

Supporting Information

Authors: Masatomo Yashima, Mio Saito, Hiromi Nakano, Tsuyoshi Takata, Kiyonori Ogisu, Kazunari Domen

Title: *Imma* Perovskite-Type Oxynitride LaTiO₂N, Structure and Electron Density

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(S1) Table S1. Space group and tolerance factor of perovskite-type oxynitride ABO₂N where the A and B are larger and smaller cations, respectively.

Space group	Composition	Tolerance factor*	Refs.
<i>Imma</i> $P\bar{1} (I\bar{1})$	LaTiO ₂ N	0.972	This Work [1]
<i>Pm</i> $\bar{3}m$	SrWO ₂ N	0.993	[2]
	BaTaO ₂ N	1.042	[3-5]
	BaNbO ₂ N	1.042	[3-5]
	EuNbO ₂ N	0.987	[6]
<i>Pnma</i>	CaTaO ₂ N	0.949	[5],[9]
	NdTiO ₂ N	0.941	[7]
	LaZrO ₂ N	0.92	[7]
<i>I4/mcm</i>	SrNbO ₂ N	0.984	[8]
	SrTaO ₂ N	0.984	[9]
<i>C2/m</i>	LaTaO ₂ N	0.956	[9]

* Tolerance factor t of perovskite-type ABX₃ was calculated by the following equations,

$$t = (r_A + r_X) / \{2^{0.5}(r_B + r_X)\}$$

$$r_X = (2r_O + r_N) / 3$$

where the r_A , r_B and r_X are ionic radii of A cation (coordination number (CN) = 12) and B cation (CN = 6) after Shannon [Ref. 10] and average ionic radius of anion X. The r_O and r_N are the ionic radii of O²⁻ and N³⁻ anions (CN = 4) after Shannon [Ref. 10]. Here we used the anion radii r_O and r_N for CN=4, because only for CN = 4, the r_N is tabulated in Ref. 10.

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(S2) Details of the synthesis of high-purity and highly crystalline LaTiO₂N sample.

A highly crystalline and high-purity LaTiO₂N sample was synthesized from the corresponding oxide precursor by ammonolysis. La(NO₃)₃·6H₂O and TiO₂ (P-25) with a molar ratio of La: Ti = 1 : 1 were mixed and ground quickly in an agate mortar. Then, the mixture was heated in air at 500 °C for 10 min to obtain a mixed oxide precursor. The precursor was heated under dry NH₃ flow of 200 mL min⁻¹ at 900 °C for 20 h with intermediate grinding. A NaCl flux was added to the obtained sample (Molar ratio, Na : La = 1 : 1), and then mixed and ground in an agate mortar. Then, the mixture was heated under dry NH₃ flow of 100 mL min⁻¹ at 900 °C for 10 h. The process of NaCl addition, mixing, grinding and heating was repeated twice. The final products were washed with distilled water to remove residual flux. The SEM-EDS indicated no Na in the final product, LaTiO₂N.

(S3) Infrared (IR) study of LaTiO₂N (Fig. S1).

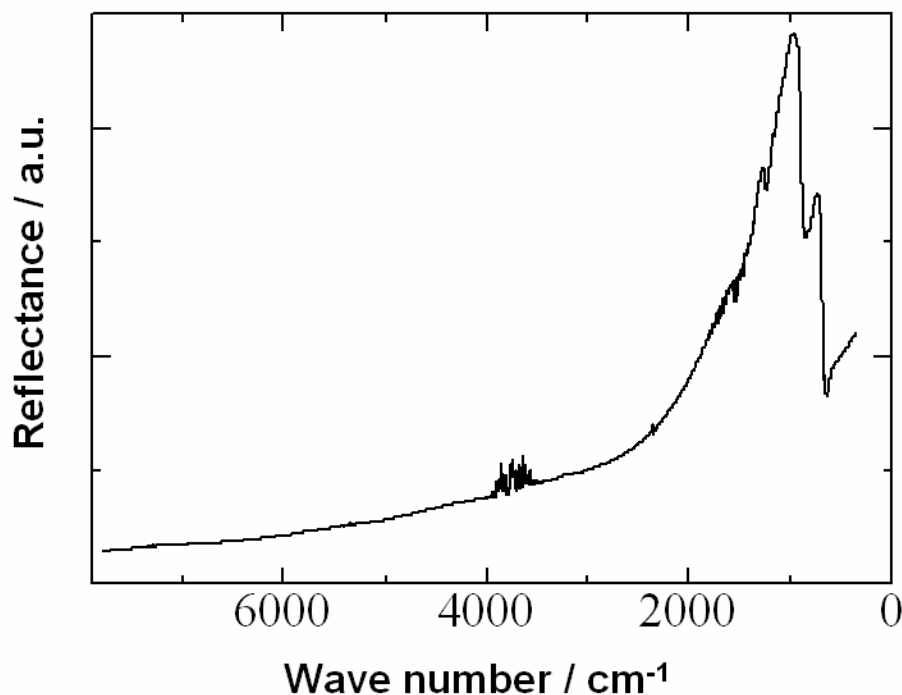


Figure S1: Infrared (IR) reflectance spectra of LaTiO₂N dispersed on a Ti metal substrate (JASCO FT/IR-6200), which were measured to investigate whether the possible OH and NH₄ species exist or not. The IR spectra indicated neither OH (around 3600 cm⁻¹) nor NH₄ species (around 3100 cm⁻¹).

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(S4) TEM study of LaTiO₂N (Figs. S2 and S3).

We investigated electron-diffraction patterns of about 10 crystallites and obtained the identical patterns and symmetry for all the crystallites.

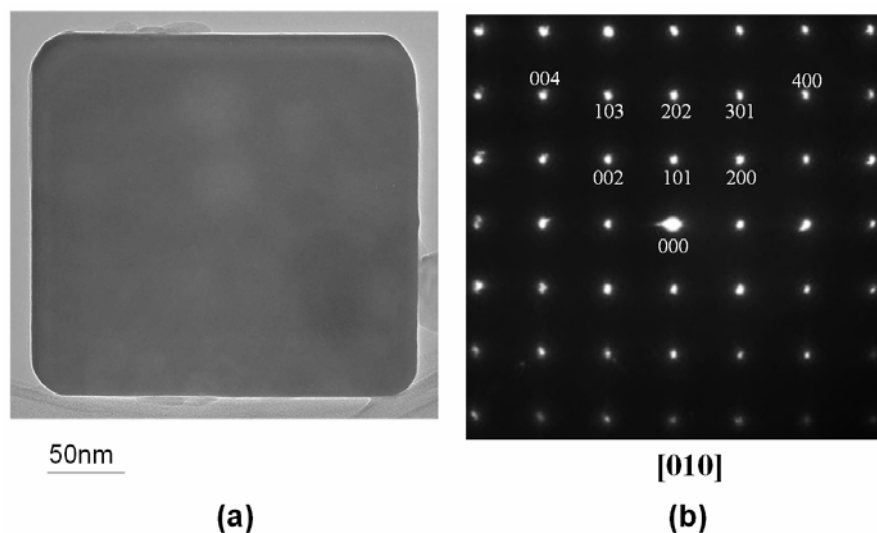


Figure S2. (a) Bright field image and (b) selected area electron diffraction (SAED) pattern of the $[010]_{\text{ortho}}$ zone axis for highly crystalline LaTiO₂N. SAED pattern indicates the reflection condition, $h0l$: $h+l = \text{even}$. The particle was single crystal with the rectangular shape. No twins were observed. TEM-EDS measurements of this particle indicated the composition La : Ti : O : N = 1.00 : 1.00 : 2 : 1. The TEM observations indicated that the crystallite sizes were ranged from 50 nm to 500 nm.

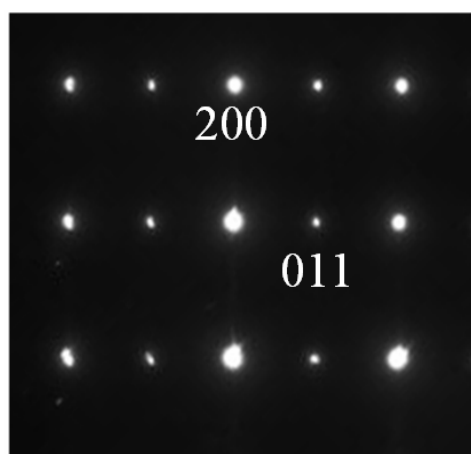


Figure S3. Selected area electron diffraction (SAED) pattern of the $[01-1]_{\text{ortho}}$ zone axis for highly crystalline LaTiO₂N. SAED pattern indicates the reflection condition, $h00$: $h = \text{even}$ and $0kl$: $k+l = \text{even}$.

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(S5) **Table S2.** Crystallographic parameters and reliability factors in Rietveld and MPF analyses for the synchrotron powder diffraction data of LaTiO₂N.*

Atom	Site	<i>g</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å ²)
La	4 <i>e</i>	1.0000(17)	0	1/4	1.0010(5)	0.01221(5)
Ti	4 <i>b</i>	1	0	0	1/2	0.00412(13)
O1	4 <i>e</i>	0.67(8)	0	1/4	0.551(2)	0.0124(10)
N1	4 <i>e</i>	0.33(8)**	0	1/4	= <i>x</i> (O1)	= <i>U</i> (O1)
O2	8 <i>g</i>	0.67(4)	1/4	0.0325(9)	1/4	= <i>U</i> (O1)
N2	8 <i>g</i>	0.33(4)**	1/4	= <i>y</i> (O2)	1/4	= <i>U</i> (O1)

*Crystal symmetry: Orthorhombic; Space group: *Imma*; Unit-cell parameters: *a* = 5.57137 (17), *b* = 7.8790(2), *c* = 5.60279(11) Å, $\alpha = \beta = \gamma = 90^\circ$; Reliability factors in Rietveld analysis: $R_{wp} = 2.87\%$, $R_I = 0.49\%$, $R_F = 0.43\%$, *S* = 1.43; Reliability factors in 1st MPF analysis: $R_{wp} = 2.87\%$, $R_I = 0.41\%$, $R_F = 0.38\%$, *S* = 1.44. The decrease of R_I and R_F from the Rietveld analysis to MPF one indicates the validity of the MEM electron density.

** Refinements of occupancy factors: *g*(*X*): Occupancy factor of *X* atom. The occupancy factors at the anion sites were refined with the linear constraints $g(\text{O1}) + g(\text{N1}) = 1$ and $g(\text{O2}) + g(\text{N2}) = 1$.

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(S6) SEM-EDS study of LaTiO_2N (Fig. S4).

To investigate the chemical composition and its homogeneity in LaTiO_2N , EDS spectra were measured for 15 particles (SEM-EDS, 10 kV, 20 μA , SU8000/Hitachi, Horiba X-max). Figure S4 shows an example of SEM photograph with the region for an EDS measurement. The chemical composition was calibrated using the standard materials BN, SiO_2 , and LaB_6 . The average chemical composition for fifteen particles was $\text{La}_{1.3(2)}\text{Ti}_{1.0(1)}\text{O}_{2.1(5)}\text{N}_{0.64(23)}$ where the number in the parenthesis denotes the standard deviation σ in the last digit. Thus, the average chemical composition $\text{La}_{1.3(2)}\text{Ti}_{1.0(1)}\text{O}_{2.1(5)}\text{N}_{0.64(23)}$ agrees with the nominal one LaTiO_2N within $\pm 3\sigma$.

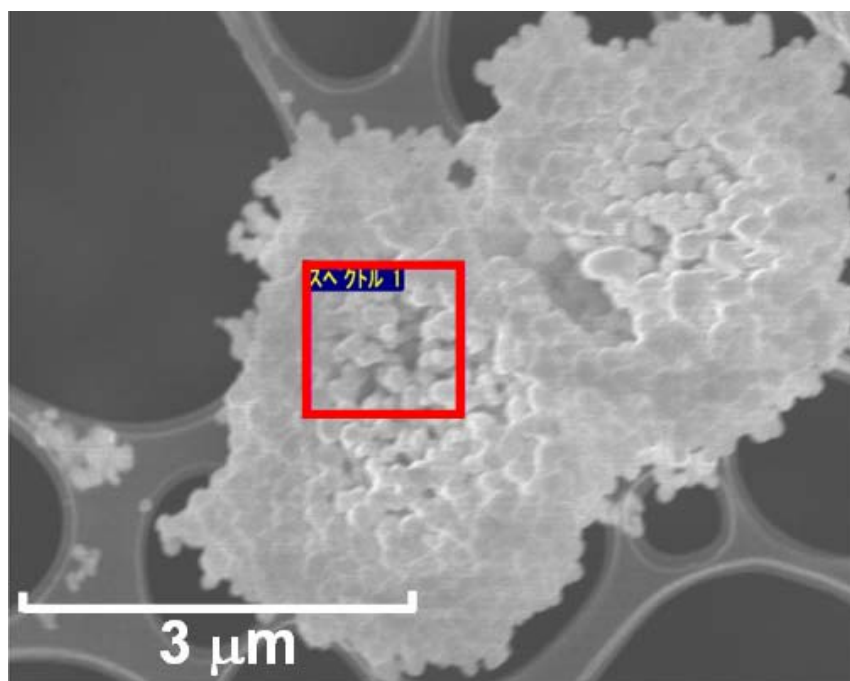


Figure S4: SEM image of LaTiO_2N . The chemical composition through the EDS measurement from the square region was La: 26.84 atomic%, Ti: 21.91 atomic%, O: 38.76 atomic%, N: 12.49 atomic%.

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(S7) Figure S5. Refined crystal structures projected on the (a) (101) and (b) (010) planes of *Imma* LaTiO₂N with the tilt system $a^0b\bar{b}$.

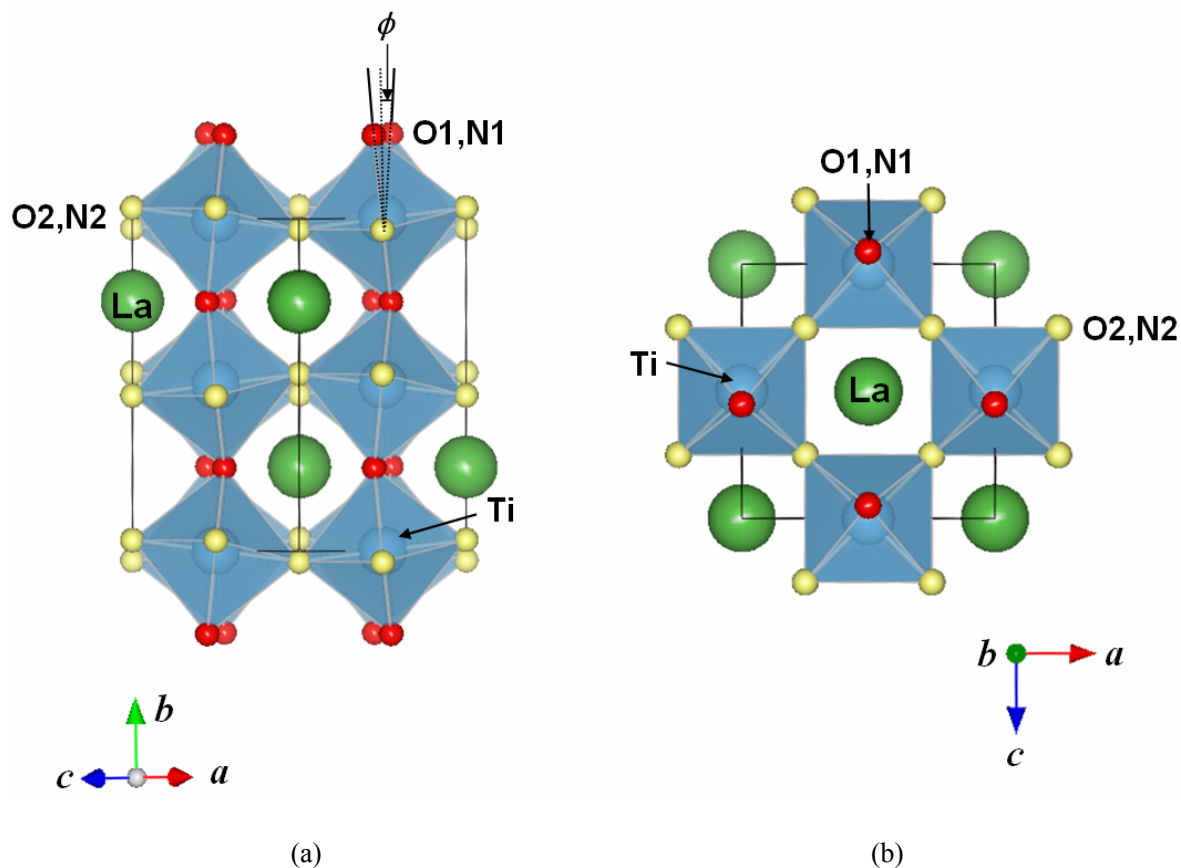


Figure S5. Refined crystal structures projected on the (a) (101) and (b) (010) planes of *Imma* LaTiO₂N with the tilt system $a^0b\bar{b}$. Fig. S5(a) indicates the anti-phase tilting, while Fig. S5(b) shows no tilting. The anti-phase tilt angle ϕ in Fig. S5(a) was estimated to be $\phi = 10.404(5)^\circ$.

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(S8) Figure S6. Refined crystal structure and MEM nuclear density distribution of *Imma* LaTiO₂N.

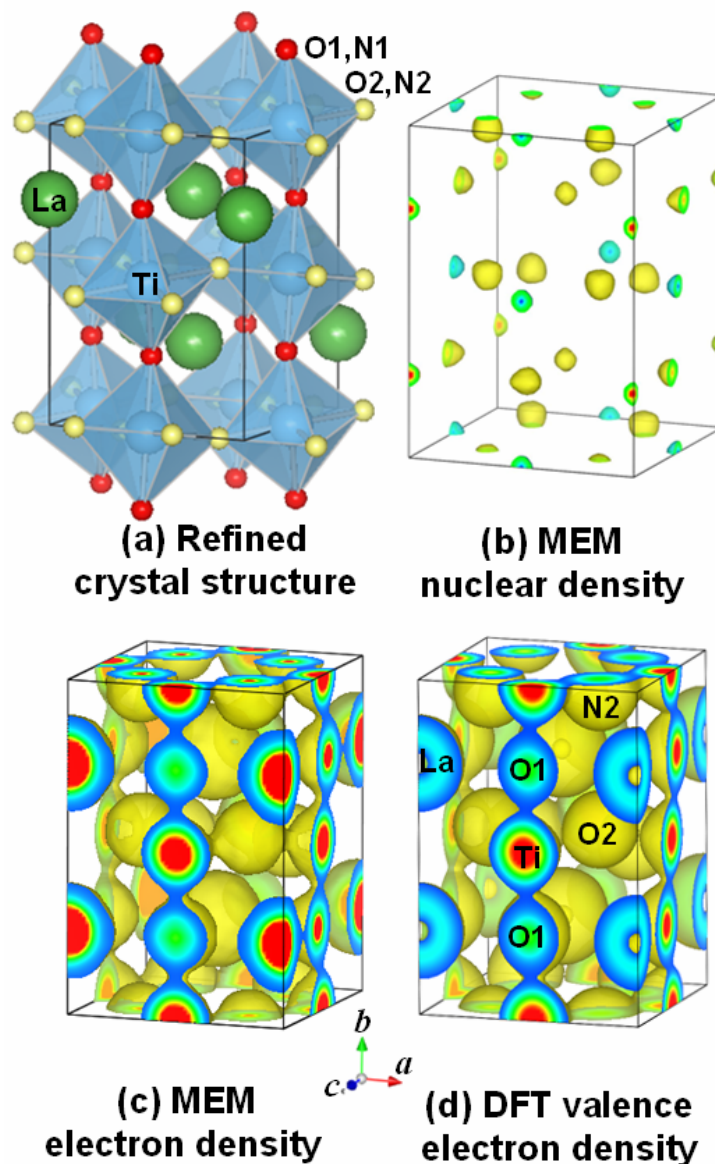


Figure S6. (a) Refined crystal structure, (b) isosurface of MEM nuclear density at $3 \text{ fm } \text{\AA}^{-3}$, (c) isosurface of MEM electron density at 0.5 \AA^{-3} , and (d) isosurface of DFT valence electron density at 0.5 \AA^{-3} (4th model in Fig. S7(d)). The nuclear density is localized at around the center of atoms, while the electron density is largely distributed forming the Ti-(O,N) covalent bonds. No nuclear density due to other species such as OH and NH₄ was observed in Fig. S6(b).

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(S9) Details of the DFT calculations and six structure models (Fig. S7).

The spin-polarized generalized gradient approximation (GGA) electronic calculations were performed with Vienna *Ab initio* Simulation Package (VASP),¹ in order to obtain the valence electron-density distribution, density of states, and band structure in $(\text{LaTiO}_2\text{N})_4$. Calculations were performed using projector augmented-wave (PAW) potentials for La, Ti, N, and O atoms.² A plane-wave basis set with a cutoff of 500 eV was used. The Perdew-Burke-Ernzerhof (PBE) GGA was employed for the exchange and correlation functionals. Sums over occupied electronic states were performed using the Monkhorst-Pack scheme³ on a $3 \times 3 \times 3$ set of a k -point mesh. Unit-cell parameters and atomic coordinates of $(\text{LaTiO}_2\text{N})_4$ were optimized with the convergence condition of 0.01 eV/Å. Initial crystallographic parameters used in the optimizations were referred from the present Rietveld analysis for *Imma* and $R\bar{3}c$, and from the literature for $P\bar{1}$.⁴

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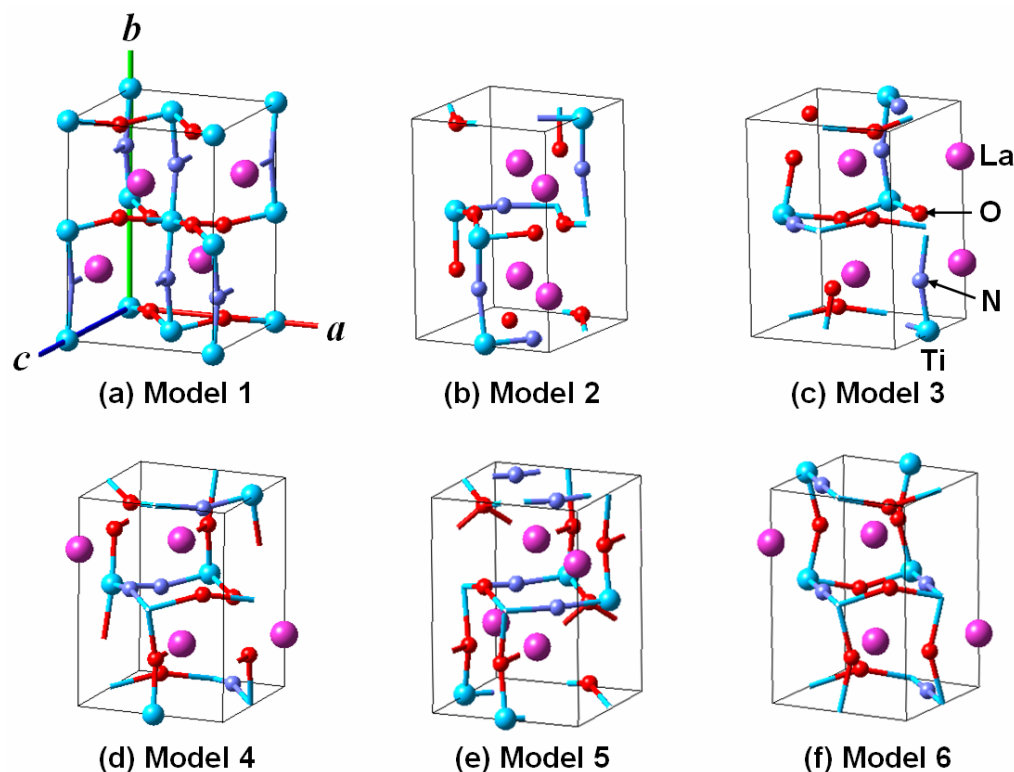


Figure S7. Six optimized *Imma* structure models of N and O atomic arrangements around a Ti atom in $(\text{LaTiO}_2\text{N})_4$.

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Model**	Relative energy / atom (meV)			Band gap [eV]		
	<i>Imma</i>	$P\bar{1}$	$R\bar{3}c$	<i>Imma</i>	$P\bar{1}$	$R\bar{3}c$
1	16	10	22	0.94	1.26	0.88
2	0	1	19	1.43	1.25	1.52
3	0	1	19	1.51	1.37	1.42
4	1.5	2	-	1.30	1.53	-
5	8	9	-	0.97	1.20	-
6	8	10	-	0.83	1.29	-

* Six structural models of O and N atoms around a Ti atom in Fig. S7 were investigated. The calculations in the *Imma* and $R\bar{3}c$ columns were done using the initial crystallographic parameters obtained by the Rietveld analysis of the synchrotron powder diffraction data in this study. The calculations in the $P\bar{1}$ columns were performed using the initial crystallographic parameters reported in the literature (Ref. 1). Since the energy difference less than 10 meV/atom is negligible, the *Imma* and $P\bar{1}$ structure models of 2, 3 and 4 are regarded as ground states. Since the positional parameters of 4th *Imma* model (Fig. S7(d)) exhibited best agreements with the refined ones from the synchrotron data, we showed the results of the 4th model in Figs. 2c, 3c, 4c and 5, Table S4 and Fig. S8.

** See Figs. S7(a), (b), (c), (d), (e) and (f) for the structural models 1, 2, 3, 4, 5 and 6, respectively.

Ref. 1: S. J. Clarke, B. P. Guinot, C. W. Michie, M. J. C. Calmont, M. J. Rosseinsky, *Chem. Mater.* **14**, (2002) 288.

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(S11) Table S4. Unit-cell and positional parameters of LaTiO₂N obtained by DFT structural optimization for 4th model of (LaTiO₂N)₄ (Fig. S7(d)) and by the *Imma* Rietveld analysis of synchrotron data (Table S2). Theoretical and experimental values agree well with each other.

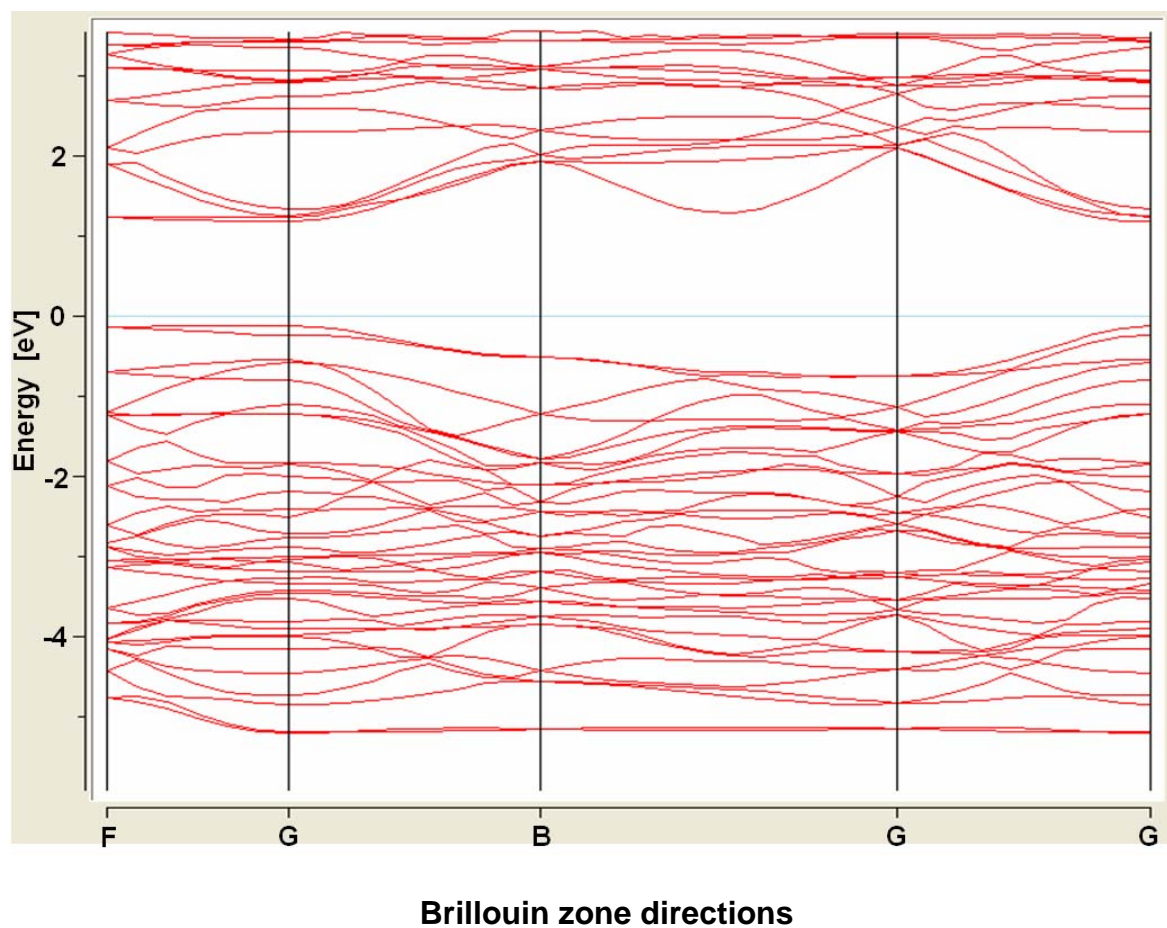
		Theoretical (4 th model)			Experimental (Table S2)		
<i>a</i> (Å)		5.647495			5.5713(2)		
<i>b</i> (Å)		7.827490			7.8790(3)		
<i>c</i> (Å)		5.660266			5.6027(2)		
α (deg)		90.0			90.0		
β (deg)		90.0			90.0		
γ (deg)		90.0			90.0		
Atom							
Coordinates	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>	
La1	0.00000	0.25000	0.00940	0.00000	0.25000	0.00103	
La2	0.00000	0.75000	0.99060	0.00000	0.75000	0.99897	
La3	0.50000	0.75000	0.50940	0.50000	0.75000	0.50103	
La4	0.50000	0.25000	0.49060	0.50000	0.25000	0.49897	
Ti1	0.97970	0.00000	0.50000	1.00000	0.00000	0.50000	
Ti2	0.02030	0.50000	0.50000	0.00000	0.50000	0.50000	
Ti3	0.47970	0.50000	0.00000	0.50000	0.50000	0.00000	
Ti4	0.52030	0.00000	0.00000	0.50000	0.00000	0.00000	
O1	0.00000	0.25000	0.57870	0.00000	0.25000	0.55066	
O2	0.50000	0.75000	0.07870	0.50000	0.75000	0.05066	
O3	0.25000	0.04900	0.25000	0.25000	0.03246	0.25000	
O4	0.25000	0.95100	0.75000	0.25000	0.96754	0.75000	
O5	0.00000	0.75000	0.42130	0.00000	0.75000	0.44934	
O6	0.75000	0.54900	0.75000	0.75000	0.53246	0.75000	
O7	0.75000	0.45100	0.25000	0.75000	0.46754	0.25000	
O8	0.50000	0.25000	0.92130	0.50000	0.25000	0.94934	
N1	0.75000	0.03720	0.25000	0.75000	0.03246	0.25000	
N2	0.25000	0.46280	0.25000	0.25000	0.46754	0.25000	
N3	0.75000	0.96280	0.75000	0.75000	0.96754	0.75000	
N4	0.25000	0.53720	0.75000	0.25000	0.53246	0.75000	

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(S12) Figure S8. Band structure of $(\text{LaTiO}_2\text{N})_4$. These curves were obtained by the DFT calculations for the 4th structure model (Fig. S7(d)).



End of the Supporting Information