Electronic Supplementary Information:

Structural Frustration Effects by Mixed Alkali Ions in Ferroelectric Dion-Jacobson Layered Perovskites (Cs,Rb)$NdNb_2O_7$

Zhen-Tao Lu[a], Sota Asaki[a], Suguru Yoshida[b], Chikako Moriyoshi[c], George Hasegawa[e], Koji Fujita[d], Venkatraman Gopalan[b], Katsuro Hayashi[a], Hirofumi Akamatsu[a,*]

[a] Department of Applied Chemistry, Kyushu University, Motooka, Fukuoka 819-0395, Japan

[b] Materials Research Institute and Department of Materials Science, Pennsylvania State University, University Park, Pennsylvania 16802, United States

[c] Graduate School of Advanced Science and Engineering, Hiroshima University, Higashihiroshima, Hiroshima 739-8526, Japan

[d] Department of Material Chemistry, Kyoto University, Nishikyo, Kyoto 615-8510, Japan

[e] Institute of Materials and Systems for Sustainability, Nagoya University, Nagoya 464-8601, Japan

*Corresponding author
E-mail address: h.akamatsu@cstf.kyushu-u.ac.jp

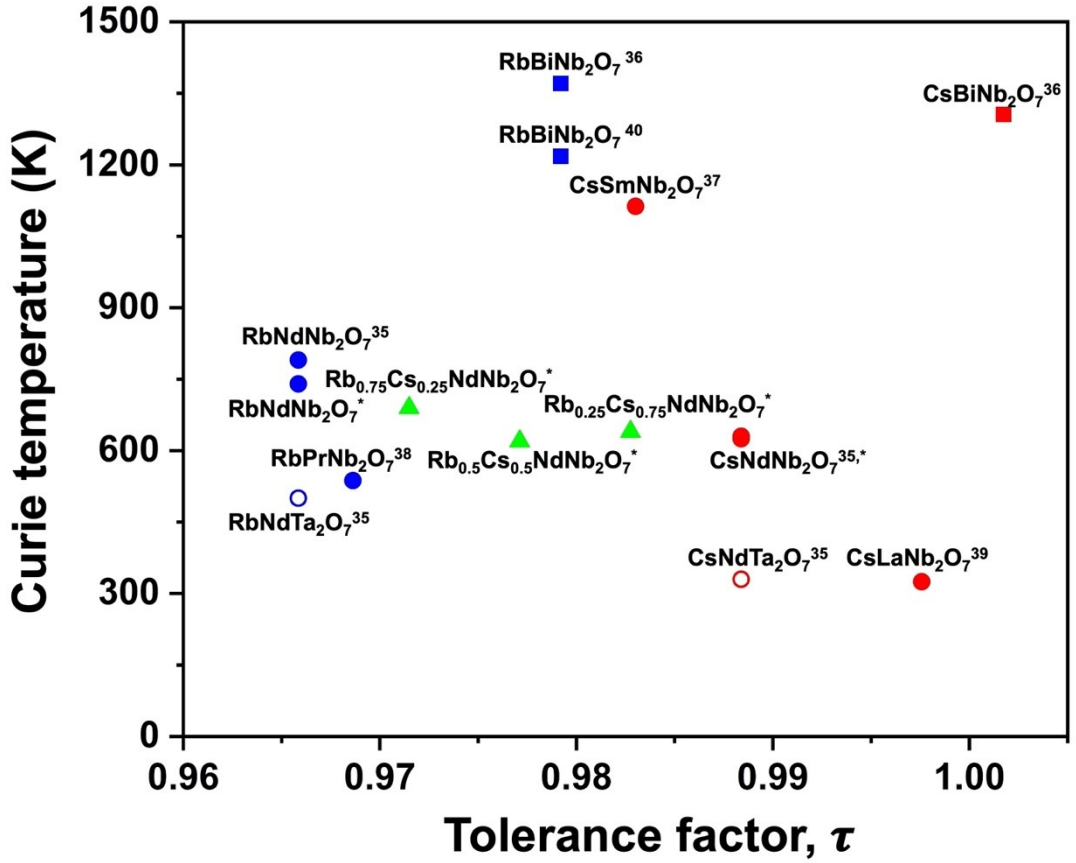

Figure S1. Relationship between Curie temperature (T_C) and tolerance factor (τ). The blue closed and open circles indicate Rb-containing niobate and tantalate DJ phases, respectively. The red closed and open circles indicate Cs-containing niobate and tantalate DJ phases, respectively. The squares indicate Bi-containing DJ phases. The green triangles indicate the solid solutions of DJ phases including Rb and Cs. The superscript numbers denote the reference numbers, while the superscript asterisks denote the T_C's reported in this work.

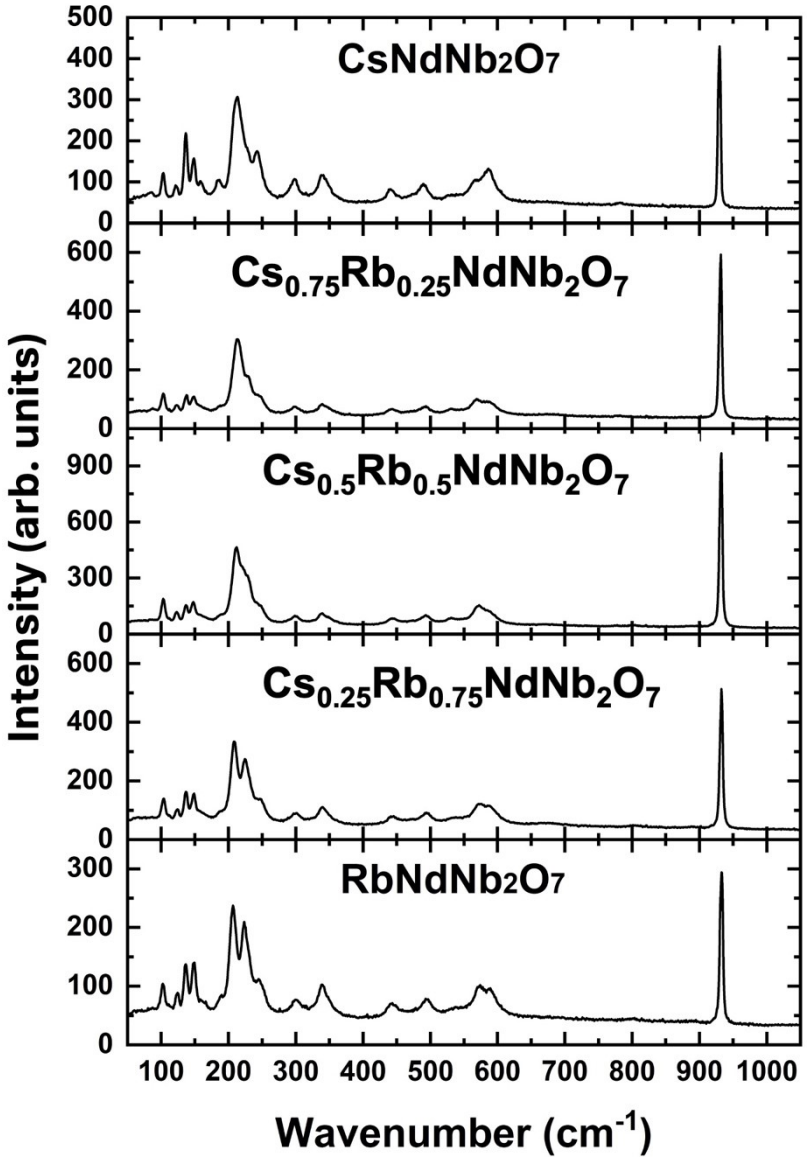

Figure S2. Raman spectra for $Cs_{1-x}Rb_xNdNb_2O_7$ (x = 0, 0.25, 0.5, 0.75, and 1) at room temperature.

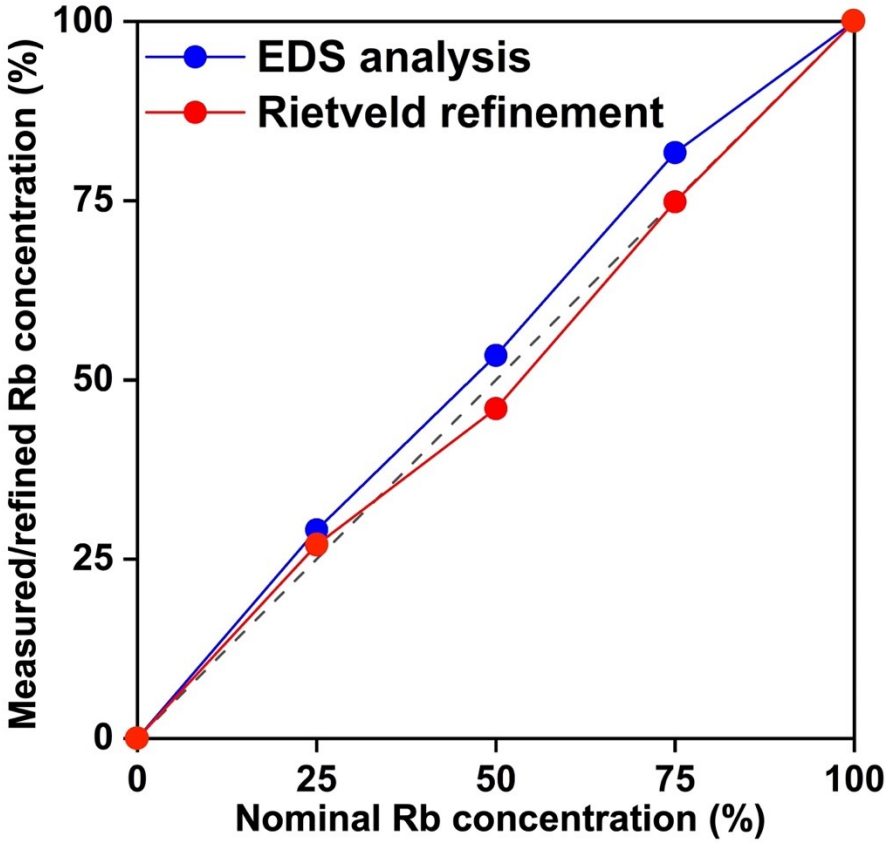

Figure S3. Rb concentration at the *A'* sites for $Cs_{1-x}Rb_xNdNb_2O_7$ (x = 0, 0.25, 0.5, 0.75, and 1) estimated by EDS analysis (blue circles) and refining the *A'*-site occupancy in Rietveld analysis (red circles). The black dashed line indicates nominal Rb concentration.

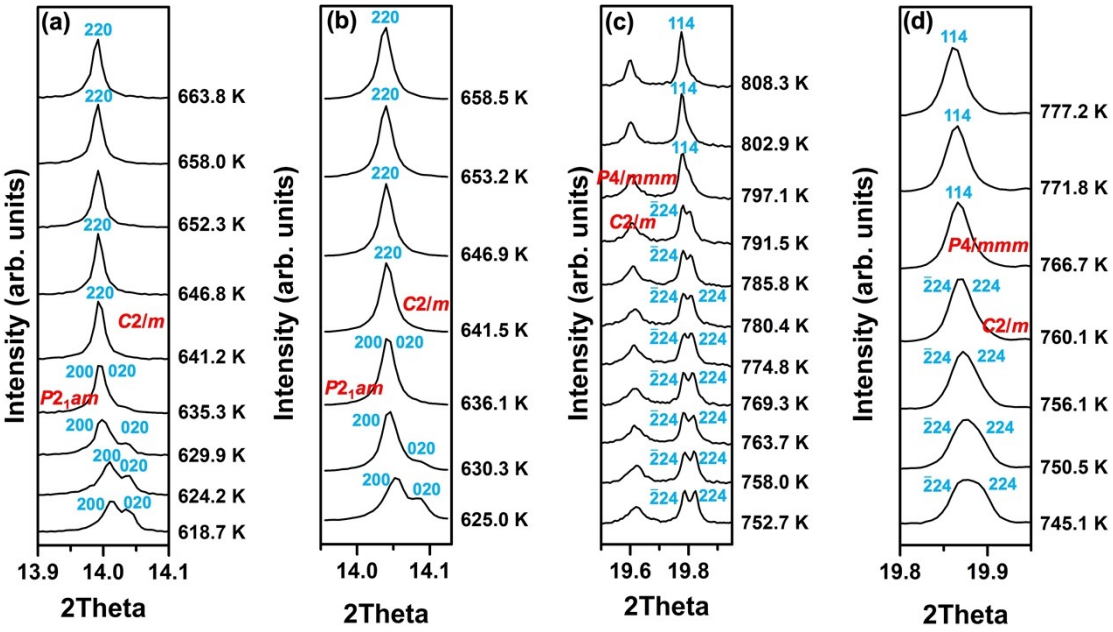

Figure S4. Variable-temperature SXRD patterns for the Cs-rich $Rb_{0.25}Cs_{0.75}NdNb_2O_7$ and $CsNdNb_2O_7$ samples. They reveal the polar-to-nonpolar phase transition $P2_1am$-to-$C2/m$ (a: $CsNdNb_2O_7$; b: $Cs_{0.75}$ $Rb_{0.25}NdNb_2O_7$) and paraelectric phase transition $C2/m$ to $P4/mmm$ (c: $CsNdNb_2O_7$; d: $Rb_{0.25}Cs_{0.75}NdNb_2O_7$).

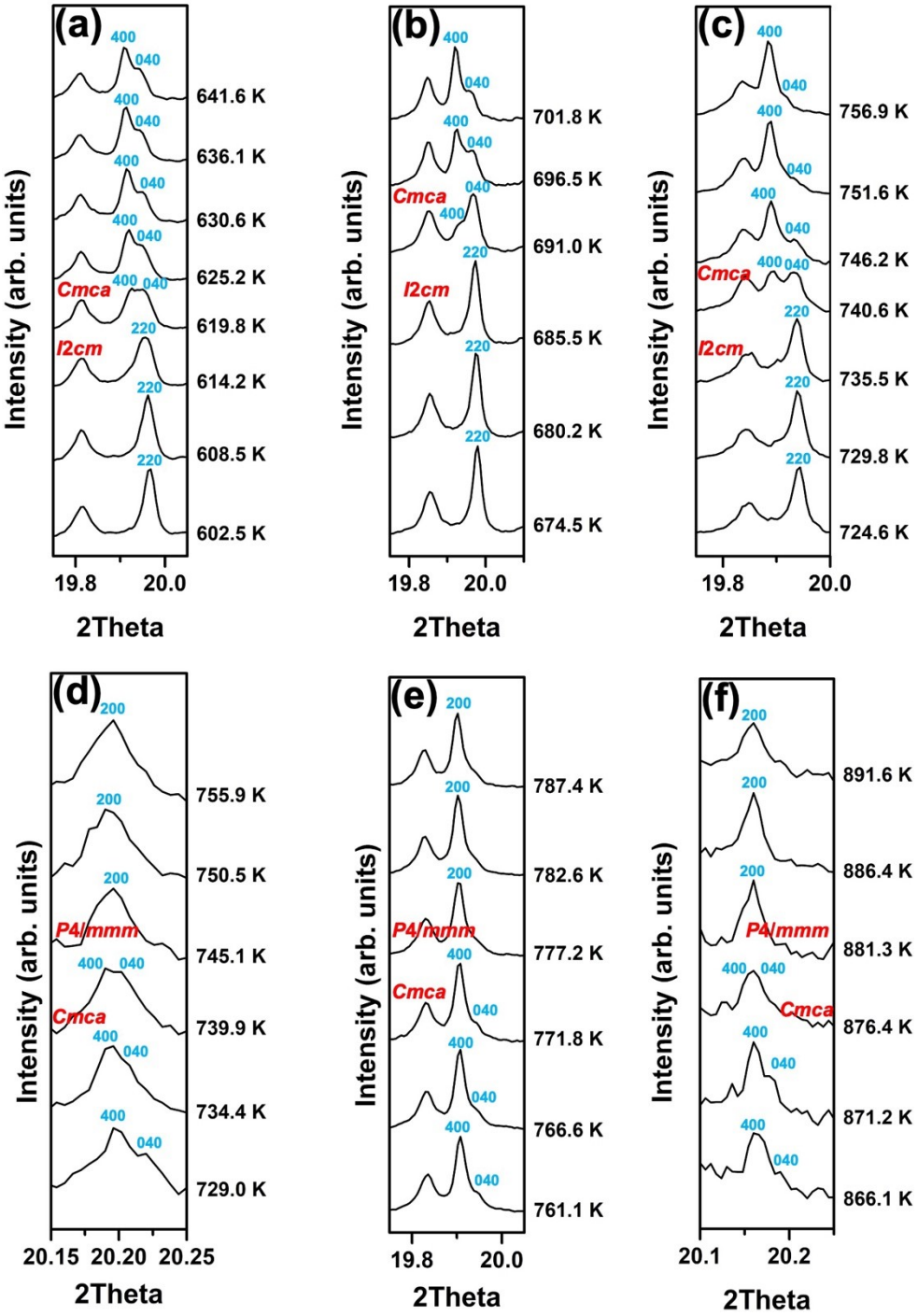

Figure S5. Variable-temperature SXRD patterns for the Rb-rich $Cs_{0.5}Rb_{0.5}NdNb_2O_7$, $Cs_{0.25}Rb_{0.75}NdNb_2O_7$ and $RbNdNb_2O_7$ samples. They reveal the polar-to-nonpolar phase transition *I*2*cm*-to-*Cmca* (a: $Cs_{0.5}Rb_{0.5}NdNb_2O_7$; b: $Cs_{0.25}Rb_{0.75}NdNb_2O_7$; c: $RbNdNb_2O_7$) and paraelectric phase transition *Cmca* to *P*4/*mmm* (d: $Cs_{0.5}Rb_{0.5}NdNb_2O_7$; e: $Cs_{0.25}Rb_{0.75}NdNb_2O_7$; f: $RbNdNb_2O_7$).

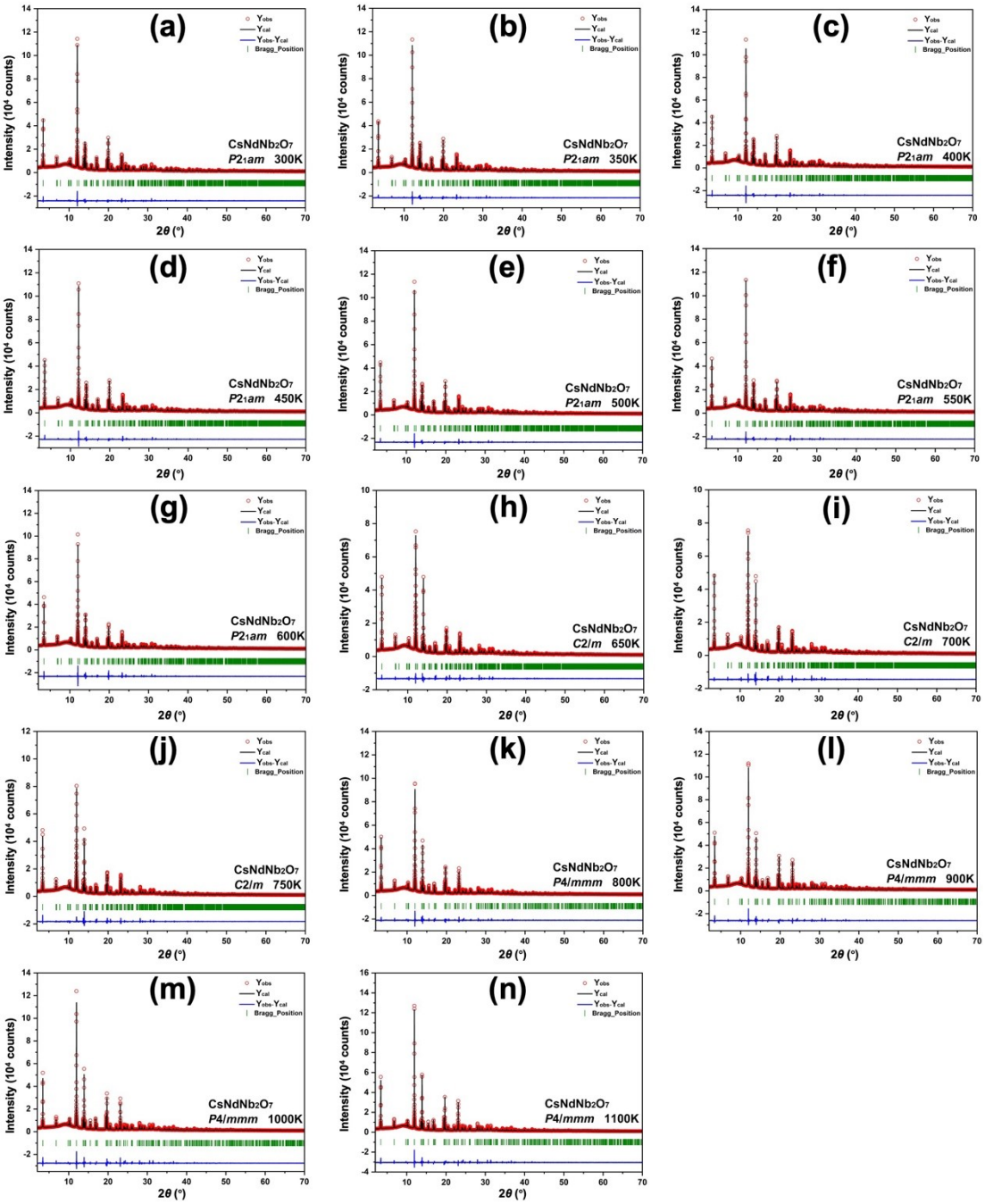

Figure S6. Rietveld refinements for temperature-dependent SXRD patterns for $CsNdNb_2O_7$ at (a) 300, (b) 350, (c) 400, (d) 450, (e) 500, (f) 550, (g) 600, (h) 650, (i) 700, (j) 750, (k) 800, (l) 900, (m) 1000, and (n) 1100 K, respectively.

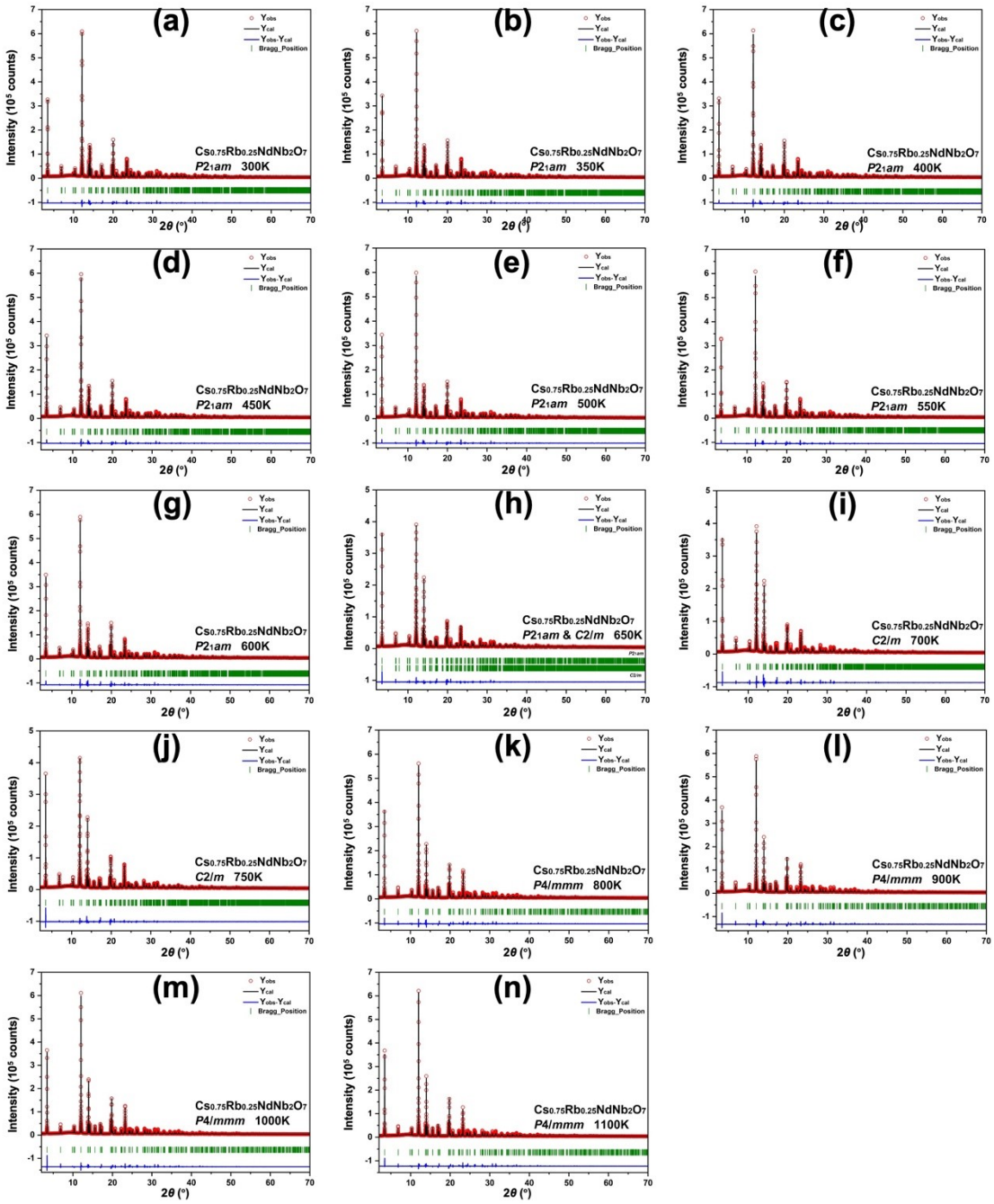

Figure S7. Rietveld refinements for temperature-dependent SXRD patterns for $Cs_{0.75}Rb_{0.25}NdNb_2O_7$ at (a) 300, (b) 350, (c) 400, (d) 450, (e) 500, (f) 550, (g) 600, (h) 650, (i) 700, (j) 750, (k) 800, (l) 900, (m) 1000, and (n) 1100 K, respectively.

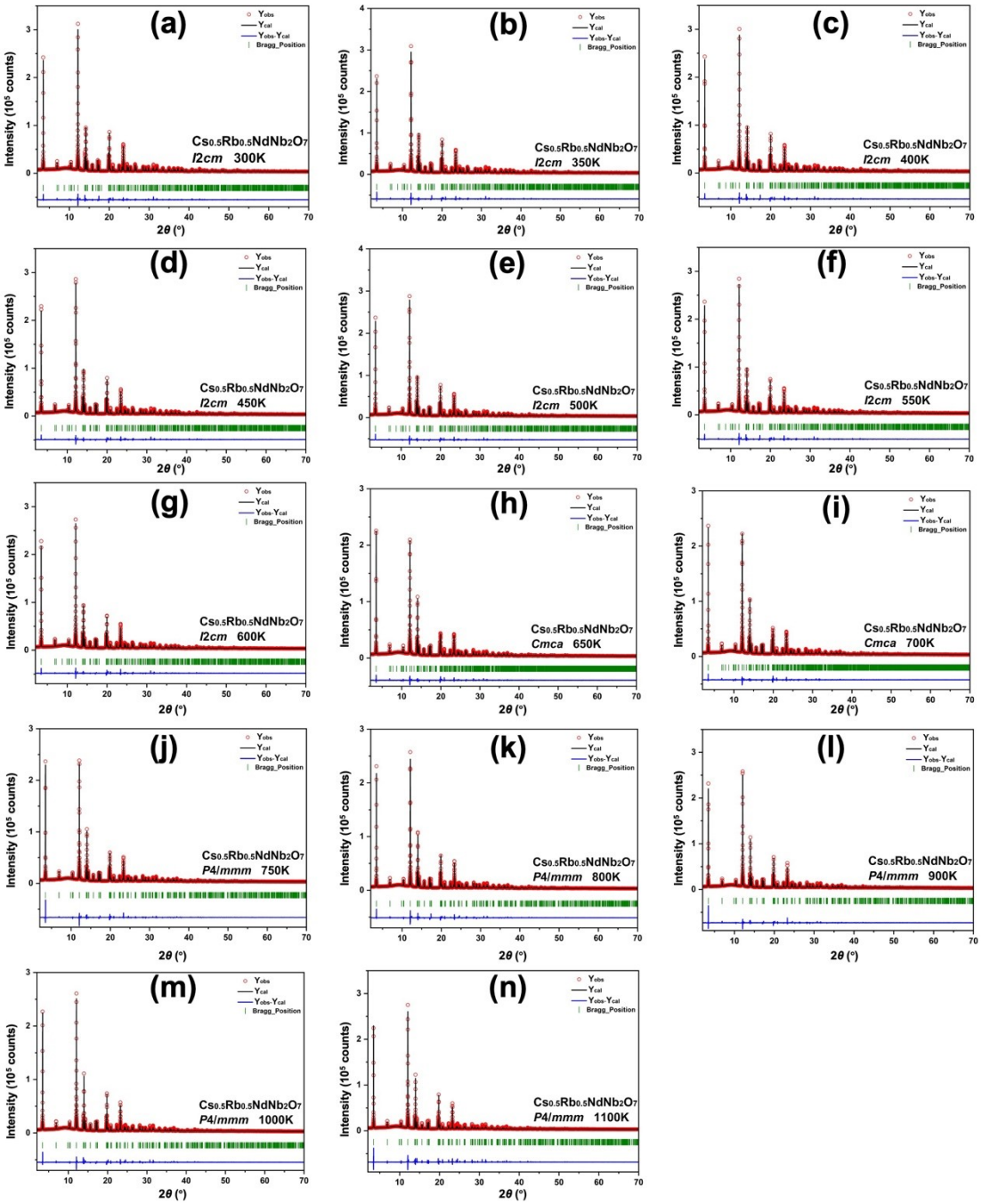

Figure S8. Rietveld refinements for temperature-dependent SXRD patterns for $Cs_{0.5}Rb_{0.5}NdNb_2O_7$ at (a) 300, (b) 350, (c) 400, (d) 450, (e) 500, (f) 550, (g) 600, (h) 650, (i) 700, (j) 750, (k) 800, (l) 900, (m) 1000, and (n) 1100 K, respectively.

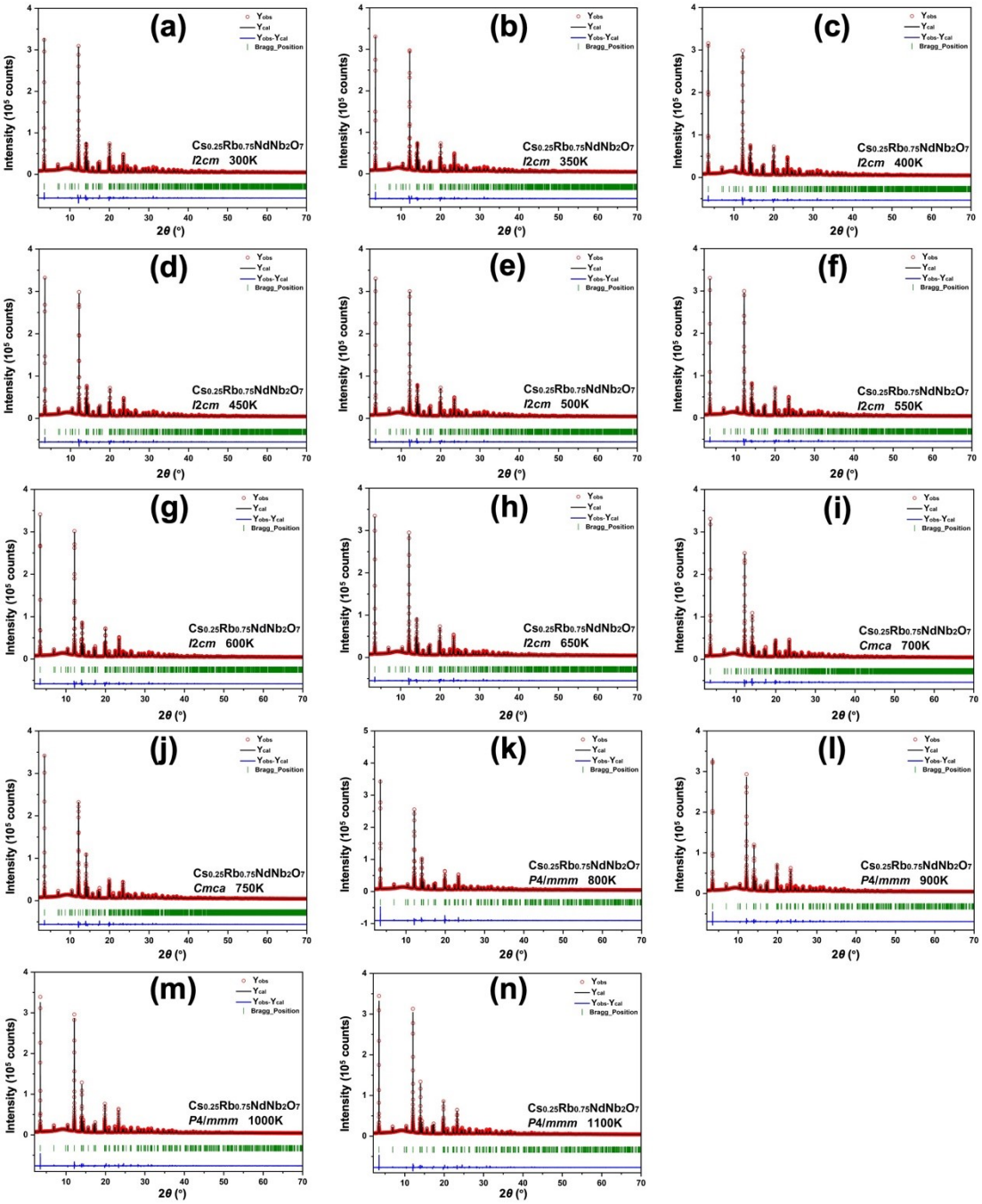

Figure S9. Rietveld refinements for temperature-dependent SXRD patterns for $Cs_{0.25}Rb_{0.75}NdNb_2O_7$ at (a) 300, (b) 350, (c) 400, (d) 450, (e) 500, (f) 550, (g) 600, (h) 650, (i) 700, (j) 750, (k) 800, (l) 900, (m) 1000, and (n) 1100 K, respectively.

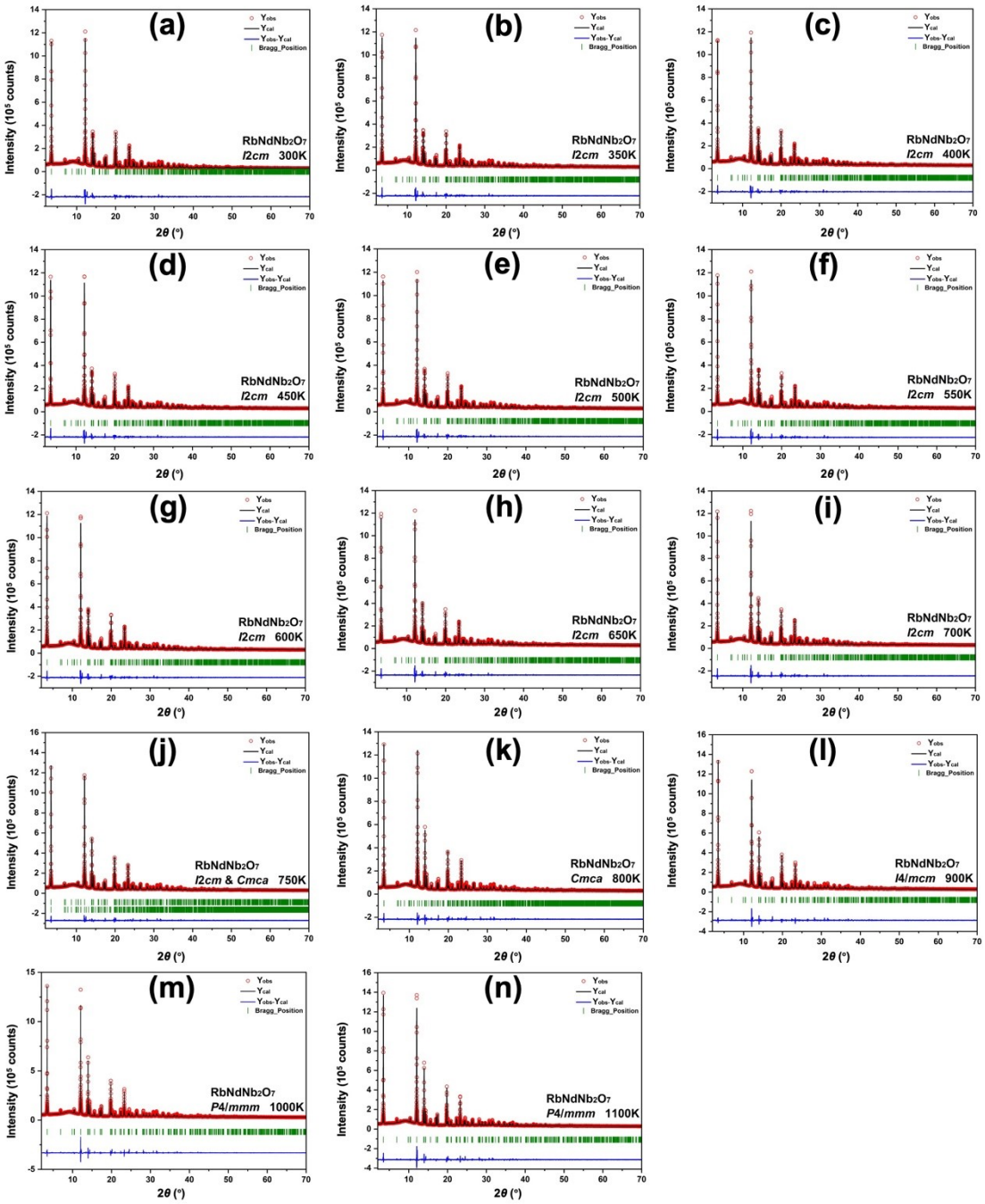

Figure S10. Rietveld refinements for temperature-dependent SXRD patterns for $RbNdNb_2O_7$ at (a) 300, (b) 350, (c) 400, (d) 450, (e) 500, (f) 550, (g) 600, (h) 650, (i) 700, (j) 750, (k) 800, (l) 900, (m) 1000, and (n) 1100 K, respectively.

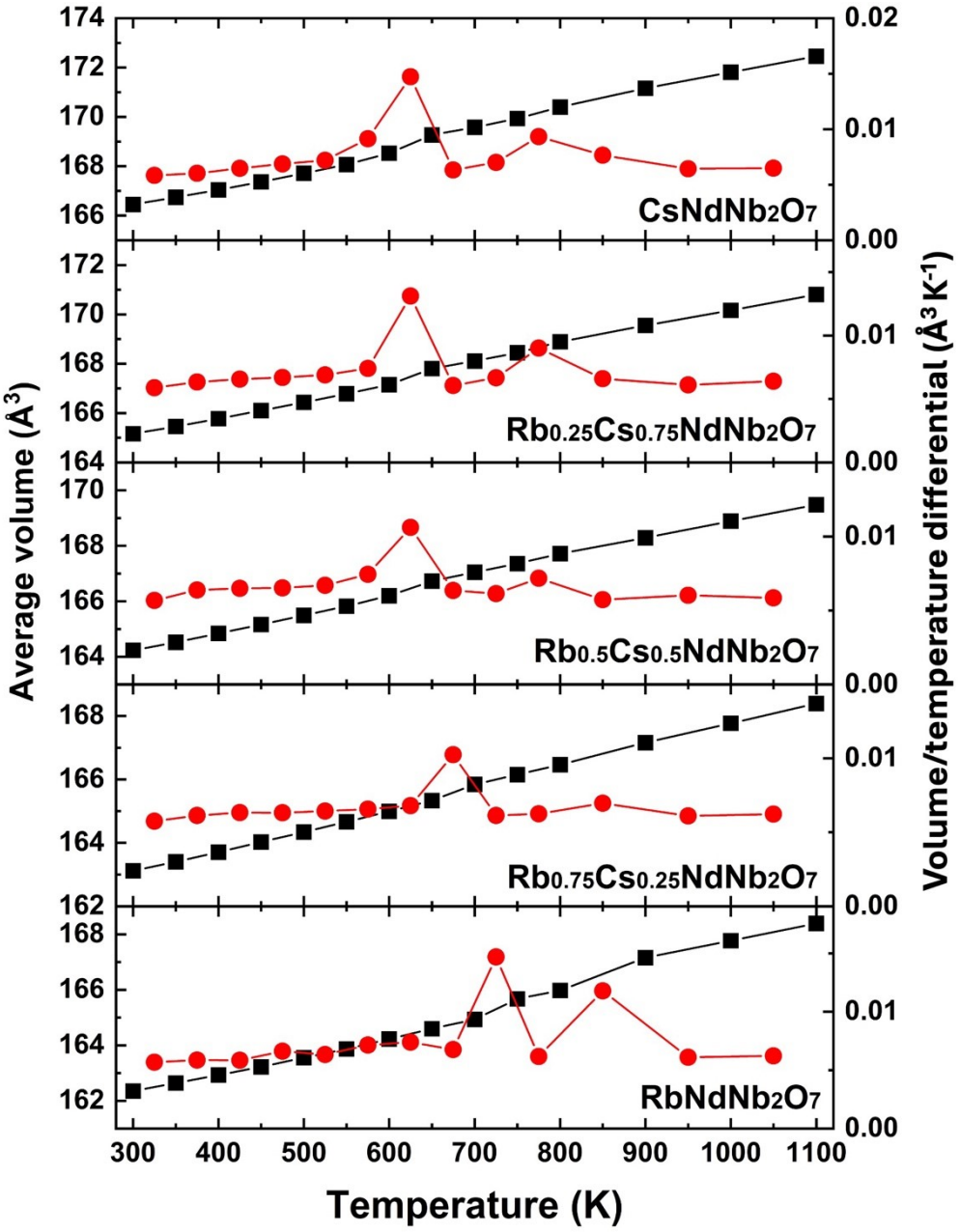

Figure S11. Average volume (black squares) and changes in volume over changes in temperature, $\frac{\Delta \bar{V}}{\Delta T}$ (red circles), as a function of temperature for $Cs_{1-x}Rb_xNdNb_2O_7$ (x = 0, 0.25, 0.5, 0.75, and 1).

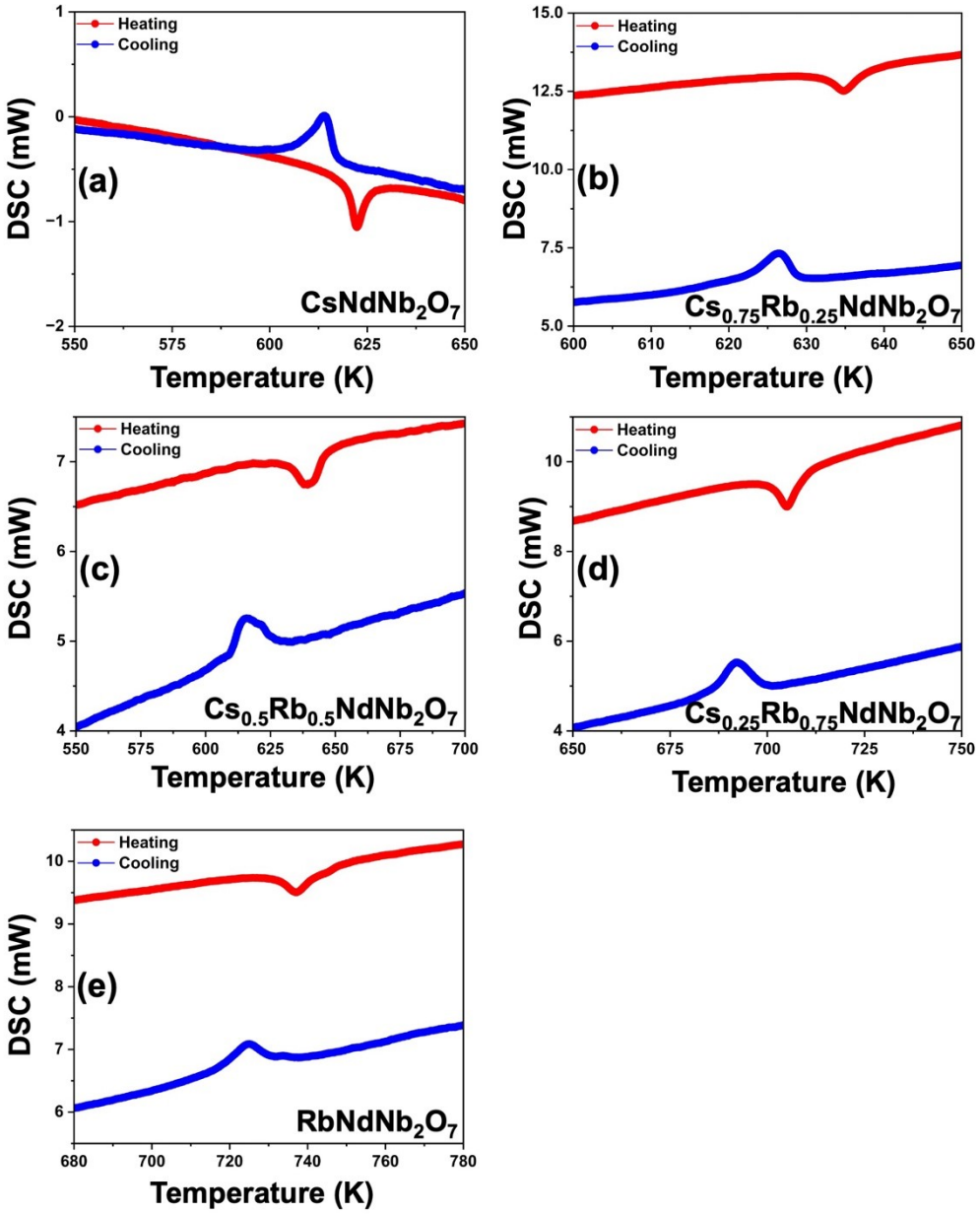

Figure S12. Enlarged view of DSC curves around endothermic and exothermic peaks on the heating and cooling processes for $Cs_{1-x}Rb_xNdNb_2O_7$ with (a) x = 0, (b) 0.25, (c) 0.5, (d) 0.75, and (e) 1.

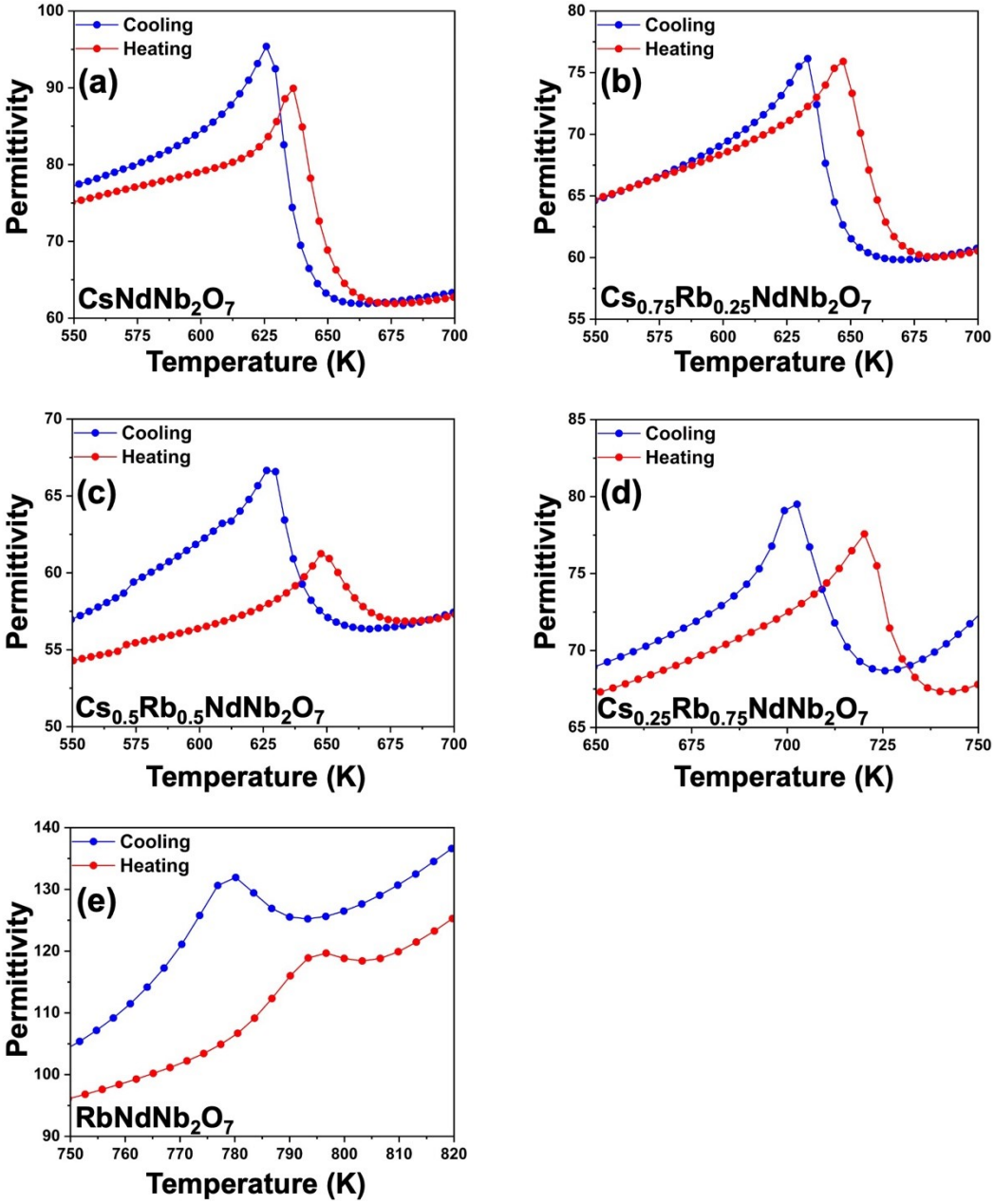

Figure S13. Enlarged view of temperature-dependent permittivity around polar-to-nonpolar phase transitions on the heating and cooling processes for $Cs_{1-x}Rb_xNdNb_2O_7$ with (a) x = 0, (b) 0.25, (c) 0.5, (d) 0.75, and (e) 1.

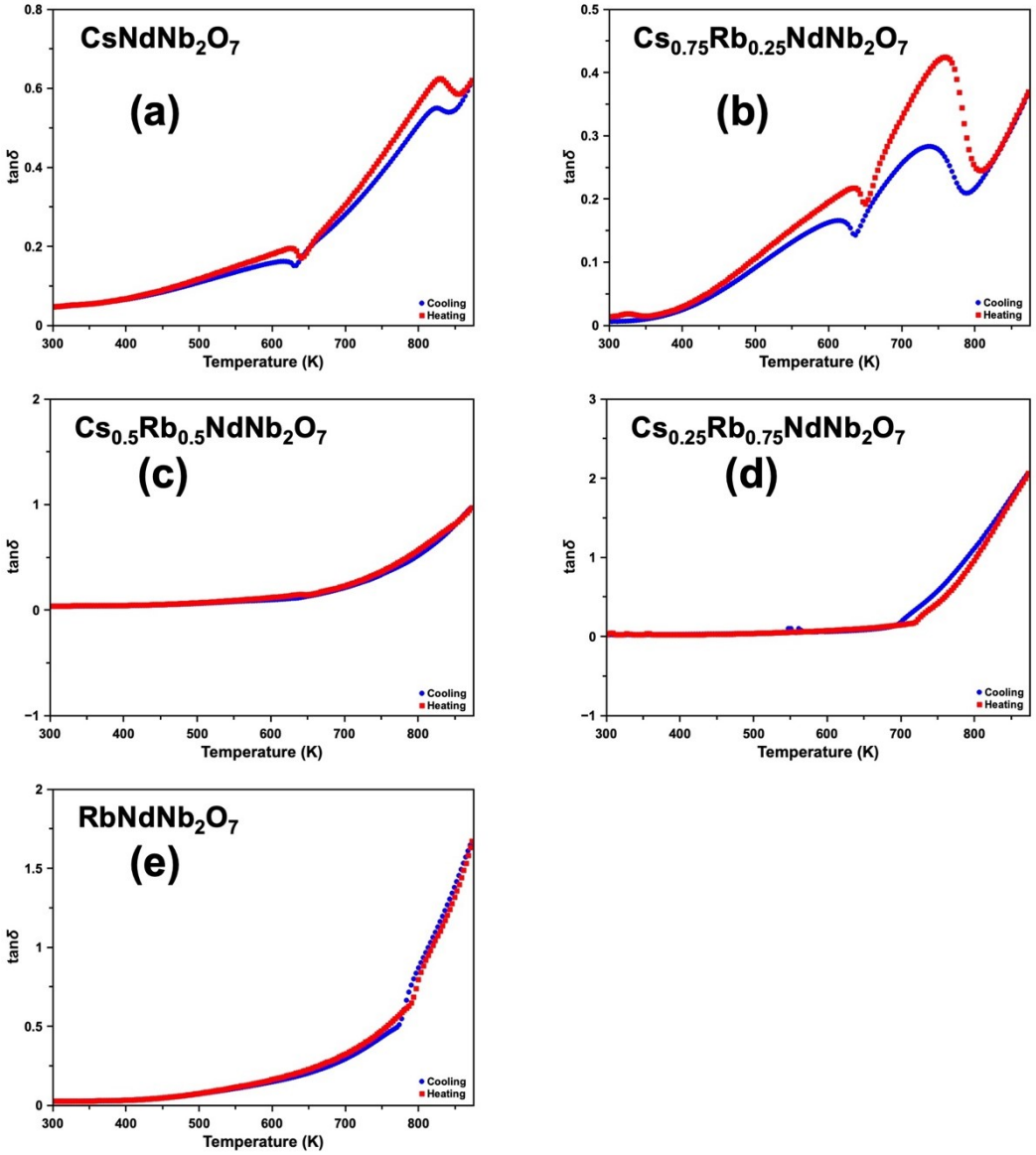

Figure S14. Dielectric loss curves on the heating and cooling processes for $Cs_{1-x}Rb_xNdNb_2O_7$ (x = 0, 0.25, 0.5, 0.75, and 1) in the high-temperature region.

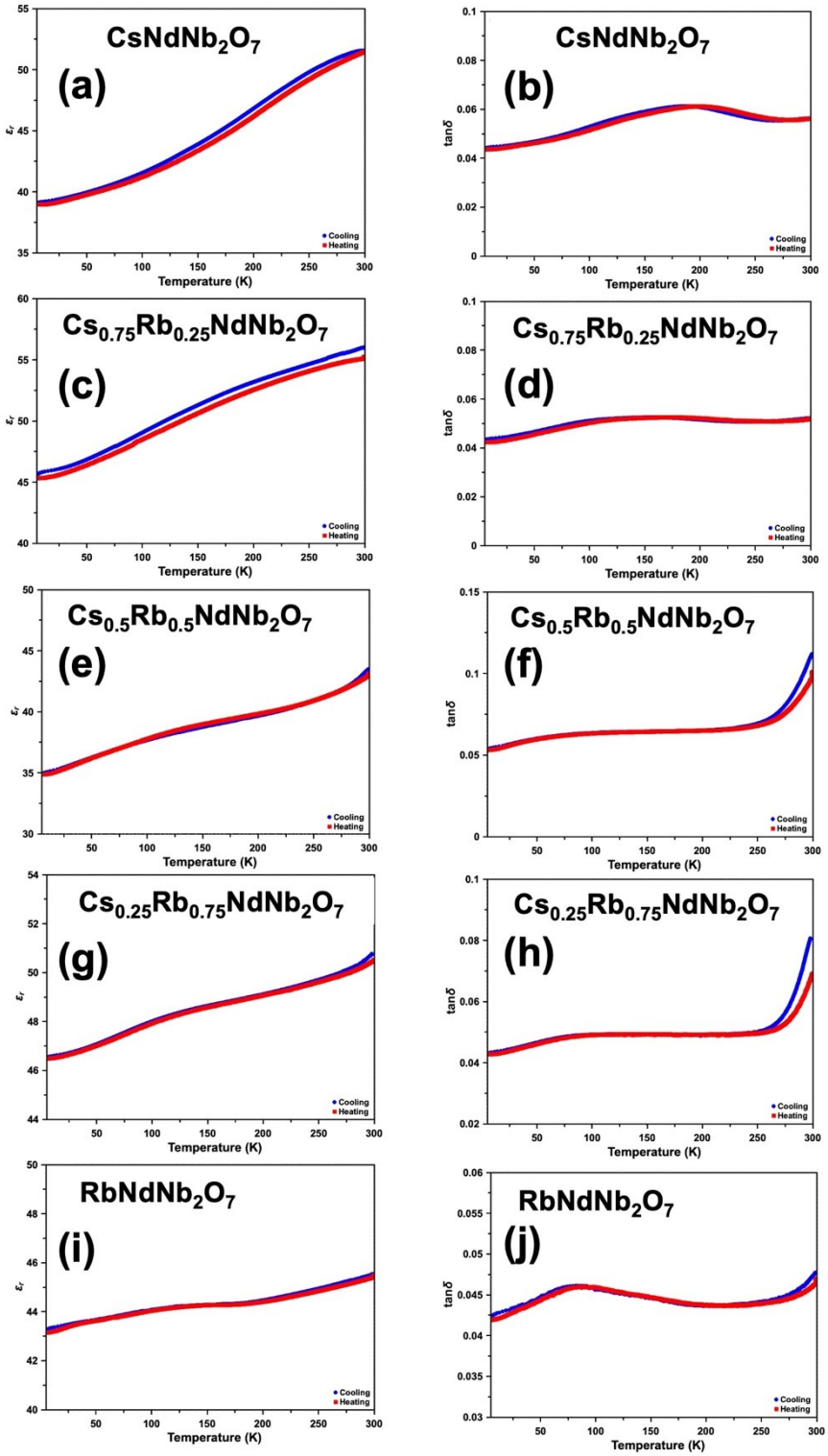

Figure S15. Permittivity and dielectric loss curves on the heating and cooling processes for $Cs_{1-x}Rb_xNdNb_2O_7$ (x = 0, 0.25, 0.5, 0.75, and 1) in the low-temperature region.

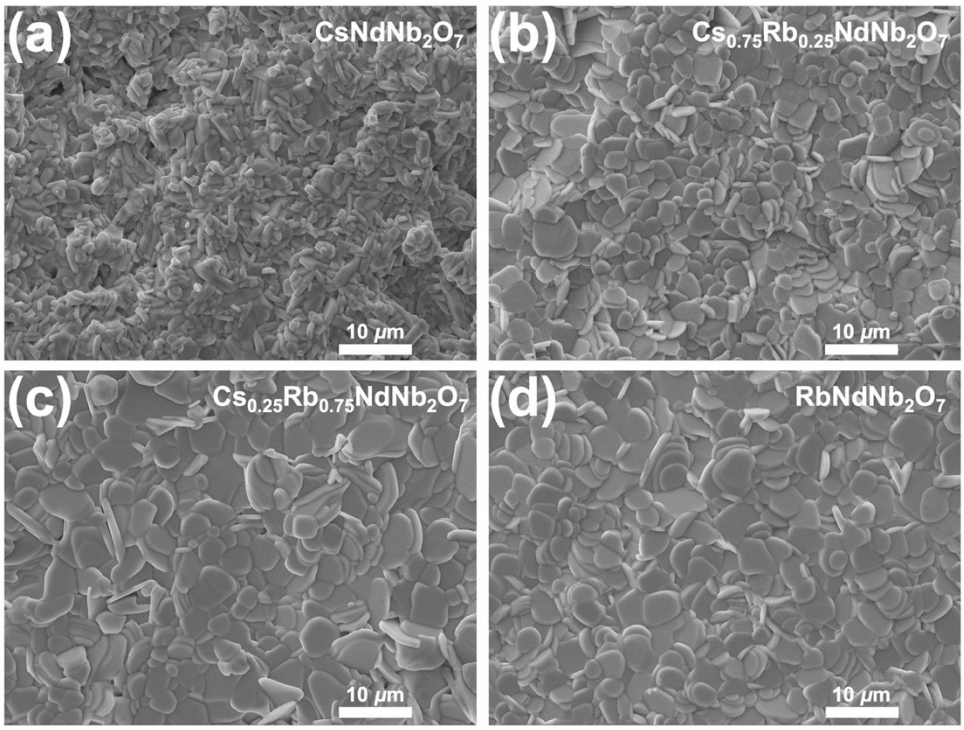

Figure S16. Plan-view SEM images for sintered (a) $CsNdNb_2O_7$, (b) $Cs_{0.75}Rb_{0.25}NdNb_2O_7$, (c) $Cs_{0.25}Rb_{0.75}NdNb_2O_7$, and (d) $RbNdNb_2O_7$ pellets.

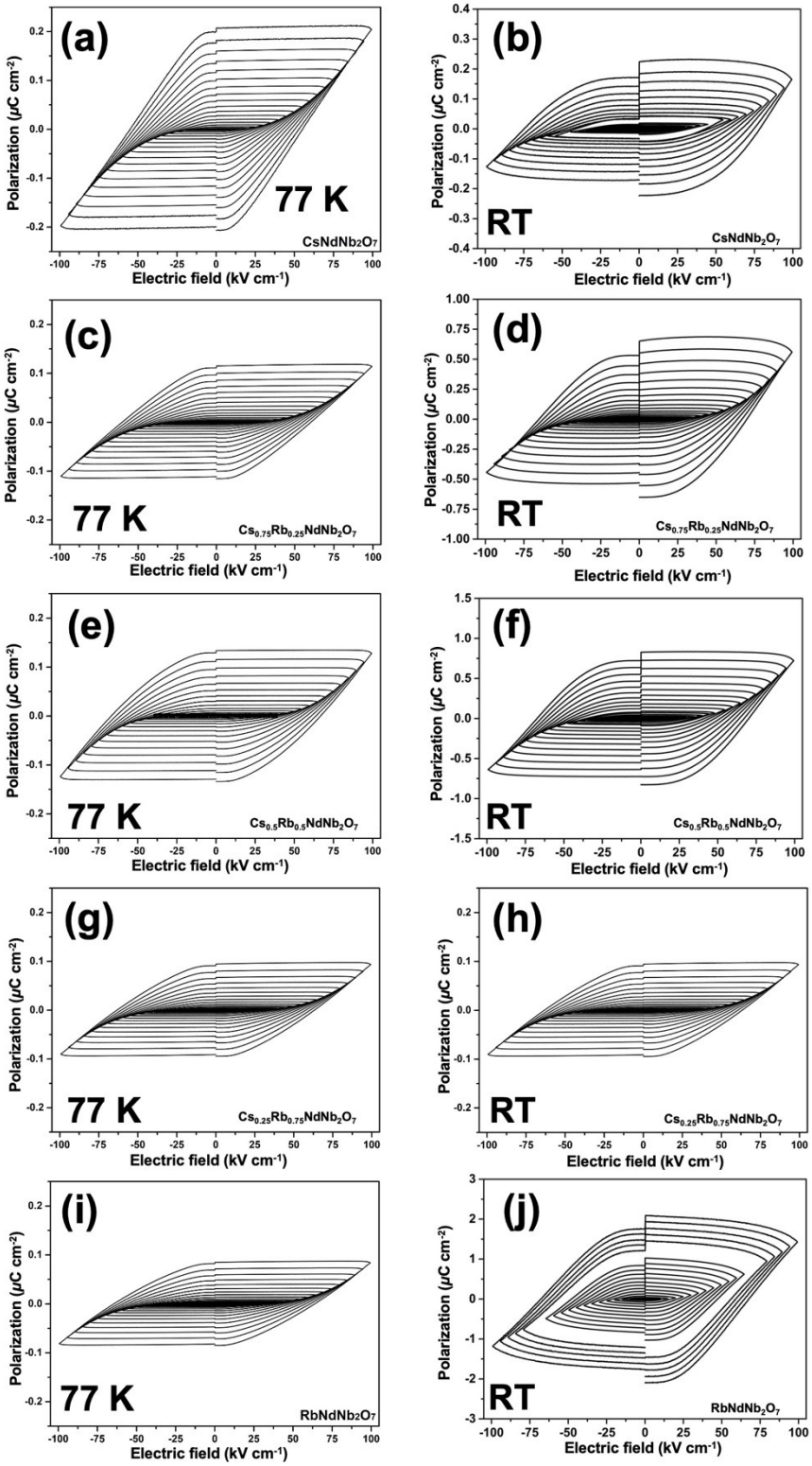

Figure S17. Remanent *P-E* hysteresis loops for $Cs_{1-x}Rb_xNdNb_2O_7$ (x = 0, 0.25, 0.5, 0.75, and 1) at 77 K and room temperature.

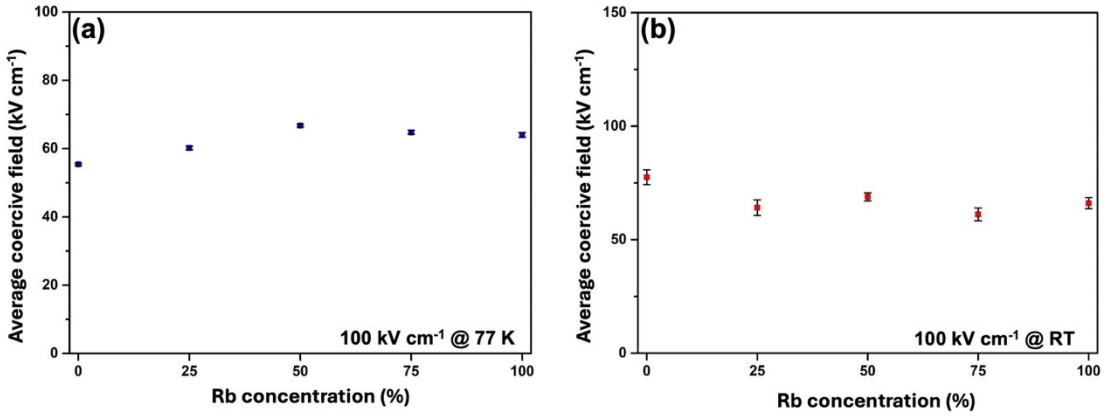

Figure S18. Average coercive fields for an electric-field amplitude of 100 kV/cm at (a) 77 K and (b) room temperature.

Table S1. Refined crystal structure parameters including Wyckoff positions, coordinates, and occupancies (g), and isotropic atomic displacement parameters (U_{iso}) for $CsNdNb_2O_7$ at 300 K.

Atom	Site	x	y	z	g	U_{iso} (Å^2)
Cs1	2*b*	0.75[a)]	0.7414(8)	0.5	1	0.02366
Nd1	2*a*	0.7634(8)	0.7462(8)	0	1	0.00770
Nb1	4*c*	0.2448(9)	0.7510(11)	0.20176(7)	1	0.00960
O1	4*c*	0.245(4)	0.7953(16)	0.6450(5)	1	0.00133
O2	4*c*	0.443(3)	0.445(3)	0.1830(7)	1	0.00936
O3	4*c*	0.040(3)	0.019(4)	0.1416(7)	1	0.00101
O4	2*a*	0.230(4)	0.6746(19)	0	1	0.00027

Space group: $P2_1am$ (No. 26), $Z = 2$ Cell parameters: a = 5.472144(13) Å, b = 5.449648(13) Å, and c = 11.16263(3) Å. R_{wp} = 12.5%, R_B = 2.72%, and χ^2 = 2.995.
[a)] Fixed to define the origin of the polar a axis.

Table S2. Refined crystal structure parameters including Wyckoff positions, coordinates, and occupancies (g), and isotropic atomic displacement parameters (U_{iso}) for $CsNdNb_2O_7$ at 700 K.

Atom	Site	x	y	z	g	U_{iso} (Å^2)
Cs1	4*i*	0.26037	0	0.48955	1	0.03756
Nd1	4*i*	0.25837	0	–0.0031(3)	1	0.01977
Nb1	8*j*	0.0034(4)	0.2459(5)	0.20004(9)	1	0.00994
O1	4*i*	0.489(4)	0	0.181(2)	1	0.00718
O2	4*i*	0.935(3)	0	0.1234(15)	1	0.00871
O3	8*j*	0.2290(18)	0.266(3)	0.8325(12)	1	0.00381
O4	8*j*	–0.009(2)	0.230(2)	0.3557(6)	1	0.01075
O5	4*g*	0	0.8086(15)	0	1	0.00293

Space group: $C2/m$ (No. 12), $Z = 4$. Cell parameters: a = 7.78768(3) Å, b =7.77081(3) Å, and c = 11.20908(6) Å, β = 90.2561(7)°. R_{wp} = 15.4%, R_B = 3.73%, and χ^2 = 4.031.

Table S3. Refined crystal structure parameters including Wyckoff positions, coordinates, and occupancies (g), and isotropic atomic displacement parameters (U_{iso}) for $CsNdNb_2O_7$ at 1100 K.

Atom	Site	x	y	z	g	U_{iso} (Å^2)
Cs1	1*b*	0	0	0.5	1	0.04560
Nd1	1*a*	0	0	0	1	0.02355
Nb1	2*h*	0.5	0.5	0.19935(10)	1	0.01042
O1	4*i*	0	0.5	0.1602(4)	1	0.01535
O2	2*h*	0.5	0.5	0.3578(6)	1	0.01879
O3	1*c*	0.5	0.5	0	1	0.02645

Space group: $P4/mmm$ (No. 123), $Z = 1$. Cell parameters: a = 3.909598(6) Å and c = 11.28291(4) Å. R_{wp} = 18.6%, R_B = 4.68%, and χ^2 = 6.462.

Table S4. Refined crystal structure parameters including Wyckoff positions, coordinates, and occupancies (g), and isotropic atomic displacement parameters (U_{iso}) for $Cs_{0.75}Rb_{0.25}NdNb_2O_7$ at 300 K.

Atom	Site	x	y	z	g	U_{iso} (Å^2)
Rb1	2*b*	0.75[a)]	0.7409(6)[b)]	0.5	0.25[c)]	0.02338
Cs1	2*b*	0.75[a)]	0.7409(6)[b)]	0.5	0.75[c)]	0.02338
Nd1	2*a*	0.7607(7)	0.7472(5)	0	1	0.00796
Nb1	4*c*	0.2413(7)	0.7502(8)	0.20286(5)	1	0.00908
O1	4*c*	0.240(3)	0.7977(13)	0.6424(4)	1	0.00278
O2	4*c*	0.4284(19)	0.4473(18)	0.1858(6)	1	0.01081
O3	4*c*	0.025(3)	0.028(2)	0.1455(5)	1	0.00246
O4	2*a*	0.221(3)	0.6822(16)	0	1	0.00172

Space group: $P2_1am$ (No. 26), Z = 2. Cell parameters: a = 5.462805(12) Å, b = 5.441063(12) Å, and c = 11.11335(2) Å. R_{wp} = 10.3%, R_B = 2.64%, and χ^2 = 17.20.

[a)] Fixed to define the origin of the polar a axis.

[b)] Constrained to be the same for Rb and Cs.

[c)] Fixed to the nominal values.

Table S5. Refined crystal structure parameters including Wyckoff positions, coordinates, and occupancies (g), and isotropic atomic displacement parameters (U_{iso}) for $Cs_{0.75}Rb_{0.25}NdNb_2O_7$ at 700 K.

Atom	Site	x	y	z	g	U_{iso} (Å^2)
Rb1	4*i*	0.2638(5)[b)]	0	0.4897(3)[b)]	0.25[c)]	0.08508
Cs1	4*i*	0.2638(5)[b)]	0	0.4897(3)[b)]	0.75[c)]	0.02125
Nd1	4*i*	0.2586(4)	0	0.0001(2)	1	0.01792
Nb1	8*j*	0.0043(3)	0.2484(4)	0.20077(8)	1	0.01017
O1	4*i*	0.537(3)	0	0.1796(16)	1	0.00623
O2	4*i*	0.934(2)	0	0.1285(13)	1	0.00777
O3	8*j*	0.2420(16)	0.2703(19)	0.8362(9)	1	0.00286
O4	8*j*	0.0093(16)	0.2285(17)	0.3551(5)	1	0.00981
O5	4*g*	0	0.7965(14)	0	1	0.00199

Space group: $C2/m$ (No. 12), Z = 4. Cell parameters: a = 7.77168(3) Å, b =7.75818(3) Å, and c = 11.15279(5) Å, β = 90.3121(6)°. R_{wp} = 14.1%, R_B = 3.48%, and χ^2 = 25.7.

[b)] Constrained to be the same for Rb and Cs.

[c)] Fixed to the nominal values.

Table S6. Refined crystal structure parameters including Wyckoff positions, coordinates, and occupancies (g), and isotropic atomic displacement parameters (U_{iso}) for $Cs_{0.75}Rb_{0.25}NdNb_2O_7$ at 1100 K.

Atom	Site	x	y	z	g	U_{iso} (Å^2)
Rb1	1*b*	0	0	0.5	0.25[c)]	0.02060
Cs1	1*b*	0	0	0.5	0.75[c)]	0.05714
Nd1	1*a*	0	0	0	1	0.01785

Nb1	2*h*	0.5	0.5	0.20043(8)	1	0.01951
O1	4*i*	0	0.5	0.1627(3)	1	0.02547
O2	2*h*	0.5	0.5	0.3534(5)	1	0.02891
O3	1*c*	0.5	0.5	0	1	0.02391

Space group: *P*4/*mmm* (No. 123), $Z = 1$. Cell parameters: $a = 3.902543(6)$ Å and $c = 11.21508(3)$ Å. $R_{wp} = 15.0\%$, $R_B = 4.56\%$, and $\chi^2 = 27.26$.

[c] Fixed to the nominal values.

Table S7. Refined crystal structure parameters including Wyckoff positions, coordinates, and occupancies (*g*), and isotropic atomic displacement parameters (U_{iso}) for $Cs_{0.5}Rb_{0.5}NdNb_2O_7$ at 300 K.

Atom	Site	*x*	*y*	*z*	*g*	U_{iso} (Å^2)
Rb1	4*a*	0.75[a]	0	0	0.5[c]	0.02683
Cs1	4*a*	0.75[a]	0	0	0.5[c]	0.02634
Nd1	4*b*	0.24742	0.5005(11)	0.25	1	0.00952
Nb1	8*c*	0.76072	0.5005(18)	0.64793(3)	1	0.00772
O1	8*c*	0.776(4)	0.524(4)	0.4308(2)	1	0.00543
O2	8*c*	0.594(4)	0.818(4)	0.6597(4)	1	0.00943
O3	8*c*	1.019(4)	0.238(4)	0.6734(4)	1	0.01163
O4	4*b*	0.321(4)	0.028(8)	0.25	1	0.00603

Space group: *I*2*cm* (No. 46), $Z = 4$. Cell parameters: $a = 5.44876(5)$ Å, $b = 5.44536(6)$ Å, and $c = 22.14150(6)$ Å. $R_{wp} = 12.2\%$, $R_B = 2.82\%$, and $\chi^2 = 10.67$.

[a] Fixed to define the origin of the polar *a* axis.

[c] Fixed to the nominal values.

Table S8. Refined crystal structure parameters including Wyckoff positions, coordinates, and occupancies (*g*), and isotropic atomic displacement parameters (U_{iso}) for $Cs_{0.5}Rb_{0.5}NdNb_2O_7$ at 700 K.

Atom	Site	*x*	*y*	*z*	*g*	U_{iso} (Å^2)
Rb1	8*f*	0	0.2654(5)[b]	0.25778(9)[b]	0.5[c]	0.02923
Cs1	8*f*	0	0.2654(5)[b]	0.25778(9)[b]	0.5[c]	0.02965
Nd1	8*f*	0	0.2529(5)	0.99985(8)	1	0.01627
Nb1	16*g*	0.7502(6)	0.9998(5)	0.10115(3)	1	0.01530
O1	8*f*	0	0.509(4)	0.5910(8)	1	0.00437
O2	8*f*	0	0.409(2)	0.0751(8)	1	0.00944
O3	16*g*	0.2279(17)	0.258(3)	0.9200(5)	1	0.00973
O4	16*g*	0.768(2)	0.013(2)	0.17738(20)	1	0.00637
O5	8*d*	0.7986(13)	0	0	1	0.00464

Space group: *Cmca* (No. 64), $Z = 8$. Cell parameters: $a = 7.76339(2)$ Å, $b = 7.75272(3)$ Å, and $c = 22.20381(5)$ Å. $R_{wp} = 11.8\%$, $R_B = 3.43\%$, and $\chi^2 = 7.857$.

[b] Constrained to be the same for Rb and Cs.

[c] Fixed to the nominal values.

Table S9. Refined crystal structure parameters including Wyckoff positions,

coordinates, and occupancies (g), and isotropic atomic displacement parameters (U_{iso}) for $Cs_{0.5}Rb_{0.5}NdNb_2O_7$ at 1100 K.

Atom	Site	x	y	z	g	U_{iso} (Å^2)
Rb1	1*b*	0	0	0.5	0.5[c)]	0.04827
Cs1	1*b*	0	0	0.5	0.5[c)]	0.04159
Nd1	1*a*	0	0	0	1	0.01800
Nb1	2*h*	0.5	0.5	0.20105(11)	1	0.01311
O1	4*i*	0	0.5	0.1651(4)	1	0.01373
O2	2*h*	0.5	0.5	0.3669(7)	1	0.01717
O3	1*c*	0.5	0.5	0	1	0.01217

Space group: *P*4/*mmm* (No. 123), $Z = 1$. Cell parameters: $a = 3.897479(7)$ Å and $c = 11.15695(5)$ Å. $R_{wp} = 19.0\%$, $R_B = 4.57\%$, and $\chi^2 = 20.21$.

[c)] Fixed to the nominal values.

Table S10. Refined crystal structure parameters including Wyckoff positions, coordinates, and occupancies (g), and isotropic atomic displacement parameters (U_{iso}) for $Cs_{0.25}Rb_{0.75}NdNb_2O_7$ at 300 K.

Atom	Site	x	y	z	g	U_{iso} (Å^2)
Rb1	4*a*	0.75[a)]	0	0	0.75[c)]	0.02528
Cs1	4*a*	0.75[a)]	0	0	0.25[c)]	0.03089
Nd1	4*b*	0.23903	0.50026	0.25	1	0.00893
Nb1	8*c*	0.76105	0.50026	0.64729	1	0.00791
O1	8*c*	0.76442	0.54047	0.42948	1	0.00265
O2	8*c*	0.57958	0.79601	0.65647	1	0.00665
O3	8*c*	0.97984	0.22020	0.67405	1	0.00885
O4	4*b*	0.28953	0.06254	0.25	1	0.00355

Space group: *I*2*cm* (No. 46), $Z = 4$. Cell parameters: $a = 5.446584(17)$ Å, $b = 5.434810(17)$ Å, and $c = 22.04192(5)$ Å. $R_{wp} = 12.2\%$, $R_B = 3.18\%$, and $\chi^2 = 6.506$.

[a)] Fixed to define the origin of the polar a axis.

[c)] Fixed to the nominal values.

Table S11. Refined crystal structure parameters including Wyckoff positions, coordinates, and occupancies (g), and isotropic atomic displacement parameters (U_{iso}) for $Cs_{0.25}Rb_{0.75}NdNb_2O_7$ at 750 K.

Atom	Site	x	y	z	g	U_{iso} (Å^2)
Rb1	8*f*	0	0.2436(11)[b)]	0.25688(12)[b)]	0.75[c)]	0.04876
Cs1	8*f*	0	0.2436(11)[b)]	0.25688(12)[b)]	0.25[c)]	0.04918
Nd1	8*f*	0	0.2524(7)	0.99980(10)	1	0.02470
Nb1	16*g*	0.7508(6)	1.0004(11)	0.10188(3)	1	0.01718
O1	8*f*	0	0.500(4)	0.5911(10)	1	0.00774
O2	8*f*	0	0.441(2)	0.0638(6)	1	0.01281

O3	16*g*	0.2177(14)	0.250(6)	0.9118(6)	1	0.01310
O4	16*g*	0.748(3)	0.0270(15)	0.17796(19)	1	0.00974
O5	8*d*	0.8033(13)	0	0	1	0.00801

Space group: *Cmca* (No. 64), $Z = 8$. Cell parameters: $a = 7.75837(2)$ Å, $b = 7.74447(2)$ Å, and $c = 22.12228(5)$ Å. $R_{wp} = 11.5\%$, $R_B = 3.46\%$, and $\chi^2 = 7.56$.

[b)] Constrained to be the same for Rb and Cs.

[c)] Fixed to the nominal values.

Table S12. Refined crystal structure parameters including Wyckoff positions, coordinates, and occupancies (g), and isotropic atomic displacement parameters (U_{iso}) for $Cs_{0.25}Rb_{0.75}NdNb_2O_7$ at 1100 K.

Atom	Site	*x*	*y*	*z*	*g*	U_{iso} (Å^2)
Rb1	1*b*	0	0	0.5	0.75[c)]	0.05489
Cs1	1*b*	0	0	0.5	0.25[c)]	0.04951
Nd1	1*a*	0	0	0	1	0.01921
Nb1	2*h*	0.5	0.5	0.20248(7)	1	0.02114
O1	4*i*	0	0.5	0.1624(3)	1	0.02412
O2	2*h*	0.5	0.5	0.3566(4)	1	0.02680
O3	1*c*	0.5	0.5	0	1	0.02256

Space group: *P*4/*mmm* (No. 123), $Z = 1$. Cell parameters: $a = 3.893111(5)$ Å and $c = 11.11039(2)$ Å. $R_{wp} = 13.0\%$, $R_B = 3.91\%$, and $\chi^2 = 9.697$.

[c)] Fixed to the nominal values.

Table S13. Refined crystal structure parameters including Wyckoff positions, coordinates, and occupancies (g), and isotropic atomic displacement parameters (U_{iso}) for $RbNdNb_2O_7$ at 300 K.

Atom	Site	*x*	*y*	*z*	*g*	U_{iso} (Å^2)
Rb1	4*a*	0.75[a)]	0	0	1	0.02743
Nd1	4*b*	0.241(2)	0.5000(16)	0.25	1	0.01914
Nb1	8*c*	0.757(2)	0.5016(19)	0.64668(5)	1	0.01723
O1	8*c*	0.766(7)	0.546(4)	0.4333(3)	1	0.00683
O2	8*c*	0.56(5)	0.817(4)	0.6537(5)	1	0.01083
O3	8*c*	0.977(8)	0.238(8)	0.6740(5)	1	0.01303
O4	4*b*	0.274(10)	0.055(5)	0.25	1	0.00773

Space group: *I*2*cm* (No. 46), $Z = 4$. Cell parameters: 5.44297(3) Å, $b = 5.43085(3)$ Å, and $c = 21.9665(8)$ Å. $R_{wp} = 15.1\%$, $R_B = 3.48\%$, and $\chi^2 = 6.32$.

[a)] Fixed to define the origin of the polar *a* axis.

Table S14. Refined crystal structure parameters including Wyckoff positions, coordinates, and occupancies (g), and isotropic atomic displacement parameters (U_{iso}) for $RbNdNb_2O_7$ at 800 K.

Atom	Site	*x*	*y*	*z*	*g*	U_{iso} (Å^2)
Rb1	8*f*	0	0.2221(6)	0.25761(17)	1	0.03489

Nd1	8*f*	0	0.2526(7)	1.00020(14)	1	0.02364
Nb1	16*g*	0.7513(7)	0.9975(5)	0.10265(4)	1	0.01508
O1	8*f*	0	0.473(4)	0.5635(8)	1	0.01063
O2	8*f*	0	0.474(4)	0.0910(14)	1	0.00304
O3	16*g*	0.224(2)	0.256(3)	0.9074(7)	1	0.00333
O4	16*g*	0.754(4)	–0.0308(18)	0.1782(3)	1	0.00346
O5	8*d*	0.8174(16)	0	0	1	0.00321

Space group: *Cmca* (No. 64), $Z = 8$. Cell parameters: $a = 7.75817(2)$ Å, $b = 7.75722(3)$ Å, and $c = 22.06393$ (8) Å. $R_{wp} = 14.4\%$, $R_B = 4.10\%$, and $\chi^2 = 5.20$.

Table S15. Refined crystal structure parameters including Wyckoff positions, coordinates, and occupancies (*g*), and isotropic atomic displacement parameters (U_{iso}) for $RbNdNb_2O_7$ at 1100 K.

Atom	Site	*x*	*y*	*z*	*g*	U_{iso} (Å^2)
Rb1	1*b*	0	0	0.5	1	0.05815
Nd1	1*a*	0	0	0	1	0.01946
Nb1	2*h*	0.5	0.5	0.20395(10)	1	0.01381
O1	4*i*	0	0.5	0.1658(4)	1	0.02949
O2	2*h*	0.5	0.5	0.3546(7)	1	0.03216
O3	1*c*	0.5	0.5	0	1	0.02793

Space group: *P*4/*mmm* (No. 123), $Z = 1$. Cell parameters: $a = 3.891510(7)$ Å and $c = 11.08495(5)$ Å. $R_{wp} = 17.5\%$, $R_B = 4.08\%$, and $\chi^2 = 8.769$.

Table S16. Bond valence sum (BVS) calculated for the refined room-temperature structures of $CsNdNb_2O_7$ and $RbNdNb_2O_7$.

$CsNdNb_2O_7$	$P2_1am$	$C2/m$	$P4/mmm$
Atom	BVS	BVS	BVS
Cs	1.1	1.0	1.0
Nd	3.1	3.2	2.4
Nb	5.0	4.8	4.9
$RbNdNb_2O_7$	$I2cm$	$Cmca$	$P4/mmm$
Atom	BVS	BVS	BVS
Rb	0.9	0.7	0.7
Nd	2.6	2.5	2.4
Nb	5.1	5.3	5.5

Table S17. Curie temperatures (T_C's) for $Cs_{1-x}Rb_xNdNb_2O_7$ (x = 0, 0.25, 0.5, 0.75, and 1) determined by DSC, optical SHG, and permittivity.

DSC	
Compound	T_C (K)
$CsNdNb_2O_7$	618.2
$Cs_{0.75}Rb_{0.25}NdNb_2O_7$	630.6
$Cs_{0.5}Rb_{0.5}NdNb_2O_7$	626.9
$Cs_{0.25}Rb_{0.75}NdNb_2O_7$	698.7
$RbNdNb_2O_7$	731.1
SHG	
Compound	T_C (K)
$CsNdNb_2O_7$	621.8
$Cs_{0.75}Rb_{0.25}NdNb_2O_7$	632.5
$Cs_{0.5}Rb_{0.5}NdNb_2O_7$	640.3
$Cs_{0.25}Rb_{0.75}NdNb_2O_7$	712.5
$RbNdNb_2O_7$	765.0
Permittivity	
Compound	T_C (K)
$CsNdNb_2O_7$	631.1
$Cs_{0.75}Rb_{0.25}NdNb_2O_7$	640.2
$Cs_{0.5}Rb_{0.5}NdNb_2O_7$	637.0
$Cs_{0.25}Rb_{0.75}NdNb_2O_7$	711.3
$RbNdNb_2O_7$	788.4