# Investigation of O/N Ordering in Perovskite-Type Oxynitrides $La_{1-x}Y_xTa(O,N)_3$ on Long Range and Short Scale

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## Supplementary Materials

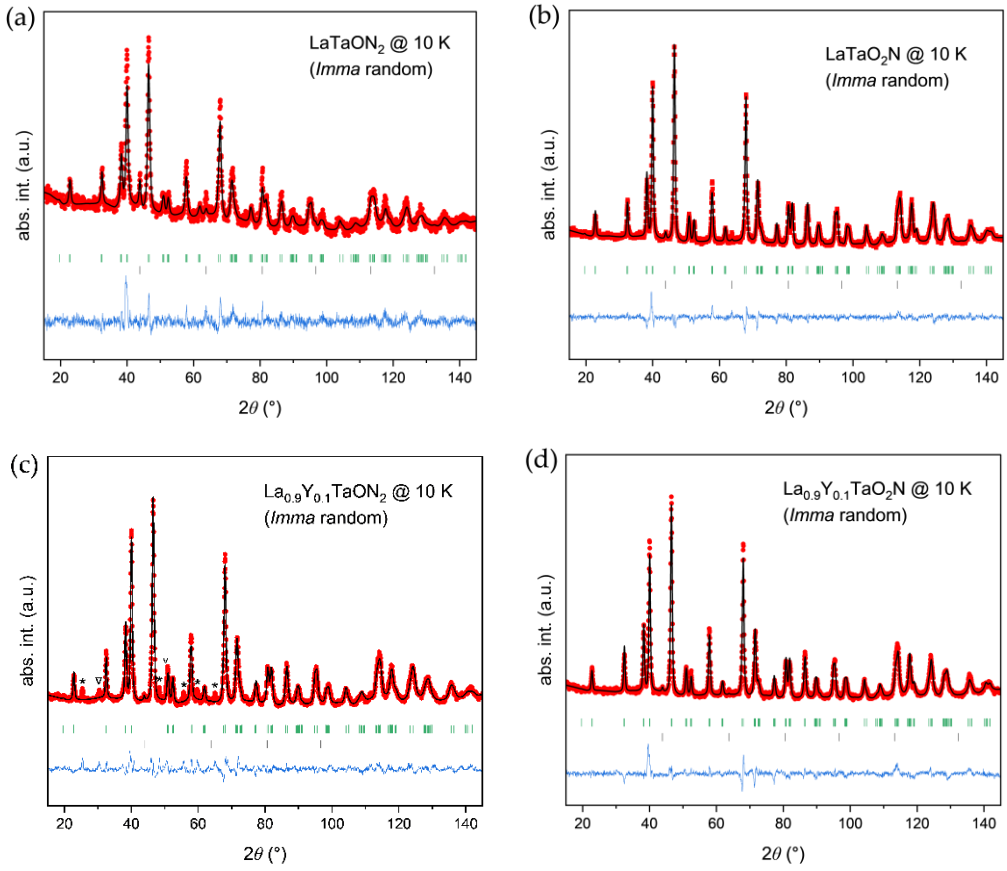


**Figure S1.** Refined neutron diffraction patterns ($\lambda$ = 1.59417(2) Å) of a) $LaTaON_2$, b) $LaTaO_2N$, c) $La_{0.9}Y_{0.1}TaON_2$, and d) $La_{0.9}Y_{0.1}TaO_2N$ at 10 K using the *Imma* random anion ordering structural model. The red dots represent experimental data, a black line the calculated 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 $Ta_3N_5$ and $Y_2O_3$, 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 $LaTaO_2N$ 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 on 4*b*, O(1)/N(1) on 4*e*, and O(2)/N(2) on 8*g*, respectively.

| **Parameter** | **300 K** | | **10 K** | |
|---|---|---|---|---|
| | **$LaTaO_2N$** | **V** | **$LaTaO_2N$** | **V** |
| Space group | *I m m a* | *I m* $\bar{3}$ *m* | *I m m a* | *I m* $\bar{3}$ *m* |
| *a* [pm] | 5.711(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* [pm$^3$] | 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$^4$ pm$^2$] | 1.0(2) | | | | 1.4(2) | |
| *z*(O(1)/N(1)) | 0.0746(8) | | | | 0.077(1) | |
| $B_{iso}$(O(2)/N(2)) [×10$^4$ pm$^2$] | 1.5(1) | | | | 1.5(1) | |
| *y*(O(2)/N(2)) | 0.9614(3) | | | | 0.9608(7) | |
| $B_{iso}$(V) [×10$^4$ pm$^2$] | | 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* [pm³] | 263.36(3) | 27.70(3) | 262.43(3) | 27.48(4) |
| $B_{iso}$(O(1)/N(1)) [×10⁴ pm²] | 0.023* | | 0.065* | |
| *z*(O(1)/N(1)) | 0.0729(5) | | 0.0748(7) | |
| $B_{iso}$(O(2)/N(2)) [×10⁴ pm²] | 0.779* | | 0.86* | |
| *y*(O(2)/N(2)) | 0.9608(3) | | 0.9595(3) | |
| $B_{iso}$(V) [×10⁴ pm²] | | 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 |

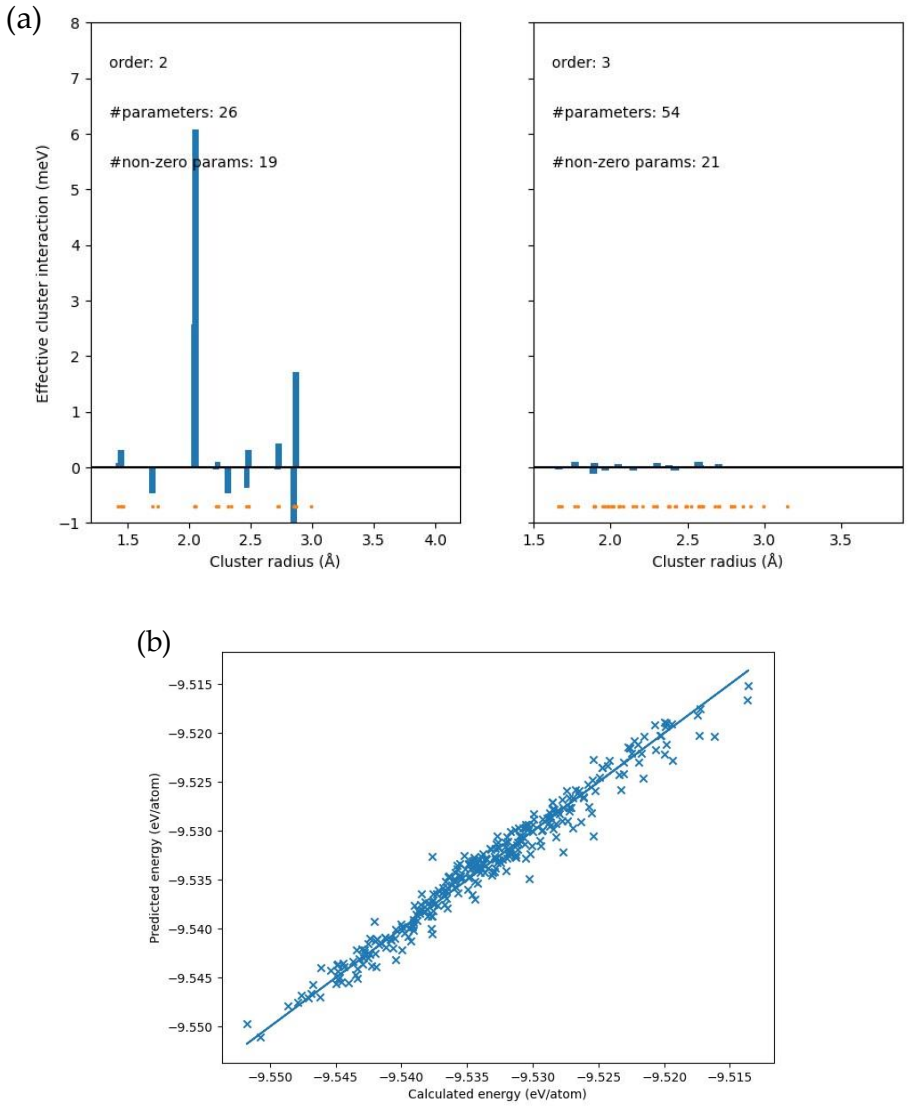


**Figure S2.** a) Effective Cluster Interactions (ECIs) of two-body and three-body clusters for the cluster expansion energy of DFT energies; b) calculated and fitted DFT energies (per atom) of the 300 configurations of *Imma* $LaTaON_2$.

**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 ≤ $r$ ≤ 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 |

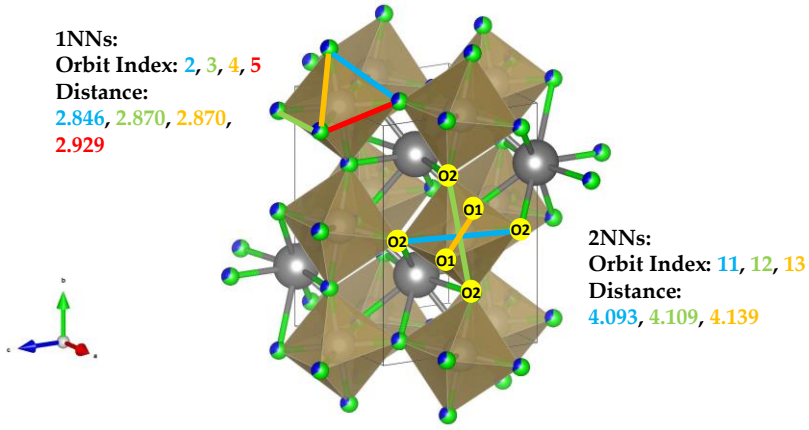


**Figure S3.** Symmetrically non-equivalent two-body clusters in the cluster expansion of the total energy as a function of O/N occupation in *Pnma* $LaTaON_2$. Number of orbit indices 2, 3, 4, and 5 represent the N–N, N–O, and O–O possible first-nearest-neighbor (1NNs) configurations; and orbit indices 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.

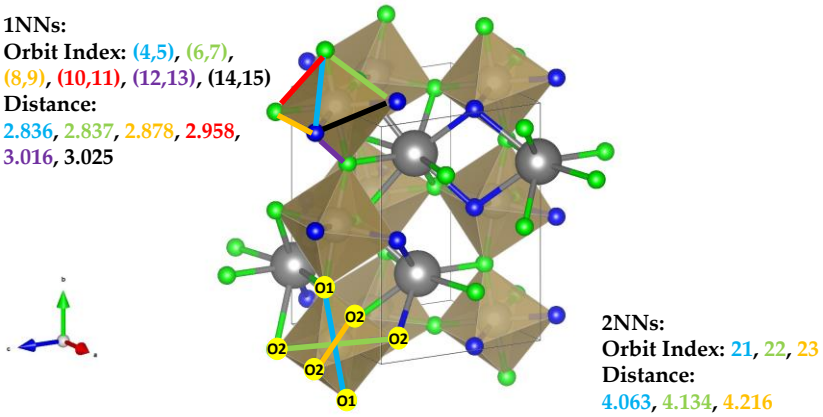


**Figure S4.** Symmetrically non-equivalent two-body clusters in the cluster expansion of the total energy as a function of O/N occupation in *Pmn*$2_1$ $LaTaON_2$. Number of orbit indices (4,5), (6,7), (8,9), (10,11), (12,13), and (14,15) represent the N–N, N–O, and O–O possible first-nearest-neighbor (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 |

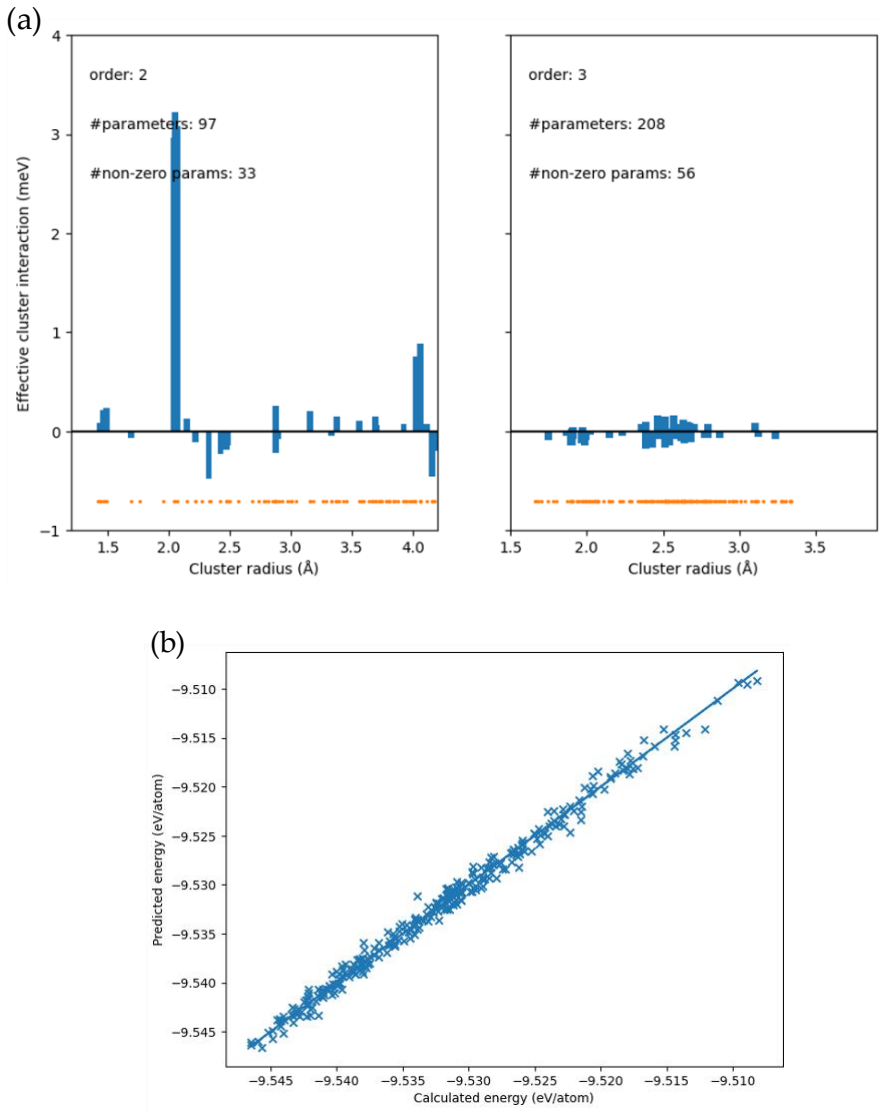


**Figure S5.** a) Effective Cluster Interactions (ECIs) of two-body and three-body clusters for the cluster expansion energy of DFT energies; b) calculated and fitted DFT energies (per atom) of the 300 configurations of *Pnma* $LaTaON_2$.

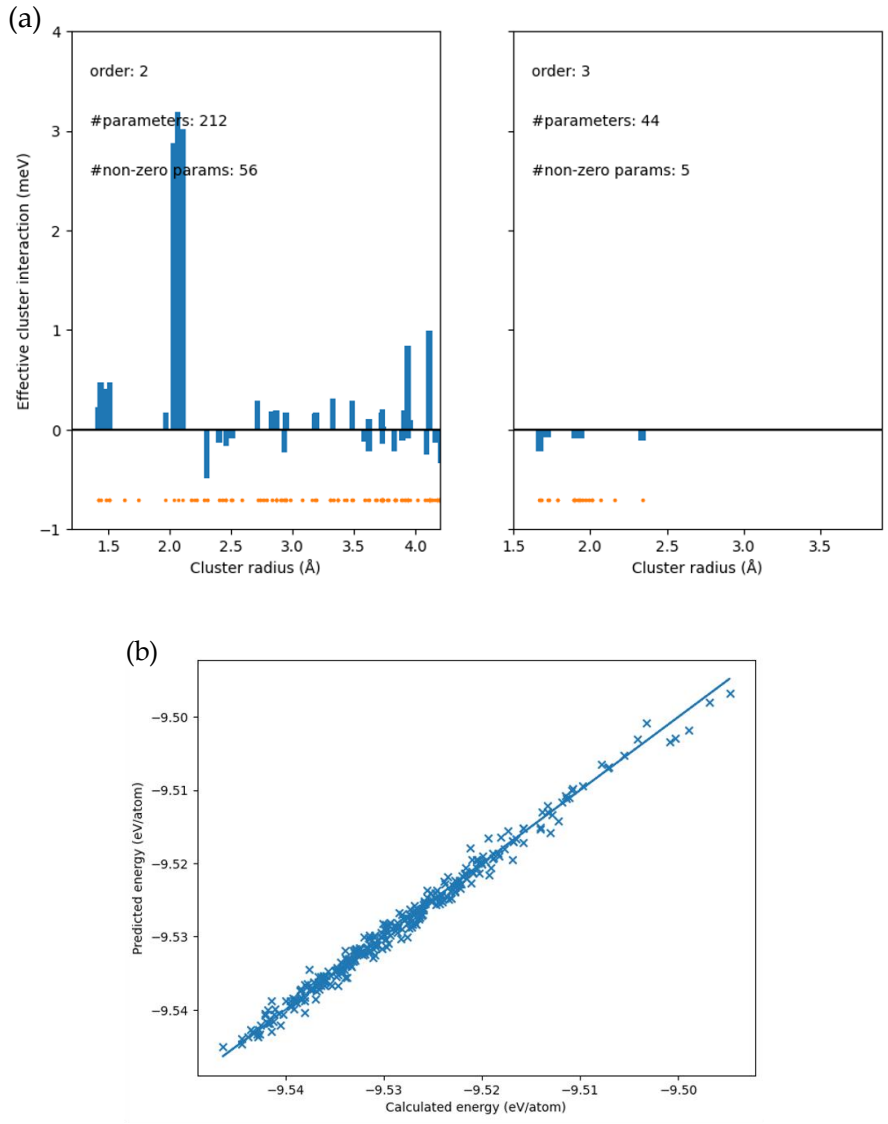


**Figure S6.** a) Effective Cluster Interactions (ECIs) of two-body and three-body clusters for the cluster expansion energy of DFT energies; b) calculated and fitted DFT energies (per atom) of the 300 configurations of *Pmn*2$_1$ $LaTaON_2$.