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


# Supplementary information – First-principles study of $Na_xTiO_2$ with trigonal bipyramid structures: An insight into sodium-ion battery anode application

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## $TiO_2$ crystalline structures in trigonal bipyramid phases

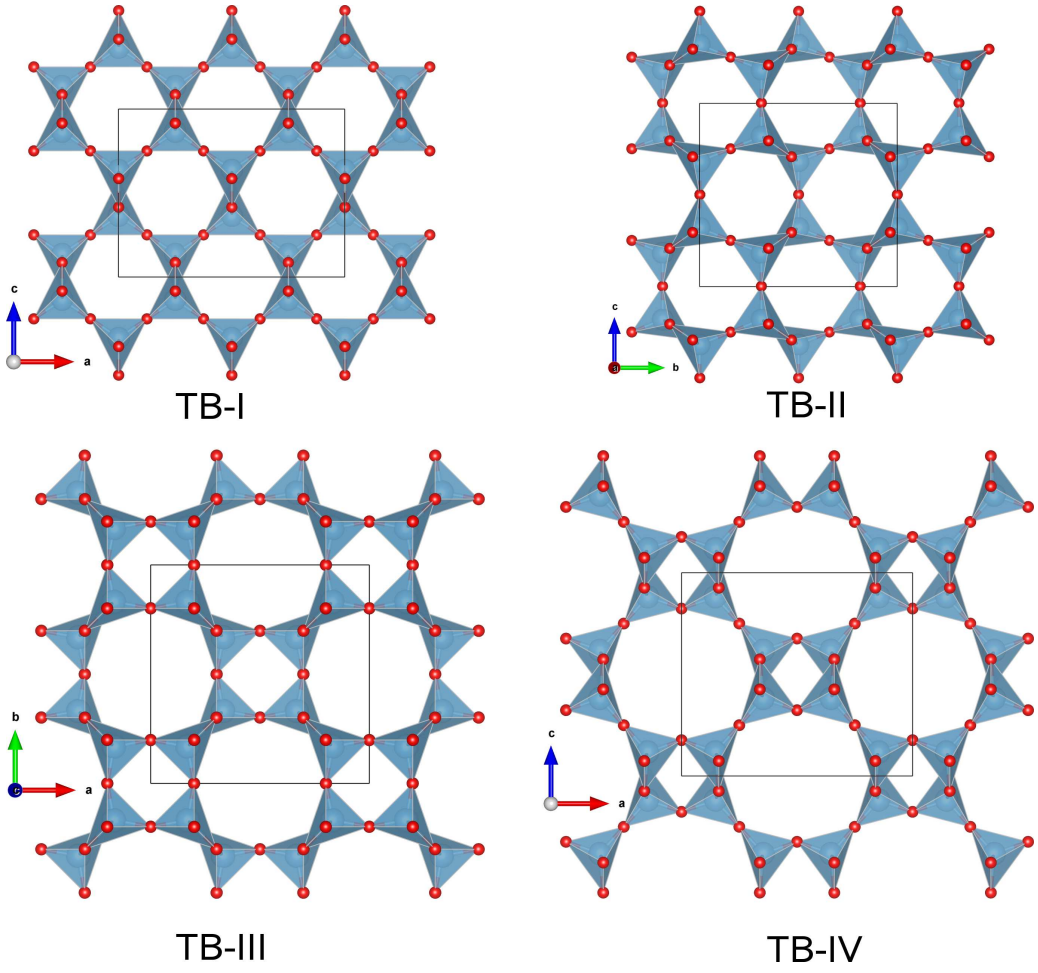


Figure S1. Crystalline structures of $TiO_2$ with four different trigonal bipyramid (TB) phases.

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## Bond valence sum

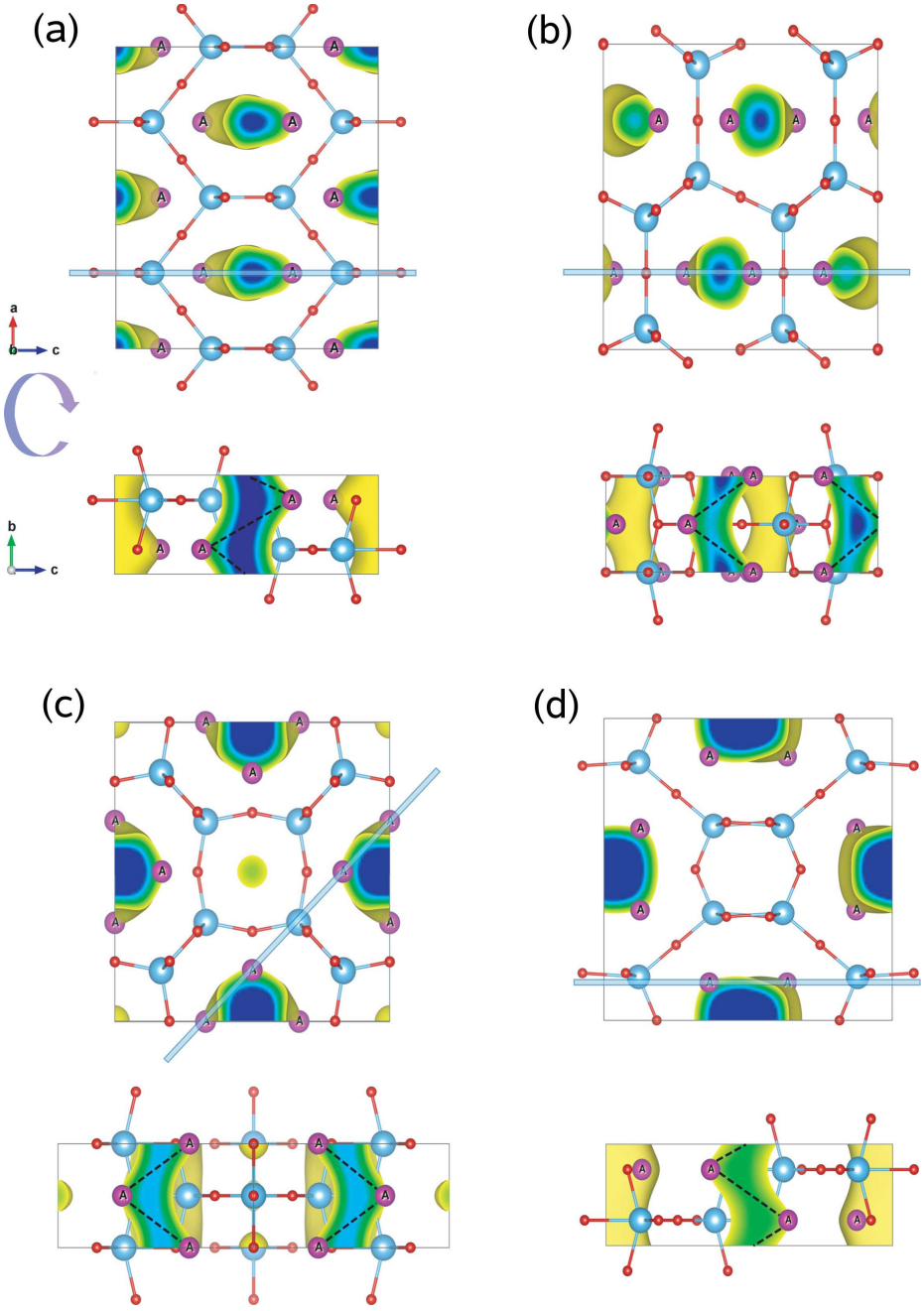


Figure S2. Isosurface view of bond valence sum (BVS) of $TiO_2$ for Na insertion into (a) TB-I, (b) TB-II, (c) TB-III and (d) TB-IV phases, projected onto *a*-*c* (top) and *b*-*c* (bottom) planes. Blue and red balls represent Ti and O atoms respectively, and yellow balls with A label denote $Na^+$ cation insertion sites. In bottom figures, ion migration paths are denoted as dashed lines.

## Structural properties and sodium binding energies

Table S1. Lattice constants $a$, $b$ and $c$ (Å), relative volume expansion rate $r_{\mathrm{vol}} = (V_x - V_0)/V_0 \times 100\%$, and sodium binding energy $E_{\mathrm{b}}$ (eV) in $Na_xTiO_2$ compounds in TB-III and -IV phases, calculated with the PBEsol functional.

| $x$ | $a$ | $b$ | $c$ | $r_{\mathrm{vol}}$ (%) | $E_{\mathrm{b}}$ |
|---|---|---|---|---|---|
| | $Na_xTiO_2$ (TB-III) | | | | |
| 0.0 | 10.54 | 3.77 | 10.54 | – | – |
| 0.125 | 10.27 | 3.82 | 10.44 | −2.27 | −2.21 |
| 0.25 | 10.18 | 3.84 | 10.27 | −4.16 | −2.03 |
| 0.375 | 10.07 | 3.88 | 10.27 | −4.10 | −1.99 |
| 0.5 | 10.23 | 3.91 | 10.10 | −3.58 | −1.89 |
| 0.625 | 10.38 | 3.94 | 10.25 | −0.13 | −1.70 |
| 0.75 | 10.88 | 3.89 | 10.53 | 6.40 | −1.61 |
| 0.875 | 10.77 | 3.94 | 10.61 | 7.51 | −1.59 |
| 1.0 | 10.71 | 3.98 | 10.72 | 9.10 | −1.58 |
| | $Na_xTiO_2$ (TB-IV) | | | | |
| 0.0 | 11.64 | 3.75 | 10.25 | – | – |
| 0.125 | 11.66 | 3.80 | 10.13 | 0.48 | −2.10 |
| 0.25 | 11.69 | 3.85 | 10.03 | 0.95 | −2.04 |
| 0.375 | 11.15 | 3.86 | 10.55 | 1.43 | −1.90 |
| 0.5 | 10.77 | 3.87 | 10.77 | 0.33 | −1.86 |
| 0.625 | 11.56 | 3.95 | 9.98 | 1.78 | −1.76 |
| 0.75 | 11.73 | 3.98 | 9.82 | 2.41 | −1.76 |
| 0.875 | 11.60 | 3.98 | 10.01 | 3.25 | −1.70 |
| 1.0 | 11.56 | 3.98 | 10.08 | 3.73 | −1.66 |

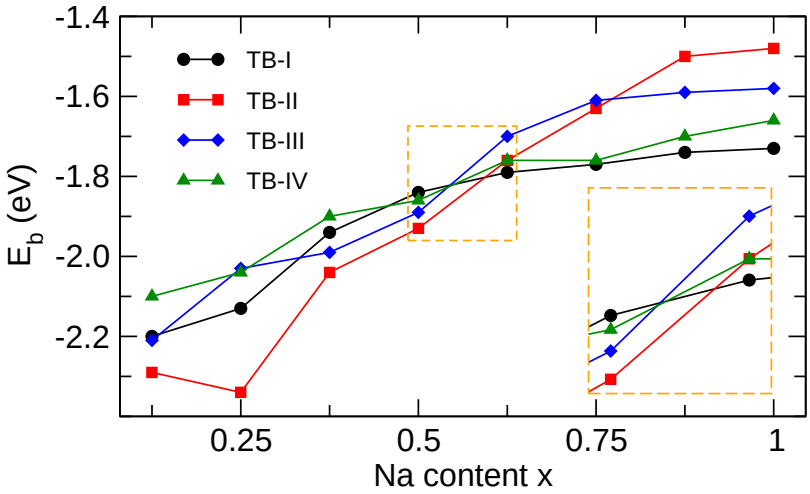


Figure S3. Binding energies of Na atom in $Na_xTiO_2$ compounds with TB phases as functions of Na content $x$.

## Activation energies for Na ion migrations

Table S2. Activation energies ($E_a$) for Na ion migrations in $Na_xTiO_2$ compounds at different Na content $x$ with different TB phases.

| | $E_a$ (eV) | | | |
|---|---|---|---|---|
| $x$ | TB-I | TB-II | TB-III | TB-IV |
| 0.125 | 0.17 | 0.19 | 0.23 | 0.58 |
| 0.25 | 0.21 | – | – | – |
| 0.375 | 0.19 | – | – | – |
| 0.5 | 0.34 | 0.46 | 0.25 | 0.46 |
| 0.625 | 0.63 | – | – | – |
| 0.75 | 0.60 | – | – | – |
| 0.875 | 0.53 | 0.26 | 0.30 | 0.65 |

## Electronic density difference

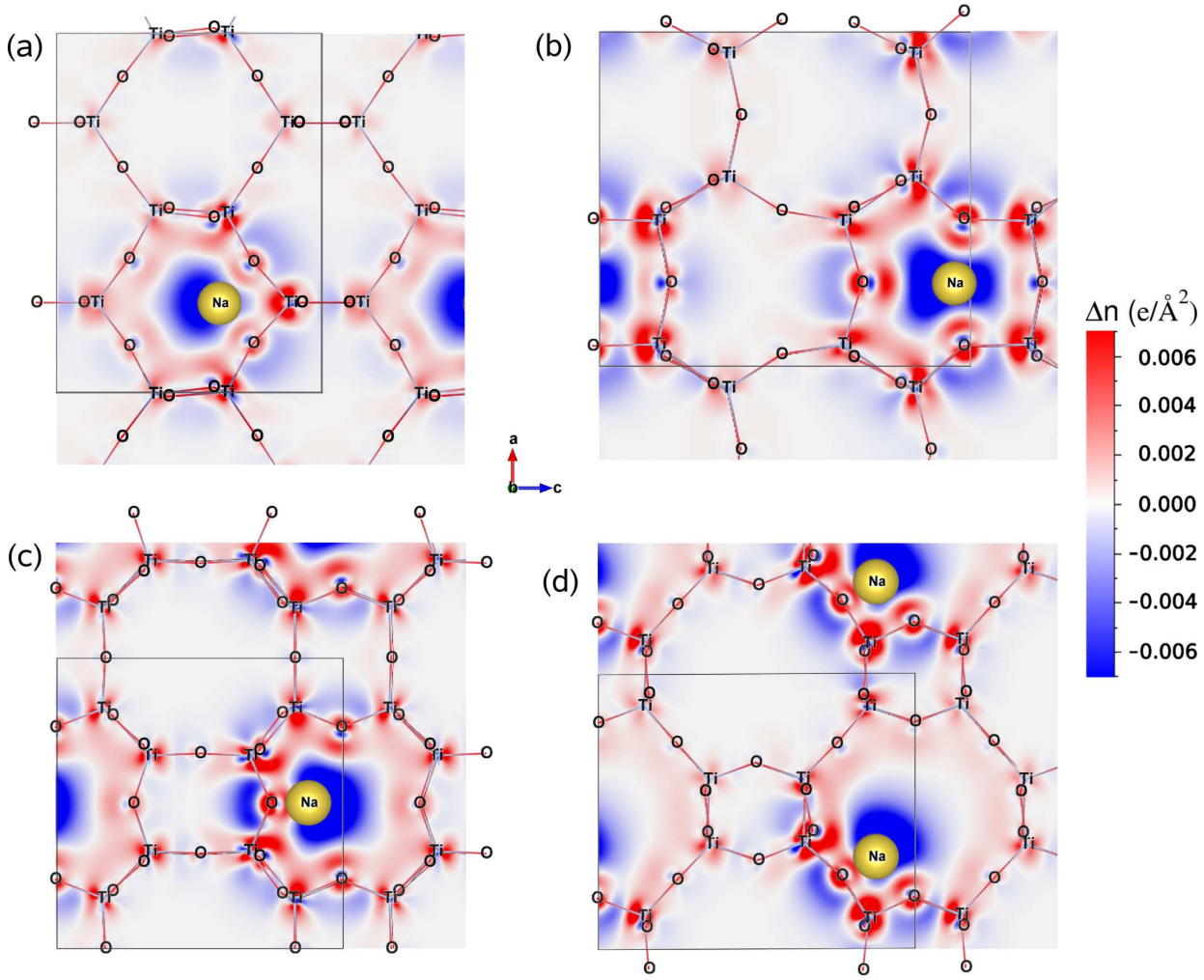


Figure S4. Electronic charge density difference integrated over $b-$axis in a) TB-I, b) TB-II, c) TB-III and d) TB-IV phases with $x = 0.125$. Positive (red) and negative (blue) values indicate the electron gain and loss, respectively.