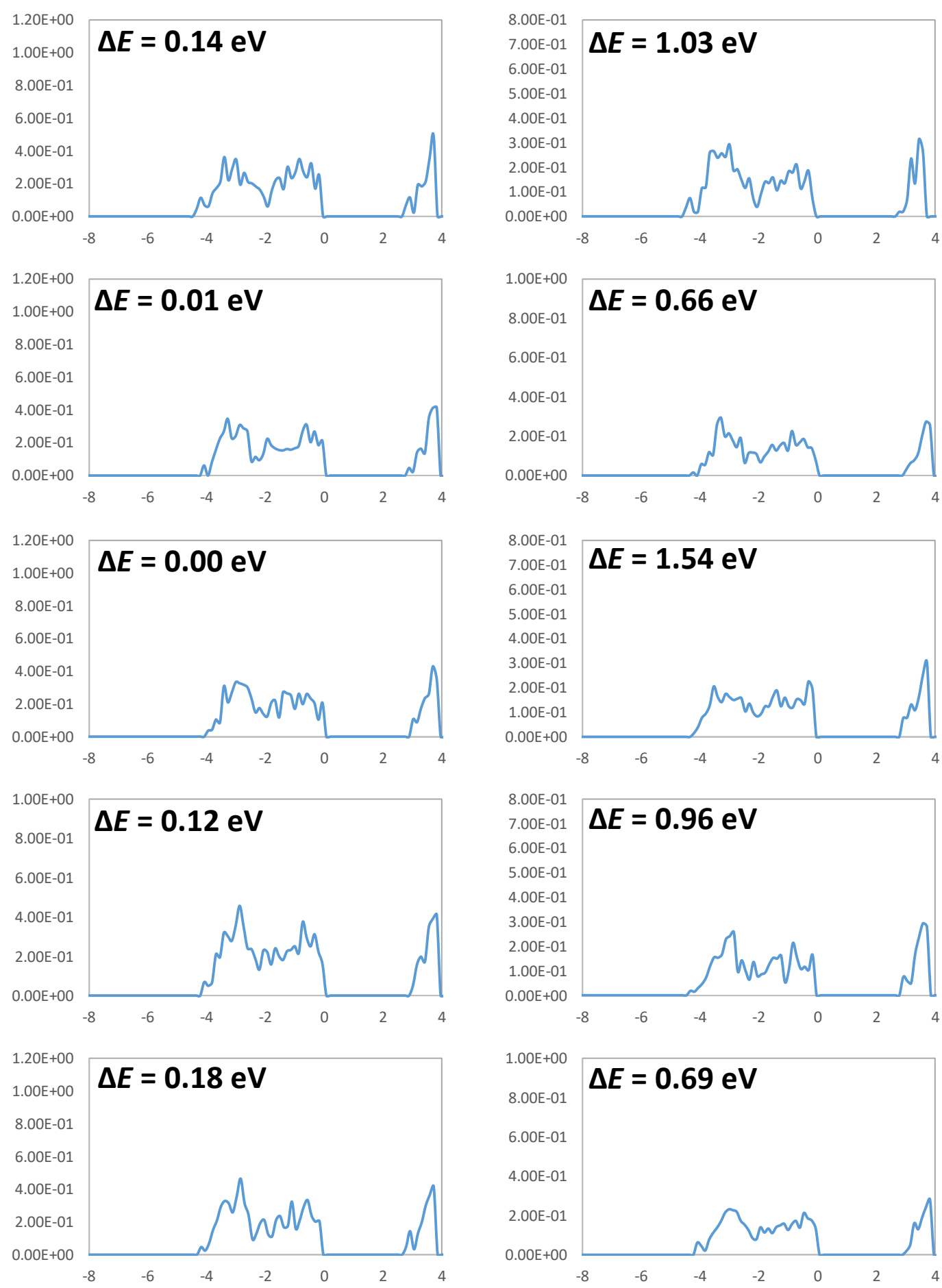


Figure S30 DOS of the ten most stable $Na_3LiTi_5O_{12}$ selected from the 58 models. The ordinate is *DOS* [eV^{-1}] and the abscissa is E - E_F (the Fermi energy) [eV]. ΔE is the energy difference in the total energy from the most stable structure.

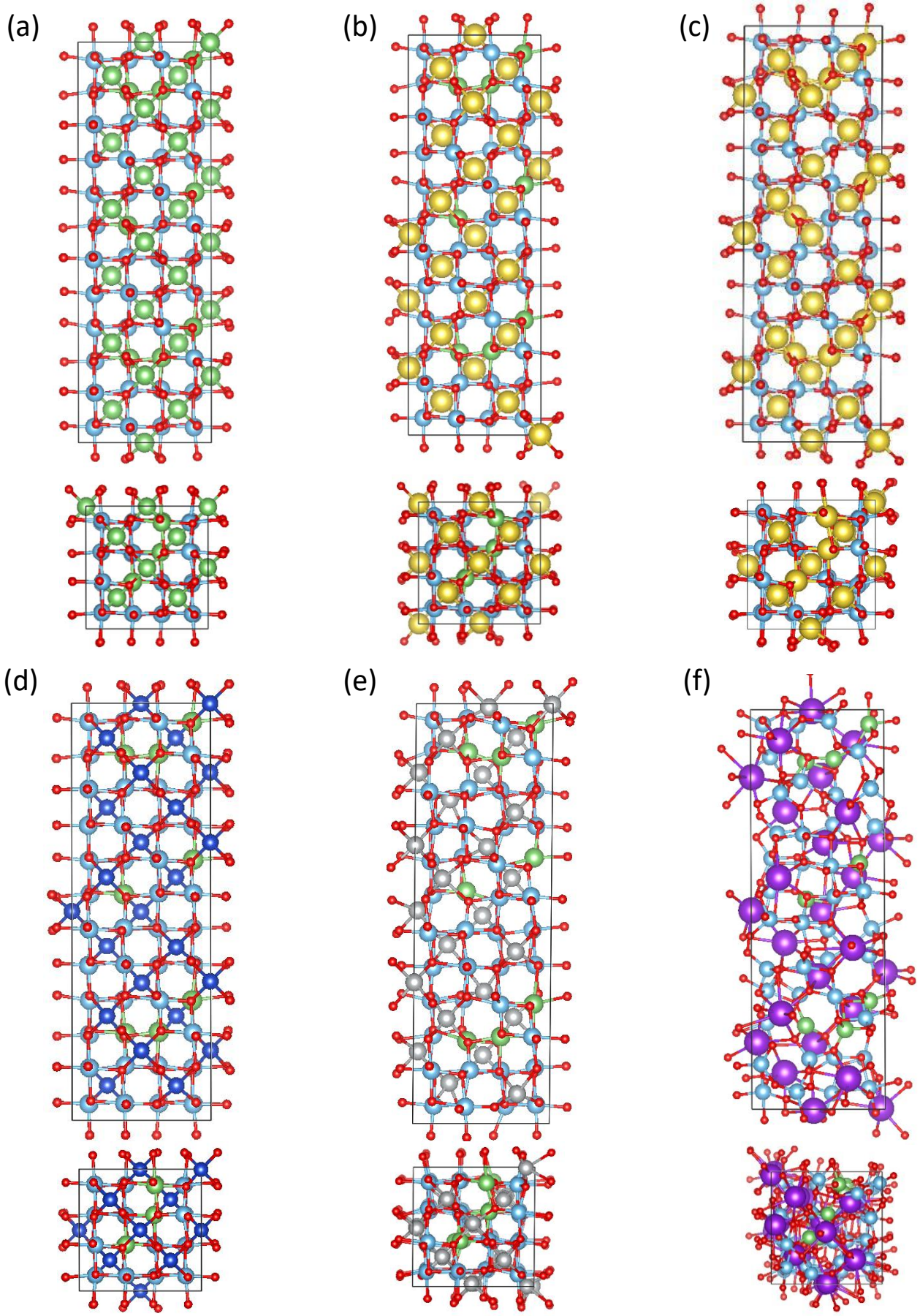


Figure S31 Side (upper panels) and top (lower panels) views of the optimized structures of (a) $Li_4Ti_5O_{12}$, (b) $Na_3LiTi_5O_{12}$, (c) $Na_4Ti_5O_{12}$, (d) $Cu_3LiTi_5O_{12}$, (e) $Ag_3LiTi_5O_{12}$, and (f) $K_3LiTi_5O_{12}$, among which the former five (a-e) retains the spinel structure while 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.

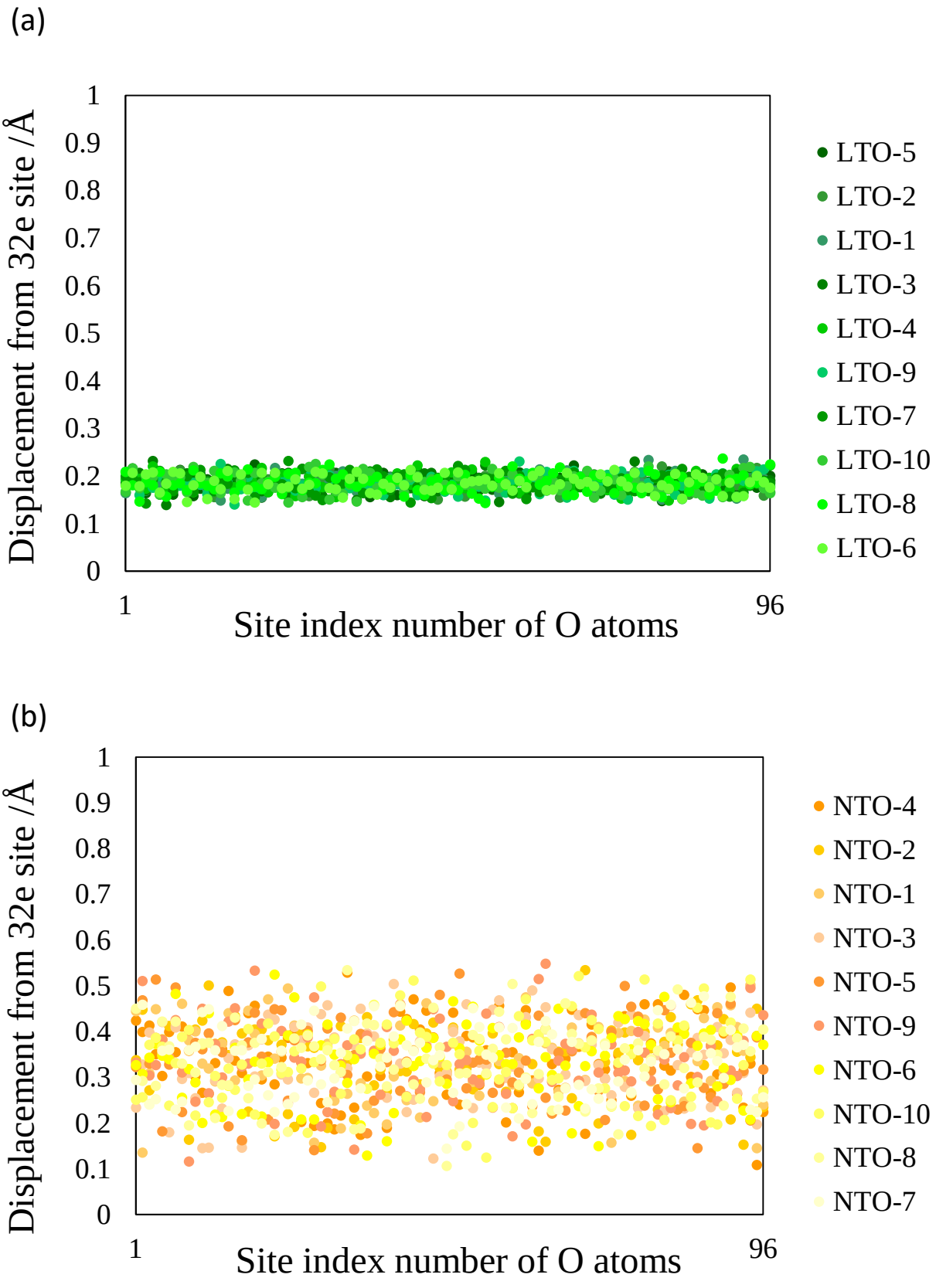


Figure S32 Displacement of O atoms from the Wyckoff positions (32e) of the $Fd\bar{3}m$ symmetry (spinel). (a) $Li_4Ti_5O_{12}$, and (b) $Na_3LiTi_5O_{12}$. LTO-1 and NTO-1 (LTO-10 and NTO-10) indicate the most stable (the 10-th stable) models.

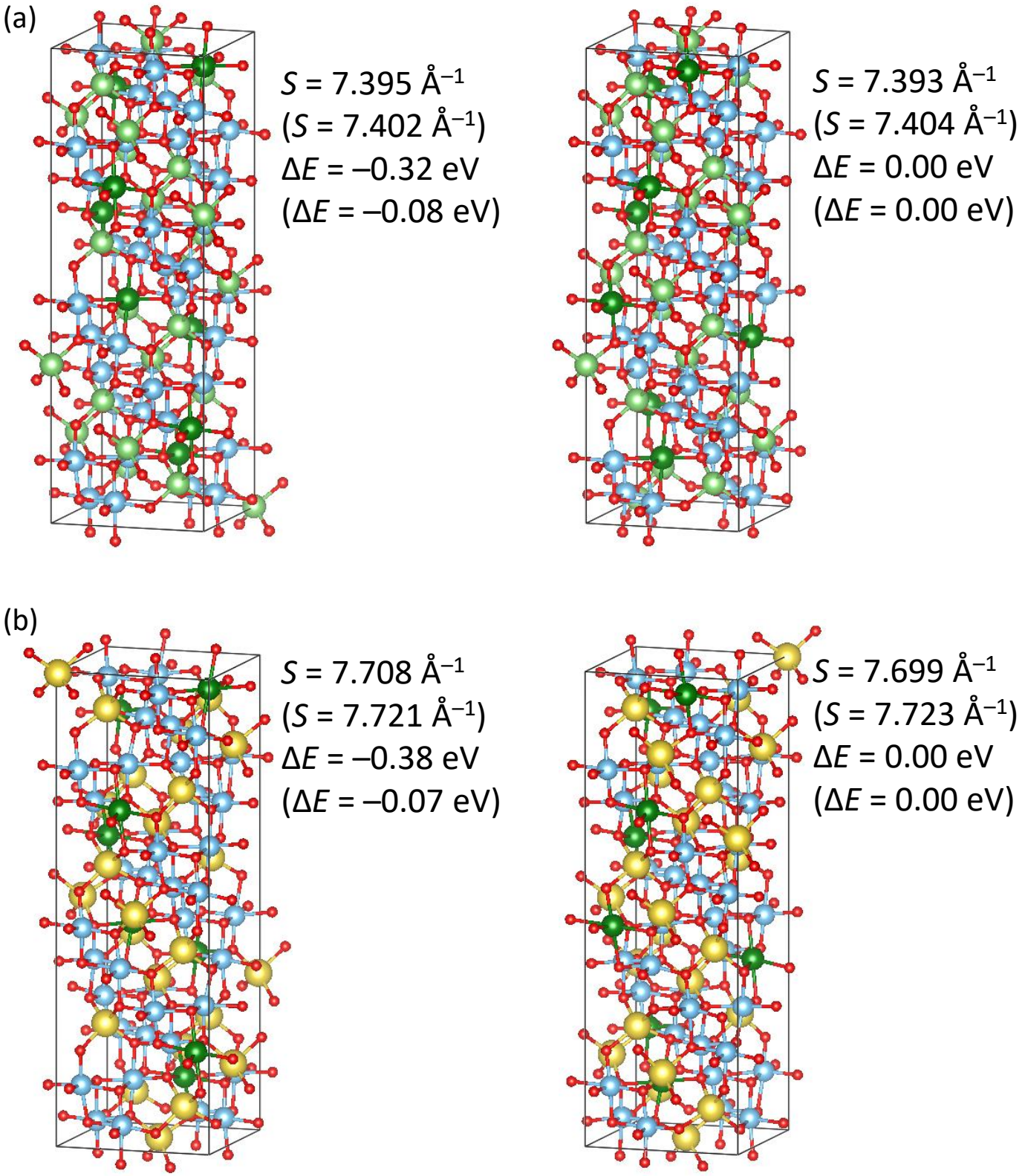


Figure S33 Comparison of the results (optimized structures, *S* values, and Δ*E* values) of spinel-titanates ((a) LTO, and (b) NTO) with the predicted configurations by previous works [30, 31] (left panels) and the most stable configurations among the 13,444 (LTO) and 8,444 (NTO) models (right panels).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