Supporting information

Figure S1. Crystal structure of Na$_{0.5}$Bi$_{0.5}$Ti$_3$O$_3$. 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$_3$O$_3$ 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$_3$O$_5$ 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.