

**Supporting Information for**  
**Temperature-Dependent Paracrystalline Nucleation in Atomically**  
**Disordered Diamonds**

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**MD simulation details.** The large-scale MD simulations were performed by the LAMMPS molecule dynamics code <sup>1</sup>. With the file provided by Prof. Marks, the environment-dependent interatomic potential (EDIP) was used <sup>2</sup>, which has been proven to be a powerful force field to describe the physical nature of amorphous carbons <sup>3-5</sup>. The initial cube simulation box with a side length of 129 Å contains 108000 carbon atoms that are stacked in FCC lattice, and the periodic boundary conditions were assigned to all directions. With the timestep of 1 fs, the initial model was compressed at 300 K from 1.0 g/cm<sup>3</sup> to around 3.3 g/cm<sup>3</sup> through 10000 steps (10 ps), followed by a heating process for 10 ps and an isothermal annealing process for 2000 ps in NVT ensemble. After compression, the system was full of high-density tetrahedral amorphous carbons. In the heating process, different annealing temperatures (3000 K, 3200K, 3800K) were achieved for different simulations. Nosé-Hoover thermostat <sup>6, 7</sup> was used to control the temperature. During the annealing simulation process, the diamond-like nuclei emerged and grew in the amorphous matrix.

**YM method.** We used the YM method <sup>8</sup> to approximately calculate the nucleation rate in p-D under different temperatures. This method was first introduced by Yasuoka and Matsumoto, where the number of grains larger than a predefined threshold ( $N_t$ ) is monitored in time. Generally, the obtained grains number curve would go through a linear rise, and the nucleation rate is calculated by dividing the slope of the linear segment by the simulation box volume. Considering that only grains larger than the critical nucleation size could be stable, the threshold  $N_t$  should be just above the critical nucleation size.

**DBSCAN cluster method.** To identify the paracrystalline grains and distinguish them from each other, we used the DBSCAN cluster method to monitor the grain size and number during annealing. In this method, two parameters,  $\epsilon$  and minPts are used to define a core point. Only the points with more than minPts neighbors inside a neighbor sphere shell of radius  $\epsilon$  could be called core points. Only when the distance of two core points is less than  $\epsilon$  are they considered to be in the same cluster. A typical set of parameters can be set as  $\epsilon = 2.6$  Å and minPts = 16.

**METAD/METAITS simulation details.** The METAD <sup>9-13</sup> and METAITS <sup>14-16</sup> simulations were performed by the open-source code PLUMED <sup>17 18</sup> patched with LAMMPS. The use of PLUMED requires an extra setup file to define CVs and the enhanced sampling method to use, while the annealing settings were the same as the large-scale MD simulations. In particular, the core code to perform METAITS was downloaded from GitHub ([https://github.com/helloyesterday/plumed2\\_its\\_full](https://github.com/helloyesterday/plumed2_its_full)).

Two specific setup files to perform METAD and METAITS simulations are attached below.

```
# an example to perform well-tempered METAD simulation
# units
UNITS LENGTH=Å TIME=ps
```

```

# select all atoms
allatoms: GROUP ATOMS=@mdatoms

# total potential energy
ene: ENERGY

#-----CV-----
Q6 ...
  LABEL=q6
  SPECIES=allatoms
  SWITCH={RATIONAL R_0=3.2 NN=12 MM=24 D_MAX=3.5}
... Q6

LOCAL_AVERAGE ...
  LABEL=la
  SPECIES=q6
  SWITCH={RATIONAL R_0=3.2 NN=12 MM=24 D_MAX=3.5}
  LESS_THAN={RATIONAL R_0=0.068 D_MAX=0.068}
  MORE_THAN={RATIONAL R_0=0.1 D_MAX=0.12}
... LOCAL_AVERAGE

CUSTOM ...
  LABEL=la2
  ARG=la.less than,la.more than
  FUNC=2048-y-x
  PERIODIC=NO
... CUSTOM

#-----METAD-----
METAD ...
  LABEL=metad
  ARG=la.more than,la2
  SIGMA=100,100
  HEIGHT=500
  PACE=1000
  TEMP=3200
  BIASFACTOR=1000
  FILE=./plumed_out/HILLS
... METAD

```

```

# an example to perform METAITS simulation
# units

```

```

UNITS LENGTH=A TIME=ps

# select all the atoms
allatoms: GROUP ATOMS=@mdatoms

# total potential energy
energy: ENERGY

#-----CV-----
Q6 ...
  LABEL=q6
  SPECIES=allatoms
  SWITCH={RATIONAL R_0=3.2 D_MAX=3.5}
... Q6

LOCAL_AVERAGE ...
  LABEL=la
  SPECIES=q6
  SWITCH={RATIONAL R_0=3.2 D_MAX=3.5}
  LESS_THAN={RATIONAL R_0=0.068 D_MAX=0.08}
  MORE_THAN={RATIONAL R_0=0.1 D_MAX=0.12}
... LOCAL_AVERAGE

CUSTOM ...
  LABEL=la2
  ARG=la.less-than,la.more-than
  FUNC=2048-y-x
  PERIODIC=NO
... CUSTOM

# -----METAD-----
METAD ...
  LABEL=metad
  ARG=la.more-than,la2
  SIGMA=60,60
  HEIGHT=300
  PACE=1000
  TEMP=3400
  BIASFACTOR=500
  GRID_MIN=-200,-200
  GRID_MAX=2200,2200
  GRID_BIN=200,200
  CALC_RCT
  RCT_USTRIDE=1

```

```

FILE=../plumed_out/HILLS
... METAD

#-----ITS-----
ITS_BIAS ...
  LABEL=its
  BIAS=metad
  ARG=energy
  NREPLICA=400
  SIM_TEMP=3400
  TEMP_MAX=3600
  TEMP_MIN=3200
  PACE=1000
  RW_TEMP=3200,3250,3300,3350,3400,3450,3500,3550,3600
... ITS_BIAS

PRINT ...
  ARG=la.morethan,la2
  FILE=../plumed_out/colvar.info.data
  STRIDE=1000
... PRINT

PRINT ...
  ARG=energy,metad.*,its.*
  FILE=../plumed_out/colvar.bias.data
  STRIDE=1000
... PRINT

```

**Local-averaged sixth Steinhardt order parameter.** The sixth Steinhardt order parameter  $Q_6$ <sup>19</sup> was used first to give a rough description of the degree of order of the local atomic environment. And the  $Q_6$  for atom  $i$  is a complex vector calculated by<sup>19</sup>

$$Q_6^i = \sqrt{\frac{4\pi}{2 \times 6 + 1} \sum_{m=-6}^{m=6} |q_{6m}(i)|^2} \quad (1)$$

where

$$q_{6m}(i) = \frac{\sum_j \sigma(r_{ij}) Y_{6m}(r_{ij})}{\sum_j \sigma(r_{ij})} \quad (2)$$

where  $Y_{6m}$  is a sixth-order spherical harmonic and the index  $m$  runs from -6 to +6.  $\sigma(r_{ij})$  is a switching function that equals to 1 when atom  $j$  is one of the neighbor atoms of atom  $i$ .

To get a more precise differentiation between different structures, we then calculated the local-averaged order parameter  $\bar{Q}_6$  <sup>(ref. 20)</sup> by taking the average value of  $Q_6$  over the atoms within the first-neighbor three atomic shells (with cutoff radius of 3.5 Å). We used the `LOCAL_AVERAGE` <sup>20</sup> command in `PLUMED` and calculated the local-averaged order parameter  $\bar{Q}_6$  by

$$\bar{Q}_6^i = \frac{Q_6^i + \sum_j \sigma(r_{ij}) Q_6^j}{1 + \sum_j \sigma(r_{ij})} \quad (3)$$

where  $r_{ij}$  represents the distance between atom  $i$  and atom  $j$ .  $\sigma(r)$  is a switching function whose parameters should be set so that the function equals to 1 when atom  $j$  is in the first-neighbor three atomic shells of atom  $i$ .

$$\sigma(r) = \frac{1 - \left(\frac{r - d_0}{r_0}\right)^6}{1 - \left(\frac{r - d_0}{r_0}\right)^{12}} \quad (4)$$

**Structure factor.** The structure factor in Fig. 2 was calculated by

$$S(q) = 1 + \frac{1}{N} \sum_{i=1}^N \sum_{j \neq i}^N \frac{\sin(qr_{ij})}{qr_{ij}} \quad (5)$$

where  $N$  is the total atom number in the simulation box.  $r_{ij}$  represents the distance between atom  $i$  and atom  $j$ .

## Reference

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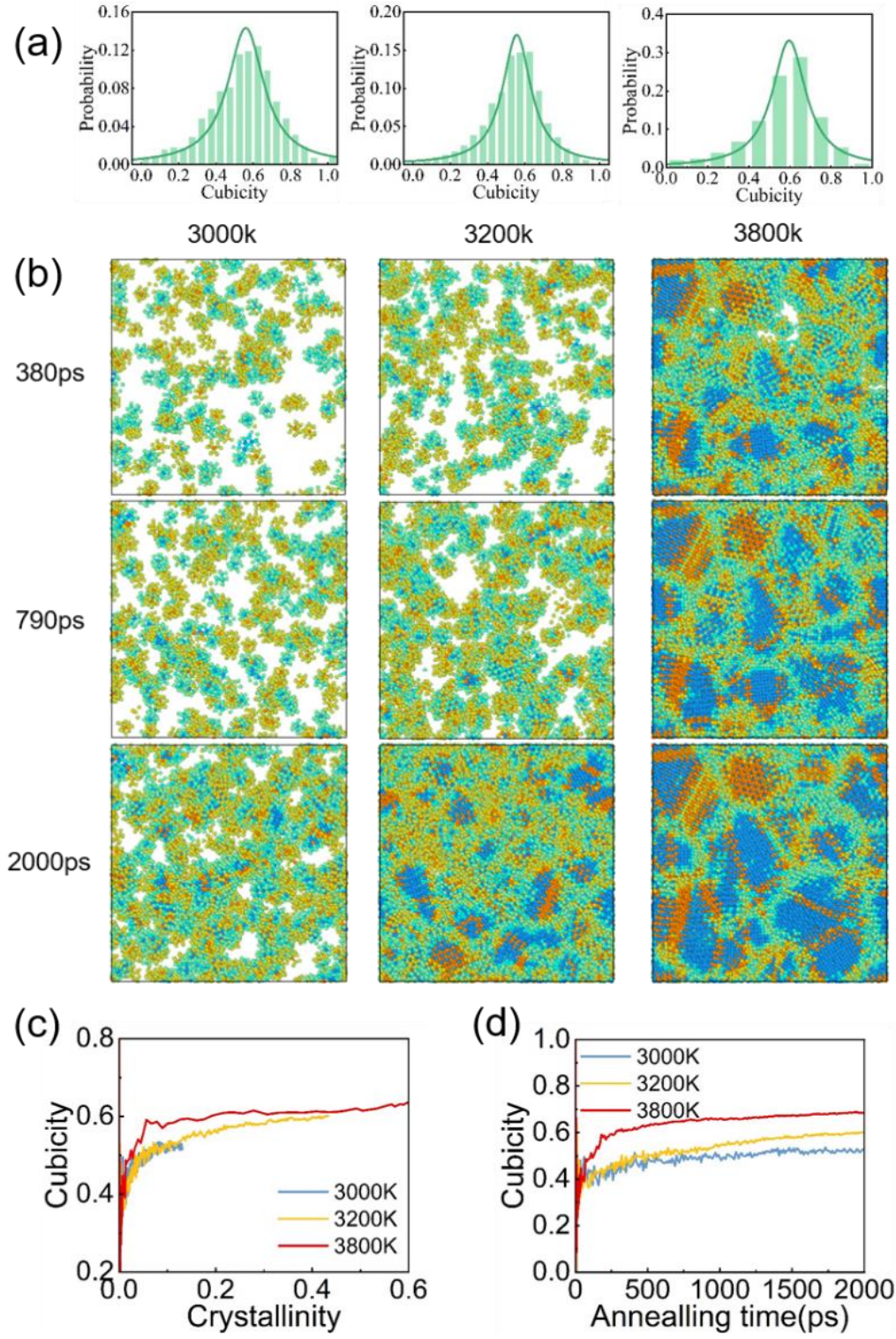


Figure S1. (a-b) Growth of diamond-like nuclei in amorphous matrix at different temperatures. (c-d) Evolution of cubicity with crystallinity and annealing time, respectively.

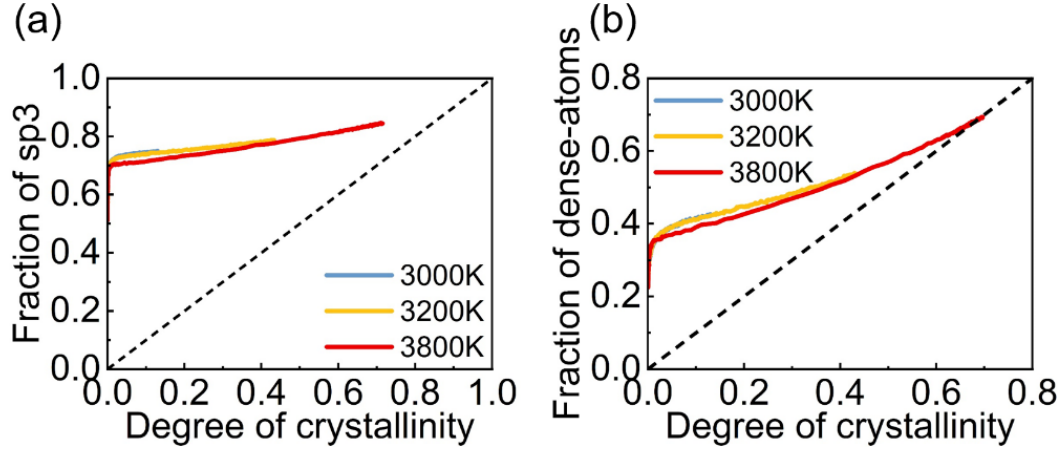


Figure S2. Relationship between the fraction of  $sp^3$  atoms (a), the fraction of dense atoms (b), and the degree of crystallinity. The  $sp^3$  atom denotes the tetrahedral carbon atom which has 4 neighbor atoms within the first atomic shells (1.85 Å). Similarly, the dense atom was defined to have more than 24 neighbors within the first-neighbor four layers of carbon atomic shells (3.5 Å). The comparison between (a) and (b) indicates that the nucleation of diamond-like grains not only depends on whether it is a  $sp^3$  hybrid atom, but also whether the atomic environment is dense enough.

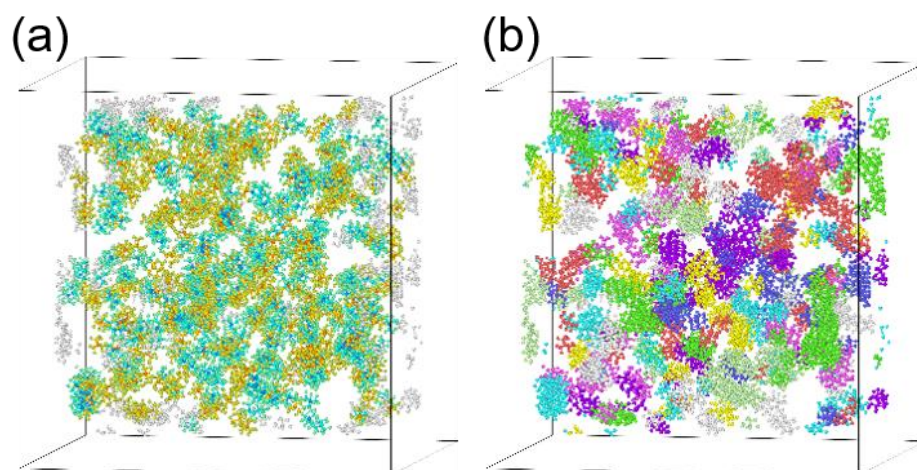


Figure S3. The DBSCAN cluster method was used to distinguish between different nuclei and calculate the nuclei size and number. As shown in (b), different clusters are assigned with different colors.

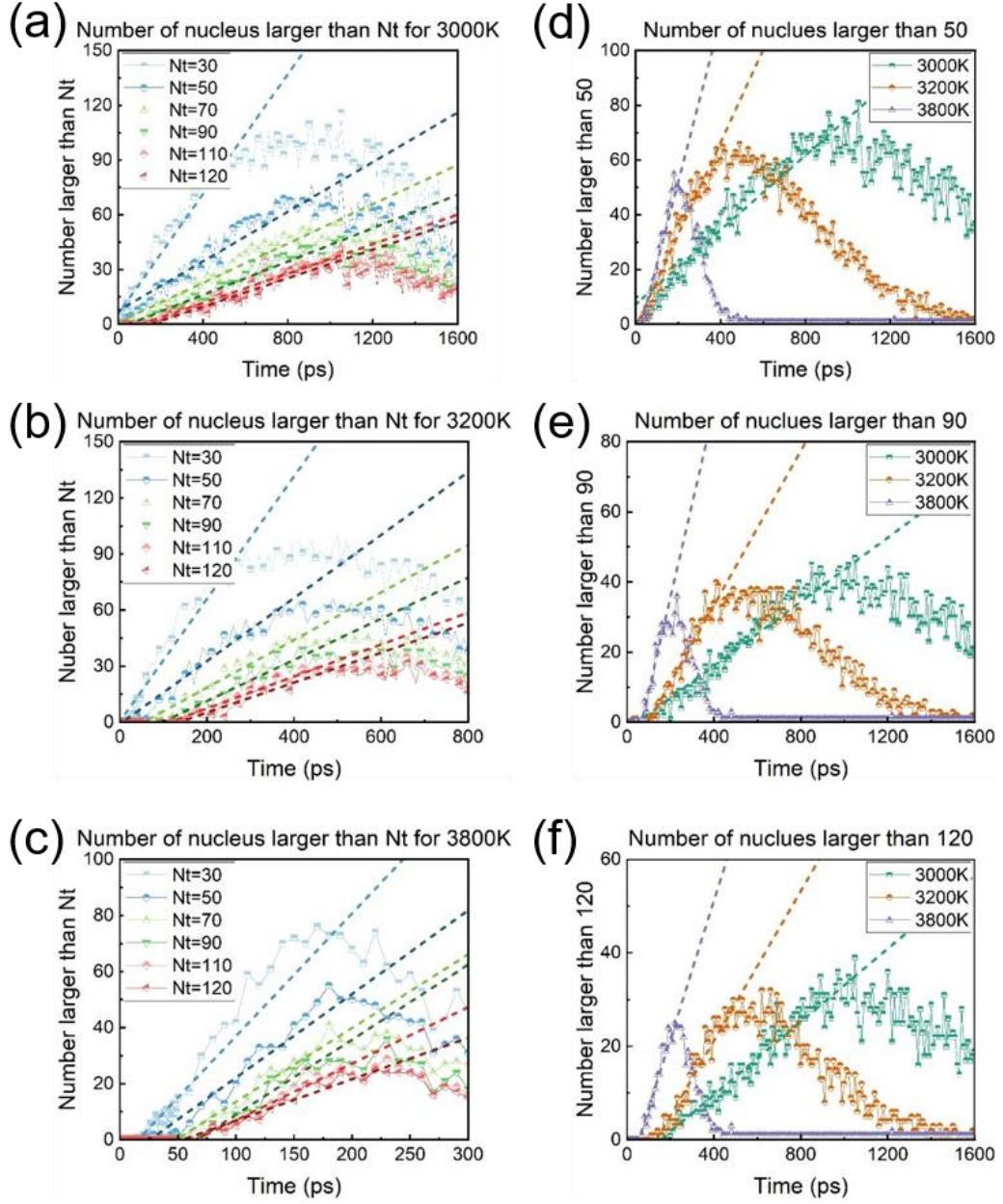


Figure S4. YM method to calculate nucleation rate. (a-c) The nuclei number curves of different  $N_t$  for 3000K, 3200K and 3800K, respectively. (b-d) The nuclei number curves of different temperatures for  $N_t = 50, 90$  and  $120$ , respectively. All curves rise first and then fall, and the higher the temperature, the earlier and faster the curves fall.



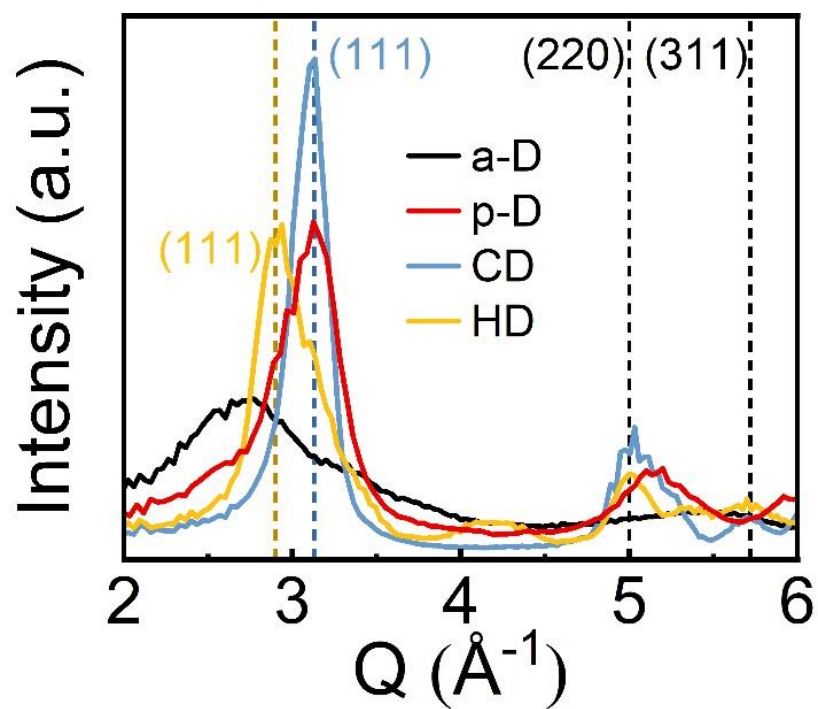


Figure S5. XRD patterns indicating the difference between a-D, p-D, CD and HD. The structures used to calculate XRD were selected from MD trajectories.

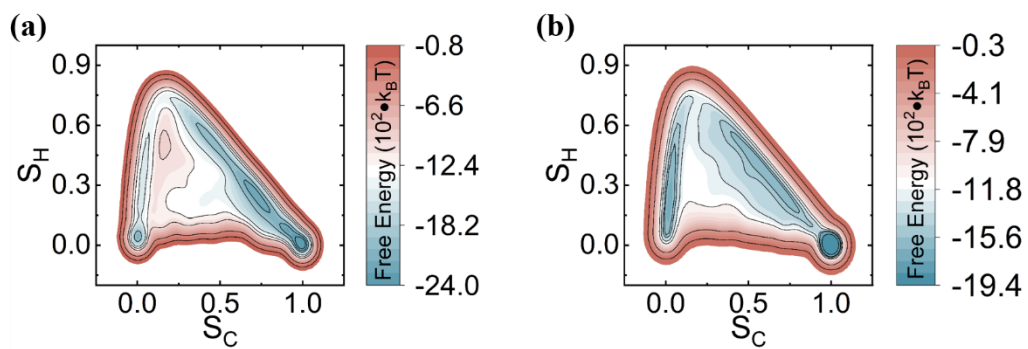


Figure S6. Free energy calculated by METAD in 3000K (a) and 3800K (b).

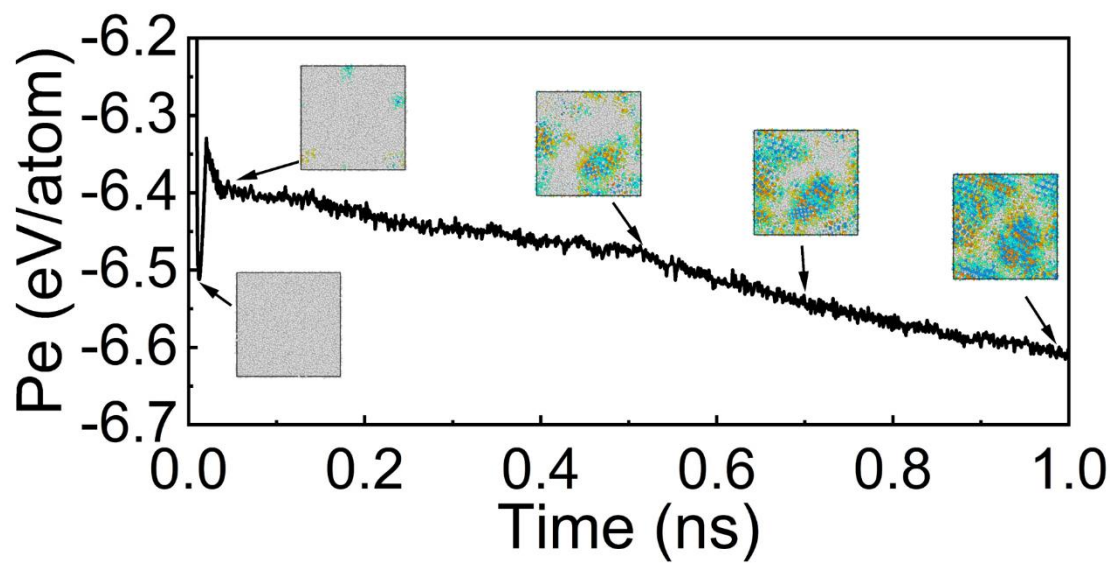


Figure S7. Solid-solid phase transition from a-D to p-D during annealing at 3500K. With the increase of the degree of paracrystallites, the average atomic potential energy drops gradually and continuously.