Ti-O System

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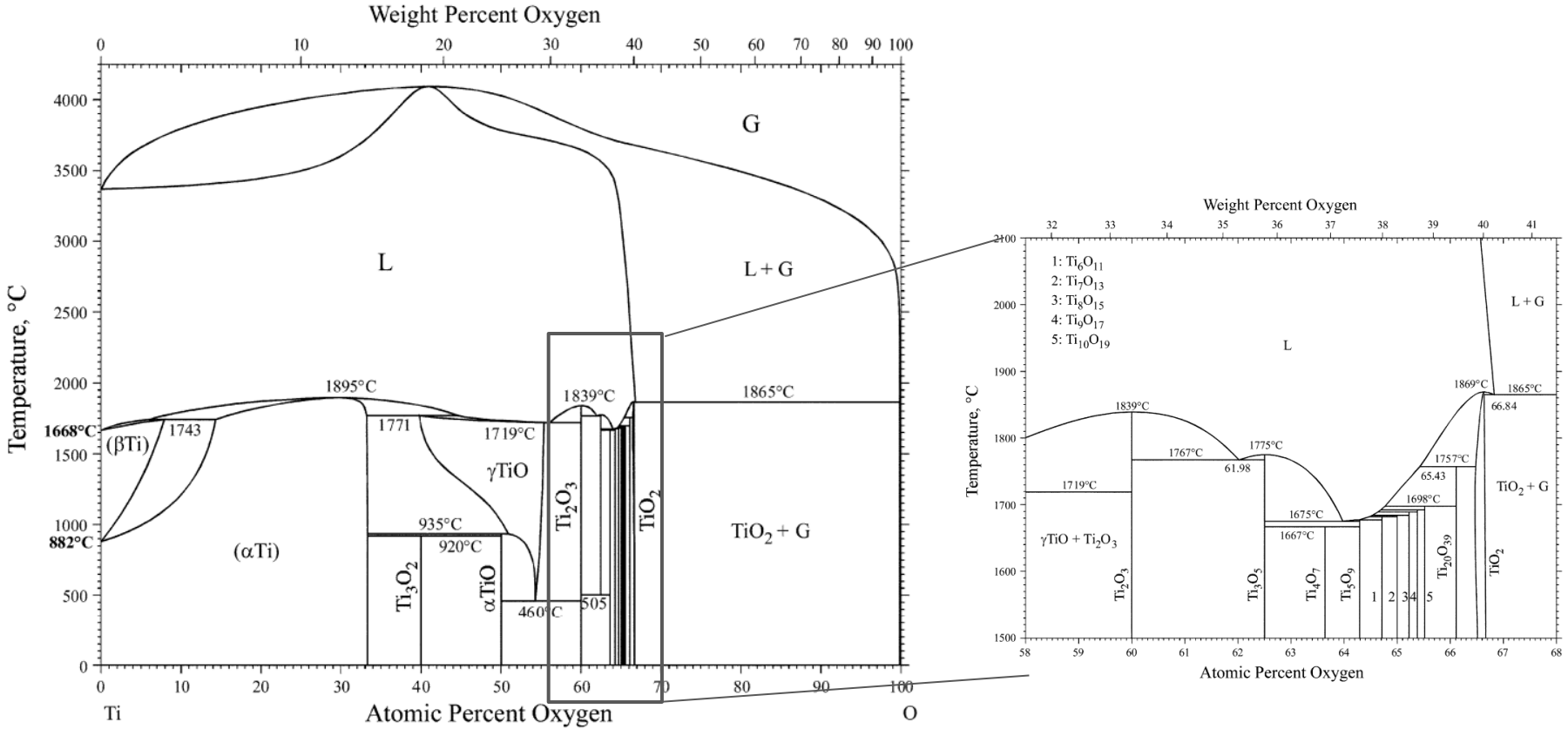
Overview

- Motivations
- TiO
  - Vacancy orderings
- TiO_2
  - Polymorph stability
  - Photocatalysis
- Magneli Phases (Substoichiometric Ti_nO_{2n-1})
- Ground states?

Motivations

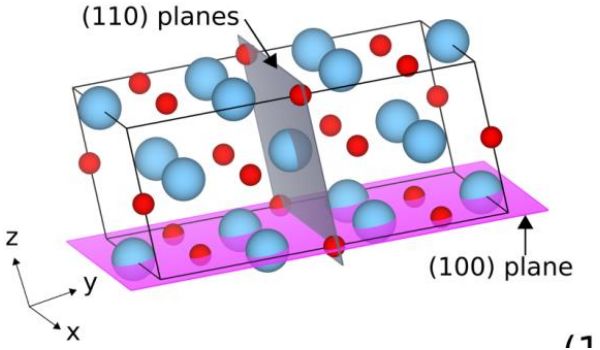
- Currently studying Ti-N-O system
- Ti-O binary full of interesting phases
  - Photocatalysis
  - Electrode materials
- Still unconfirmed equilibrium phases

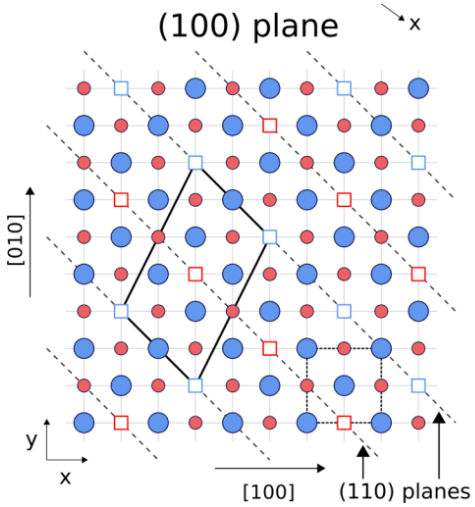


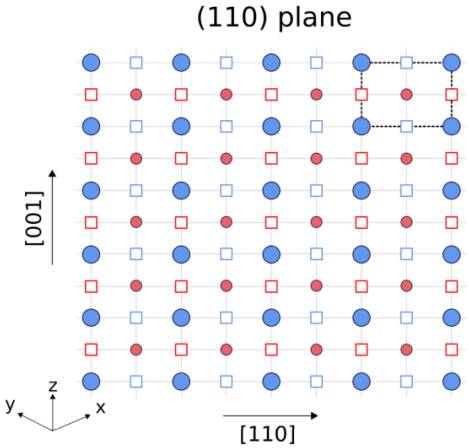
H. Okamoto, Journal of Phase Equilibria and Diffusion. 2011

α-TiO - experimental ground state

- Rocksalt structure
  - ⅙ vacancies (Ti_5O_5 unit cell)
- Different from other transition metal oxides
  - ex. NbO takes a Nb_3O_3 (¼ vacancies) structure
  - Defect free rock-salts (NiO)



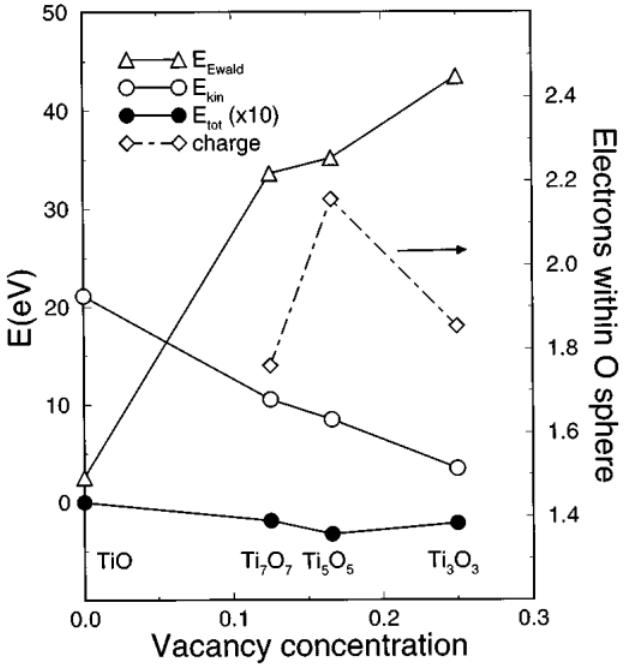




N. S. Harsha Gunda, B. Puchala, A. Van der Ven, Phys. Rev. Materials. 2018.
C. Leung, M. Weinert, P. Allen, R. Wentzcovitch, Phys Rev. B, 1996.

Why ⅙ vacancy ordering for TiO?

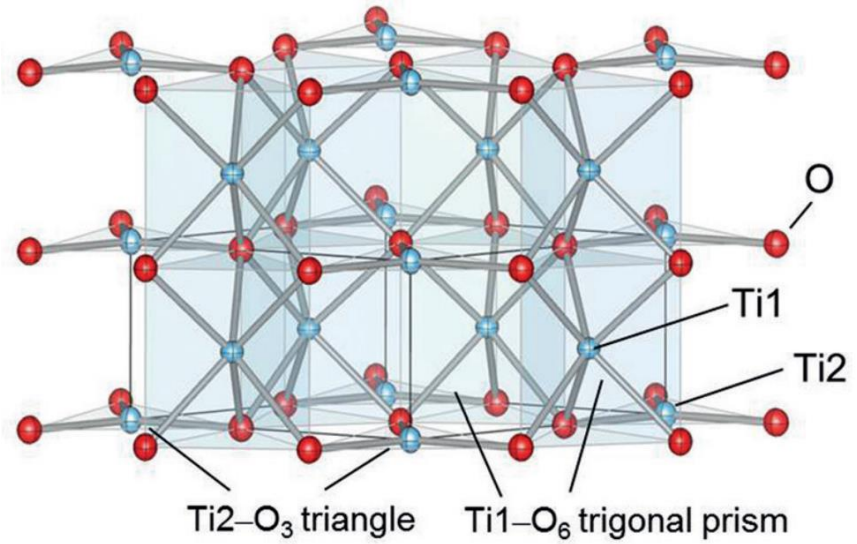
- Adding vacancies decreases Madelung energy
- Vacancy-induced perturbation breaks rocksalt energy-level degeneracy
  - O orbitals form antibonding states with Ti orbitals
    - Pushes more electron density towards vacancy site
    - Lowers electron kinetic energy
    - Recovers part of the lost Madelung energy
- Smaller d-orbital (later transition metals)
  - less kinetic energy reduction -> vacancy-free orderings
  - more ionic moving to the right



C. Leung, M. Weinert, P. Allen, R. Wentzcovitch, Phys Rev. B, 1996.

ω-TiO: More stable structure

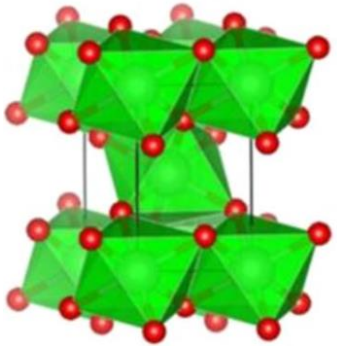
- New (more stable) monoxide structure
  - 8kJ/mol difference in enthalpy vs. α-TiO
- Experimentally synthesized
  - Required synthesis in a Bi flux
- Stronger Ti-O bonds
- Fewer antibonding states below E_f
- More ionicity



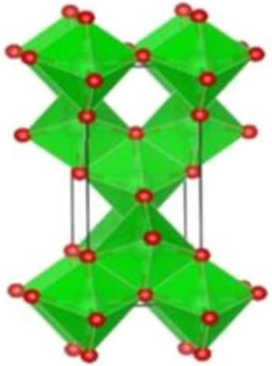
S. Amano, D. Bogdanovski, H. Yamane, M. Terauchi, R. Dronskowski, Angew. Chem. Int. Ed. 2016.

TiO_2: Rutile vs Anatase

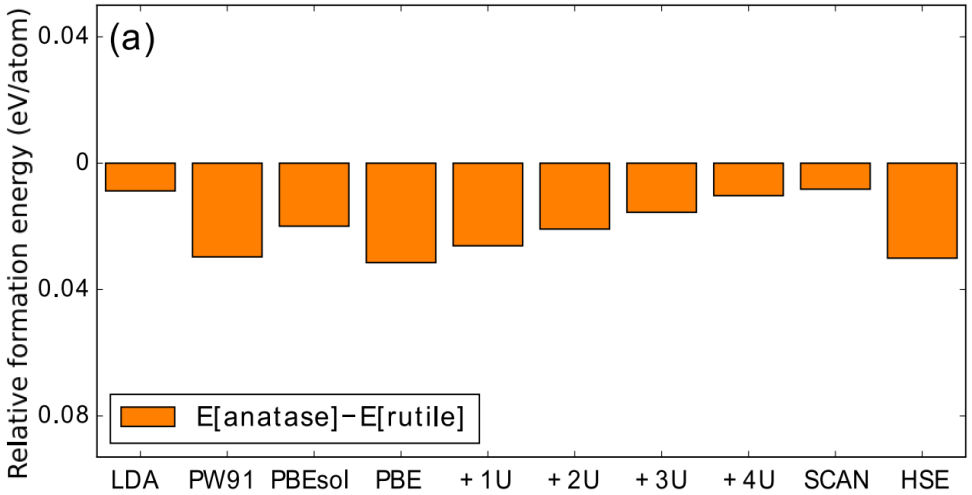
- Experimental literature reports rutile as the equilibrium phase
- Calculations report that anatase is slightly more stable



Rutile



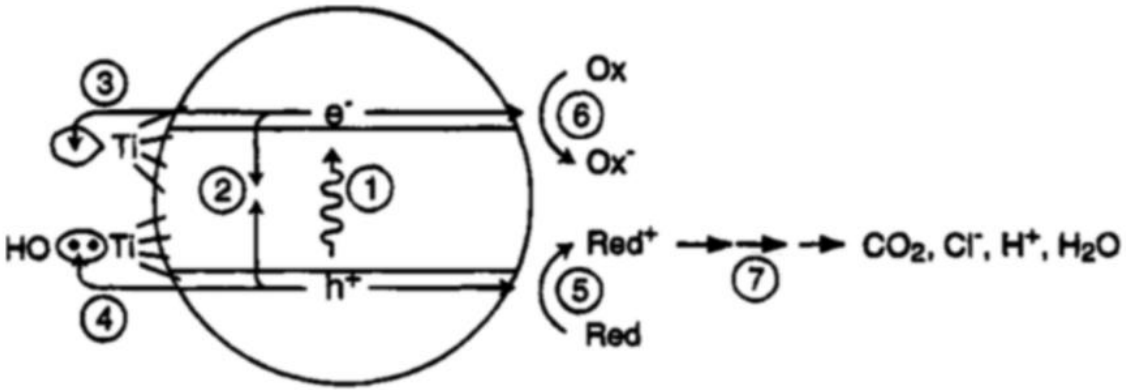
Anatase



J. Murray, H. A. Wriedt, Bulletin of Alloy Phase Diagrams, 1987.
M. Mikami, S. Nakamura, O. Kitao, H. Arakawa, X. Gonze, Jpn. J. Aplp. Phys., 2000.
N. S. Harsha Gunda, B. Puchala, A. Van der Ven, Phys. Rev. Materials. 2018.

TiO_2: Photocatalysis

- Widely used (and studied) photocatalysts
  - Chemically stable
  - Non-toxic
  - Inexpensive
  - UV active (~3eV band gap)



J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, D. W. Bahnemann, Chem. Rev. 2014.

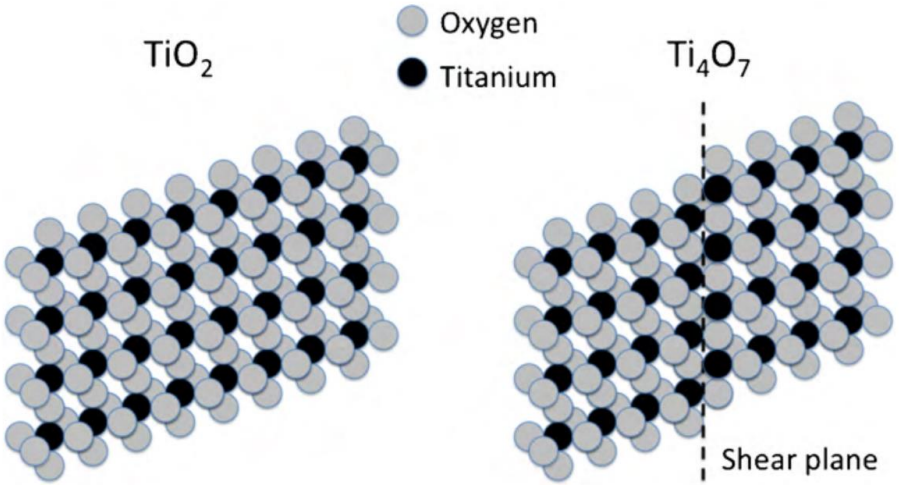
TiO_2: Rutile vs Anatase - Photocatalysis

- Anatase is perceived as more photoactive than rutile in the literature
- Anatase has a higher band gap (~3.2eV vs ~3.0eV)
- Rutile has higher surface reducibility
- Anatase has greater stability as high surface area nanoparticles
- Charge carriers excited deeper in the bulk contribute to surface reactions in anatase compared to rutile

M. Henderson, Surface Science Reports, 2011.
T. Luttrell, S. Halpegamage, J. Tao, A. Kramer, E. Sutter, M. Batzill, Scientific Reports, 2014

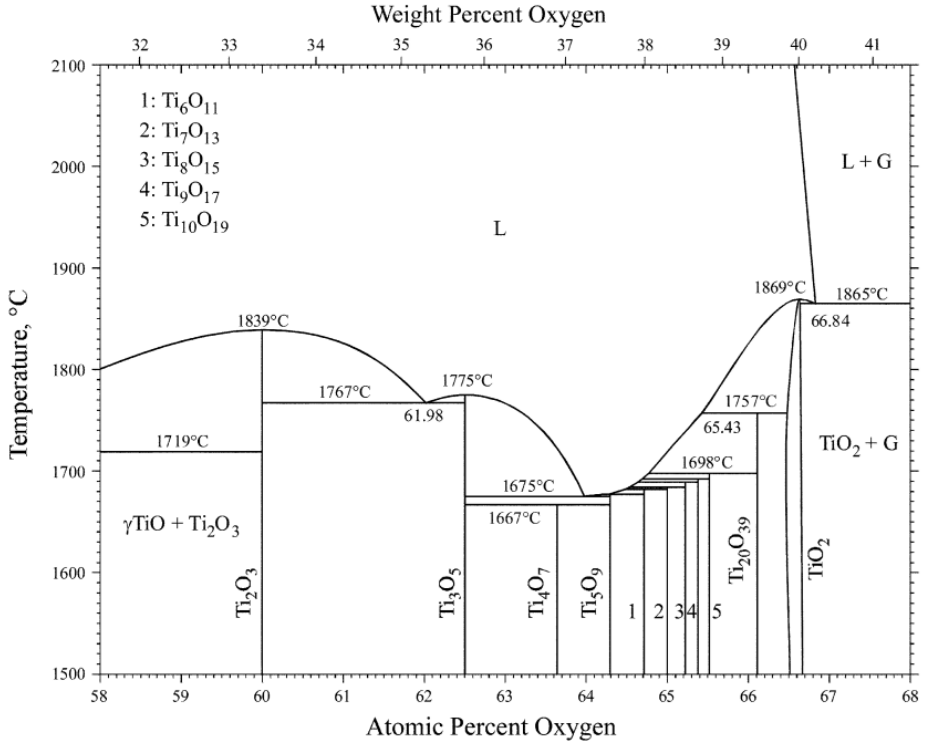
Magneli Phases (Ti_nO_{2n-1}) n=4-10

- Shear structures of rutile (TiO_2)
  - Shear planes lead to O vacancies
- Corrosion resistant
- Conductor
  - Delocalized d electrons due to oxygen deficiencies
  - Shear planes act as electron pathways
  - Higher for low n (~1900 S/cm)
- Used as electrode materials



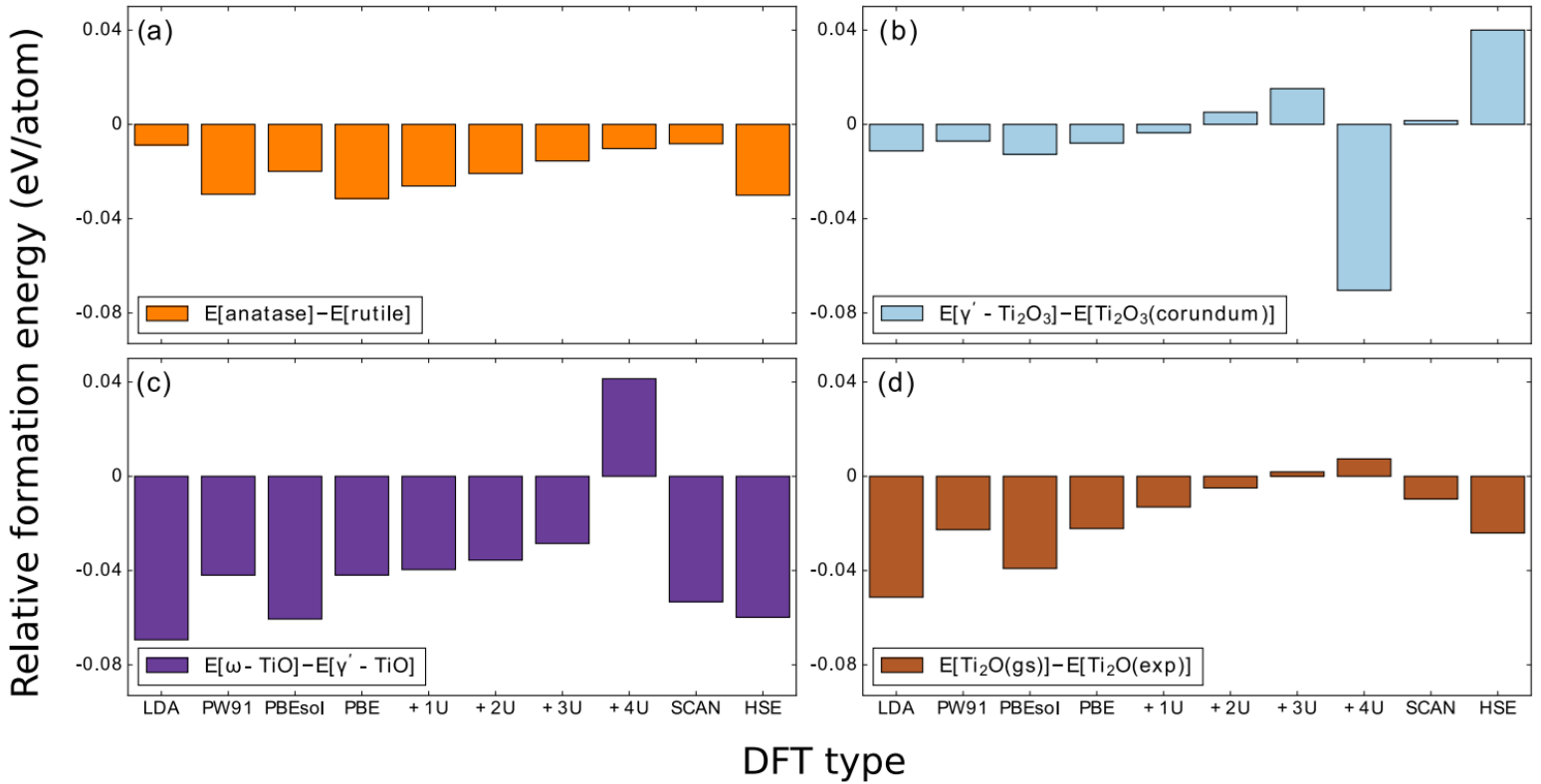
F.C. Walsh, R.G.A. Wills, Electrochimica Acta, 2010.

Magneli Phases (Ti_nO_{2n-1}) n=4-10



H. Okamoto, Journal of Phase Equilibria and Diffusion. 2011

What are the Ti-O Ground states?



N. S. Harsha Gunda, B. Puchala, A. Van der Ven, Phys. Rev. Materials. 2018.

Challenges in experimentally observing calculated ground states

- N & C interstitials stabilize rock-salt orderings in Ti
  - These orderings are predicted to be meta-stable in DFT
- Kinetic barriers may suppress ω-TiO_x formation from hcp orderings
- Note: DFT is a 0K, 0 pressure method

N. S. Harsha Gunda, B. Puchala, A. Van der Ven, Phys. Rev. Materials. 2018
.H. Okamoto, J. Phase Equilib. Diffusion, 1998.

Conclusion

- Despite being studied for decades, continuous new discoveries in Ti-O system (including new ground states)
- First-principles calculations raise some uncertainty in experimentally observed phases (namely rutile vs anatase)
- Photocatalytic TiO_2
- Conductive substoichiometric Ti_nO_{2n-1}

Questions?