Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


**Supporting information**

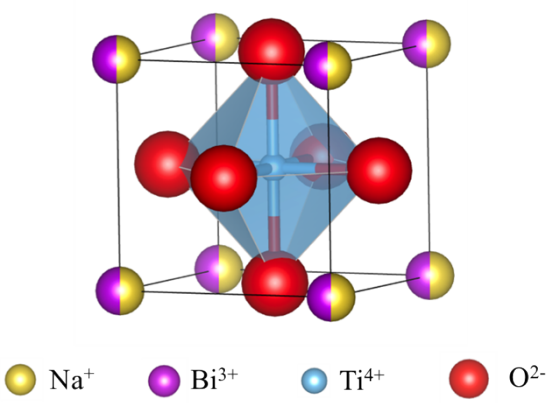


**Figure S1.** Crystal structure of $Na_{0.5}Bi_{0.5}Ti_3O_3$. Na and Bi ions share the A sites and Ti ions occupy the B sites. The octahedral of $TiO_6$ is shown for clarity.

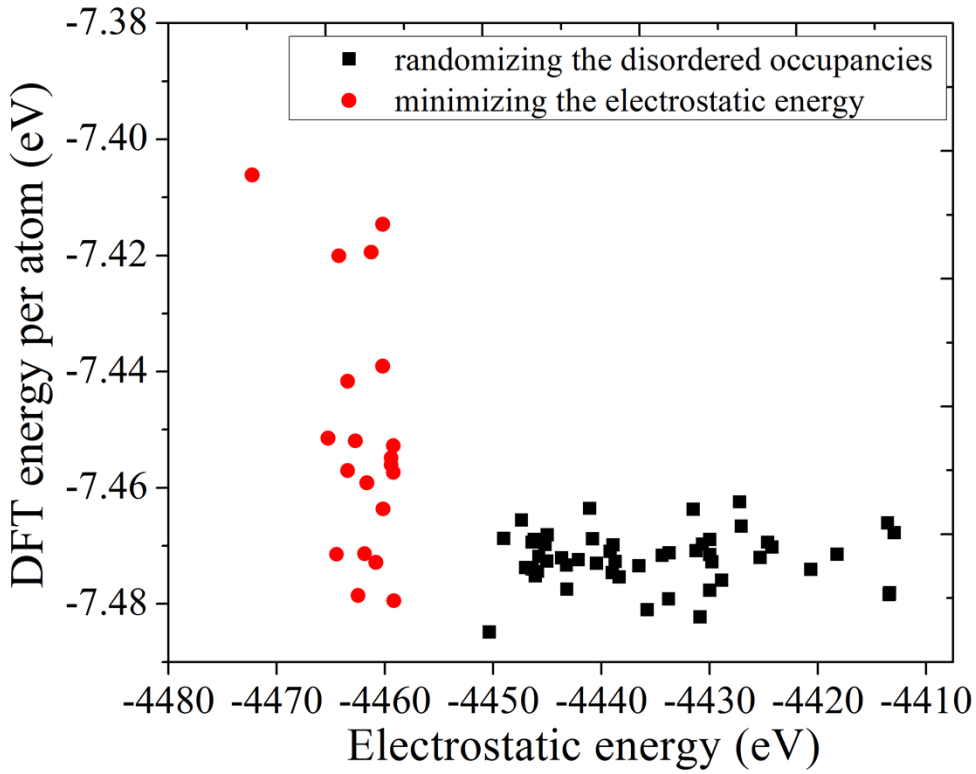


**Figure S2.** Electrostatic energy versus DFT energy for the $Na_{0.5}Bi_{0.5}Ti_3O_3$ with different A-site configurations, which were generated by randomizing the disordered occupancies (black) and by minimizing the electrostatic energy (red) of A-site Na and Bi sublattice.

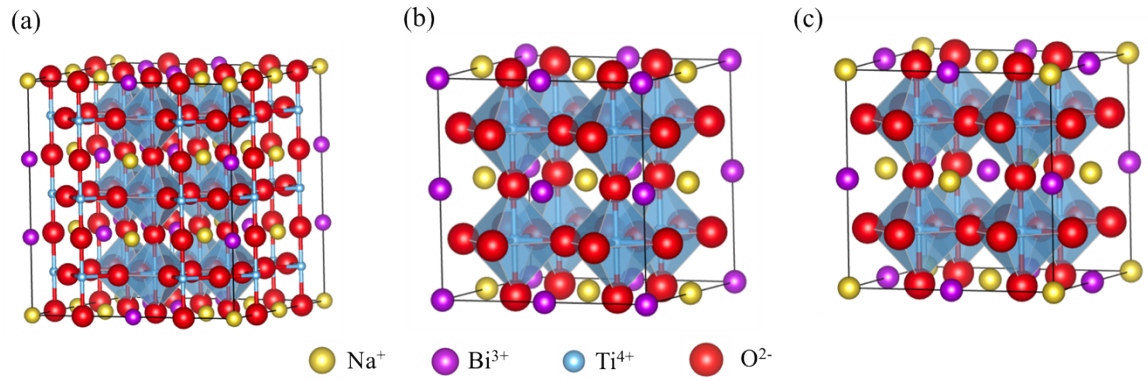


**Figure S3.** Crystal structures of $Na_{0.5}Bi_{0.5}Ti_3O_3$ with different A-site Na/Bi sublattice, which has (a) the lowest DFT energy, (b) the {001} layered ordering, or (c) the rock-salt ordering. The octahedral of $TiO_6$ is shown for clarity. The DFT energies for these three structures are: (a) -7.485 eV/atom, (b) -7.437 eV/atom, (c) -7.397 eV/atom, respectively.