Temperature Effects on Phase Stability of Metal Oxide Polymorphs

Prateek Mehta and John R. Kitchin
Department of Chemical Engineering,
Carnegie Mellon University

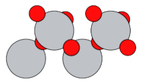
INTRODUCTION

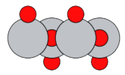
OBJECTIVE: To use quantum chemical methods and simple thermodynamic models to study the phase stability of BO_2 oxide polymorphs and identify candidates for epitaxial synthesis

Polymorphs are solid materials that can exist in more than one form or crystal structure. Example: diamond and graphite are polymorphs of carbon.

Why are we interested in Metal Oxide Polymorphs?

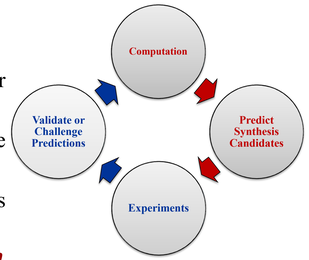
- BO_2 (B = Ti, V, Ru, Ir, Sn) polymorphs have applications in catalysis, energy, electronics, thermal barrier coatings, etc.
- Metastable polymorphs exhibit unique and sometimes superior properties
  - Example: Anatase TiO_2 is a superior photocatalyst than Rutile TiO_2





How do we look for new polymorphs?

- Looking for a new material is like looking for a needle in a haystack
  - Exploratory methods are tedious, involve trial and error
  - Likely that many nearly stable polymorphs have not been discovered

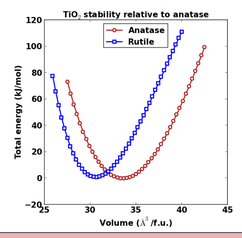


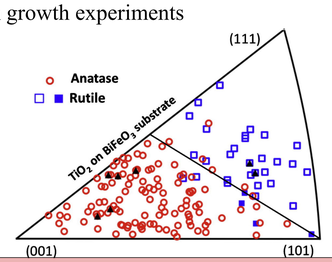
Answer: Predictive Materials Synthesis!

METHODS

Metastable polymorphs can be accessed using pressure and epitaxial methods

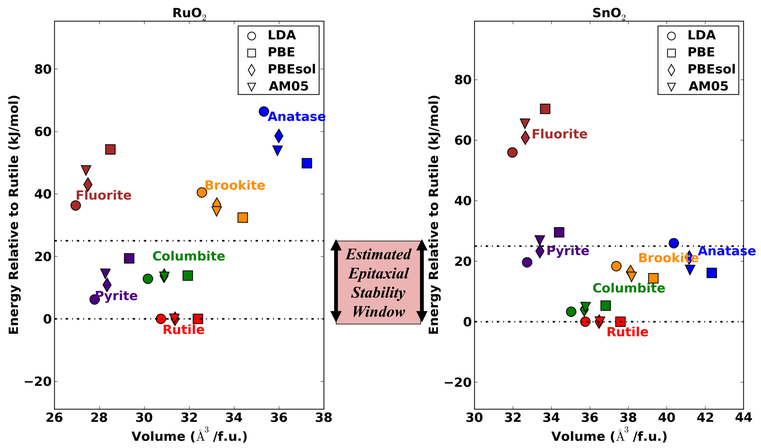
- Predictive materials synthesis is a much-used approach in high pressure research
- It is under utilized in epitaxy
- Combinatorial Substrate Epitaxy (CSE)
  - High-throughput
  - Allows hundreds of parallel film growth experiments





First Step: Use Density Functional Theory to identify potential synthesis candidates

EPITAXIAL CANDIDATES



Interpretation

- The main idea is that metastable polymorph has to be sufficiently close in energy to the ground state polymorph to be a target for epitaxial synthesis
- Interfacial energies between the thin polymorph film and a suitable substrate may cause re-ordering of relative stability
- Low volume polymorphs can be obtained by high pressure compression
- Results should be used to guide future efforts towards a more comprehensive investigation of identified targets

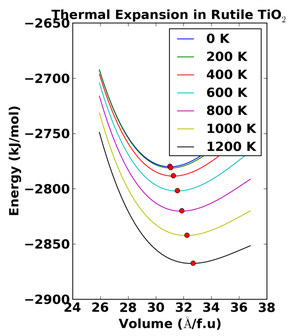
Challenges

- A complete investigation of epitaxial growth would involve incorporation of interfacial energy and surface energy, which are not easily measured experimentally
- DFT results are calculated at 0 K. Do stability trends change at higher temperatures?

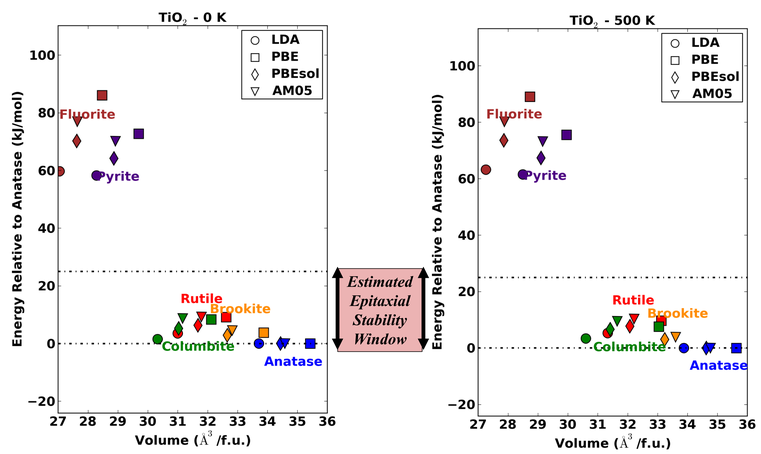
THERMODYNAMICS

$$G(V,T) = E(V) + F_{el}(V,T) + F_{vib}(V,T) + pV$$

- $E(V)$ is the 0 K DFT energy
- $F_{el}(V,T)$ is the electronic contribution to the free energy
  - Derived from density of states calculations
- $F_{vib}(V,T)$ is the vibrational contribution to the free energy
  - Described by phonon calculations – computationally expensive
  - Or by the Debye model – less expensive, less accurate
- pV is the pressure-volume energy



TEMPERATURE EFFECTS



Interpretation

- There is a negligible change in relative stability – both plots look essentially the same!
- There is a slight increase in the volume at 500 K
- Predicted epitaxial candidates do not change

Challenges

- Approximate model – error increases with temperature
- Dependent on choice of DFT exchange correlation functional – works for some functionals, fails for others
  - See two missing data points for Brookite at 500 K

CONCLUSIONS

- ***A methodology for the accelerated discovery of metastable BO_2 polymorphs has been proposed***
- ***Results show that there are many potential candidates for epitaxial synthesis***
- ***Epitaxial synthesis is particularly important to stabilize polymorphs that are metastable in both temperature or pressure space***
- ***Models indicate that temperature does not significantly affect the window for epitaxial synthesis***
- ***The results do not indicate a clear or consistent way to use simple models to study phase behavior at high temperatures using 0 K data alone***

[1] Zhang *et al. Acta Materialia* **60,** 6486–6493 (2012)
[2] Shang et al. *Computational Materials Science* **47,** 1040–1048 (2010)