# Striking many-body effects in a simple ($B_2O_3$) oxide

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***1ère réunion générale du GDR NBODY***

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PHYSICAL REVIEW MATERIALS 3, 063603 (2019)

## van der Waals forces stabilize low-energy polymorphism in $B_2O_3$: Implications for the crystallization anomaly

Guillaume Ferlat,[1] Maria Hellgren,[1] François-Xavier Coudert,[2] Henri Hay,[1] Francesco Mauri,[1,3] and Michele Casula[1]
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(Received 13 December 2018; published 10 June 2019)

## Many-body effects at the origin of structural transitions in $B_2O_3$

Cite as: J. Chem. Phys. 151, 224508 (2019); doi: 10.1063/1.5131763
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nature materials

LETTERS

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PHYSICAL REVIEW B 92, 144111 (2015)

## Dispersion effects in $SiO_2$ polymorphs: An *ab initio* study

Henri Hay,[1,*] Guillaume Ferlat,[1] Michele Casula,[1] Ari Paavo Seitsonen,[1,2,3] and Francesco Mauri[1]

[1]*Institut de Minéralogie, Physique des Matériaux et Cosmochimie, Sorbonne Universités - UPMC Univ Paris 06, UMR CNRS 7590, 4 Place Jussieu, F-75005 Paris, France*

[2]*Institut für Chimie, Universität Zurich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland*

[3]*École Normale Supérieure, Paris Sciences et Lettres (PSL) Research University, Département de Chimie, Sorbonne Universités, Université Pierre et Marie Curie (UPMC), Université Paris 06, CNRS UMR 8640 Pasteur, F-75005 Paris, France*

(Received 22 July 2015; revised manuscript received 5 October 2015; published 30 October 2015)

PHYSICAL REVIEW MAT

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## Implications for the crystallization anomaly

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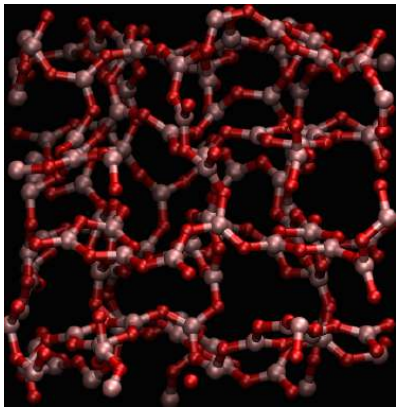
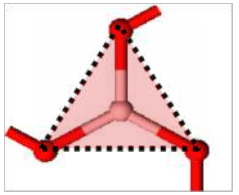
# $B_2O_3$ (and borates): Motivations

- Major component of industrial glasses (ceramics, biomaterials, optical fibers, waste storage matrix, …)
- A prototypical **network-forming** system based on **trigonal units**



(simulated) glass configuration



basic building block ($BO_3$)

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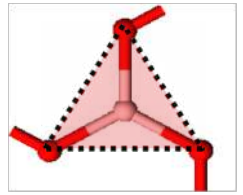
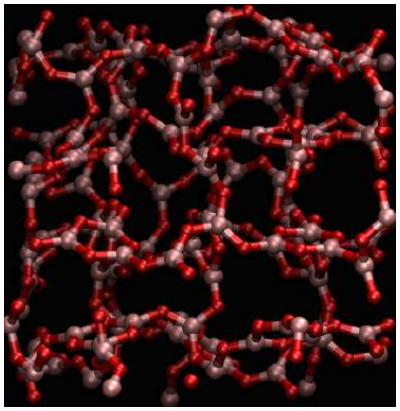


basic building block ($BO_3$)



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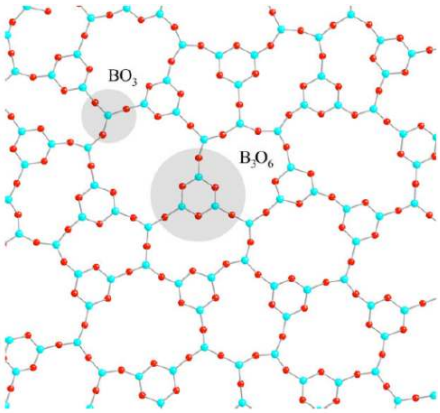
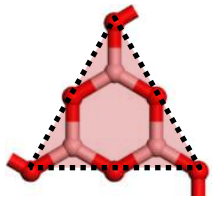



2D schematic representation of the glass structure (from A.C. Hannon)

- A glass with significant **medium-range** order (**superstructural units**)

  *G. Ferlat et al., Phys. Rev. Lett., **101**, 065504 (2008)*



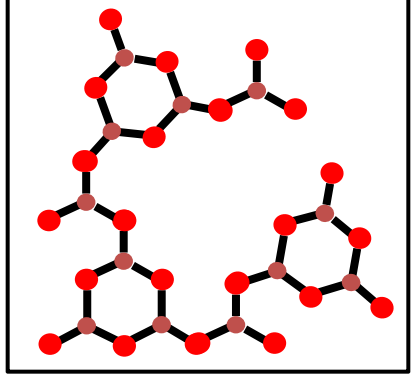
boroxol ring

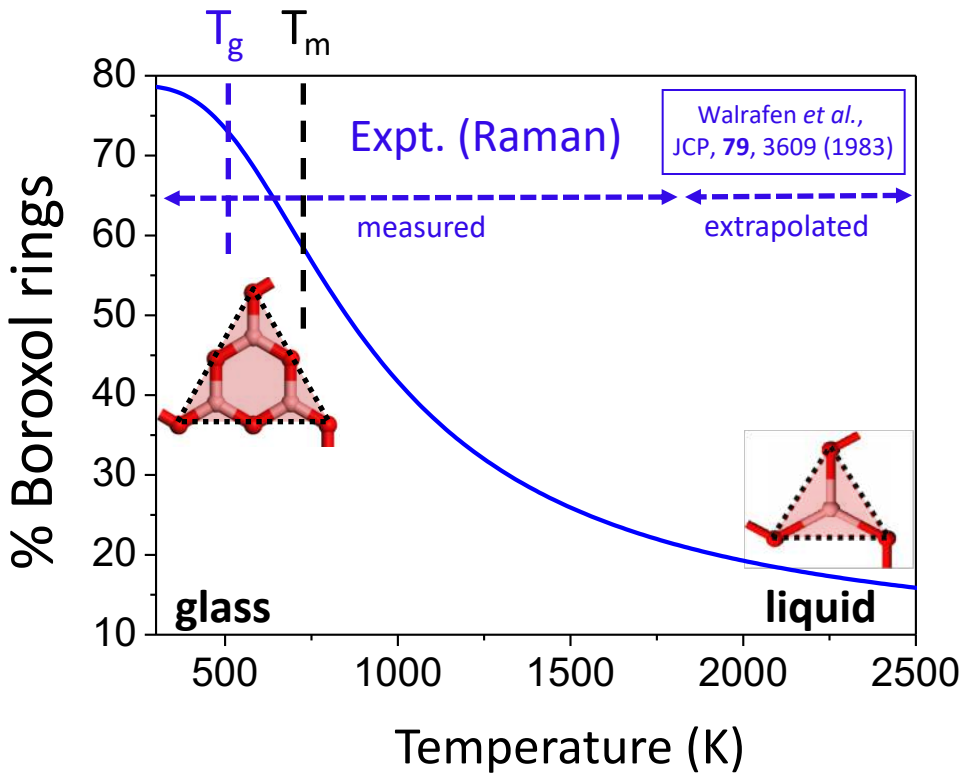
- The **glass former** *par excellence* (abnormal reluctance to crystallisation)

# Experimental facts

Glass

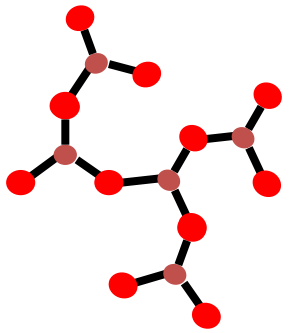
boroxol-dominated network






Liquid

triangle-dominated network



✓ Marked **structural transformation** (for 500 < T < 1500 K)

[Existence of a boroxol ring stabilisation energy: $\Delta E \approx -6$ *kcal/mol* ]

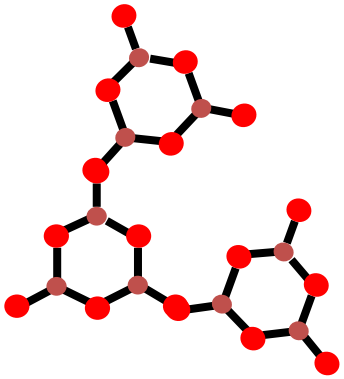
**What is the driving force ? …**

# Experimental facts

Why is the glass so (structurally) different from the known crystal?

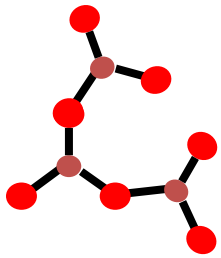
**$B_2O_3$ anomaly n°1**: the glass has a very different medium-range structure, dominated by **boroxol** rings

In the glass:



✓ **Large amounts** (~70%) of boroxol rings

In the crystal:

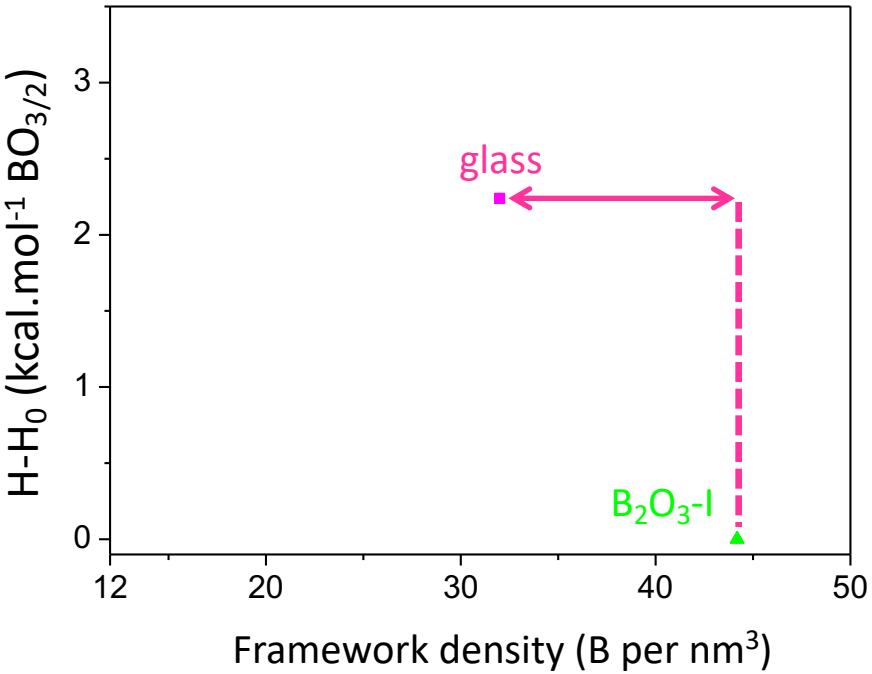


✓ **NO** boroxols at all in $B_2O_3$-I

**$B_2O_3$ anomaly n°2**: the glass has a **low density** (1.84 $g.cm^{-3}$) compared to the known crystal ($B_2O_3$-I: 2.55 $g.cm^{-3}$)

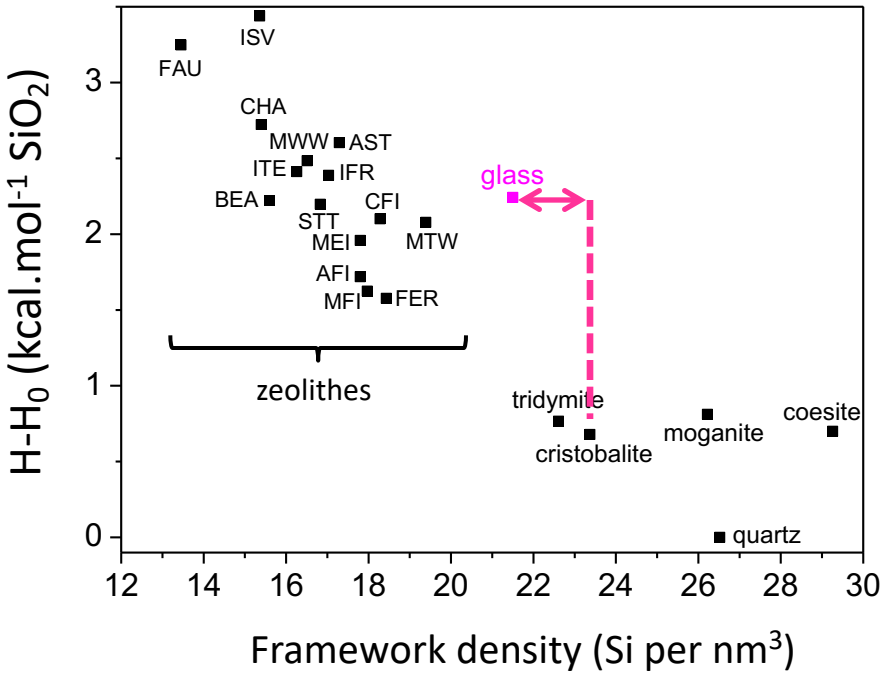
# Experimental facts

## $B_2O_3$




$\rho_{glass} \sim 0.71\ \rho_{crystal}$

## $SiO_2$



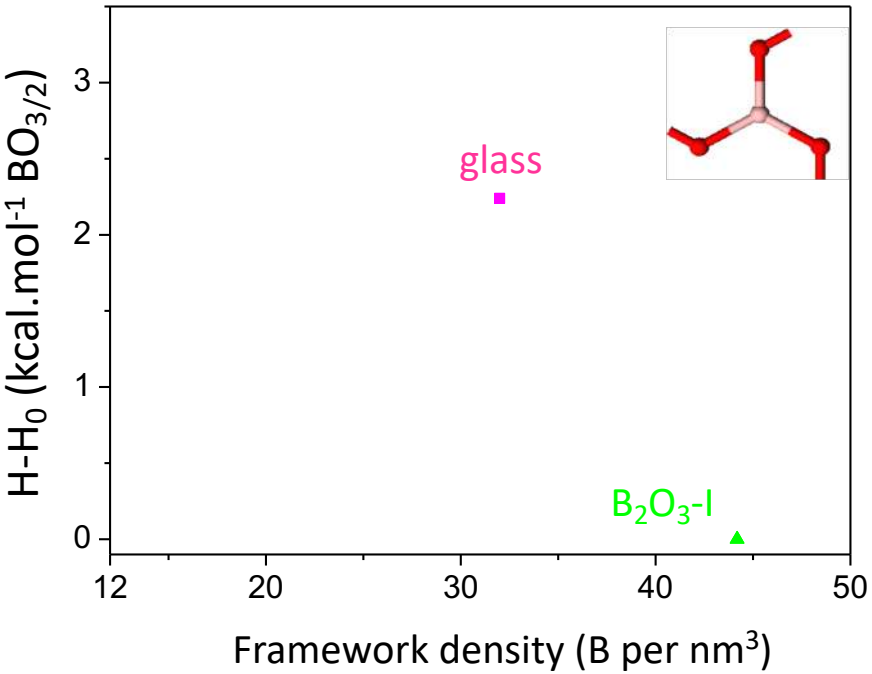

$\rho_{glass} \sim 0.95\ \rho_{tridymite}$

$\rho_{glass} \sim 0.92\ \rho_{cristobalite}$

**$B_2O_3$ anomaly n°2**: the glass has a low density compared to the known crystal

# Experimental facts

## $B_2O_3$

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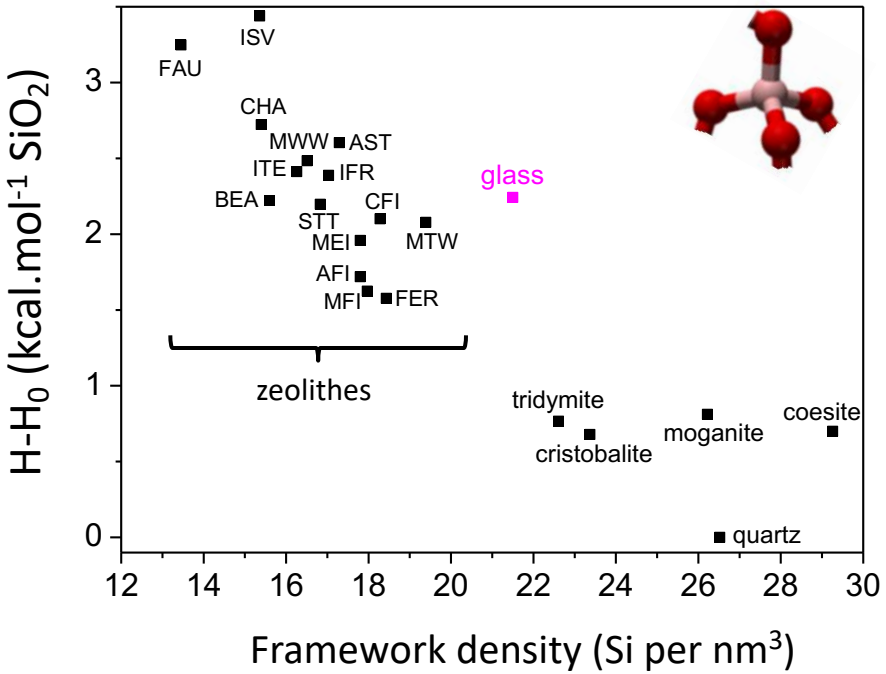
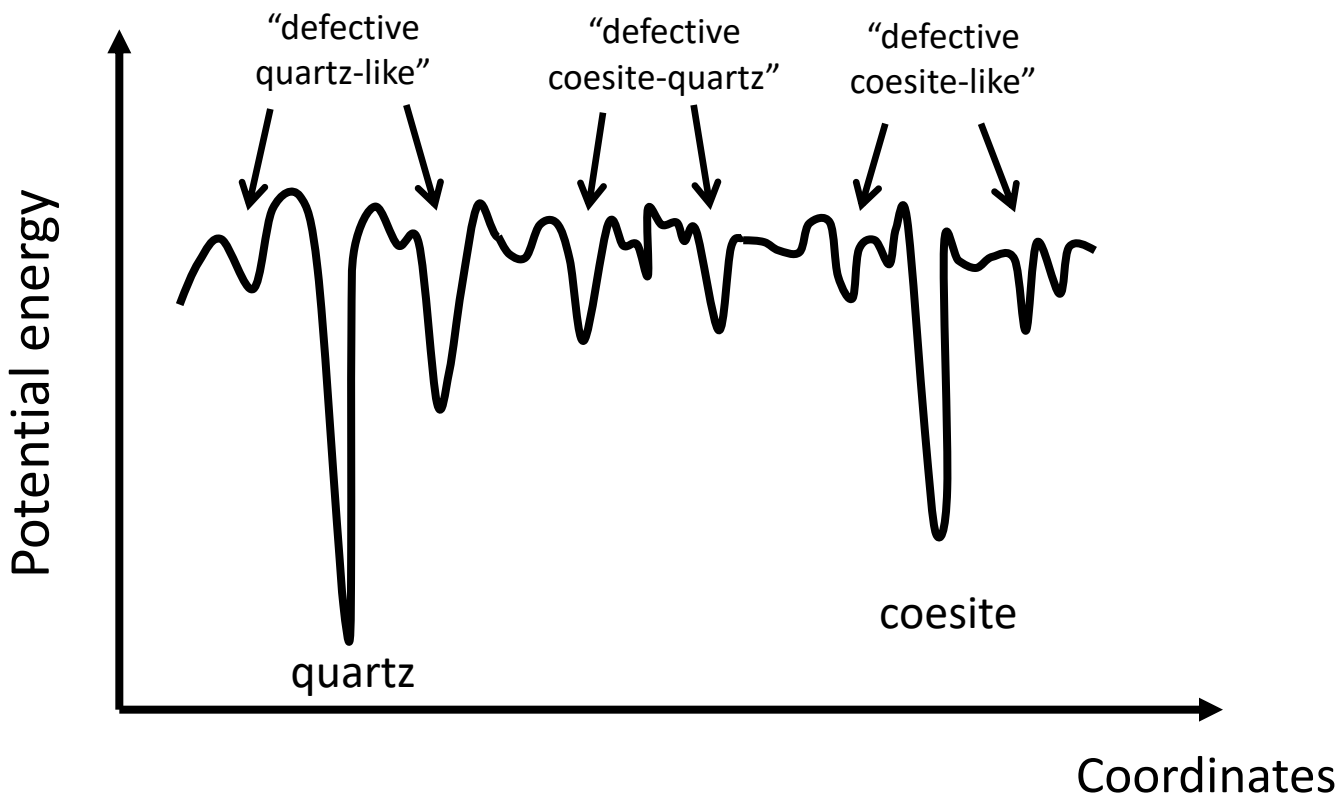



✓ $B_2O_3$ : - poor polymorphism
- (very) good glass former

✓ $SiO_2$ : - rich polymorphism
- good glass former

**$B_2O_3$ anomaly n°3**: Poor polymorphism (despite very high aptitude to vitrify)

# Polymorphism and ease of vitrification

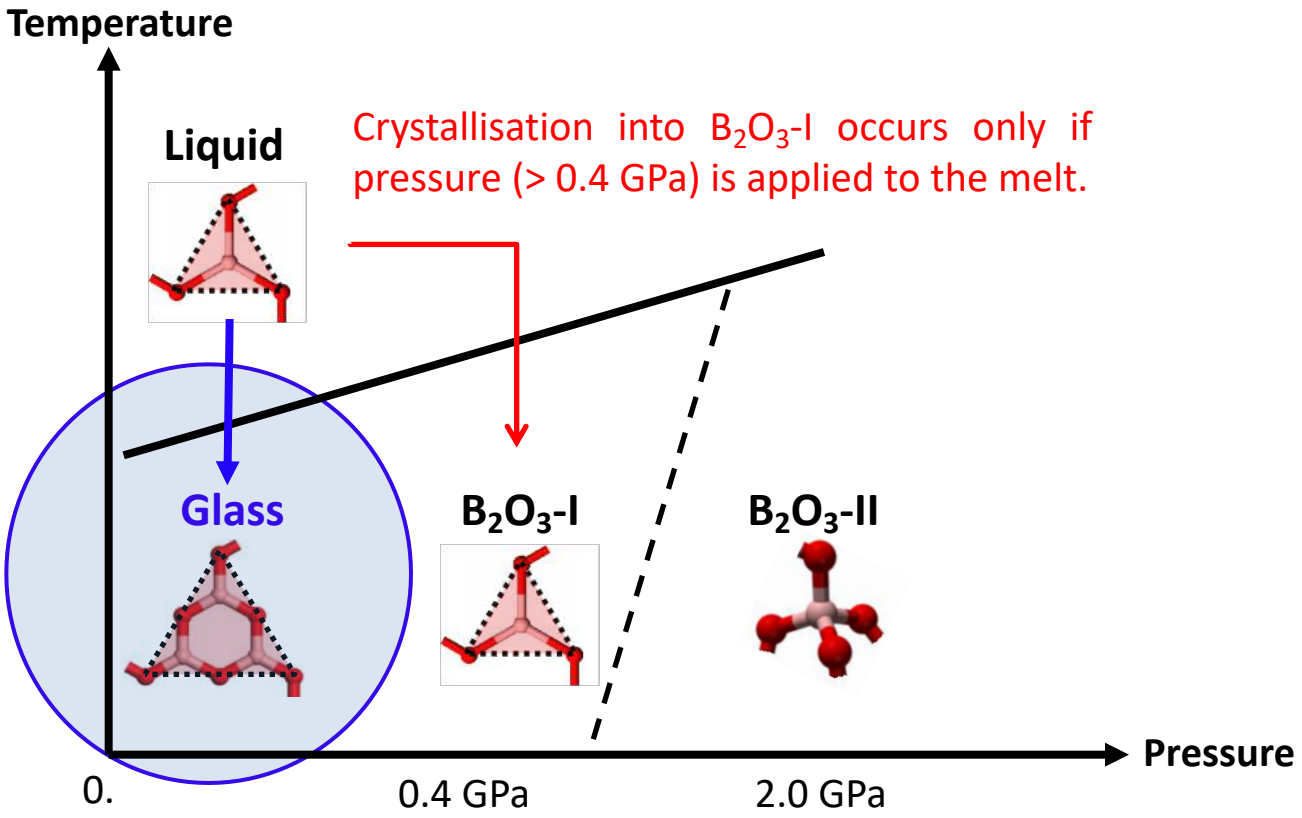



Rich (low-energy) polymorphism (many competing crystals)
→ *rugged* energy landscape → favours amorphisation

See *e.g.* Goodman, Nature (1975), Wang & Merz, Nature (1976), Perrin *et al.* Nature Comm. (2016), …

# Experimental facts

**Anomaly n°4:** The crystallisation of $B_2O_3$-I from the melt at ambient pressure has never been observed (even if seeded with crystals).
No crystal growth (of $B_2O_3$-I) at any imposed cooling rate unless pressure is applied (***crystallisation anomaly***).



# The $B_2O_3$ anomalies: summary

## Why is the glass so (structurally) different from the known crystal?

**anomaly n°1**: glass has a very different medium-range structure (boroxol rings)

**anomaly n°2**: glass has a low density (-30 %) compared to the known crystal

## Why does $B_2O_3$ vitrify so easily and never crystallise from the melt?

**anomaly n°3:** poor polymorphism (despite very high aptitude to vitrify)

**anomaly n°4**: crystallisation from the melt at ambient pressure never observed unless pressure is applied (***crystallisation anomaly***).

→ The origin of these anomalies is to be found in the existence of yet ***unknown*** polymorphs

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**Hidden polymorphs drive vitrification in $B_2O_3$**

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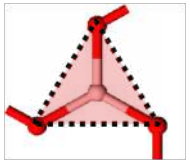
# Systematic construction of polymorphs

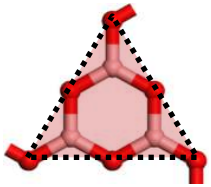
## ⇨ Using decoration of topological networks

✓ Relevant **building units** (for ambient polymorphs):

[Constraints to be fulfilled: every boron is three-fold coordinated
every oxygen is two-fold coordinated]



$BO_3$ triangle



$B_3O_6$ super-triangle

N.B.: the boroxol units are **self-similar** to the $BO_3$ units.

# Systematic construction of polymorphs

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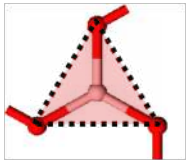

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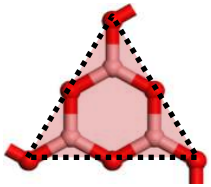

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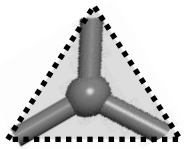
✓ Use of topological databases of **three-fold coordinated networks**

Winkler *et al*. (CPL, 2001): from **graph theory**, prediction of all possible **three-coordinated 3D** frameworks with up to 6 atoms in the primitive cell: **12 networks** (originally applied to $sp^2$-carbon structures)

**+ 2D** network of graphite**: 13 networks**



✓ **Decoration** of the networks vertices by the relevant **building units:**

# Systematic construction of polymorphs

## ➡ Using decoration of topological networks

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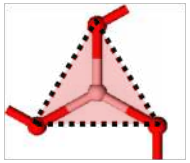

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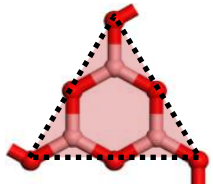

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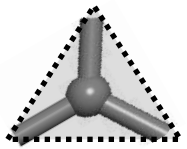

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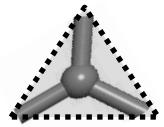
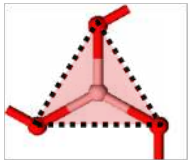
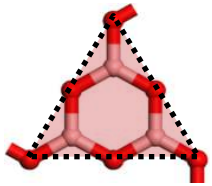


**13 networks**



**T1 to T13**



**T1-*b* to T13-*b***

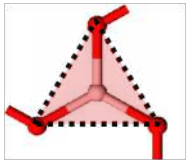
2*13 -1 = **25 new $B_2O_3$ crystals**
(with 10 to 135 atoms per unit cell)

N.B.: T13 is the known $B_2O_3$-I crystal

# Systematic construction of polymorphs

## ➡ Using decoration of topological networks

✓ Relevant **building units** (for ambient polymorphs):



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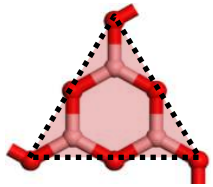

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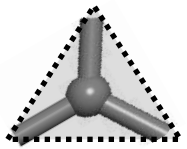
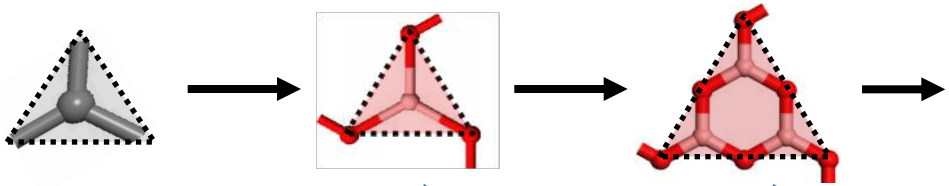


✓ **Decoration** of the networks vertices by the relevant **building units:**



**13 networks**

**T1 to T13**

**T1-*b* to T13-*b***

**$B_2O_3$-I**

**$B_2O_3$-I-*b***

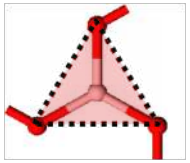
2*13 -1 = **25 new $B_2O_3$ crystals**
(with 10 to 135 atoms per unit cell)

N.B.: T13 is the known $B_2O_3$-I crystal
T8 and T10: some nodes belong to 3-fold rings

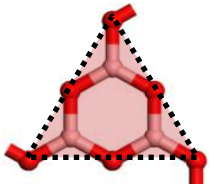
# Systematic construction of polymorphs

## ➡ Using decoration of topological networks

✓ Relevant **building units** (for ambient polymorphs):



$BO_3$ triangle

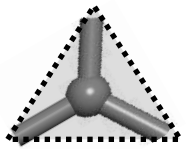


$B_3O_6$ super-triangle

✓ Use of topological databases of **three-fold coordinated networks**

Winkler *et al*. (CPL, 2001): from **graph theory**, prediction of all possible **three-coordinated 3D** frameworks with up to 6 atoms in the primitive cell: **12 networks** (originally applied to $sp^2$-carbon structures)

**+ 2D** network of graphite**: 13 networks**



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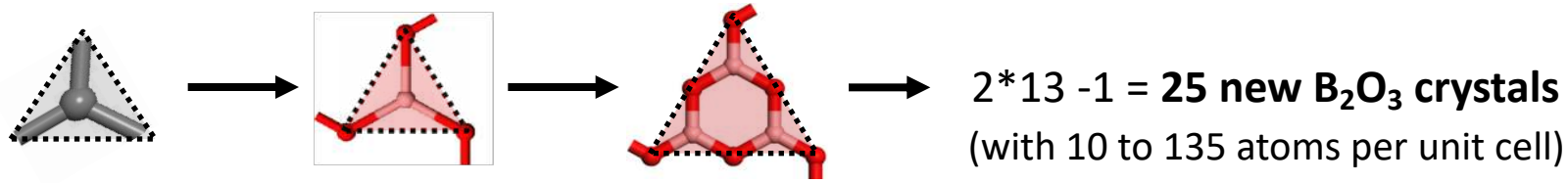
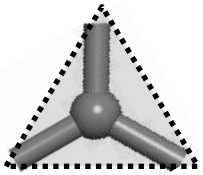


**13 networks** **T1 to T13** **T1-*b* to T13-*b***

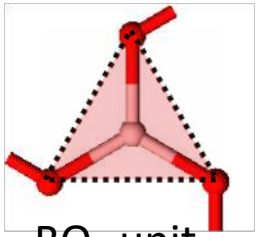
2*13 -1 = **25 new $B_2O_3$ crystals**
(with 10 to 135 atoms per unit cell)

✓ **Relaxation** (positions and unit cell) of the structures by ***first-principles*** calculations within Density Functional Theory (GGA-PBE, ultra-soft pseudos, PW basis, CASTEP code)

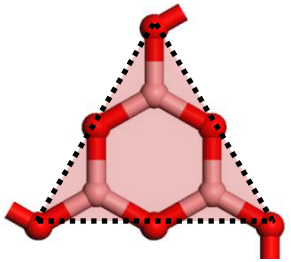
# Exploiting isomorphism: graphite-like



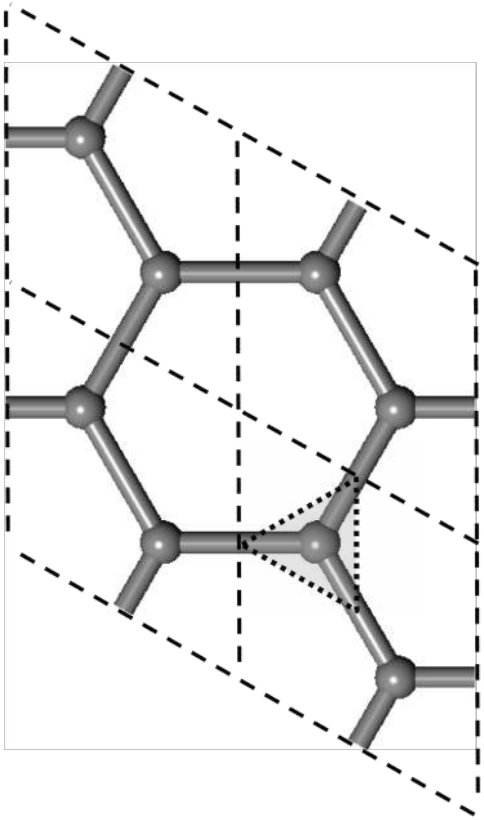
3-coordinated vertex



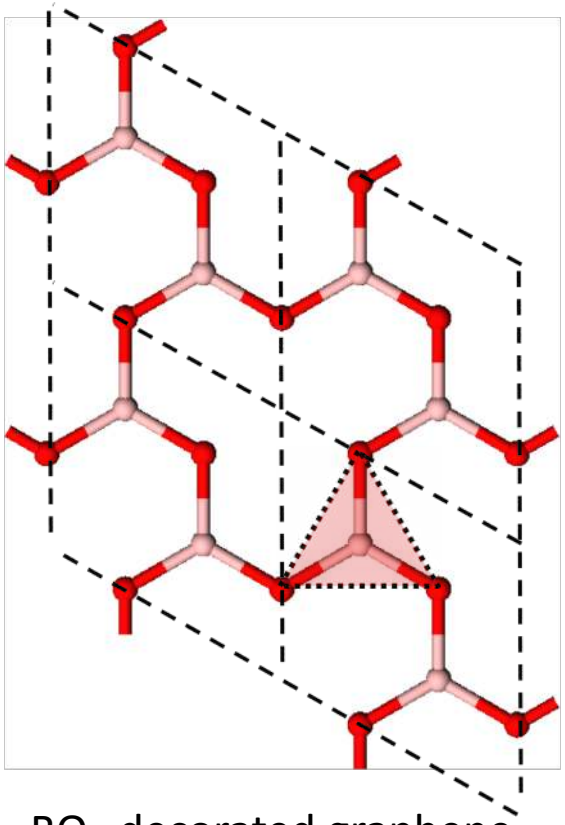
$BO_3$ unit



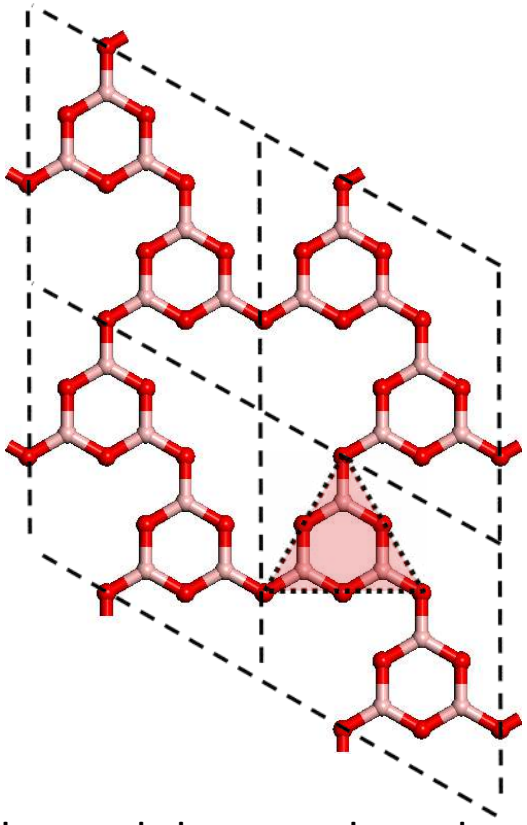
Boroxol ring



*sp*$^2$-carbon graphene

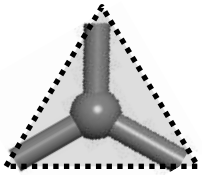


$BO_3$-decorated graphene

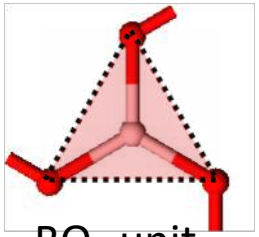


boroxol-decorated graphene

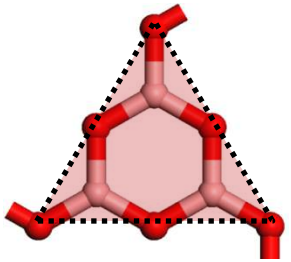
# Exploiting isomorphism: graphite-like



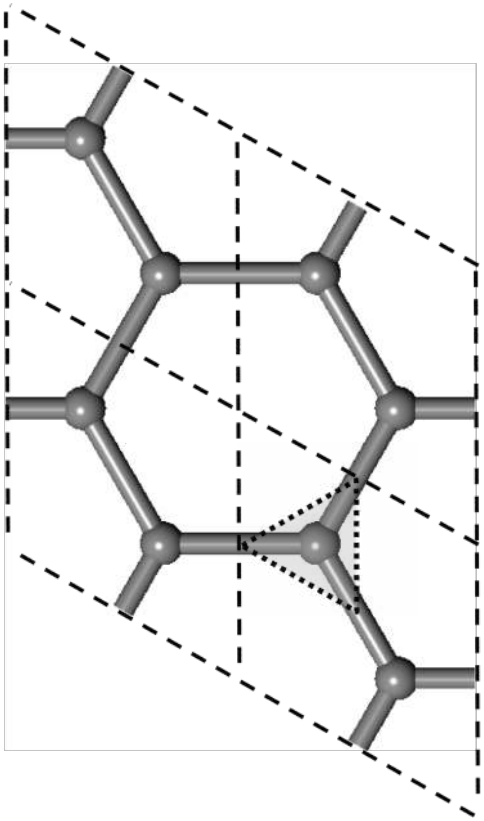
3-coordinated vertex



$BO_3$ unit

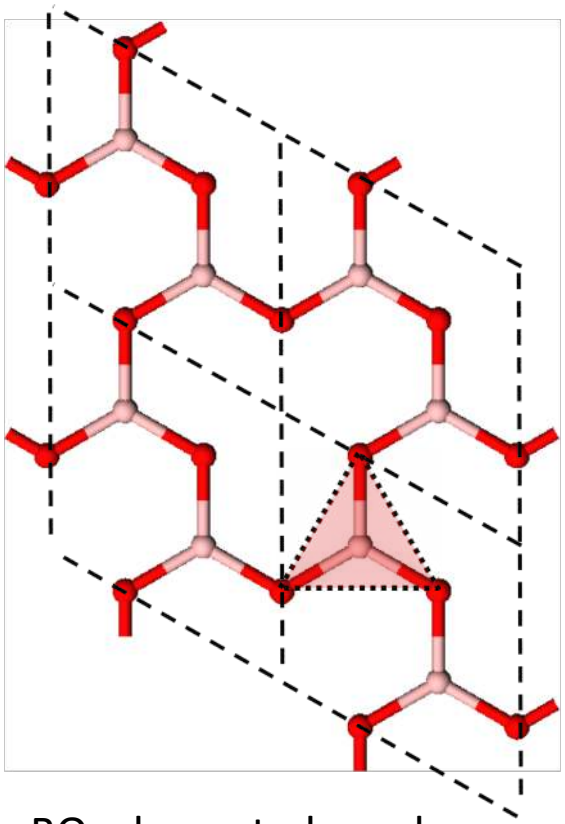


Boroxol ring



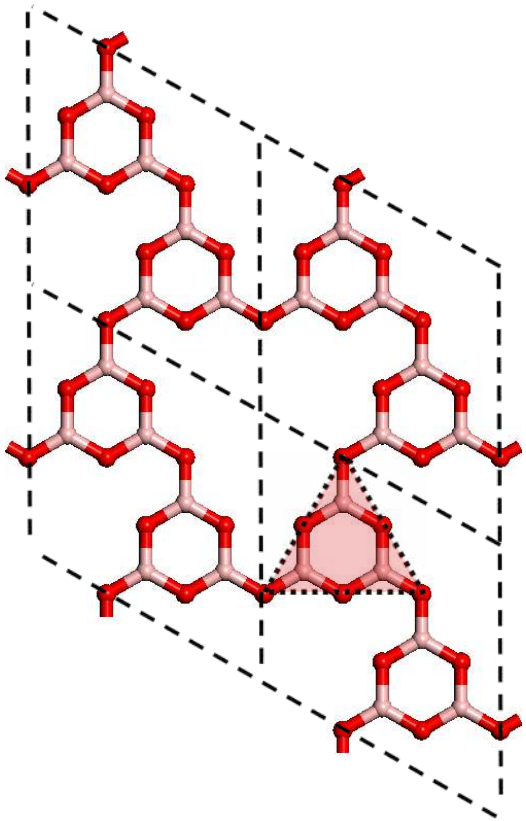
$sp^2$-carbon graphene

**graphite**



$BO_3$-decorated graphene

**T0**

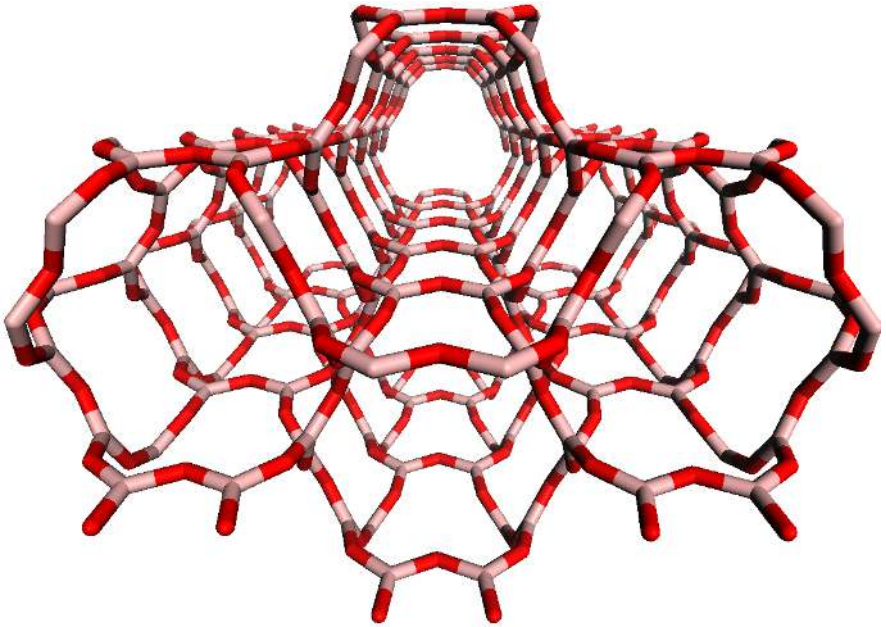


boroxol-decorated graphene

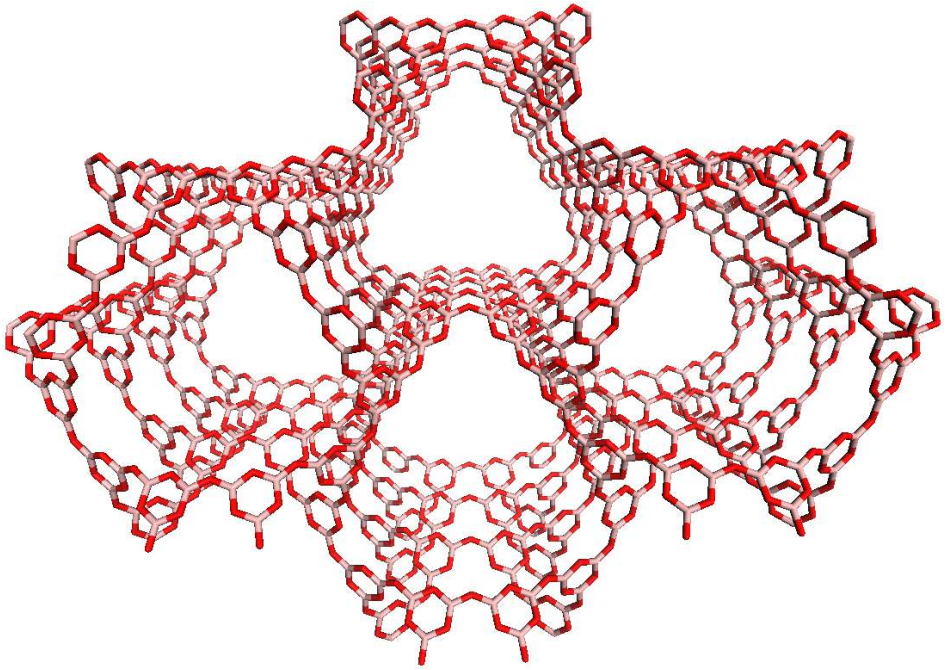
**T0-*b***

# New $B_2O_3$ polymorphs

G. Ferlat *et al.,* Nature Materials (2012)



($BO_3$-decorated) T7



(boroxol-decorated) T7-*b*

✓ Some crystals show *cage*- or *channel-like* structures

**Light**, **crystalline** and **porous**: possible applications as *e.g.* molecular sieves, hydrogen storage matrices, ... ?

✓ Negative linear compressibility, auxeticity (negative poisson ratio) …

# New $B_2O_3$ polymorphs

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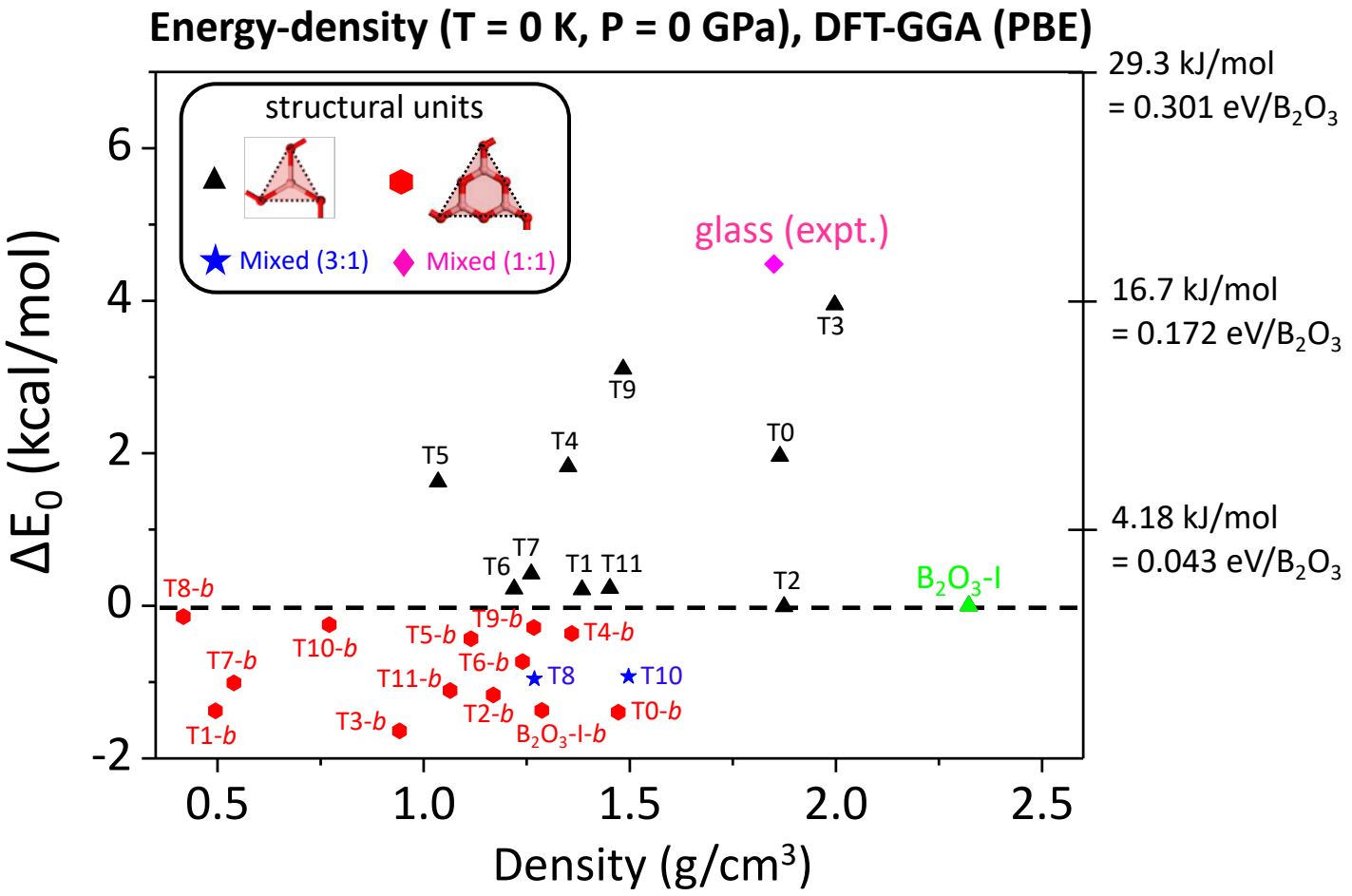


✓ Many low-energy crystals (lower than the glass, close to that of $B_2O_3$-I)

Are these predictions experimentally realisable? Is $B_2O_3$-I the true ground state ?

# New $B_2O_3$ polymorphs

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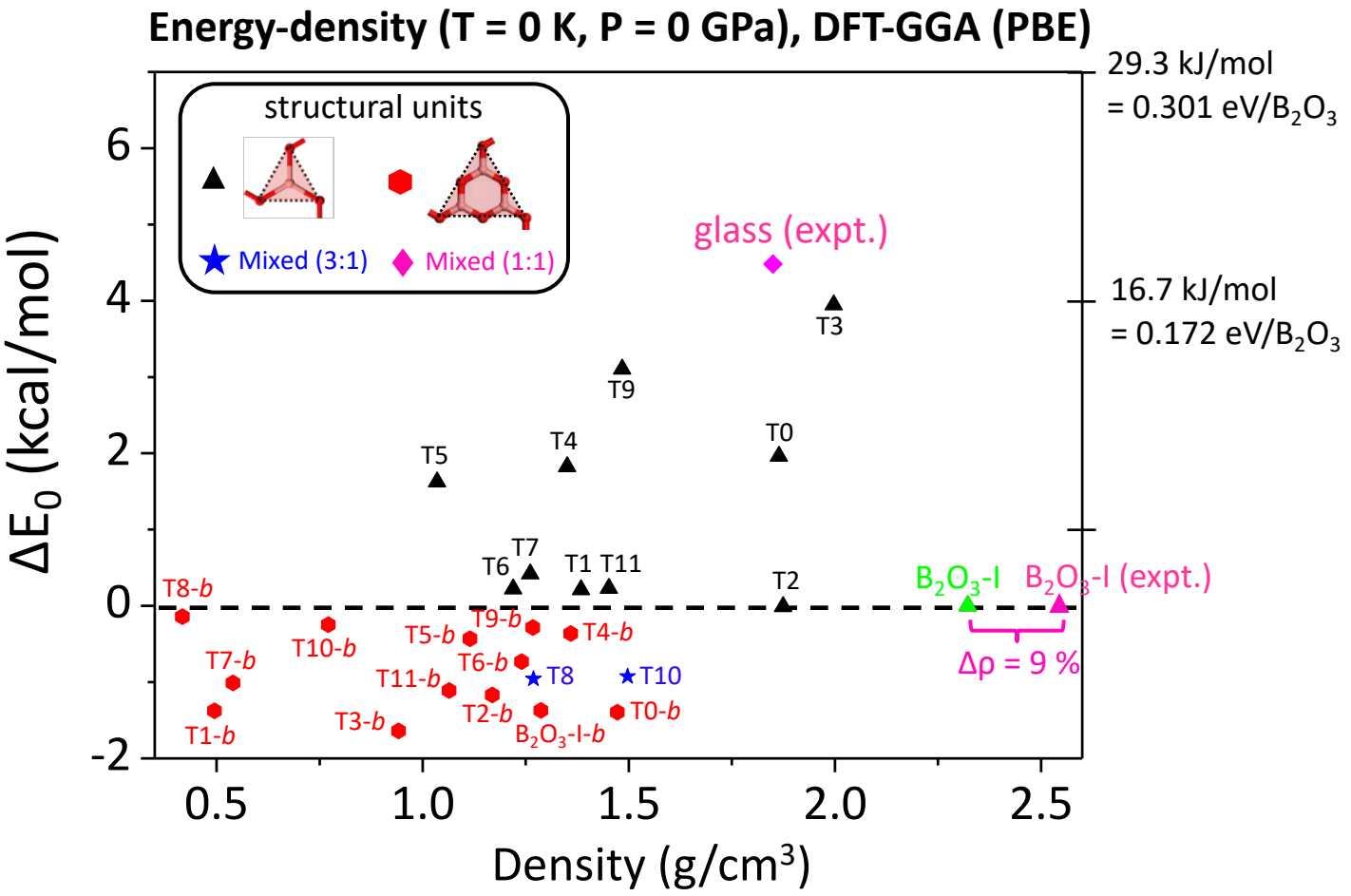
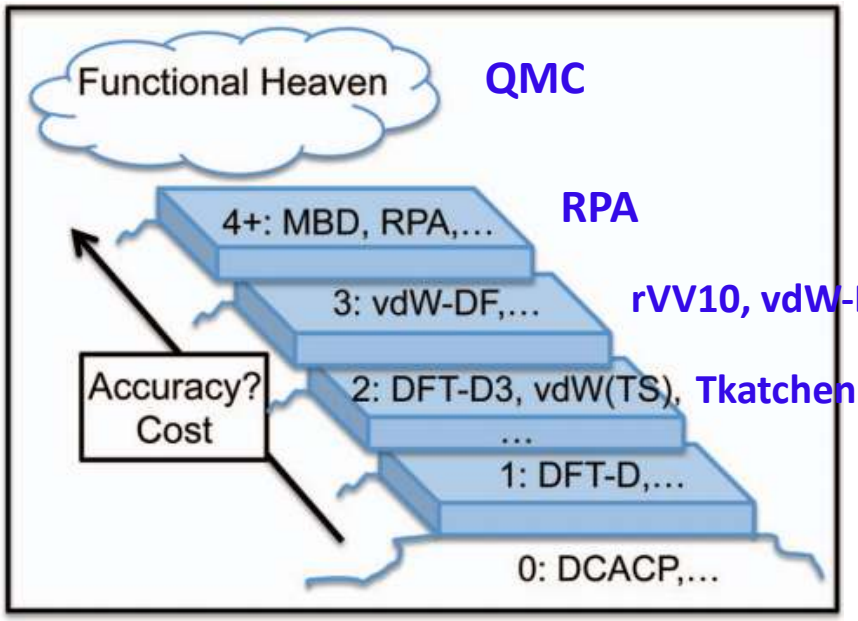



✓ Many low-energy crystals (lower than the glass, close to that of $B_2O_3$-I)

Are these predictions experimentally realisable? Is $B_2O_3$-I the true ground state ?
How robust are these predictions (DFT-GGA errors)?

# New $B_2O_3$ polymorphs: vdW and many-body contributions

- Assessing the van der Waals contributions (using DFT-vdW schemes)
- Beyond DFT: RPA (*collab. M. Hellgren*), Quantum Monte-Carlo *(M. Casula)*




**Classification of DFT-based dispersion correction schemes.**
**From Klimeš & Michaelides, J. Chem. Phys. (2012)**
step 0: no account of long range asymptotics;
step 1: simple $C_6$ correction;
step 2: environment-dependent $C_6$ corrections;
step 3: long range density functionals.
Above: beyond pairwise additive determinations.

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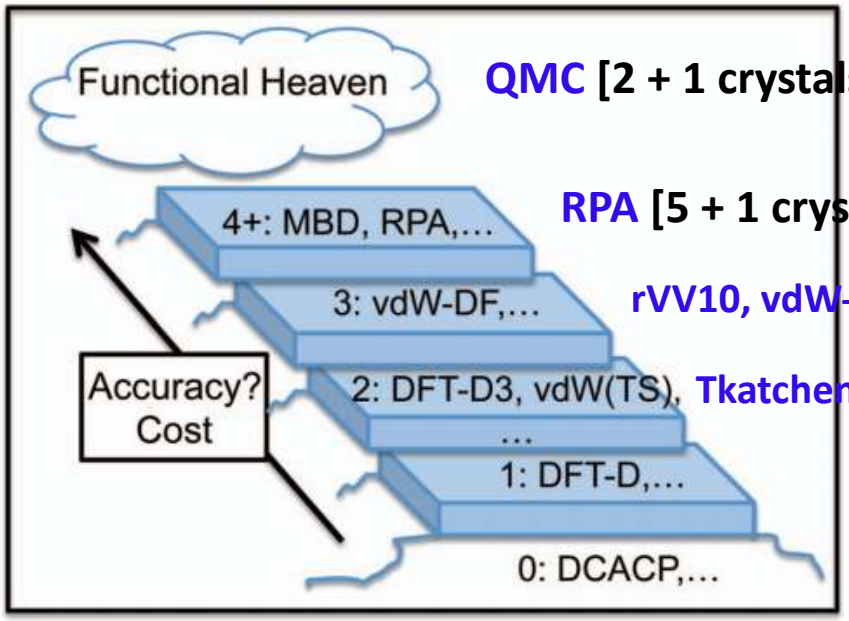


**QMC [2 + 1 crystals]**

**RPA [5 + 1 crystals]**

**rVV10, vdW-DF2 (2010)**

**Tkatchenko-Scheffler (2009): PBE + TS**

**Grimme D2 (2006): PBE + D2**

**[all 26 crystals]**

**Classification of DFT-based dispersion correction schemes.**
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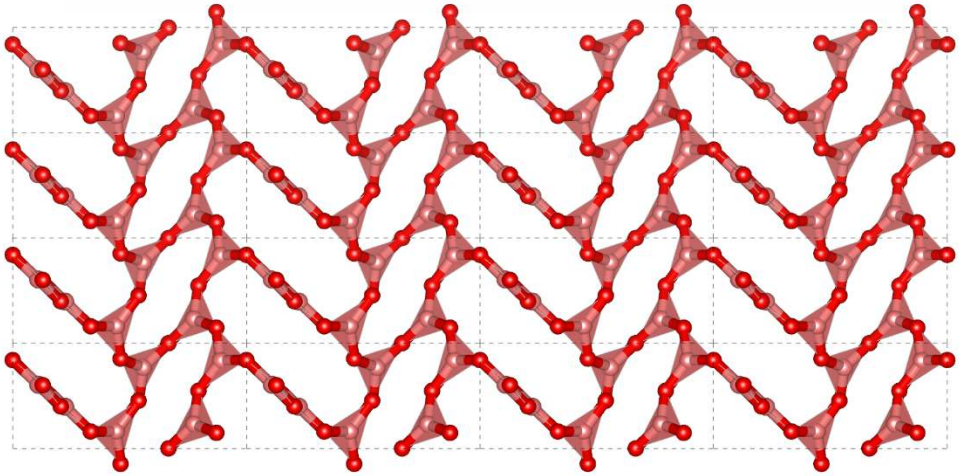
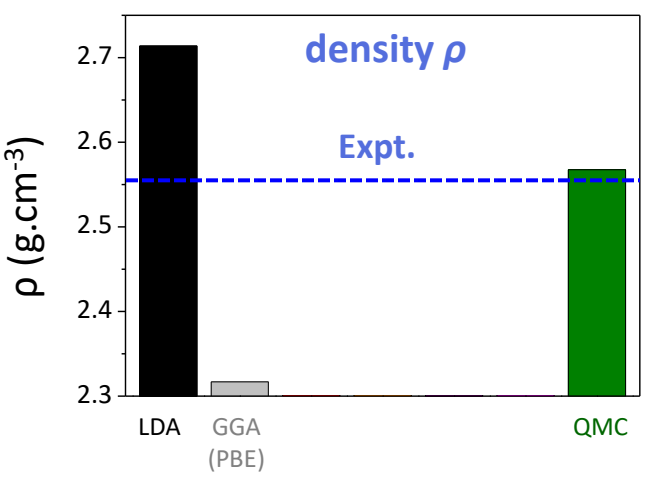
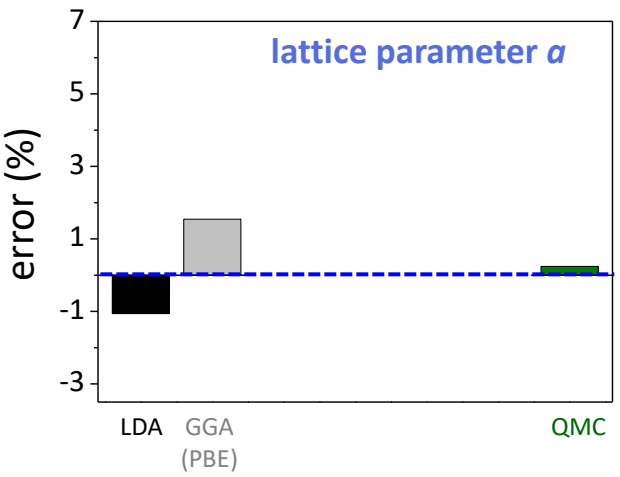
step 0: no account of long range asymptotics;
step 1: simple $C_6$ correction;
step 2: environment-dependent $C_6$ corrections;
step 3: long range density functionals.
Above: beyond pairwise additive determinations.

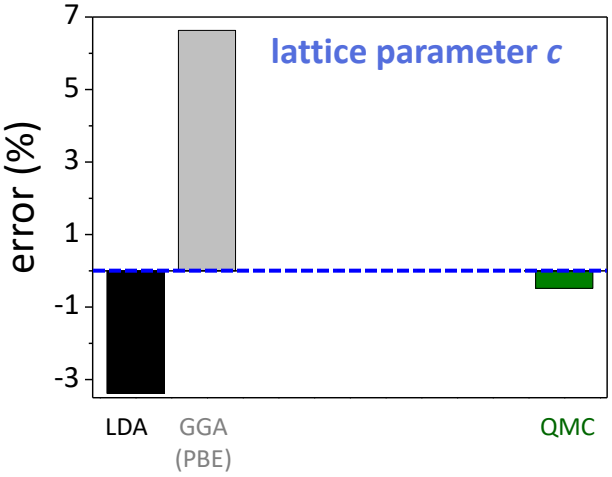
# Benchmarking DFT: structure

**$B_2O_3$-I**
**(known polymorph)**





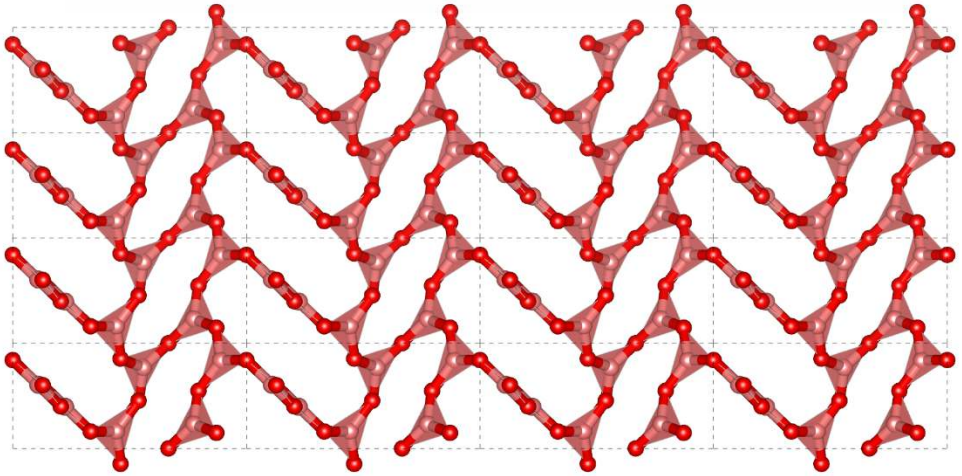



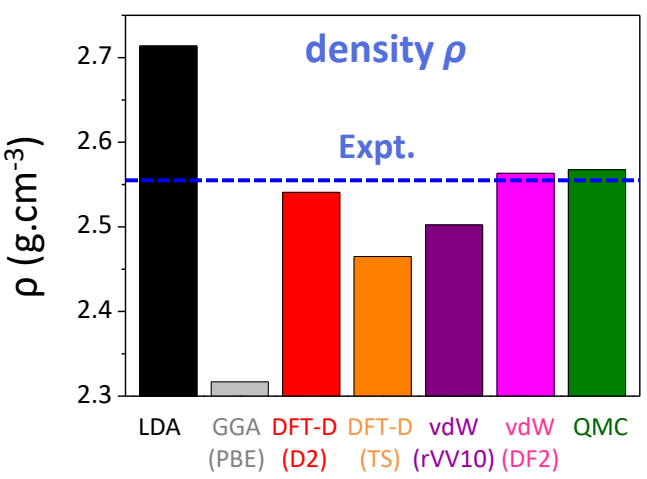



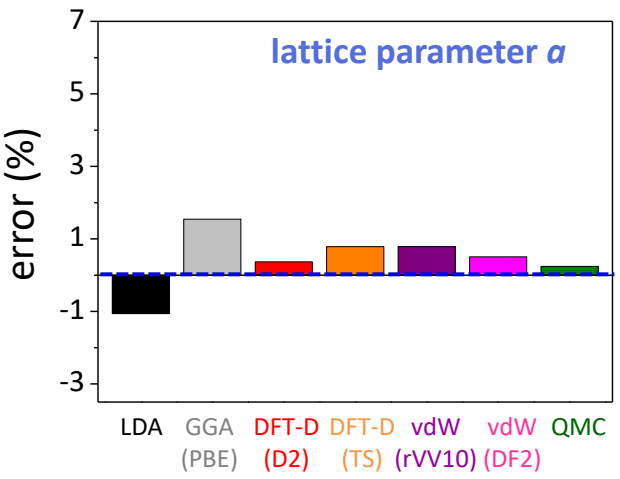

- ✓ PBE: very significant underbinding (and overbinding with LDA)
- ✓ very anisotropic variation (there is a “soft” direction)

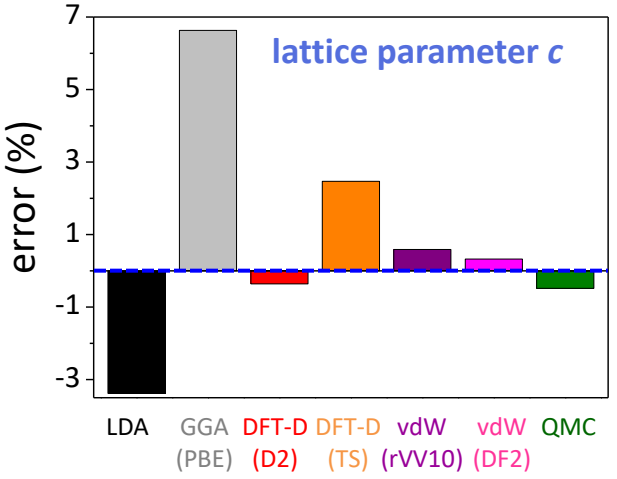
# Benchmarking DFT: structure

**$B_2O_3$-I**
**(known polymorph)**





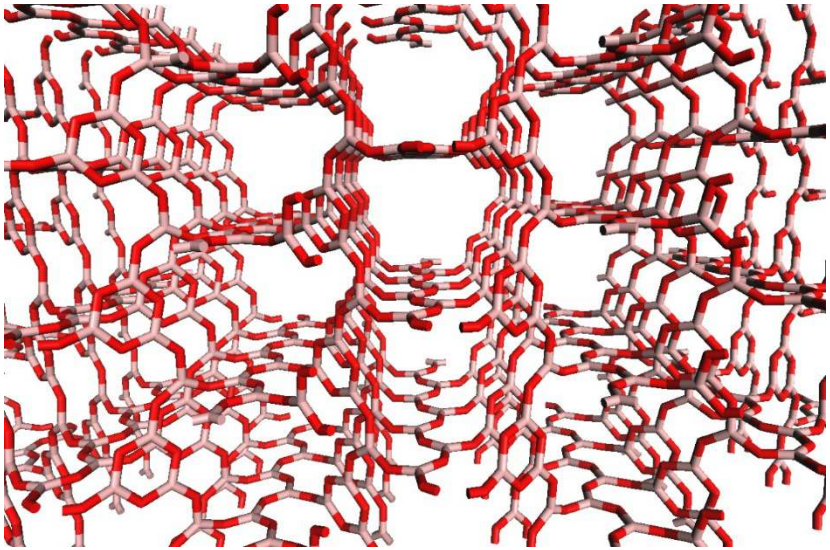



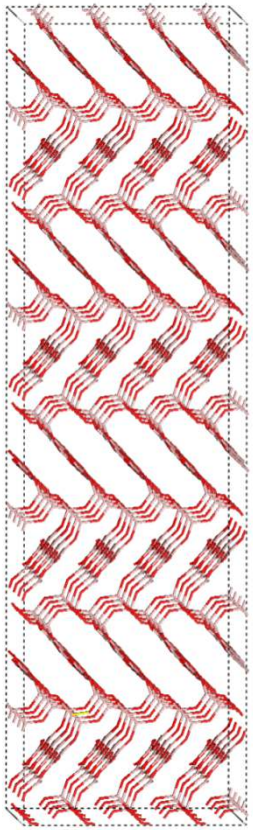



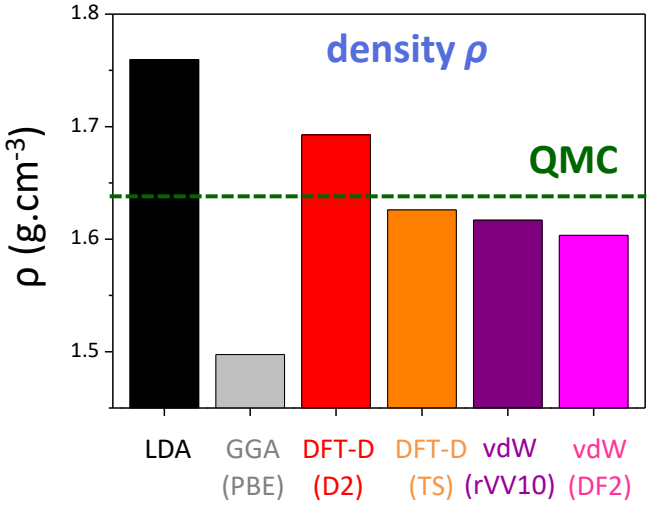

✓ All DFT-vdW schemes perform quite well
(and bring significant improvements)

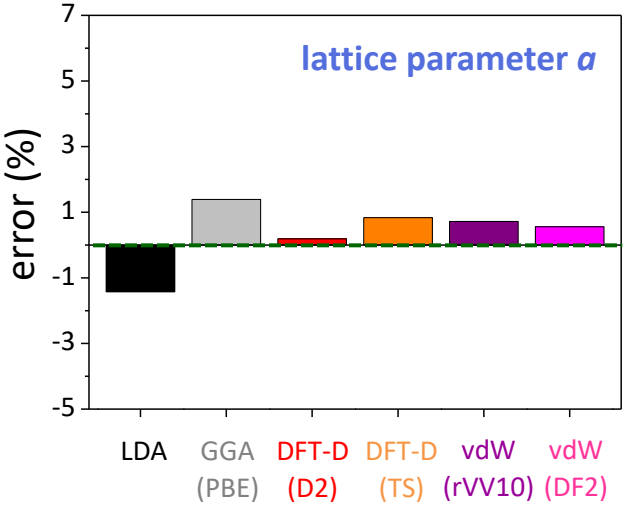
# Benchmarking DFT: structure

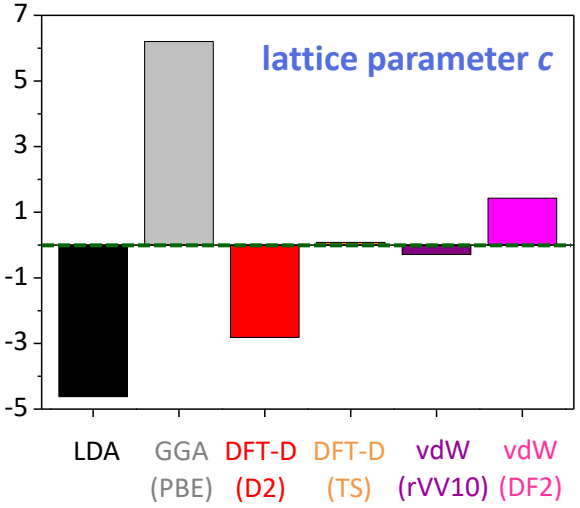
**T10 (new polymorph)**





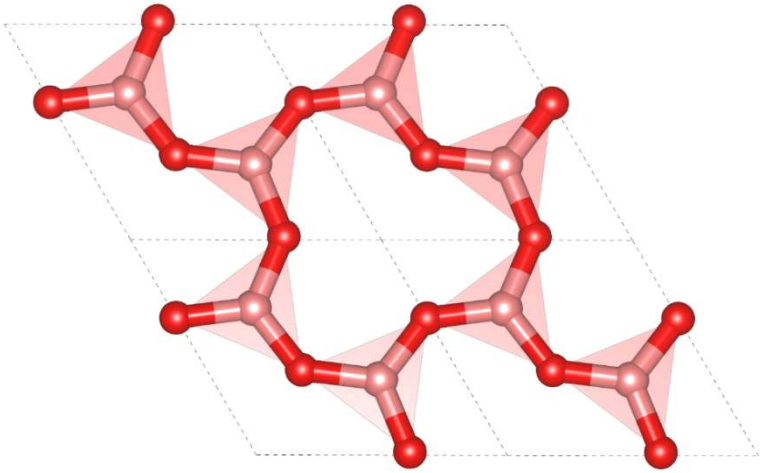


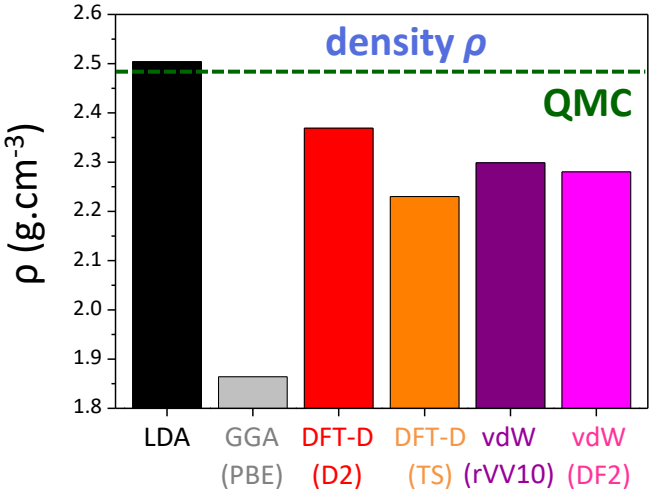



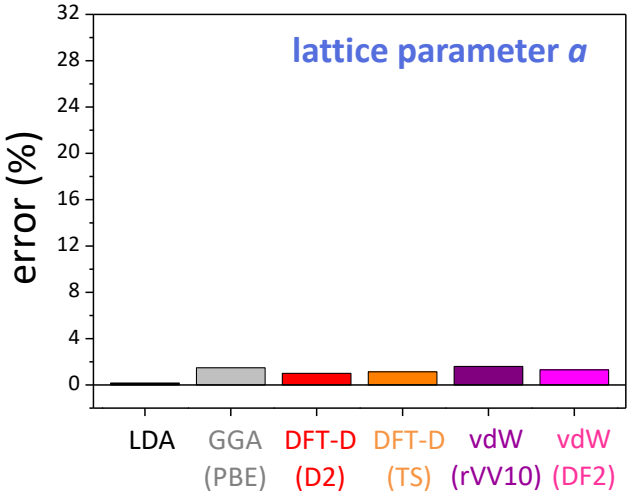



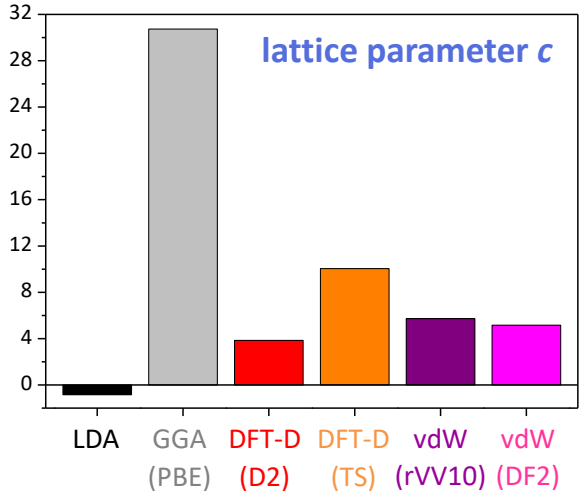
# Benchmarking DFT: structure

**T0 (new polymorph)**



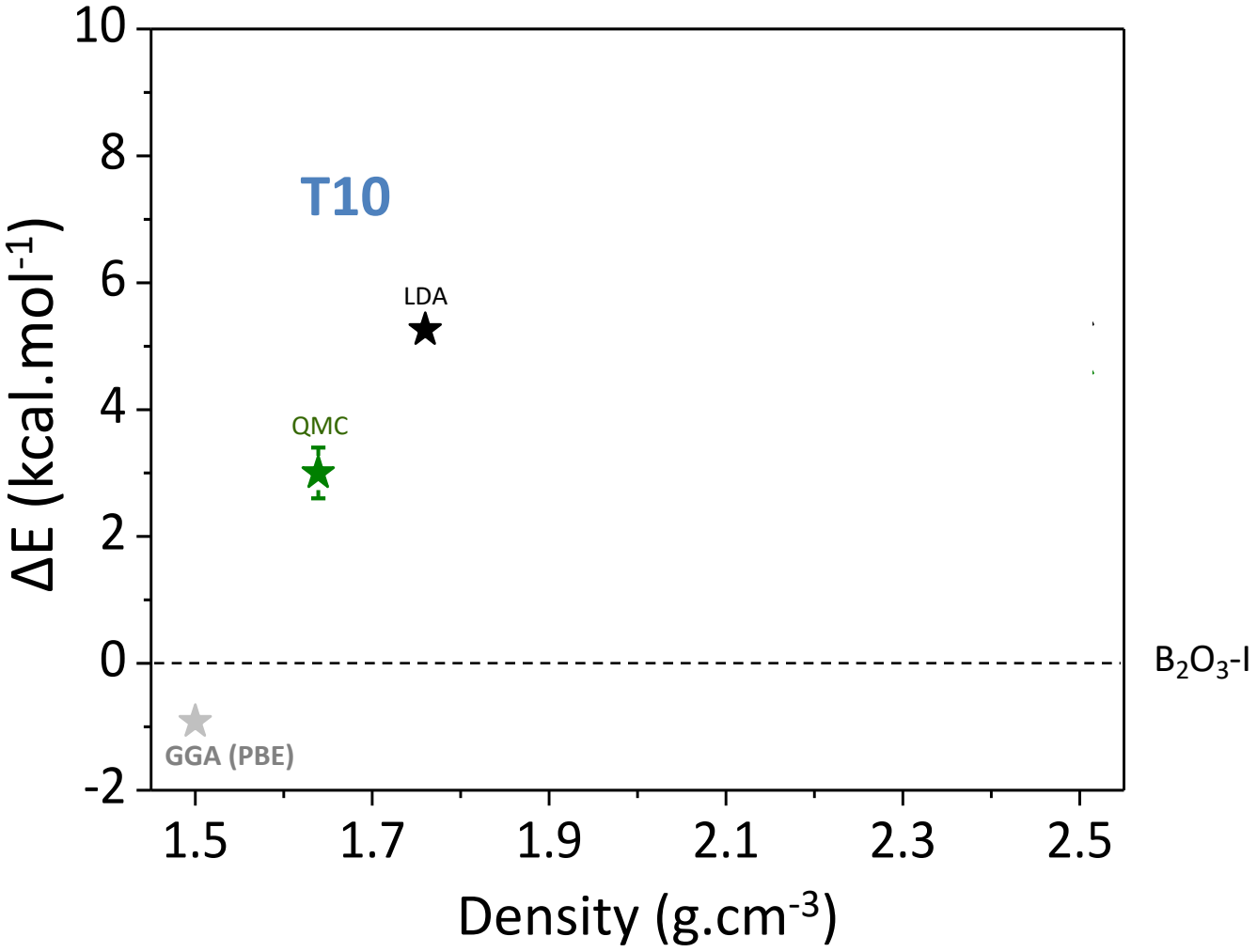



✓ Large GGA error (best result with LDA). Situation reminiscent of *h*-BN.

# Benchmarking DFT: energy



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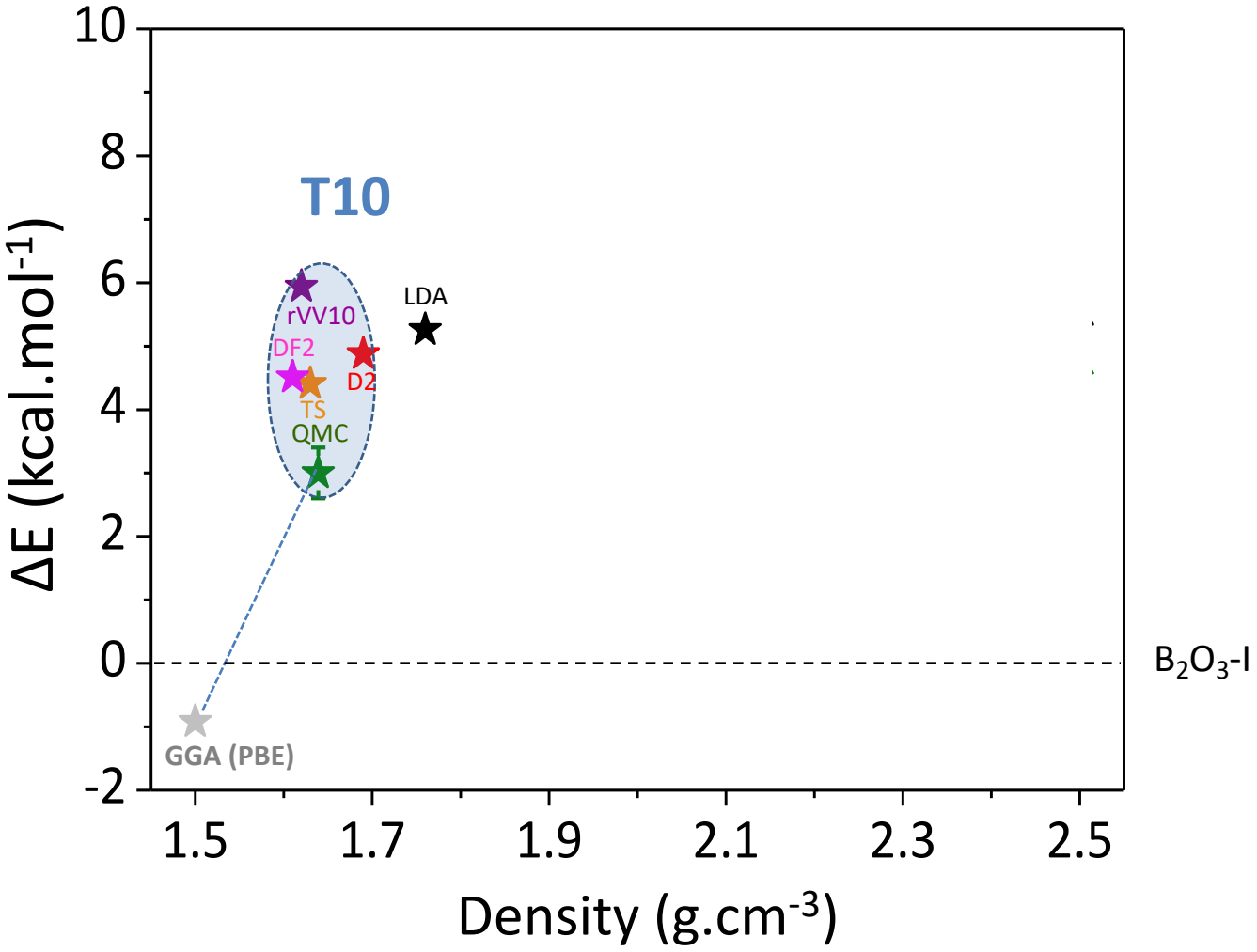
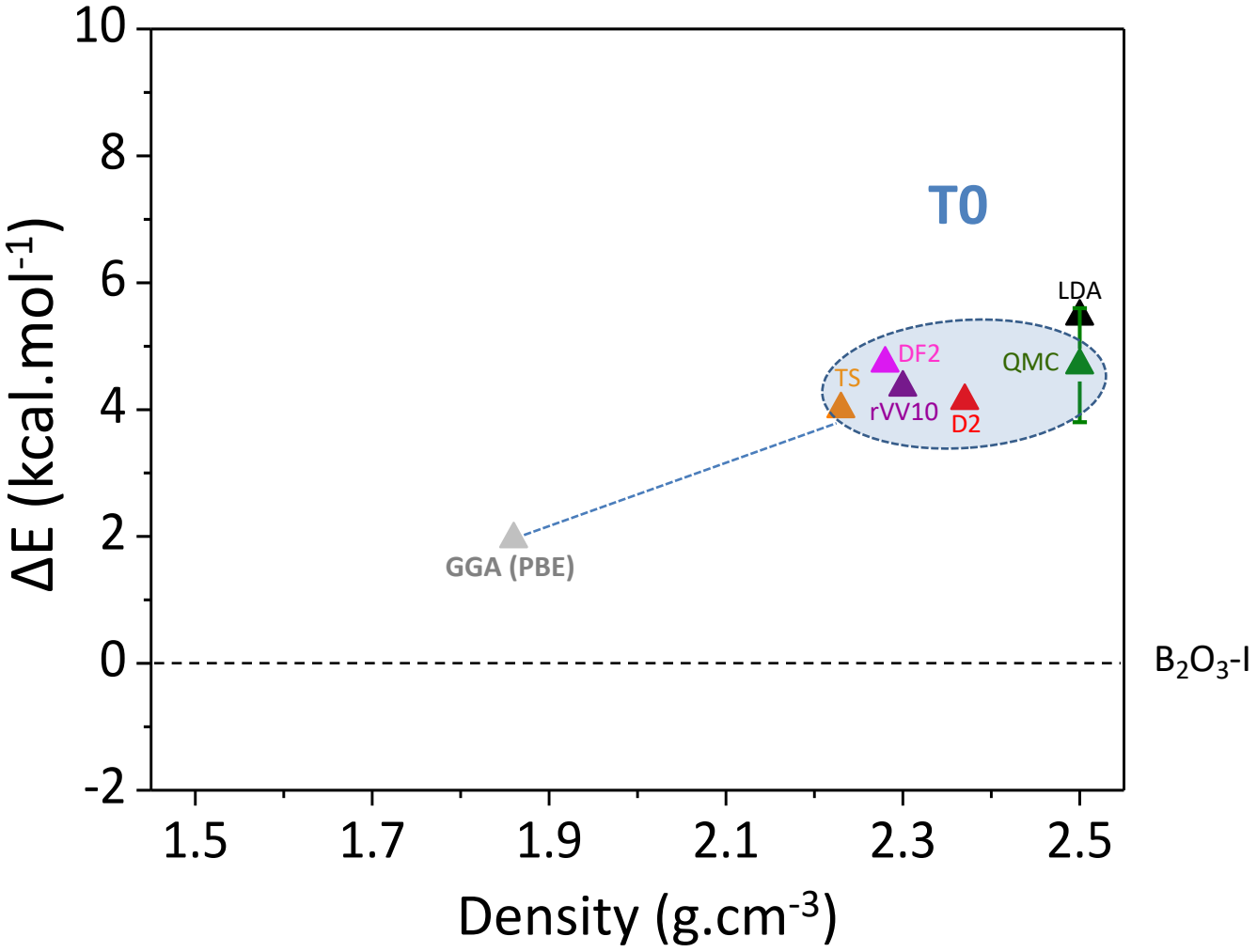



✓ Large GGA error. DFT + vdW reasonably well

# Benchmarking DFT: energy

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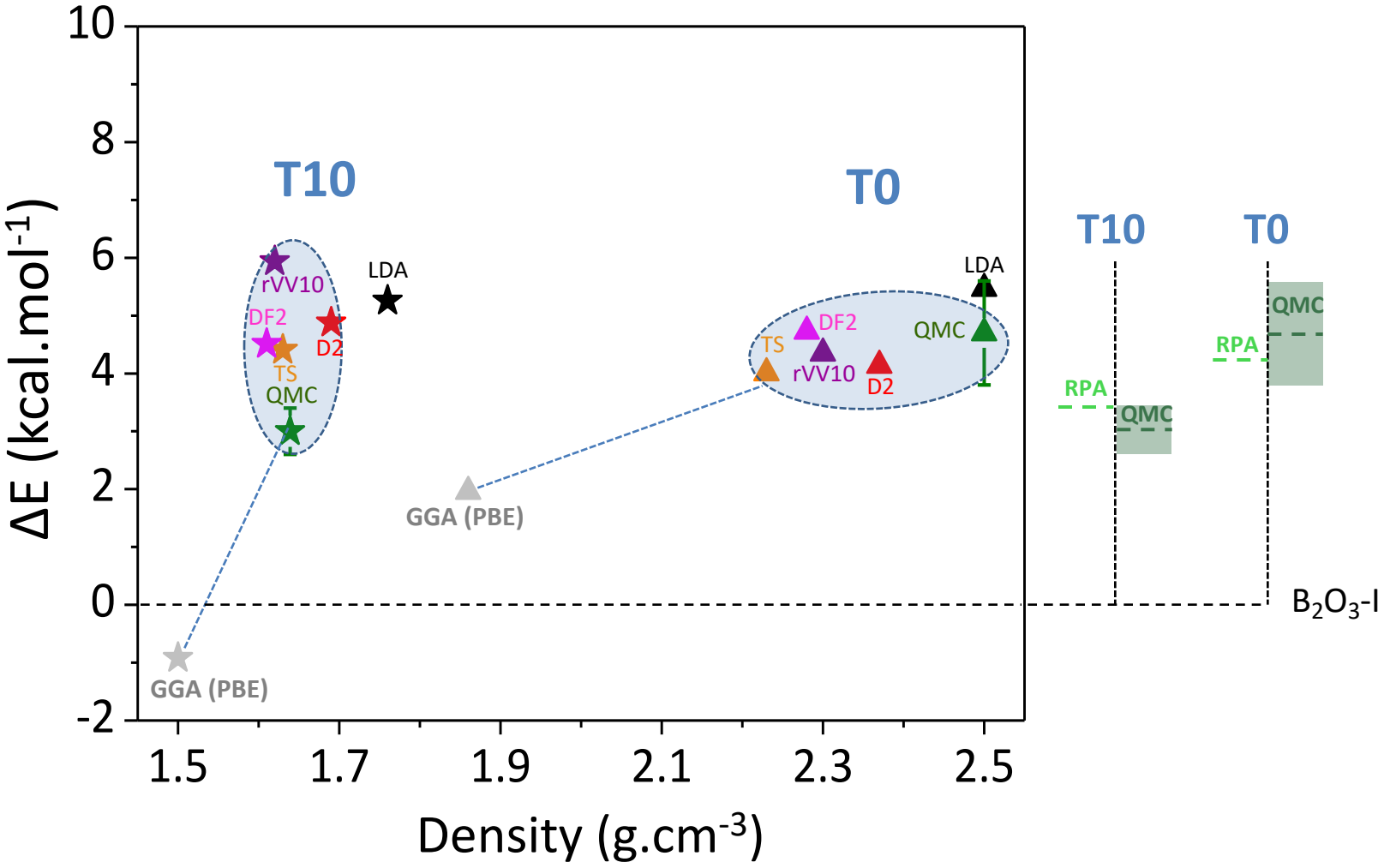
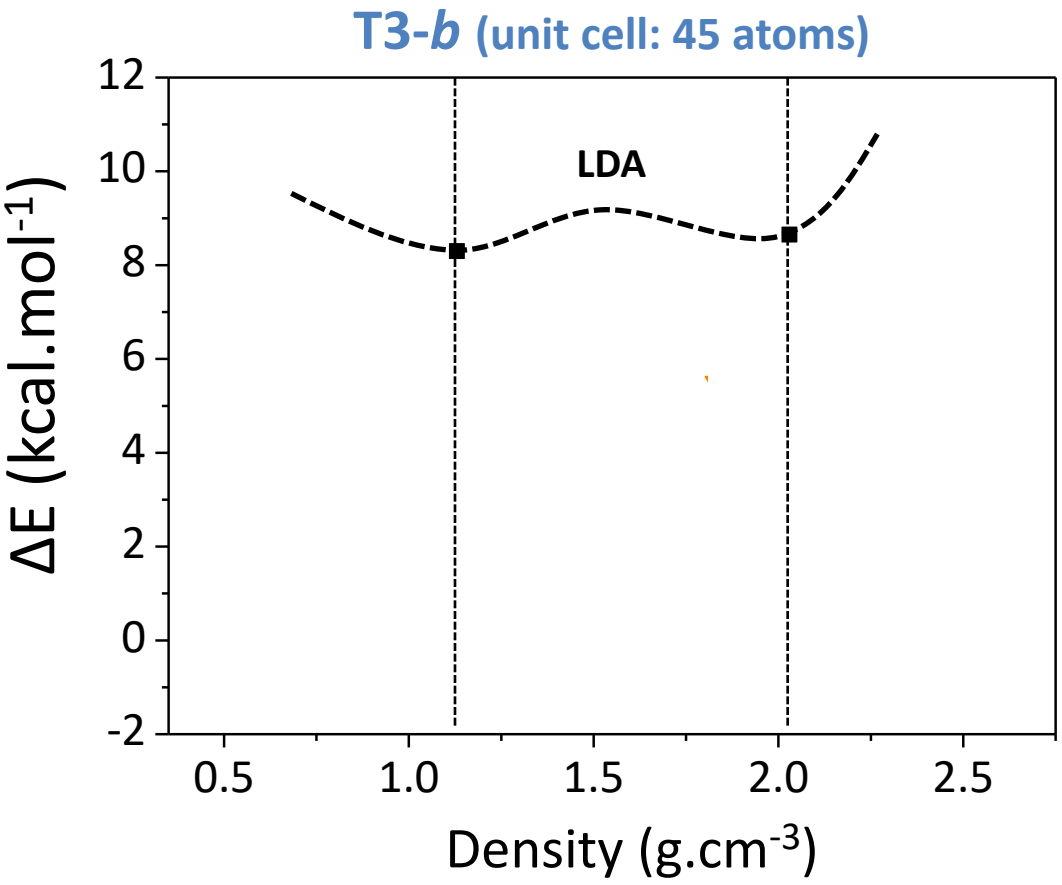


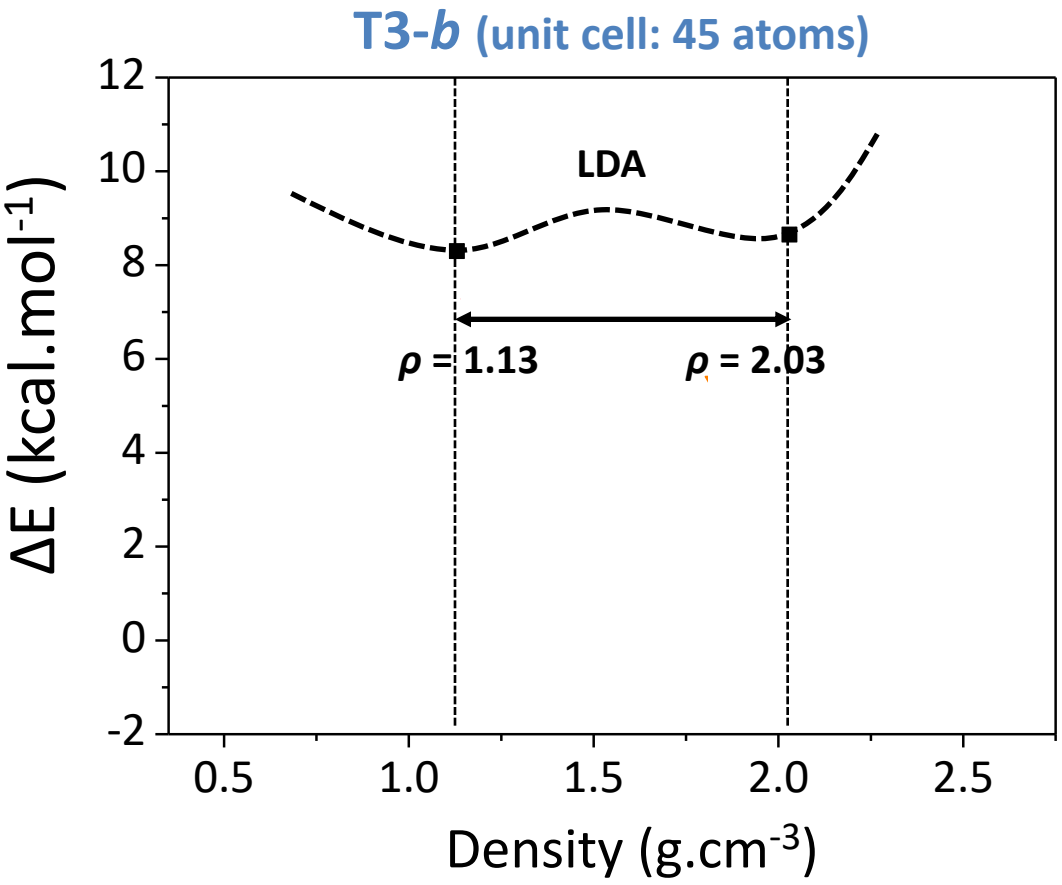
# DFT energy landscape




✓ For a given topology (and a given XC), existence of **several minima (*i.e. stable* geometries)**

→ ***Rugged* energy landscape**

# DFT energy landscape

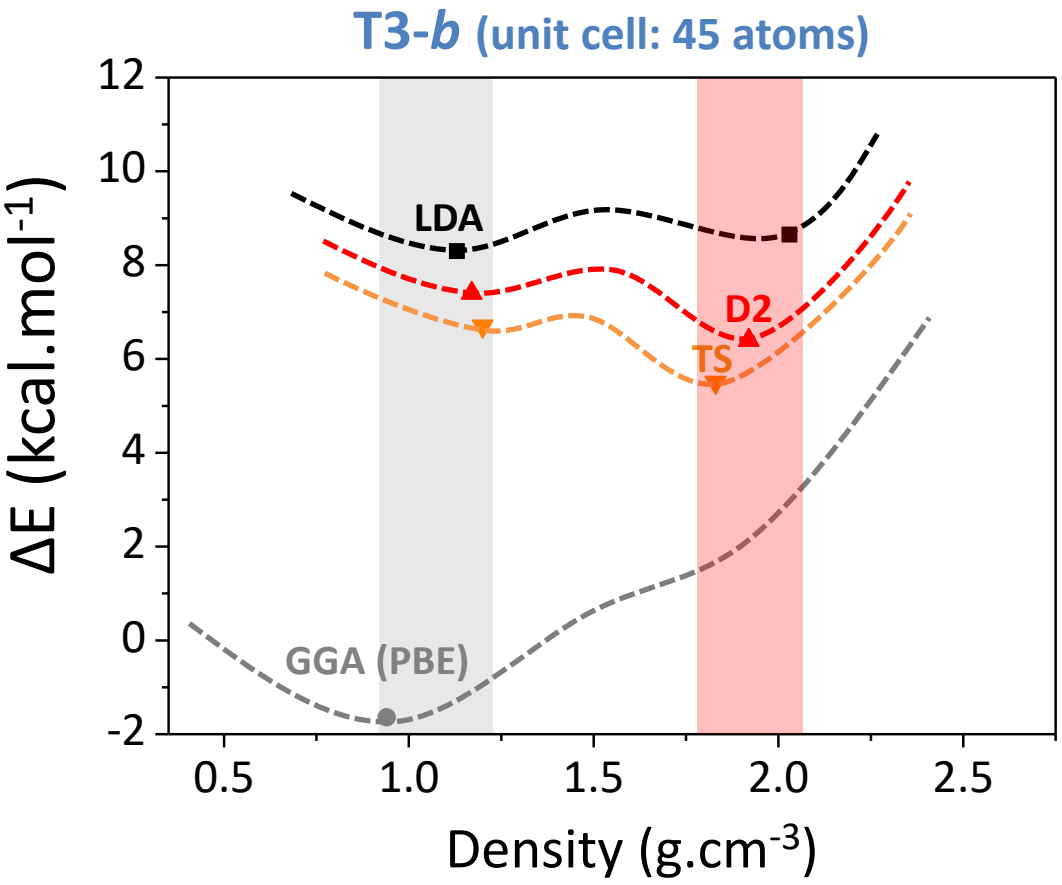



✓ For a given topology (and a given XC), existence of **several minima (*i.e. stable* geometries)**

→ ***Rugged* energy landscape**

[small energy differences while huge density differences → hard to « converge »]

# DFT energy landscape



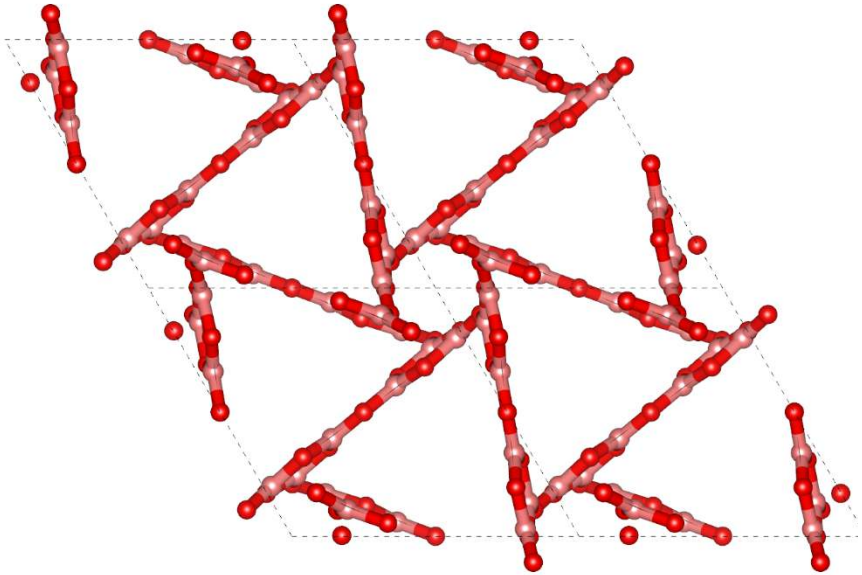

✓ For a given topology (and a given XC), existence of **several minima (*i.e. stable* geometries)**

PBE — tends to favour → low-density geometry

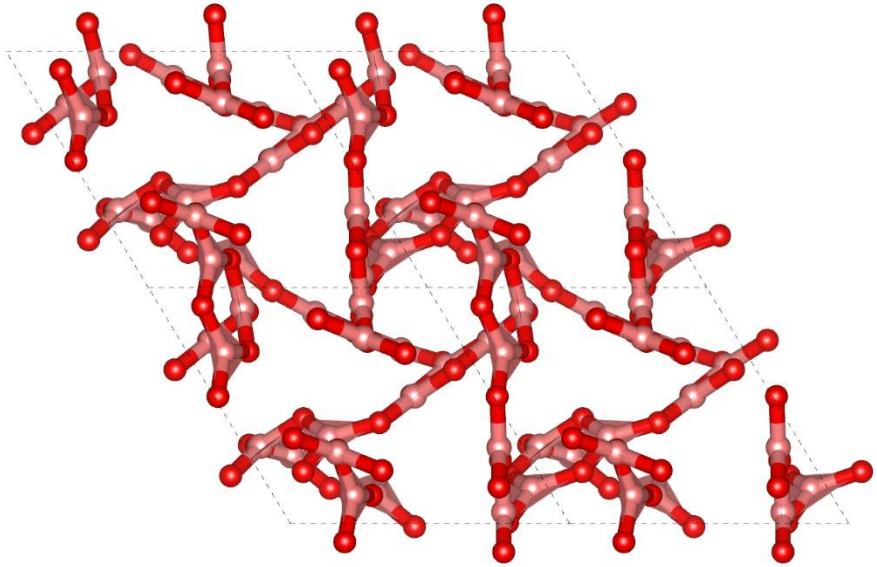
vdW — high-density geometry

# DFT energy landscape

## T3-*b* (unit cell: 45 atoms)



**Low-density**: highly symmetric, « puffed » rings
(as in $SiO_2$ β-cristobalite)



**High-density**: less symmetric, « puckered » rings
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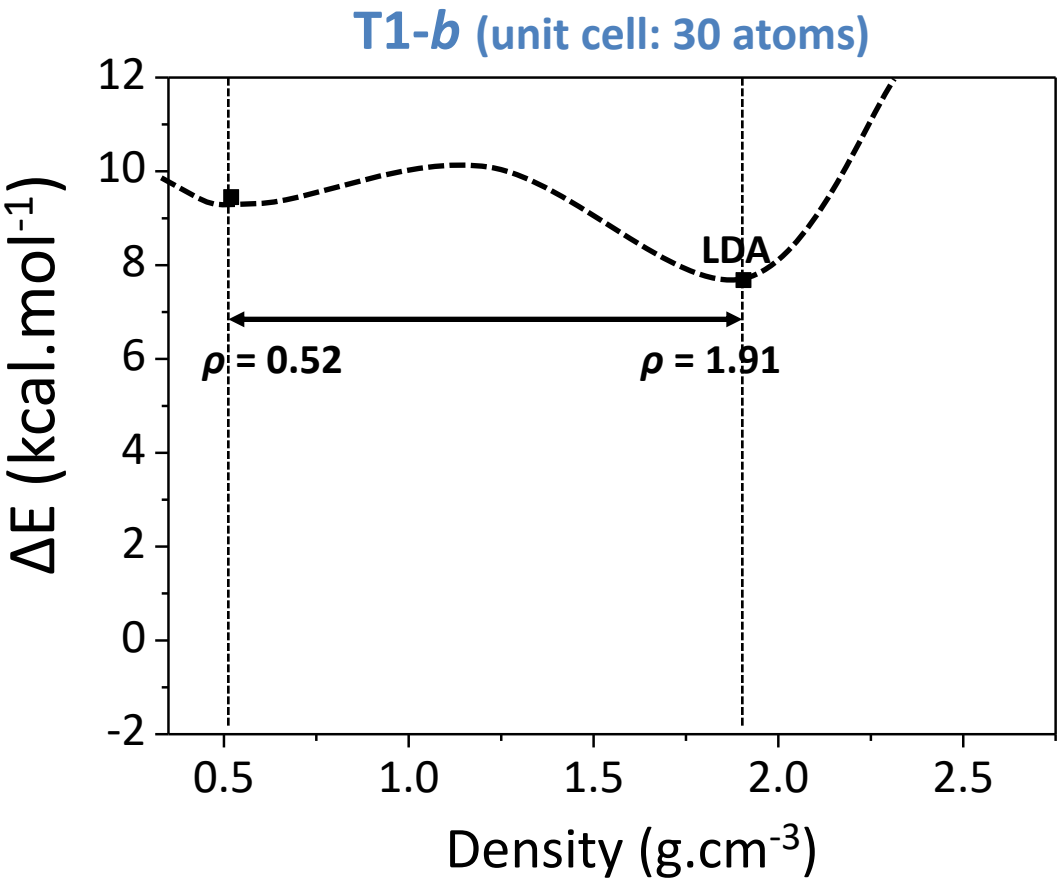
# DFT energy landscape

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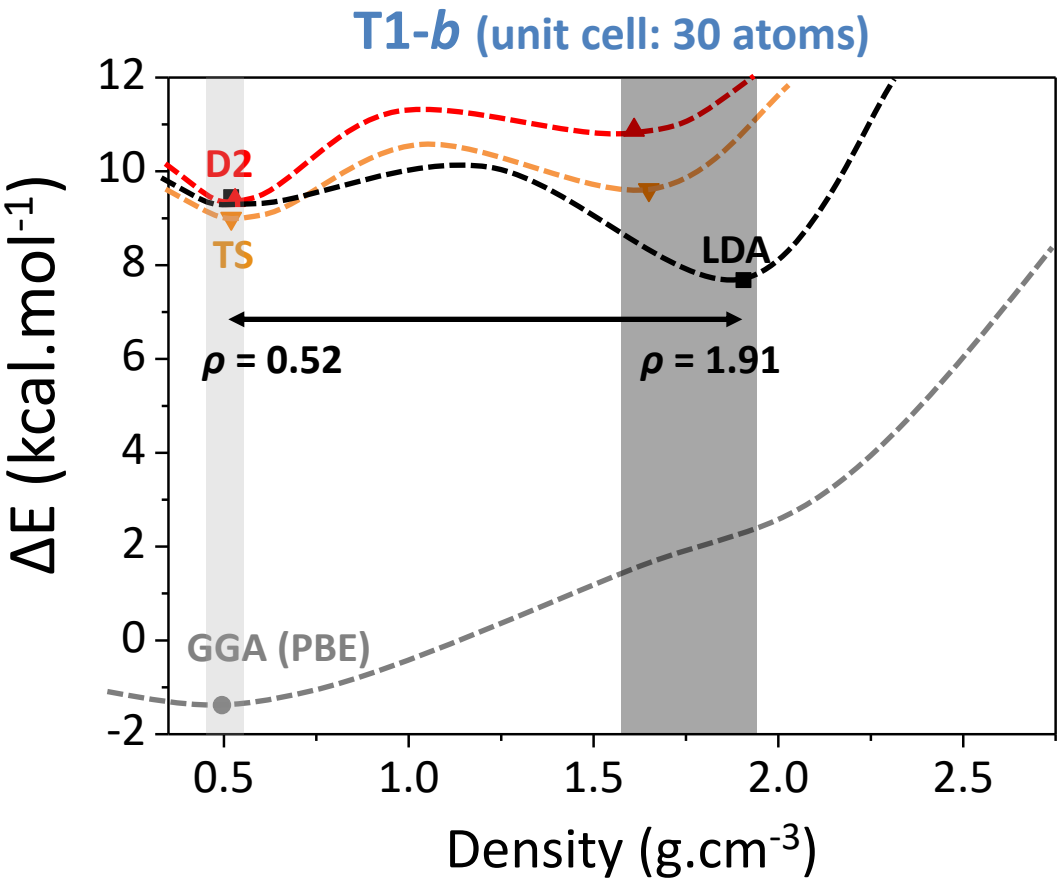
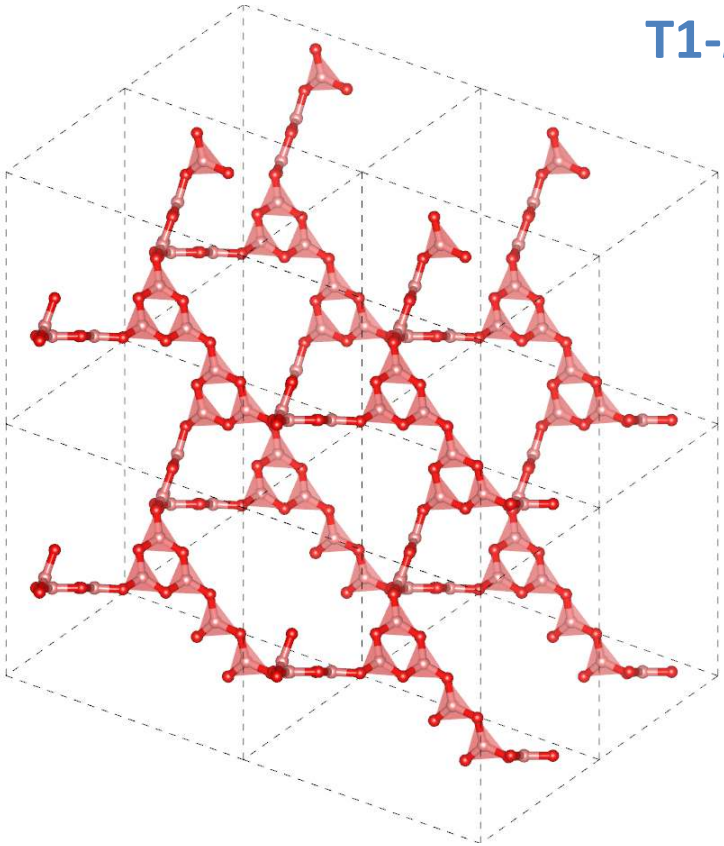
# DFT energy landscape



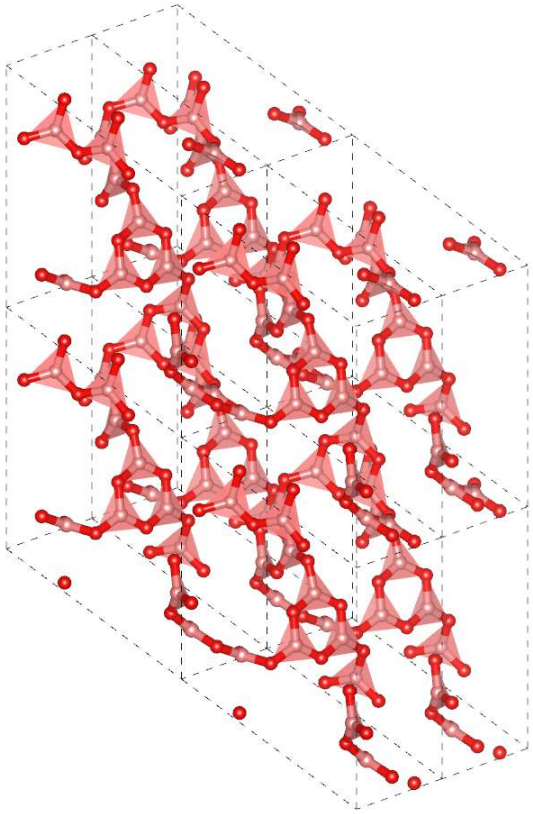

✓ For a given topology (and a given XC), existence of **several minima (*i.e. stable* geometries)**

# DFT energy landscape

## T1-*b* (unit cell: 30 atoms)



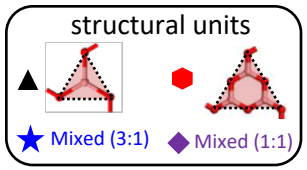
**Low-density**: highly symmetric, « puffed » rings
(as in $SiO_2$ β-cristobalite)

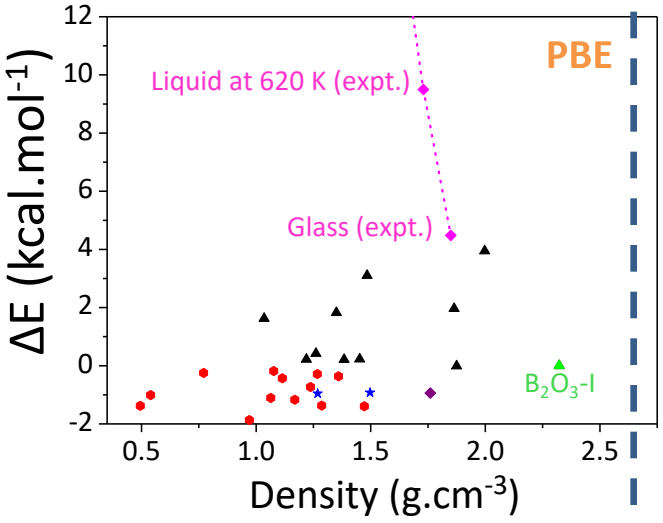


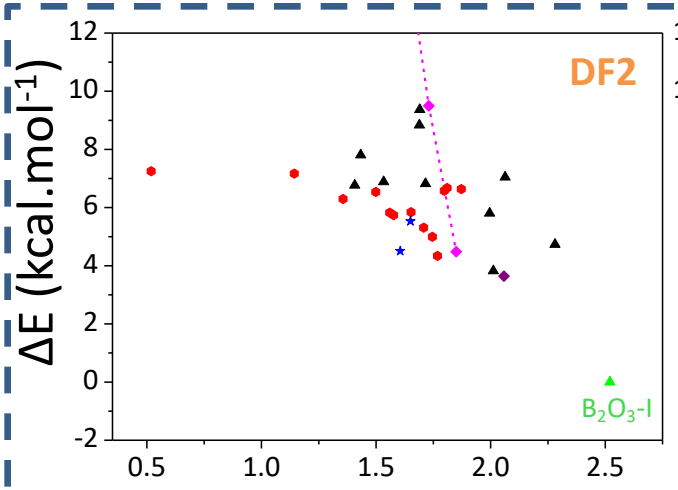
**High-density**: less symmetric, « puckered » rings
(as in $SiO_2$ α-cristobalite)

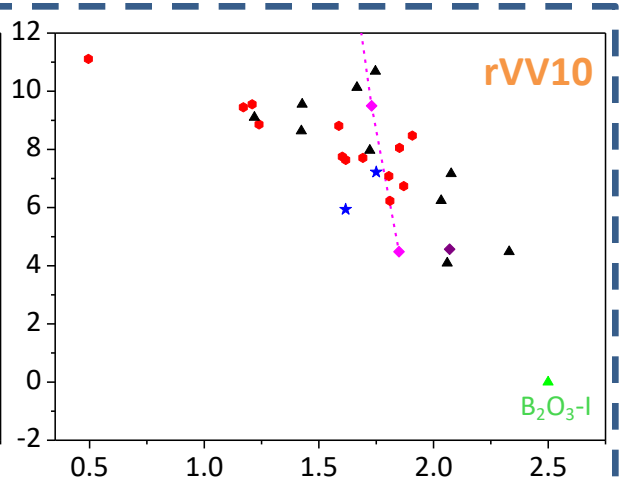
# DFT (full set)

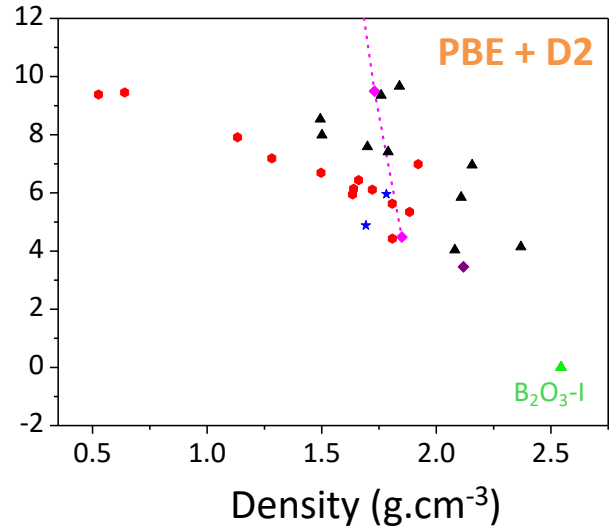
## vdW

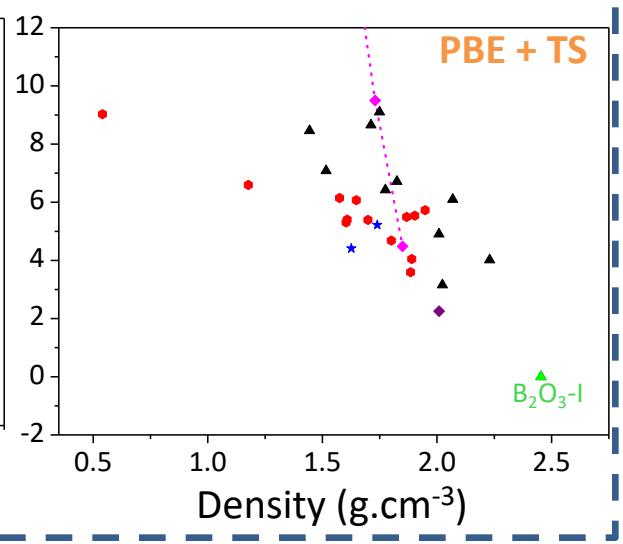


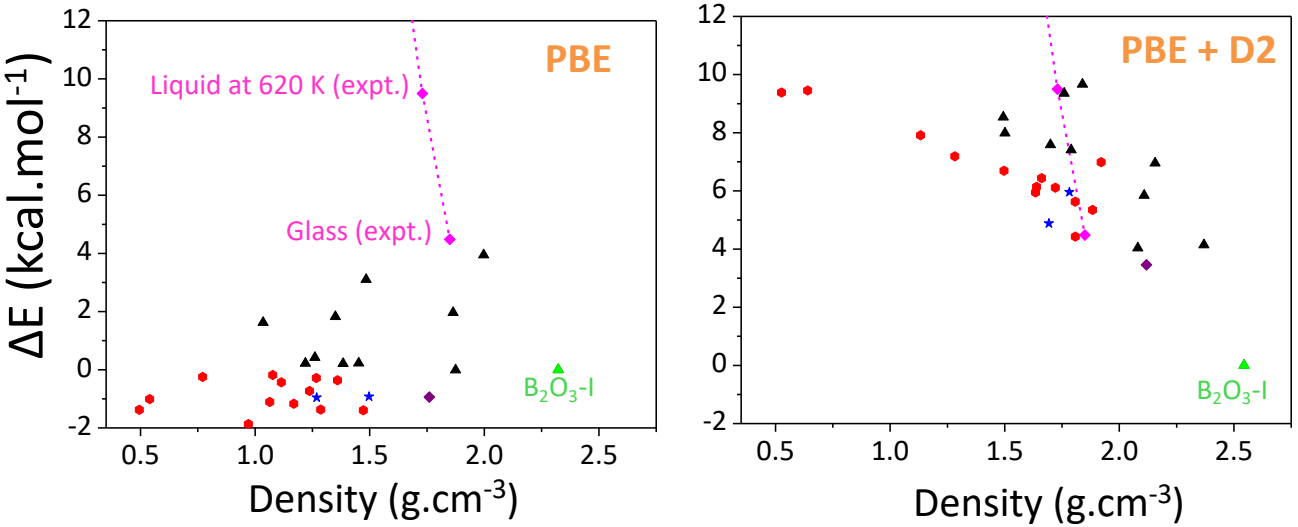




- ✓ Significant changes from PBE to “vdW”
- ✓ Good agreement between the various DFT-vdW schemes [$B_2O_3$-I consistently found as ground state]

# PBE versus DFT-D

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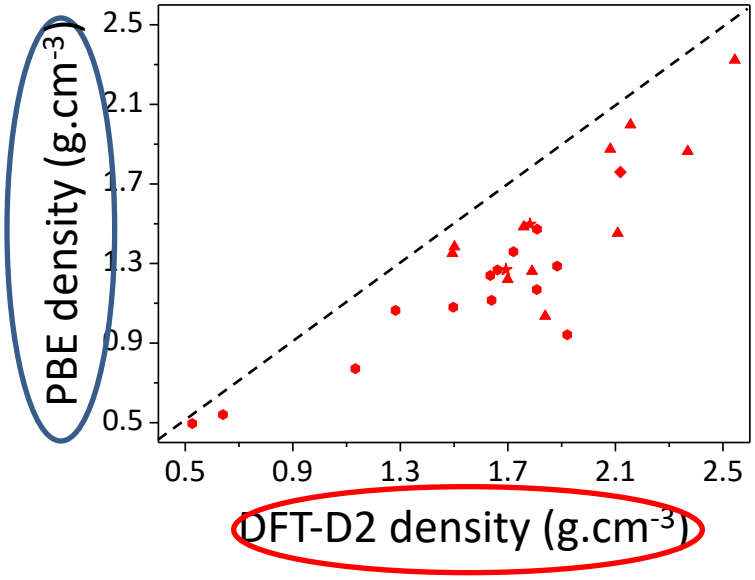
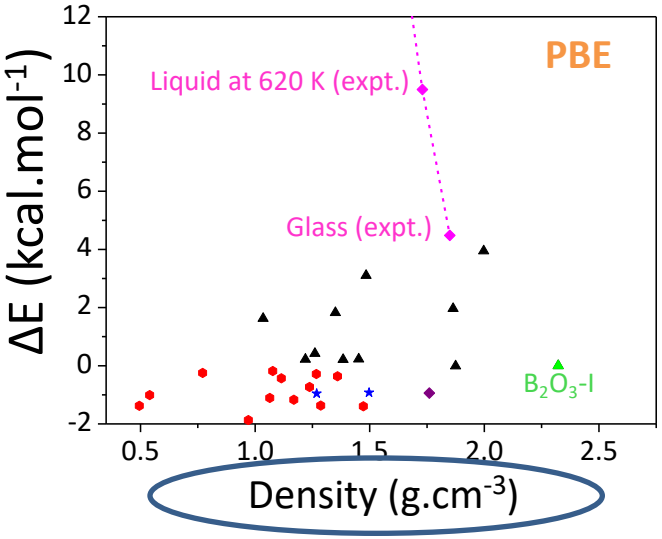
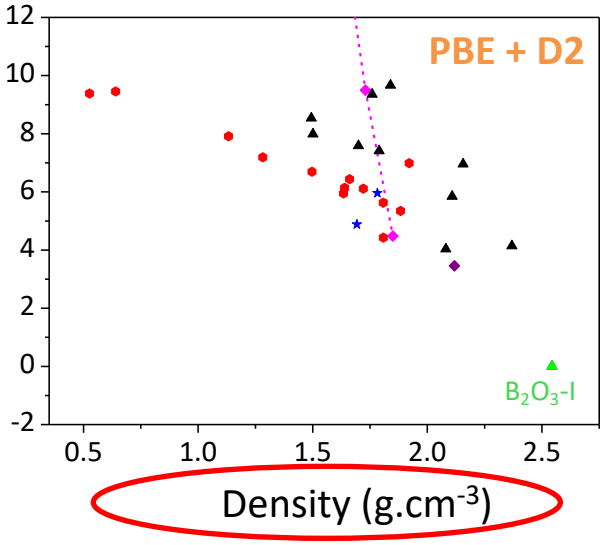
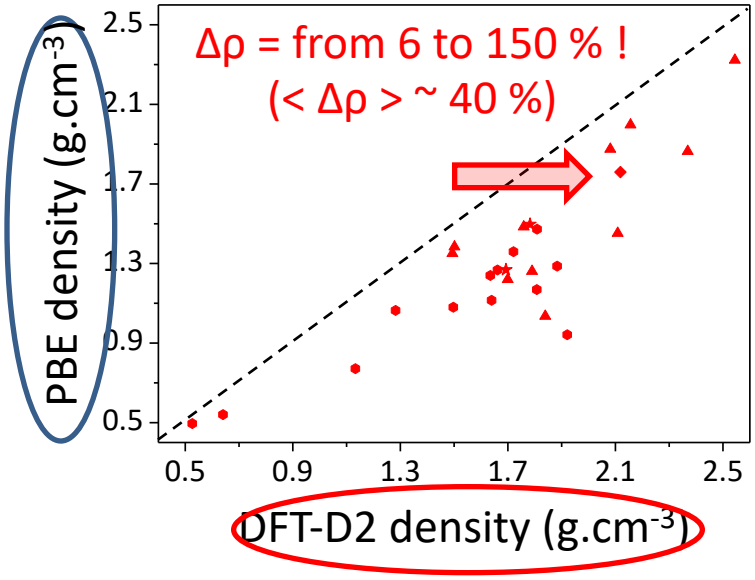
# PBE versus DFT-D: density corrections

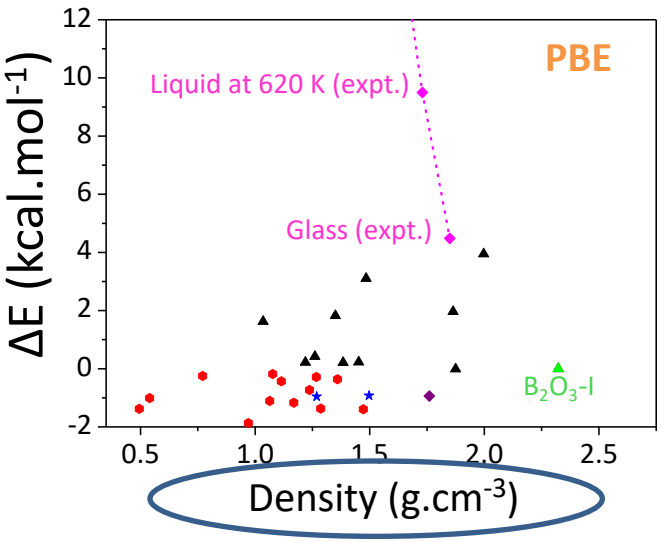


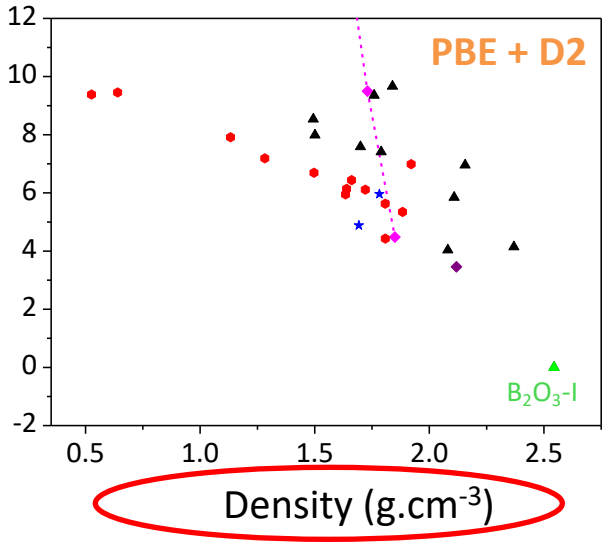



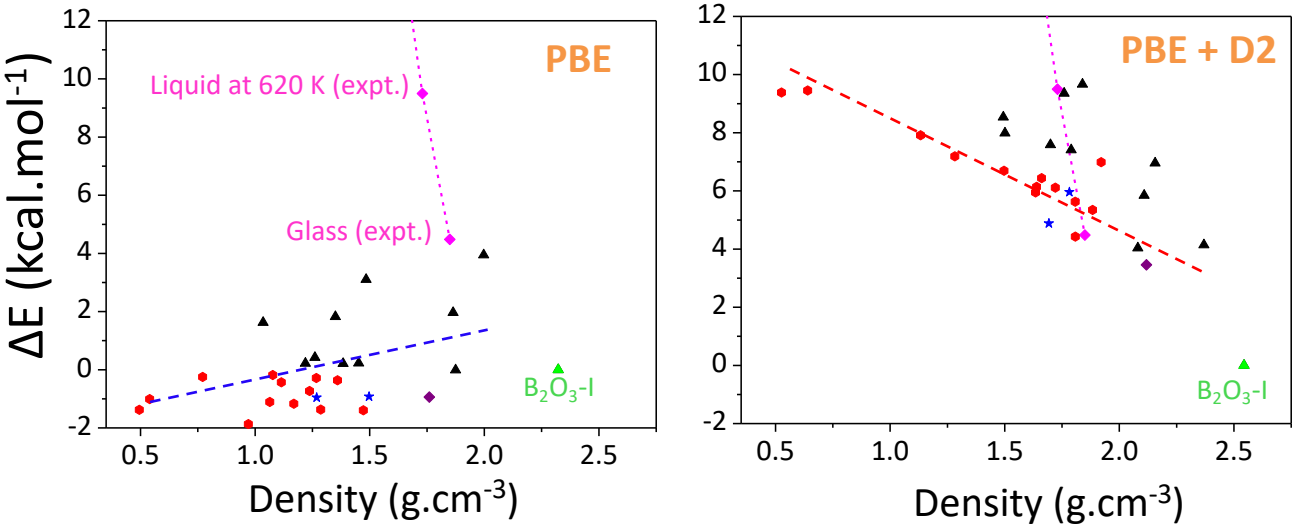
# PBE versus DFT-D: density corrections



# PBE versus DFT-D: energy corrections



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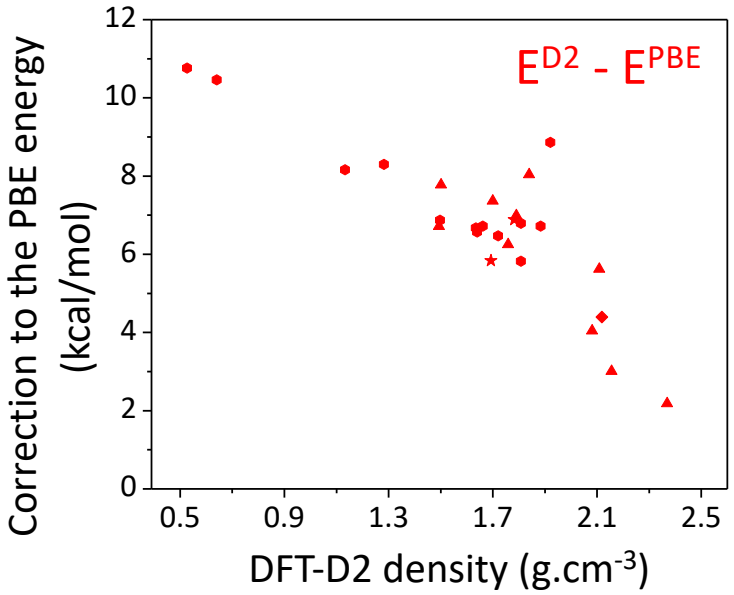
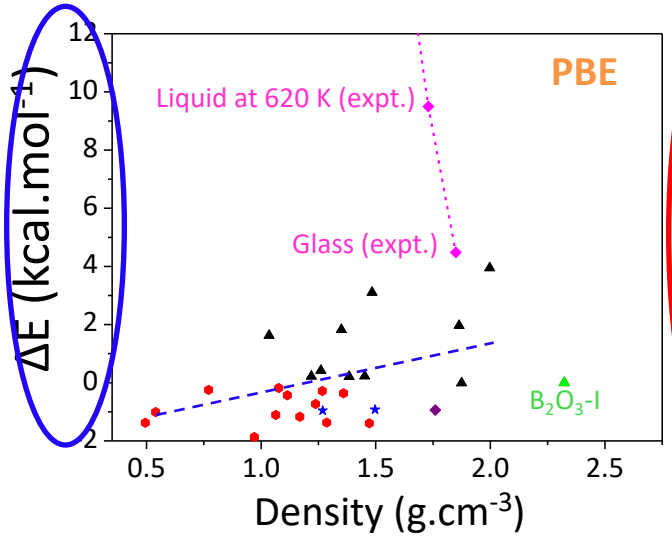
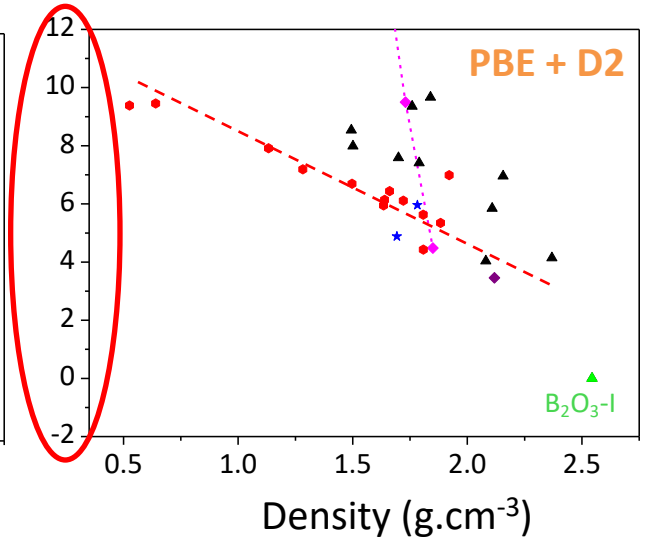
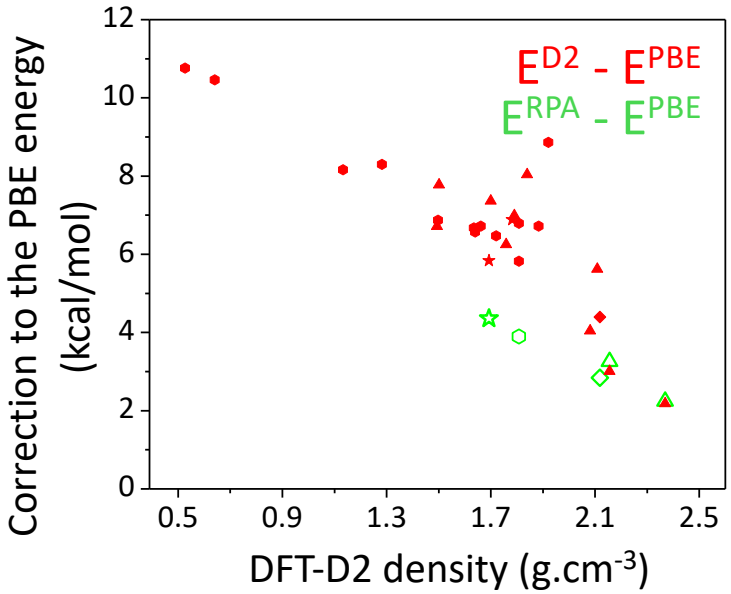



vdW: increasing energy penalty with decreasing density



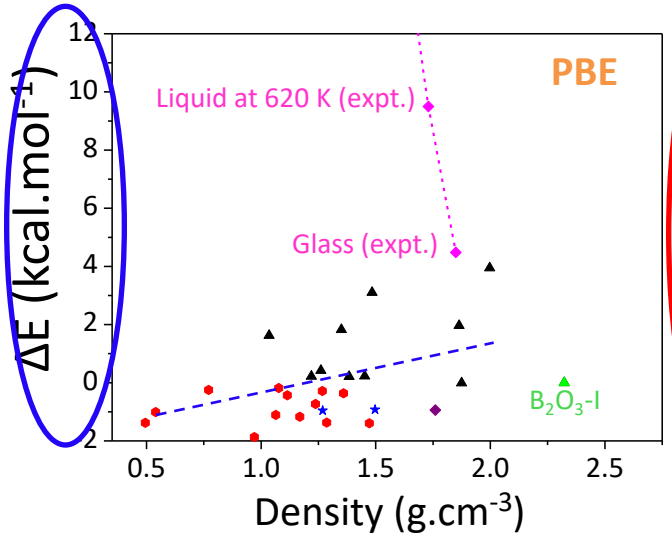



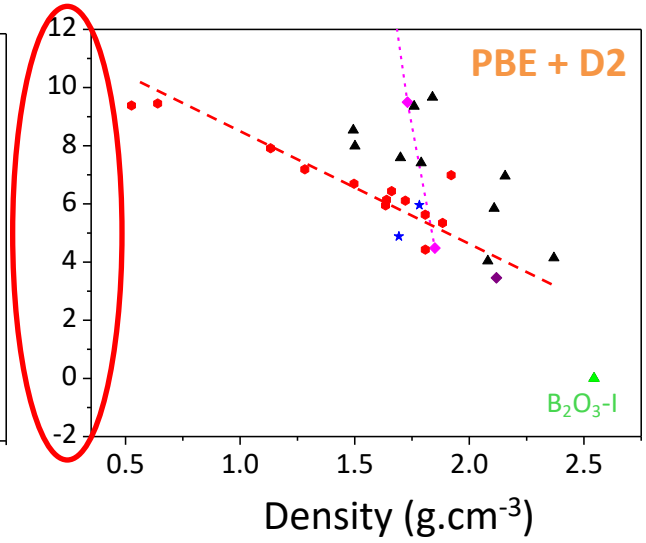
# PBE versus DFT-D: energy corrections



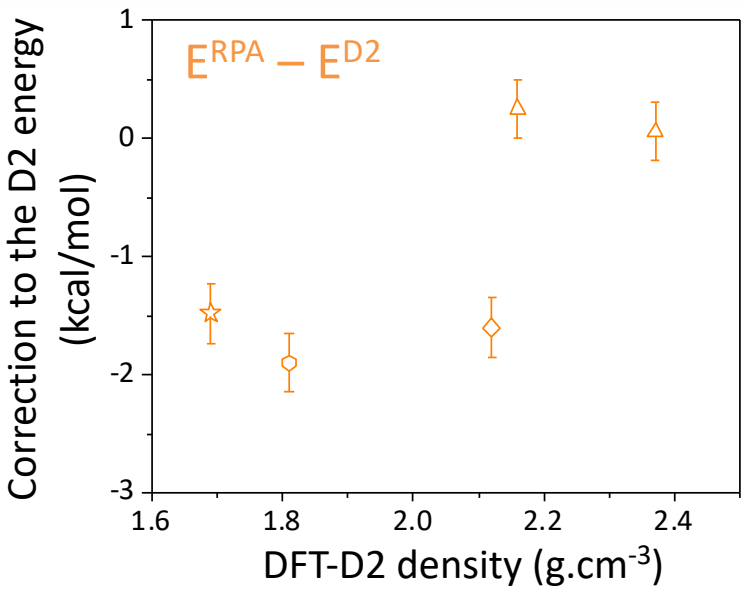

vdW: increasing energy penalty with decreasing density

Trend confirmed by RPA



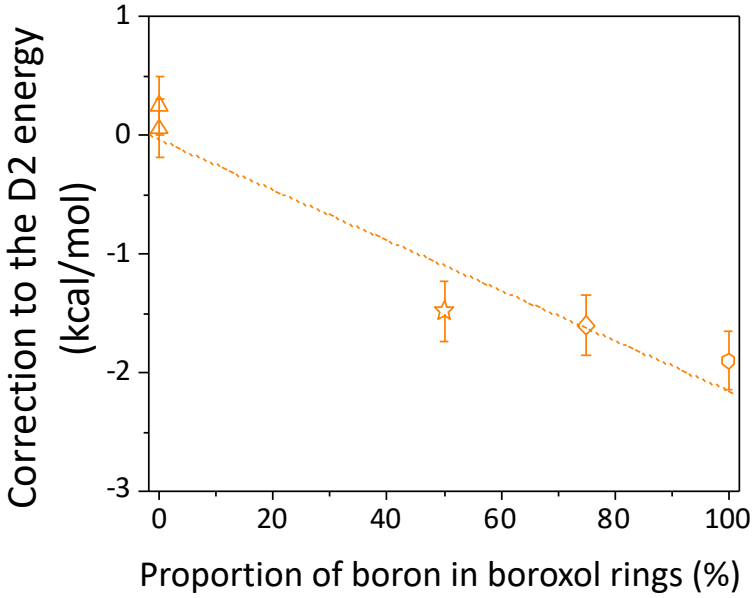
# Many-body beyond vdW ?




$E^{RPA} - E^{DFT\text{-}vdW} \equiv$

Many-body contribution ?

(on top of vdW, not captured by DFT)

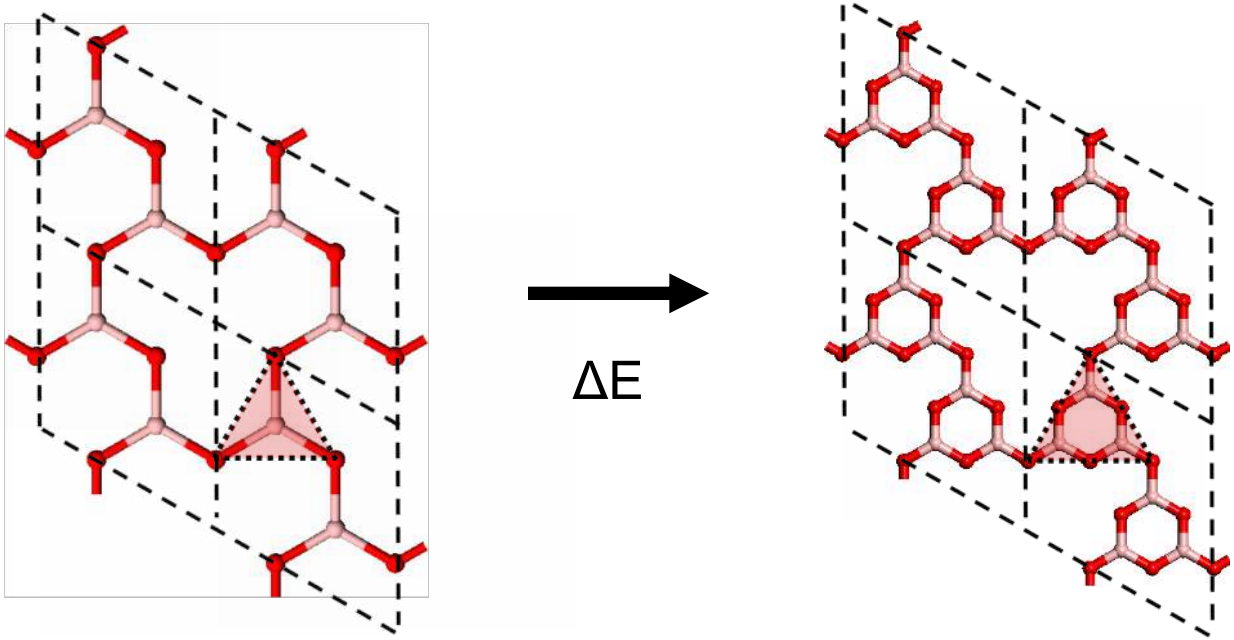



Related to the boroxol-ring stabilisation energy?

Work in progress …

# Boroxol stabilisation energy

- « graphite » iso-structural crystals




100 % triangles “graphite”: T0

100 % boroxols “graphite”: T0-*b*

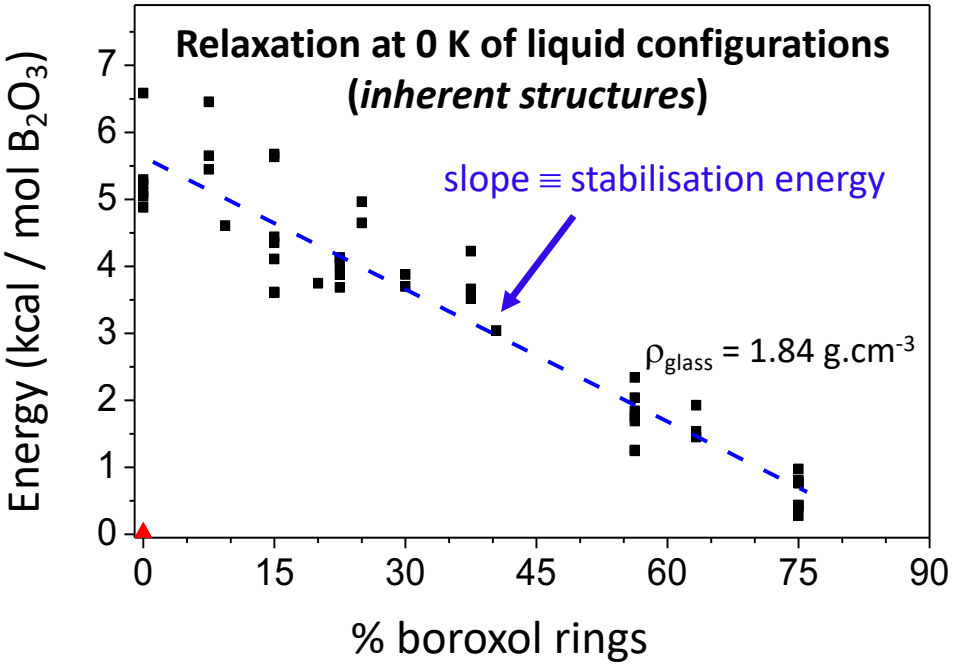
No relaxation (B-O-B angles fixed to 120°): $\Delta E^{DFT}$ ~ -10 kcal/mol

After relaxation: $\Delta E^{DFT}$ ~ 0 kcal/mol

$\Delta E^{RPA}$ ~ -2 kcal/mol

# Boroxol stabilisation energy

*G. Ferlat, T. Charpentier, A.P. Seitsonen, A. Takada, M. Lazzeri, L. Cormier, G. Calas, F. Mauri, Phys. Rev. Lett., **101**, 065504 (2008)*




✓At the glass density, *boroxol*-rich are more stable than *triangle*-rich structures

✓Numerical evidence of a boroxol stabilisation-energy (in ~ good agreement with expt.)

PBE + D2: $E_{stab}$ = - 9 ± 2 kcal/(mol boroxol) for a glass with *f* = 75 % boroxol rings

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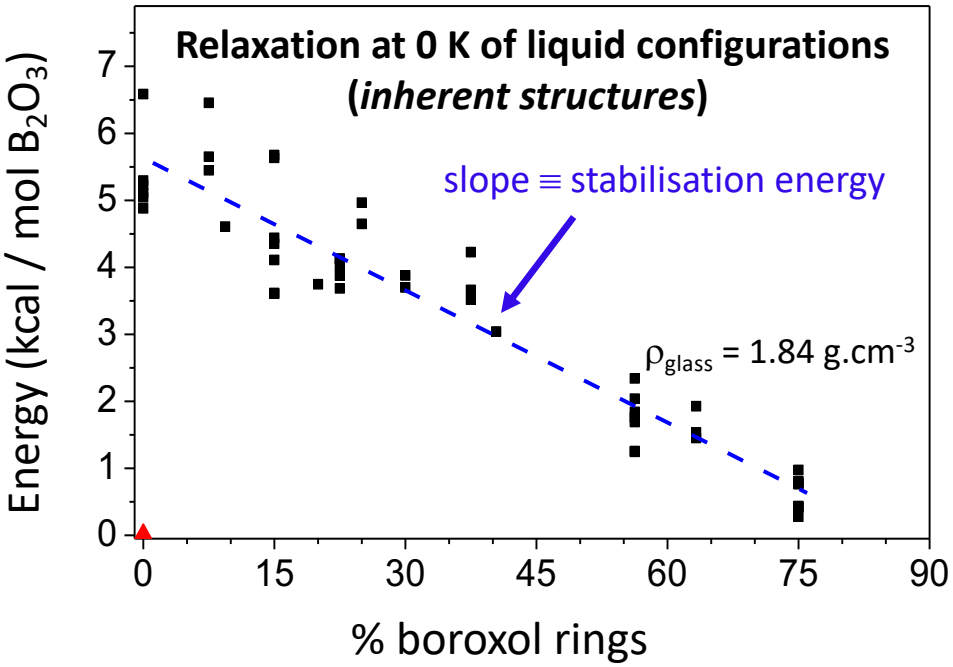


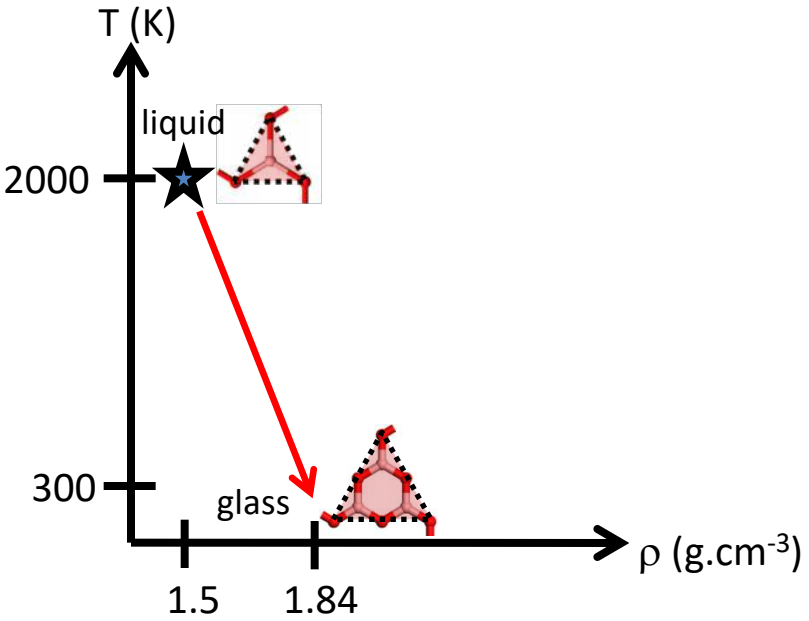


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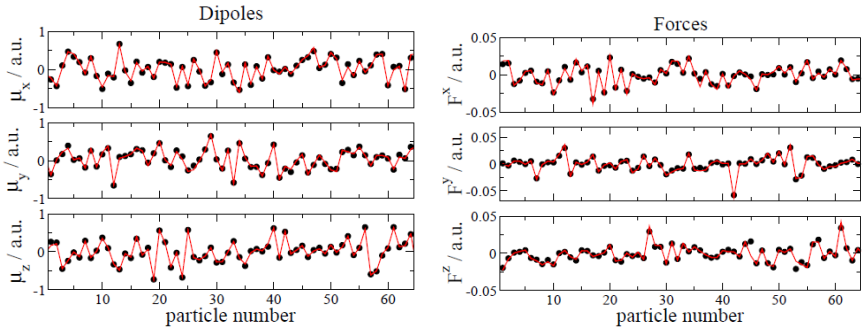
Expt.: $E_{stab}$ ~ - 6 ± 1 kcal/(mol boroxol)

# Polarisable force-fields from *first-principles*

Collab. M. Salanne (PHENIX, Sorbonne Univ.)

*Phys. Rev. B (2014), J. Phys. Condens. Matter (2015), J. Chem. Phys. (2019)*

- *first-principles* (CPMD) simulations used as benchmarks
- Force- and dipole-matching to calibrate the parameters

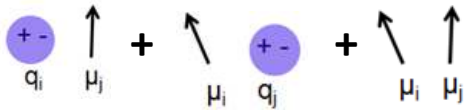



*CPMD – Fitted polarisable ion model*

Rotenberg, Salanne, Simon, Vuilleumier, Phys. Rev. Lett. (2010)

The potential includes:

- electrostatics
- short-range repulsion
- dispersion
- polarisation

$V^{pol}$ = 


$\mu_i$ : induced dipoles
additional degrees of freedom

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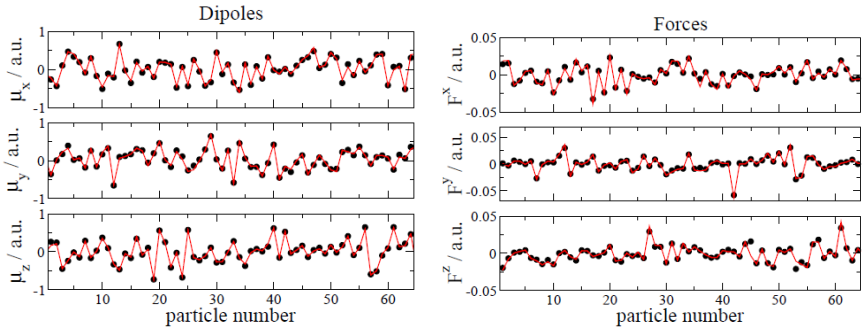


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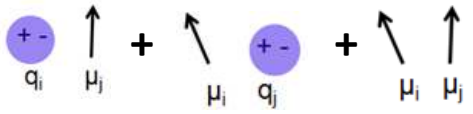
$V^{pol}$ = 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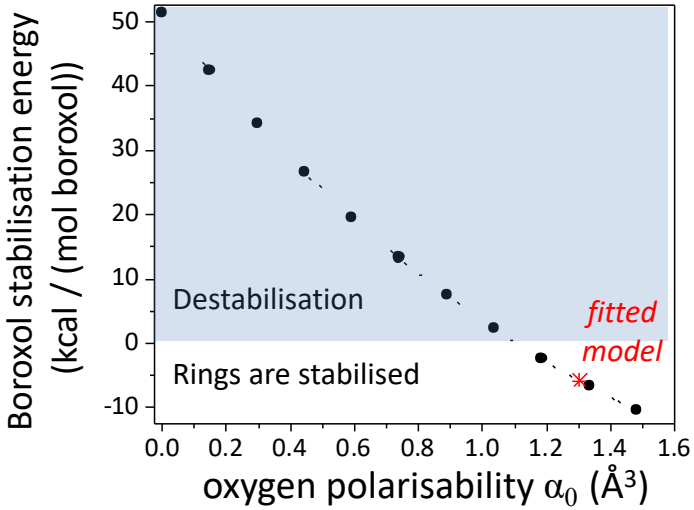
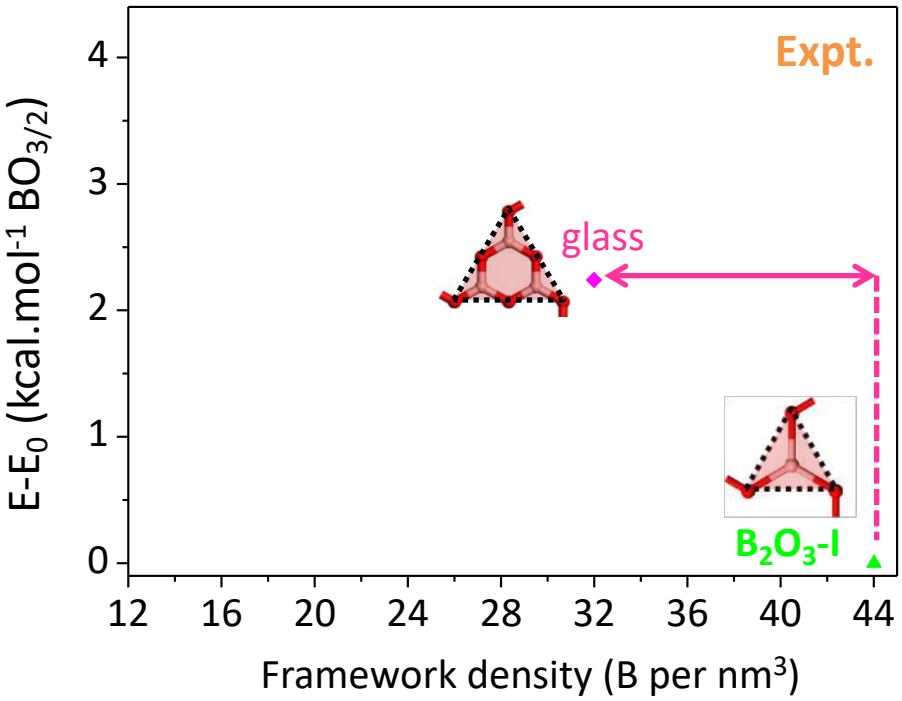



✓ strong dependence of the boroxols' stabilisation energy upon the **oxygen polarisability**

# Back to the $B_2O_3$ anomalies

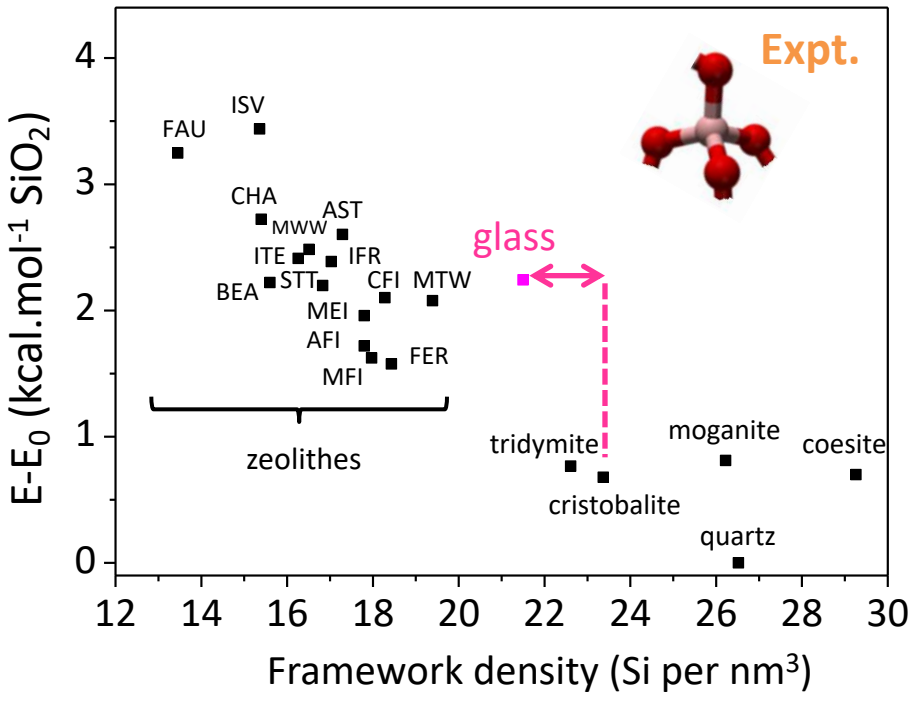
## $B_2O_3$




✓ $B_2O_3$ : - glass structure ≠ crystal

- $\rho_{glass}$ ~ 0.71 $\rho_{crystal}$
- poor polymorphism

## $SiO_2$

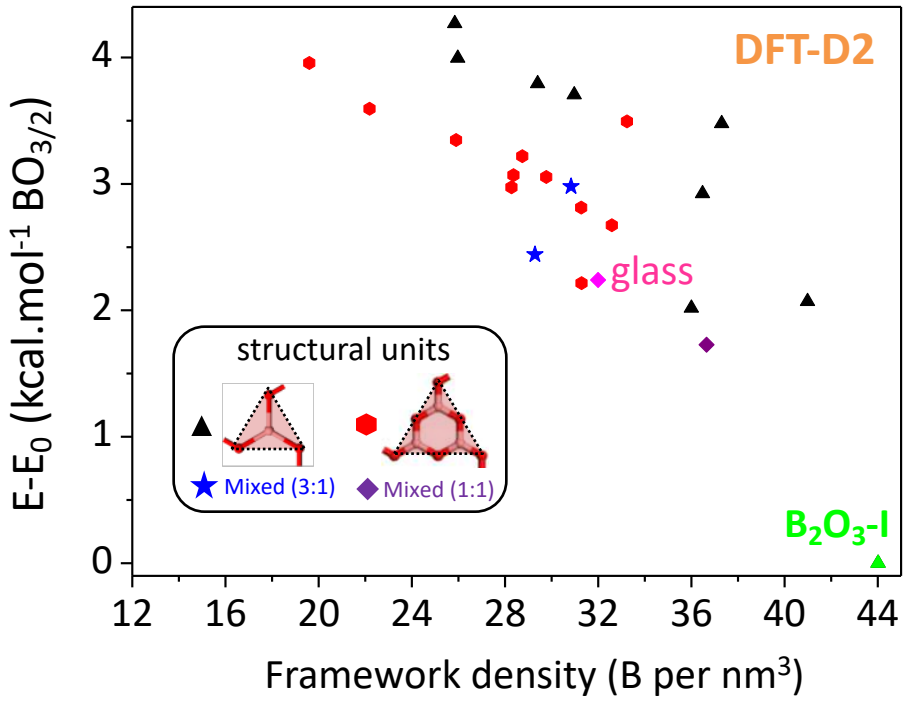



✓ $SiO_2$ : - glass ~ cristobalite

- $\rho_{glass}$ ~ 0.92 $\rho_{cristobalite}$
- rich polymorphism

# Back to the $B_2O_3$ anomalies

## $B_2O_3$

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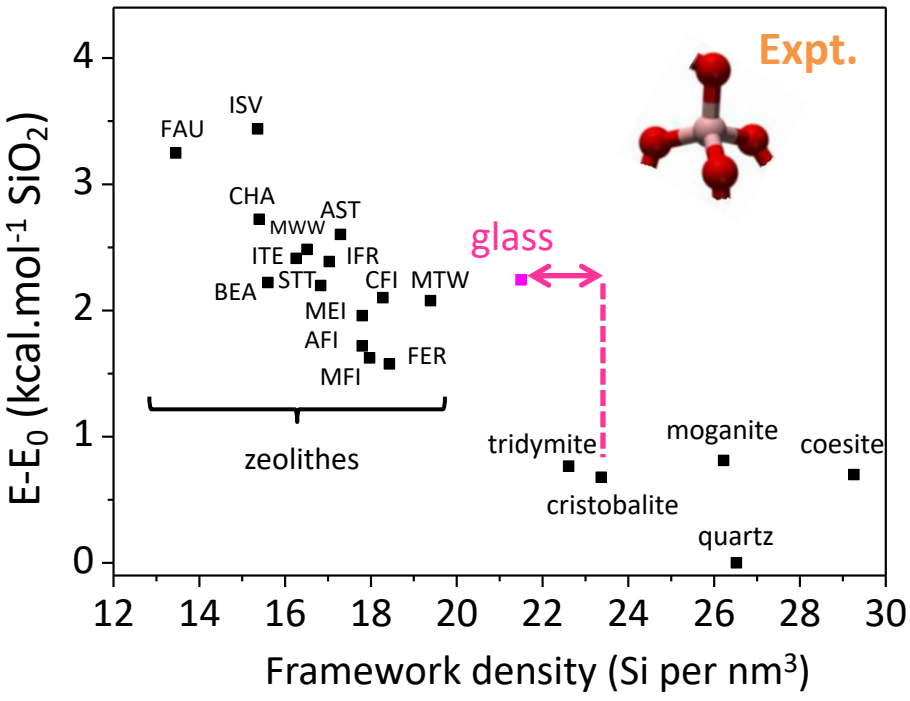



✓ $B_2O_3$ : - glass structure ~ crystals

~~$\rho_{glass} \sim 0.71\ \rho_{crystal}$~~ $\rho_{glass} \sim \rho_{crystal}$

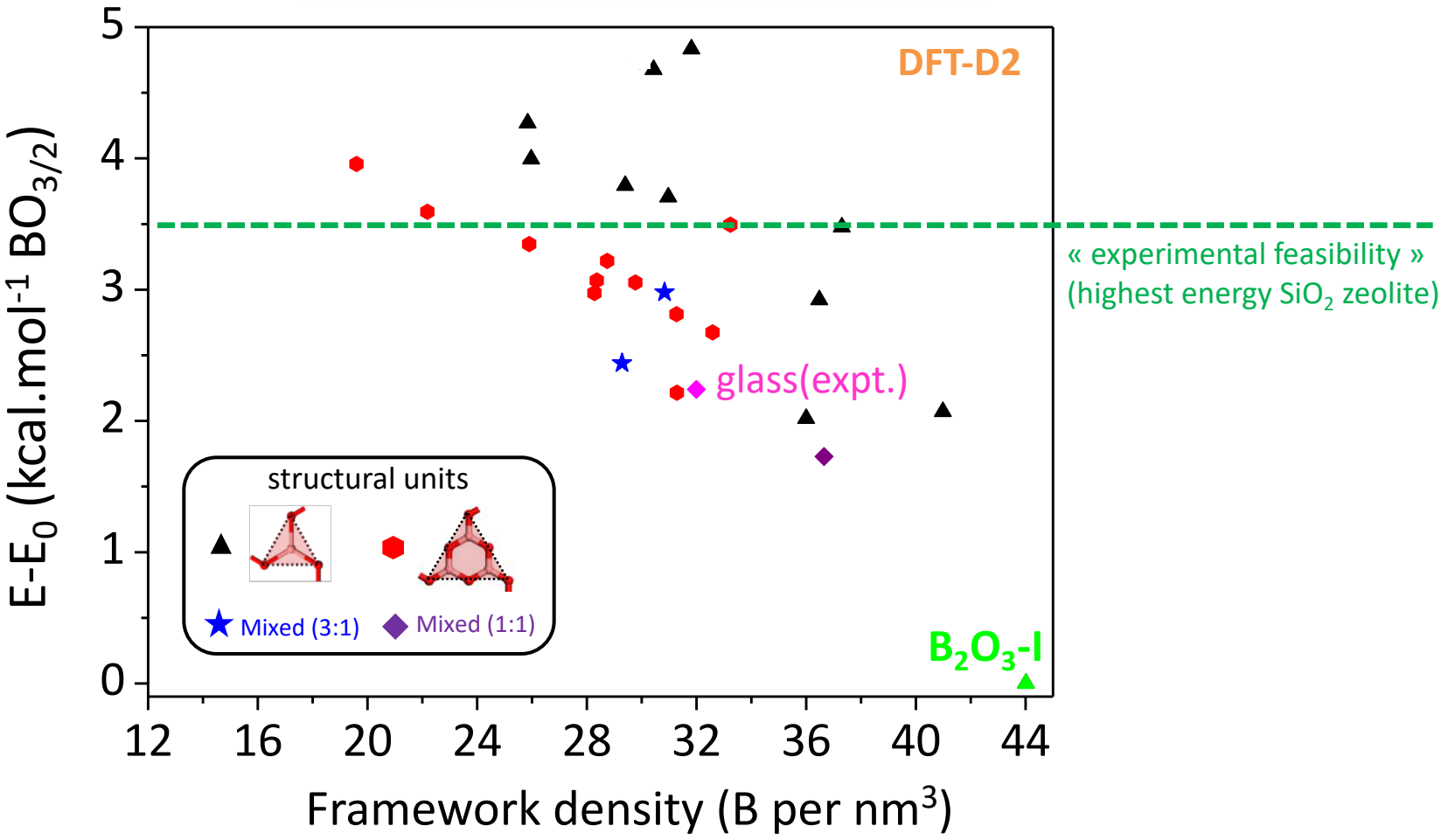
- ~~poor~~ rich polymorphism

✓ $SiO_2$ : - glass ~ cristobalite

- $\rho_{glass} \sim 0.92\ \rho_{cristobalite}$
- rich polymorphism

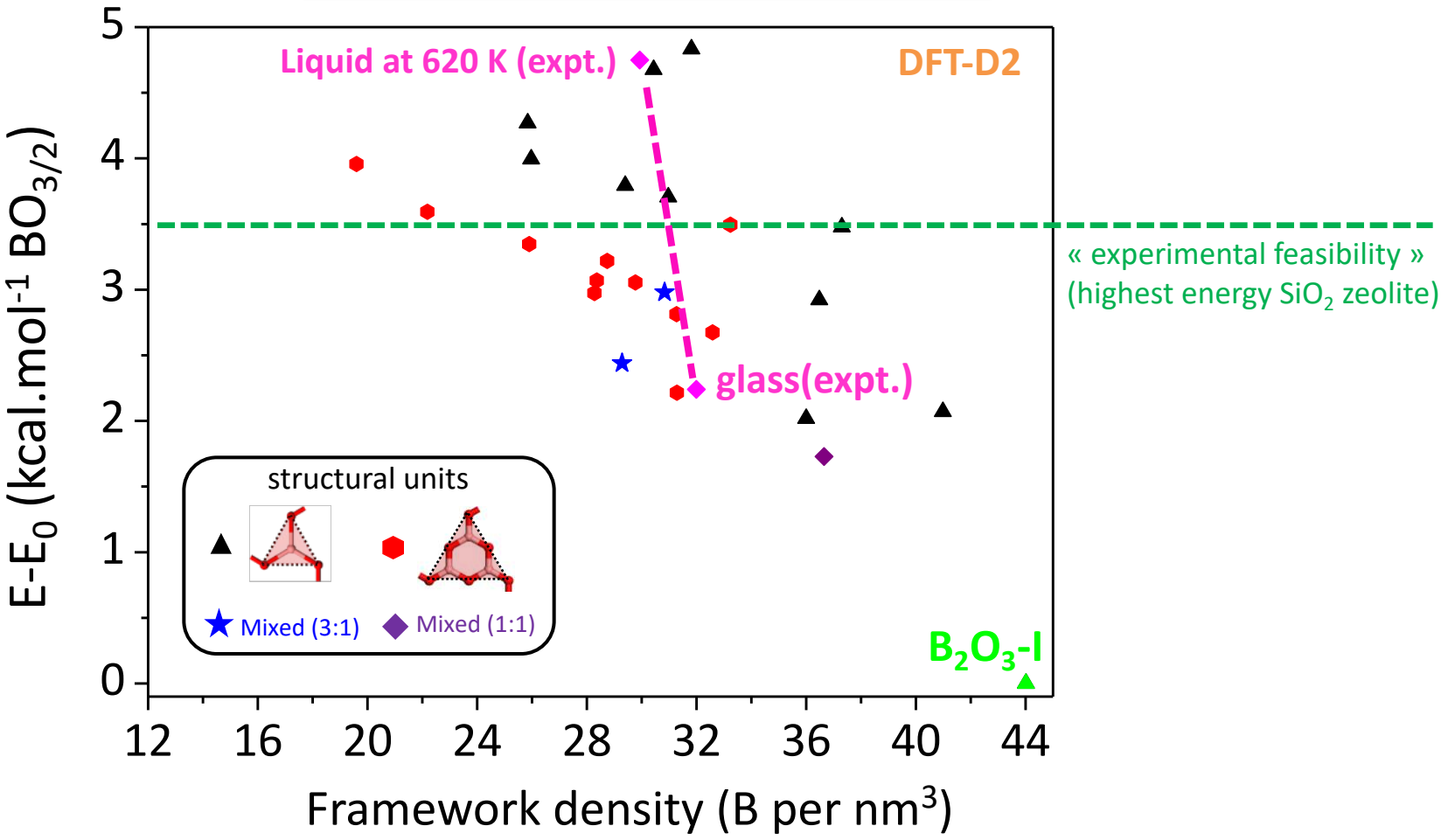
✓ New polymorphs more relevant (than $B_2O_3$-I) for understanding the glass properties

# $B_2O_3$ polymorphism: energy




✓ Most polymorphs in thermodynamically accessible energy range. Why not yet observed?

# $B_2O_3$ polymorphism: energy




- ✓ Most polymorphs in thermodynamically accessible energy range. Why not yet observed?
- ✓ Spontaneous vitrification (***crystallisation anomaly***) likely results from 2 factors:
  1) rich degeneracy of competing polymorphs (*rugged* energy landscape)
  2) poor mechanical strength [not shown in this talk]

# Take-home messages

- Prediction of 26 new $B_2O_3$ crystalline polymorphs of low-energy

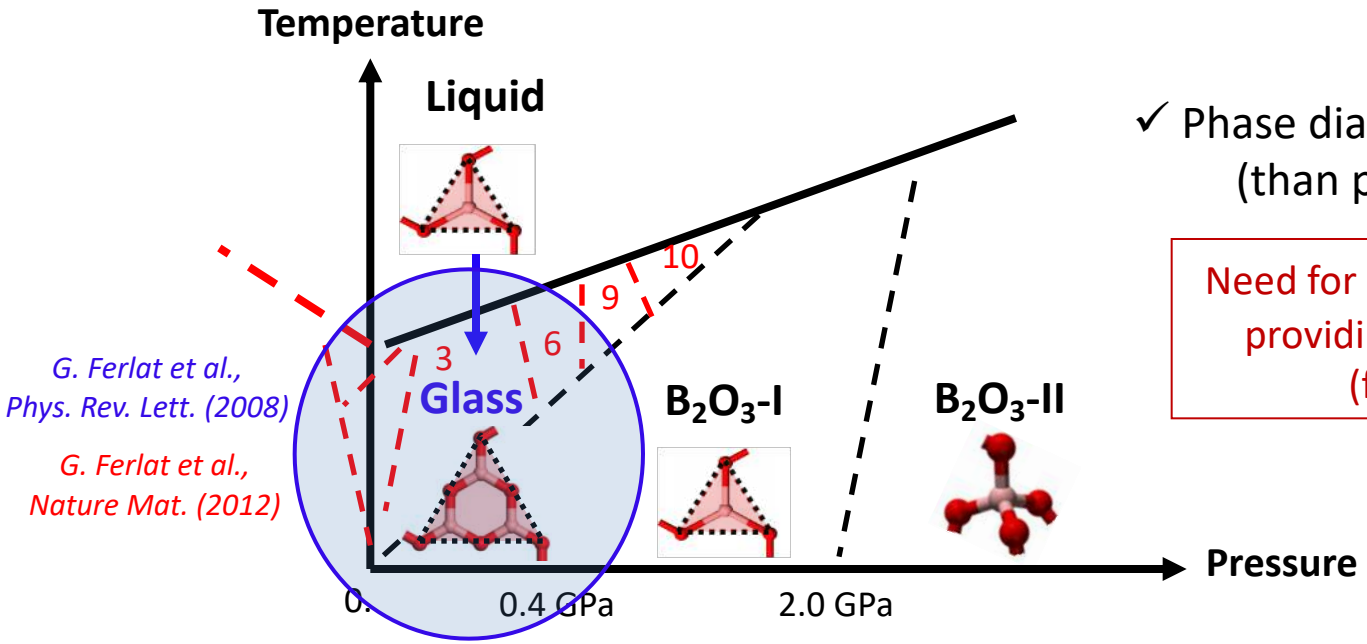
  Ferlat *et al.,* Nature Materials (2012)
  Ferlat, Hellgren, Coudert, Hay, Mauri, Casula, Phys. Rev. Materials (2019)

  → Data set used here to **benchmark DFT against RPA and QMC**

- $B_2O_3$: strong (iono-covalent) bonds, fully connected 3D networks. Yet, very significant effects of **vdW interactions**: qualitative (not only quantitative) changes. This is related to the flexibility of the bonds between units and to the existence of « soft » directions.

- **Challenging system** for DFT.

# Perspectives




*G. Ferlat et al., Phys. Rev. Lett. (2008)*

*G. Ferlat et al., Nature Mat. (2012)*

✓ Phase diagram could be much richer (than presently determined)

Need for an efficient atomistic method providing the transition pathways (free-energy barriers)

- parametrisation of $B_2O_3$ **accurate force-fields** from *ab-initio*:

  *Phys. Rev. B (2014), J. Phys. Condens. Matter (2015), J. Chem. Phys. (2019)*

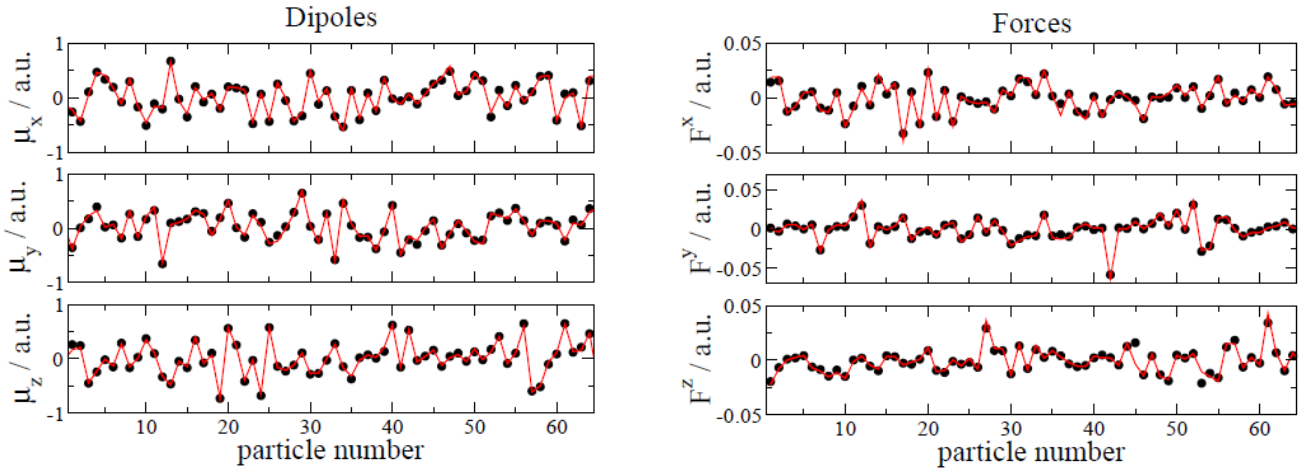
- ***enhanced sampling:***

  *Navigating at will on the water phase diagram, Phys. Rev. Lett (2017)*

*Collaboration: M. Salanne, F. Pietrucci (Sorbonne Université)*

# Polarisable force-fields from *first-principles*

- *First-principles* MD simulations (CPMD) used as benchmark trajectories
- Force- and dipole-matching approach to calibrate the force-field parameters




*CPMD – Fitted polarisable ion model*

*V* is an analytical function of the positions. It includes:

- electrostatics
- short-range repulsion
- dispersion
- polarisation

✓ Transferable parameters for a family of compounds

B. Rothenberg, M. Salanne, C. Simon, R. Vuilleumier *"From Localized Orbitals to Material Properties: Building Classical Force Fields for Nonmetallic Condensed Matter Systems",* Phys. Rev. Lett. **104**, 138301 (2010)

# Polarisable Ion Model (PIM)

✓ Pairwise additive components:

- Charge-charge interactions:

$$V_{\text{charge-charge}} = \sum_{i,j>i} \frac{q^i q^j}{r^{ij}}$$

- Short-range repulsion:

$$V_{\text{repulsion}} = \sum_{i,j>i} B^{ij} \exp(-a^{ij} r^{ij})$$

- Dispersion interactions:

$$V_{\text{dispersion}} = -\sum_{i,j>i} \left[ f_6^{ij}(r^{ij}) \frac{C_6^{ij}}{(r^{ij})^6} + f_8^{ij}(r^{ij}) \frac{C_8^{ij}}{(r^{ij})^8} \right]$$

✓ Polarisation component:

- Charge-dipole and dipole-dipole interactions

$$\begin{aligned} V_{\text{polarization}} = & \sum_{i,j>i} \left( q^i \mu_\alpha^j g_D^{ij}(r^{ij}) - q^j \mu_\alpha^i g_D^{ji}(r^{ij}) \right) \nabla_\alpha \frac{1}{r^{ij}} \\ & \sum_{i,j>i} -\mu_\alpha^i \mu_\beta^j \nabla_\alpha \nabla_\beta \frac{1}{r^{ij}} \\ & + \sum_i \frac{1}{2\alpha^i} \mid \vec{\mu}^i \mid^2 \end{aligned}$$

$\vec{\mu}^i$ are the induced dipoles $\longrightarrow$ Additional degrees of freedom

- Self-consistent calculation of $\vec{\mu}^i$ by conjugate gradients

# Aspherical Ion Model (AIM)

Modified repulsion term:

$$V^{\mathrm{rep}} = \sum_{j>i} \left( A^{ij} \mathrm{e}^{-a^{ij}\rho^{ij}} + B^{ij} \mathrm{e}^{-b^{ij}\rho^{ij}} + C^{ij} \mathrm{e}^{-c^{ij} r^{ij}} \right) \tag{1}$$

$$+ \sum_{i \in \mathrm{O}} \left[ D^i (\mathrm{e}^{\beta^i \delta\sigma^i} + \mathrm{e}^{-\beta^i \delta\sigma^i}) + (\mathrm{e}^{\zeta^i |\nu^i|^2} - 1) + (\mathrm{e}^{\eta^i |\kappa^i|^2} - 1) \right]$$

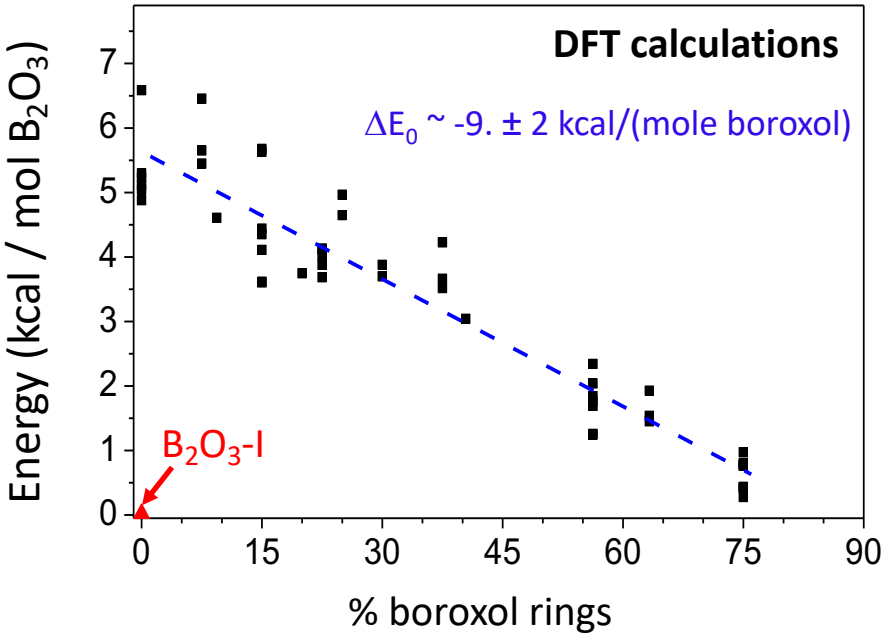
$$\rho^{ij} = r^{ij} - \delta\sigma^i - S^{(1)}_{\alpha} \nu^i_{\alpha} - S^{(2)}_{\alpha\beta} \kappa^i_{\alpha\beta} \tag{2}$$

Additional degrees of freedom (SCF calculation):

- $\delta\sigma^i$: "Breathing" of the ion
- $\nu^i_{\alpha}$: Dipolar distorsion of the ion
- $\kappa^i_{\alpha\beta}$: Quadrupolar distorsion of the ion

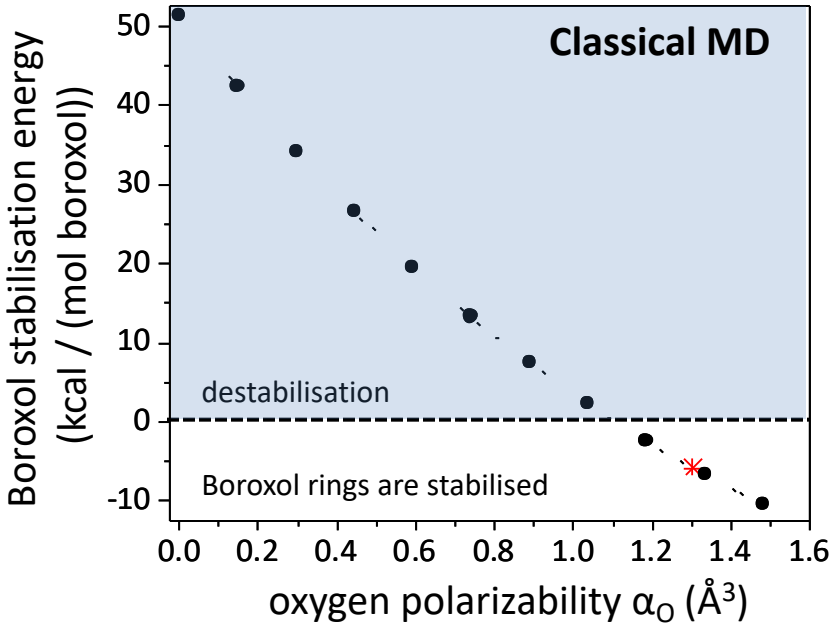
# Boroxol stabilisation energy

**Relaxation at 0 K of *glassy* configurations**




Phys. Rev. Letters, **101**, 065504 (2008)

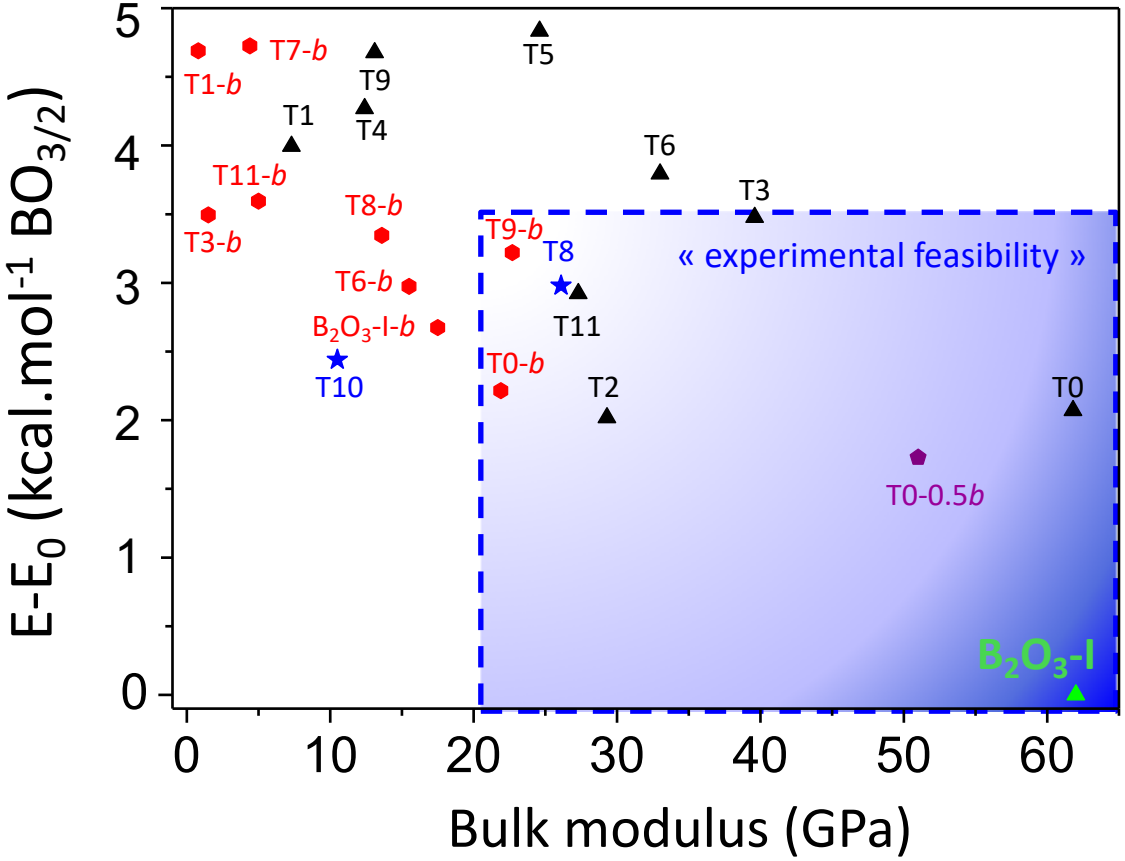
**Polarizability in classical force-fields**




J. Chem. Phys., **151**, 224508 (2019)

# $B_2O_3$ polymorphism: mechanical properties

**Computation of bulk (B), shear (E) and Young (Y) moduli**




- ✓ New polymorphs are mechanichally much “weaker” than $B_2O_3$-I
- ✓ Prone to “collapse”. Reason for not being observed ?
  Part of the *crystallisation anomaly* explanation ?
  [applying pressure favours higher density and stiffer structures → $B_2O_3$-I ]

# $B_2O_3$ polymorphism: mechanical properties

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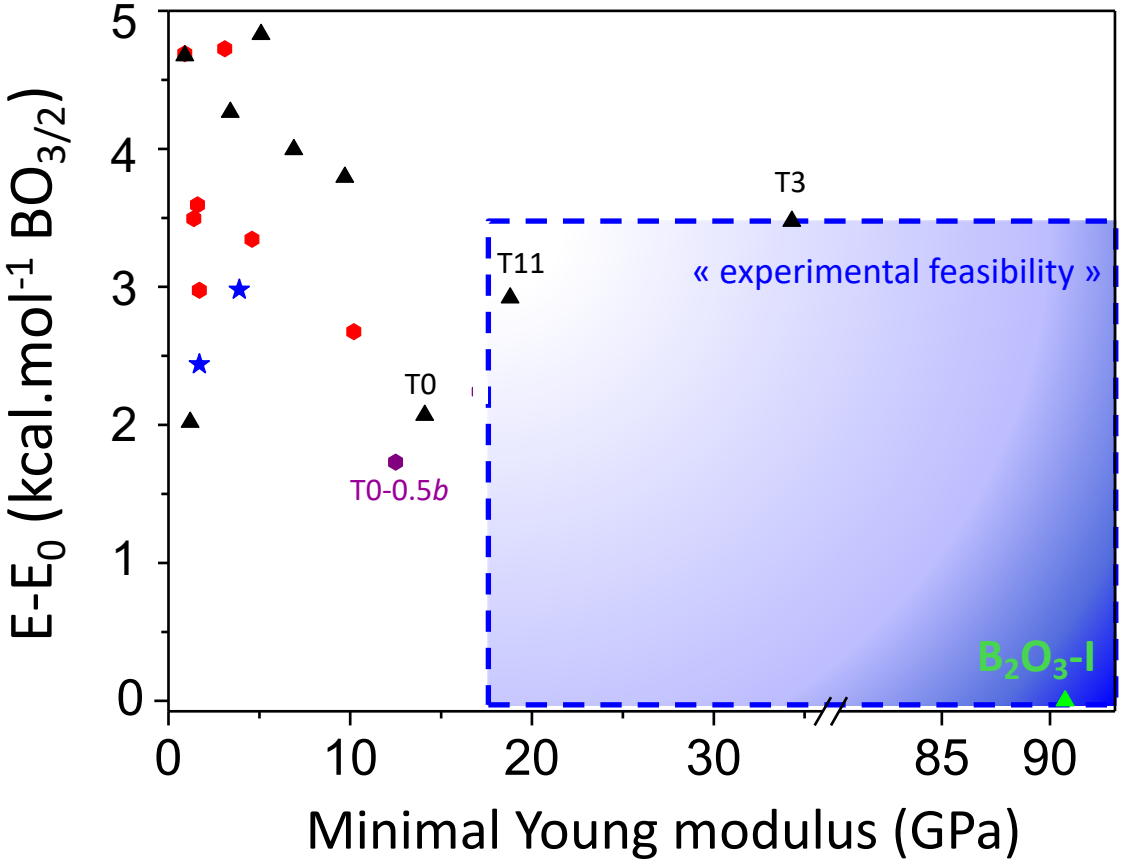


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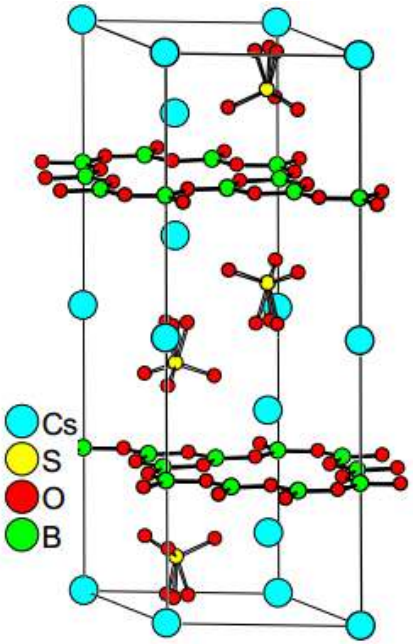
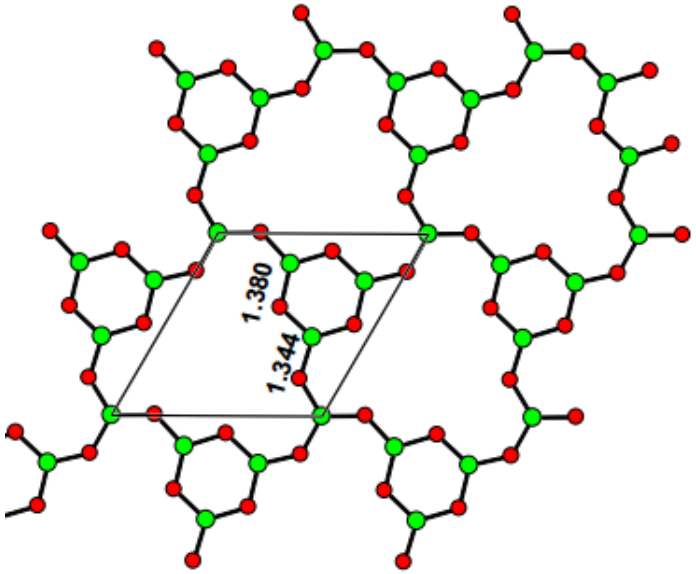
  Part of the *crystallisation anomaly* explanation ?
  [applying pressure favours higher density and stiffer structures → $B_2O_3$-I ]

# Hints for synthesis?
# $B_2O_3$ layers in borates

Experiment from H. Hillebrecht *et al.* (Eur. J. Inorg. Chem. 2015)




$Cs_3H(SO_4)_2$-$2B_2O_3$

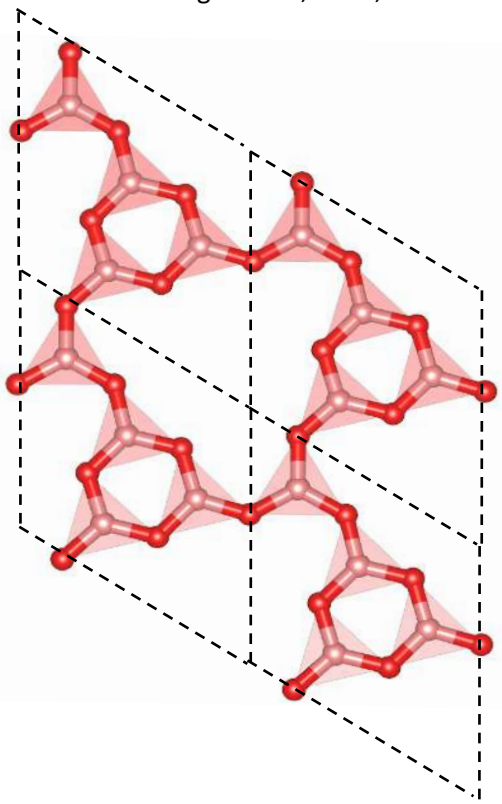



The $B_2O_3$ layer in $Cs_3H(SO_4)_2$-$2B_2O_3$

Could a pure $B_2O_3$ phase obtained from deintercalation?

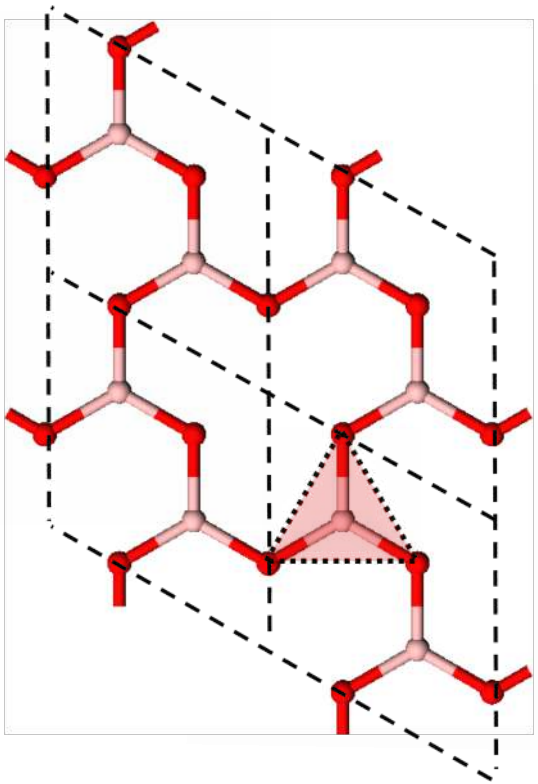
# $B_2O_3$ layered polymorphs

Built upon M. Daub, H. Hillebrecht,
Eur. J. Inorg. Chem., **2015**, 4176



# $B_2O_3$ layered polymorphs

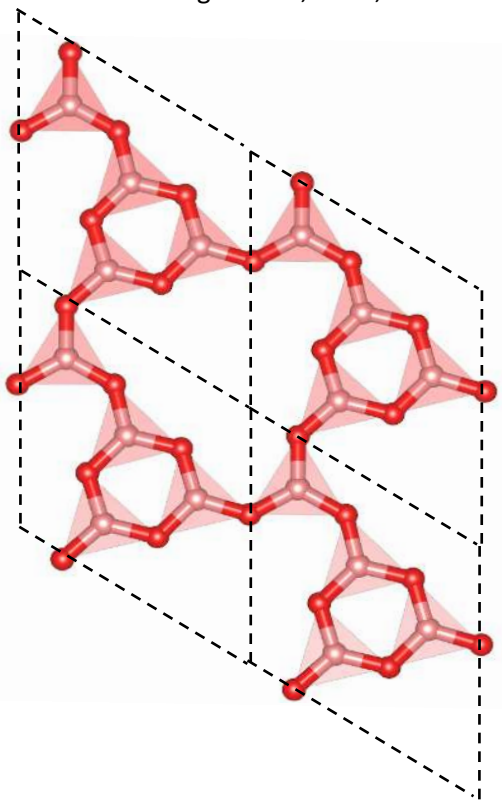
**T0**



Motif: triangle

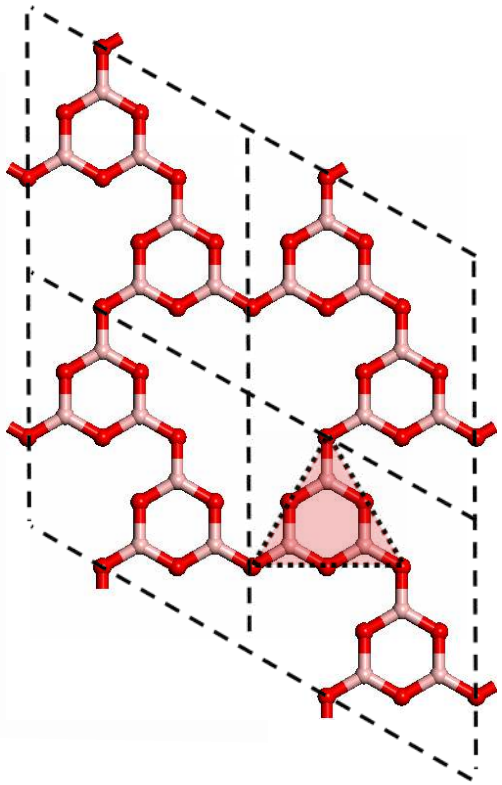
**T0-0.5*b***

Built upon M. Daub, H. Hillebrecht, Eur. J. Inorg. Chem., **2015**, 4176



Motif: triangle and boroxol

**T0-*b***



Motif: boroxol

*Calculations: lowest energy !*

# Experimental realisations of other $B_2O_3$ polymorphs?

- There are at least two reports of low-density crystals (incorrectly assigned as $B_2O_3$-I):

✓ S. S. Cole, N. W. Taylor, J. Am. Ceram. Soc., **18**, 55 (1935) : $\rho$= 1.805 g.cm$^{-3}$

✓ S. Kocakusak *et al.*, Chem. Eng. Proc. **35**, 311 (1996) : $\rho$= 0.69 g.cm$^{-3}$ !

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Chemical Engineering and Processing 35 (1996) 311–317

Chemical Engineering and Processing

Production of anhydrous, crystalline boron oxide in fluidized bed reactor

S. Kocakuşak, K. Akçay, T. Ayok, H.J. Köroğlu, M. Koral, Ö.T. Savaşçi, R. Tolun

*Tübitak–Marmara Research Center, Chemical Engineering Department, P.O Box 21, 41470, Gebze/Kocaeli, Turkey*

Received 21 September 1995; accepted 28 November 1995

**Abstract**

Industrial production of boron oxide is via fusion of boric acid at 550–1000 °C. The glassy melt thus obtained is then cooled until solid; crushed, ground and then sieved to allow classification according to particle size and distribution. The melting of boric acid is both the most critical and costly stage of all these operations, because boron oxide is highly corrosive to refractories and steel.

Our study allows the production of commercial quality anhydrous and crystalline boron oxide without the melting and other processes mentioned above. This is achieved by dehydrating boric acid in a fluidized bed with a gradual increase in the bed temperature up to 250 °C. During this process as the bed temperature is increased gradually, particular attention is paid to keep the dehydration rate below a certain value to prevent melting or sticking, and to secure the desired bulk density value of the product.

- Chemical synthesis, using Chemical Vapor Deposition (CVD) techniques: MOCVD, Atomic Layer Deposition (ALD) , ...

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Physica E 27 (2005) 319–324

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Crystalline boron oxide nanowires on silicon substrate

Qing Yang[a], Jian Sha[b], Lei Wang[a], Yu Zou[a], Junjie Niu[a], Can Cui[a], Deren Yang[a,*]

[a]*State Key Laboratory of Silicon Materials, Zhejiang University, 20 Yu Gu Road, Hangzhou 310027, People's Republic of China*
[b]*Department of Physics, Zhejiang University, 20 Yu Gu Road, Hangzhou 310027, People's Republic of China*

Received 26 November 2004; accepted 20 December 2004

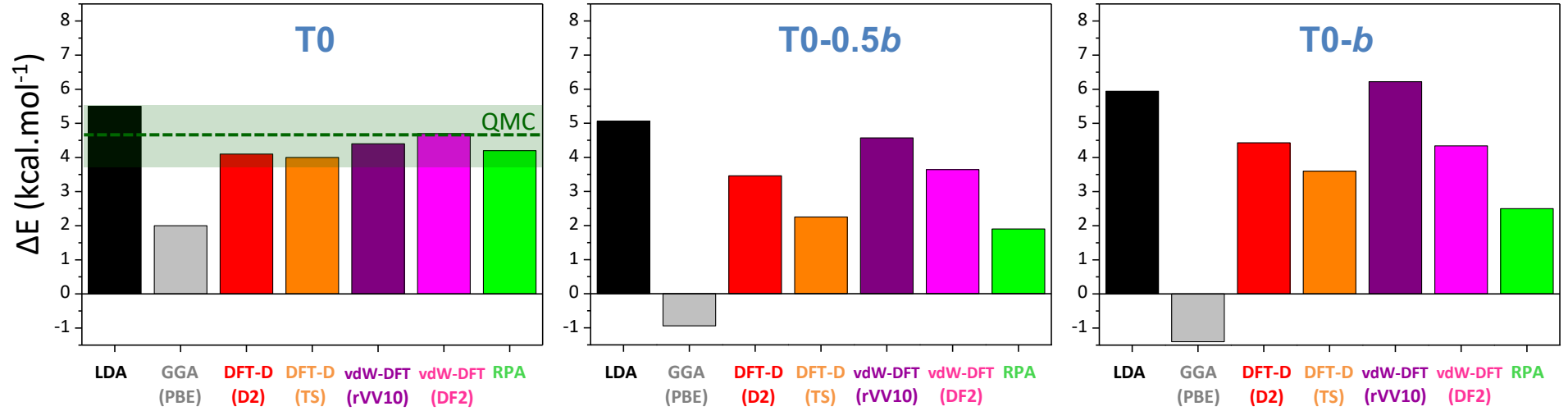
**Abstract**

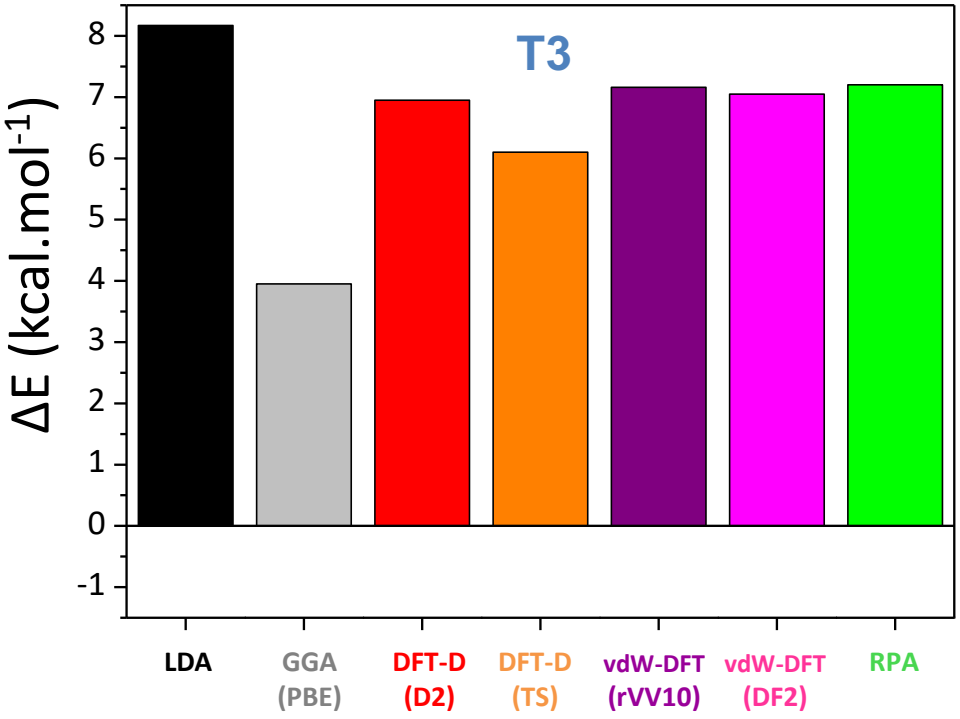
Crystalline boron oxide nanowires have been synthesized on silicon substrates by chemical vapor deposition (CVD) process without the use of catalysts or templates. It is pointed out that the boron oxide nanowires are cubic and single crystalline, and the diameter of the nanowires is in the range of 20–80 nm. Some of the nanowires branched, and the diameters of the branches and stems of the branched boron oxide nanowires are in the range of 20–80 and 100–200 nm, respectively. The crystallinity, morphology, and structure features of the as-prepared boron oxide nanowires were investigated by field emission scanning electron microscopy, X-ray diffraction, transmission electron microscopy, and selected area electron diffraction. Furthermore, Raman spectrum and Fourier transform infrared spectroscopy of the nanowires were also investigated.

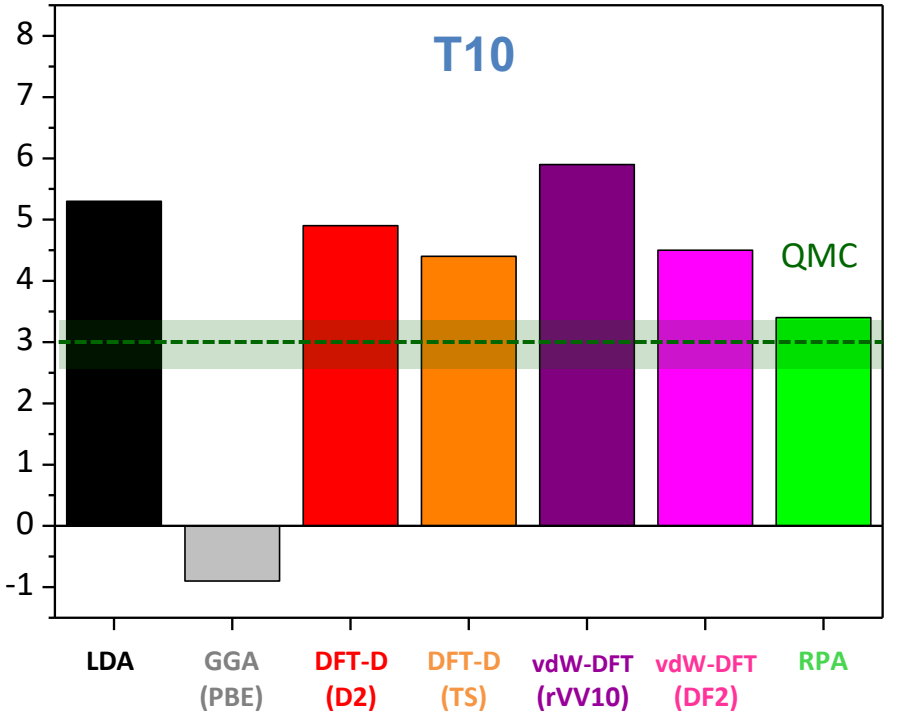
✓ cubic phase? That originally seen in J. Am. Ceram. Soc., **18**, 55 (1935)?

$\rho$= 1.805 g.cm$^{-3}$

# Benchmarking DFT: energy

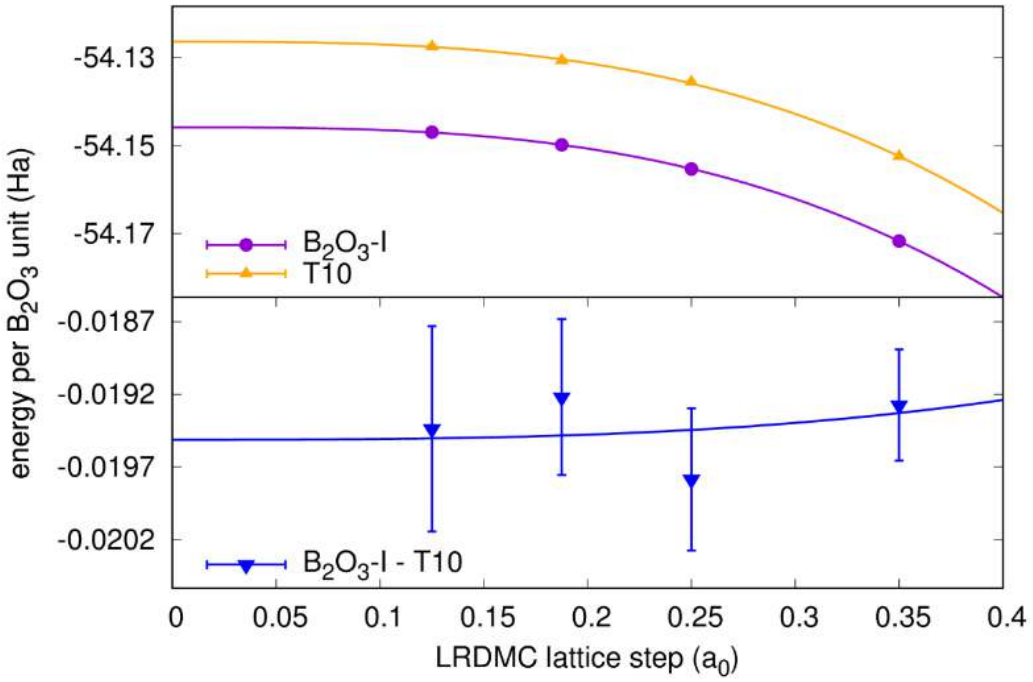


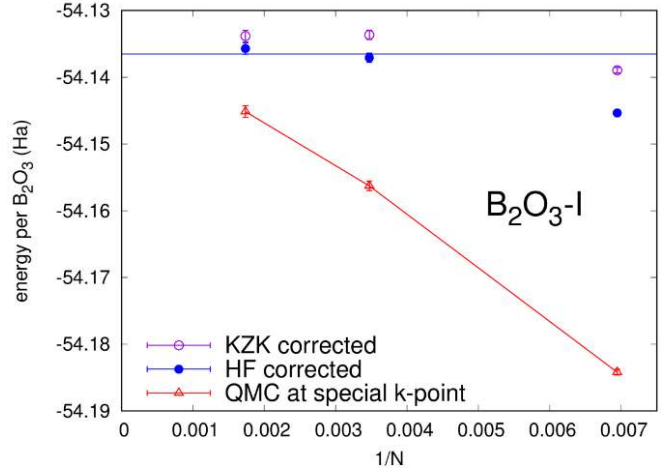



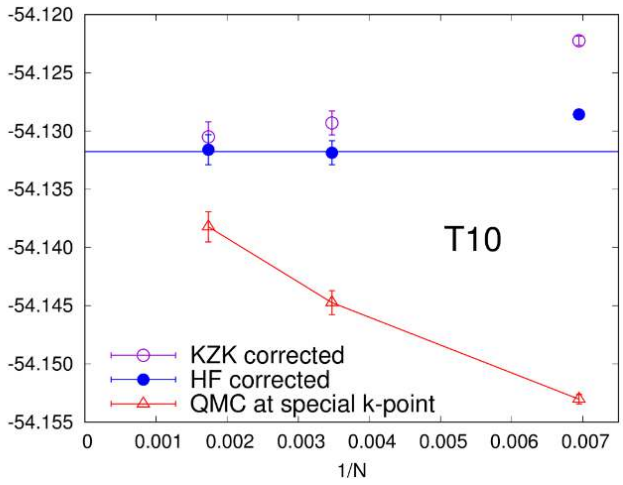



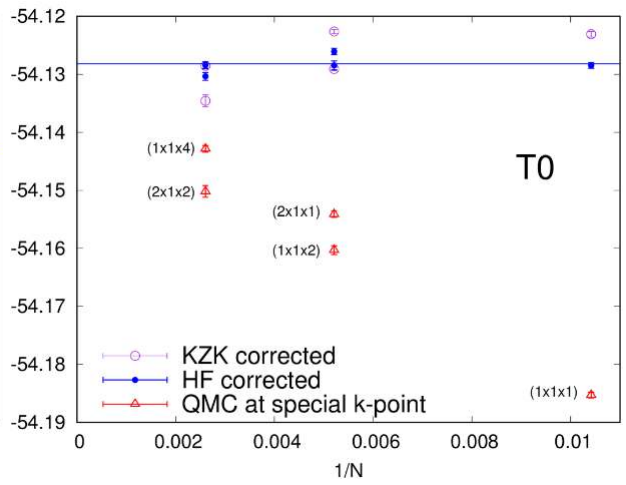
| | LDA | PBE | HSE06 | PBE+D2 | PBE+TS | rVV10 | DF2 | RPA | QMC |
|---|---|---|---|---|---|---|---|---|---|
| T0 | 5.5 | 2.0 | 2.1 | 4.1 | 4.0 | 4.5 | 4.7 | 4.2 | 4.7 ± 0.9 |
| T0-0.5$b$ | 5.1 | -0.9 | -1.4 | 3.5 | 2.2 | 4.6 | 3.6 | 1.9 | |
| T0-$b$ | 5.9 | -1.4 | | 4.4 | 3.6 | 6.2 | 4.3 | 2.5 | |
| T3 | 8.2 | 3.9 | | 7.0 | 6.1 | 7.2 | 7.0 | 7.2 | |
| T10 | 5.3 | -0.9 | -0.9 | 4.9 | 4.4 | 5.9 | 4.5 | 3.4 | 3.0 ± 0.4 |

| | LDA | PBE | PBE+D2 | PBE+TS | DF2 | DF-cx | RPA | QMC |
|---|---|---|---|---|---|---|---|---|
| T0 | 5.5 | 2.0 | 4.1 | 4.0 | 4.7 | 4.6 | 4.2 | 4.7 ± 0.9 |
| T0-0.5$b$ | 5.1 | -0.9 | 3.5 | 2.2 | 3.7 | 3.5 | 1.9 | - |
| T0-$b$ | 5.9 | -1.4 | 4.4 | 3.6 | 4.3 | 4.4 | 2.5 | - |
| T3 | 8.2 | 3.9 | 7.0 | 6.1 | 7.0 | 6.9 | 7.2 | - |
| T10 | 5.3 | -0.9 | 4.9 | 4.4 | 4.5 | 4.9 | 3.4 | 3.0 ± 0.4 |

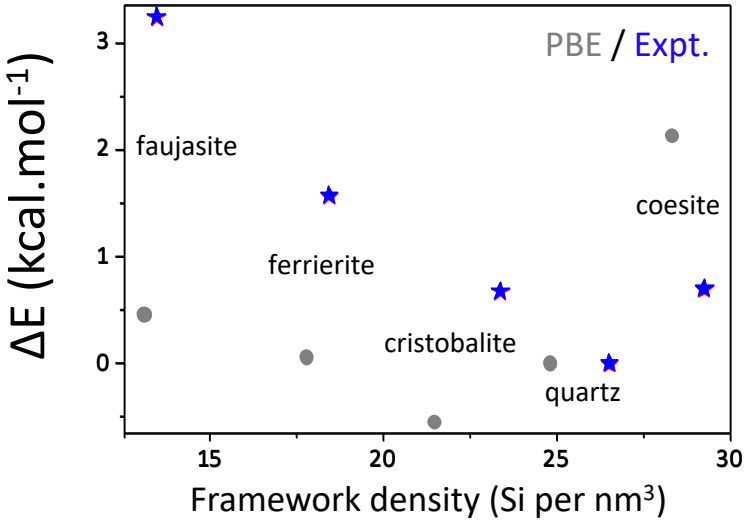

energy per $B_2O_3$ unit (Ha)
-54.13
-54.15
-54.17
$B_2O_3$-I
T10
-0.0187
-0.0192
-0.0197
-0.0202
$B_2O_3$-I - T10
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
LRDMC lattice step ($a_0$)

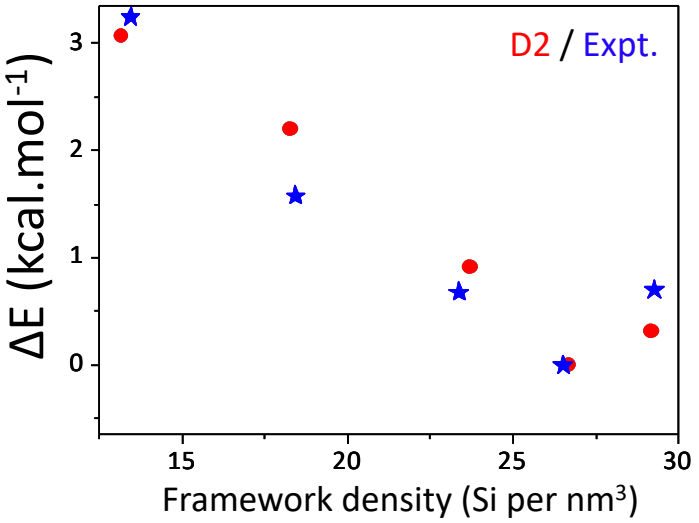

energy per $B_2O_3$ (Ha)
$B_2O_3$-I
KZK corrected
HF corrected
QMC at special k-point
1/N

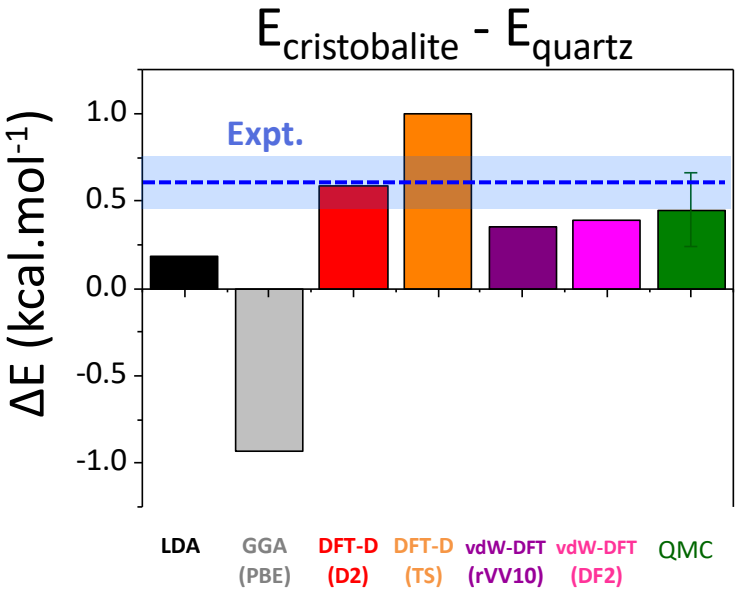

T10
KZK corrected
HF corrected
QMC at special k-point
1/N


T0
(1x1x4)
(2x1x2)
(2x1x1)
(1x1x2)
(1x1x1)
KZK corrected
HF corrected
QMC at special k-point
1/N

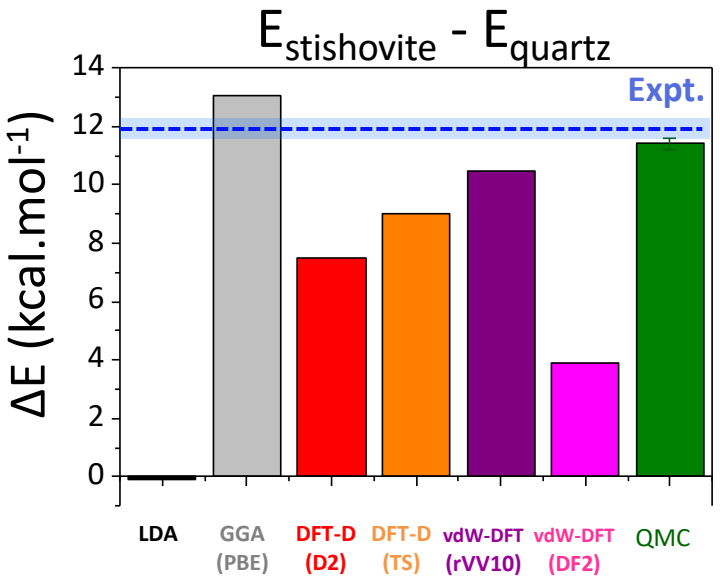
# Energy of $SiO_2$ polymorphs



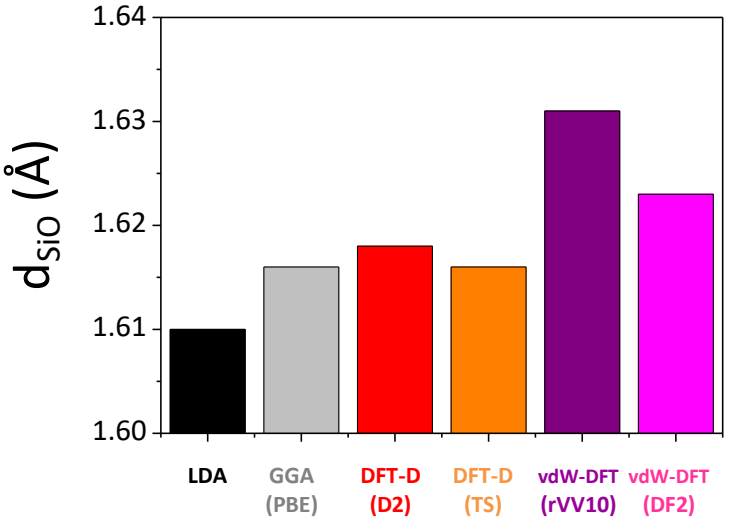

[PBE very bad]

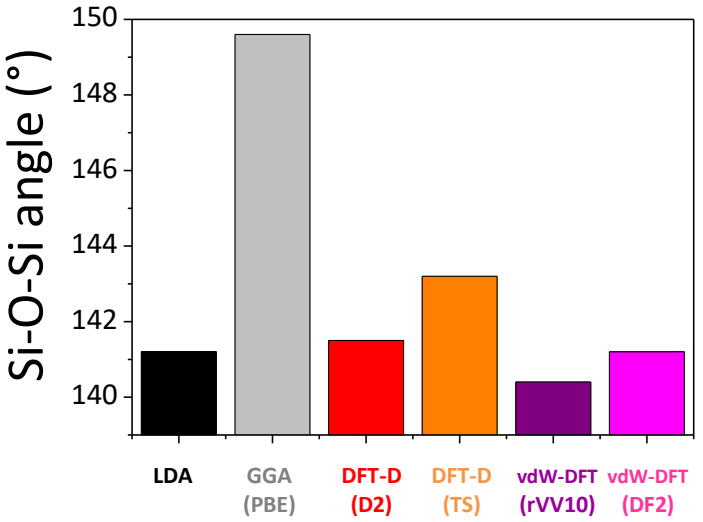



[PBE quite good]

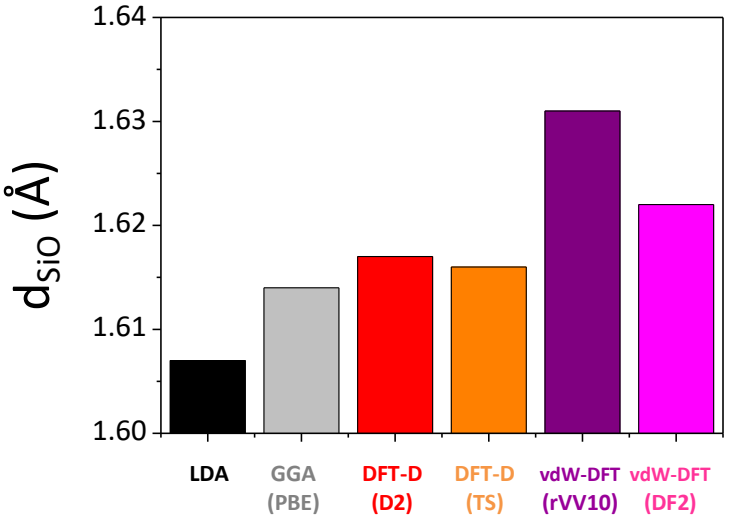
# Structure of $SiO_2$ polymorphs

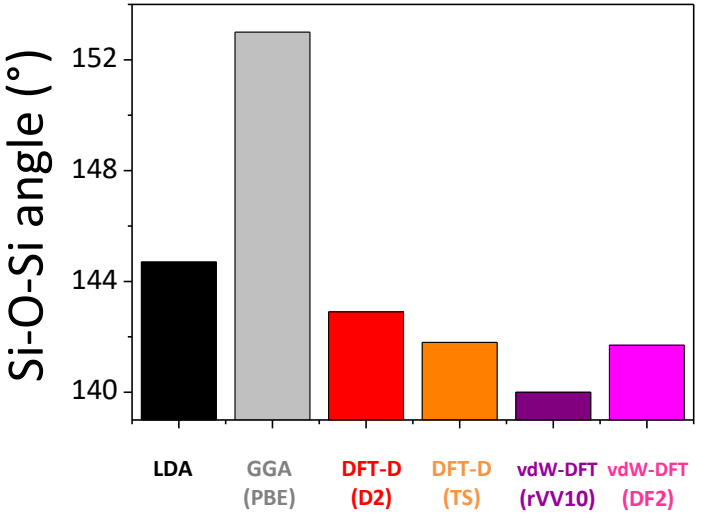
## quartz




## cristobalite



# DFT relaxation: details

| | |
|---|---|
| General framework | • Density Functional Theory (DFT)<br>• Exchange-correlation: GGA (PBE)<br>• Pseudo-potentials (PP) |

**Aim:** for each topology, we want to determine the lowest-energy minimum

- Preliminary *first-principles* **Molecular Dynamics** at 500 K (*Siesta* code):
  DZP basis, Born-Oppenheimer, Trouiller-Martins PP, real-space grid 600 Ry

- **Relaxations (T = 0 K)** of positions and unit cell (*CASTEP* code):
  PW basis set: 60 Ry, Ultra-soft PP, *k*-points grid $\leq 0.05$ Å$^{-1}$

- For some networks, several local minima were observed
  (compressing/decompressing the obtained structures helped to found better geometries)

- Vibrational contribution: $E_{vib} = \sum_i \frac{\hbar\omega_i}{2}$ Zero-point energy

$$F_{vib} = k_B T \sum_i \ln\left[2\sinh\left(\frac{\hbar\omega_i}{k_B T}\right)\right]$$ Free-energy

Vibrational contribution negligible at T = 0 K (< 0.5 kcal/mol), small at T ~ $T_g$ (~ 1 kcal/mol)

→ contribution not included in the following

There is no *crystallization anomaly* !

**Review:**

*Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B*, April 2018, 59 (2), 65–87

# The structural chemistry of $B_2O_3$

*Adrian C. Wright**

*J.J. Thomson Physical Laboratory, University of Reading, Whiteknights, Reading, RG6 6AF, UK*

*The structural chemistry of $B_2O_3$ has been the subject of considerable controversy in the literature, especially in the case of the vitreous phase. A brief review is presented as to the present state of knowledge concerning the structures of crystalline, liquid and vitreous $B_2O_3$, and it is demonstrated that the key to the structural chemistry of $B_2O_3$ lies in understanding that of the liquid state, which is dominated by the equilibrium reaction between $B_3O_3Ø_3$ boroxol groups and independent $BØ_3$ basic structural units (i.e. those not in boroxol groups): $B_3O_3Ø_3 \rightleftharpoons 3BØ_3$. The failure of the low pressure polymorph, $B_2O_3$-I, to form, either by crystallisation from the supercooled liquid at ambient pressure, or on devitrification of vitreous $B_2O_3$, is due to the high activation energy involved both in the break-up of boroxol groups and as a result of the large difference in number density between the crystal and supercooled liquid/glass. SAXS studies of vitreous and supercooled liquid $B_2O_3$ by V. V. Golubkov indicate that, in addition to the scattering due to thermal density fluctuations, there is extra small-Q scattering, centred at Q=0, arising from regions of inhomogeneity ~15 Å in size. These disappear for $B_2O_3$ equilibriated at temperatures below 240°C, and are interpreted as being linked with the above equilibrium reaction. The fact that the time scale for establishing the equilibrium boroxol fraction, $x_B$, in the supercooled liquid state is very much longer than that associated with the thermal density fluctuations means that the structural rearrangements during quenching to the vitreous state are more complex than for $SiO_2$, thus explaining the wide range of glass transition temperatures, $T_g$, and number densities, $\rho°$, reported in the literature for vitreous $B_2O_3$. Golubkov's SAXS data also mitigate against a two-phase nanoheterogeneous structure for vitreous $B_2O_3$, based on nanodomains rich in either boroxol groups or independent $BØ_3$ triangles. Contrary to conventional wisdom, it is indeed possible to crystallise $B_2O_3$ from the supercooled liquid just above $T_g$. However, this takes considerable time, and the resulting long forgotten polymorph is **not** $B_2O_3$-I, but one that has an average number density within the range of that exhibited by the glass, and which almost certainly has a structure that includes boroxol groups.*

# There is no *crystallization anomaly* !

*Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B*, April 2018, 59 (2), 65–87

## Review:

## The structural chemistry of $B_2O_3$

*Adrian C. Wright**

*J.J. Thomson Physical Laboratory, University of Reading, Whiteknights, Reading, RG6 6AF, UK*

✓ S. S. Cole, N. W. Taylor, J. Am. Ceram. Soc., **18**, 55 (1935)

$\rho$= 1.805 g.cm$^{-3}$

crystal structure analysis. Even if their x-ray analysis is incorrect, the fact remains that they succeeded in preparing a crystalline $B_2O_3$ polymorph with an average number density within the range exhibited by vitreous $B_2O_3$.

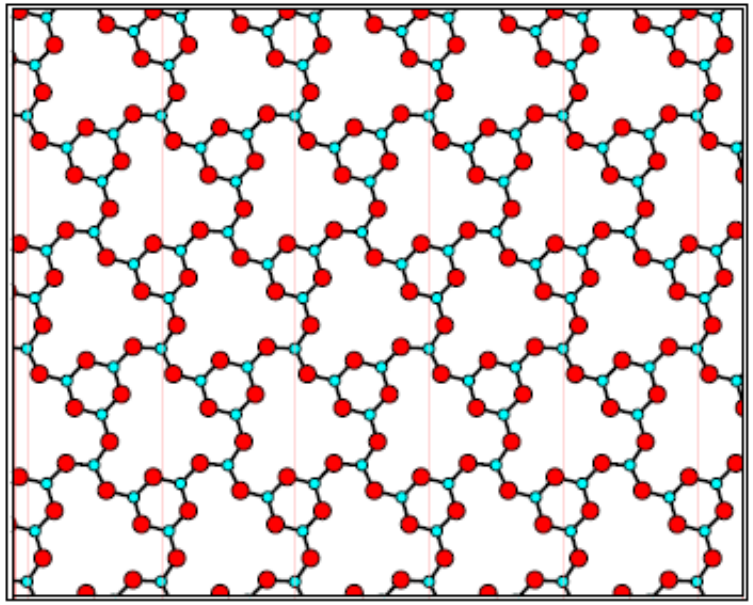
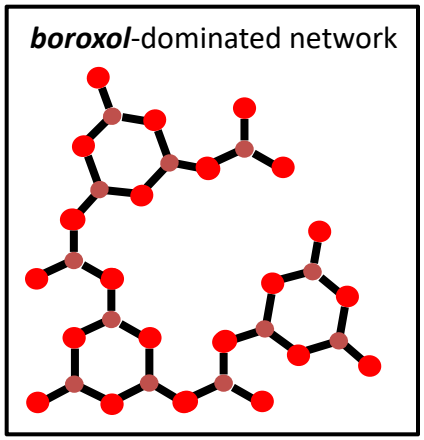
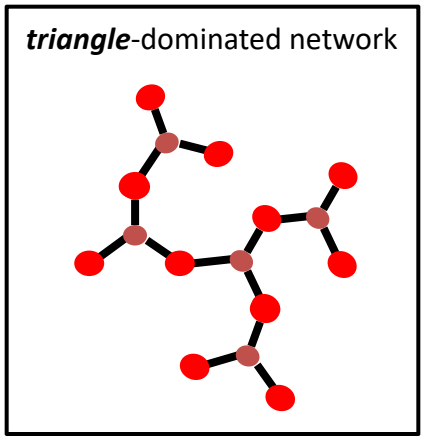


*Figure 17. A two-dimensional crystalline layer formed from alternate boroxol groups and independent $BØ_3$ triangles (Key as Figure 2) [Colour available online]*

# Medium-range order in v-$B_2O_3$

## The *boroxol dispute* (30s to 2008)



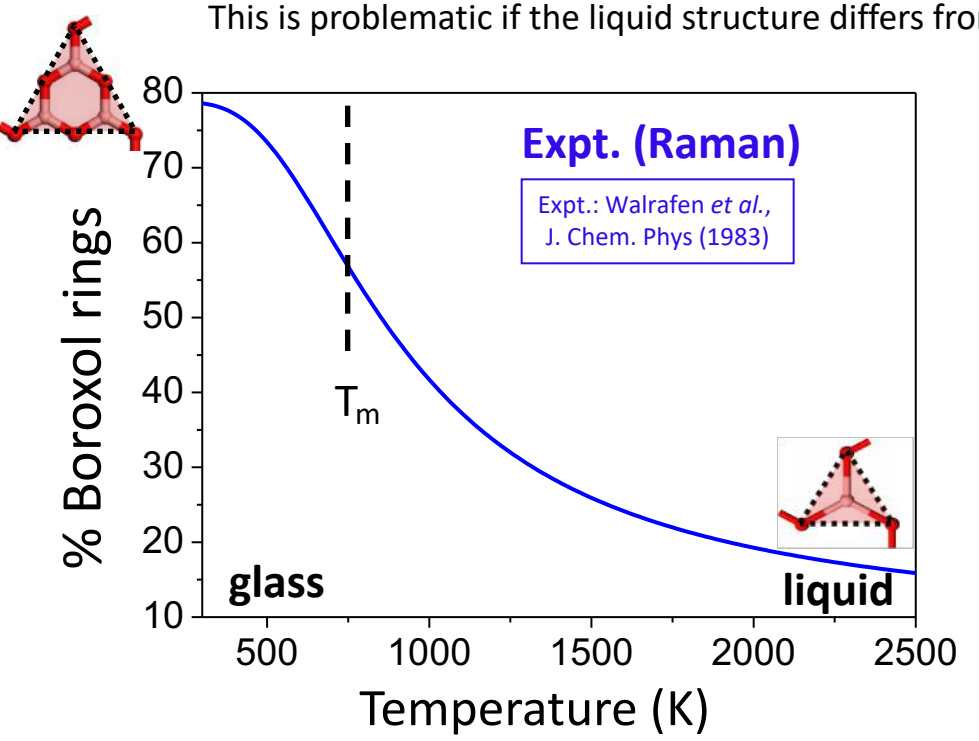

**Fraction of (boron atoms in) boroxol rings:**

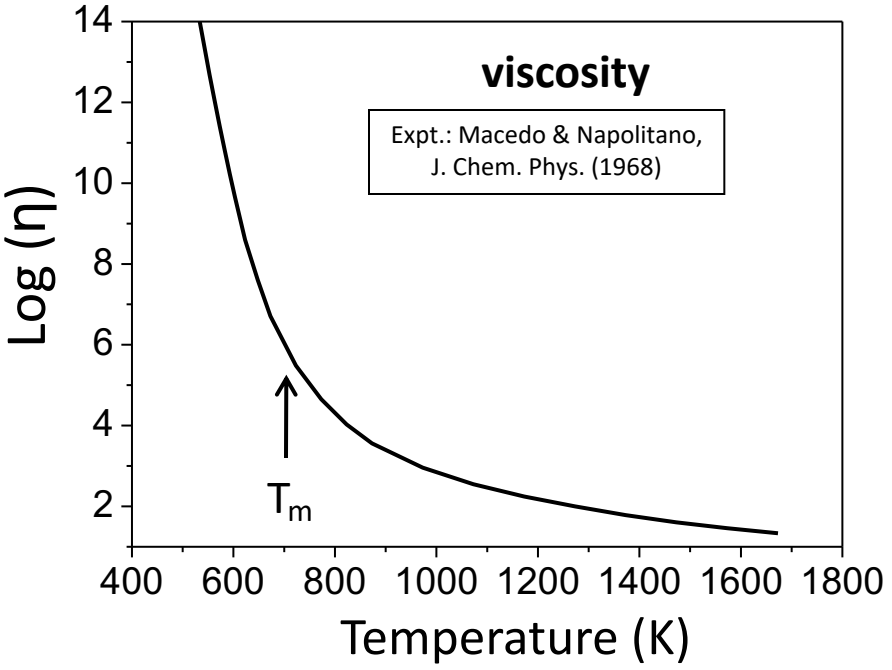
Some XRD/ND interpretations: 60-85 %
Raman: 64-79 %
NMR, NQR: ~ 75-85 %
INS: ~ 75 %
Statistical model: ~ 80 %

Some XRD/ND (or IR) interpretations: 0 %
RMC (XRD, ND): < 30 %
MD (2-body potentials): 0 %
MD (3-, 4-body or polarisable): < 30 %
FPMD (from quenched melts): 9 - 22%

# Glass ←→ liquid $B_2O_3$
# MD simulations: a timescale problem

(Brute-force) MD simulations produce glasses from liquid at a much **too fast** quenching rate (> $10^{11}$ K/s).
This is problematic if the liquid structure differs from that of the glass ($B_2O_3$!)



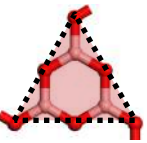

✓ Structural changes occur for T < 1500 K (concomitant with huge viscosity increase)

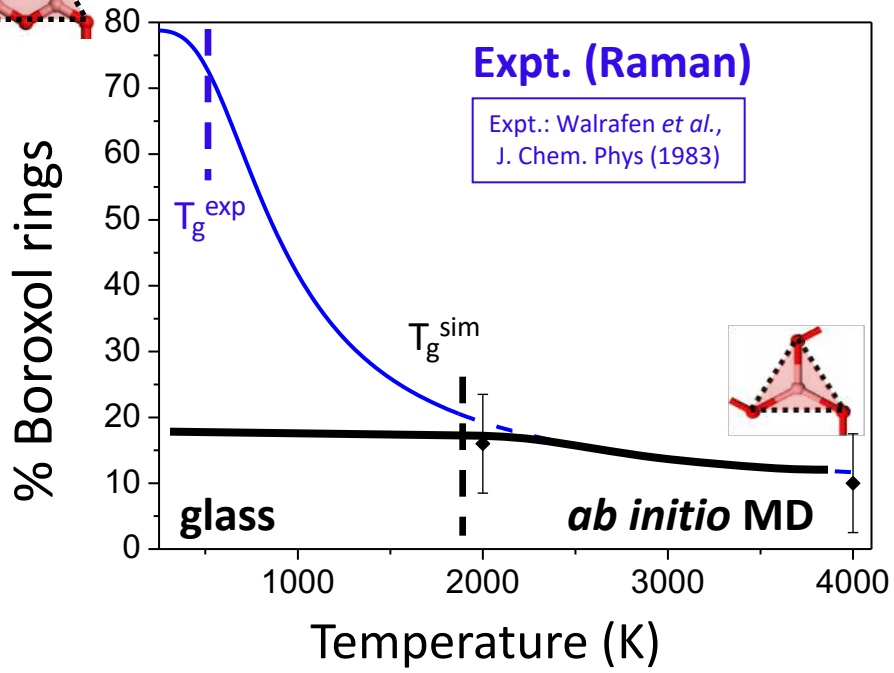
+ small *driving force* (stabilisation energy of boroxol ring: $\Delta E \approx -4$ *kcal/mol*)

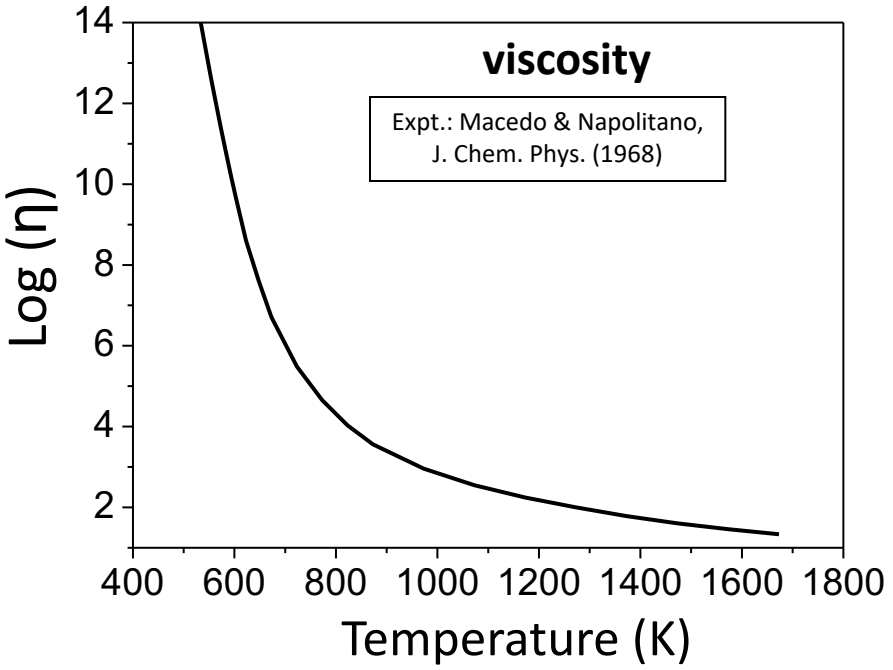
Numerically, these structural changes are extremely **challenging** to reproduce
(dynamics much too slow given the available simulation time)

# Glass ←→ liquid $B_2O_3$
# MD simulations: a timescale problem

(Brute-force) MD simulations produce glasses from liquid at a much **too fast** quenching rate (> $10^{11}$ K/s).
This is problematic if the liquid structure differs from that of the glass ($B_2O_3$!)





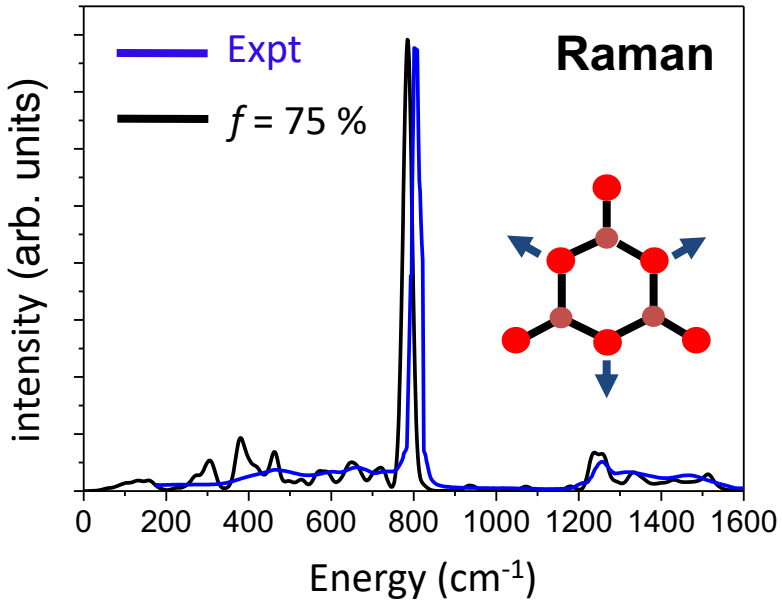

conventional numerical quench ➡ *Cannot follow the structural rearrangement*

# Our previous works (summary)

*G. Ferlat, T. Charpentier, A.P. Seitsonen, A. Takada, M. Lazzeri, L. Cormier, G. Calas, F. Mauri, Phys. Rev. Lett., **101**, 065504 (2008)*

From *first-principles* (DFT) calculations:

- **liquid: dominated by triangles**
- **glass: dominated by boroxol rings (~ 65–75 %)**
- Reconciliation of numerical models with expts (diffraction, Raman, NMR)
- Previous underestimated values were due to methodological limitations (quenching rate)
- Confirmation of a **boroxol stabilisation energy**



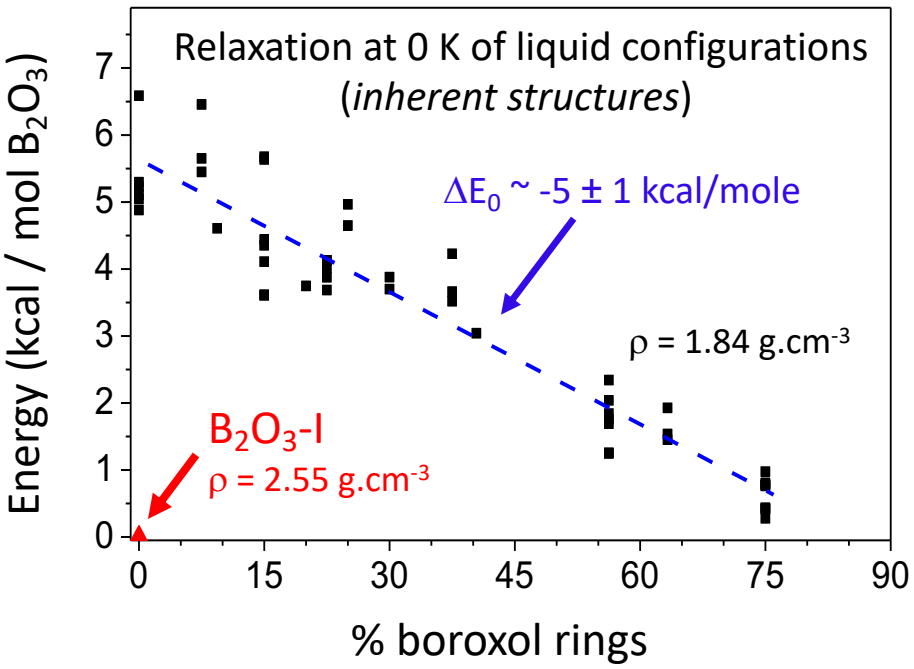

N.B. : the glass model was *'hand-made'* (by tweaking a $Cs_2O$-$B_2O_3$ crystal)

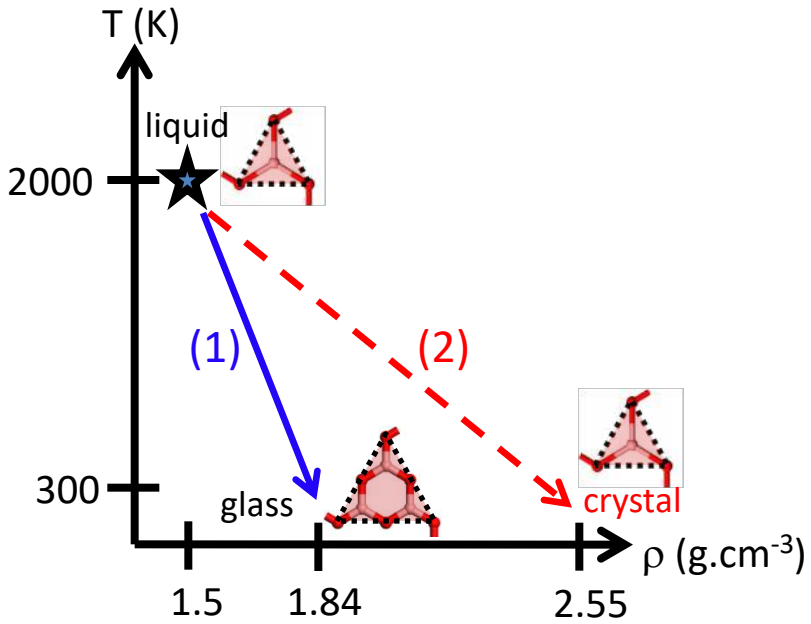
→ we still lack a (good) numerical model obtained from the liquid quench

Need for good (*many-body*) force-fields **and** efficient sampling methods (*enhanced sampling*)

# Our previous works (summary)

*G. Ferlat, T. Charpentier, A.P. Seitsonen, A. Takada, M. Lazzeri, L. Cormier, G. Calas, F. Mauri, Phys. Rev. Lett., **101**, 065504 (2008)*




✓ Why does the liquid always follow path (1) (vitrification) rather than path (2) (crystallisation)?

***Crystallisation anomaly***: crystallisation from the liquid is **never** observed unless pressure is applied.

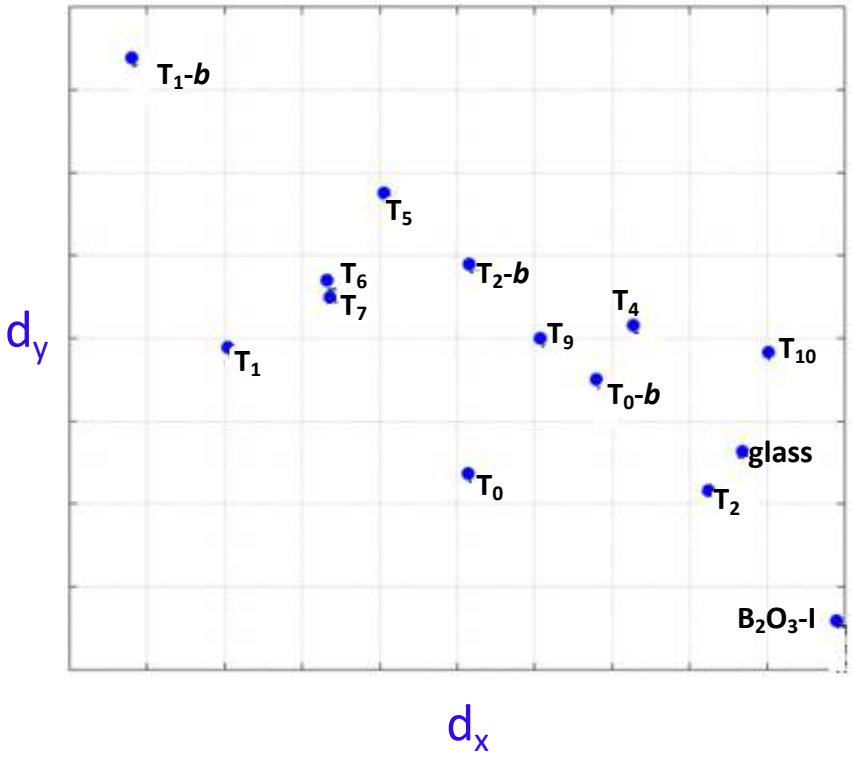
# Work in progress: PIV metric

Using polarisable force-fields (previously calibrated from AIMD and tested against structural experiments)

*O. Alderman et al., J. Phys.: Condens. Matter (2015)*

*A. Zeidler et al. Phys. Rev. B (2014)*

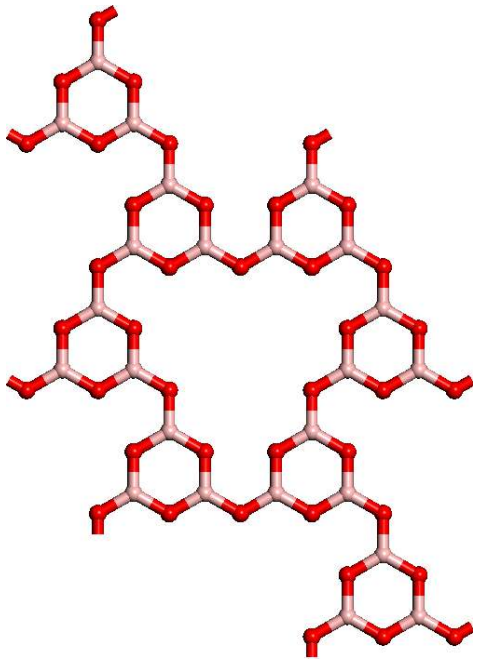
**Map of topological distances** using the PIV metric




✓ The PIV metric distinguishes $B_2O_3$ phases

# $B_2O_3$ layers in borates

✓ The layers from our *graphite-like* $B_2O_3$ polymorphs are found in synthetised borates



**T0-*b***

Motif: boroxol (*f* = 100 %)

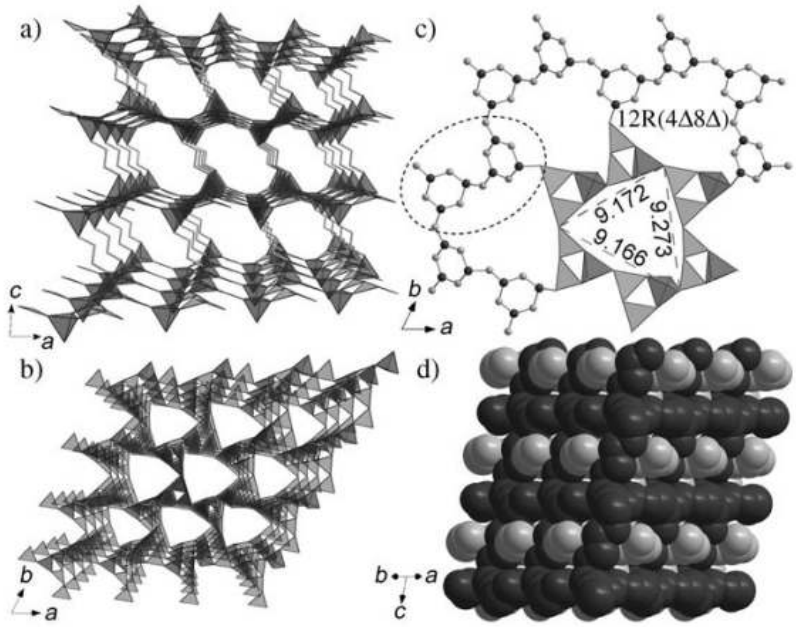


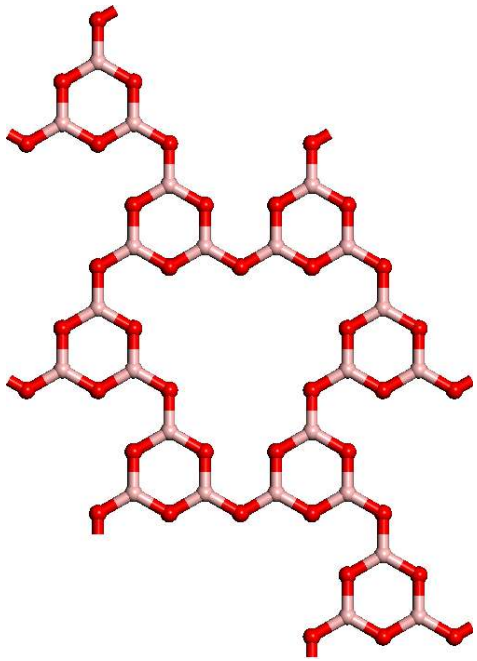

***Figure 1.*** 3D open frameworks of **1** along the *b* (a) and *c* (b) directions, 2D layer of 3,12-membered rings with the dashed circle showing the FBB (c), and the twofold interpenetrating crystal structure (d).

The $B_2O_3$ layer in $B_6O_9$(en) (en = ethylenediamine)

Wang *et al.*, Angew. Chem. Int. Ed. **46**, 3909 (2007)

# $B_2O_3$ layers in borates

✓ The layers from our *graphite-like* $B_2O_3$ polymorphs are found in synthetised borates



**T0-*b***

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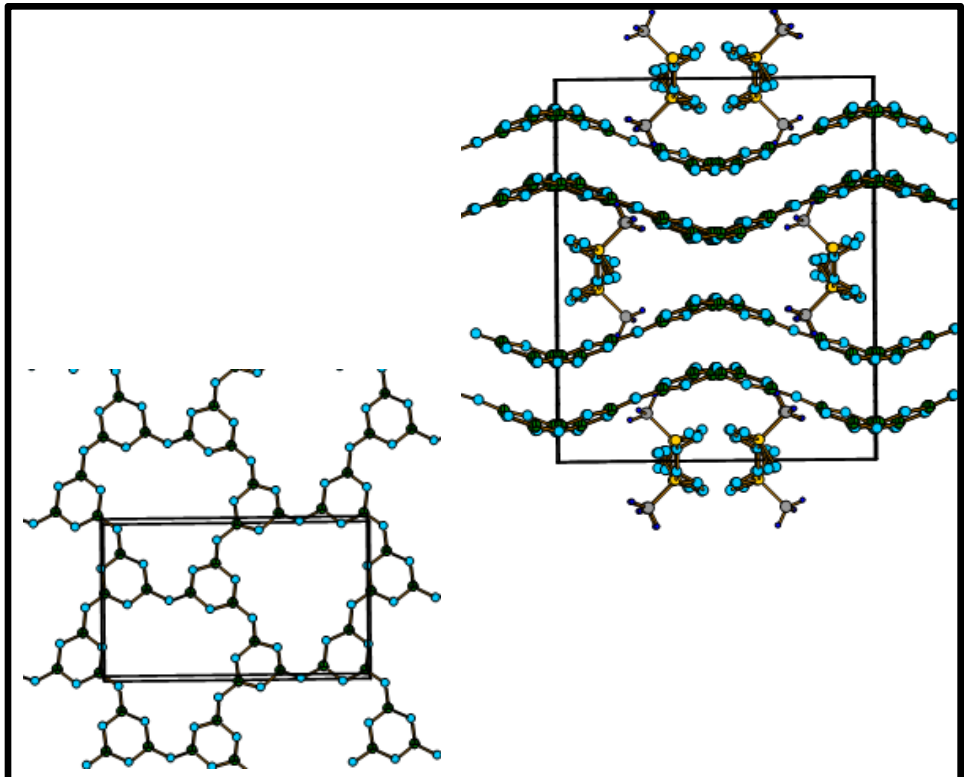

The $B_2O_3$ layer in a borosulphate compound

H. Hillebrecht *et al.*, in prep.

# Other experimental routes ?

- Chemical Vapor Deposition techniques: MOCVD, Atomic Layer Deposition (ALD), ...

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Physica E 27 (2005) 319–324
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## Crystalline boron oxide nanowires on silicon substrate

Qing Yang[a], Jian Sha[b], Lei Wang[a], Yu Zou[a], Junjie Niu[a], Can Cui[a], Deren Yang[a,*]

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[b]Department of Physics, Zhejiang University, 20 Yu Gu Road, Hangzhou 310027, People's Republic of China

Received 26 November 2004; accepted 20 December 2004

**Abstract**

Crystalline boron oxide nanowires have been synthesized on silicon substrates by chemical vapor deposition (CVD) process without the use of catalysts or templates. It is pointed out that the boron oxide nanowires are cubic and single crystalline, and the diameter of the nanowires is in the range of 20–80 nm. Some of the nanowires branched, and the diameters of the branches and stems of the branched boron oxide nanowires are in the range of 20–80 and 100–200 nm, respectively. The crystallinity, morphology, and structure features of the as-prepared boron oxide nanowires were investigated by field emission scanning electron microscopy, X-ray diffraction, transmission electron microscopy, and selected area electron diffraction. Furthermore, Raman spectrum and Fourier transform infrared spectroscopy of the nanowires were also investigated.

✓ cubic phase? That originally seen in J. Am. Ceram. Soc., **18**, 55 (1935) ?

- Physical Vapor Deposition techniques: Magnetron sputtering, IR irradiation, ...

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## Analysis of magnetron sputtered boron oxide films

Dalibor Buc[a], Igor Bello[b], Maria Caplovicova[c], Milan Mikula[a], Jaroslav Kovac[a], Ivan Hotovy[a], Yat Min Chong[b], Guei Gu Siu[b,*]

[a] Slovak University of Technology in Bratislava, Slovak Republic
[b] City University of Hong Kong, Kowloon, Hong Kong
[c] Comenius University in Bratislava, Slovak Republic

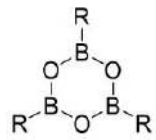
Available online 5 April 2007

**Abstract**

Boron oxide films were grown on silicon substrates by radio-frequency (rf) unbalanced magnetron sputtering of a boron target in argon–oxygen gas mixtures with different compositions. Microscopic analyses show that overall boron oxide films are amorphous. The film prepared at oxygen/argon flow rate ratio >0.05 developed large crystallites of boric acid in localize areas of amorphous boron oxide matrices. These crystallites were unstable and at electron microscopic analysis they continuously transformed to a cubic $HBO_2$ phase and then completely vanished leaving an underlying amorphous boron oxide film behind. The analyses indicate the coexistence of $B_6O$, $HBO_2$ crystallites and amorphous boron oxide matrices. Fourier transform infrared (FTIR) spectra revealed spectral bands of BOH, BO, BOB and BH groups. Nanohardness and elastic modulus of a film prepared at low oxygen concentration approach 30 and 300 GPa, respectively. These parameters however vary with deposition conditions.


- Chemical synthesis using sol-gel techniques:

Starting from e.g. an alkyl (R) substituted metaboric acid, $R_3B_3O_6$ :

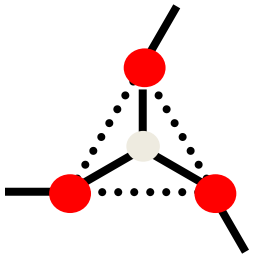



R = alkyl, alkoxy or aryl

- Physical synthesis at *negative pressure* (Berthelot tubes)

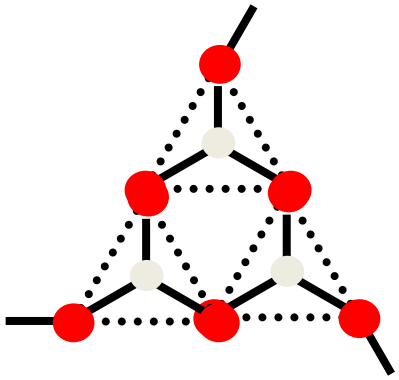
# Self-similarity

**In a given structure:**



self-similar

transformation



N atoms

length: L

volume: V

density: $\rho$

N * 3 atoms

L * 2

V * $2^2$ (2D) or $2^3$ (3D)

$\rho$ * 3/4 (2D) or 3/8 (3D)

$B_2O_3$-I: $\rho$ = 2.56 g.cm$^{-3}$ 

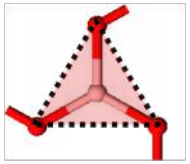
$B_2O_3$-I-*b* (3D unrelaxed) $\rho$ = 0.96 g.cm$^{-3}$

$B_2O_3$-I-*b* (relaxed) $\rho$ ~ 1.4 g.cm$^{-3}$

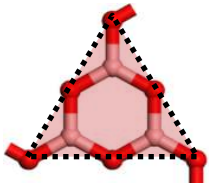
# (potentially exhaustive) search

## ➡ Using decoration of topological networks

✓ Relevant **building units** (for ambient polymorphs):



$BO_3$ triangle

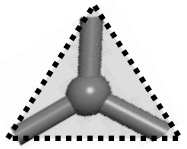


$B_3O_6$ super-triangle

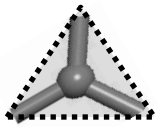
✓ Use of previously determined topological databases of **three-fold coordinated networks**

Winkler *et al*. (CPL, 2001): from **graph theory**, prediction of all possible **three-coordinated 3D** frameworks with up to 6 atoms in the primitive cell: **12 networks** (originally applied to $sp^2$-carbon structures)

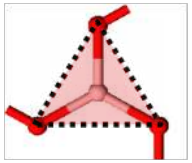
**+ 2D** network of graphite **: 13 networks**



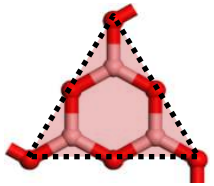
✓ **Decoration** of the networks vertices by the relevant **building units:**



**13 networks**



**T1 to T13**



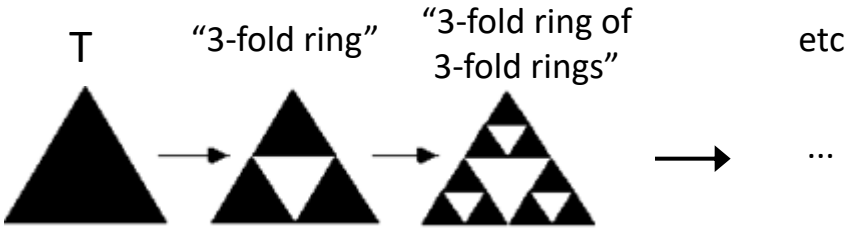
**T1-*b* to T13-*b***

2*13 -1 = **25 new $B_2O_3$ crystals**
(with 10 to 135 atoms per unit cell)

✓ **Relaxation** (positions and unit cell) of the structures by ***first-principles*** calculations within Density Functional Theory (GGA-PBE, ultra-soft pseudos, PW basis, CASTEP code)

# Some more predictions?

- Our search is not fully exhaustive since :
  - the number of nodes per unit cell is limited
  - 100 % of the nodes were decorated by a single type of decoration unit (triangle or boroxol). Mixtures (e.g. 50-50 %) could be considered.
  - Larger (self-similar) decoration units could be considered.



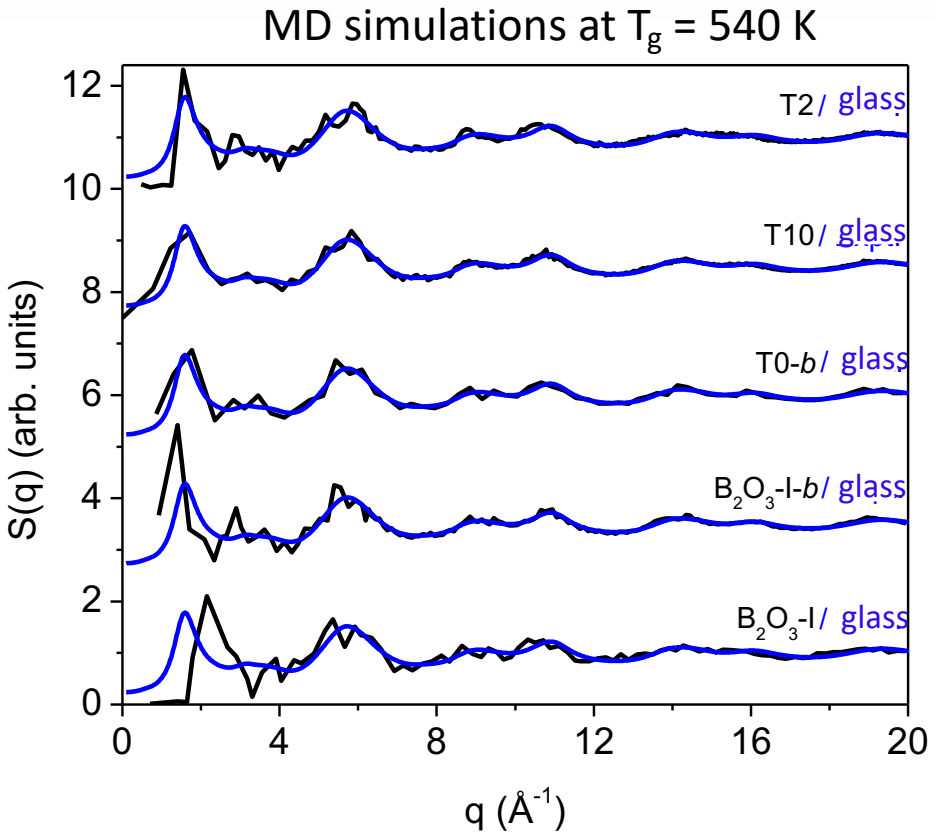

- Two additional predictions have since been published

  F. Claeyssens *et al.*, Adv. Funct. Mater., **23**, 5887 (2013)

- PCOD database : > 800 predicted $B_2O_3$ structures! (energies not determined)

  http://www.crystallography.net/pcod (A. Le Bail, Univ. Le Mans, France)

# New polymorphs versus glass: structure factors




✓ Overall good match between the novel polymorphs' S(q) and that of the glass. The novel crystals bear greater structural similarity with the glass than $B_2O_3$-I.

*Glass expt. data: A. C. Hannon et al., JNCS **177** 299 (1994)*

# Polymorphism and amorphisation

E. Perim *et al.*, Nat. Comm. **7**, 12315 (2016)

"We postulate that the existence of **multiple phases with similar energies**, implying similar probabilities of being formed, but dissimilar structures, will lead to the formation of several distinct clusters, which will intimately compete and thus keep each other from reaching the critical size needed for crystallization."

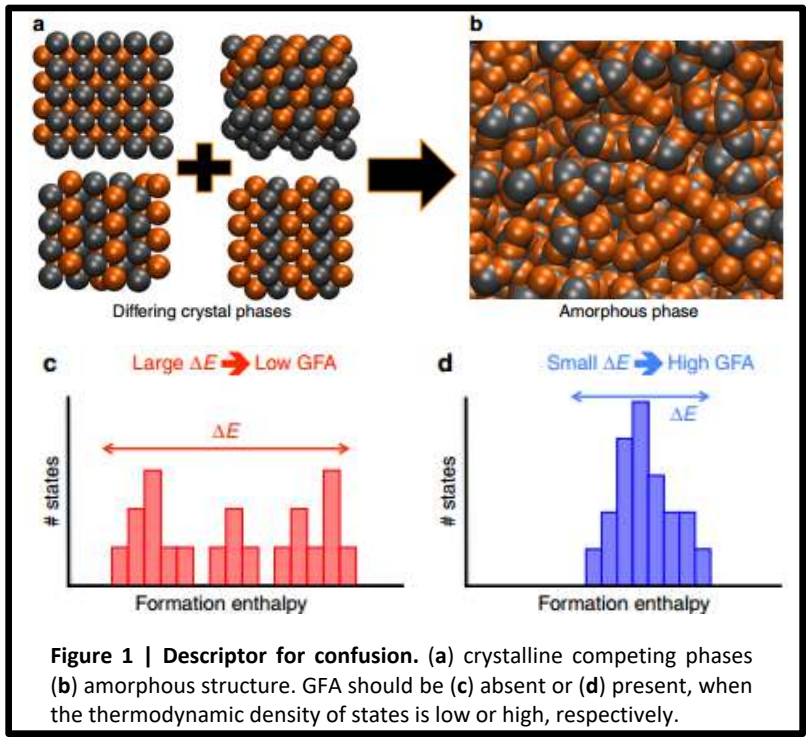



**Figure 1 | Descriptor for confusion.** (**a**) crystalline competing phases (**b**) amorphous structure. GFA should be (**c**) absent or (**d**) present, when the thermodynamic density of states is low or high, respectively.

**Simple descriptor for glass formation.** To quantify the level of disorder, we identify the most stable structures and **count all of the available phases**, ordered by their formation enthalpy difference above the ground state, $\Delta H$. This leads to a cumulative distribution, $N_p(\Delta H)$. We also count the **number of different Bravais lattice types** $N_{BL}(\Delta H)$ and **space groups** $N_{SG}(\Delta H)$ among the phases. These three quantities are combined into a single heuristic descriptor, called the 'entropic factor':

$$\chi_F(\Delta H) = \sqrt[3]{N_P(\Delta H) \times N_{BL}(\Delta H) \times N_{SG}(\Delta H)}$$

$\chi_F(\Delta H)$ should be related to the configurational entropy but, by taking into account the different symmetries available to the system, it is more generally representative of **the frustration of the crystallization** of a single homogeneous crystal structure. Compositions with large $\chi_F(\Delta H)$ are expected to present structures with more disorder, thus leading to high GFA.

**Glass Forming Ability descriptor**, evaluated by summing through structures *i* at fixed stoichiometry *{x}*

$$\chi_{\mathrm{GFA}}(\{x\}) = \frac{\sum_i f(H_i) g(|\psi_i\rangle)}{h(\{x\})}$$

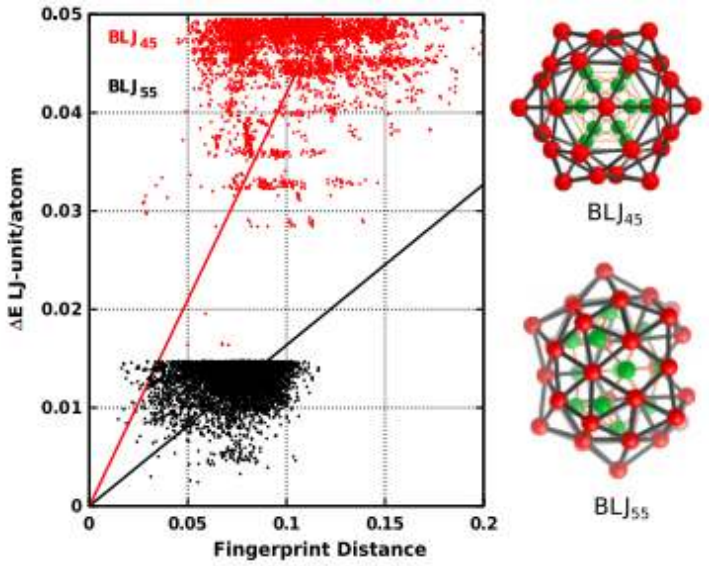
**Enthalpy proximity** (to the ground state)

$$f(H_i) = \exp\left(\frac{-|H_i - H_0|}{k_B T_0}\right) \times \begin{cases} 1, & H_i < 0 \\ e^{-H_i/k_B T_0}, & 0 \le H_i < 50\,\mathrm{meV} \\ 0, & 50\,\mathrm{meV} \le H_i \end{cases}$$

**Structure dissimilarity.** To correlate properties of structures having different decorations of the underlying lattice, we use a lattice-free formalism, the expansion in local atomic environments (AEs)[64]. (g = 0 for similar structures)

# Polymorphism and energy landscape

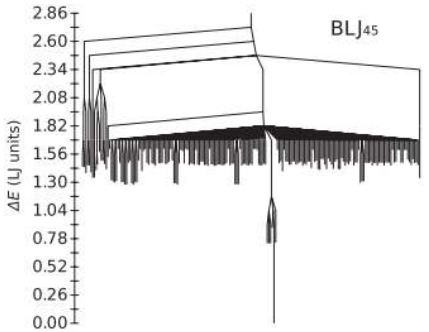
S. De *et al.*, Phys. Rev. Lett. **112**, 083401 (2014)



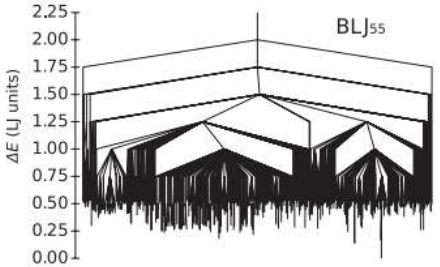







*« non-glassy»*




*« glassy »*

« … All the investigated clusters that were synthesized experimentally exhibit a nonglassy energy landscape. This suggests that a landscape of this type is a prerequisite for experimental synthesis. »

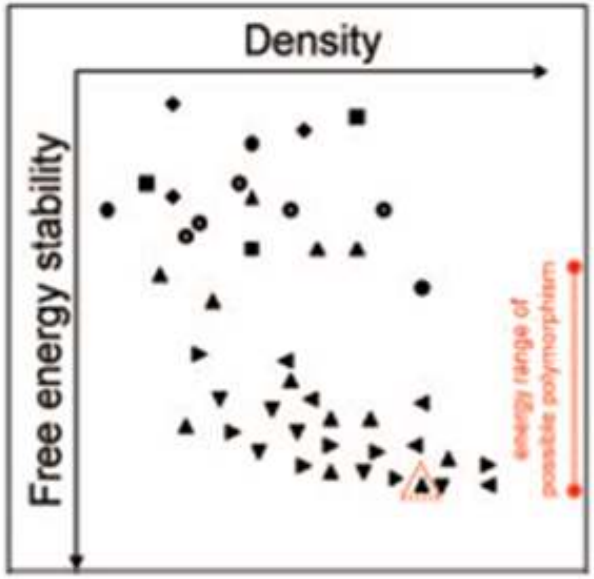
Common criteria for allotropes that have been experimentally isolated:
- occupy deep potential wells
- surrounding wells are higher in energy and/or « funneling » toward the stable form
- barriers to subsequent conversion are high

➡ Structure lie at the apex of a disconnectivity graph, occupying a unique energetically isolated position

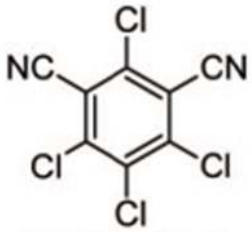
C. P. Ewels *et al.*, PNAS, **112**, 15609 (2015)

# Polymorphism and ease of amorphization

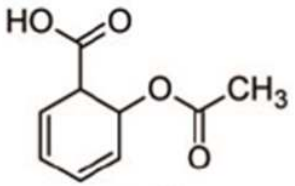
## Case (a): There are several polymorphs of similar energy




Examples (organic molecules):




Chlorothalonil



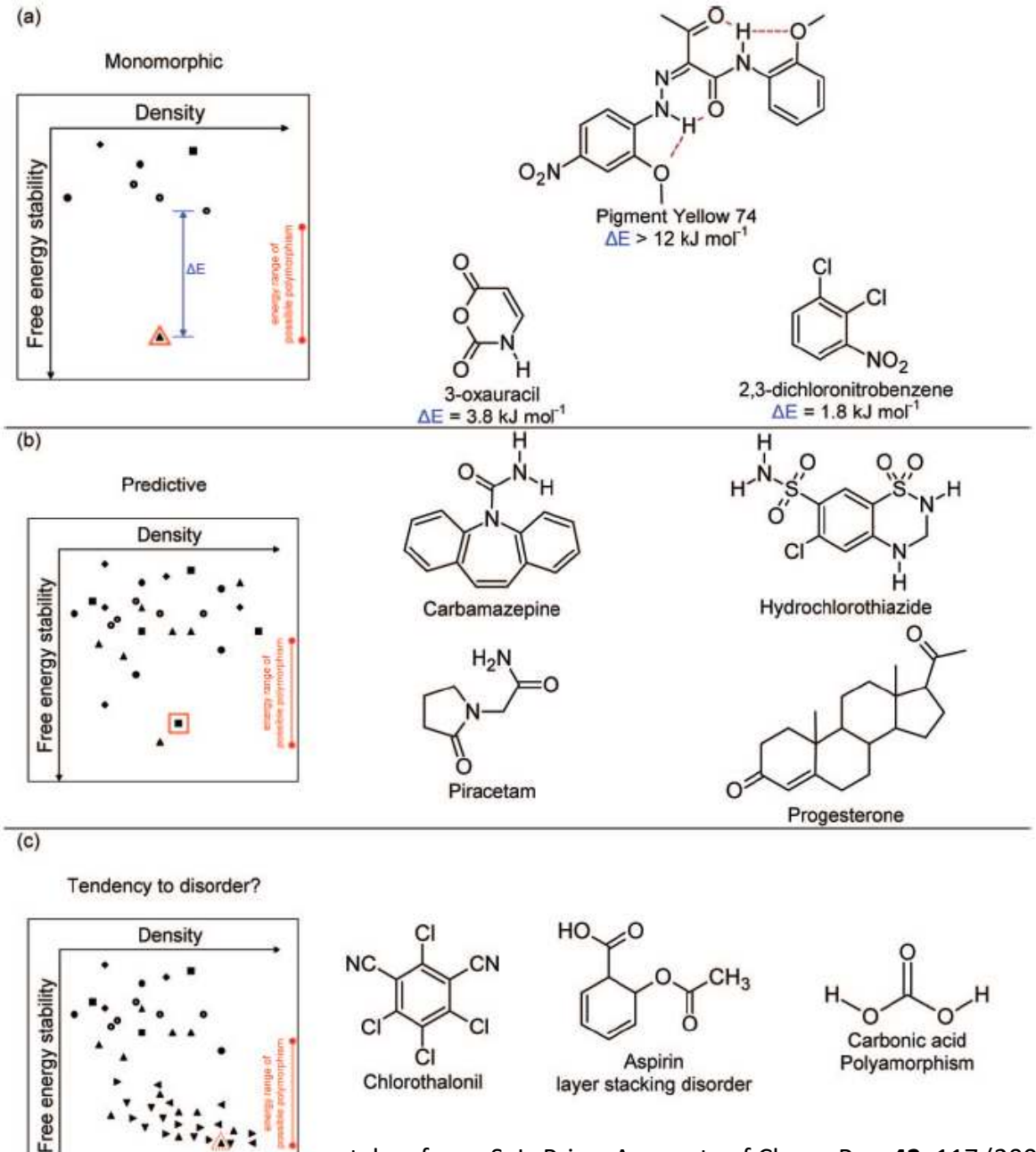

Aspirin
layer stacking disorder

from: S. L. Price, Accounts of Chem. Res. **42**, 117 (2009)

➡ The system easily amorphizes (= hardly crystallizes a given polymorph)

This is typically the case for $SiO_2$, ...

# Polymorphism and the amorphisation




taken from: S. L. Price, Accounts of Chem. Res. **42**, 117 (2009)

(a) The lowest-energy polymorph is well separated from the others ($\Delta E \geq 10$ kJ/mol~3 kcal/mol)

✓ monomorphic behaviour, hard to vitrify (easy to crystallise)

This is typically the case for Si, Ge, ...

(b) There is a small number of polymorphs (and they are structurally unrelated)

✓ these polymorphs may be observed

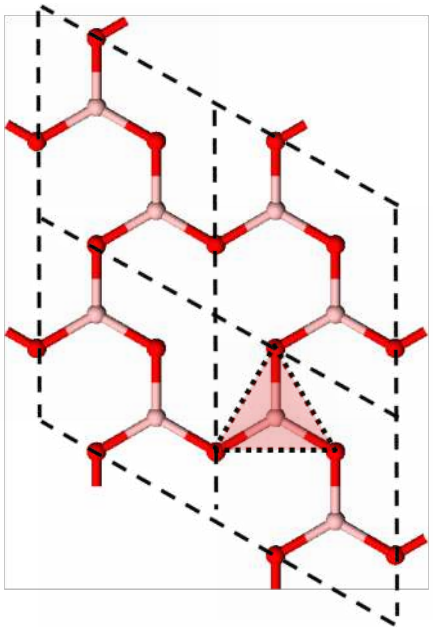
(c) There are many polymorphs of similar energy

✓ easy to amorphise (hard to crystallise a given polymorph)

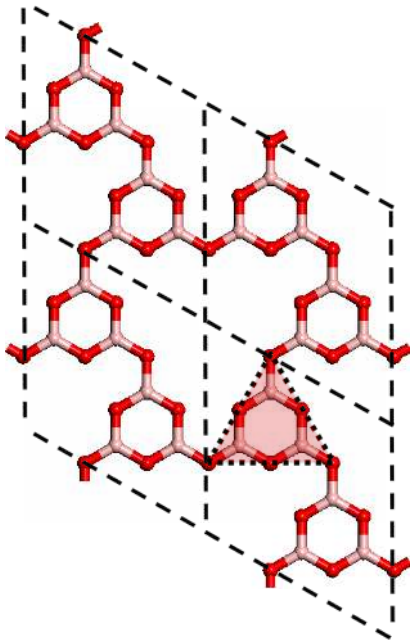
This is typically the case for $SiO_2$, ...

# Boroxol stabilisation energy

- « graphene » iso-structural layers



$\Delta E_{layer}$



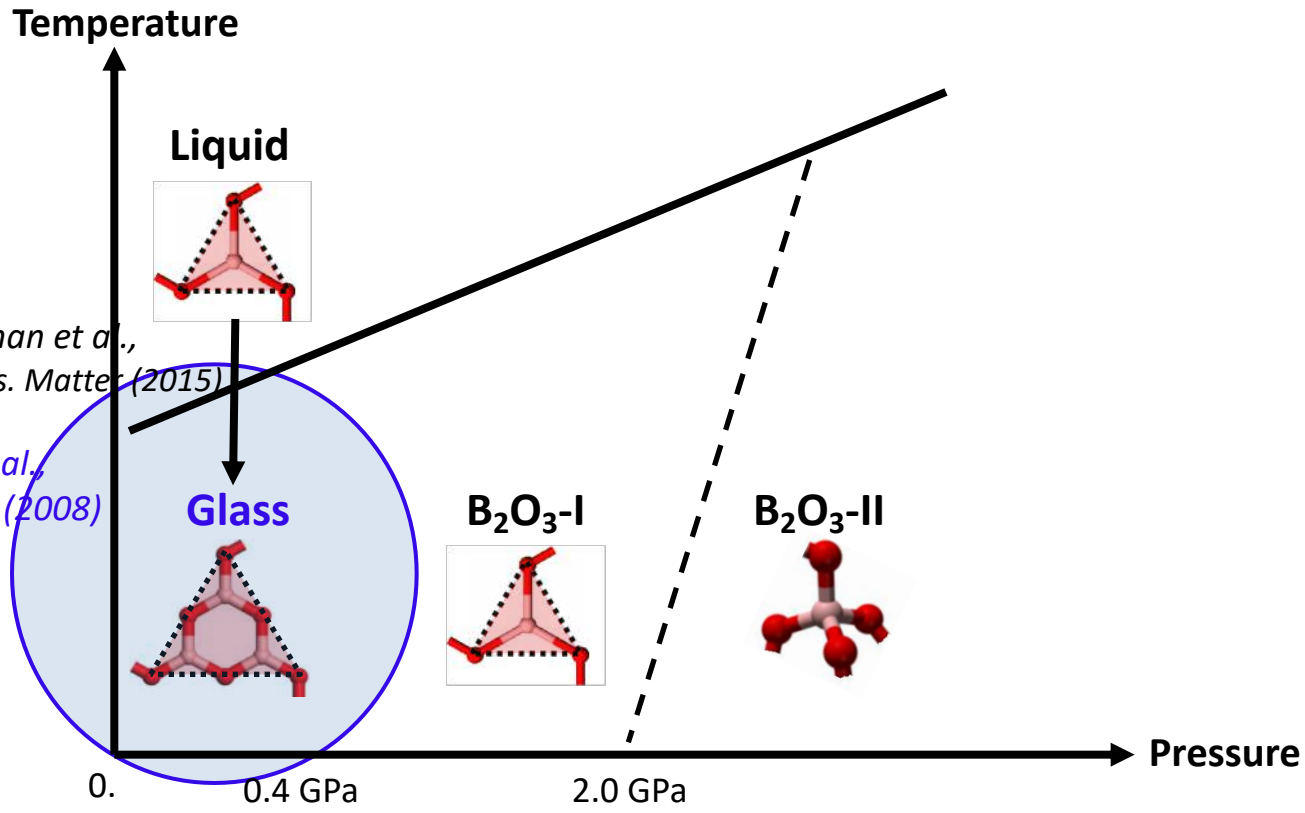
100 % triangles monolayer

100 % boroxols monolayer

No relaxation (B-O-B angles = 120°): $\Delta E_{Layer}$ ~ -10.0 kcal / mole

[ After relaxation: $\Delta E_{Layer}$ ~ -1.0 kcal / mole ]

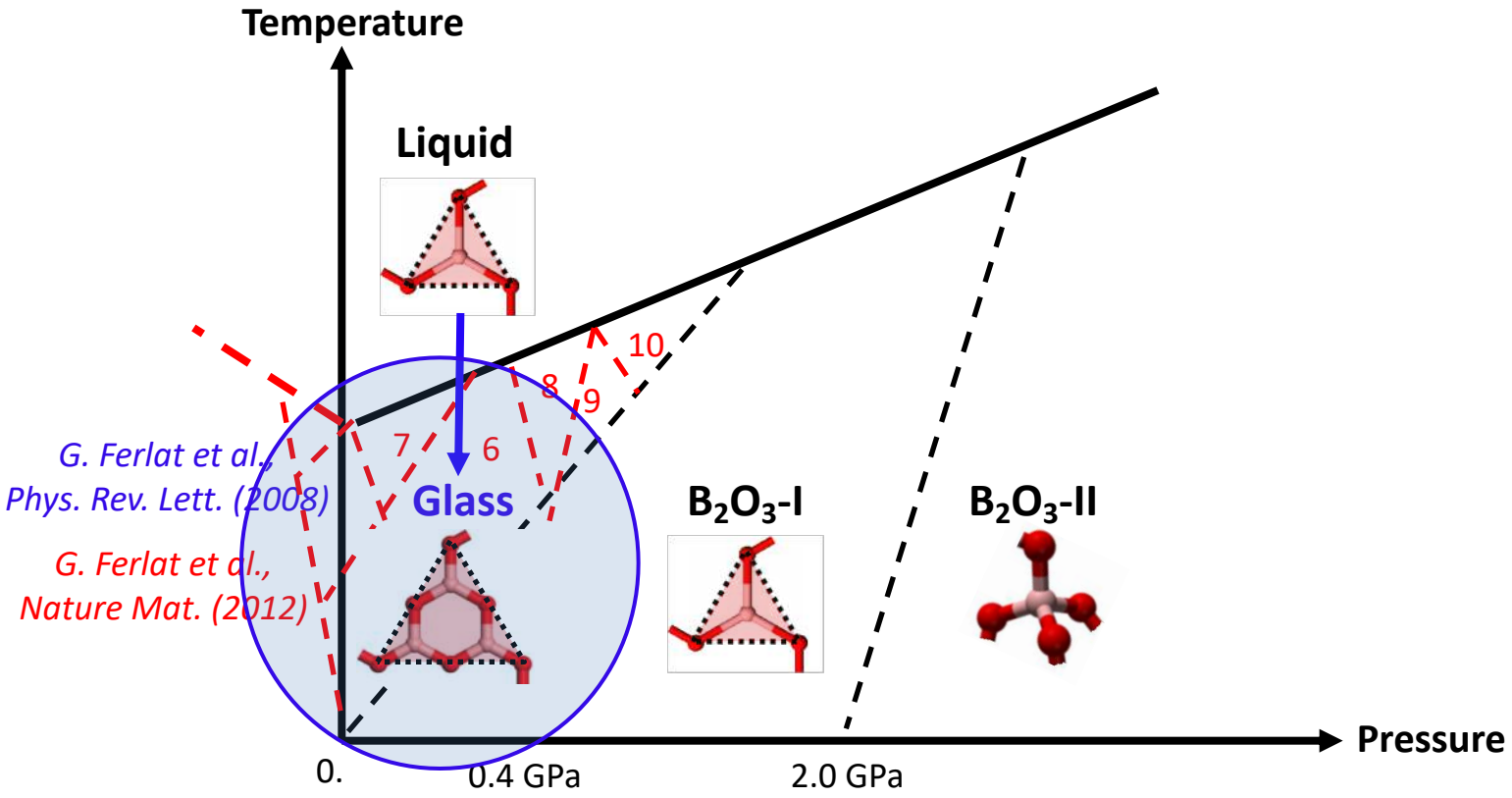
# Previous (MD) works: summary




✓ a **network-forming glass** with significant **medium-range order** (3-fold rings)

*Rings in network glasses: the $B_2O_3$ case*. G. Ferlat. Chapter 14 in "Frontiers and challenges in molecular dynamics simulations of structurally disordered materials: from network glasses to phase change memory alloys", Springer (2015).

# Previous (MD) works: summary




✓ a **network-forming glass** with significant **medium-range order** (3-fold rings)

✓ many (**new**) polymorphs structurally similar to the glass

*Rings in network glasses: the $B_2O_3$ case*. G. Ferlat. Chapter 14 in "Frontiers and challenges in molecular dynamics simulations of structurally disordered materials: from network glasses to phase change memory alloys", Springer (2015).

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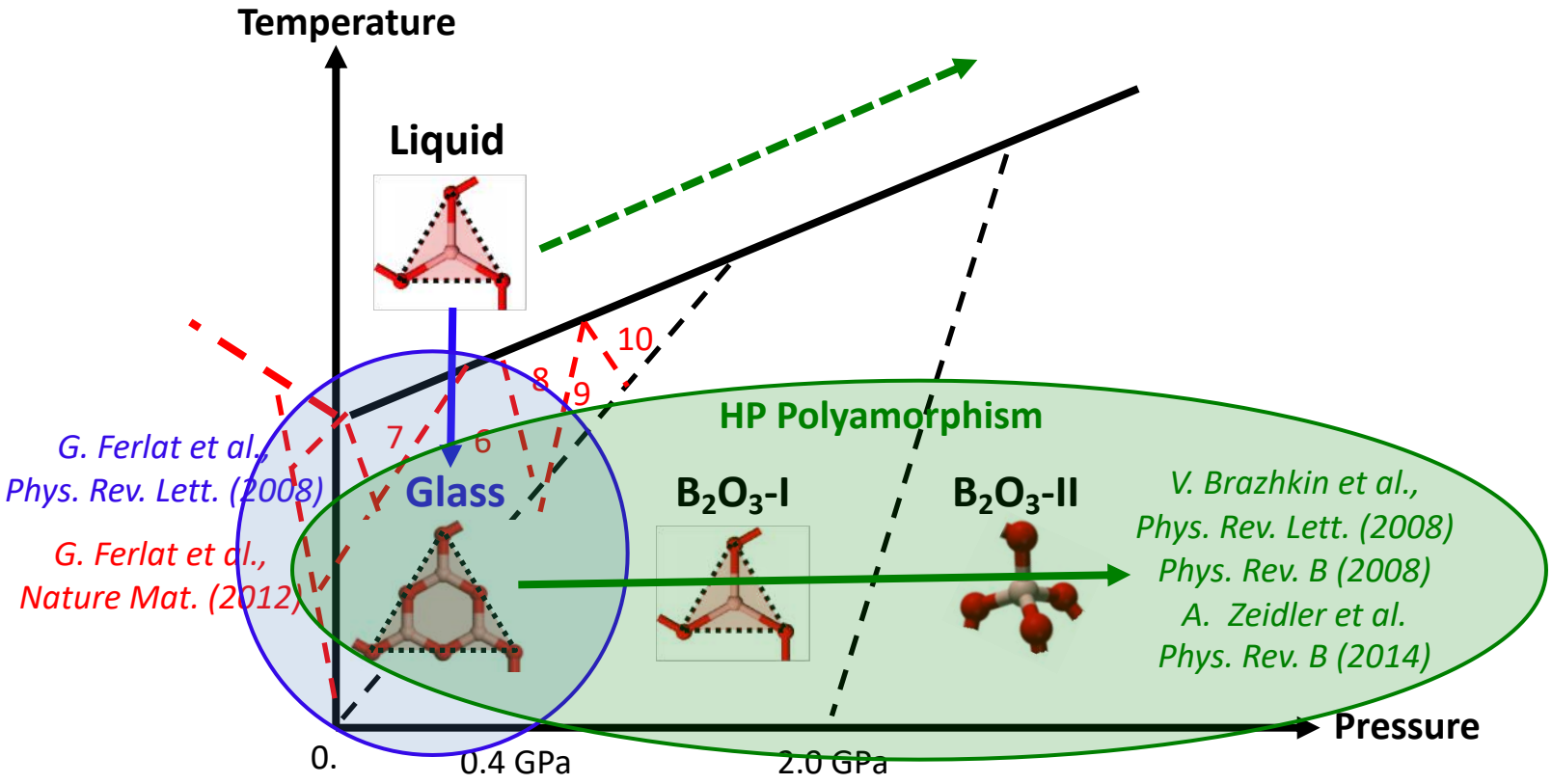


✓ a **network-forming glass** with significant **medium-range order** (3-fold rings)

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✓ a system prone to polyamorphism and liquid-liquid transitions (?)

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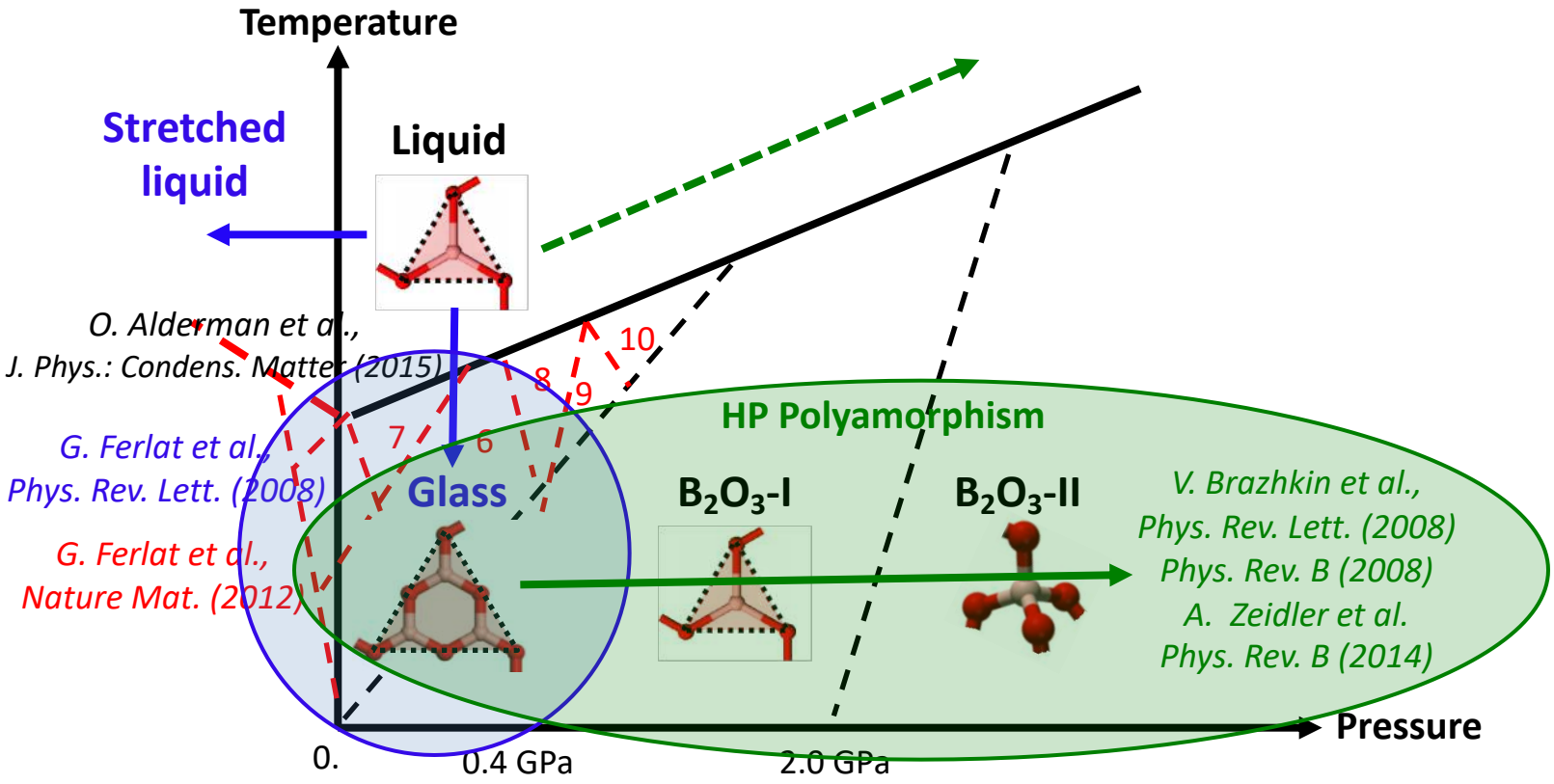


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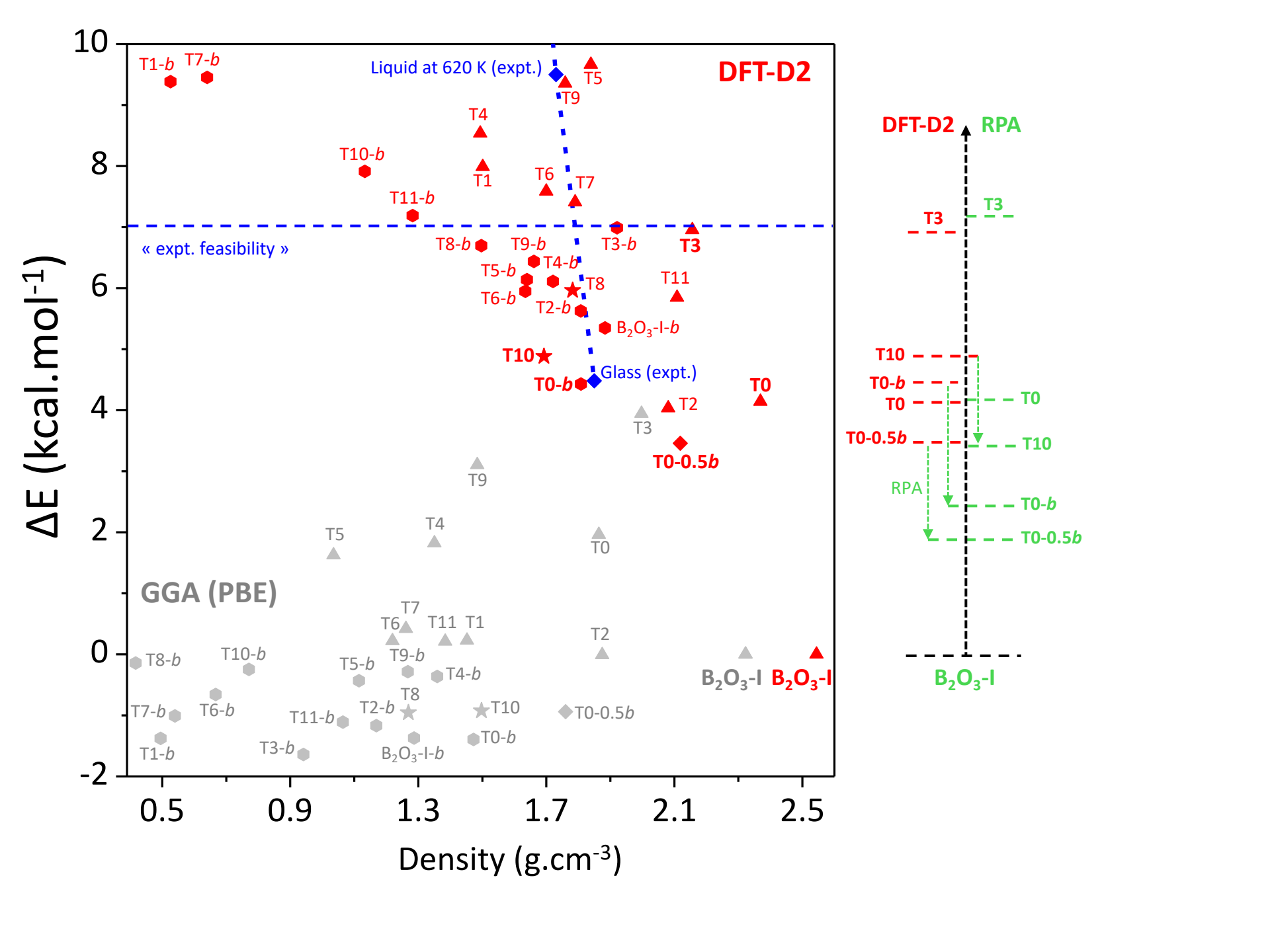
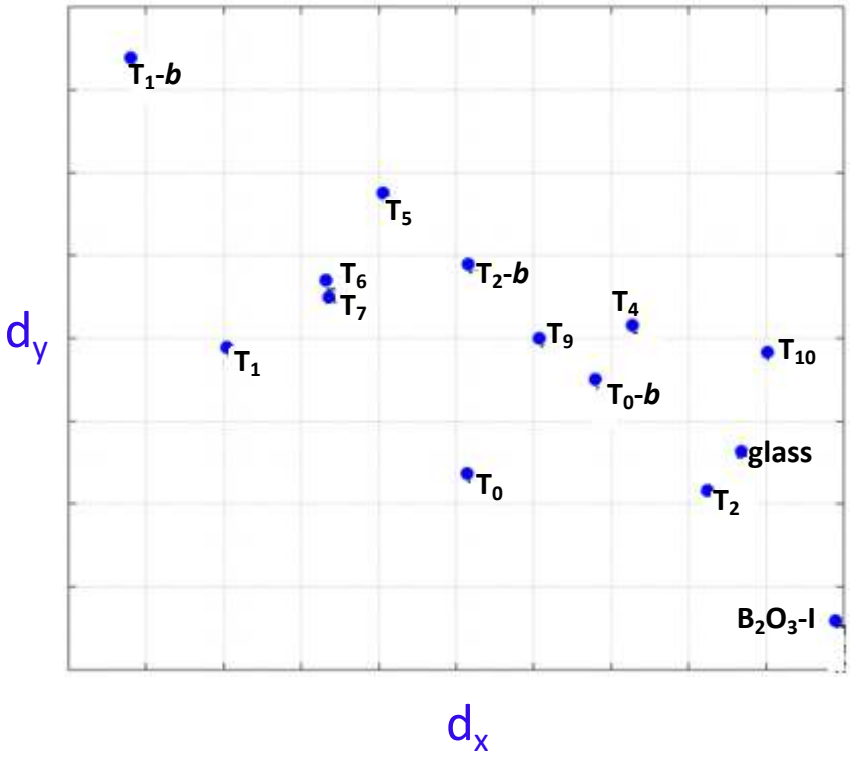

ΔE (kcal.mol-1)
Density (g.cm-3)
10
8
6
4
2
0
-2
0.5
0.9
1.3
1.7
2.1
2.5
DFT-D2
GGA (PBE)
Liquid at 620 K (expt.)
Glass (expt.)
« expt. feasibility »
T1-b
T7-b
T5
T9
T4
T10-b
T1
T6
T7
T11-b
T8-b
T9-b
T3-b
T3
T5-b
T4-b
T8
T11
T6-b
T2-b
B2O3-I-b
T10
T0-b
T0
T2
T0-0.5b
T9
T5
T4
T0
T7
T6
T11
T1
T2
T8-b
T10-b
T5-b
T9-b
T4-b
B2O3-I
T8
T7-b
T6-b
T11-b
T2-b
T10
T0-0.5b
T1-b
T3-b
T0-b
B2O3-I-b
DFT-D2
RPA
T3
T3
T10
T0-b
T0
T0
T0-0.5b
T10
RPA
T0-b
T0-0.5b
B2O3-I

# Work in progress: PIV



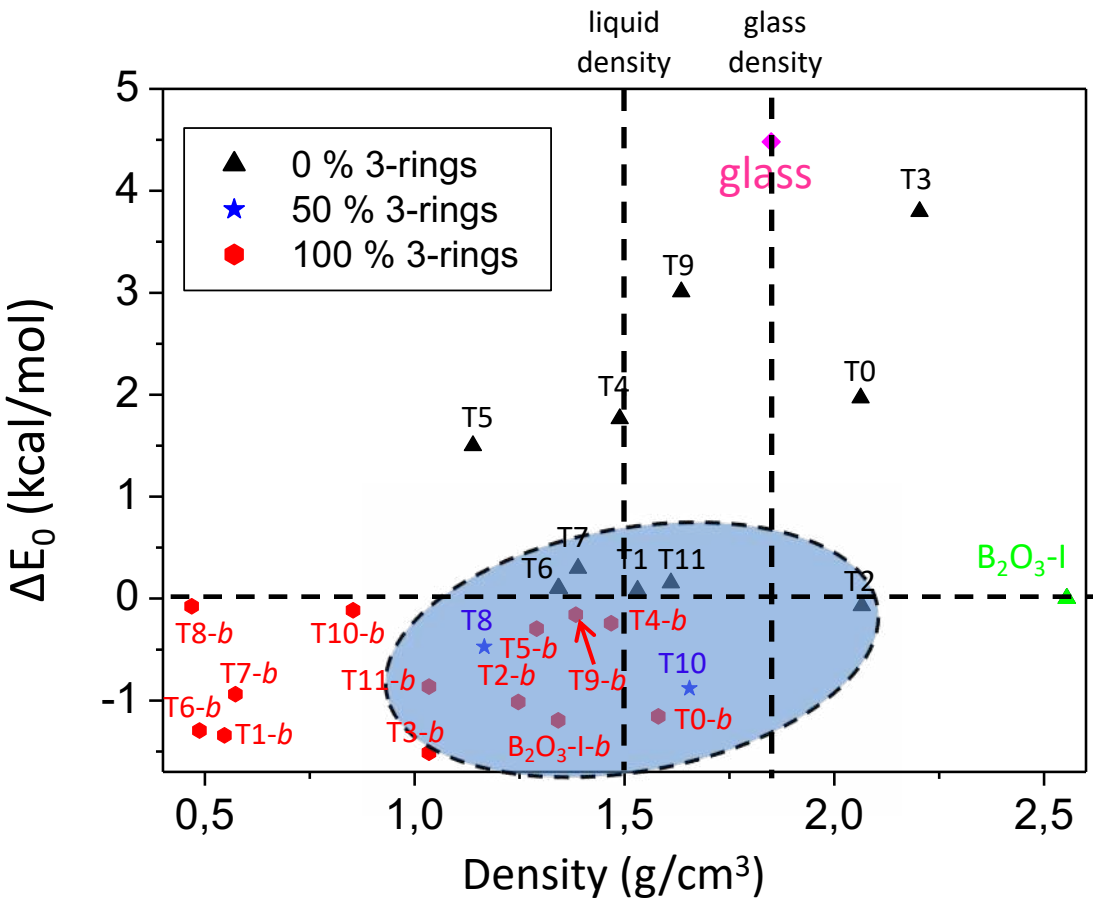

Starting from the PIV distances between all pairs of structures in a given set, for the sake of visualization and clarity, a two-dimensional map can be constructed employing the following Monte Carlo optimization algorithm. A representative point in a plane is assigned to each structure, initially with random position ($0 < x < 1$, $0 < y < 1$). Next, a cost function is defined as

$$U = \sum_{i<j} (\mathcal{D}_{ij} - d_{ij})^2, \qquad (3)$$

where the sum runs over all pairs of structures and each harmonic term grows with the difference between the PIV distance $\mathcal{D}_{ij}$ and the in-plane distance $d_{ij}$. In the case of liquid water and amorphous ices in Fig. 3, a set of 50 configurations is considered for each disordered phase but for the sake of clarity, a single point is shown for each phase, with $\mathcal{D}_{ij}$ defined as the average distance between the configurations of phase $i$ and those of phase $j$. $U$ is minimized through a sequence of moves, each move consisting in the random displacement (maximum amplitude 0.0005) of one point in the plane. Moves are accepted or rejected according to a Metropolis criterion at thermal energy $kT = 1 \times 10^{-7}$ (in $U$ units) until obtaining a Pearson's correlation coefficient = 0.999 between PIV distances and in-plane distances (in the case of water phases in Fig. 3, $10^5$ moves were sufficient).

✓The PIV metric distinguishes $B_2O_3$ phases

# Energy-density (from DFT-GGA)




✓ Many low-energy crystals, most with high % of boroxols

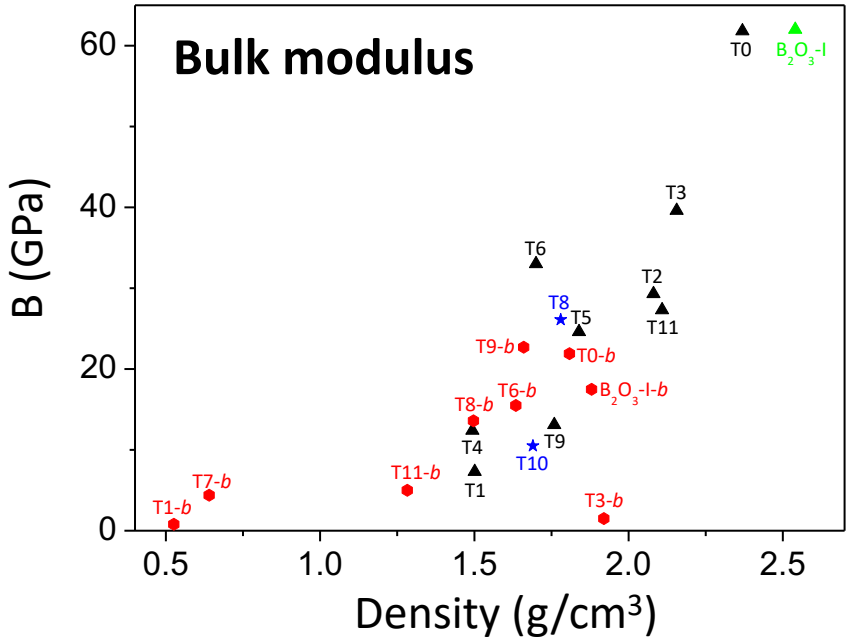
✓ Many of similar energy at densities ~ close to those of the liquid/glass

➡ This **rich polymorphism** induces the vitrification in a low-density glass

# Work in progress: mechanical properties

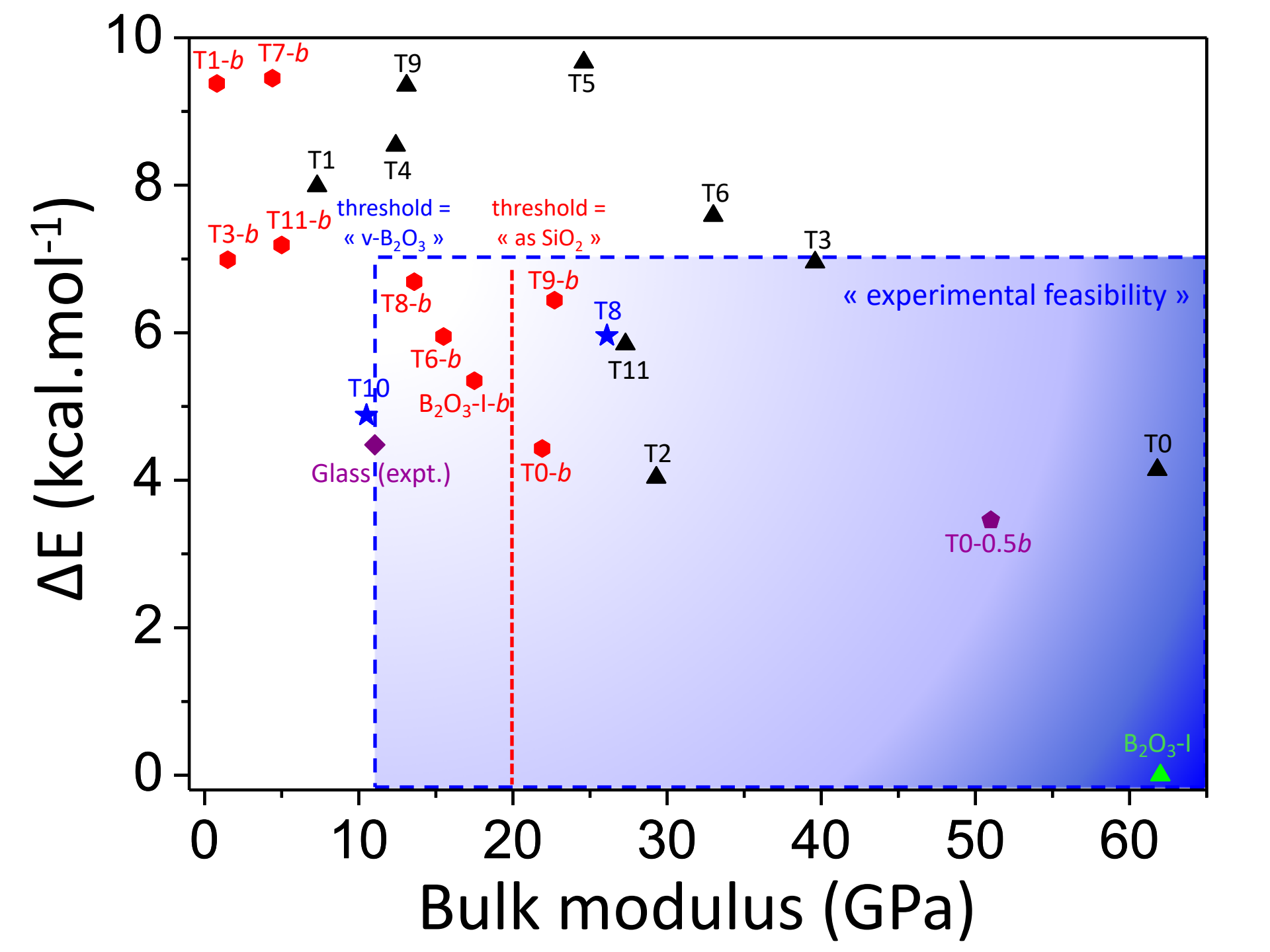
Coll. F.-X. Coudert (Chimie-ParisTech)

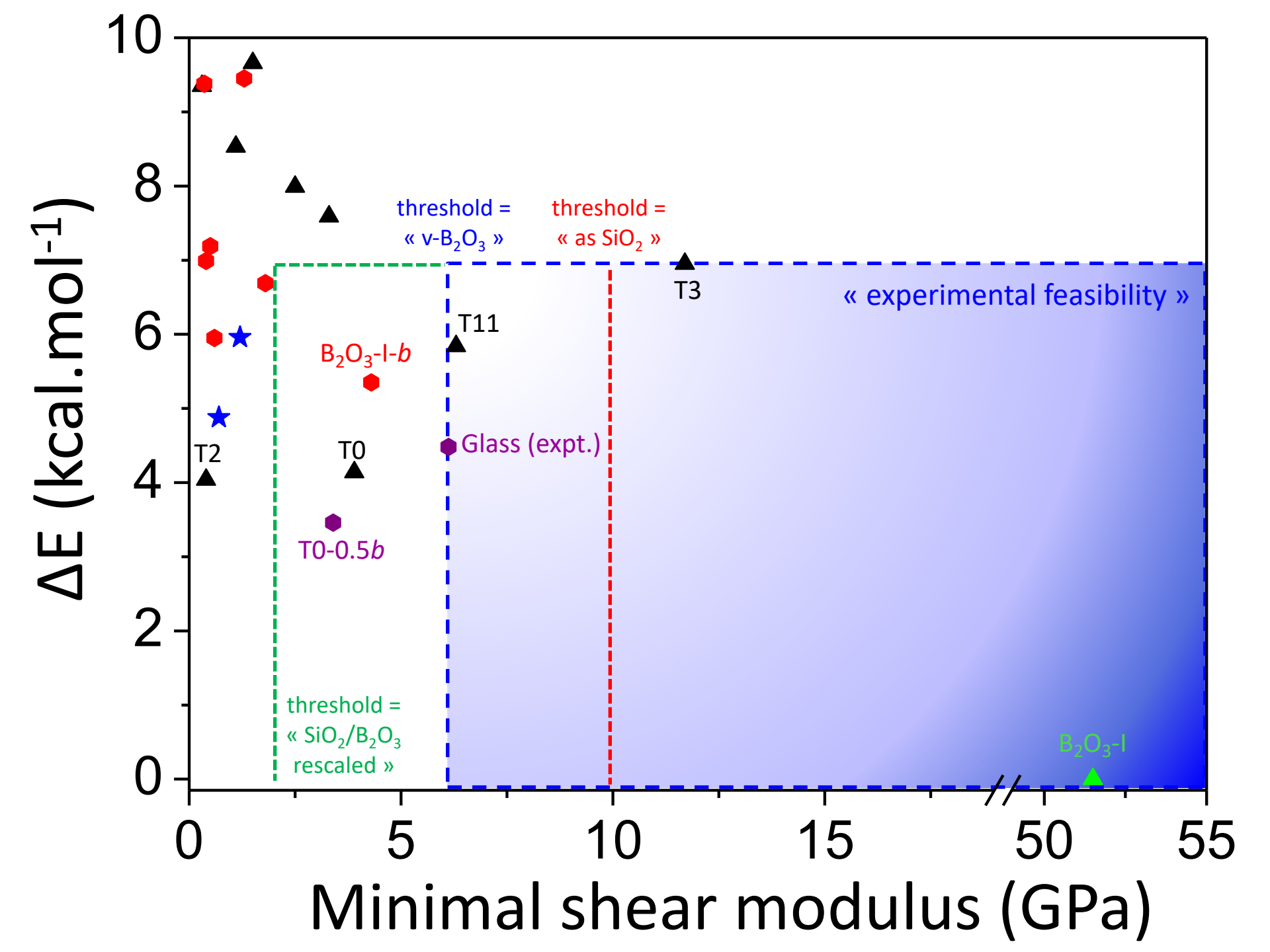
Computation of bulk, Young and Shear moduli + poisson ratio (and their anisotropy)

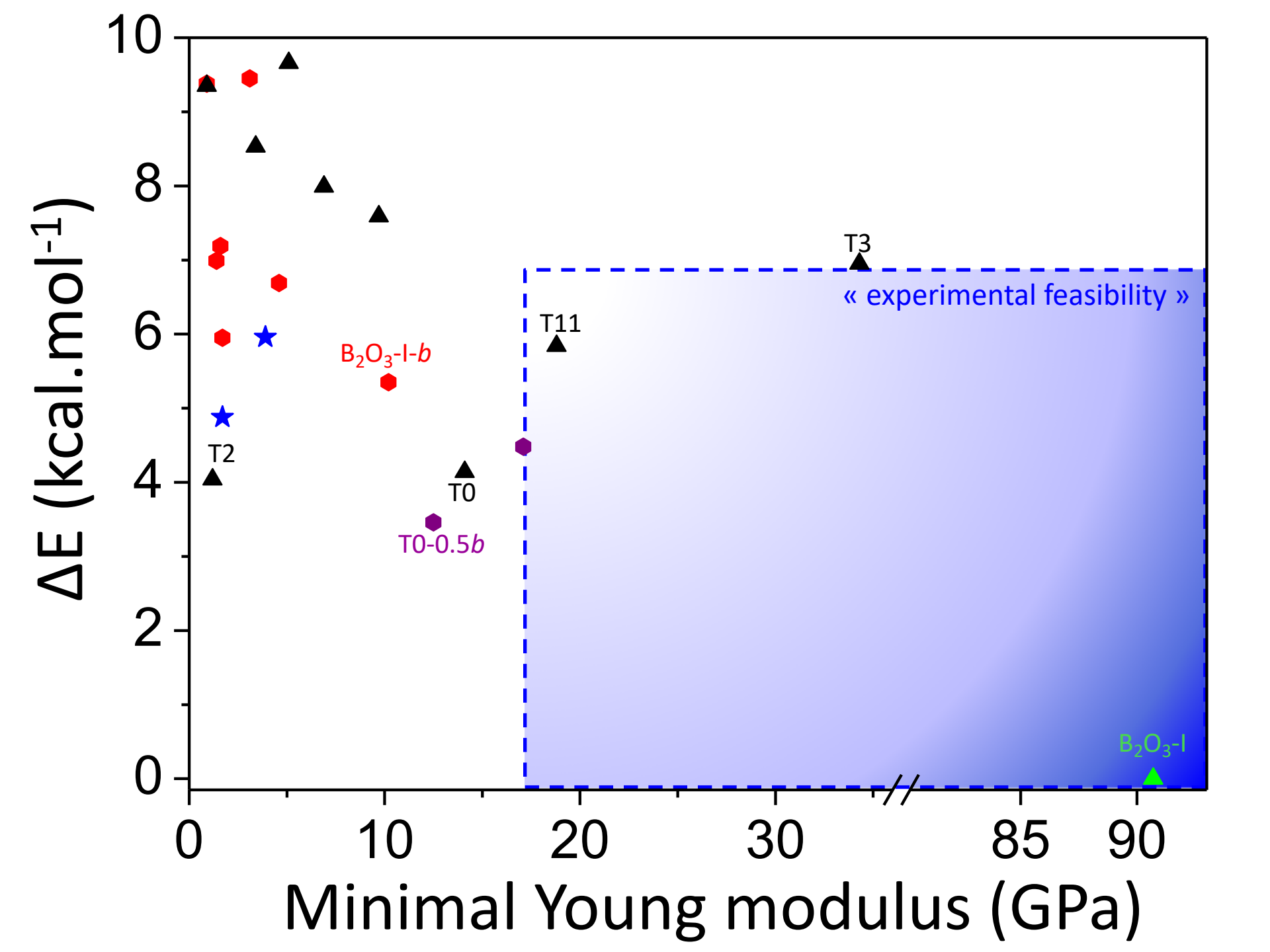



✓ most predicted polymorphs have **low** mechanical moduli (low *stiffness*)

✓ some show intriguing mechanical properties (*e.g.* **negative linear compressibility**)


ΔE (kcal.mol-1)
Bulk modulus (GPa)
0
2
4
6
8
10
0
10
20
30
40
50
60
T1-b
T7-b
T9
T5
T1
T4
T6
T3-b
T11-b
threshold = « v-B2O3 »
threshold = « as SiO2 »
T3
T9-b
« experimental feasibility »
T8-b
T8
T6-b
T11
T10
B2O3-I-b
Glass (expt.)
T0-b
T2
T0
T0-0.5b
B2O3-I


ΔE (kcal.mol-1)
Minimal shear modulus (GPa)
threshold = « v-B2O3 »
threshold = « as SiO2 »
« experimental feasibility »
threshold = « SiO2/B2O3 rescaled »
T3
T11
T2
T0
B2O3-I-b
Glass (expt.)
T0-0.5b
B2O3-I


ΔE (kcal.mol-1)
Minimal Young modulus (GPa)
« experimental feasibility »
T3
T11
T2
T0
B2O3-I-b
T0-0.5b
B2O3-I
0
2
4
6
8
10
0
10
20
30
85
90

# Conclusions

• Predictions of yet unknown crystals. This motivates renewed efforts to experimentally synthesise them (hints of possible synthesis do exist)

• The predicted crystals share structural similarities with the glass (low-density, high proportion of boroxol rings)

• Rich polymorphism + mechanical softness ←→ ease of vitrification

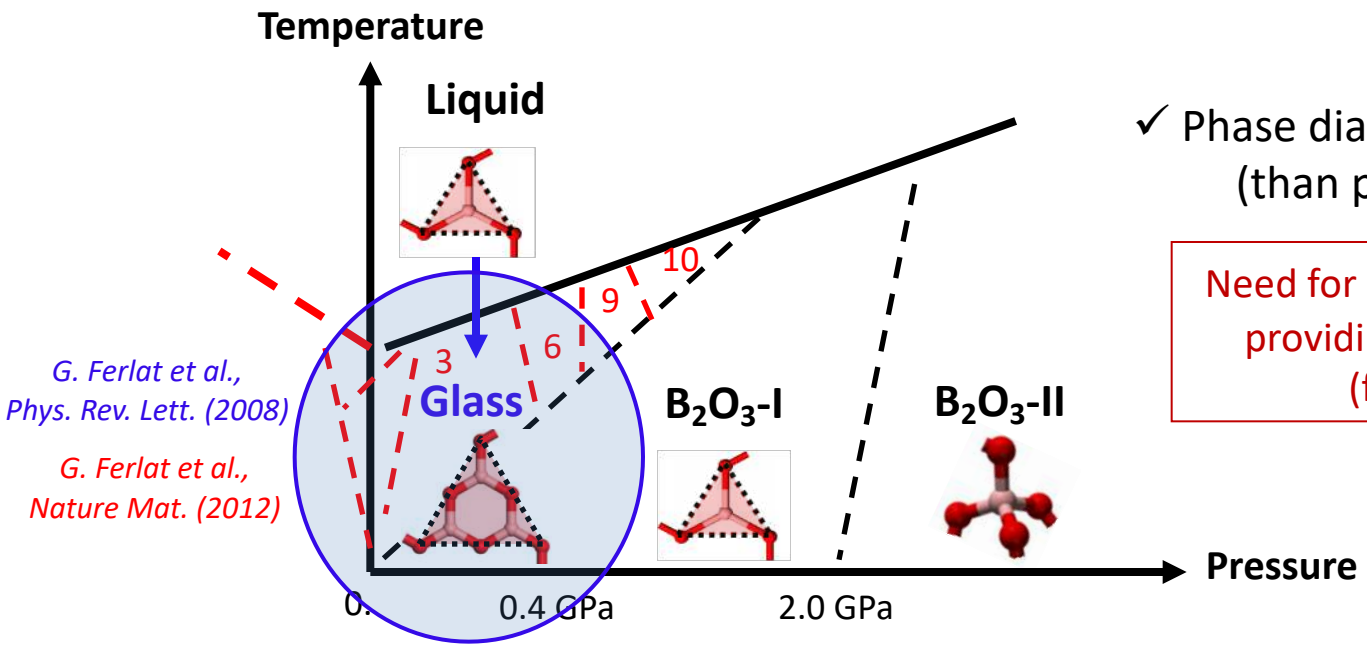
• Large flexibility of the B-O-B bonds. Importance of vdW interactions

• Evidence of a boroxol stabilisation energy of ~ 10 kcal/mol

# Perspectives

▪ Exploration of the phase diagram: Metadynamics + PIV metric
*collaboration F. Pietrucci (Sorbonne U.), M. Salanne (Sorbonne U.)*

# Perspectives




*G. Ferlat et al., Phys. Rev. Lett. (2008)*

*G. Ferlat et al., Nature Mat. (2012)*

✓ Phase diagram could be much richer (than presently determined)

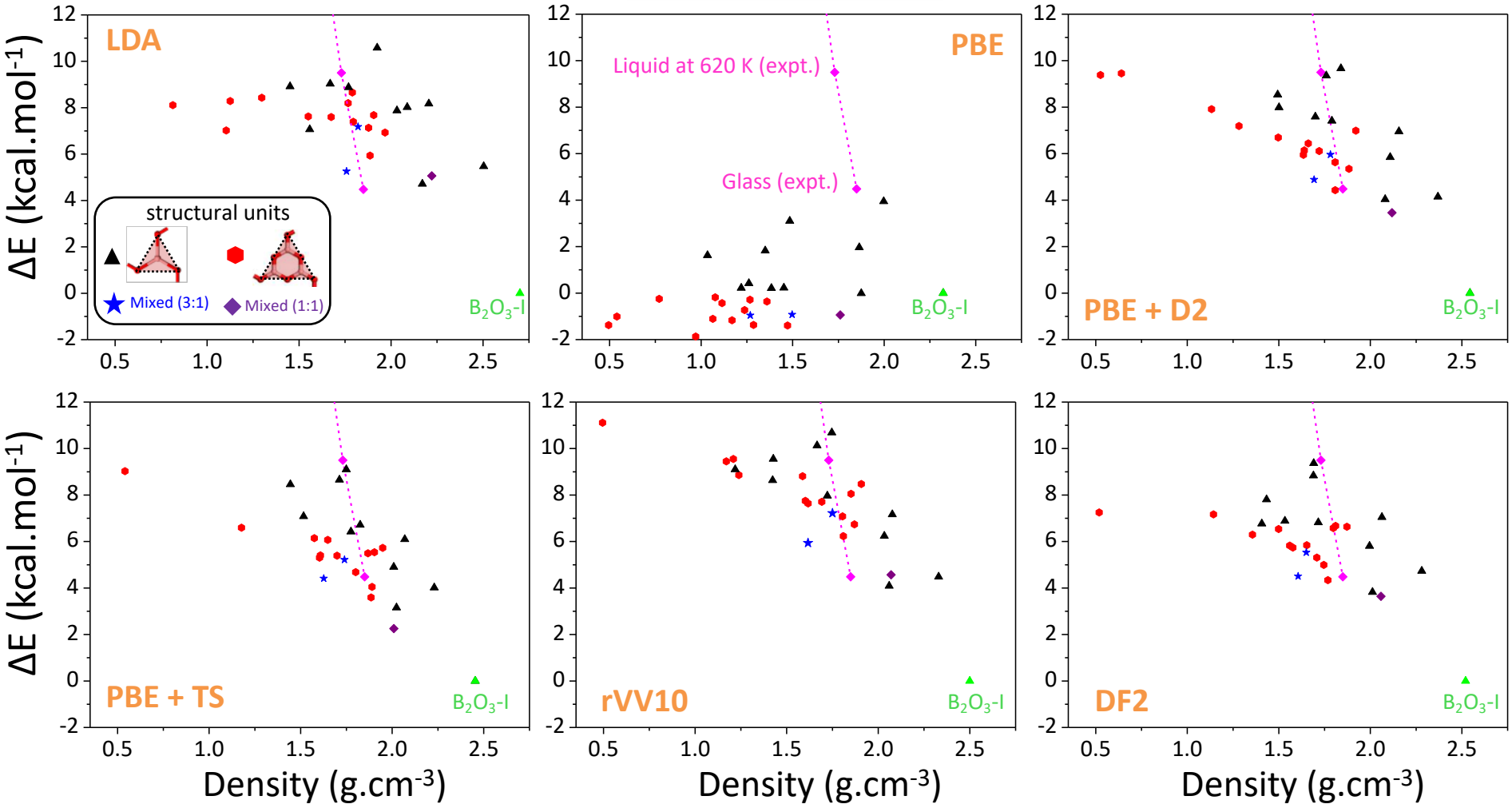
Need for an efficient atomistic method providing the transition pathways (free-energy barriers)

**Perspectives:** - determine the p-T conditions of stability for the novel phases
- track the structural transformations as the liquid is cooled down

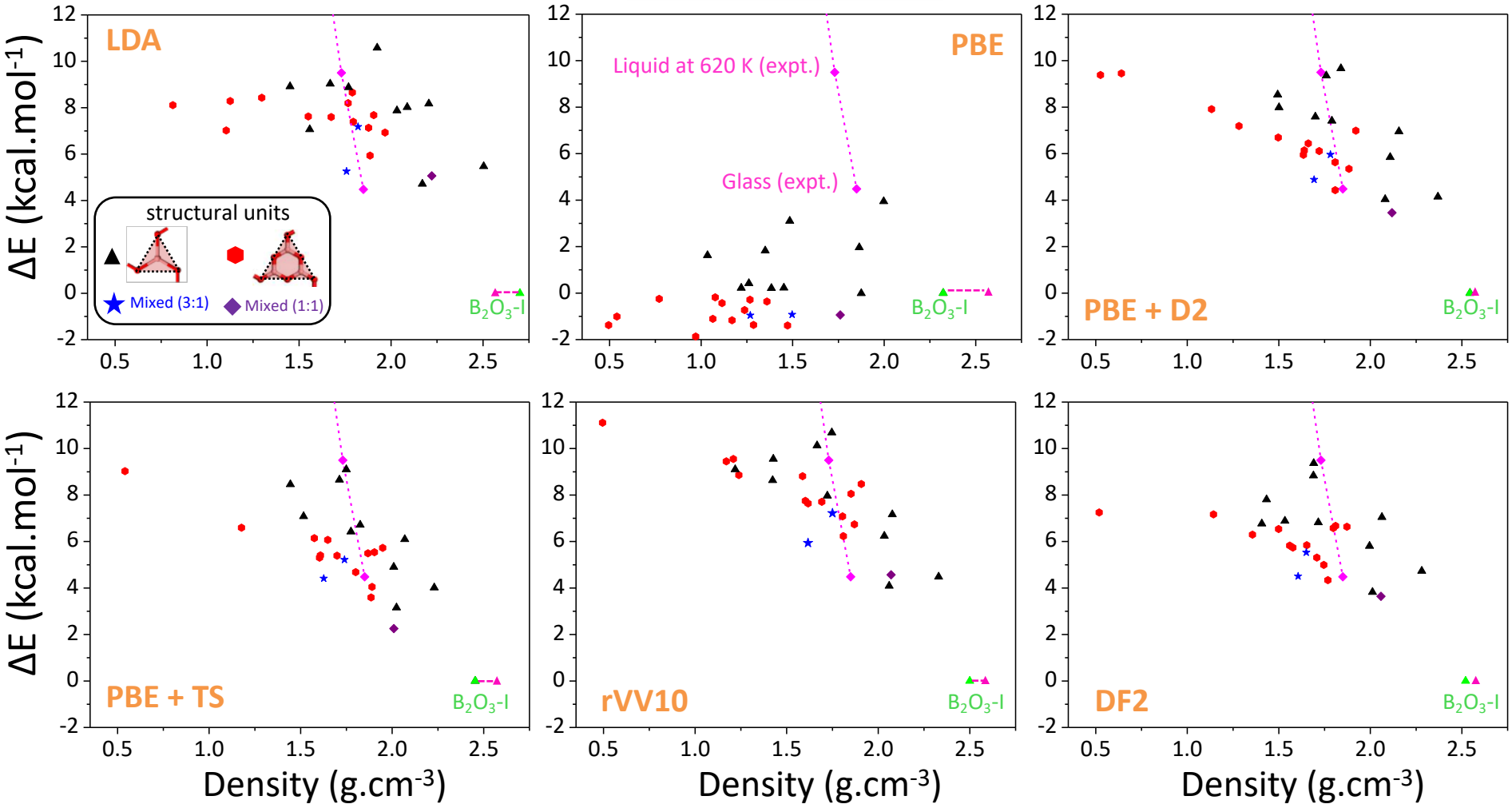
• What are the **structural connections between the known and the novel crystals** ? (*i.e.* can we obtain a novel polymorph by *e.g.* shearing $B_2O_3$-I) ?

• What are the **structural connections between the glass and the novel crystals** ? Can the glass be devitrified ? What is the glass **nanoscale organisation** ?

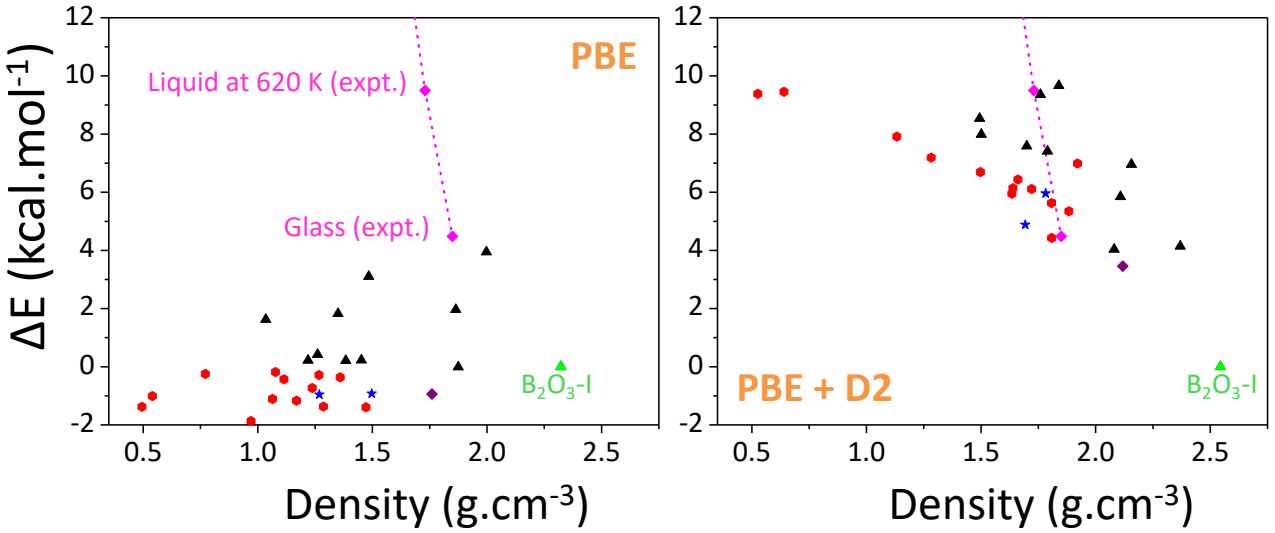
# DFT scenari


LDA
PBE
PBE + D2
PBE + TS
rVV10
DF2
Liquid at 620 K (expt.)
Glass (expt.)
structural units
Mixed (3:1)
Mixed (1:1)
B2O3-I
ΔE (kcal.mol-1)
Density (g.cm-3)

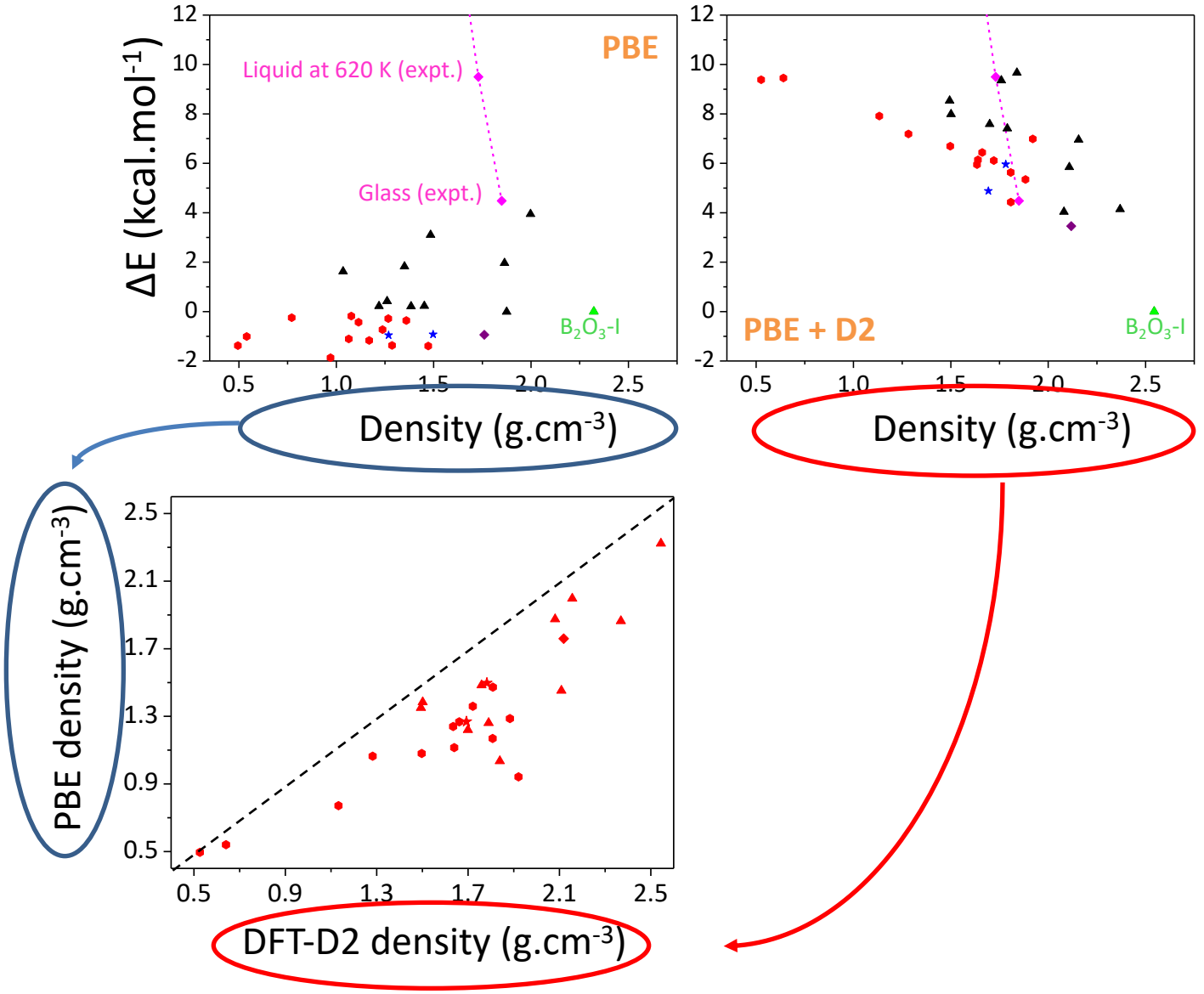
# DFT scenari


LDA
PBE
PBE + D2
PBE + TS
rVV10
DF2
Liquid at 620 K (expt.)
Glass (expt.)
structural units
Mixed (3:1)
Mixed (1:1)
B2O3-I
ΔE (kcal.mol-1)
Density (g.cm-3)

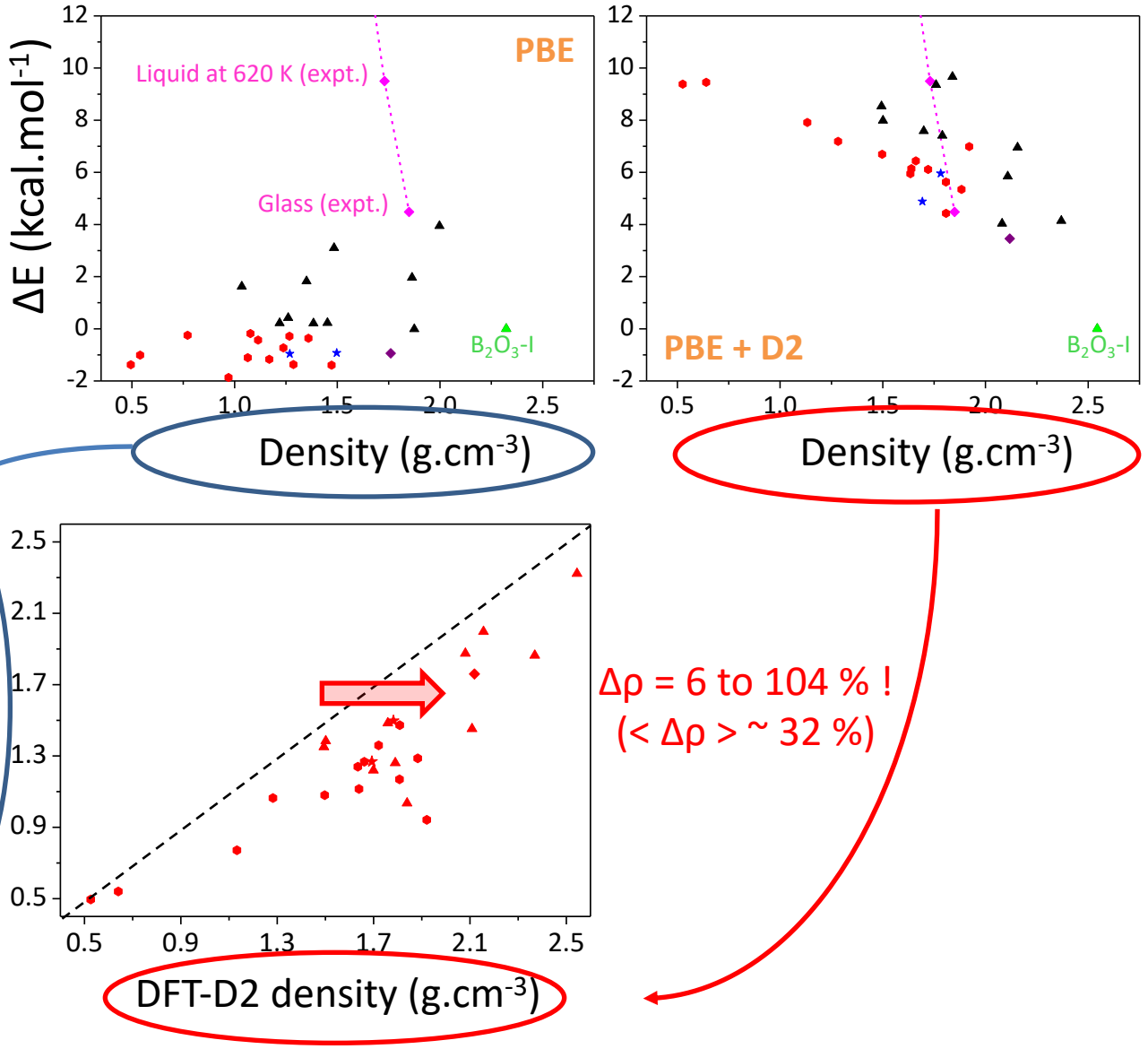
# DFT-GGA versus DFT-D



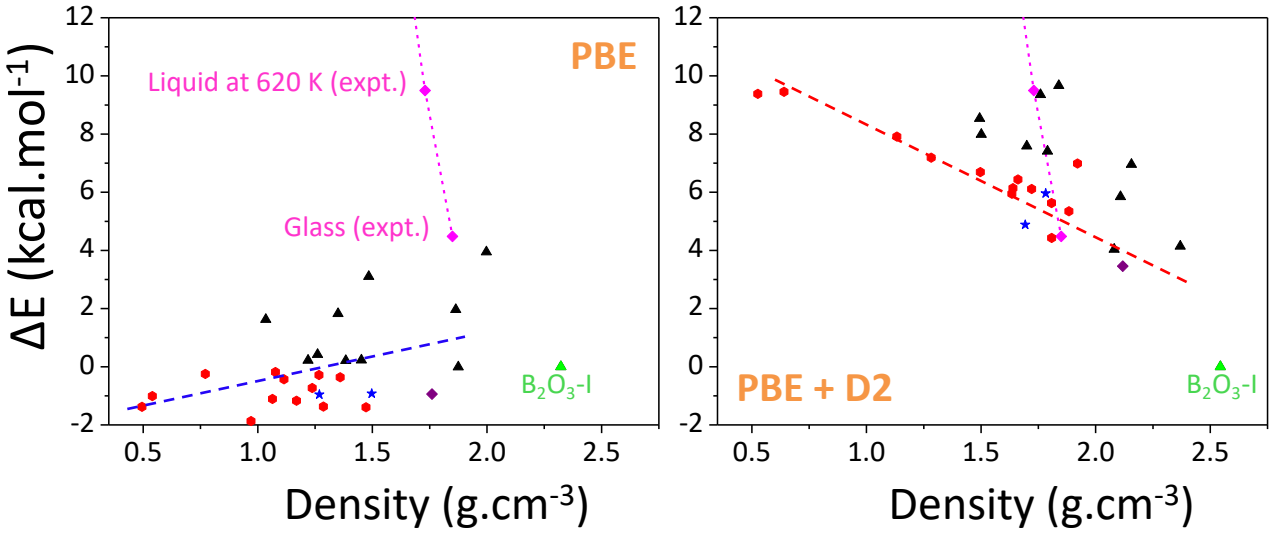
# DFT-GGA versus DFT-D



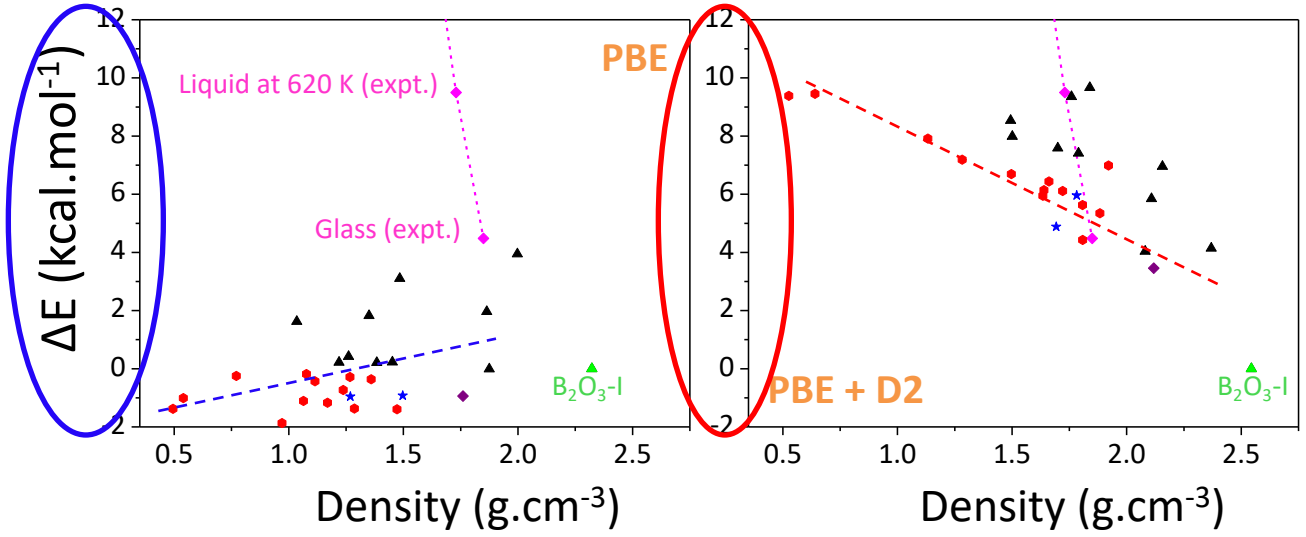
# DFT-GGA versus DFT-D

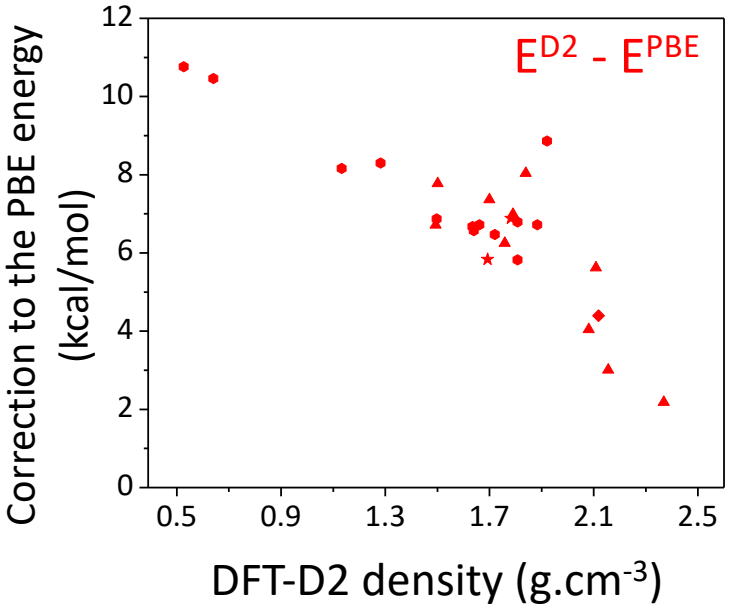


# DFT-GGA versus DFT-D



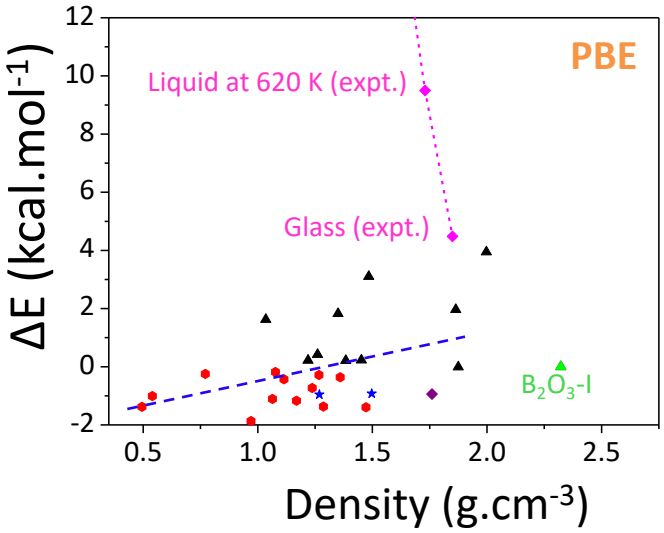
# DFT-GGA versus DFT-D

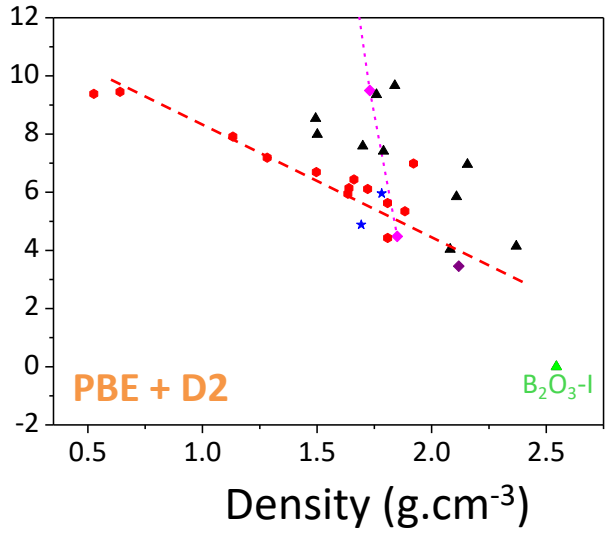


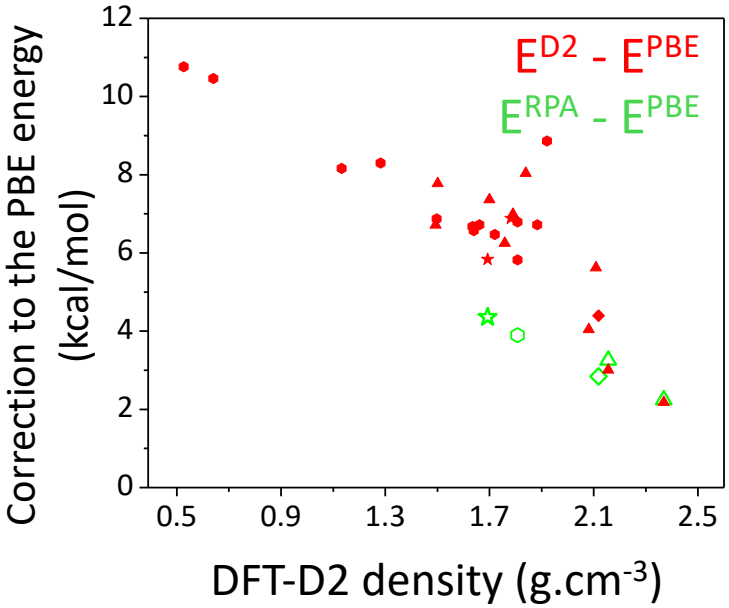




vdW: increasing energy penalty with decreasing density

# DFT-GGA versus DFT-D



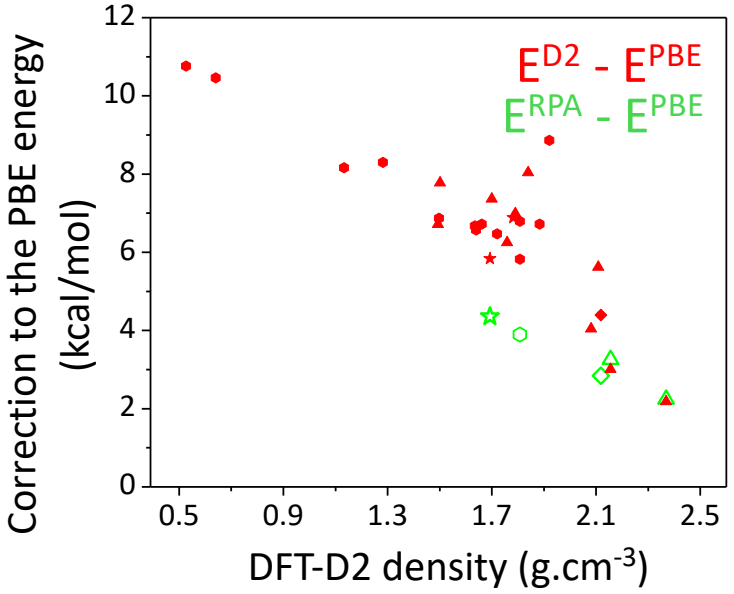



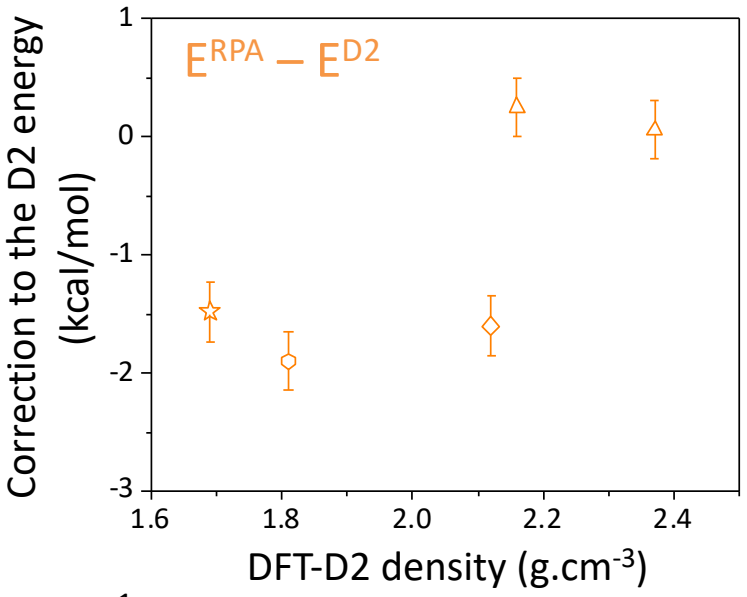



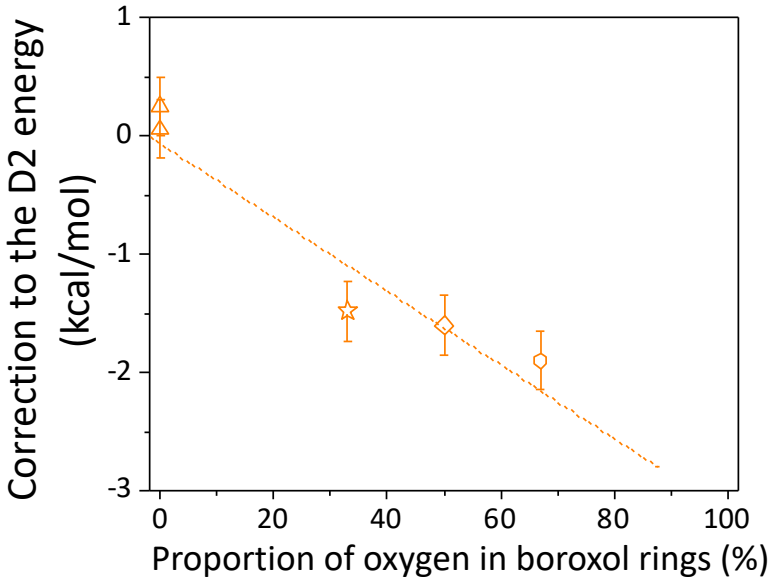

vdW: increasing energy penalty with decreasing density

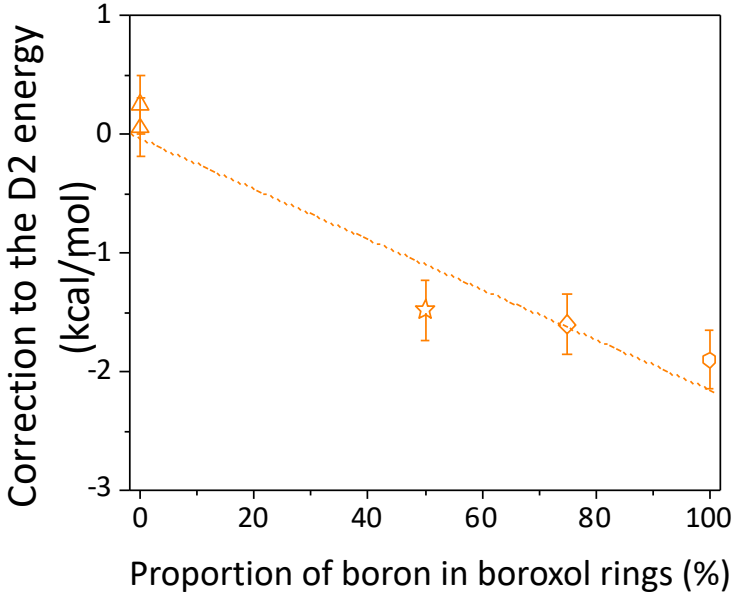
Trend confirmed by RPA

# Many-body beyond vdW



# Polymorphism and ease of vitrification

Nature **257**, 370 (1975)

## Strained mixed-cluster model for glass structure

C. H. L. Goodman

Standard Telecommunication Laboratories Ltd, London Road, Harlow, Essex, UK

*Many features of glass behaviour can be explained by a new approach to glass structure based on two ideas. First, glass-forming melts generate 'clusters' of structurally non-related polymorphs which associate on cooling but cannot nucleate, and second, inter-cluster thermal strain can be relieved by subsequent 'plating-out' of modifier impurities.*

Nature **260**, 35 (1976)

## Non-crystallinity and polymorphism in elemental solids

Rong Wang
Martin D. Merz

THIS paper shows a universal correlation of the non-crystalline state with polymorphism in elemental solids. This is demonstrated by a map constructed on a plot of the number of polymorphic forms (NPF) against the group number (GN) for all solid elements in the Periodic Table (Fig. 1). From this result, we propose that both the structure and occurrence of a non-crystalline solid are governed by the structures shown by crystalline states of the element.

nature COMMUNICATIONS

ARTICLE

Received 29 Jan 2016 | Accepted 22 Jun 2016 | Published 2 Aug 2016

DOI: 10.1038/ncomms12315

## Spectral descriptors for bulk metallic glasses based on the thermodynamics of competing crystalline phases

Eric Perim[1,2,*], Dongwoo Lee[3,*], Yanhui Liu[4,*], Cormac Toher[1,2], Pan Gong[4], Yanglin Li[4], W. Neal Simmons[1,2], Ohad Levy[1,2], Joost J. Vlassak[3], Jan Schroers[4] & Stefano Curtarolo[1,2]

Metallic glasses attract considerable interest due to their unique combination of superb properties and processability. Predicting their formation from known alloy parameters remains the major hindrance to the discovery of new systems. Here, we propose a descriptor based on the heuristics that structural and energetic 'confusion' obstructs crystalline growth, and demonstrate its validity by experiments on two well-known glass-forming alloy systems. We then develop a robust model for predicting glass formation ability based on the geometrical and energetic features of crystalline phases calculated *ab initio* in the AFLOW framework. Our findings indicate that the formation of metallic glass phases could be much more common than currently thought, with more than 17% of binary alloy systems potential glass formers. Our approach pinpoints favourable compositions and demonstrates that smart descriptors, based solely on alloy properties available in online repositories, offer the sought-after key for accelerated discovery of metallic glasses.

# QMC details

- Variational ansatz: Jastrow-Slater wave-function
- Pseudos-potentials of Burkatzki-Filippi-Dolg,
- Supercells of up to 60 atoms, special Baldereschi *k*-point

**Geometry relaxation at VMC level:**

- contracted basis set: (6s4p)/[2s1p] for B and (5s4p)/[2s1p] for O,
- fully optimised wave-function (Jastrow + Slater orbitals)

**Energetics at LRDMC level**

Large uncontracted basis set:

- for the determinant: (10s10p1d) gaussian type orbitals for both B and O,
- for the Jastrow three- and four-body terms: (2s2p1d) gaussian type orbitals

TurboRVB package