

Supporting information

Identification of oxygen diffusion mechanisms in $\text{Nd}_{1-x}\text{AE}_x\text{BaInO}_{4-x/2}$ (AE=Ca, Sr, Ba) compounds through molecular dynamics

Chenyi Li^a, Hichem Dammak^a, Guilhem Dezanneau^{*a}

^aLaboratoire Structures, Propriétés et Modélisation des Solides, UMR 8580 CNRS, CentraleSupélec, Université Paris-Saclay, 91190, Gif-sur-Yvette, France

Email: guilhem.dezanneau@centralesupelec.fr

Outline of supporting information:

1. Example input files of NcBIO c6.25% 1500K (NσT) for DLPOLY calculations
2. Matlab code for producing the complex information cell
3. Matlab code for 3D convex hull classification method
4. Figure S1 The complete information cell of NBIO at 1900K.
5. Figure S2 The lattice parameters **a b c** of pure and AE-doped NBIO as a function of temperature and dopant amount. (AE= Ca, Sr, Ba).
6. Figure S3 One representative oxygen ion trajectory.
7. Figure S4 jumps conditions of NcBIO c9.375% 1500K.
8. Figure S5 jumps conditions of NcBIO c15.625% 1500K.
9. Figure S6 The MSD curves of all oxygen ions of NcBIO c18.75% 1900K along different direction.

Example input files of NcBIO c6.25% 1500K (NσT) for DLPOLY calculations

CONTROL file

NCBIO maille	3*4*4	stack	500
integrator	leapfrog	stats	1000
temperature	1500.0	timestep	0.0005
pressure	0.001	cutoff	10.00
ensemble	nst Hoover 0.1 0.1	delr width	0.5000
steps	100000	ewald precision	1.0E-6
equil	20 000	job time	144000.00
scale	10	close time	100000.00
print	1000	finish	

FIELD file

NCBIO maille 3*4*4
UNITS eV
MOLECULES 8
Neodymium
NUMMOLS 180
ATOMS 1
Nd 144.242 3.000
FINISH
Calcium
NUMMOLS 12
ATOMS 1
Ca 40.078 2.000
FINISH

Barium
NUMMOLS 192
ATOMS 1
Ba 137.327 2.000
FINISH
Indium
NUMMOLS 192
ATOMS 1
In 114.818 3.000
FINISH
Oxygen1
NUMMOLS 192
ATOMS 1
O1 15.9994 -2.000

FINISH				O2 Ca buck	1228.9	0.3372	0.00
Oxygen2				O2 Ba buck	931.7	0.3949	0.00
NUMMOLS 192				O2 In buck	1495.6	0.3310	4.325
ATOMS 1				O3 Nd buck	1379.9	0.36072	22.59
O2	15.9994	-2.000		O3 Ca buck	1228.9	0.3372	0.00
FINISH				O3 Ba buck	931.7	0.3949	0.00
Oxygen3				O3 In buck	1495.6	0.3310	4.325
NUMMOLS 189				O4 Nd buck	1379.9	0.36072	22.59
ATOMS 1				O4 Ca buck	1228.9	0.3372	0.00
O3	15.9994	-2.000		O4 Ba buck	931.7	0.3949	0.00
FINISH				O4 In buck	1495.6	0.3310	4.325
Oxygen4				O1 O1 buck	22764.30	0.1490	43.00
NUMMOLS 189				O1 O2 buck	22764.30	0.1490	43.00
ATOMS 1				O1 O3 buck	22764.30	0.1490	43.00
O4	15.9994	-2.000		O1 O4 buck	22764.30	0.1490	43.00
FINISH				O2 O2 buck	22764.30	0.1490	43.00
VDW 26				O2 O3 buck	22764.30	0.1490	43.00
O1 Nd buck	1379.9	0.36072	22.59	O2 O4 buck	22764.30	0.1490	43.00
O1 Ca buck	1228.9	0.3372	0.00	O3 O3 buck	22764.30	0.1490	43.00
O1 Ba buck	931.7	0.3949	0.00	O3 O4 buck	22764.30	0.1490	43.00
O1 In buck	1495.6	0.3310	4.325	O4 O4 buck	22764.30	0.1490	43.00
O2 Nd buck	1379.9	0.36072	22.59	CLOSE			

Matlab code for producing the complex information cell

```
clear
close all

% Read the trajectories coordinates of all ions obtained by MD simulation, e.g. the coordinates
% generated by HISTORY file with VMD.1
DATA=load('data_MD.dat','-ascii');

% The lattice parameter of compounds.  $\mathbf{a}=[a_x \ a_y \ a_z]$ .  $n_a$  is the number of unit cells along  $\mathbf{a}$  direction,
% the same is for  $\mathbf{b}$  and  $\mathbf{c}$  respectively.
ax=27.4569856338;
ay=0;
az=0.1645871838;

bx=0;
by=24.3745847321;
bz=0;

cx=-7.7636119933;
cy=0;
cz=32.3640450323;

na = 3;
nb = 4;
nc = 4;

% Because the origin of all coordinates in HISTORY file produced by DLPLOY is  $[0.5*(a_x+b_x+c_x),$ 
%  $0.5*(a_y+b_y+c_y), 0.5*(a_z+b_z+c_z)]$ , Now we transfer the origin of coordinate from  $([0.5*(a_x+b_x+c_x),$ 
%  $0.5*(a_y+b_y+c_y), 0.5*(a_z+b_z+c_z)]$  to  $[-0.5*(a_x+b_x+c_x),-0.5*(a_y+b_y+c_y),-0.5*(a_z+b_z+c_z)]$ . Then all the
% coordinates will be positive.
origin=[0.5*(ax+bx+cx) 0.5*(ay+by+cy) 0.5*(az+bz+cz)];
DATA=DATA+origin;

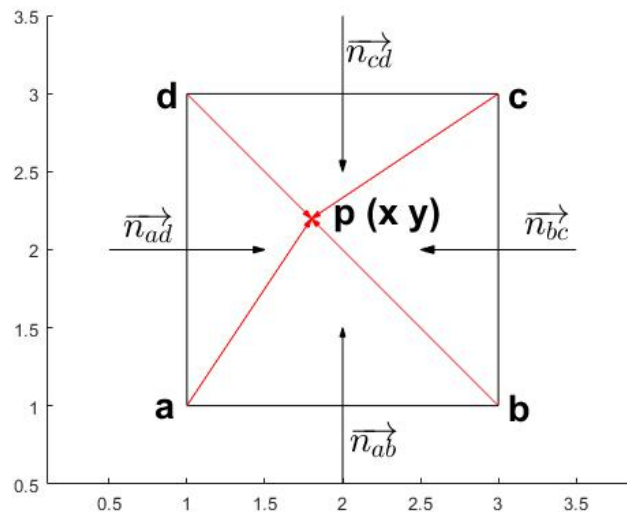
% A is the reduced-unit cell in which all the coordinates will be transferred by periodic boundary
% condition.
A = [ax/na ay/na az/na;
     bx/nb by/nb bz/nb;
     cx/nc cy/nc cz/nc];
InvA=inv(A');

% MD data in a reduced cell with fractional positions
DATA2=mod((InvA*DATA)',1);

% MD data in a reduced cell with xyz positions
DATA3=(A'*DATA2)';
```

Matlab code for 3D convex hull classification method

%% Here the Matlab code of 3D convex hull classification method (Figure 3) is attached. The geometric criterion of whether the point is inside the 2D or 3D convex hull is: when a point is inside or on the convex hull, the dot production between the vector from any convex vertex to this point and any normal vector of this convex vertex is more than 0. The normal vector of this convex vertex means that all the normal vectors of line segments (2D) or faces (3D) including this vertex. For example, as shown in the figure behind, when an arbitrary point p is inside or on the square abcd, we can get $\vec{ap} \cdot \vec{n}_{ab} \geq 0$ and $\vec{ap} \cdot \vec{n}_{ad} \geq 0$. The same is for \vec{bp} with \vec{n}_{ab} and \vec{n}_{bc} etc. ²



```
clear
close all
```

```
%coexp is the coefficient of expansion of standard convex hull.
coexp=1.15;
```

```
%read the standard convex hull and then adjust the size of this convex hull. In this work, the standard
convex hull is the 3D data of NdBaInO4 1900K (Figure S1) and the coefficient expansion is 15%.
```

```
data=textread('points of standard convex hull.txt');
dataN(:,1)=(data(:,1)-mean(data(:,1)))*coexp+mean(data(:,1));
dataN(:,2)=(data(:,2)-mean(data(:,2)))*coexp+mean(data(:,2));
dataN(:,3)=(data(:,3)-mean(data(:,3)))*coexp+mean(data(:,3));
convexH=convhulln(dataN);
[nc,~]=size(convexH);
```

```
% read all the test points, here the test points are all 3D oxygen coordinates.
```

```
testP=textread('test points.txt');
[n,~]=size(testP);
```

```
% build normal vectors
```

```
ab=dataN(convexH(:,1),:)-dataN(convexH(:,2),:);
ac=dataN(convexH(:,1),:)-dataN(convexH(:,3),:);
normalV=cross(ab,ac,2);
```

```
% scale normal vectors to unit length
```

```
module=sqrt(sum(normalV.^2,2));
```

```

normalV = normalV.*repmat(1./ module,1,3);

% center point of the convex hull
center = mean(dataN,1);

% all vertexes in the plane of each simplex in the convex hull
vertex = dataN (convexH (:,1),:);

% ensure the normal vectors pointing inwards
difference = sum((repmat(center,nc,1) - vertex).* normalV,2);
k = difference<0;
normalV (k,:) = - normalV (k,:);

% We want to test if: dot production ((testpoint - vertex),Normal) >= 0, if so for all faces of the
convex hull, then p is inside the convex hull. Change this to dot production (testpoint, Normal) >=
dot(vertex, Normal)
NorVer = sum(normalV.* vertex,2);

% if n is too large, we need to worry about the dot product grabbing huge chunks of memory.
in = false(n,1);
memblock = 1e6;
blocks = max(1,floor(n/(memblock/nc)));
NorVerN = repmat(NorVer,1,length(1:blocks:n));

for i = 1:blocks
    j = i:blocks:n;
    if size(NorVerN,2) ~= length(j)
        NorVerN = repmat(NorVer,1,length(j));
    end
    in(j) = all((normalV * testP (j,:) - NorVerN) >= 0,1)';
end

```

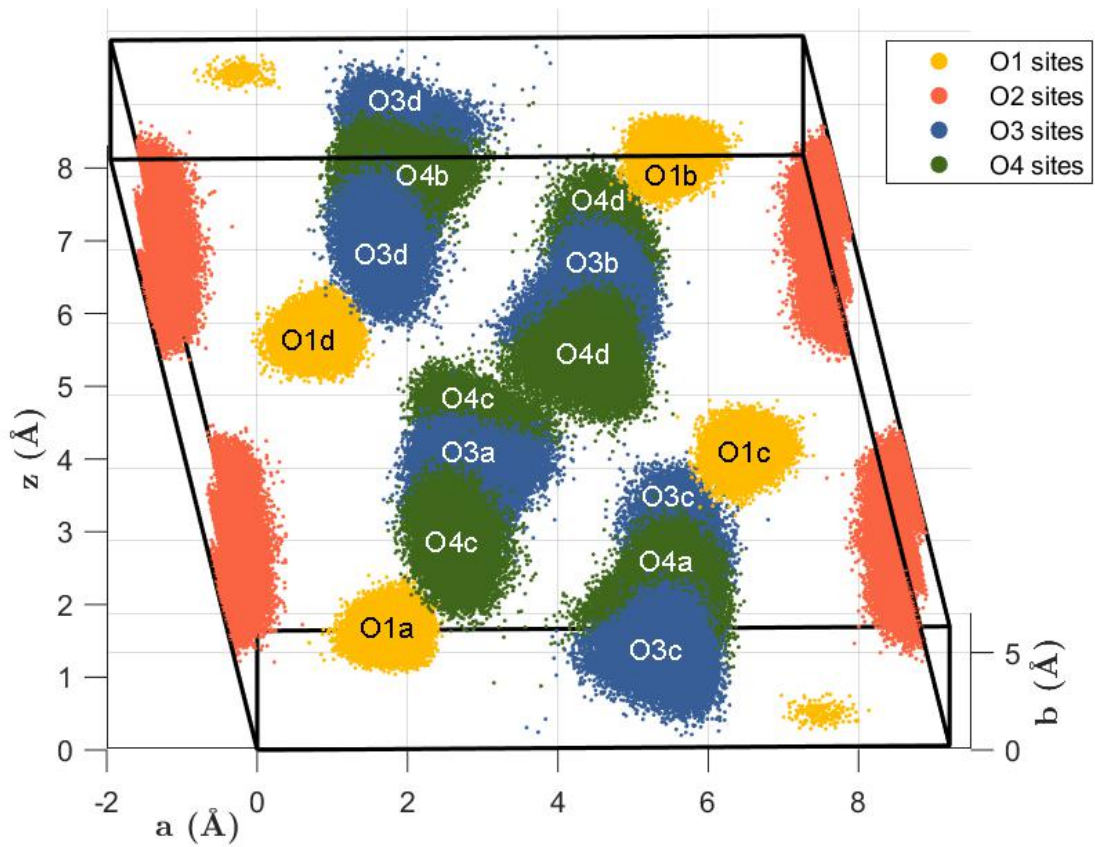
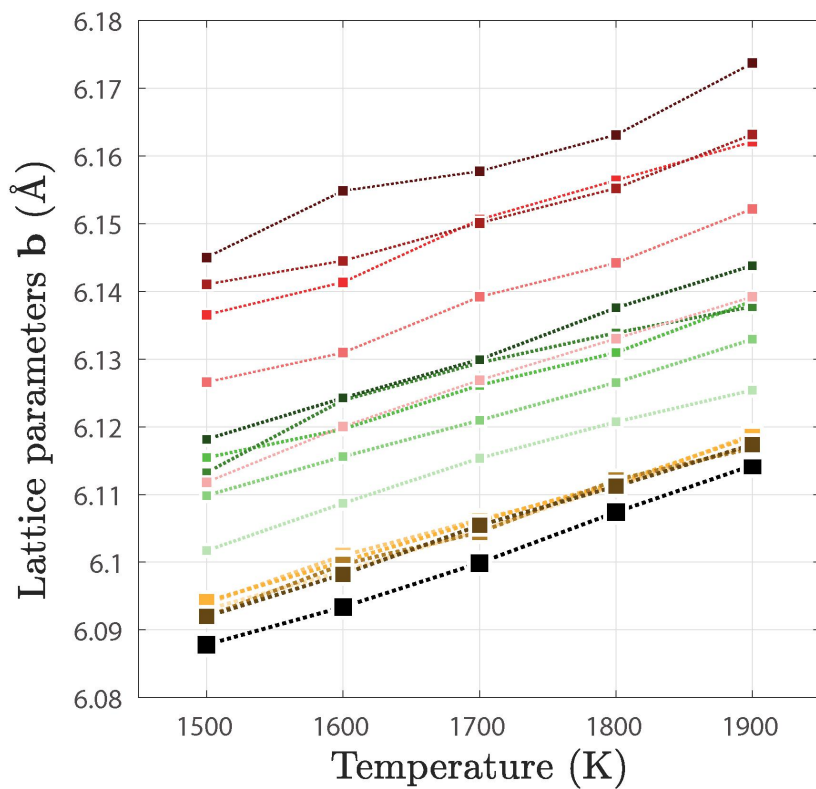
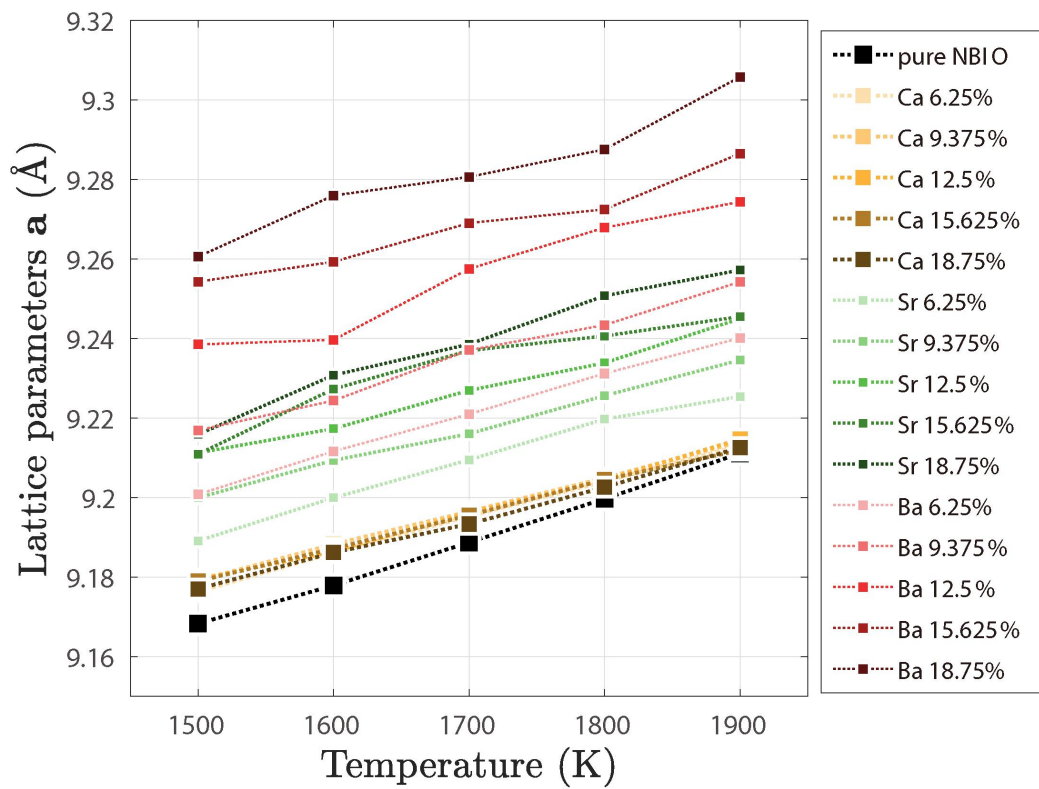


Figure S1 The complete information cell of NBIO at 1900K.

Compared with the complete information cell of NBIO at 1500K (**Figure 2**), the size of each oxygen site clusters increase due to a higher temperature.



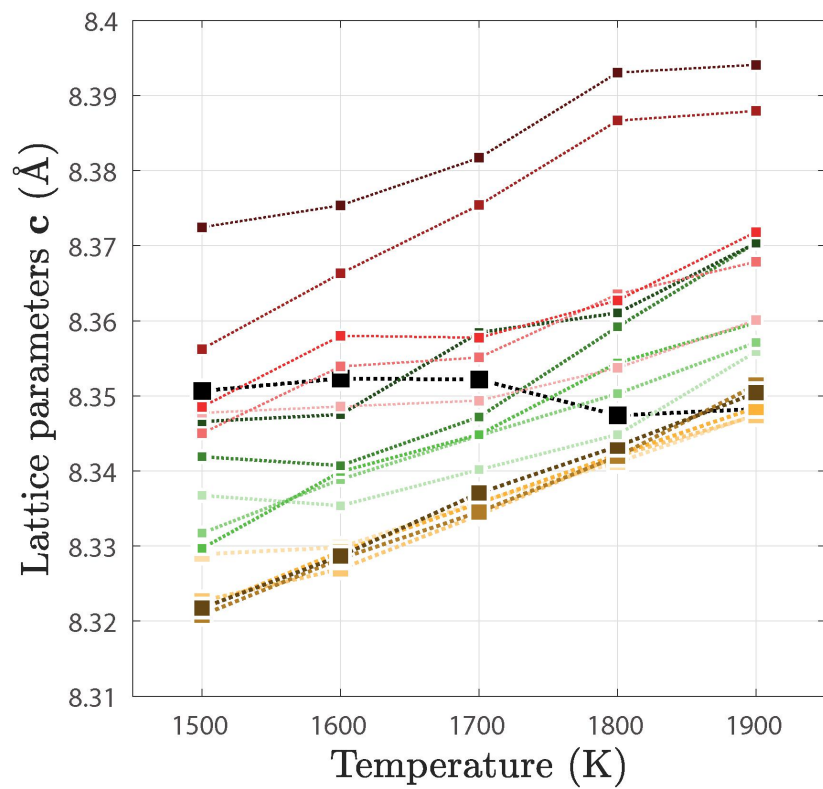


Figure S2 The lattice parameters a b c of pure and AE-doped NBO as a function of temperature and dopant amount. (AE= Ca, Sr, Ba).

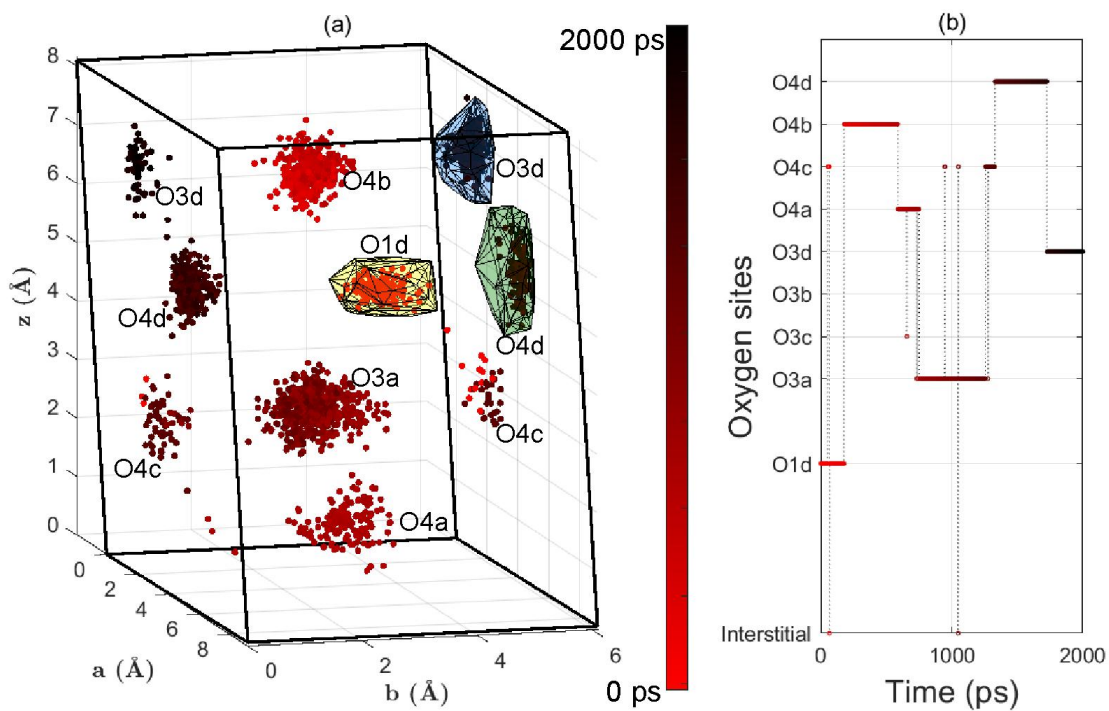


Figure S3 One representative oxygen ion trajectory in NcBIO c18.75% 1500K.

One oxygen ion was traced by using convex hull classification method. The color change of color bar (from red to black) represent the evolution of simulation time, all these dots stand for this oxygen ion at different timesteps, the darker color, the later timestep. We can find clearly the variation of the belonging cluster of this oxygen ion with the pass of simulation time by recognizing the changing dots colors. The change clusters of this ion can be described roughly as O1d (178ps) → O4b (410ps) → O4a (144ps) → O3a (544ps) → O4c (52ps) → O4d (399ps) → O3d (273ps).

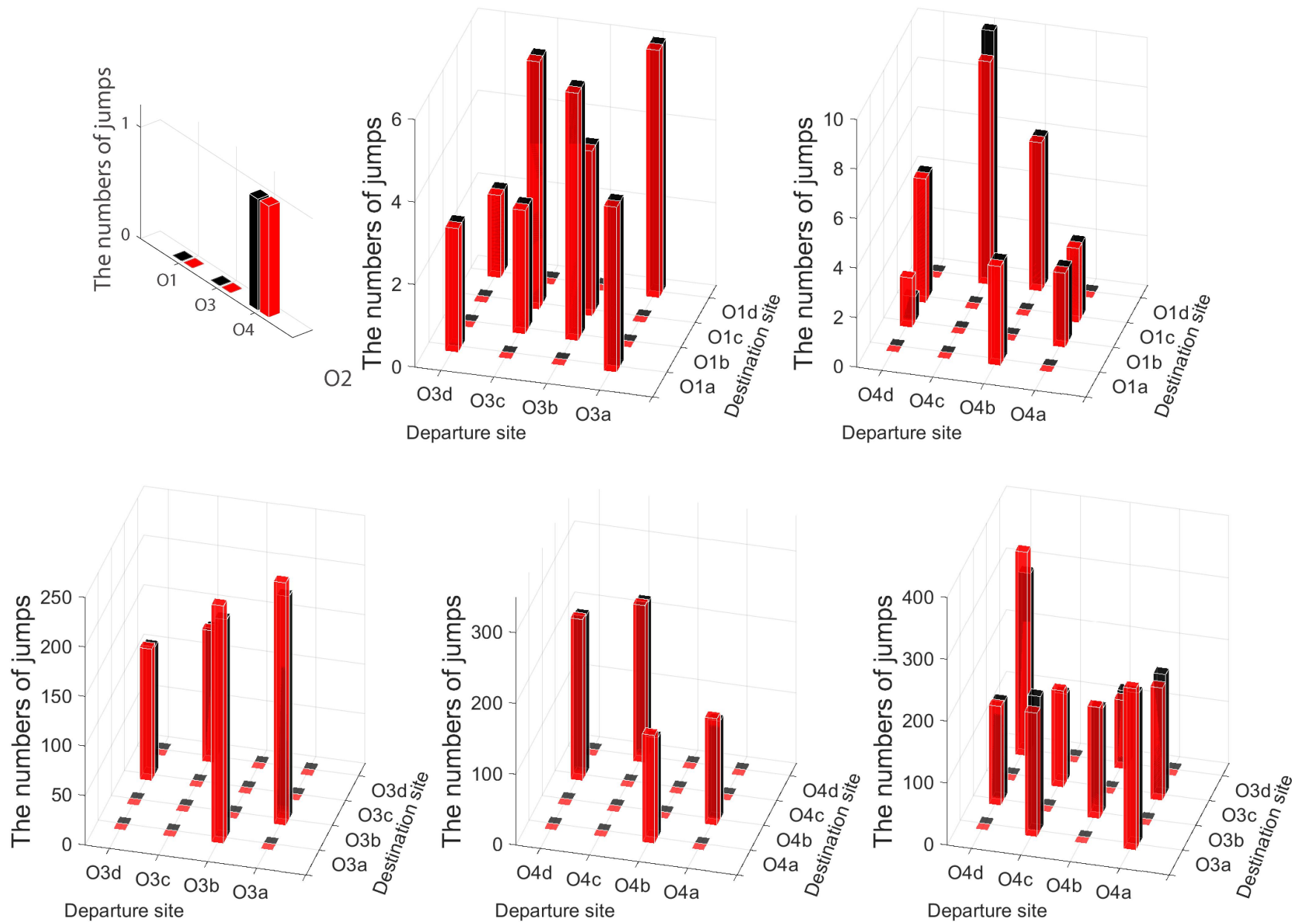


Figure S4 Detailed jump analysis between different sites in NcBio c9.375% 1500K. Red column represents results by convex hull classification methods (CHC), while black stands for DBSCAN.

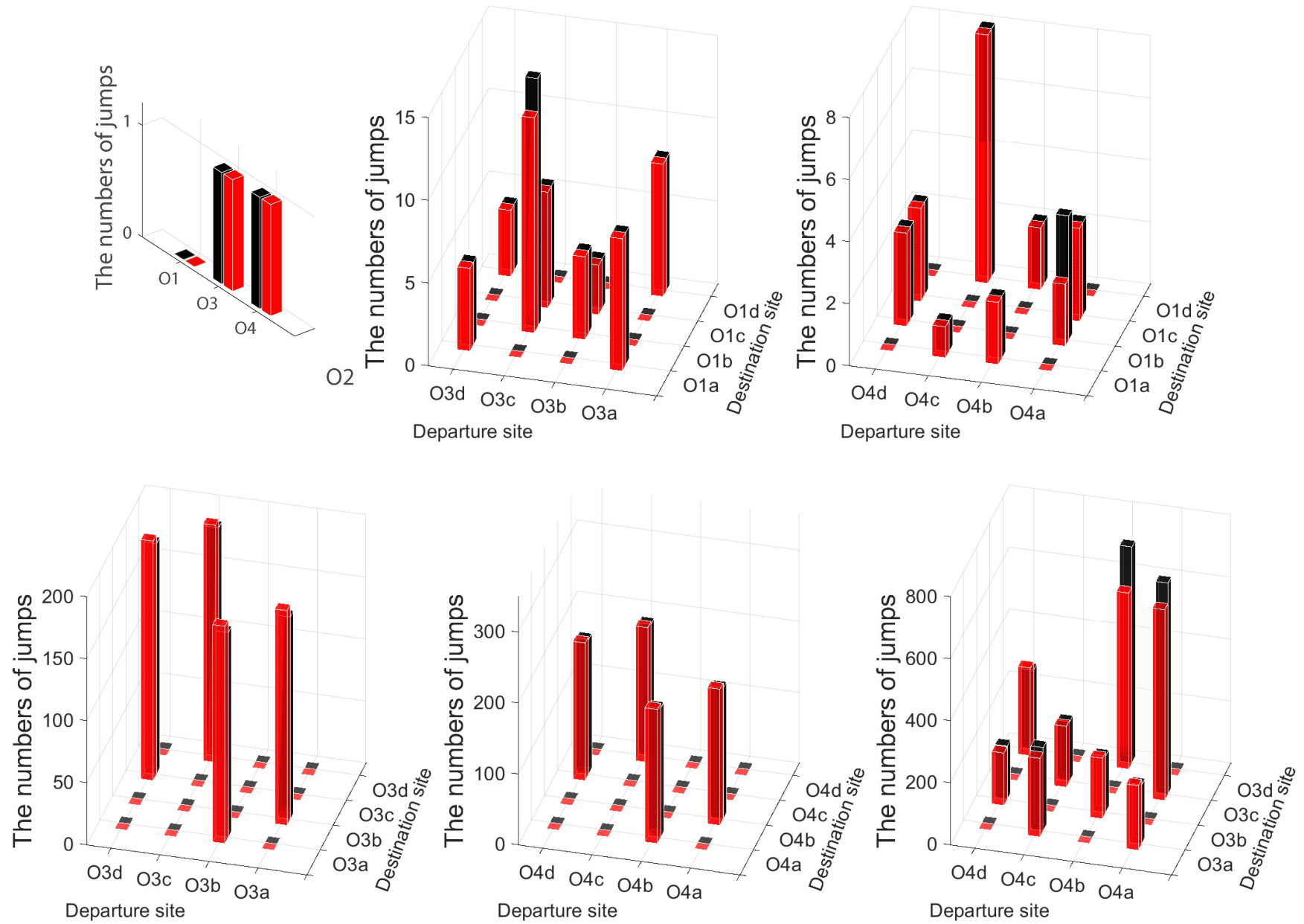


Figure S5 Detailed jump analysis between different sites in NcBIO c15.625% 1500K. Red column represents results by convex hull classification methods (CHC), while black stands for DBSCAN.

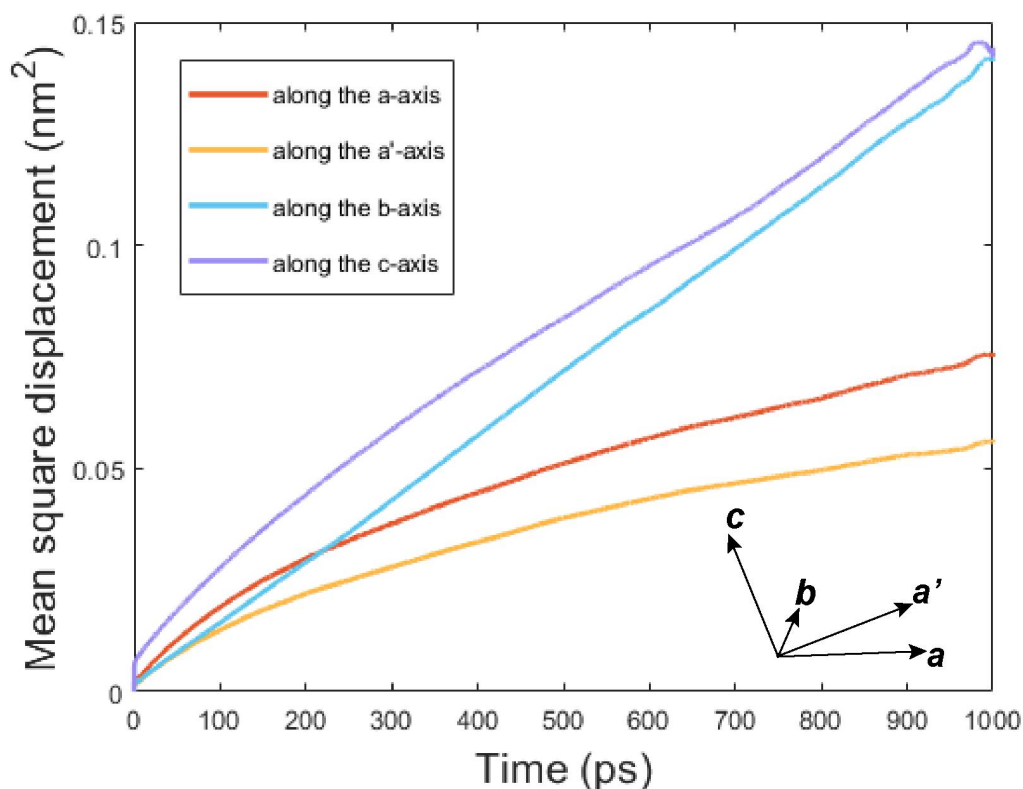


Figure S6 The MSD curves of all oxygen ions of NcBIO c18.75% 1900K along different direction.

In figure S6, the MSD curves along four different directions are presented: \mathbf{a} , \mathbf{b} , \mathbf{c} and \mathbf{a}' , where \mathbf{a} , \mathbf{b} , \mathbf{c} are the primitive vectors of unit cell along $[1\ 0\ 0]$, $[0\ 1\ 0]$ and $[\cot\beta, 0, 1]$ respectively, β is the angle between \mathbf{a} and \mathbf{c} . \mathbf{a}' , with the direction of $[1, 0, -\cot\beta]$, is on the \mathbf{ac} plane and perpendicular to \mathbf{c} . Though O2 is the barrier for oxygen diffusion along the \mathbf{a} direction, oxygen ions diffuse inside unit cell resulting in the values of MSD of \mathbf{a} and \mathbf{a}' are not 0. Besides the oxygen ions diffuse along \mathbf{c} direction will contribute to \mathbf{a} direction, resulting in the values of MSD \mathbf{a} is larger than MSD \mathbf{a}' . The oxygen diffusion mainly happens along \mathbf{b} and \mathbf{c} direction, which is also proved in Figure S6, the MSD curves of \mathbf{b} and \mathbf{c} are similar and the top two highest.

References

1. Humphrey, W., Dalke, A. and Schulten, K., "VMD - Visual Molecular Dynamics", *J. Molec. Graphics*, 1996, vol. 14, pp. 33-38.
2. <https://uk.mathworks.com/matlabcentral/fileexchange/10226-inhull>