Investigation of O/N Ordering in Perovskite-Type Oxynitrides La$_{1-x}$Y$_x$Ta(O,N)$_3$ on Long Range and Short Scale

Margarida Barroso [1], Mian Dai [2], Cora Bubeck [1], Marco Scavini [3], Gabriel J. Cuello [4], Hongbin Zhang [2], Anke Weidenkaff [1,5], and Marc Widenmeyer [1*]

[1] Department of Materials- and Geosciences, Materials and Resources, Technische Universität Darmstadt, Peter-Grünberg-Str. 2, 64287 Darmstadt, Germany

[2] Department of Materials- and Geosciences, Theory of Magnetic Materials, Technische Universität Darmstadt, Otto-Berndt-Str. 3, 64287 Darmstadt, Germany

[3] Department of Chemistry, University of Milan, Via C. Golgi 19, 20133 Milan, Italy

[4] Institut Laue Langevin, 71 Avenue des Martyrs, 38047 Grenoble, France

[5] Fraunhofer Research Institution for Materials Recycling and Resource Strategies IWKS, Aschaffenburger Str. 121, 63457 Hanau, Germany

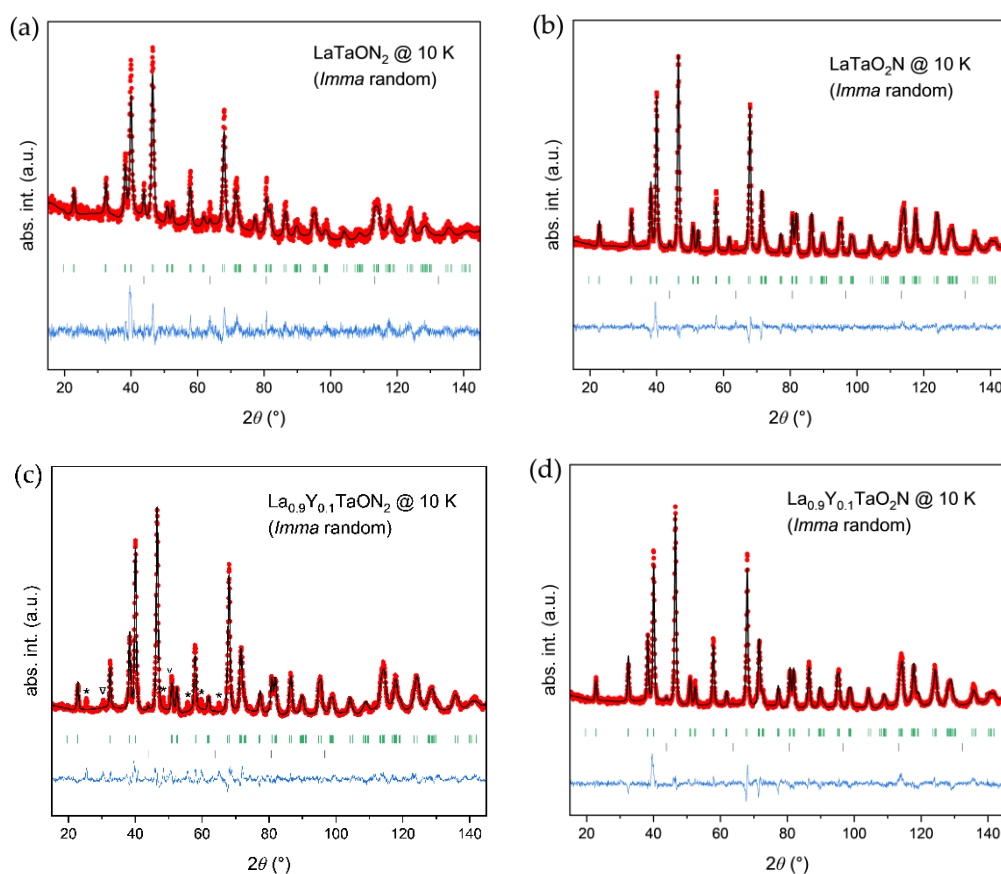* marc.widenmeyer@mr.tu-darmstadt.de;

Supplementary Materials

Figure S1. Refined neutron diffraction patterns (λ = 1.59417(2) Å) of a) LaTaON$_2$, b) LaTaO$_2$N, c) La$_{0.9}$Y$_{0.1}$TaON$_2$, and d) La$_{0.9}$Y$_{0.1}$TaO$_2$N at 10 K using the *Imma* random anion ordering structural model. The red dots represent experimental data, a black line the calculated pattern, and a blue line the difference curve. Upper green hash marks represent the indexed reflections of the oxynitrides, and lower gray hash marks the indexed reflections of the vanadium sample holder. Additional reflections marked with * and ∇ in (c) were indexed to belong to Ta$_3$N$_5$ and Y$_2$O$_3$, respectively.

Table S1.(a) Structural data from Rietveld refinements of the neutron diffraction patterns of $LaTaON_2$ in the space group *Imma* both at 300 K and 10 K. At both temperatures a second phase (vanadium, V) was seen, as a result of the vanadium sample holder. Parameters marked with * were fixed during the refinements. Tantalum is located on Wyckoff site 4*a*, lanthanum on 4*b*, O(1)/N(1) on 4*e*, and O(2)/N(2) on 8*g*, respectively.

Parameter	300 K		10 K	
	LaTaON$_2$	V	LaTaON$_2$	V
Space group	$I\,m\,m\,a$	$I\,m\,\bar{3}\,m$	$I\,m\,m\,a$	$I\,m\,\bar{3}\,m$
a [pm]	5.7110(8)	3.0243(7)	5.701(3)	3.017(2)
b [pm]	8.052(1)		8.042(3)	
c [pm]	5.7498(9)		5.739(3)	
V [pm^3]	264.42(6)	27.66(1)	263.1(2)	27.45(3)
B_{iso}(O(1)/N(1)) [×10^4 pm^2]	0.5(2)		0.7(5)	
z(O(1)/N(1))	0.072(1)		0.073(3)	
B_{iso}(O(2)/N(2)) [×10^4 pm^2]	1.8(1)		1.6(3)	
y(O(2)/N(2))	0.9633(5)		0.963(2)	
B_{iso}(V) [×10^4 pm^2]		0.5*		0.5*
P(O(1))	0.67(6)		0.332*	
P(O(2))	0.18(5)		0.334*	
P(N(1))	0.33(6)		0.668*	
P(N(2))	0.82(5)		0.666*	
R_p [%]	1.98		1.96	
R_{wp} [%]	2.51		2.62	
R_{Bragg} [%]	6.76	11.8	4.40	6.99

Table S1.(b) Structural data from Rietveld refinements of the neutron diffraction patterns of LaTaO$_2$N in the space group *Imma* both at 300 K and 10 K. At both temperatures a second phase (vanadium, V) was seen, as a result of the vanadium sample holder. Parameters marked with * were fixed during the refinements. Tantalum is located on Wyckoff site 4*a*, lanthanum on 4*b*, O(1)/N(1) on 4*e*, and O(2)/N(2) on 8*g*, respectively.

Parameter	300 K		10 K	
	LaTaO$_2$N	V	LaTaO$_2$N	V
Space group	$I\,m\,m\,a$	$I\,m\,\bar{3}\,m$	$I\,m\,m\,a$	$I\,m\,\bar{3}\,m$
a [pm]	5.711(2)	3.023(5)	5.703(1)	3.018(1)
b [pm]	8.064(2)		8.052(1)	
c [pm]	5.744(2)		5.736(1)	
V [pm^3]	264.5(1)	27.65(8)	263.4(8)	27.49(2)
B_{iso}(O(1)/N(1)) [×10^4 pm^2]	0.3(3)		0.1(1)	
z(O(1)/N(1))	0.070(3)		0.072(3)	
B_{iso}(O(2)/N(2)) [×10^4 pm^2]	1.0(3)		1.0(2)	
y(O(2)/N(2))	0.963(1)		0.962(1)	
B_{iso}(V) [×10^4 pm^2]		0.5*		0.5*
P(O(1))	0.667*		0.667*	
P(O(2))	0.667*		0.667*	
P(N(1))	0.333*		0.333*	
P(N(2))	0.333*		0.333*	
R_p [%]	5.60		5.01	
R_{wp} [%]	7.15		7.46	
R_{Bragg} [%]	19.2	30.3	21.8	19.5

Table S1.(c) Structural data from Rietveld refinements of the neutron diffraction patterns of $La_{0.9}Y_{0.1}TaON_2$ in the space group *Imma* both at 300 K and 10 K. At both temperatures a second phase (vanadium, V) was seen, as a result of the vanadium sample holder. Parameters marked with * were fixed during the refinements. Tantalum is located on Wyckoff site 4*a*, lanthanum/yttrium on 4*b*, O(1)/N(1) on 4*e*, and O(2)/N(2) on 8*g*, respectively.

Parameter	300 K				10 K	
	$La_{0.9}Y_{0.1}TaON_2$	V	Ta_3N_5[1]	Y_2O_3[2]	$La_{0.9}Y_{0.1}TaON_2$	V
Space group	$I\,m\,m\,a$	$I\,m\,\bar{3}\,m$	$C\,m\,c\,m$	$I\,a\,\bar{3}$	$I\,m\,m\,a$	$I\,m\,\bar{3}\,m$
a [pm]	5.7061(5)	3.024(3)	3.892(1)	10.572(4)	5.698(1)	3.018(3)
b [pm]	8.0469(7)		10.216(4)		8.037(1)	
c [pm]	5.7393(6)		10.27*		5.731(1)	
V [pm³]	263.53(4)	27.66(4)	408.4(2)	1181.8(8)	262.44(8)	27.46(8)
B_{iso}(O(1)/N(1)) [×10^4 pm²]	1.0(2)				1.4(2)	
z(O(1)/N(1))	0.0746(8)				0.077(1)	
B_{iso}(O(2)/N(2)) [×10^4 pm²]	1.5(1)				1.5(1)	
y(O(2)/N(2))	0.9614(3)				0.9608(7)	
B_{iso}(V) [×10^4 pm²]		0.5*				0.5*
P(O(1))	0.48(5)				0.332*	
P(O(2))	0.25(4)				0.334*	
P(N(1))	0.52(5)				0.668*	
P(N(2))	0.75(4)				0.666*	
R_p [%]	3.36				4.09	
R_{wp} [%]	4.35				5.38	
R_{Bragg} [%]	5.6	11.2	15.0	25.6	4.78	9.34

[1] The structural data of Ta_3N_5 not stated in Table S1.(c) were taken as given by N. E. Brese et al., Acta Cryst. C (1991) 47, 2291-2294. [2] The structural data of Y_2O_3 not stated in Table S1.(c) were taken as given by M. G. Paton, E. N. Maslen, Acta Cryst. (1965) 19, 307-310.

Table S1.(d) Structural data from Rietveld refinements of the neutron diffraction patterns of $La_{0.9}Y_{0.1}TaO_2N$ in the space group *Imma* both at 300 K and 10 K. At both temperatures a second phase (vanadium, V) was seen, as a result of the vanadium sample holder. Parameters marked with * were fixed during the refinements. Tantalum is located on Wyckoff site 4*a*, lanthanum/yttrium on 4*b*, O(1)/N(1) on 4*e*, and O(2)/N(2) on 8*g*, respectively.

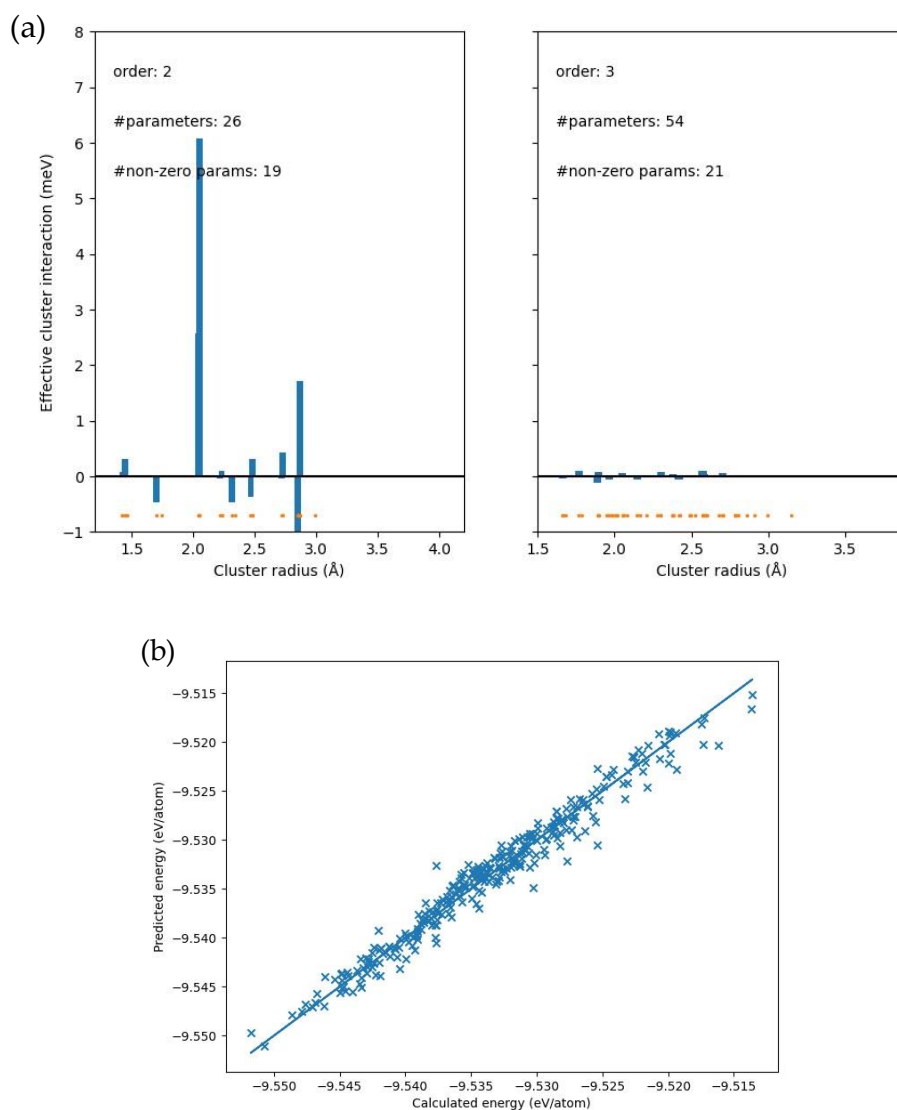| Parameter	300 K		10 K	
	$La_{0.9}Y_{0.1}TaO_2N$	V	$La_{0.9}Y_{0.1}TaO_2N$	V
Space group	$I\,m\,m\,a$	$I\,m\,\bar{3}\,m$	$I\,m\,m\,a$	$I\,m\,\bar{3}\,m$
a [pm]	5.7059(3)	3.026(2)	5.6992(4)	3.018(3)
b [pm]	8.0536(5)		8.0438(5)	
c [pm]	5.7312(4)		5.7245(4)	
V [pm^3]	263.36(3)	27.70(3)	262.43(3)	27.48(4)
B_{iso}(O(1)/N(1)) [×10^4 pm^2]	0.023*		0.065*	
z(O(1)/N(1))	0.0729(5)		0.0748(7)	
B_{iso}(O(2)/N(2)) [×10^4 pm^2]	0.779*		0.86*	
y(O(2)/N(2))	0.9608(3)		0.9595(3)	
B_{iso}(V) [×10^4 pm^2]		0.5*		0.5*
P(O(1))	0.58(3)		0.58(3)	
P(O(2))	0.50(2)		0.45(2)	
P(N(1))	0.42(3)		0.42(3)	
P(N(2))	0.50(2)		0.55(2)	
R_p [%]	3.09		3.57	
R_{wp} [%]	4.13		4.94	
R_{Bragg} [%]	5.22	18.5	6.30	23.80

Figure S2. a) Effective Cluster Interactions (ECIs) of two-body and three-body clusters for the cluster expansion energy of DFT energies; b) calculated and fitted DFT energies (per atom) of the 300 configurations of *Imma* LaTaON$_2$.

Table S2. R_w values obtained using various distinct anisotropic thermal parameters in the PDF analysis for space group *Imma* LaTaON$_2$ at 10 K, in the short (1.5 Å $\leq r \leq$ 5.5 Å) range. Values marked by # indicate that the refinements involve non-physically meaningful parameters.

Thermal Parameters	Rw (1.5 - 5.5Å)
U_{iso}	0.146
All U_{aniso}	0.114#
$U(La,N(2))_{aniso}$	0.117
$U(N(1),N(2))_{aniso}$	0.122
$U(N(2))_{aniso}$	0.123
$U(La)_{aniso}$	0.122

1NNs:
Orbit Index: 2, 3, 4, 5
Distance:
2.846, 2.870, 2.870,
2.929

2NNs:
Orbit Index: 11, 12, 13
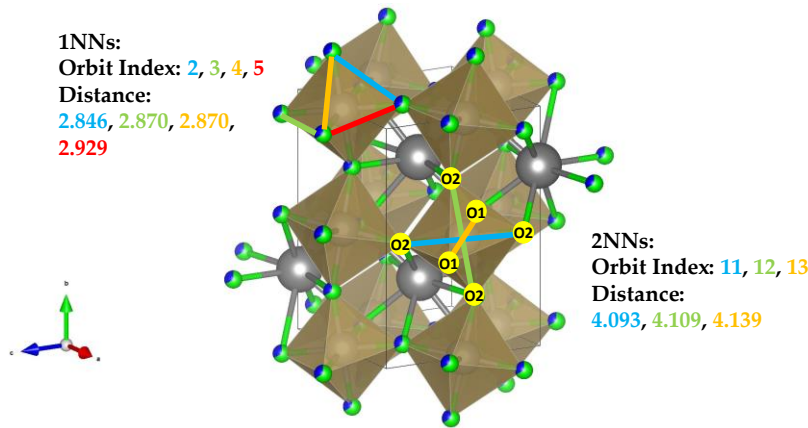**Distance:**
4.093, 4.109, 4.139

Figure S3. Symmetrically non-equivalent two-body clusters in the cluster expansion of the total energy as a function of O/N occupation in *Pnma* LaTaON$_2$. Number of orbit indices 2, 3, 4, and 5 represent the N−N, N−O, and O−O possible first-nearest-neighbor (1NNs) configurations; and orbit indices 11, 12, and 13 represent the N−N, N−O, and O−O possible second-nearest-neighbor (2NNs) configurations. The gray ions represent lanthanum, the blue/green ions represent the anions, oxygen and nitrogen, and the ions inside the octahedral structure represent tantalum.
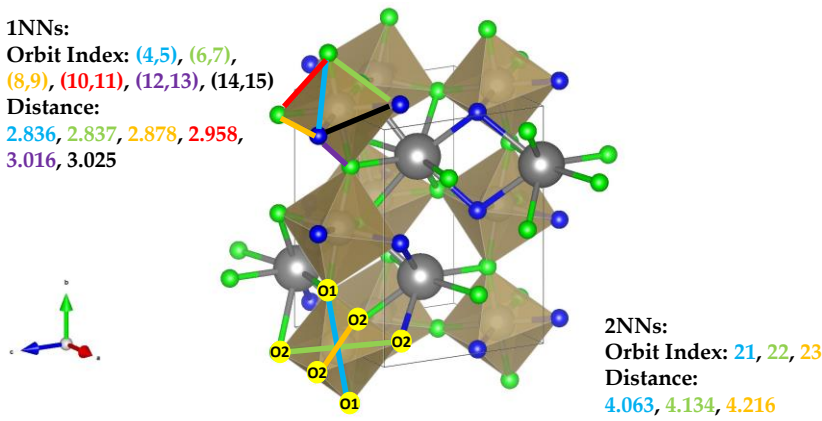

1NNs:
Orbit Index: (4,5), (6,7),
(8,9), (10,11), (12,13), (14,15)
Distance:
2.836, 2.837, 2.878, 2.958,
3.016, 3.025

2NNs:
Orbit Index: 21, 22, 23
Distance:
4.063, 4.134, 4.216

Figure S4. Symmetrically non-equivalent two-body clusters in the cluster expansion of the total energy as a function of O/N occupation in *Pmn*2$_1$ LaTaON$_2$. Number of orbit indices (4,5), (6,7), (8,9), (10,11), (12,13), and (14,15) represent the N−N, N−O, and O−O possible first-nearest-neighbor (1NNs) configurations; and orbit indices 21, 22, and 23 represent the N−N, N−O, and O−O possible second-nearest-neighbor (2NNs) configurations. The gray ions represent lanthanum, the blue/green ions represent the anions, oxygen and nitrogen, and the ions inside the octahedral structure represent tantalum.

Table S3. The experimental and calculated lattice parameters of *Pnma* and *Pmn*2$_1$ LaTaON$_2$, as determined by density-functional theory analysis.

		a (Å)	*b* (Å)	*c* (Å)
Pnma	Experimental	5.376	8.045	5.751
LaTaON$_2$	Calculated	5.7358	8.0448	5.6887
*Pmn*2$_1$	Experimental	7.878	5.743	5.893
LaTaON$_2$	Calculated	7.8783	5.7434	5.7422

(a)

order: 2

#parameters: 97

#non-zero params: 33

order: 3
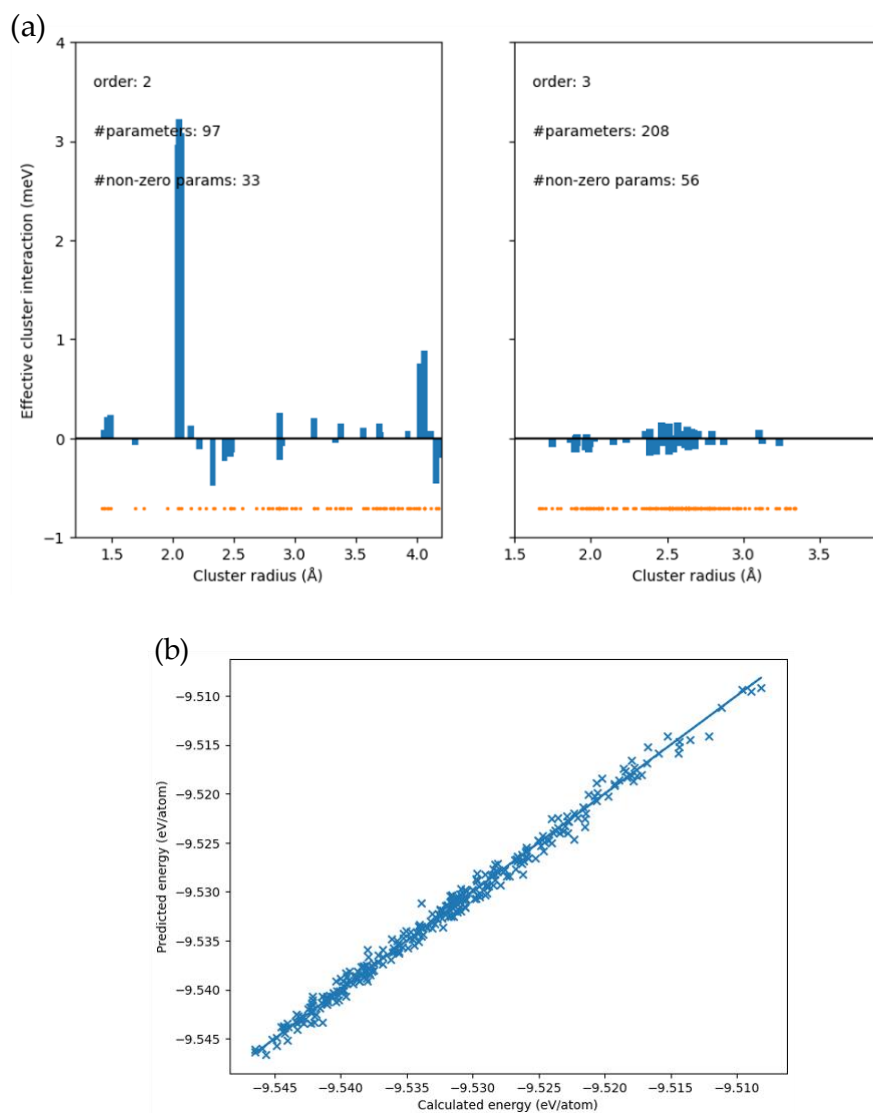
#parameters: 208

#non-zero params: 56

(b)

Figure S5. a) Effective Cluster Interactions (ECIs) of two-body and three-body clusters for the cluster expansion energy of DFT energies; b) calculated and fitted DFT energies (per atom) of the 300 configurations of *Pnma* LaTaON₂.
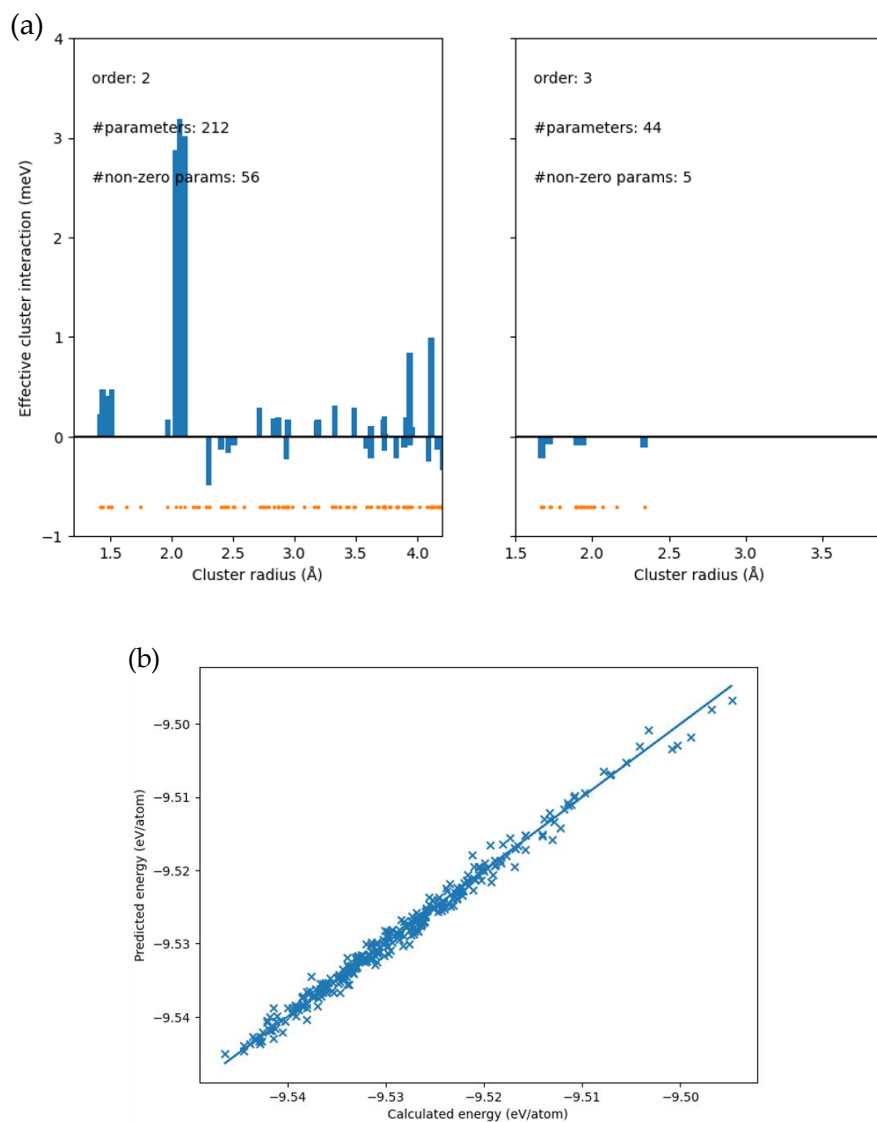
Figure S6. a) Effective Cluster Interactions (ECIs) of two-body and three-body clusters for the cluster expansion energy of DFT energies; b) calculated and fitted DFT energies (per atom) of the 300 configurations of *Pmn*2$_1$ LaTaON$_2$.