Learning how oxide materials evolve from nano to bulk

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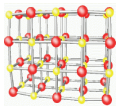
For the majority of inorganic solids only very few dense crystalline phases are known...

Examples:
- MgO (rocksalt), CdS (wurtzite, zincblende),
- TiO_2 (anatase, rutile, brookite)...

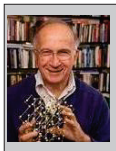


Questions:
- Are there constraints on viable crystal types for inorganic compounds?
  - (Current) experimental constrains?
  - Fundamental (e.g. Energetic, structural)?
- If not fundamental where are the missing phases?

Apparent Scarcity of Low-Density Polymorphs of Inorganic Solids. M. A. Zwijnenburg F. Illas, STB, Phys. Rev. Lett, 104,175503. (2010)

Learning to get from structures to materials…

Reasonably reliable calculated data sets of structures, energies…



Hoffmann – human chemical insight aided by calculations (human learning)

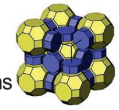
+

Turing – Let the computer do all the work (big data / machine learning)

New insights and discovery of novel inorganic polymorphs

Deriving large datasets of structures

1. Structure Enumeration: systematic generation of structures from bonding patterns characteristic of the material

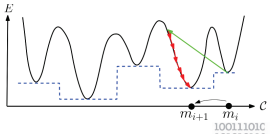


Tilings of 3D space

3D embedding of graphs

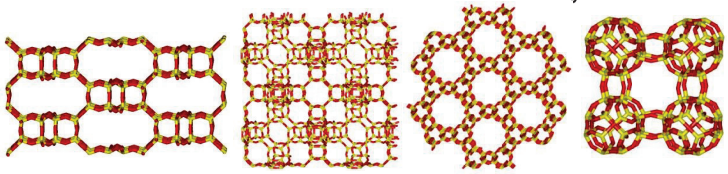
2. Data mining: using experimental and/or hypothetical crystal structures for material A as guesses for new stable phases for material B.

3. Global optimisation: simulating annealing, evolutionary algorithms, basin hopping, minima hopping, particle swarm, lid method…



Enumeration of tetrahedral frameworks

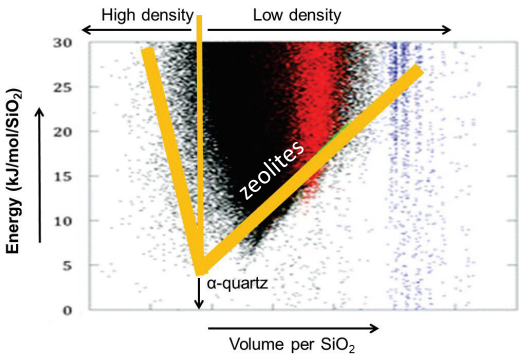
- Attempts to enumerate all possible topologies (nets) for a given connectivity (usually 4-connected nets).
- Some subclasses of nets have been exhaustively enumerated.



- More than one million unique 4-connected (tetrahedral) nets enumerated. (see: rcsr.anu.edu.au, www.hypotheticalzeolites.net, www.crystallography.net/pcod)

Treacy M.M.J. *et al Z. Kristalogr.* **1997**, 212, 768.
Delgado-Friedrichs O. *et al Nature* **1999**, 400, 644

From enumerated nets to viable materials?

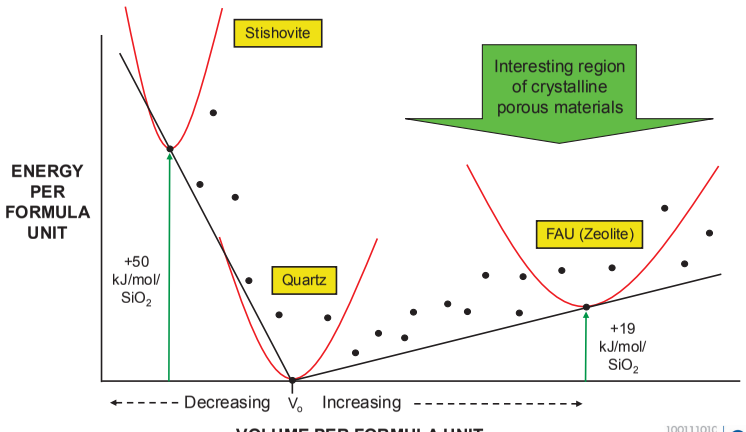


Accurate empirically fitted Interatomic Potentials (IPs) available for bulk silicates

However only 190 zeolites synthesised…

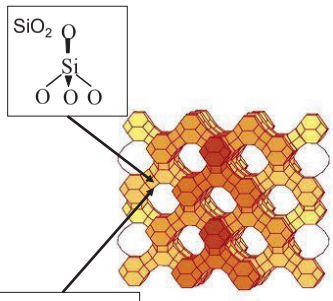
Pore size analysis of >250000 hypothetical zeolites
(E. Haldoupis et al. Phys. Chem. Chem. Phys., 2011,13, 5053)

Generic energy *versus* volume behaviour

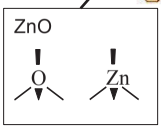


Data-mining the zeolite dataset

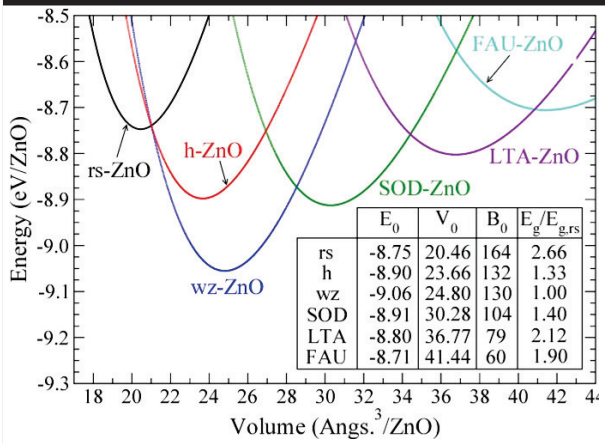
- The underlying topology of a zeolite is a 4-connected net.
- Such nets have 4-connected vertices and 2-connected edges
- In the zeolite the vertices are Si atoms and edges are -O- linkages.



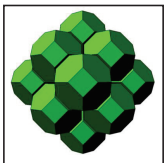
- In ZnO we have 4-connected vertices (Zn/O) and 2-connected edges.(Zn-O) bonds
- New ZnO polymorphs?



Stability of zeolitic ZnO polymorphs?



	E_0	V_0	B_0	$E_g/E_{g,rs}$
rs	-8.75	20.46	164	2.66
h	-8.90	23.66	132	1.33
wz	-9.06	24.80	130	1.00
SOD	-8.91	30.28	104	1.40
LTA	-8.80	36.77	79	2.12
FAU	-8.71	41.44	60	1.90



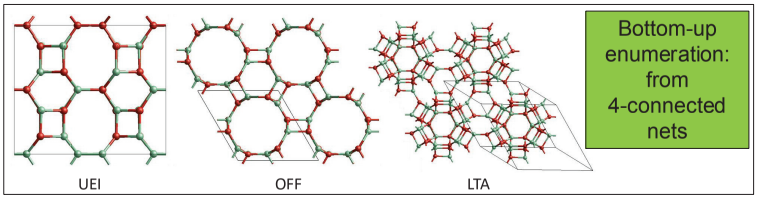
SOD-ZnO
+0.14 eV/ZnO

Theory: DFT PW91 415eV cut-off.

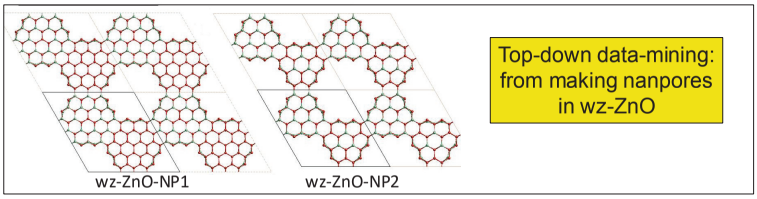
Data fitted to Birch-Murnaghan equation of state.

J. Carrasco, F. Illas, STB, Phys. Rev. Lett., 99, 235502 (2007).

Building a dataset of nanoporous ZnO polymorphs



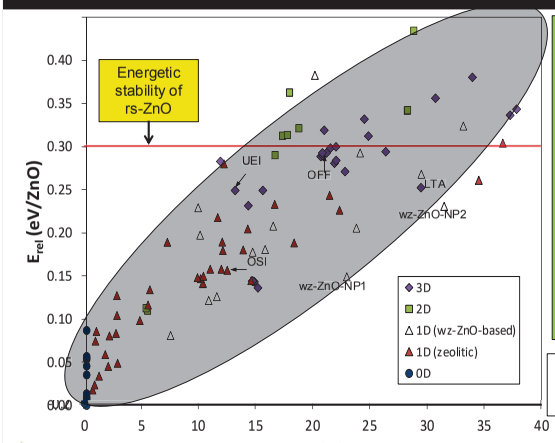
Bottom-up enumeration: from 4-connected nets



Top-down data-mining: from making nanpores in wz-ZnO

M. A. Zwijnenburg, F. Illas, STB, *Phys. Rev. Lett.*, 104, 175503, 2010.
I. Demiroglu, S. Tosoni, F. Illas, STB, Nanoscale, 6, 1181, 2014.

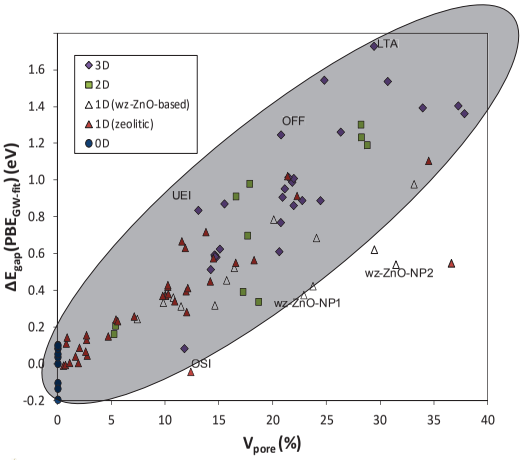
Energetic stability of nanoporous ZnO



- >100 nanoporous ZnO polymorphs generated
- >70% more stable than rocksalt ZnO
- General tendency for increasing metastability with increasing nanoporosity

I. Demiroglu, S. Tosoni, F. Illas, STB, Nanoscale, 6,1181 (2014)

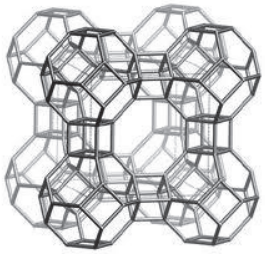
Band gap shifts for nanoporous ZnO polymorphs



- Low density ZnO polymorphs have direct band gaps varying up to ~1.6 eV above that of wurtzite
- Porosity correlates with band gap
- Greater band gap range than $Zn_{1-x}Mg_xO$ wurtzite alloys.

I. Demiroglu, S. Tosoni, F. Illas, STB, Nanoscale, 6,1181 (2014)

Nanoporosity *versus* Low Density



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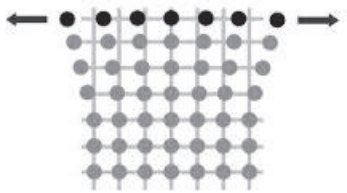
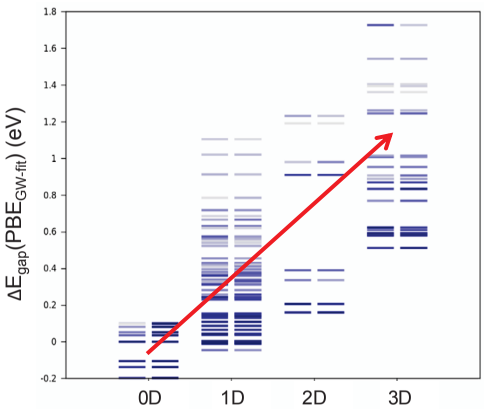


Nanoporous structures have low density but relatively unstrained bonds

Tensile strain induces low density but stretches bonds (reduces band gap)

Effect of pore system dimensionality

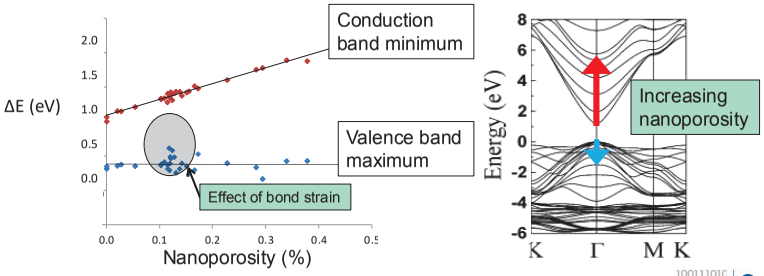


- Increasing the dimensionality of the pore system tends to increase the band gap shift

I. Demiroglu, S Tosoni, F. Illas, STB, Nanoscale, 6, 1181, 2014.

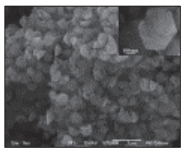
What determines the band gap variance?

- Nanoporosity can be used to tailor band gaps.
- Reducing bandwidths of the valence and conduction band increases ΔE_{gap}.
- .Dispersive conduction band in ZnO is more affected than the flatter valence band.

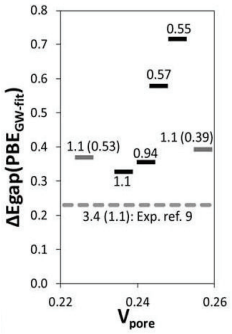


I. Demiroglu, S Tosoni, F. Illas, STB, Nanoscale, 6, 1181, 2014.

ZnO nanoporosity in experiment – top down



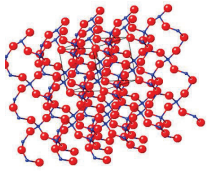
S. Bhattacharyya and A. Gedanken, Microporous Mesoporous Mater., 2008, 110, 533.



- A template-free, sonochemical method has produced nanoporous ZnO with a band gap shift of +0.23 eV.
- Unknown degree of nanoporosity but can compare with our top-down nanoporous wurzite structures
- The same degree of nanoporosity achieved with larger pores yields lower band gap shifts

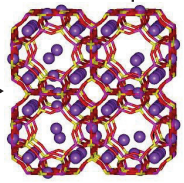
ZnO nanoporosity – learning from zeolite synthesis?

Dense quartz SiO_2

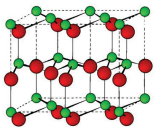


→ Substitute % of Si^{4+} by Al^{3+} and X^+ →

Al^{3+} replaces Si^{4+}, X^+ creates nanopores



Dense wurtzite ZnO



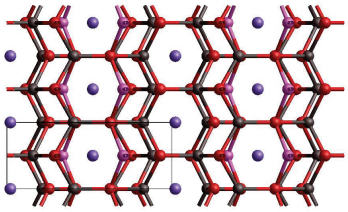
→ Substitute % of Zn^{2+} by Li^+ and X^+ → ?

M. A. Zwijnenburg and STB, *J. Mater. Chem* 21, 15255 (2011).

Formation of substituted/stuffed ZnO frameworks

For ≤33% Zn substitution cage-like materials formed

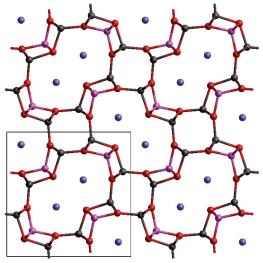
25% substitution of Zn with Li/K



- Same topology as zeolite framework ATN
- Also found experimentally for $RbLiMn_3O_4$

R. Hoppe *et al J. Solid State Chem.* **1988**, 72, 52.

33% substitution of Zn with Li/Rb



R. Baier *et al Z. Anorg. Allg. Chem.* **1989**, 568, 136.

M. A. Zwijnenburg and STB, *J. Mater. Chem* 21, 15255 (2011).

$(X,Li)_xZn_{(1-x)}O$ alloys for 4-5 eV band gaps?

- For UV optoelectronics would like stable materials with controllable band gaps between approx. 3.5 and 6 eV

- Region of approx. 4-5 eV difficult to obtain through $Mg_xZn_{(1-x)}O$ alloys due to structural phase segregation.

- Band gap increases in $(X,Li)_xZn_{(1-x)}O$ alloys can be tailored by the:
  1. Type of nanoporous framework structure formed
  2. Level of (X,Li) substitution
  3. Choice of X cation

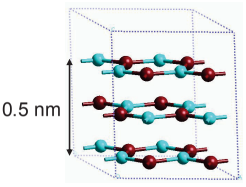
	Predicted Band gap (eV)
Wurtzite	3.4
[ZnO]-ATN	3.8
|K|[$LiZn_3O_4$]-	4.2

Increase framework structure

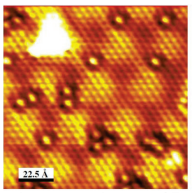
Increase due to dopant choice

M. A. Zwijnenburg and STB, *J. Mater. Chem* 21, 15255 (2011).

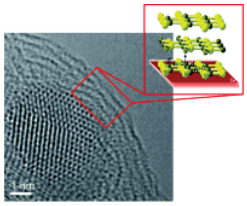
Novel 2D ZnO polymorphs: from prediction to reality



A new layered phase of ZnO (h-BN structure) was predicted to be stable in nanofilms – Freeman et al. PRL 96, 066102 (2006).

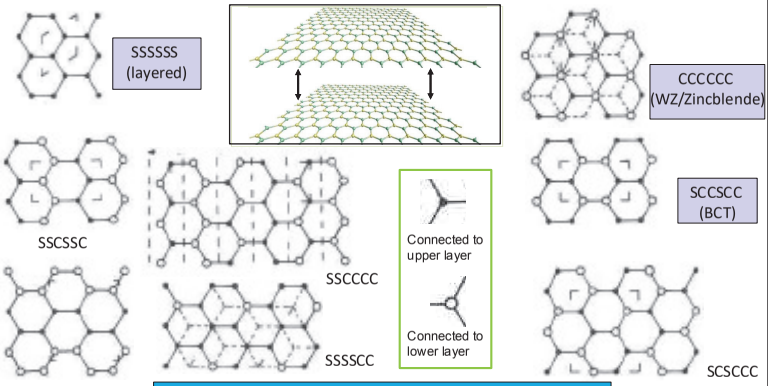


Surface science experiments of ZnO deposited on Ag(111) confirm prediction in very thin films - Tusche et al PRL 99, 026102 (2007).



Formation of a ZnO overlayer in industrial Cu/ZnO/Al_2O_3 catalysts - T. Lunkenbein et al. Angew. Chemie Int. Ed., 54, 4544 (2015).

Enumeration of new ZnO thin film polymorphs based on linking hexagonal layers



Method first used to enumarate and classify bulk silicates (Smith, V. J., Amer. Minerologist, 62, 703, 1977)

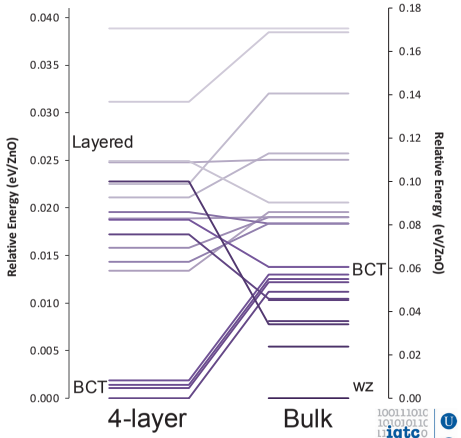
Comparison of 3D versus 2D polymorphism for ZnO

- Many other similar polymorphs lie lower in energy than the layered phase for >3 layers.

- BCT-ZnO and its polytypes are most stable as 4-layer nanofilms.

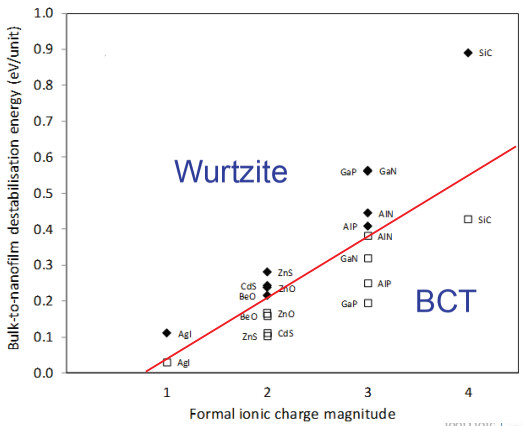
- Nanofilm energetic stability ordering totally distinct to that of bulk polymorphs

I. Demiroglu, STB, Phys. Rev. Lett. 110, 245501 (2013)



General bulk-to-nanofilm tendency of AB wurtzite materials

- All materials are destabilised upon size reduction
- For AB wurtzite materials the bulk-to-nanofilm transition is less destabilising for the BCT phase.
- BCT is a promising new phase for AB nanofilms



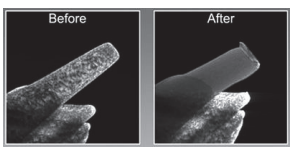
When enumeration fails for nanofilms: Simulated Mechanical Annealing (SMA)

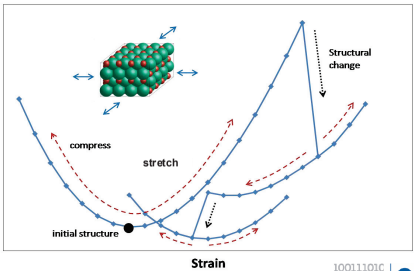
- Mechanical Annealing used experimentally to rid nanostructures of defects.
  W. Shan et al. Nature Materials 7, 115 (2007).
- Simulated Mechanical Annealing uses virtual cycles of stress and strain to find low energy structures.
- SMA sucessfully applied to nanotubes, nanowires, nanosheets:

W. Sangthong Limtrakul, F. Illas, STB, Nanoscale 2, 72 (2010).

N. Krainara, J. Limtrakul, F. Illas, STB, J. Phys. Chem. C 117, 22908 (2013).

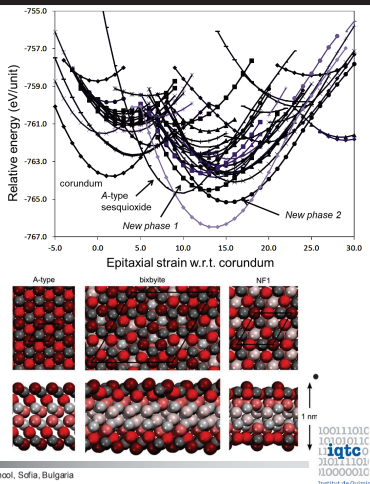
N. Krainara, J. Limtrakul, F. Illas, STB, Phys. Rev. B 83, 233305 (2011).





Simulated Mechanical Annealing of unsupported Ce_2O_3 nanofilms

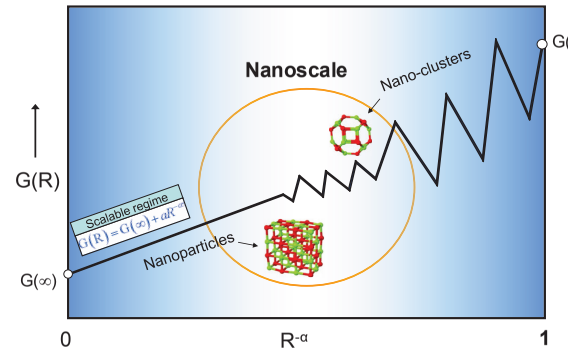
- Enumeration not practicable for Ce_2O_3 thin films as no known regular growth pattern
- Use global optimisation starting from known A_2B_3 bulk structures
- Many non-bulk low energy structures found.
- Unlike A-type and bixbyite, NF1 cannot be extended into a bulk polymorph



S. Kozlov, I. Demiroglu, K. Neyman, STB, Nanoscale 7, 4361 (2015).

Size-dependency of properties of materials…

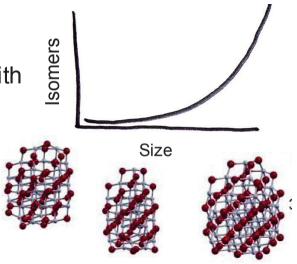
For an arbitrary property, G(R), of a particle with radius R



STB, I. de P. R. Moreira, K. M. Neyman, F. Illas, *Chem. Soc. Rev.* (2009) 2657-2670

Obtaining the structure of low energy nanoclusters:

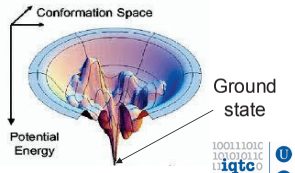
- Exponential growth of the number of energetically reasonable cluster isomers with increasing size



- Even for small clusters (e.g. ~20 atoms) there are an "astronomical" number of possible structural isomers.

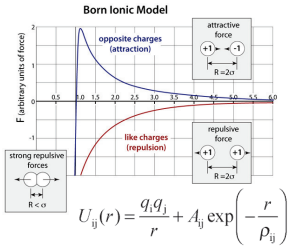
- Want to find most stable structures in complex space of structure and energy

Global Optimisation



Obtaining the structure of low energy nanoclusters

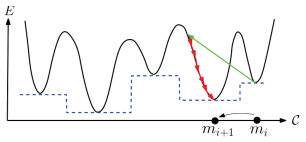
1. Basin hopping global optimisation using interatomic potentials to give reasonable low energy candidates



$$U_{ij}(r) = \frac{q_i q_j}{r} + A_{ij}\exp\left(-\frac{r}{\rho_{ij}}\right) - \frac{C_{ij}}{r^6}$$

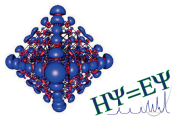
(+ polarisation)

+

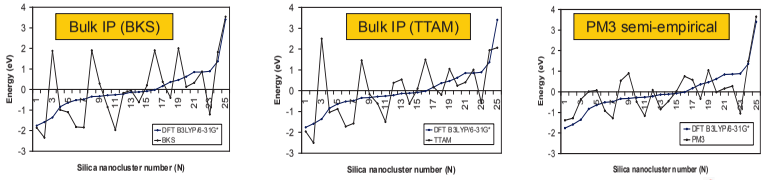


- Basin Hopping combines Monte Carlo with regular energy minimisations.
- Potential energy surface is transformed into a step-wise surface.
- Local energy barriers are eliminated.

2. Evaluate/refine properties using *ab initio* quantum mechanical methods (typically DFT)



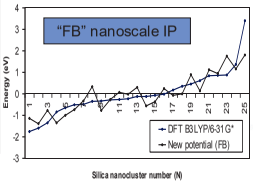
Tailoring interatomic potentials (IPs) for the nanoscale

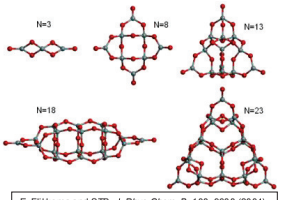


New IP trained for $(SiO_2)_N$ with N=2-6

Test set shown for N=7 isomers

Structure: Most clusters < 0.1Å max RMS diff w.r.t. DFT energy minimised (6-31G*/B3LYP) structures





E. Flikkema and STB, *Chem. Phys. Lett.* 378, (2003) 36.

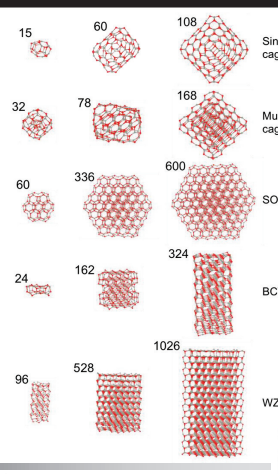
E. Flikkema and STB, *J. Phys.Chem. B*, 108, 9638 (2004)
STB and E. Flikkema, *Phys. Rev. Lett.* 95, 185505 (2005)
E. Flikkema and STB, *Phys. Rev. B* 80, 035402 (2009)

Structural size dependence of ZnO

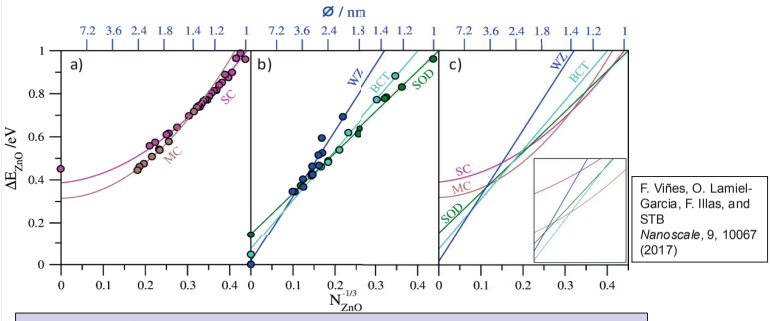
For nanoclusters IP-based global optimisation IPs show single-layered and multi-layered cages are most stable

"Polymorph prediction" studies have identified the SOD and BCT polymorphs as relatively low energy bulk structures for ZnO

Wulff cuts from the thermodynamic ground state wurtzite structure known to dominate for moderate/large sizes ZnO



Structural size dependence of ZnO



F. Viñes, O. Lamiel-Garcia, F. Illas, and STB *Nanoscale*, 9, 10067 (2017)

- Dataset of over 300 DFT-optimised structures used to track size-evolution of ZnO from nanocluster to bulk
- Transition to bulk wurtzite predicted to occur for $(ZnO)_N$ nanoparticles with ~4.7nm diameter / ~4600 atoms – in line with experiment

Structural size dependence of TiO_2

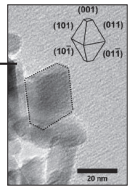
Increasing size

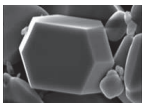
Non-crystalline nanoclusters → Bulk crystalline nanoparticles (Anatase, Rutile)

~1 nm

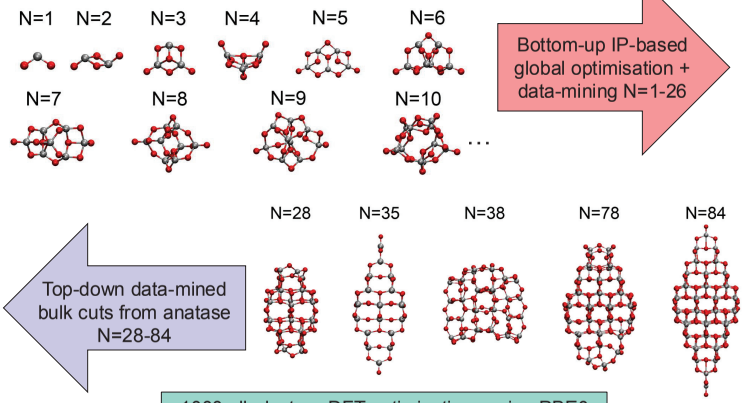
$(TiO_2)_8$

Cluster to bulk crossover size ?





Dataset of considered $(TiO_2)_N$ species

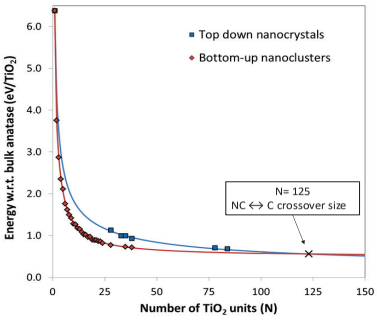


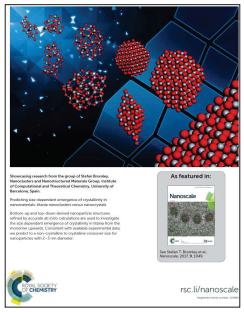
Bottom-up IP-based global optimisation + data-mining N=1-26

Top-down data-mined bulk cuts from anatase N=28-84

~1000 all-electron DFT optimisations using PBE0

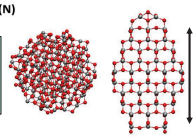
Predicting the lower size limit for anatase nanocrystals





O. Lamiel-Garcia, A. Cuko, M. Calatayud, F. Illas, STB, Nanoscale 9, 1049 (2017)

Crossover from non-crystalline to crystalline (anatase) predicted to occur at ~125 TiO_2 units

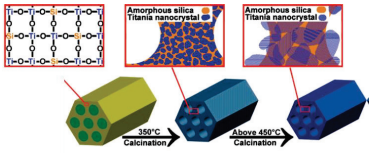


Stabilising nano-TiO_2 - mixed SiO_2-TiO_2 oxides

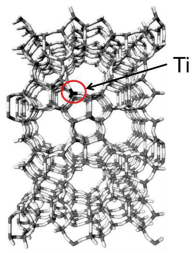
J|A|C|S ARTICLES
Published on Web 10/17/2007

Controllable and Repeatable Synthesis of Thermally Stable Anatase Nanocrystal−Silica Composites with Highly Ordered Hexagonal Mesostructures

Weiyang Dong,*† Yaojun Sun,§ Chul Wee Lee,|| Weiming Hua,‡ Xinchun Lu,§ Yifeng Shi,‡ Shicheng Zhang,‡ Jianmin Chen,† and Dongyuan Zhao*‡



Higher photocatalytic activity than commercial nano-TiO_2 catalyst Degussa-P25 for the degradation of rhodamine B.

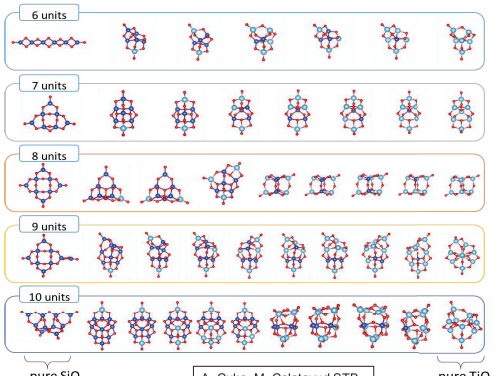


TS-1
$Ti_xSi_{1-x}O_2$ titanosilicate zeolitic material – MFI structure.

M. Taramasso, G Perego, B. Notari, U.S. Patent No. 4410501, 1983.

- TS-1 catalyzes reactions (e.g., propylene epoxidation) **– but is not photoactive**
- **Only low loading of Ti possible in the silica zeolite framework – max 10-15 wt% before phase segregation**

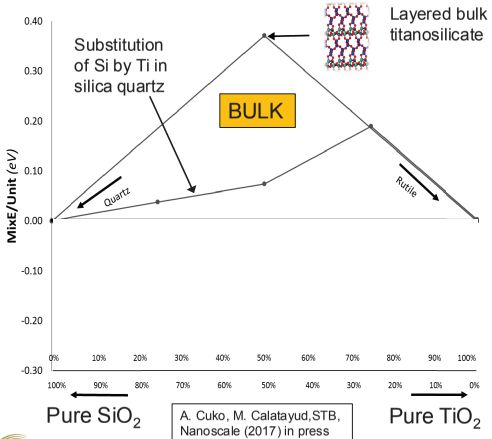
Increasing Ti content in SiO_2-TiO_2 composites without segregation - nanoclusters?



A. Cuko, M. Calatayud,STB, Nanoscale (2017) in press

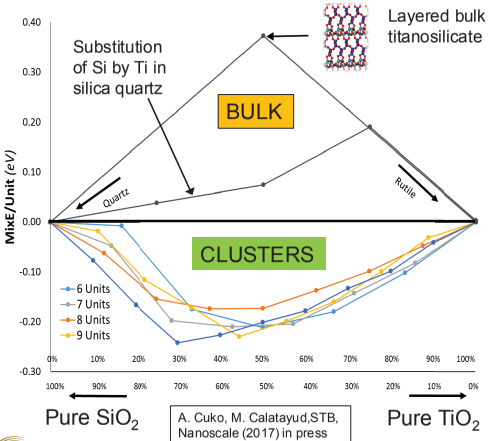
- Use global optimisation to search for stable mixed $(SiO_2)_m(TiO_2)_n$ clusters
- Lowest energy mixed oxide isomers often have new structures compared to pure end members
- Is segregation size dependent?

Mixing energy: gauging the tendency to segregate



A. Cuko, M. Calatayud,STB, Nanoscale (2017) in press

Mixing energy: gauging the tendency to segregate

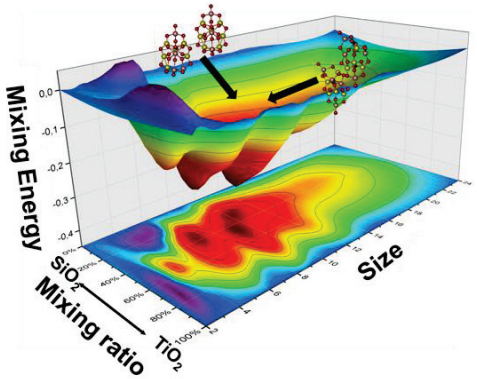


Bulk mixing of SiO_2 and TiO_2 not energetically favoured

Mixing of SiO_2 and TiO_2 in clusters energetically favoured

A. Cuko, M. Calatayud,STB, Nanoscale (2017) in press

Size-dependency of nano-SiO_2-TiO_2 mixing



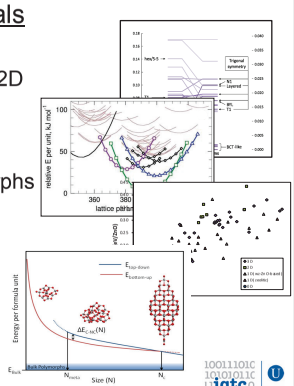
- Valley of stability for mixed $(SiO_2)_n(TiO_2)_m$ nanoclusters with n:m ratio close to 1:1
- Non-segregated mixing most energetically favourable for nanoclusters with 18-30 atoms
- Mixing energy becomes less negative with increasing size

A. Cuko, M. Calatayud,STB, Nanoscale (2017) in press

Summary

<u>Enumeration, data-mining and global optimisation together can provide reliable datasets for studying size-dependent transitions in materials</u>

- Relative stability of polymorphs very different in 2D nanofilms w.r.t. 3D bulk
- Numerous low density/nanoporous bulk polymorphs and nanofilms shown to be potentially viable
- Size at which bulk crystallinity emerges strongly dependent on the material



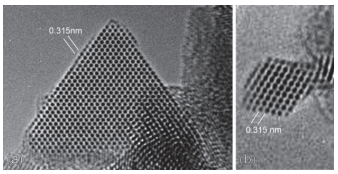
Acknowledgements

- Edwin Flikkema
- Oriol Lamiel
- Sergey Kozlov
- Ilker Demiroglu
- Andi Cuko
- Konstantin Neyman
- Francesc Illas

Structure of ceria nanoparticles

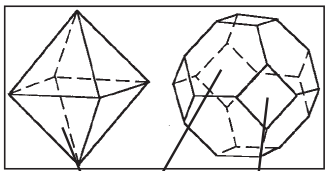
Some experimentally prepared nanoparticles are structurally characterized

- CaF_2–type fluorite structure of bulk CeO_2
- Exposed {111} and {100} facets
- Size Ø ≥ 2 nm
- Octahedral → Cuboctahedral



HRTEM: nanoparticle with (111) facets and a small (100) facet

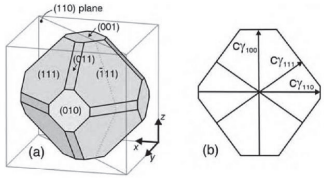
Chem. Mater. 20 (2008) 5460



Structure of small ceria nanoparticles?

- Same as for size Ø ≥ 2 nm as observed in experiment ?
- Assuming a CaF_2–type fluorite crystal structure, observed octahedral/cuboctahedral nanocrystallite shapes can be rationlised using the Wulff construction:

The length of a vector drawn normal to a crystal face is proportional to its surface energy. Each vector is the "height" of the corresponding face, and is drawn from the center of the crystal to the face.



Using atomistic modelling we can test if this top-down construction also holds for ceria nanoparticles with size Ø < 2 nm

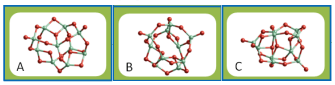
Searching for stable oxide nanocluster structures from the bottom-up…

Global Optimisation:

- Aim: to efficiently search the massive and complex space of structural possibilities for the most stable atomic configurations
- Many methods (e.g. Evolutionary algorithms, Basin Hopping, Particle Swarm)
- Current limits: using DFT max. ~30-40 atoms, using classical potentials max. ~1000 atoms.

BUT, very system dependent:

Many $(CeO_2)_N$ ground states known up to ~300 atoms BUT still debating ground state structure of $Ti_{10}O_{20}$!

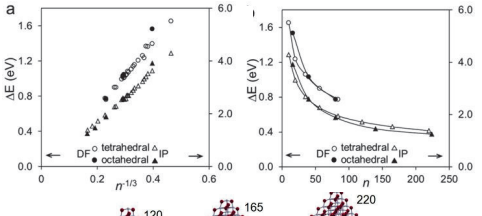


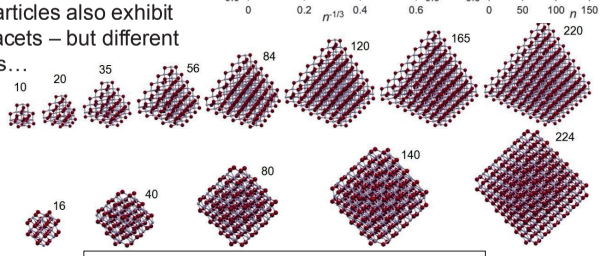
"Nanoclusters and Nucleation" PCCP *Perspective* 12, 786 (2010)

"Approaching Nanoscale Oxides: Models and Theoretical Methods" *Chem.Soc. Rev.* 9, *2657* (2009).

$(CeO_2)_N$ Tetrahedral to (Cubo)Octahedral crossover

- At smaller ceria nanoparticle sizes tetrahedral morphologies are more stable
- Like octahedral nanoparticles also exhibit {111} facets – but different vertices…

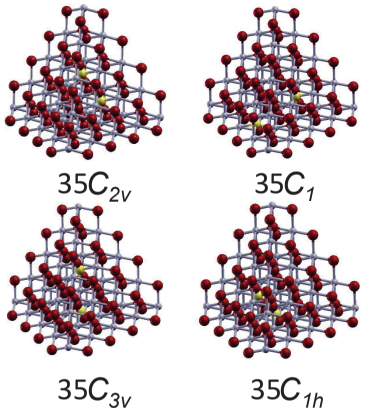




A. Migasni, K. Neyman and STB, Chem Commun. 48, 4199 (2012).

Tetrahedral nanoparticles with gaps in the oxygen sub-lattice

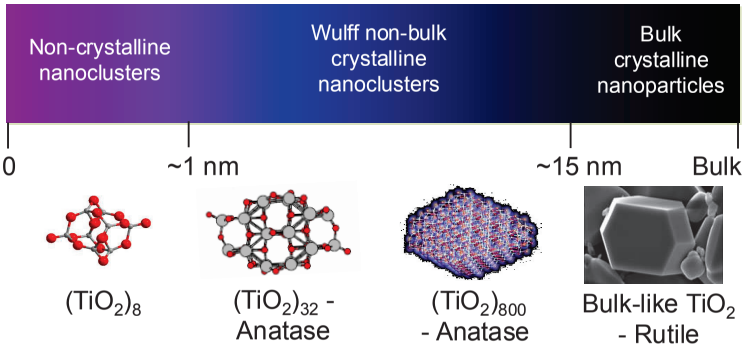
- In order to maintain CeO_2 stoichiometry in a tetrahedral bulk cut need to remove oxygen atoms
- Found that oxygen sub-lattice gaps preferred within the nanoparticle core.
- Distinct internal atomic structure and nanomorphology could yield new properties.



A. Migasni, K. Neyman and STB, Chem Commun. 48, 4199 (2012).

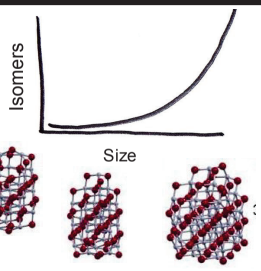
Structural size dependence

Less Ionic 1:2 oxide: TiO_2



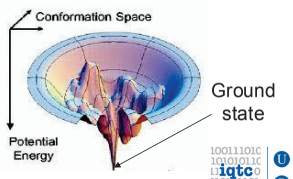
Obtaining the structure of low energy nanoclusters:

- Exponential growth of the number of energetically reasonable cluster Isomers with increasing size



- Even for small clusters (e.g. ~40 atoms) there are an "astronomical" number of possible structural isomers.
- Want to find most stable structures but space of structure and energy is extremely complex

Global Optimisation



Global optimisation of $(SiO_2)_N$ clusters

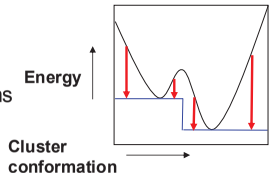
1.) interatomic potential specifically parameterised for nano-SiO_2 (also including long-range electrostatics).

$$V_{ab}^{Buck} = A_{ab}\exp(\frac{-r}{B_{ab}}) - \frac{C_{ab}}{r^6}$$

a, b ∈ {Si, O}

E. Flikkema S. T. Bromley, Chem. Phys. Lett. **378**, (2003) 36.

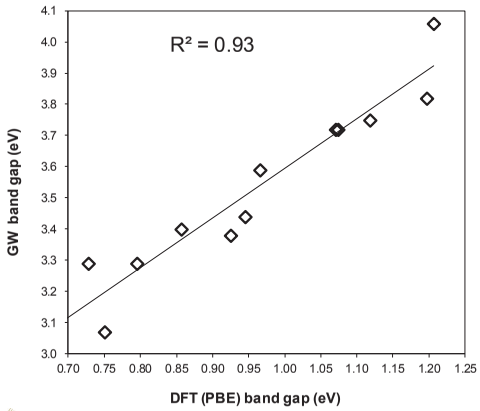
2.) Use "Basin Hopping" global optimisation to search through **100000s** of structural configurations for low energy cluster isomers



- Combines Monte Carlo with regular energy minimisations.
- Potential energy surface is transformed into a step-wise surface.
- Local energy barriers are eliminated.

3.) Energy minimise best candidates using Density Functional Theory

Band gaps: DFT versus GW



- Many body GW and DFT results show same tendency

GW calculations:

- Initial eigenvalues and eigenvectors generated with a PBE pre-run.
- GW scheme, as implemented in VASP 5.2

I. Demiroglu, S Tosoni, F. Illas, STB, Nanoscale, 6, 1181, 2014.

ICREA Stefan T. Bromley , Computational Modeling of Materials School, Sofia, Bulgaria 2017