Predictions of $\text{B}_2\text{O}_3$ polymorphs from first-principles: implications for the glassy phase

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From first-principles calculations of experimental data (diffraction, IR, Raman, NMR), determination of the rings’ proportion in the glass.

The glass structure is dominated by boroxol rings.
Marked structural changes occur for $500 < T < 1500$K

Existence of a (boroxol) ring stabilisation energy: $\Delta E = -5.6 \pm 1.0$ kcal/mol

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

**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$_2$O$_3$-I

**Anomaly n 2:** the glass has a **low density** (1.84 g.cm$^{-3}$) compared to the known crystal (B$_2$O$_3$-I: 2.55 g.cm$^{-3}$)
**B₂O₃ versus SiO₂ polymorphism**

**B₂O₃**

- H-H₀ (kcal.mol⁻¹BO₃/₂) vs Framework density (B per nm³)

  - Glass
  - B₂O₃-I

**SiO₂**

- H-H₀ (kcal.mol⁻¹SiO₂) vs Framework density (Si per nm³)

  - Zeolites
  - Tridymite
  - Cristobalite
  - Moganite
  - Coesite
  - Quartz

\[ \rho_{\text{glass}} \approx 0.71 \rho_{\text{B₂O₃-I}} \]

\[ \rho_{\text{glass}} \approx 0.95 \rho_{\text{tridymite}} \]

\[ \rho_{\text{glass}} \approx 0.92 \rho_{\text{cristobalite}} \]

**B₂O₃ anomaly n 2**: the glass has a low density compared to the known crystal
**B₂O₃ versus SiO₂ polymorphism**

**B₂O₃**

- Poor polymorphism
- (very) good glass former

**SiO₂**

- Rich polymorphism
- Good glass former

**B₂O₃ anomaly n 3:** Poor polymorphism (despite very high aptitude to vitrify)
Case (a): There are several polymorphs of similar energy

Examples (organic molecules):

- Chlorothalonil
- Aspirin layer stacking disorder


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

This is typically the case for SiO$_2$, ...
Polymorphism and energetic landscape

Potential energy

Coordinates

“defective quartz-like”
“defective coesite-quartz”
“defective coesite-like”
coesite
quartz
Case (b) There is a polymorph of much lower energy
\( \Delta E \geq 10 \text{ kJ/mol} \sim 3 \text{ kcal/mol} \)


monomorphic behaviour,
hard to vitrify (easy to crystallize)

This is typically the case for Ag, Si, Ge, ...
B$_2$O$_3$: Anomaly n 4

Why does B$_2$O$_3$ vitrify so easily and never crystallize from the melt?

Anomaly n 4: the crystallisation of B$_2$O$_3$-I from the melt at ambient pressure has never been observed (even when seeded with crystals). No crystal growth at any imposed cooling rate unless pressure is applied (crystallization anomaly).
Why does $\text{B}_2\text{O}_3$ vitrify so easily and never crystallize from the melt?

**Anomaly n 4**: the crystallisation of $\text{B}_2\text{O}_3$-I from the melt at ambient pressure has never been observed (even when seeded with crystals). No crystal growth at any imposed cooling rate unless pressure is applied (crystallization anomaly).

Crystallization into $\text{B}_2\text{O}_3$-I occurs only if a small pressure ($\sim 0.4$ GPa) is applied to the melt.
Why does \( \text{B}_2\text{O}_3 \) vitrify so easily and never crystallize from the melt?

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Crystallization into \( \text{B}_2\text{O}_3 \)-I occurs only if a small pressure (\( \sim 0.4 \) GPa) is applied to the melt.

N.B.: \( \text{B}_2\text{O}_3 \)-I can also be obtained by dehydration of \( \text{H}_3\text{BO}_3 \).
Why does \( \text{B}_2\text{O}_3 \) vitrify so easily and never crystallize from the melt?

**Anomaly n 4**: the crystallisation of \( \text{B}_2\text{O}_3\)-I from the melt at ambient pressure has never been observed (even when seeded with crystals). No crystal growth at any imposed cooling rate unless pressure is applied (*crystallization anomaly*).

Crystallization into \( \text{B}_2\text{O}_3\)-I occurs only if a small pressure (~0.4 GPa) is applied to the melt.
The $\text{B}_2\text{O}_3$ anomalies (summary)

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

**Anomaly n 1:** the glass has a low density ($1.84 \text{ g.cm}^{-3}$) compared to the known crystal ($\text{B}_2\text{O}_3$-I: $2.55 \text{ g.cm}^{-3}$)

**Anomaly n 2:** the glass has a very different medium-range structure, dominated by boroxol rings.

**Why does $\text{B}_2\text{O}_3$ vitrify so easily and never crystallize from the melt?**

**Anomaly n 3:** Poor polymorphism despite very high aptitude to vitrify

**Anomaly n 4:** Crystallization from the melt at ambient pressure never observed unless pressure is applied (*crystallization anomaly*).

The origin of these anomalies is to be found in the existence of yet *unknown* polymorphs.
There are at least two reports of low-density crystals (incorrectly assigned as $\text{B}_2\text{O}_3\text{-I}$):

- S. S. Cole, N. W. Taylor, J. Am. Ceram. Soc., 18, 55 (1935) : $\rho = 1.805 \text{ g.cm}^{-3}$
- S. Kocakusak et al., Chem. Eng. Proc. 35, 311 (1996) : $\rho = 0.69 \text{ g.cm}^{-3}$!

Production of anhydrous, crystalline boron oxide in fluidized bed reactor


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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.
(exhaustive) search for new $\text{B}_2\text{O}_3$ 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]

N.B. : the boroxol units are **self-similar** to the $\text{BO}_3$ units.

\[\text{BO}_3 \text{ triangle} \quad \text{B}_3\text{O}_6 \text{ super-triangle}\]
(exhaustive) search for new $\text{B}_2\text{O}_3$ polymorphs

⇒ Using decoration of topological networks

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

- BO$_3$ triangle
- B$_3$O$_6$ 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:
  - **13 networks** (originally applied to $sp^2$-carbon structures)

✓ **Decoration** of the networks vertices by the relevant **building units**:
(exhaustive) search for new $\text{B}_2\text{O}_3$ polymorphs

⇒ Using decoration of topological networks

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

![BO$_3$ triangle and $\text{B}_3\text{O}_6$ super-triangle](images)

✓ 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:

- **13 networks** (originally applied to $sp^2$-carbon structures)

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

- **13 networks**
- **T1 to T13**
- **T1-b to T13-b**
- $2 \times 13 - 1 = 25$ new $\text{B}_2\text{O}_3$ crystals (with 10 to 135 atoms per unit cell)

N.B.: T13 is the known $\text{B}_2\text{O}_3$-I crystal

T8 and T10: half of 3-fold rings (50%)
(exhaustive) search for new $\text{B}_2\text{O}_3$ polymorphs

⇒ Using decoration of topological networks

✓ Relevant building units (for ambient polymorphs):

✓ 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: 13 networks (originally applied to $sp^2$-carbon structures)

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

13 networks $\rightarrow$ T1 to T13 $\rightarrow$ T1-$b$ to T13-$b$ $\rightarrow$ $2\times13 - 1 = 25$ new $\text{B}_2\text{O}_3$ 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, CASTEP code)
New $\text{B}_2\text{O}_3$ polymorphs: *First-principles* relaxation

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

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

- Relaxations of positions and unit cell at 0 K (*CASTEP* code):  
  PW basis set: 40 Ry, Ultra-soft PP, k-point grid $\leq 0.05 \text{ Å}^{-1}$

N.B. : for most networks, many local minima could be found. In the following, we show only the lowest-energy minimum for a given topology.
Exploiting isomorphism: graphene-like

3-coordinated vertex

$sp^2$-carbon graphene

$BO_3$ unit

$BO_3$-decorated graphene

Boroxol ring

boroxol-decorated graphene
Exploiting the self-similarity

In a given structure:

\[ N \text{ atoms} \]
\[ \text{length: } L \]
\[ \text{volume: } V \]
\[ \text{density: } \rho \]

\[ \text{B}_2\text{O}_3-\text{l}: \rho = 2.56 \text{ g.cm}^{-3} \]

\[ \text{B}_2\text{O}_3-\text{l-b (3D unrelaxed)}: \rho = 0.96 \text{ g.cm}^{-3} \]
\[ \text{B}_2\text{O}_3-\text{l-b (relaxed)}: \rho \sim 1.4 \text{ g.cm}^{-3} \]
Wacław Franciszek Sierpiński (1882-1969)

The Sierpiński carpet (1915)

Wacław Franciszek Sierpiński (1882-1969)
New B$_2$O$_3$ polymorphs: energy-density

Many low-energy crystals (lower than the glass, close to that of B$_2$O$_3$-I).

The lowest energy crystals have high amounts of boroxol rings (50 or 100%).
There are many crystals of similar energy and density.

This polymorphic cloud is close to the liquid and glass densities.

This polymorphism induces the vitrification in a low-density glass.

Overall good agreement between the novel polymorphs’ S(q) and that of the glass. The novel crystals bear greater structural similarity with the glass than B$_2$O$_3$-I.

Glass expt. data: A. C. Hannon et al., JNCS 177 299 (1994)
New B$_2$O$_3$ polymorphs: effect of pressure

![Graph showing the relationship between Δ$H_0$ (kcal/mol) and density (g/cm$^3$) for different polymorphs of B$_2$O$_3$. The graph indicates the effect of pressure on the stability of these polymorphs.](image)
New $\text{B}_2\text{O}_3$ polymorphs: effect of pressure

$\Delta H_0$ (kcal/mol)

Density (g/cm$^3$)

0.5 GPa

- $\blacktriangle$ 0 % 3-rings
- $\blacktriangle$ 50 % 3-rings
- $\bullet$ 100 % 3-rings

New $\text{B}_2\text{O}_3$ polymorphs:

Effect of pressure
New B$_2$O$_3$ polymorphs: effect of pressure

For pressures $\geq$ 0.5 GPa, B$_2$O$_3$-I is the most stable crystal.

Fully consistent with the experimental observations (a small pressure is required to nucleate B$_2$O$_3$-I from the melt).
The $\text{B}_2\text{O}_3$ anomalies (summary)

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

- **Anomaly n 1**: the glass has a low density (1.84 g.cm\(^{-3}\)) compared to the known crystal ($\text{B}_2\text{O}_3$-I: 2.55 g.cm\(^{-3}\))

- **Anomaly n 2**: the glass has a very different medium-range structure, dominated by boroxol rings.

Why does $\text{B}_2\text{O}_3$ vitrify so easily and never crystallize from the melt?

- **Anomaly n 3**: Poor polymorphism despite very high aptitude to vitrify

- **Anomaly n 4**: Crystallization from the melt at ambient pressure never observed unless pressure is applied (crystallization anomaly).

because there are other (more relevant) crystals

because of the energetic degeneracy of the polymorphs (hidden polymorphism)

the polymorphic degeneracy is lifted by pressure
SiO$_2$ versus B$_2$O$_3$ polymorphism

- B$_2$O$_3$ behaviour is reconciled with that from SiO$_2$ (richness of polymorphism)
SiO$_2$ versus B$_2$O$_3$ polymorphism

✓ B$_2$O$_3$-I, an equivalent of silica coesite?
New $\text{B}_2\text{O}_3$ polymorphs: Can we observe them?

- All predicted crystals lie in the ‘thermodynamically accessible’ energy range (~4 kcal/mol). However, they could be kinetically hindered.

- Part of the difficulty to synthesize a given polymorph may lie in the crystals degeneracy (since one must avoid the amorphization).

The obtained polymorphism is *hidden* (by the vitrification): revealing it would require to produce conditions such that one crystal is energetically favored over all the others.

- However, there are at least two experimental reports of low-density crystals (uncorrectly assigned as $\text{B}_2\text{O}_3$ -I):

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

  ✓ S. Kocakusak *et al.*, Chem. Eng. Proc. 35, 311 (1996) : $\rho = 0.69 \text{ g.cm}^{-3}$
Chemical synthesis, using sol-gel techniques:

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

1) Hydrolysis: $R_2B_3O_5$-$OR + H_2O \leftrightarrow R_2B_3O_5$-OH + ROH

Followed by either:
2a) alcohol condensation:
   $R_2B_3O_5$-OH + RO-$R_2B_3O_5 \leftrightarrow R_2B_3O_5$-O-$R_2B_3O_5 + ROH$

or: 2b) water condensation:
   $R_2B_3O_5$-OH + HO-$R_2B_3O_5 \leftrightarrow R_2B_3O_5$-O-$R_2B_3O_5 + H_2O

Formation of boroxol-boroxol linkages
New B$_2$O$_3$ polymorphs: Are they synthesisable?

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


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

Boroxol modes at 875 cm$^{-1}$ ?!
New $\text{B}_2\text{O}_3$ polymorphs: Are they synthesisable?

- Physical synthesis, using PVD techniques: Magnetron sputtering, Infrared irradiation, ...

- Physical synthesis, using negative pressure...
Most (22) of the new crystals have a low density (< 2.0 g/cm³)
Some crystals have a very low density (< 1.1 g/cm³)
Nanoporous $\text{B}_2\text{O}_3$ polymorphs

- $\text{BO}_3$-decorated structure T7
- Boroxol-decorated structure T7-b

✓ Some crystals show cage- or channel-like structures

**Light, crystalline** and **porous** matrices: high potential for applications such as molecular sieves, hydrogen storage, ...

**Collaboration:** F.X. Coudert (Chimie-Paris)
Nanoporous $\text{B}_2\text{O}_3$ polymorphs

T10: 50% triangle - 50% boroxol

✓ Some crystals show cage- or channel-like structures
A hydrogen storage medium is provided, where the medium is comprised of boron oxide and closely related compounds such as orthoboric acid, metaboric acid, hydrated boric acid, and disodium borohydride. The medium is substantially an amorphous glassy network, albeit with local regions of order, pores, and networks that provide surface area. Hydrogen is adsorbed by the medium with a heat of adsorption of about 9 kJ/mol to about 13 kJ/mol, a value which is higher than that of the heat of adsorption of hydrogen on carbon. The value for the heat of adsorption of hydrogen on the inventive storage medium is provided by computation, and corroborated by experimental observation. The higher heat of adsorption of the medium provides for operation at temperatures higher than those provided by carbon. Further provided are methods by which the storage medium can be prepared in such a form so as to permit high capacity hydrogen storage, as well as an apparatus, with the inventive medium disposed therein, for storing hydrogen.
Boroxine chemistry and applications: A perspective

Andrew L. Koriche and Peter M. Iovine

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This perspective summarizes the chemistry of boroxines and outlines progress towards incorporating these ring structures into functional materials and macromolecular architectures. Special attention is paid to the dynamic covalent chemistry of boroxine ring construction and how these processes lead to novel molecular architectures and functional materials. Also highlighted in this perspective is the rich chemistry surrounding boroxine-ligand interactions and how these interactions favor many areas of boroxine chemistry.

Introduction

Boroxines, sometimes termed boronic acid anhydrides or boroxines, are the dehydration products of organoboronate acids. Substitution on the boroxine ring generally falls into three categories: trialkyl, trialkoxyl, or triaryl (Fig. 1).

![Generalized structure of boroxine ring-containing compounds.](image)

Fig. 1 Generalized structure of boroxine ring-containing compounds.

Historically, there were two common themes in boroxine-related research. First was the question of aromaticity. In 1936 Snyder et al. proposed "the relatively great stability of the cyclic trimer may be due in part to resonance effects involving an unsaturated electron pair of the oxygen atom and the open sextet of 3-covalent boron." Over the years a large number of papers have followed up on this proposition, but it is now generally accepted that organoboroxines possess little aromatic character. The second line of investigation focused on the propensity of aryloboroxines to form Lewis acid-base adducts with nitrogen-containing ligands. As early as 1932, Bröcker and Yano proposed an addition compound of diethylamine and phenylboronic acid.

Boroxine research has traditionally enjoyed a balanced existence between fundamental academic interests (e.g. structural considerations, thermodynamics, boroxine-ligand interactions and applications-driven research (phosphorus redox, lithium ion battery materials, etc.). In 2005, boroxines were thrust into the spotlight when the Yagi group published a landmark paper describing the synthesis and characterizations of the first crystalline aryloboroxine-based covalent organic framework (COF-1) material (Fig. 2).

The flurry of COF-related publications appearing since the disclosure of COF-1 has significantly expanded interest in boroxine-containing materials and has also highlighted the versatility of the boroxine ring system.

In this perspective we intend to summarize the diverse chemistry of boroxines and present a sampling of how these ring structures are used.

Introduction

Boronic acids easily react with diolulates to give boronate esters (Scheme 1a). An interesting feature of this condensation reaction is that it is fast and reversible, despite the fact that the covalent B-O bonds are stronger than typical C-O bonds. In the absence of alcohols, boronic acids can undergo self-condensation reactions to give six-membered boroxines (Scheme 1b). Again, these reactions are fast and reversible. In fact, trimerization already occurs to some extent if boronic acids are dissolved in dry chloroform. The condensation products of boronic acids, boronate esters and boroxines, are mild Lewis acids that can bind to N-donor ligands (Scheme 1c and 1d). The diverse B-N bonds are significantly less stable than the covalent B-O bonds. Nevertheless, the formation of tetra-coordinated adducts can be important, in particular in non-polar organic solvents.

All four reactions have been studied by chemists in various contexts. Most notably, the formation of boronate esters has been used extensively in carbohydrate chemistry, where boronic acids have found applications as protecting group or as receptors and sensors. In the following section it is described how these reversible reactions can be used to assemble complex molecular nanoarchitectures and polymeric materials.

2. Macrocycles

In a series of publications by Farman, Högl, Barber, and co-workers, the reactions of boronic acids with trivalent imine ligands derived from salicylaldehyde and anilinoalcohols are described. The reactions were found to depend on the nature of the anilinoalcohol, but in many cases it was possible to isolate macroyclic condensation products (I) containing two tetravalent boron centers (Scheme 2 and Fig. 3). The highest yields were generally obtained when the reactions were performed in borane or toluene using a Dean–Stark trap in order to remove the water byproduct.

Scheme 1 Reversible reactions of boronic acids. (a) condensation with diols to give boronate esters; (b) self-condensation to give boroxines; (c) addition formation of boronate esters with N-donor ligands NR; and (d) addition formation of boronines with N-donor ligands NR.
The design and synthesis of crystalline extended organic structures in which the building blocks are linked by strong covalent bonds are undeveloped areas of research. It is widely believed that the required microscopic reversibility of the crystallization of linked organic molecules into such solids is difficult if not impossible to achieve (the crystallization problem). The lack of crystalline cross-linked polymers is often cited as evidence in support of this view (7). Recently, we embarked on a program aimed at challenging this notion by constructing porous, crystalline, covalent organic frameworks (COFs) solely from light elements (H, B, C, N, and O) that are known to form strong covalent bonds in well-established and useful materials such as diamond, graphite, and boron nitride. The successful realization of COF materials through molecular building blocks would provide covalent frameworks that could be functionalized into lightweight materials optimized for gas storage, photonic, and catalytic applications.

We report a general design strategy and its implementation for the synthesis and crystallization of micro- and mesoporous crystalline COFs. These materials have rigid structures, exceptional thermal stabilities (to temperatures up to 600°C), and low densities, and they exhibit permanent porosity with specific surface areas surpassing those of well-known zeolites and porous silicates. The first two members, COF-1 ([(C<sub>H</sub>BO)<sub>x</sub>·y(C<sub>H</sub>O)]<sub>x</sub>) and COF-5 (C<sub>6</sub>H<sub>12</sub>BO<sub>x</sub>), can be synthesized using a simple “one-pot” procedure under mild reaction conditions that are efficient and high-yielding.
The expt. data (ΔH) were carried out at 300 K while the calculations at 0 K. However, calculations of the Zero-Point Energy (ZPE) show that vibrational contributions are negligible at 300K (and even tend to further stabilise, by ~1 kcal/mol, the novel polymorphs at T_g).

Contribution from London dispersions (van der Waals) were not included.

Typical DFT-GGA error bars are « commonly »: ~ 1 - 5 kcal/mol on ΔE
3-10 % on ρ
Assessing the London dispersions (using DFT-D functionals)

Beyond DFT-GGA: Quantum Monte-Carlo (*collaboration M. Casula*)

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**Figure 4.** In analogy with the Jacob's ladder classification of functionals the "stairway to heaven" is used here to classify and group DFT-based dispersion correction schemes. At ground level are methods which do not describe the long range asymptotics. Simple \( C_6 \) correction schemes sit on the first step, on the second step are approaches that utilise environment dependent \( C_6 \) corrections. The long range density functionals sit on step 3 and on step 4 and above are approaches which go beyond pairwise additive determinations of dispersion. Upon climbing each step of the stairway the level of approximation is reduced and the overall accuracy is expected to increase.

Work in progress: a polarisable force-field from *first-principles*

collaboration M. Micoulaut (LPTMC), M. Salanne (PECSA), A. Baroni (PhD)

- Ab-initio MD simulations (CPMD) used as benchmark trajectories
- “Force-matching” like approach to calibrate a polarisable force-field

B. Rothenberg, M. Salanne, C. Simon, R. Vuilleumier

✓ Perspectives:
- crystals: extension of the number of predictions
- liquids/glasses: extension to larger system sizes and longer simulation times, extensive exploration of the phase-diagram, ...
Conclusions

• Predictions of yet unknown crystals. This may motivate renewed efforts to experimentally synthesize the predicted crystals.

• The polymorphism richness is likely the reason for the ease of vitrification. The behavior of $\text{B}_2\text{O}_3$ is reconciled with that of e.g. $\text{SiO}_2$.

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

• The predictions are fully consistent with the experimentally observed crystallisation anomaly.

• Existence of a rings’ stabilisation energy (which has both electronic and topologic origins).