

Supporting Information

Dion–Jacobson-type oxide-ion conductor $\text{CsLa}_2\text{Ti}_2\text{NbO}_{10-\delta}$ without phase transitions

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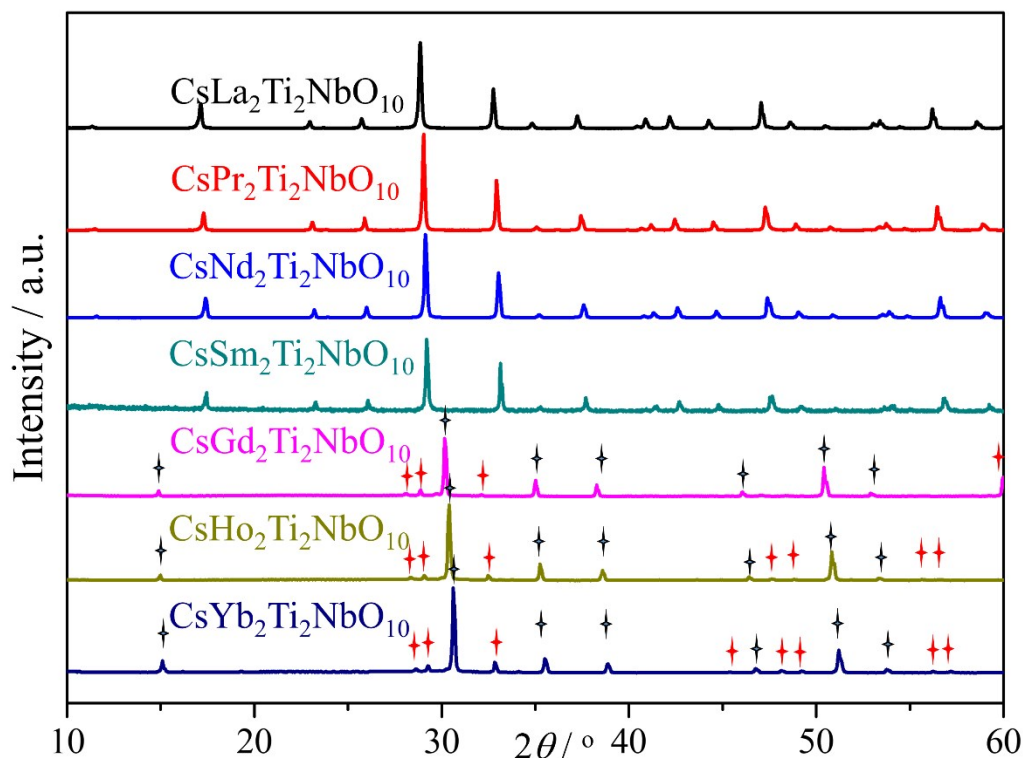


Fig. S1 X-ray diffraction patterns of $\text{CsR}_2\text{Ti}_2\text{NbO}_{10}$ ($R = \text{La, Pr, Nd, Sm, Gd, Ho}$ and Yb). The black star marks in $\text{CsR}_2\text{Ti}_2\text{NbO}_{10}$ ($R = \text{Gd, Ho}$ and Yb) denote the X-ray diffraction peaks of $\text{R}_2\text{Ti}_2\text{O}_7$ ($R = \text{Gd, Ho}$ and Yb). The red star marks stand for the unknown peaks.

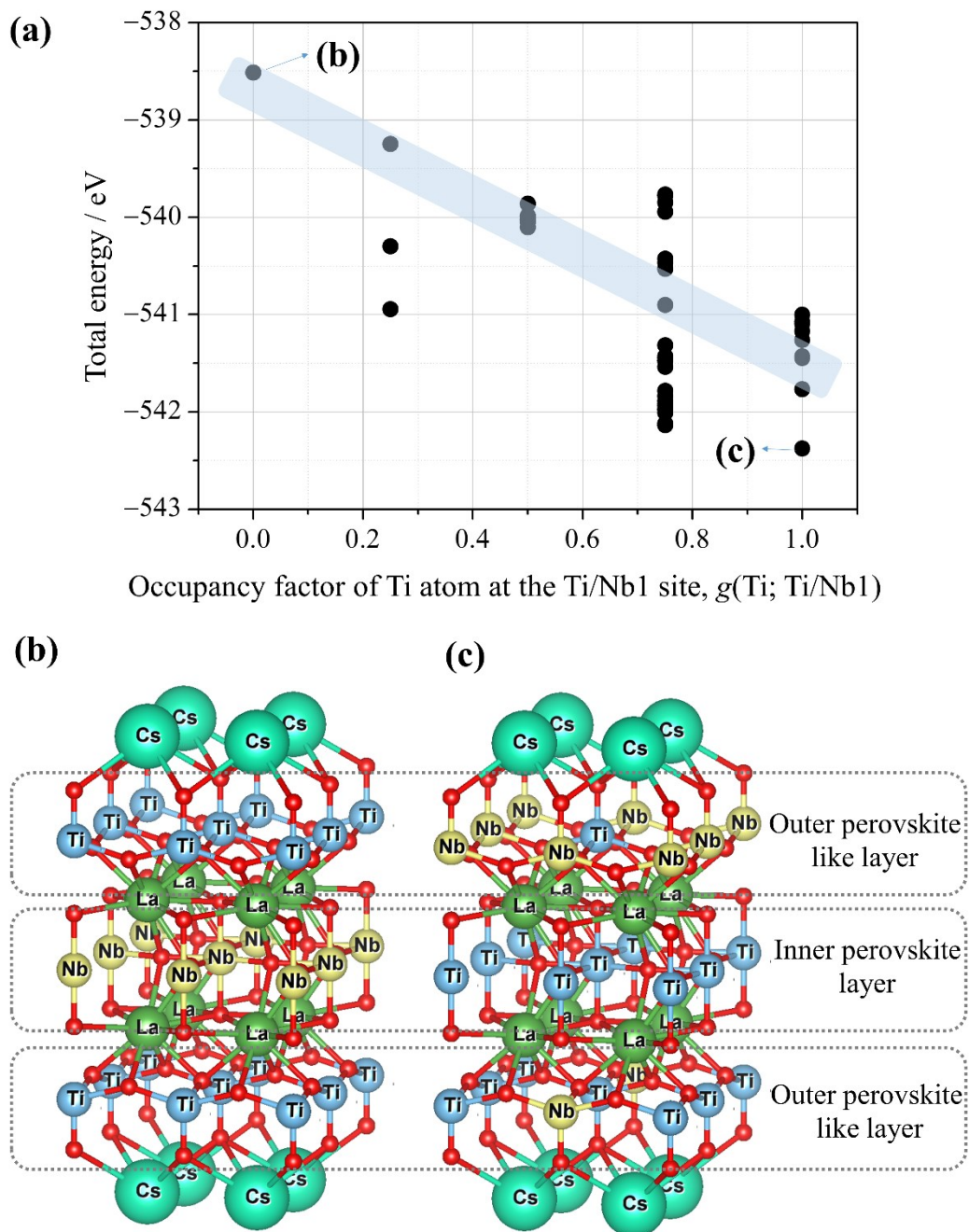


Fig. S2 (a) Total energies of 49 kinds of models (all the possible arrangements of the Ti and Nb cations in the supercells $(\text{CsLa}_2\text{Ti}_2\text{NbO}_{10})_4$) using DFT-based calculations, (b) the most unstable model and (c) the most stable model of the $2 \times 2 \times 1$ tetragonal supercells $(\text{CsLa}_2\text{Ti}_2\text{NbO}_{10})_4$.

We constructed $2 \times 2 \times 1$ tetragonal supercells $(\text{CsLa}_2\text{Ti}_2\text{NbO}_{10})_4$ with different arrangements of the Ti and Nb cations. The Ti and Nb cations were allowed to exist in the inner perovskite layer and also in the outer perovskite layer (**Fig. S2**). **Fig. S2b** shows the most unstable model where all the Nb cations exist in the inner perovskite layer and all the Ti cations are located in the outer perovskite-like layers.

This model is inconsistent with the experimental results. **Fig. S2c** shows the most stable model where only Ti cations exist in the inner perovskite layer and Ti and Nb cations exist in the outer perovskite-like layer, which is consistent with the refined crystal structure with the inner perovskite layer $\text{LaTi}_{0.985}\text{Nb}_{0.015}\text{O}_3$ and the outer perovskite-like layer $\text{La}_{0.5}\text{Ti}_{0.508}\text{Nb}_{0.492}\text{O}_3$ (**Fig. 3**).

The different occupation of *B*-site cations (Ti and Nb) in $\text{CsLa}_2\text{Ti}_2\text{NbO}_{10}$ was explained using the electrostatic stabilization, in addition to the ionic radii and charge differences by Hong in 2000.^[1] They concluded that the insertion of a CsO layer with negative charge ($[\text{CsO}]^{-1}$) into a 3-dimensional perovskite structure contributes to the ordering of Ti^{4+} and Nb^{5+} cations along the *z*-axis by electrostatic stabilization. They imagined $\text{CsLa}_2\text{Ti}_2\text{NbO}_{10}$ as the composite of a $[\text{CsO}]$ layer and a $[\text{La}_2\text{Ti}_2\text{NbO}_9]$ layer. Then, the compound was depicted as a chain of $[\text{CsO}]^{-1}-[\text{La}_{0.5}(\text{Ti}_{1-x}\text{Nb}_x)\text{O}_3]^{x-0.5}-[\text{La}(\text{Ti}_{2x}\text{Nb}_{1-2x})\text{O}_3]^{-2x+2}-[\text{La}_{0.5}(\text{Ti}_{1-x}\text{Nb}_x)\text{O}_3]^{x-0.5}-[\text{CsO}]^{-1}$ depending on the distribution of *B*-site cations. They considered the $x = 0.5$ gives the charge distribution of $[\text{CsO}]^{-1}-[\text{La}_{0.5}(\text{Ti}_{0.5}\text{Nb}_{0.5})\text{O}_3]^0-[\text{LaTiO}_3]^{+1}-[\text{La}_{0.5}(\text{Ti}_{0.5}\text{Nb}_{0.5})\text{O}_3]^0-[\text{CsO}]^{-1}$ with the ideal charge separation, which means *B*-site cation arrangement in $\text{CsLa}_2\text{Ti}_2\text{NbO}_{10}$ was determined by the electrostatic stabilization.

References

1. Y.-S. Hong, S.-J. Kim, S.-J. Kim and J.-H. Choy, *J. Mater. Chem.*, 2000, **10**, 1209.

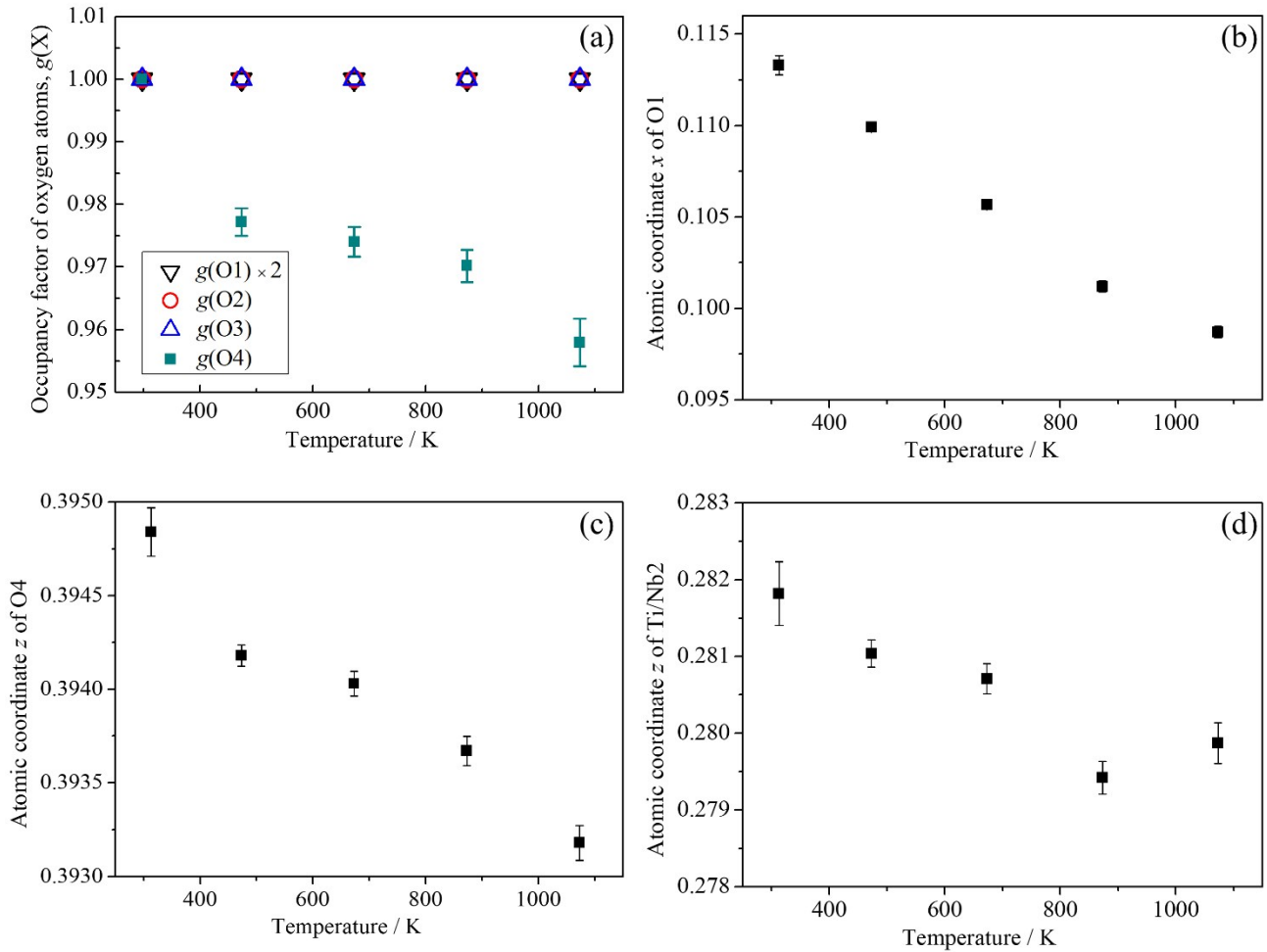


Fig. S3 Temperature dependencies of (a) the occupancy factors of oxygen atoms at the O_i site $g(O_i)$, (b) the atomic coordinate x of the oxygen atom at the O1 site, $x(\text{O1})$, (c) the atomic coordinate z of the oxygen atom at the O4 site, $z(\text{O4})$, and (d) the atomic coordinate z of the $\text{Ti}_{0.5102}\text{Nb}_{0.4898}$ atom at the Ti/Nb2 site, $z(\text{Ti/Nb2})$, in $\text{CsLa}_2\text{Ti}_2\text{NbO}_{10-\delta}$, which were refined using high-temperature neutron-diffraction data. The equatorial oxygen atom at the O4 site in the CsO layer has a higher oxygen vacancy concentration than the others and the oxygen vacancy concentration increases with an increase of temperature. The atomic coordinates of $x(\text{O1})$, $z(\text{O4})$ and $z(\text{Ti/Nb2})$ decrease with an increase of temperature.

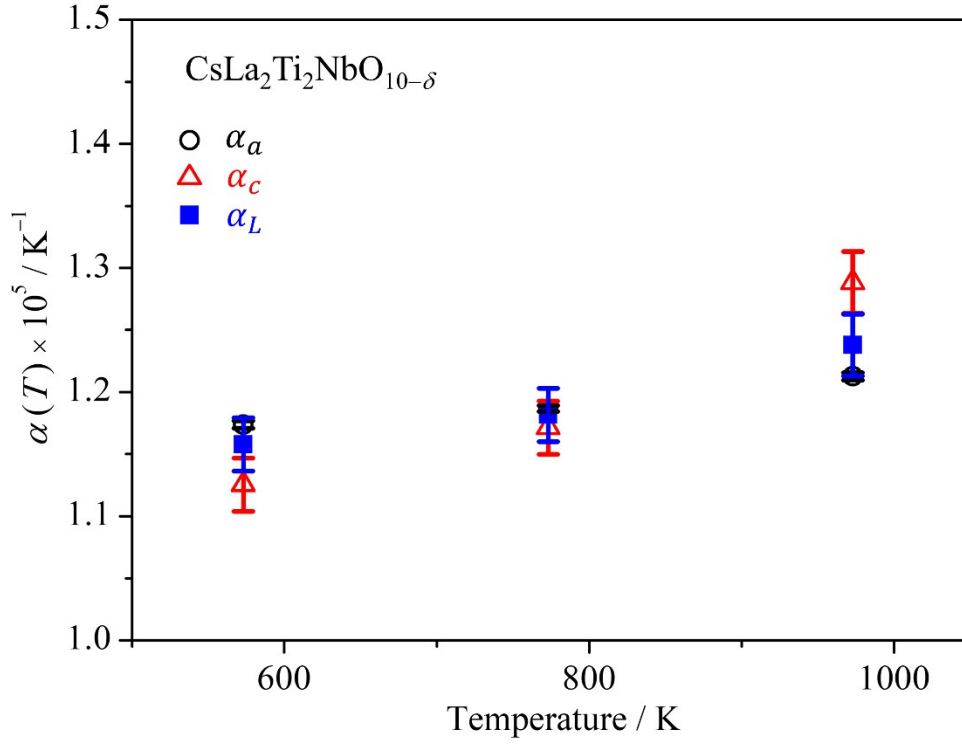


Fig. S4 Thermal expansion coefficients (TECs) of $\text{CsLa}_2\text{Ti}_2\text{NbO}_{10-\delta}$. The TECs were estimated using the lattice parameters refined by the Rietveld analyses of the neutron diffraction data. TECs of $\text{CsLa}_2\text{Ti}_2\text{NbO}_{10-\delta}$ are defined as follows.

$$\alpha_a\left(\frac{(T_{i+1}) + (T_i)}{2}\right) = (a(T_{i+1}) - a(T_i)) \times 2 / (a(T_{i+1}) + a(T_i)) / (T_{i+1} - T_i)$$

$$\alpha_c\left(\frac{(T_{i+1}) + (T_i)}{2}\right) = (c(T_{i+1}) - c(T_i)) \times 2 / (c(T_{i+1}) + c(T_i)) / (T_{i+1} - T_i)$$

$$\alpha_L\left(\frac{(T_{i+1}) + (T_i)}{2}\right) = (v(T_{i+1}) - v(T_i)) \times 2 / (v(T_{i+1}) + v(T_i)) / (T_{i+1} - T_i)$$

$$\text{where } v(T_i) = [a(T_i) \cdot b(T_i) \cdot c(T_i)]^{1/3}$$

Here, the i is 1, 2 and 3; $T_1 = 473$ K, $T_2 = 673$ K, $T_3 = 873$ K and $T_4 = 1073$ K for $\text{CsLa}_2\text{Ti}_2\text{NbO}_{10-\delta}$. The α_a , α_c and α_L increase with an increase of temperature.

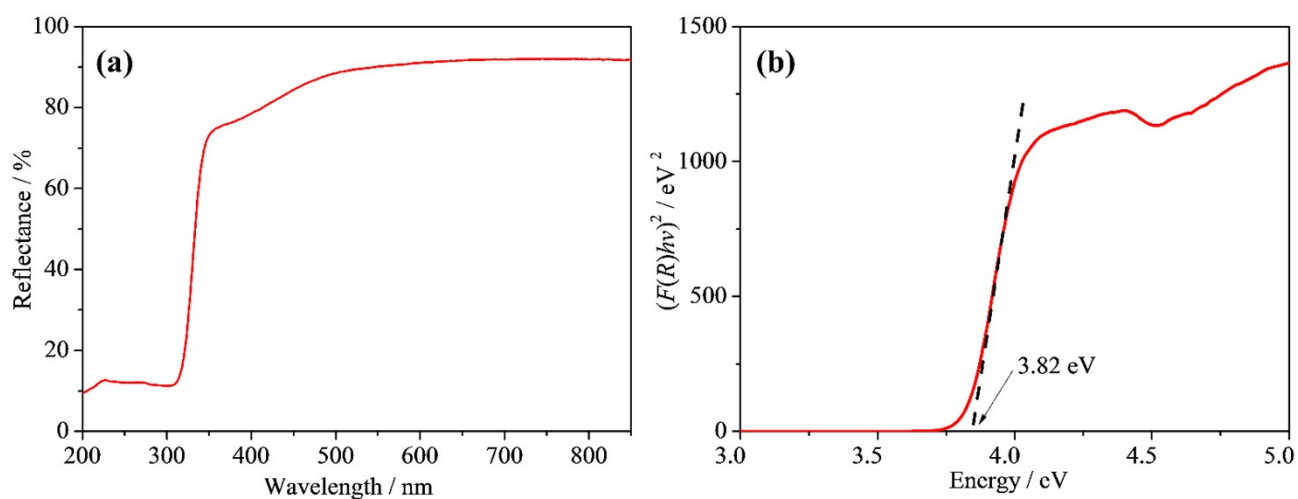


Fig. S5 (a) Diffuse reflectance spectrum and (b) Tauc plot for the direct band gap of CsLa₂Ti₂NbO₁₀.

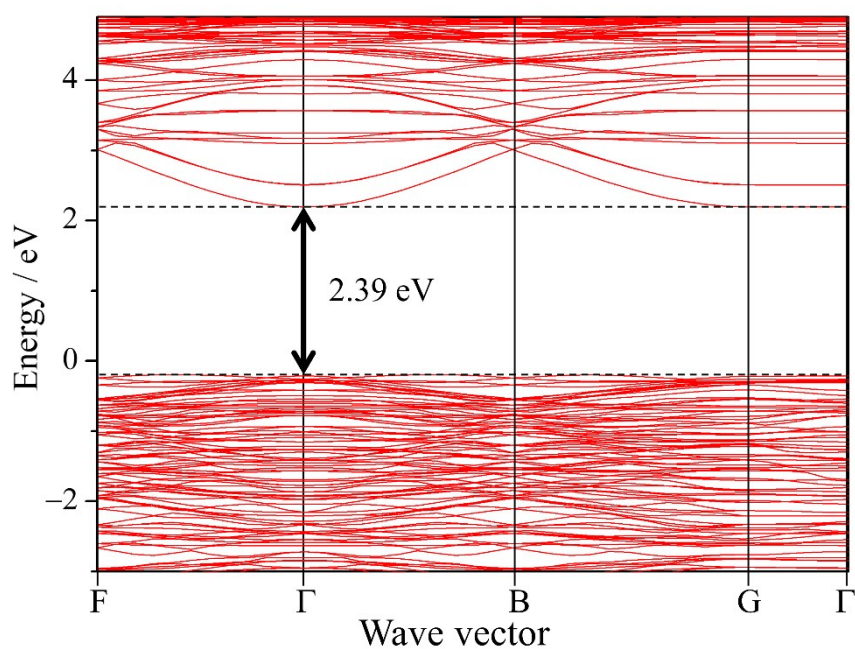


Fig. S6 Band structure of CsLa₂Ti₂NbO₁₀ based on DFT calculations using the most stable model in Fig. S2, which indicates the direct band gap at the Γ point. Lower E_g value (2.39 eV) in the DFT calculations compared with the experimental value (3.82 eV) is usual.

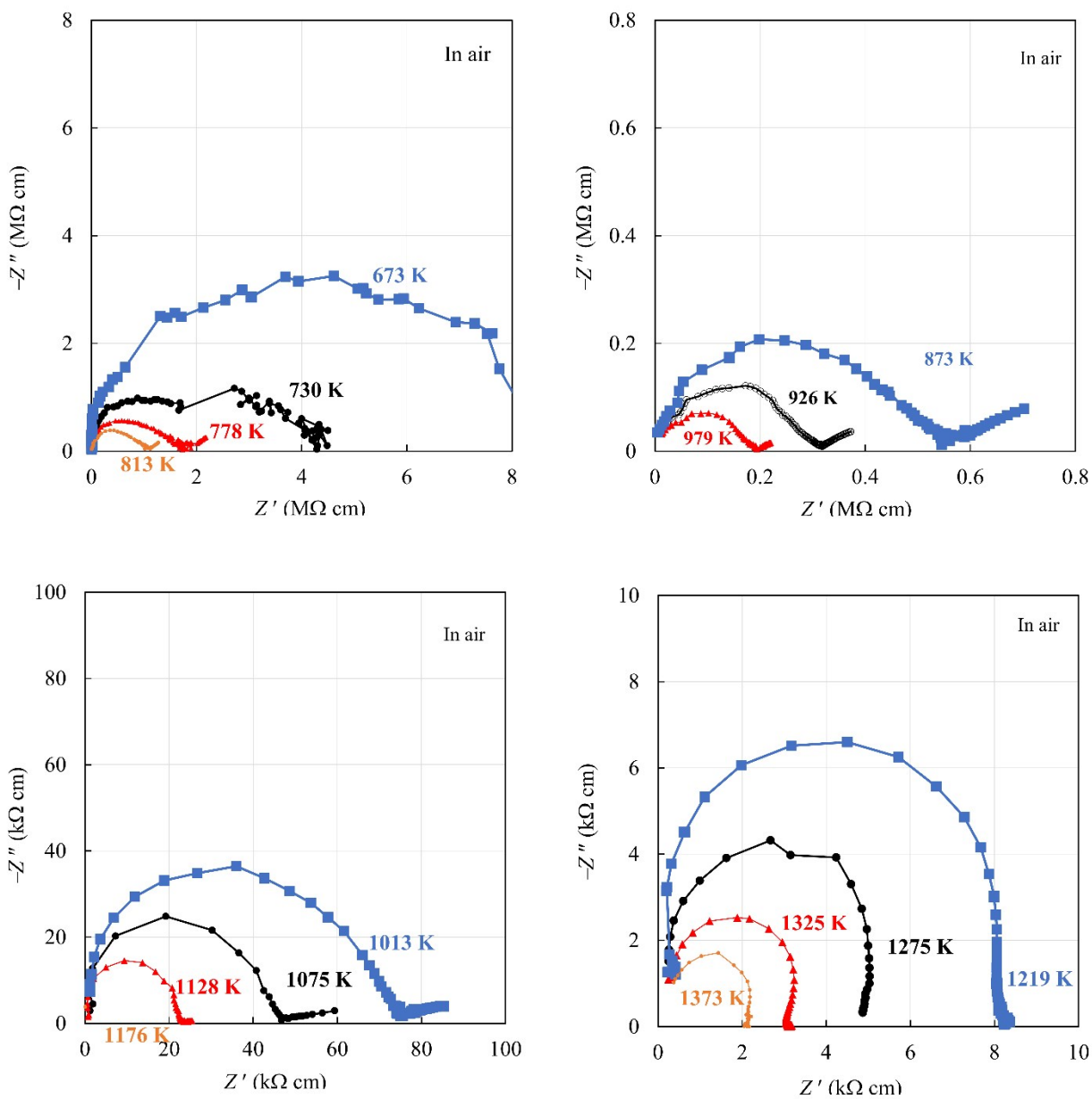


Fig. S7 Complex impedance plot recorded from 673 K to 1373K in following dry air.

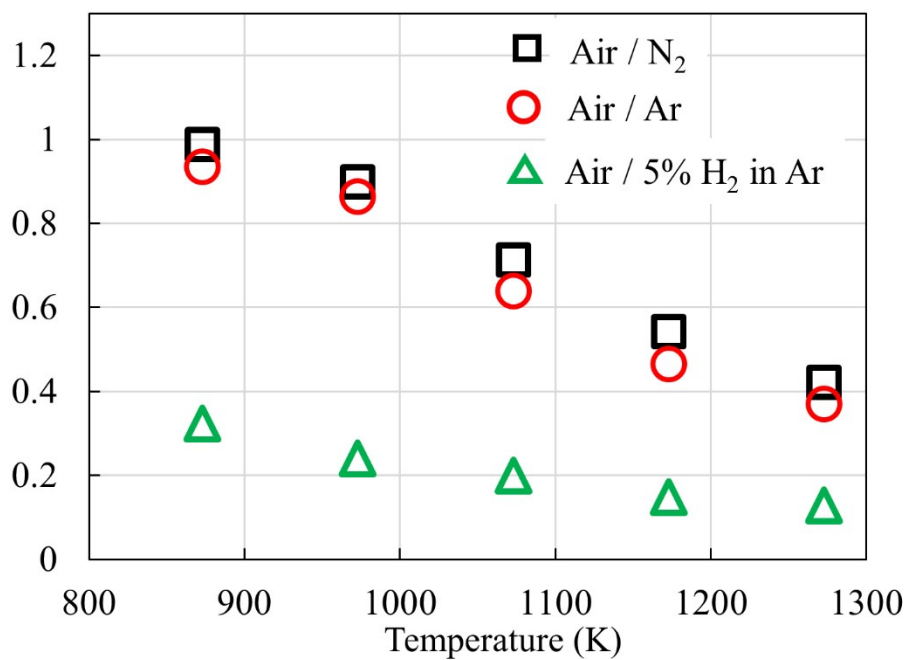


Fig. S8 Oxide-ion transport number of CsLa₂Ti₂NbO_{10- δ} over the temperature range 873–1273 K measured by the oxygen concentration cell method.

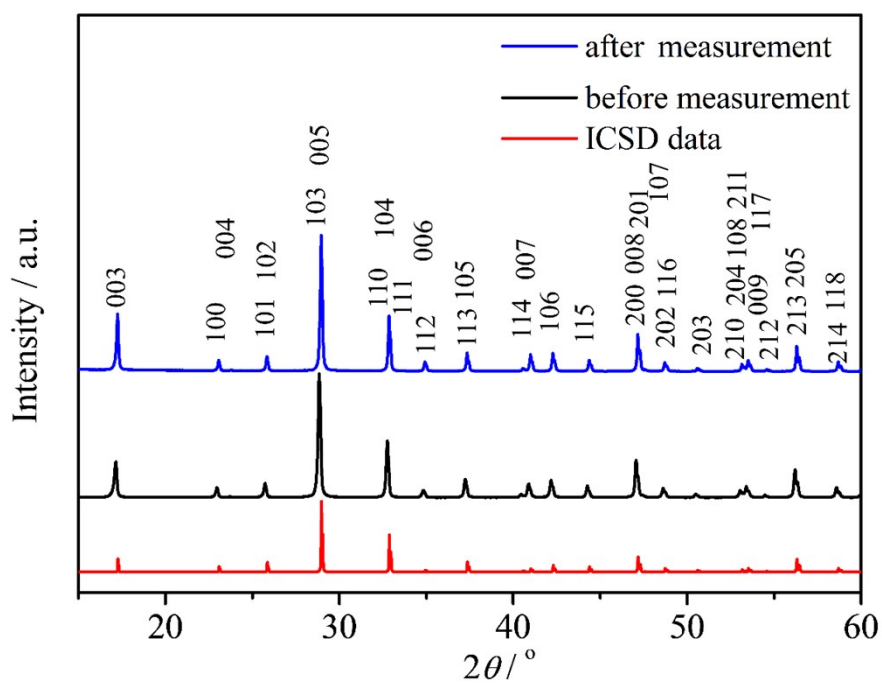


Fig. S9 X-ray powder diffraction patterns of CsLn₂Ti₂NbO_{10- δ} before and after the electrical-conductivity measurements at different oxygen partial pressures.

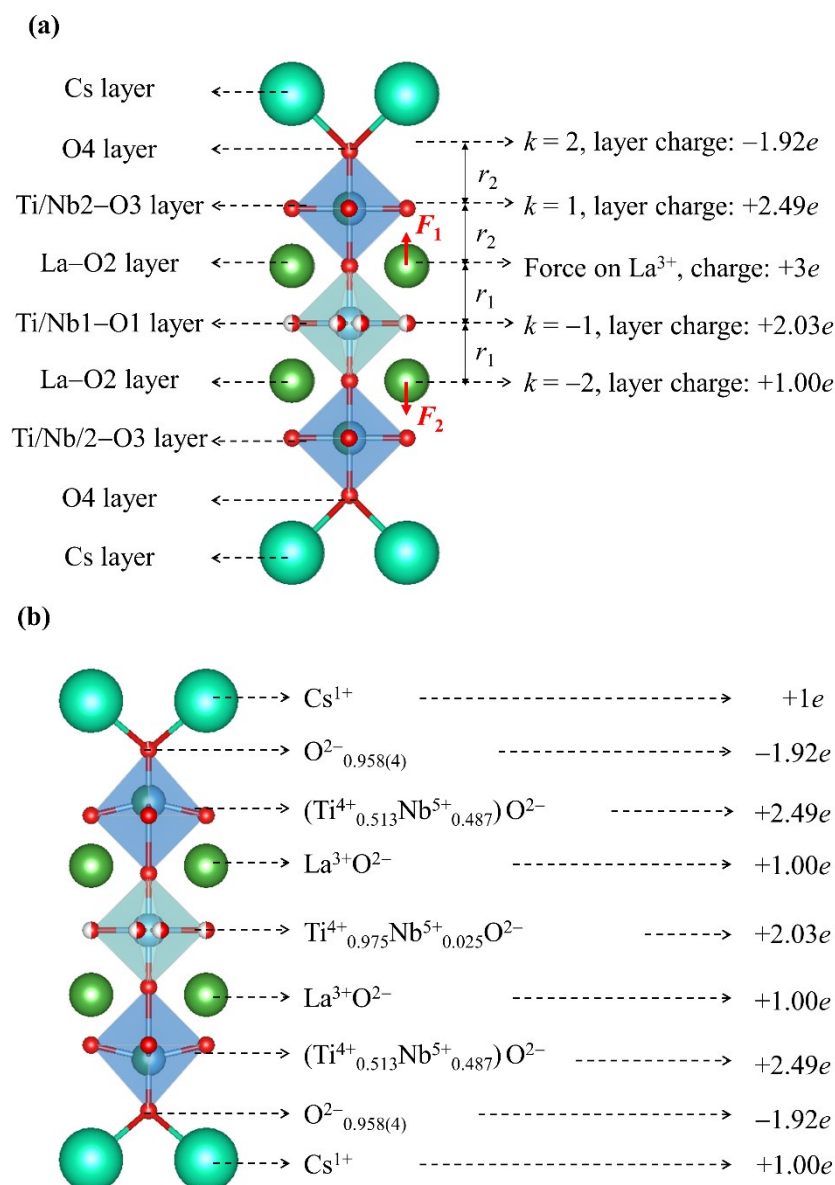


Fig. S10 La^{3+} displacement from the La-O2 layer due to electrostatic forces. (a) Hypothetical crystal structure of $\text{CsLa}_2\text{Ti}_2\text{NbO}_{9.916(8)}$ without cation and anion displacements. (b) Refined crystal structure of $\text{CsLa}_2\text{Ti}_2\text{NbO}_{9.916(8)}$, which was obtained using neutron-diffraction data at 1073 K.

The r_1 stands for the distance between La^{3+} and Ti/Nb1-O1 layer, while the r_2 denotes the distance between La^{3+} and Ti/Nb2-O3 layer. The interatomic distance r_2 is assumed to be r_1 . F_1 and F_2 in (a) are the electrostatic forces on the La^{3+} cations. To estimate the F_1 and F_2 , the Coulomb's forces between the La^{3+} cation and four layers of $k = \pm 2$ and ± 1 are considered. The calculated results show $F_1 > 0$ and $F_2 < 0$, indicating that the La^{3+} cations in $\text{CsLa}_2\text{Ti}_2\text{NbO}_{9.916(8)}$ can be displaced apart from the Ti/Nb1-O1 layer due to the electrostatic forces.

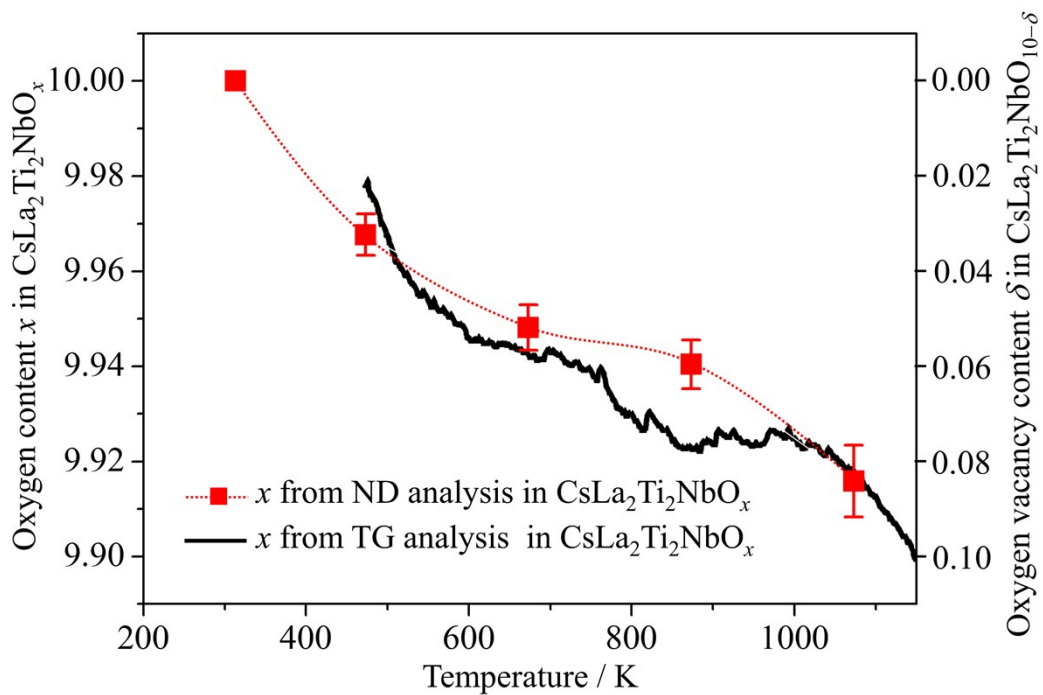


Fig.S11 Oxygen contents x in $\text{CsLa}_2\text{Ti}_2\text{NbO}_x$ and oxygen vacancy content δ in $\text{CsLa}_2\text{Ti}_2\text{NbO}_{10-\delta}$, which were obtained through a thermogravimetric analysis and calculated using occupancy factors refined using the ND data.

Table S1. Lattice parameters a , c and volume V of $\text{CsR}_2\text{Ti}_2\text{NbO}_{10-\delta}$ ($R = \text{La, Pr, Nd}$ and Sm) which were refined by the Rietveld analysis using the XRPD data.

Composition	a	c	V
$\text{CsLa}_2\text{Ti}_2\text{NbO}_{10-\delta}$	3.84951(2) Å	15.3964(11) Å	228.1551(11)
$\text{CsPr}_2\text{Ti}_2\text{NbO}_{10-\delta}$	3.83714(12) Å	15.3099(8) Å	225.4175(8)
$\text{CsNd}_2\text{Ti}_2\text{NbO}_{10-\delta}$	3.83292(3) Å	15.2874(2) Å	224.5914(2)
$\text{CsSm}_2\text{Ti}_2\text{NbO}_{10-\delta}$	3.8178(2) Å	15.2544(12) Å	222.3420(12)

Table S2. Crystallographic parameters of CsLa₂Ti₂NbO_{9.954(4)} which were refined using neutron-diffraction data at 473 K.

Site <i>s</i>	Atom <i>X</i> , Oxidation number	Wyckoff position	$g(X; s)^a$	<i>x</i>	<i>y</i>	<i>z</i>	
Cs	Cs +1	1 <i>d</i>	1	1/2	1/2	1/2	
La	La +3	2 <i>h</i>	1	1/2	1/2	0.14035(4)	
Ti/Nb1	Ti	1 <i>a</i>	0.9855(11)	0	0	0	
	Nb		0.0145(11)				
Ti/Nb2	Ti	2 <i>g</i>	0.5072(5)	0	0	0.28106(2)	
	Nb		0.4928(5)				
O1	O -2	4 <i>n</i>	0.5	0.1099(2)	1/2	0	
O2	O -2	2 <i>g</i>	1	0	0	0.12432(5)	
O3	O -2	4 <i>i</i>	1	0	1/2	0.24963(4)	
O4	O -2	2 <i>g</i>	0.977(2)	0	0	0.39421(6)	
Site <i>s</i>	U_{iso}^b or U_{eq}^c (Å ²)	U_{11} (Å ²) ^d	U_{22} (Å ²) ^d	U_{33} (Å ²) ^d	U_{12} (Å ²) ^d	U_{13} (Å ²) ^d	U_{23} (Å ²) ^d
Cs	$U_{\text{eq}} = 0.0190(4)$	0.0083(5)	0.0083(5)	0.0403(12)	0	0	0
La	$U_{\text{iso}} = 0.0043(14)$	-	-	-	-	-	-
Ti/Nb1	$U_{\text{iso}} = 0.0039(10)$	-	-	-	-	-	-
Ti/Nb2	$= U_{\text{iso}}(\text{Ti}; \text{Ti/Nb1})$ $= U_{\text{iso}}(\text{Nb}; \text{Ti/Nb1})$	-	-	-	-	-	-
O1	$U_{\text{iso}} = 0.0161(4)$	-	-	-	-	-	-
O2	$U_{\text{eq}} = 0.0188(3)$	0.0119(4)	0.0119(4)	0.0326(11)	0	0	0
O3	$U_{\text{iso}} = 0.0075(11)$	-	-	-	-	-	-
O4	$U_{\text{eq}} = 0.0077(3)$	0.0088(5)	0.0088(5)	0.0055(6)	0	0	0

Crystal system: tetragonal; Space group: *P4/mmm*; Lattice parameters: $a = b = 3.858267(6)$ Å and $c = 15.43165(4)$ Å

Reliability factors: $R_{\text{wp}} = 3.23\%$, $R_{\text{p}} = 2.36\%$, $R_{\text{B}} = 3.24\%$ and $R_{\text{F}} = 3.32\%$.

^a $g(X; s)$: Occupancy factor of *X* atom at the *s* site.

^b $U_{\text{iso}}(X; s)$: Isotropic atomic displacement parameter of *X* atom at the *s* site.

^c U_{eq} : Equivalent isotropic atomic displacement parameter.

^d U_{ij} : Anisotropic atomic displacement parameter.

^e The following linear constraints were used in the refinement: $U_{\text{iso}}(\text{Ti}; \text{Ti/Nb1}) = U_{\text{iso}}(\text{Nb}; \text{Ti/Nb1}) = U_{\text{iso}}(\text{Ti}; \text{Ti/Nb2}) = U_{\text{iso}}(\text{Nb}; \text{Ti/Nb2})$.

^f The occupancy factors of Cs, La, O1×2, O2, O3 and O4 were fixed to be 1 because the refined value was 1 within 3 times of the estimated deviation or higher than 1.

Table S3. Crystallographic parameters of CsLa₂Ti₂NbO_{9.948(5)} which were refined using neutron-diffraction data at 673 K.

Site <i>s</i>	Atom <i>X</i> , Oxidation number	Wyckoff position	$g(X; s)^a$	<i>x</i>	<i>y</i>	<i>z</i>	
Cs	Cs +1	1 <i>d</i>	1	1/2	1/2	1/2	
La	La +3	2 <i>h</i>	1	1/2	1/2	0.14020(4)	
Ti/Nb1	Ti Nb	+ 4.02	1 <i>a</i>	0.9796(11)	0	0	0
				0.0204(11)			
Ti/Nb2	Ti Nb	+ 4.49	2 <i>g</i>	0.5102(6)	0	0	0.28071(2)
				0.4898(6)			
O1	O -2	4 <i>n</i>	0.5	0.1056(2)	1/2	0	
O2	O -2	2 <i>g</i>	1	0	0	0.12407(5)	
O3	O -2	4 <i>i</i>	1	0	1/2	0.25005(4)	
O4	O -2	2 <i>g</i>	0.974(2)	0	0	0.39403(7)	
Site <i>s</i>	U_{iso}^b or U_{eq}^c (Å ²)	U_{11} (Å ²) ^d	U_{22} (Å ²) ^d	U_{33} (Å ²) ^d	U_{12} (Å ²) ^d	U_{13} (Å ²) ^d	U_{23} (Å ²) ^d
Cs	$U_{\text{eq}} = 0.0306(5)$	0.0201(5)	0.0201(5)	0.0526(2)	0	0	0
La	$U_{\text{eq}} = 0.0074(13)$	0.0033(2)	0.0033(2)	0.0156(5)	0	0	0
Ti/Nb1	$U_{\text{iso}} = 0.0040(2)$	-	-	-	-	-	-
Ti/Nb2	$= U_{\text{iso}}(\text{Ti}; \text{Ti/Nb1})$ $= U_{\text{iso}}(\text{Nb}; \text{Ti/Nb1})$	-	-	-	-	-	-
O1	$U_{\text{iso}} = 0.0217(6)$	-	-	-	-	-	-
O2	$U_{\text{eq}} = 0.0210(3)$	0.0173(5)	0.0173(5)	.0285(13)	0	0	0
O3	$U_{\text{eq}} = 0.0157(2)$	0.0066(11)	0.0064(9)	0.0350(10)	0	0	0
O4	$U_{\text{eq}} = 0.0160(8)$	0.0180(5)	0.0180(5)	0.0122(8)	0	0	0

Crystal system: tetragonal; Space group: *P4/mmm*; Lattice parameters: $a = b = 3.867334(5)$ Å and $c = 15.46637(4)$ Å

Reliability factors: $R_{\text{wp}} = 2.93\%$, $R_{\text{p}} = 2.18\%$, $R_{\text{B}} = 3.87\%$ and $R_{\text{F}} = 3.86\%$.

^a $g(X; s)$: Occupancy factor of *X* atom at the *s* site.

^b $U_{\text{iso}}(X; s)$: Isotropic atomic displacement parameter of *X* atom at the *s* site.

^c U_{eq} : Equivalent isotropic atomic displacement parameter.

^d U_{ij} : Anisotropic atomic displacement parameter.

^e The following linear constraints were used in the refinement: $U_{\text{iso}}(\text{Ti}; \text{Ti/Nb1}) = U_{\text{iso}}(\text{Nb}; \text{Ti/Nb1}) = U_{\text{iso}}(\text{Ti}; \text{Ti/Nb2}) = U_{\text{iso}}(\text{Nb}; \text{Ti/Nb2})$.

^f The occupancy factors of Cs, La, O1×2, O2, O3 and O4 were fixed to be 1 because the refined value was 1 within 3 times of the estimated deviation or higher than 1.

Table S4. Crystallographic parameters of CsLa₂Ti₂NbO_{9.940(5)} which were refined using neutron-diffraction data at 873 K.

Site <i>s</i>	Atom <i>X</i> , Oxidation number	Wyckoff position	$g(X; s)^a$	<i>x</i>	<i>y</i>	<i>z</i>	
Cs	Cs +1	1 <i>d</i>	1	1/2	1/2	1/2	
La	La +3	2 <i>h</i>	1	1/2	1/2	0.14063(5)	
Ti/Nb1	Ti	+ 4.02	1 <i>a</i>	0.9845(11)	0	0	0
	Nb			0.0155(11)			
Ti/Nb2	Ti	+ 4.49	2 <i>g</i>	0.5077(6)	0	0	0.2794(2)
	Nb			0.4923(6)			
O1	O -2	4 <i>n</i>	0.5	0.10124(3)	1/2	0	
O2	O -2	2 <i>g</i>	1	0	0	0.12363(6)	
O3	O -2	4 <i>i</i>	1	0	1/2	0.24996(4)	
O4	O -2	2 <i>g</i>	0.970(3)	0	0	0.39367(8)	
Site <i>s</i>	U_{iso}^b or U_{eq}^c (Å ²)	U_{11} (Å ²) ^d	U_{22} (Å ²) ^d	U_{33} (Å ²) ^d	U_{12} (Å ²) _{<i>d</i>}	U_{13} (Å ²) _{<i>d</i>}	U_{23} (Å ²) _{<i>d</i>}
Cs	$U_{\text{eq}} = 0.0438(6)$	0.0286(7)	0.0286(7)	0.0744(2)	0	0	0
La	$U_{\text{eq}} = 0.0129(2)$	0.0062(2)	0.0062(2)	0.0264(6)	0	0	0
Ti/Nb1	$U_{\text{iso}} = 0.0059(6)$	-	-	-	-	-	-
Ti/Nb2	$= U_{\text{iso}}(\text{Ti}; \text{Ti/Nb1})$	-	-	-	-	-	-
	$= U_{\text{iso}}(\text{Nb}; \text{Ti/Nb1})$	-	-	-	-	-	-
O1	$U_{\text{iso}} = 0.0274(5)$	-	-	-	-	-	-
O2	$U_{\text{eq}} = 0.0290(3)$	0.0282(6)	0.0282(6)	0.0306(2)	0	0	0
O3	$U_{\text{eq}} = 0.0187(2)$	0.0154(4)	0.0043(5)	0.0364(11)	0	0	0
O4	$U_{\text{eq}} = 0.0262(4)$	0.0297(6)	0.0297(6)	0.0190(10)	0	0	0

Crystal system: tetragonal; Space group: *P4/mmm*; Lattice parameters: $a = b = 3.876526(5)$ Å and $c = 15.50272(4)$ Å; Reliability factors: $R_{\text{wp}} = 2.81\%$, $R_{\text{p}} = 2.11\%$, $R_{\text{B}} = 4.36\%$ and $R_{\text{F}} = 4.20\%$.

^a $g(X; s)$: Occupancy factor of *X* atom at the *s* site. ^b $U_{\text{iso}}(X; s)$: Isotropic atomic displacement parameter of *X* atom at the *s* site. ^c U_{eq} : Equivalent isotropic atomic displacement parameter.

^d U_{ij} : Anisotropic atomic displacement parameter. ^e The following linear constraints were used in the refinement: $U_{\text{iso}}(\text{Ti}; \text{Ti/Nb1}) = U_{\text{iso}}(\text{Nb}; \text{Ti/Nb1}) = U_{\text{iso}}(\text{Ti}; \text{Ti/Nb2}) = U_{\text{iso}}(\text{Nb}; \text{Ti/Nb2})$.

^f The occupancy factors of Cs, La, O1×2, O2, O3 and O4 were fixed to be 1 because the refined value was 1 within 3 times of the estimated deviation or higher than 1.

Table S5. Crystallographic parameters of CsLa₂Ti₂NbO₁₀ which were refined using synchrotron X-ray powder diffraction data at 297 K.

Site <i>s</i>	Atom <i>X</i>	Oxidation number	Wyckoff position	$g(X; s)^a$	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}(X; s)^b$
Cs	Cs	+1	1 <i>d</i>	1	1/2	1/2	1/2	0.02796(13)
La	La	+3	2 <i>h</i>	1	1/2	1/2	0.141986(13)	0.00601(6)
Ti/Nb 1	Ti	+ 4.0	1 <i>a</i>	1	0	0	0	0.0185(3)
	Nb			0				
Ti/Nb 2	Ti	+ 4.5	2 <i>g</i>	0.5	0	0	0.28053(3)	0.01852(14)
	Nb			0.5				
O1	O	-2	4 <i>n</i>	0.5	0.0938(7)	1/2	0	0.0127(7)
O2	O	-2	2 <i>g</i>	1	0	0	0.12544(9)	= $U_{\text{iso}}(\text{O}; \text{O1})$
O3	O	-2	4 <i>i</i>	1	0	1/2	0.22754(7)	= $U_{\text{iso}}(\text{O}; \text{O1})$
O4	O	-2	2 <i>g</i>	1	0	0	0.381972(11)	= $U_{\text{iso}}(\text{O}; \text{O1})$

Crystal system: tetragonal; Space group: *P4/mmm*;

Lattice parameters: $a = b = 3.850752(3)$ Å and $c = 15.401752(22)$ Å;

Reliability factors: $R_{\text{wp}} = 8.48\%$, $R_{\text{p}} = 5.15\%$, $R_{\text{B}} = 8.87\%$ and $R_{\text{F}} = 6.22\%$.

^a $g(X; s)$: Occupancy factor of *X* atom at the *s* site.

^b $U_{\text{iso}}(X; s)$: Isotropic atomic displacement parameter of *X* atom at the *s* site.

^c The following linear constraints were used in the refinement: $U_{\text{iso}}(\text{Ti}; \text{Ti/Nb1}) = U_{\text{iso}}(\text{Nb}; \text{Ti/Nb1})$; $U_{\text{iso}}(\text{Ti}; \text{Ti/Nb2}) = U_{\text{iso}}(\text{Nb}; \text{Ti/Nb2})$; $U_{\text{iso}}(\text{O}; \text{O1}) = U_{\text{iso}}(\text{O}; \text{O2}) = U_{\text{iso}}(\text{O}; \text{O3}) = U_{\text{iso}}(\text{O}; \text{O4})$; $g(\text{O}; \text{O1}) \times 0.5 = g(\text{O}; \text{O2}) = g(\text{O}; \text{O3}) = g(\text{O}; \text{O4})$.

^d The occupancy factors of Cs, La, O1×2, O2, O3 and O4 were fixed to be 1 because the refined value was 1 within 3 times of the estimated deviation or higher than 1, the occupancy factors of Ti and Nb were fixed.

Table S6. Crystallographic parameters of CsLa₂Ti₂NbO₁₀ which were refined using synchrotron X-ray powder diffraction data at 473 K.

Site <i>s</i>	Atom <i>X</i>	Oxidation number	Wyckoff position	$g(X; s)^a$	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}(X; s)^b$
Cs	Cs	+1	1 <i>d</i>	1	1/2	1/2	1/2	0.04202(14)
La	La	+3	2 <i>h</i>	1	1/2	1/2	0.141888(13)	0.01008(6)
Ti/Nb 1	Ti	+ 4.0	1 <i>a</i>	1	0	0	0	0.00836(3)
	Nb			0				
Ti/Nb 2	Ti	+ 4.5	2 <i>g</i>	0.5	0	0	0.28025(3)	0.02471(15)
	Nb			0.5				
O1	O	-2	4 <i>n</i>	0.5	0.0821(6)	1/2	0	0.0238(2)
O2	O	-2	2 <i>g</i>	1	0	0	0.12268(9)	= $U_{\text{iso}}(\text{O}; \text{O1})$
O3	O	-2	4 <i>i</i>	1	0	1/2	0.22759(6)	= $U_{\text{iso}}(\text{O}; \text{O1})$
O4	O	-2	2 <i>g</i>	1	0	0	0.384138(11)	= $U_{\text{iso}}(\text{O}; \text{O1})$

Crystal system: tetragonal; Space group: *P4/mmm*;

Lattice parameters: $a = b = 3.857901(3)$ Å and $c = 15.428681(26)$ Å;

Reliability factors: $R_{\text{wp}} = 7.69\%$, $R_{\text{p}} = 4.69\%$, $R_{\text{B}} = 9.02\%$ and $R_{\text{F}} = 6.28\%$.

^a $g(X; s)$: Occupancy factor of *X* atom at the *s* site.

^b $U_{\text{iso}}(X; s)$: Isotropic atomic displacement parameter of *X* atom at the *s* site.

^c The following linear constraints were used in the refinement: $U_{\text{iso}}(\text{Ti}; \text{Ti/Nb1}) = U_{\text{iso}}(\text{Nb}; \text{Ti/Nb1})$; $U_{\text{iso}}(\text{Ti}; \text{Ti/Nb2}) = U_{\text{iso}}(\text{Nb}; \text{Ti/Nb2})$; $U_{\text{iso}}(\text{O}; \text{O1}) = U_{\text{iso}}(\text{O}; \text{O2}) = U_{\text{iso}}(\text{O}; \text{O3}) = U_{\text{iso}}(\text{O}; \text{O4})$; $g(\text{O}; \text{O1}) \times 0.5 = g(\text{O}; \text{O2}) = g(\text{O}; \text{O3}) = g(\text{O}; \text{O4})$.

^d The occupancy factors of Cs, La, O1×2, O2, O3 and O4 were fixed to be 1 because the refined value was 1 within 3 times of the estimated deviation or higher than 1, the occupancy factors of Ti and Nb were fixed.

Table S7. Crystallographic parameters of CsLa₂Ti₂NbO₁₀ which were refined using synchrotron X-ray powder diffraction data at 673 K.

Site <i>s</i>	Atom <i>X</i>	Oxidation number	Wyckoff position	$g(X; s)^a$	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}(X; s)^b$
Cs	Cs	+1	1 <i>d</i>	1	1/2	1/2	1/2	0.05782(15)
La	La	+3	2 <i>h</i>	1	1/2	1/2	0.142156(14)	0.01596(6)
Ti/Nb1	Ti	+ 4.0	1 <i>a</i>	1	0	0	0	0.0162(3)
	Nb			0				
Ti/Nb2	Ti	+ 4.5	2 <i>g</i>	0.5	0	0	0.27976(3)	0.02983(16)
	Nb			0.5				
O1	O	-2	4 <i>n</i>	0.5	0.0752(7)	1/2	0	0.0354(3)
O2	O	-2	2 <i>g</i>	1	0	0	0.12345(9)	= $U_{\text{iso}}(\text{O}; \text{O1})$
O3	O	-2	4 <i>i</i>	1	0	1/2	0.22614(6)	= $U_{\text{iso}}(\text{O}; \text{O1})$
O4	O	-2	2 <i>g</i>	1	0	0	0.381114(12)	= $U_{\text{iso}}(\text{O}; \text{O1})$

Crystal system: tetragonal; Space group: *P4/mmm*;

Lattice parameters: $a = b = 3.867959(4)$ Å and $c = 15.5465635(27)$ Å;

Reliability factors: $R_{\text{wp}} = 7.50\%$, $R_{\text{p}} = 4.55\%$, $R_{\text{B}} = 9.38\%$ and $R_{\text{F}} = 6.69\%$.

^a $g(X; s)$: Occupancy factor of *X* atom at the *s* site.

^b $U_{\text{iso}}(X; s)$: Isotropic atomic displacement parameter of *X* atom at the *s* site.

^c The following linear constraints were used in the refinement: $U_{\text{iso}}(\text{Ti}; \text{Ti/Nb1}) = U_{\text{iso}}(\text{Nb}; \text{Ti/Nb1})$; $U_{\text{iso}}(\text{Ti}; \text{Ti/Nb2}) = U_{\text{iso}}(\text{Nb}; \text{Ti/Nb2})$; $U_{\text{iso}}(\text{O}; \text{O1}) = U_{\text{iso}}(\text{O}; \text{O2}) = U_{\text{iso}}(\text{O}; \text{O3}) = U_{\text{iso}}(\text{O}; \text{O4})$; $g(\text{O}; \text{O1}) \times 0.5 = g(\text{O}; \text{O2}) = g(\text{O}; \text{O3}) = g(\text{O}; \text{O4})$.

^d The occupancy factors of Cs, La, O1×2, O2, O3 and O4 were fixed to be 1 because the refined value was 1 within 3 times of the estimated deviation or higher than 1, the occupancy factors of Ti and Nb were fixed.

Table S8. Crystallographic parameters of CsLa₂Ti₂NbO₁₀ which were refined using synchrotron X-ray powder diffraction data at 873 K.

Site <i>s</i>	Atom <i>X</i>	Oxidation number	Wyckoff position	$g(X; s)^a$	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}(X; s)^b$
Cs	Cs	+1	1 <i>d</i>	1	1/2	1/2	1/2	0.07944(17)
La	La	+3	2 <i>h</i>	1	1/2	1/2	0.141998(14)	0.02443(6)
Ti/Nb 1	Ti	+ 4.0	1 <i>a</i>	1	0	0	0	0.0180(3)
	Nb			0				
Ti/Nb 2	Ti	+ 4.5	2 <i>g</i>	0.5	0	0	0.27949(3)	0.03765(17)
	Nb			0.5				
O1	O	-2	4 <i>n</i>	0.5	0.0643(8)	1/2	0	0.0425(3)
O2	O	-2	2 <i>g</i>	1	0	0	0.12248(9)	= $U_{\text{iso}}(\text{O}; \text{O1})$
O3	O	-2	4 <i>i</i>	1	0	1/2	0.22676(7)	= $U_{\text{iso}}(\text{O}; \text{O1})$
O4	O	-2	2 <i>g</i>	1	0	0	0.38925(12)	= $U_{\text{iso}}(\text{O}; \text{O1})$

Crystal system: tetragonal; Space group: *P4/mmm*;

Lattice parameters: $a = b = 3.876614(4)$ Å and $c = 15.501699(26)$ Å;

Reliability factors: $R_{\text{wp}} = 7.51\%$, $R_{\text{p}} = 4.74\%$, $R_{\text{B}} = 10.29\%$ and $R_{\text{F}} = 8.10\%$.

^a $g(X; s)$: Occupancy factor of *X* atom at the *s* site.

^b $U_{\text{iso}}(X; s)$: Isotropic atomic displacement parameter of *X* atom at the *s* site.

^c The following linear constraints were used in the refinement: $U_{\text{iso}}(\text{Ti}; \text{Ti/Nb1}) = U_{\text{iso}}(\text{Nb}; \text{Ti/Nb1})$; $U_{\text{iso}}(\text{Ti}; \text{Ti/Nb2}) = U_{\text{iso}}(\text{Nb}; \text{Ti/Nb2})$; $U_{\text{iso}}(\text{O}; \text{O1}) = U_{\text{iso}}(\text{O}; \text{O2}) = U_{\text{iso}}(\text{O}; \text{O3}) = U_{\text{iso}}(\text{O}; \text{O4})$; $g(\text{O}; \text{O1}) \times 0.5 = g(\text{O}; \text{O2}) = g(\text{O}; \text{O3}) = g(\text{O}; \text{O4})$.

^d The occupancy factors of Cs, La, O1×2, O2, O3 and O4 were fixed to be 1 because the refined value was 1 within 3 times of the estimated deviation or higher than 1, the occupancy factors of Ti and Nb were fixed.

Table S9. Crystallographic parameters of CsLa₂Ti₂NbO₁₀ which were refined using synchrotron X-ray powder diffraction data at 1073 K.

Site <i>s</i>	Atom <i>X</i>	Oxidation number	Wyckoff position	$g(X; s)^a$	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}(X; s)^b$
Cs	Cs	+1	1 <i>d</i>	1	1/2	1/2	1/2	0.09446(19)
La	La	+3	2 <i>h</i>	1	1/2	1/2	0.142078(15)	0.02741(6)
Ti/Nb 1	Ti	+ 4.0	1 <i>a</i>	1	0	0	0	0.0222(3)
	Nb			0				
Ti/Nb 2	Ti	+ 4.5	2 <i>g</i>	0.5	0	0	0.27904(3)	0.04343(18)
	Nb			0.5				
O1	O	-2	4 <i>n</i>	0.5	0.0549(9)	1/2	0	0.0486(3)
O2	O	-2	2 <i>g</i>	1	0	0	0.12152(9)	= $U_{\text{iso}}(\text{O}; \text{O1})$
O3	O	-2	4 <i>i</i>	1	0	1/2	0.22379(7)	= $U_{\text{iso}}(\text{O}; \text{O1})$
O4	O	-2	2 <i>g</i>	1	0	0	0.378359(12)	= $U_{\text{iso}}(\text{O}; \text{O1})$

Crystal system: tetragonal; Space group: *P4/mmm*;

Lattice parameters: $a = b = 3.886112(4)$ Å and $c = 15.542047(28)$ Å;

Reliability factors: $R_{\text{wp}} = 7.97\%$, $R_{\text{p}} = 5.01\%$, $R_{\text{B}} = 10.9\%$ and $R_{\text{F}} = 9.17\%$.

^a $g(X; s)$: Occupancy factor of *X* atom at the *s* site.

^b $U_{\text{iso}}(X; s)$: Isotropic atomic displacement parameter of *X* atom at the *s* site.

^c The following linear constraints were used in the refinement: $U_{\text{iso}}(\text{Ti}; \text{Ti/Nb1}) = U_{\text{iso}}(\text{Nb}; \text{Ti/Nb1})$; $U_{\text{iso}}(\text{Ti}; \text{Ti/Nb2}) = U_{\text{iso}}(\text{Nb}; \text{Ti/Nb2})$; $U_{\text{iso}}(\text{O}; \text{O1}) = U_{\text{iso}}(\text{O}; \text{O2}) = U_{\text{iso}}(\text{O}; \text{O3}) = U_{\text{iso}}(\text{O}; \text{O4})$; $g(\text{O}; \text{O1}) \times 0.5 = g(\text{O}; \text{O2}) = g(\text{O}; \text{O3}) = g(\text{O}; \text{O4})$.

^d The occupancy factors of Cs, La, O1×2, O2, O3 and O4 were fixed to be 1 because the refined value was 1 within 3 times of the estimated deviation or higher than 1, the occupancy factors of Ti and Nb were fixed.