Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Supplementary Information

High Temperature Phases of Borophene: Borophene Glass and Liquid

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Decomposed coordinate numbers (DCNs) and their coefficients

We formulated the potential energy surface using the decomposed coordinate numbers (DCNs) as a local descriptor. DCNs describe the central boron atom together with its environment by checking the arrangement of boron atoms and holes in its neighborhood. Figure S1 (a) shows all possible DCN configurations. We considered the equivalent DCNs by the 6-fold rotation symmetry (C_6) and reflections over the six vertical planes passing through the central boron atom. In the cases of DCN=5 and 6, we further separated the DCNs, considering the numbers of boron atoms in the second-nearest neighbor sites, such as DCN=$5_{0\sim6}$, 5_7, …, 5_{11}, 5_{12} and $6_{0\sim6}$, 6_7, …, 6_{11}, 6_{12}. Figure S1 (b) shows how to determine these DCNs. For example, if there is only one hole in the first-nearest neighbor layer of the central boron atom, then the central boron atom has DCN=5. If there are also two vacancy sites in the second-nearest neighbor layer, then the central boron atom has DCN=5_{10}. We provide a constant term b and 25 formation energy regression coefficients related to the DCNs in Table S1.

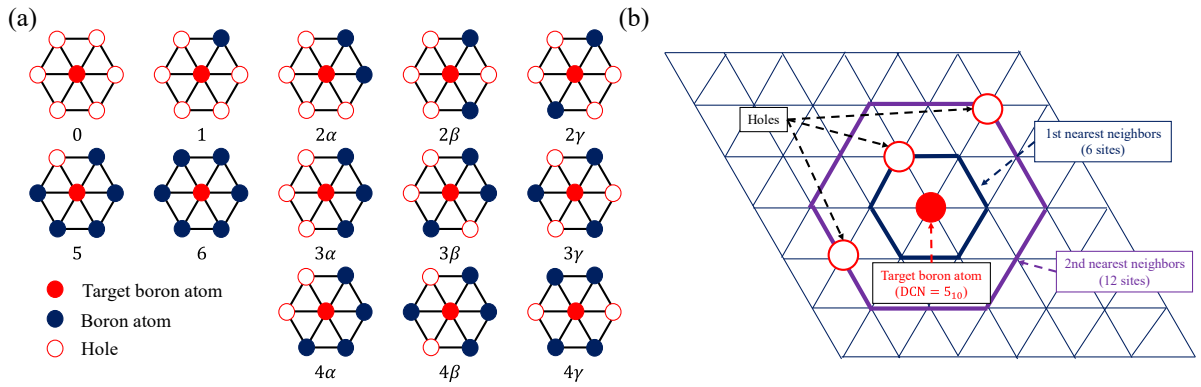


Fig. S1 (a) Arrangement of the boron atoms and the vacancy sites for each DCN, (b) example for DCN=5_{10}.

Table. S1 Regression coefficients for the formation energy described by the DCNs (Unit: eV/atom). The constant term (regression intercept) is b.

Type	b	0	1	2α	2β	2γ	
Coef.	0.0049	4.0011	3.3123	2.6126	0.9424	0.8965	
Type	3α	3β	3γ	4α	4β	4γ	
Coef.	1.0365	0.5365	0.3979	0.0556	−0.2538	0.1425	
Type	$5_{0\sim6}$	5_7	5_8	5_9	5_{10}	5_{11}	5_{12}
Coef.	−0.2754	−0.3112	−0.2861	−0.2835	−0.3052	−0.3500	−0.3454
Type	$6_{0\sim6}$	6_7	6_8	6_9	6_{10}	6_{11}	6_{12}
Coef.	−0.0829	−0.2509	−0.2504	−0.2294	−0.1656	−0.0928	0

Other fitting results for the formation energies and structures for calculation of the transition energies

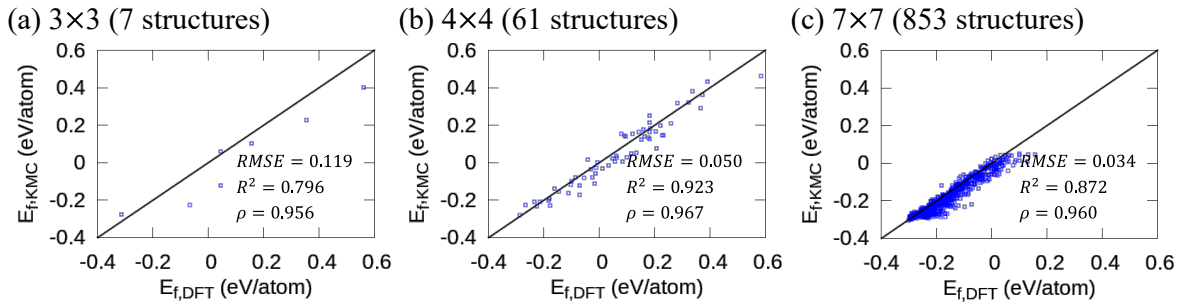


Fig. S2 The fitting of our model to the formation energies calculated by DFT for borophene structures with the parallelogram-unit cell with the size of (a) 3×3, (b) 4×4, and (c) 7×7.

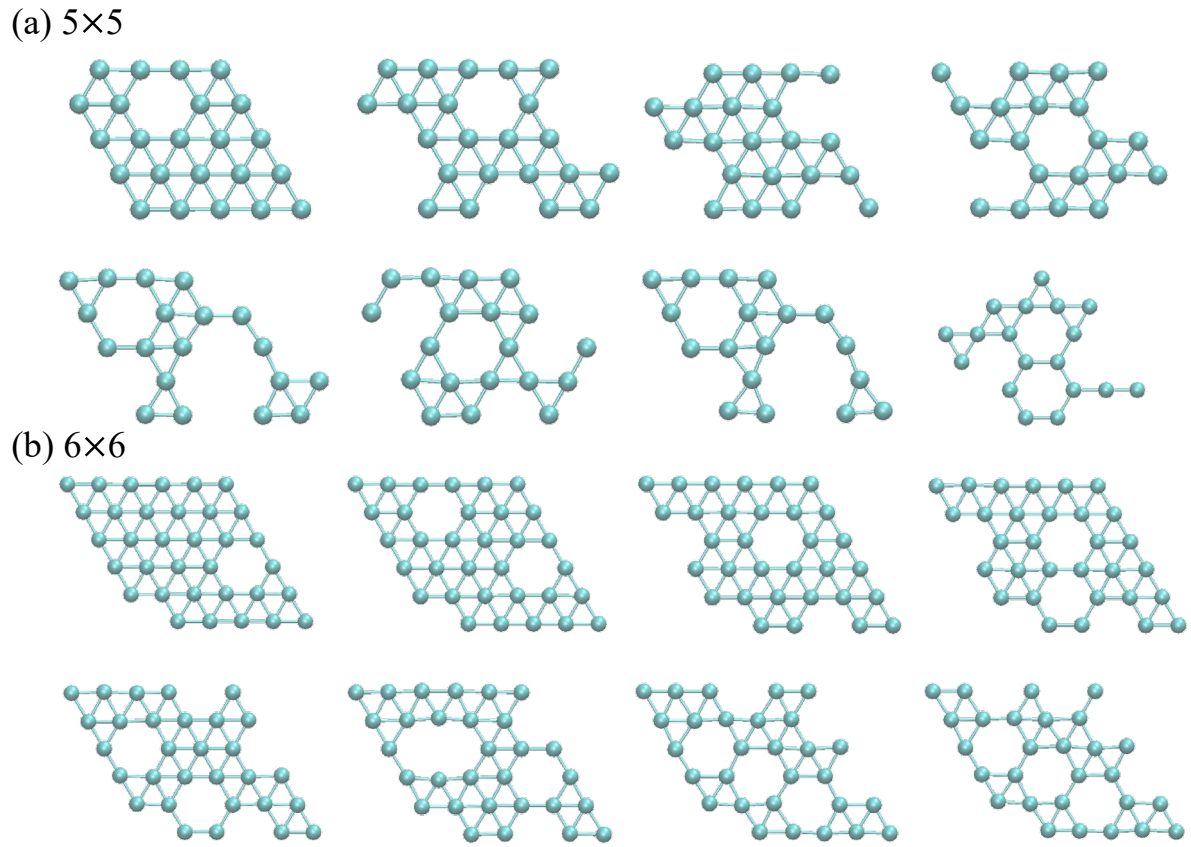
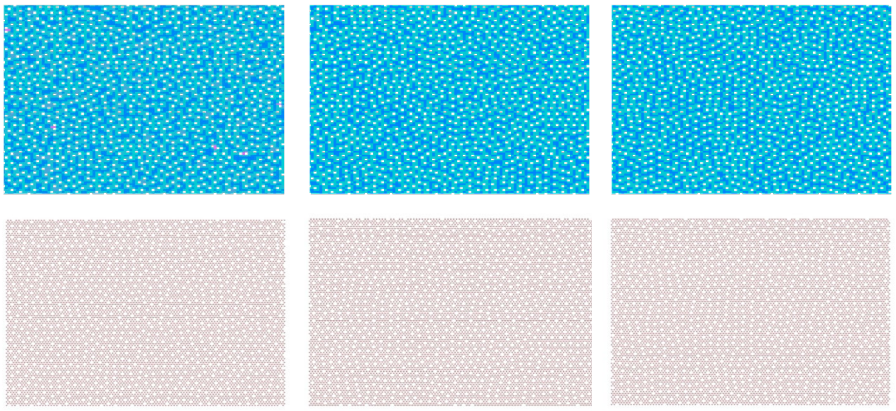


Fig. S3 Various borophene structures used for the fitting. These structures are based on stable structures of Fig. 1 and 2 with (a) 5×5 and (b) 6×6-unit cell sizes.

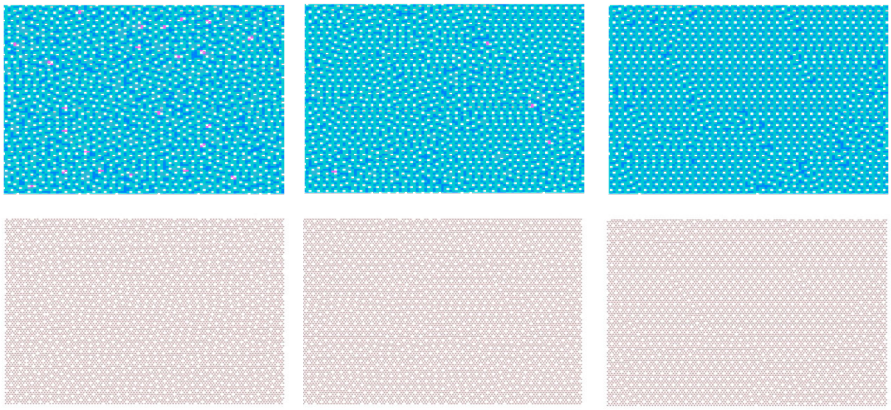
Configurations for different hole concentrations at selected temperatures

(a) $\eta = 0.10$



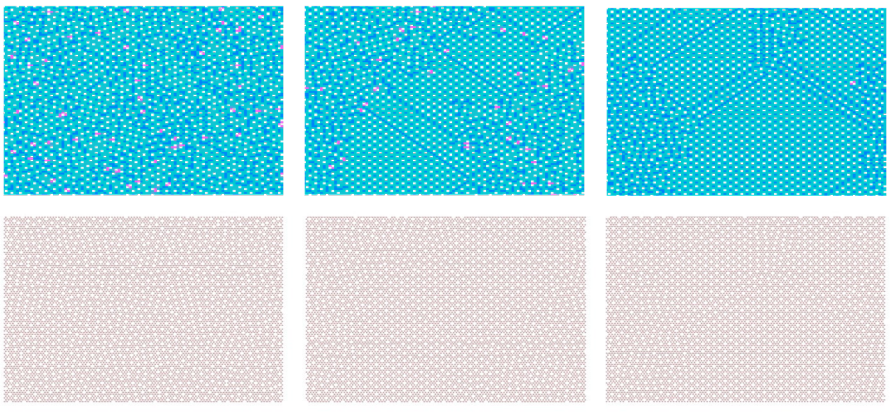
1400 K 800 K 500 K

(b) $\eta = 0.11$



1400 K 1050 K 500 K

(c) $\eta = 0.12$



1100 K 1050 K 500 K

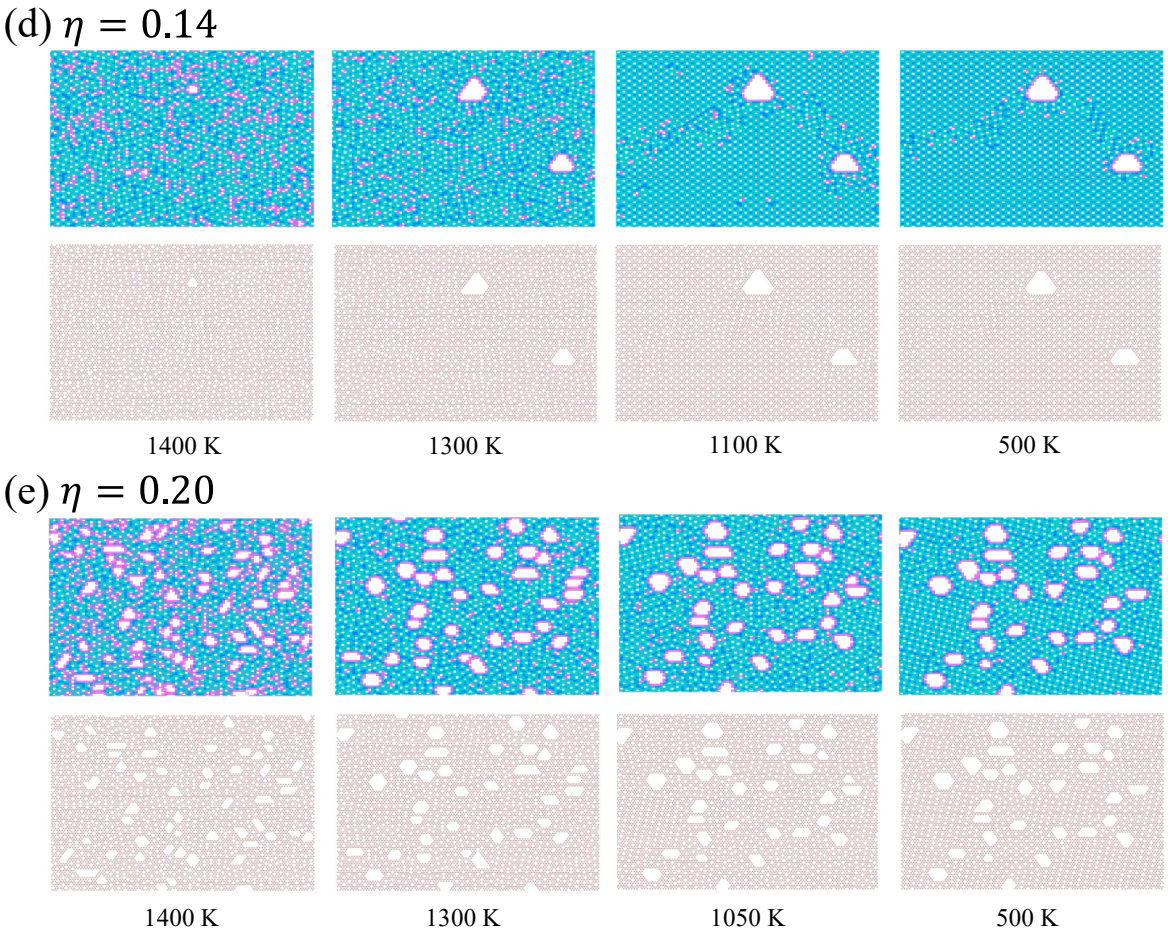


Fig. S4 Configuration changes for each vacancy concentration (a) η=0.10, (b) η=0.11, (c) η=0.12, (d) η=0.14, and (e) η=0.20 represented by VMD software[1]. Colors in the borophene structures at different temperatures denote the boron density: blue is high, cyan is average, magenta is low, and white is a hole.

A classification algorithm for distinguishing identical DCNs induced by symmetry operations using Gödel number-like values.

To classify equivalent DCNs generated by a 6-fold rotation symmetry (C_6) with a rotation axis perpendicular to the flat borophene and by reflections over six vertical planes passing through the center, we applied an algorithm for classification of the DCNs with Gödel number-like values, γ. Logical variables "*or*" and "*and*" within *if*-statements are used many times in the code, which implies that the code would be inefficient and spend long time for the classification. Gödel numbering (or encoding) was designed to prove one of the Hilbert's problems[2]. The encoding is that mathematical statements are converted to unique natural numbers by multiplying a sequence of prime numbers with exponents to denote a mathematical symbol. This relationship is bijective by the unique factorization theorem[3-4]. We applied this method with the binary numbers to distinguish the equivalent DCNs. We consider $\sigma(i,j)$ to be binary numbers: $\sigma = 1$ if there is a boron atom at (i,j) where i and j are the row/column indices, otherwise $\sigma = 0$. Then, $\gamma(i,j) = 2^{\sigma(i+1,j+1)}3^{\sigma(i,j+1)}5^{\sigma(i-1,j)}7^{\sigma(i-1,j-1)}11^{\sigma(i,j-1)}13^{\sigma(i+1,j)}$. For example, Figure S5 shows how to calculate the Gödel number-like value γ, in which case, only $\sigma(i+1,j+1)$, $\sigma(i,j+1)$ and $\sigma(i-1,j-1)$ are one, and the others are zero. So, $\gamma(i,j) = 2^1 3^1 5^0 7^1 11^0 13^0 = 42$. Next, we check where γ has same number in one of the lists including equivalent Gödel number-like values generated by DCNs and count the number of the boron atoms to have that DCN. This method is outlined in Algorithm.

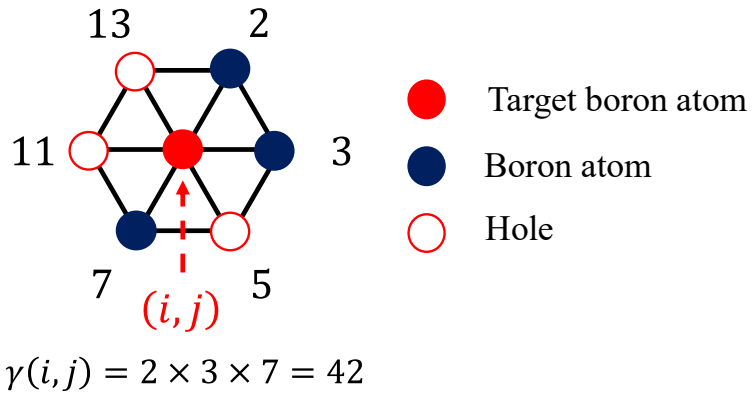


Fig. S5 Gödel number-like value of DCN=3β.

Algorithm: Classification of the equivalent DCNs with Gödel number-like value

1: **Input** $\sigma(i,j) \in \{0,1\}$, $i \in \{1,\dots,N_{col}\}$ and $j \in \{1,\dots,N_{row}\}$,
where $\sigma(i,j) = 0$ if a hole or 1 if the boron atom at (i,j), and N_{col} and N_{row} are column and row sizes of borophene.
Let $\Lambda = \{0,1,2\alpha,\dots,6_{10},6_{11},6_{12}\}$ be a DCN set and Γ: $k \in \Lambda \rightarrow \gamma_k$ be a mapping onto a Gödel number-like value γ_k (e.g., $\Gamma(1) = \{2,3,5,7,11,13\}$ and $\Gamma(2\alpha) = \{6,15,26,35,77,143\}$).

2: **for all** (i,j) **do**

3: $\gamma \leftarrow 2^{\sigma(i+1,j+1)}3^{\sigma(i,j+1)}5^{\sigma(i-1,j)}7^{\sigma(i-1,j-1)}11^{\sigma(i,j-1)}13^{\sigma(i+1,j)}$ *// Get Gödel number-like value γ*

4: **if** $\gamma \in \Gamma(k)$ **then** *// Check where γ is in $\Gamma(k)$ (k: a DCN type)*

5: **if** $k = 5$ or 6 **then** *// Check subscript for $DCN = 5$ or 6*

6: **Count** $N_{B,2nd}$ *// Count the number of boron atoms in 2nd layer.*

7: **end if**

8: $N_k \leftarrow N_k + 1$ *// Count one if γ is in $\Gamma(k)$*

9: **end if**

10: **end for** .

11: **Return** $N_{DCN} = (N_1,\dots,N_k,\dots,N_{6_{12}})$ *// Return N_{DCN}*

This algorithm is for classification of same DCN by rotation, and reflection.

Classification between glass and liquid

There are many definitions of glass. One of them is "a solid having a non-crystalline structure, which continuously converts to a liquid upon heating"[5]. In this perspective, the order of the diffusion coefficient can be used to determine if the structure is glass or liquid.

To calculate the diffusion coefficient, we performed isothermal kMC simulations on the temperature interval between 500K and 1400K at a 10K step. The initial configurations are obtained by kMC of the cooling process for the hole concentrations, $\eta = 0.1$ and 0.14. These concentrations have glass and crystalline phases at low temperature, respectively.

Next, we calculate the mean-squared displacement, $\left\langle (r_i(t) - r_i(0))^2 \right\rangle_i$ at each temperature, where $r_i(t)$ is the ith hole position at time t and $\langle \cdot \rangle$ means the average of the squared displacements for all holes. The diffusion coefficients for each temperature are calculated by the ordinary least squares (see Fig. S6a).

The diffusion coefficients as a function of temperature for $\eta = 0.1$ and 0.14 are plotted in Fig. S6b and c. For borophene with $\eta = 0.1$, the diffusion coefficient varies smoothly in the whole temperature range. In contrast, for borophene with $\eta = 0.14$, a transition of the diffusion coefficient at temperature of ~1130K is clearly seen. So, we classified the configuration of $\eta = 0.1$ at low temperature as glass and that of $\eta = 0.14$ as crystalline phase. In the main text, the crystal structure of $\eta = 0.14$ is the α_1 borophene with large holes.

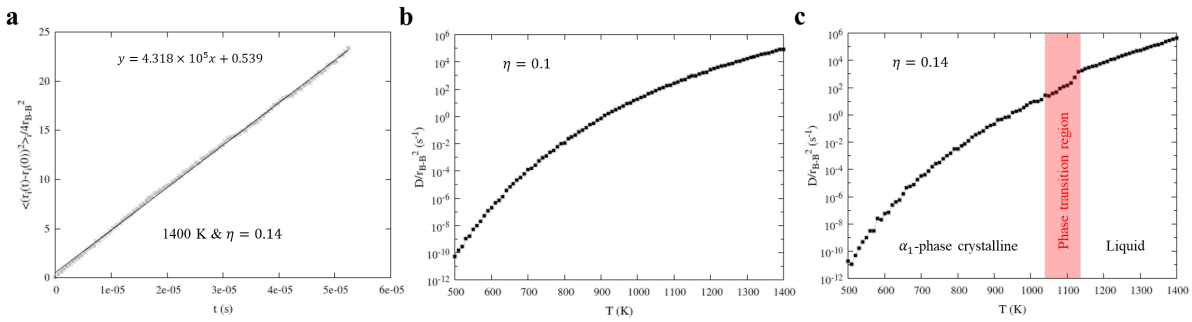


Fig. S6 Diffusion coefficient D of η=0.1 (glass) and 0.14 (α_1-crystalline) systems. (a) An example of the diffusion coefficient for =1400 K and =0.14 calculated from the mean-squared displacements at each time t. The diffusion coefficient D/r_{B-B}^2 (r_{B-B} is the bond length) is determined by the slope of the black line. Gray points are from an isothermal kMC simulation, and the line is the least squares regression line. The diffusion coefficients as a function of temperature for (b) $\eta = 0.1$ and (c) 0.14. Two phases at low/high temperature and the red region in (c) are based on Fig. 4a and b.

References

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2 K. Gödel disproved “the axioms of arithmetic are consistent” of Hilbert’s problems by “Gödel’s incompleteness theorems”.

3 K. Gödel, *Monatshefte für mathematik und physic,* 1931, **38**, 173.

4 E. Mendelson, *Introduction to Mathematical Logic* Springer, Boston, 3rd edn., 1987.

5 E. D. Zanotto, J. C. Mauro, *J. Non-Cryst. Solids* 2017, **471**, 490.