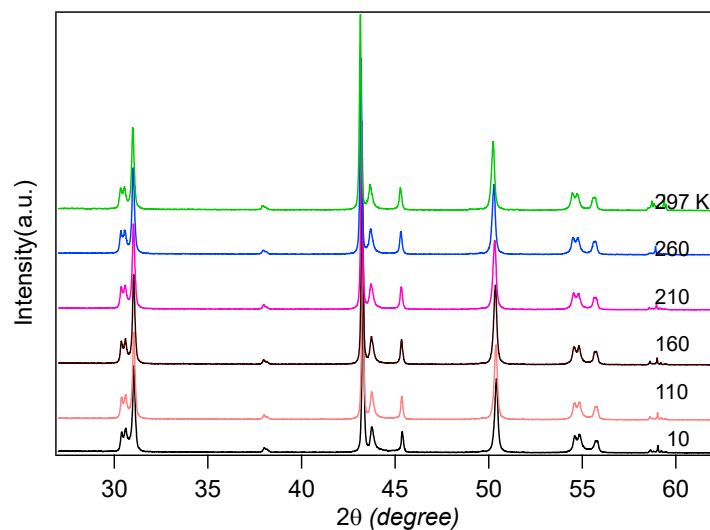


Supplemental materials figures and tables

(a)



(b)

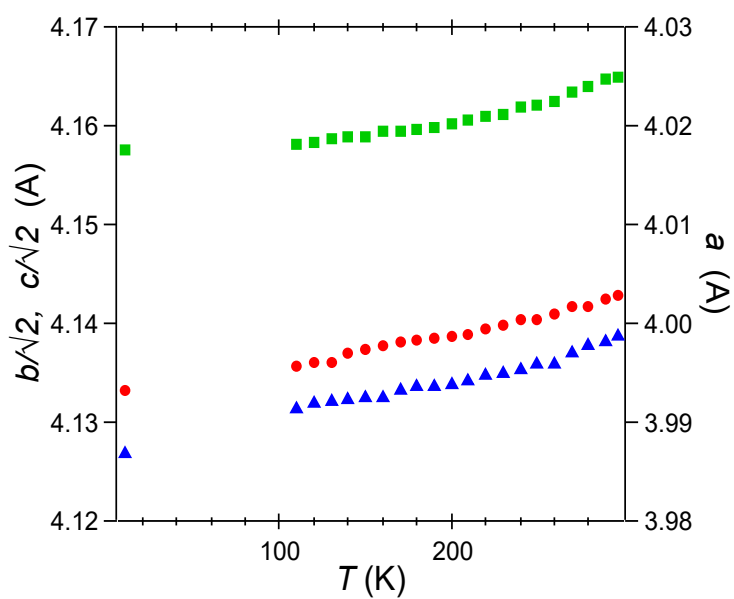


Fig. S1 (a) Temperature dependence of powder XRD patterns of high-pressure phase (HPP)-RbNbO₃, and (b) Temperature dependence of lattice parameters of HPP-RbNbO₃.

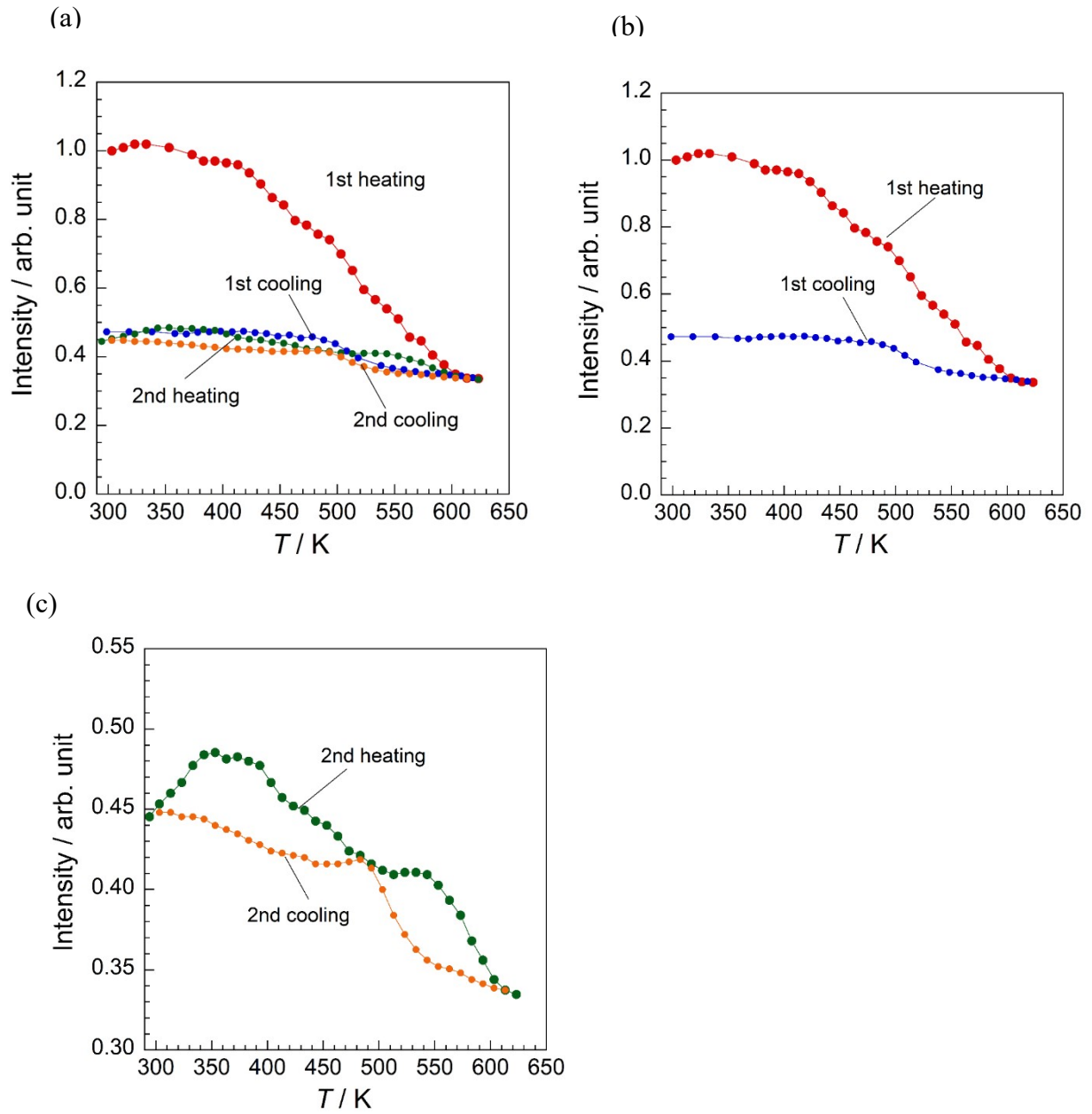


Fig. S2 Temperature dependences of intensity of SHG signals of HPP-RbNbO₃. (a) 1st and 2nd runs, (b) zoom-up figure of 1st run, and (c) zoom-up figure of 2nd run. The kinks observed around 500 K and 620 K with a hysteresis suggest the phase transition Ortho-Tetra1 and Tetra1-Tetra2, respectively.

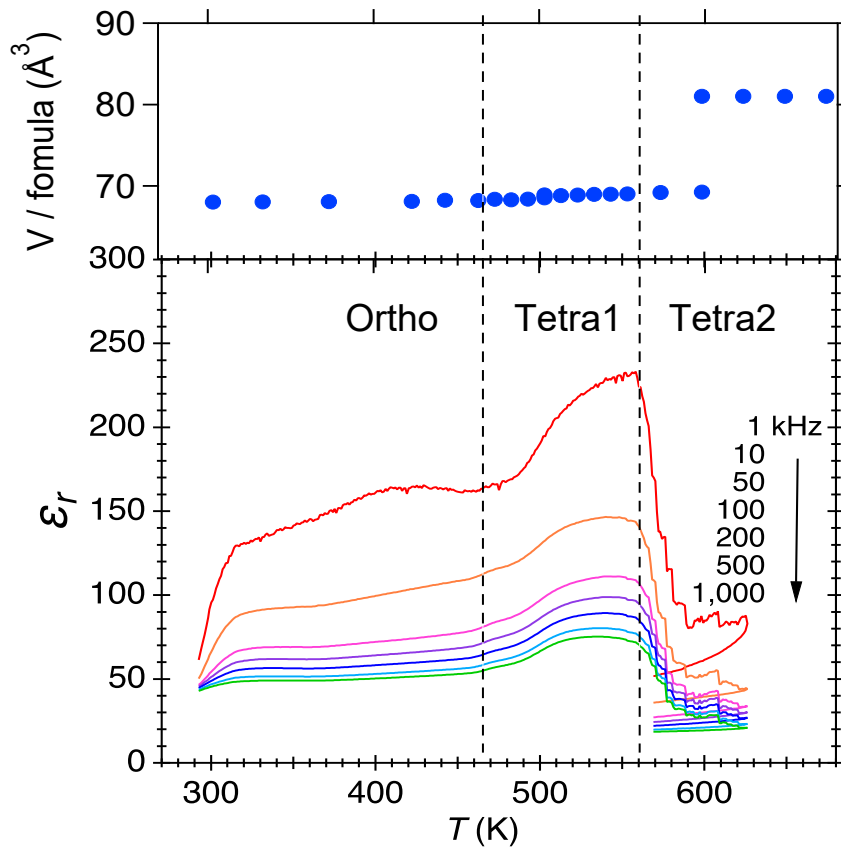
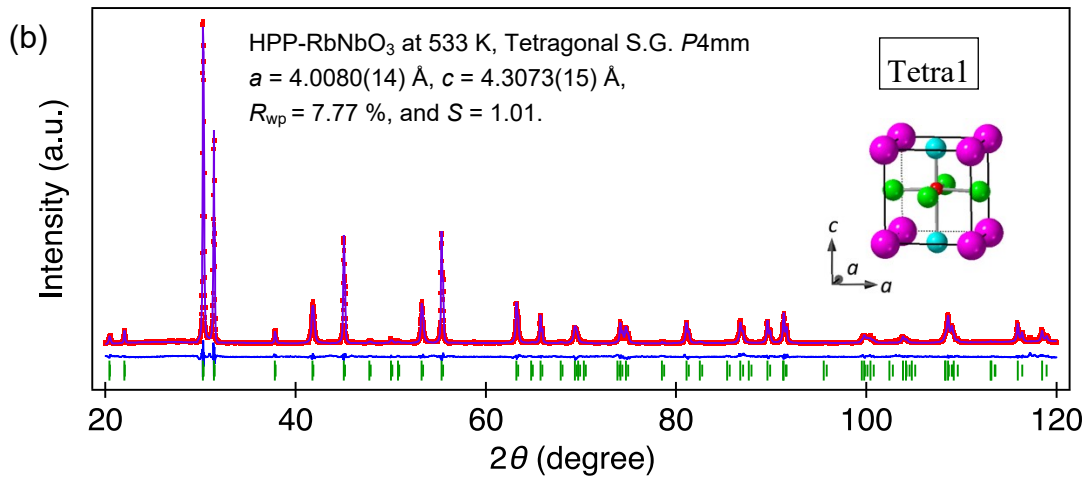
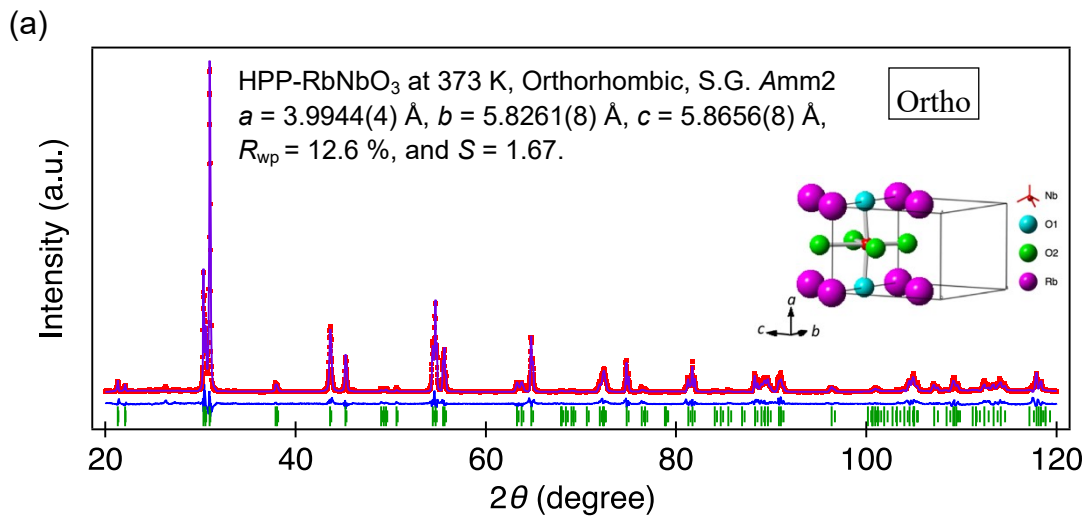


Fig. S3 Temperature dependence of relative permittivity of HPP-RbNbO₃. The sample collapsed with heating above 560 K, probably due to the sudden expansion with holding in place by a spring.



(to be continued)

(continued)

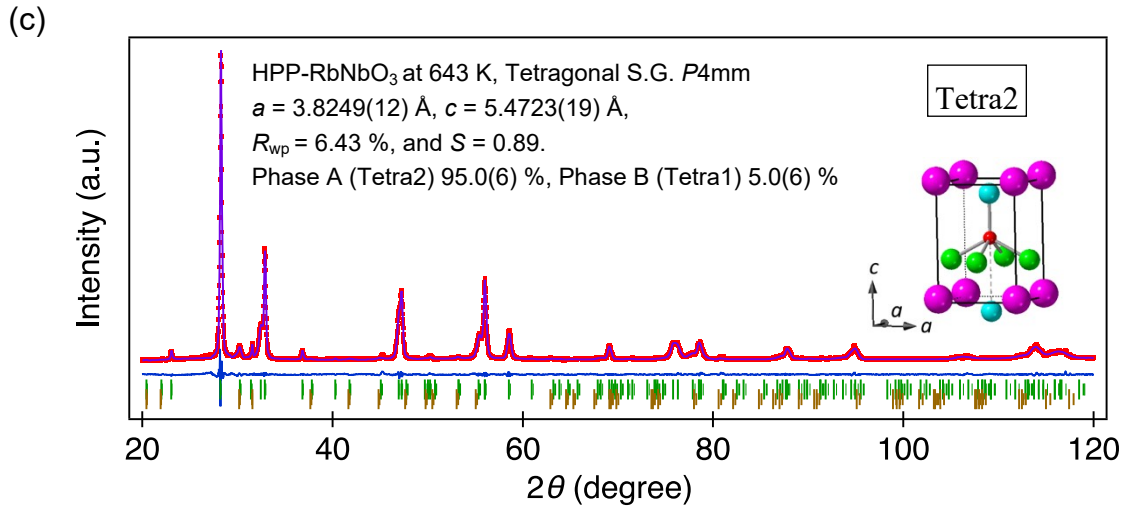


Fig. S4 Observed and calculated powder XRD pattern of RbNbO₃ at (a) 373 K, (b) 533 K, and (c) 643 K. Inset figures are local structure around Nb ion. The data were collected by the lab-powder XRD machine (Rigaku Ultima with high temperature furnace with using Bragg-Brentano diffractometer with CuK α). The structure was refined by the Rietveld method with the software “Z-Rietveld”²¹). Red dot: experimental intensity, purple line: calculated intensity, blue line: residual intensity, green tick: peak position of main phase, brown tick: peak position of secondary phase. Refined parameters are listed in Table S3. The space group both tetragonal phases were determined as *P4mm*. Both Tetra1 and Tetra2 phases showed SHG signal indicating non-centrosymmetric (polar), and no reflection conditions are found in the diffraction patterns (all possible peaks were appeared). Therefore, *P4mm* is only solution to satisfy the experimental results. We tried to obtain pure Tetra2 phase, however, data collection above 650 K over 24 h with lab-powder XRD machine led another phase transition to ambient phase. Therefore, we measured Tetra2 phase at the temperature coexisting very small amount of Tetra1 phase.

Table S1 Refinement details of single X-ray diffraction analysis of high-pressure phase of RbNbO₃

Crystal data	
Formula weight	226.38
Crystal system	Orthorhombic
Space group	<i>Amm</i> 2 (#38)
Temperature (K)	294(2)
<i>a</i> (Å)	3.99374(19)
<i>b</i> (Å)	5.8217(3)
<i>c</i> (Å)	5.8647(2)
<i>v</i> (Å ³)	136.355(10)
<i>Z</i>	2
Radiation type	Mo <i>K</i> _α
Crystal size (mm)	0.031×0.020×0.020
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, Hypix
Absorption correction	Numerical <i>CrysAlis PRO</i> (Rigaku OD)
Refinement	
Number of reflection	635
$R[F^2 > 2\sigma(F^2)]/wR(F^2)$	0.0158/0.0366
Flack parameter	0.244(7)
<i>S</i>	1.031

Table S2 Anisotropic displacement parameters U_{ij} of single X-ray diffraction analysis of high-pressure phase of RbNbO_3 . $U_{12} = U_{13} = 0 \text{ \AA}^2$

Atom	site	Occ.	$U_{11} (\text{\AA}^2)$	$U_{22} (\text{\AA}^2)$	$U_{33} (\text{\AA}^2)$	$U_{23} (\text{\AA}^2)$
Nb	$2b$	1	0.00397(16)	0.00406(14)	0.0035(4)	0
Rb	$2a$	1	0.00642(19)	0.00678(18)	0.0054(6)	0
O1	$2a$	1	0.0048(13)	0.0075(12)	0.0073(13)	0
O2	$4e$	1	0.0066(9)	0.0058(9)	0.0055(9)	0.0013(8)

Table S3 Positional parameters of high-pressure phase of RbNbO₃ analyzed by the Rietveld method. The experimental and calculated XRD patterns are plotted in the Fig. S4.

(1) At 373 K, Orthorhombic (Space group: *Amm2*), $a = 3.9944(4)$ Å, $b = 5.8261(8)$ Å, $c = 5.8656(8)$ Å, $R_{wp} = 12.6$ %, and $S = 1.67$. U_{eq} s were fixed the value obtained by the single crystal analysis.

Atom	site	Occ.	x	y	z	U_{iso} (Å ²)
Nb	$2b$	1	1/2	0	0.5057(8)	0.004
Rb	$2a$	1	0	0	0	= U_{iso} (Nb)
O1	$2a$	1	0	0	0.548(3)	0.006
O2	$4e$	1	1/2	0.02	0.299(2)	= U_{iso} (O1)

(2) At 533 K, Tetragonal (Space group: *P4mm*), $a = 4.0080(14)$ Å, $c = 4.3073(15)$ Å. $R_{wp} = 7.77$ %, and $S = 1.01$, U_{eq} s were fixed roughly expected value. The lattice parameters at 540 K determined by Fukuda *et al.* (*J. Ceram. Soc. Jpn.*, 2023, **131**, 126) are $a = 4.00874(2)$ Å, and $c = 4.31520(2)$ Å are very close to our refined parameters.

Atom	site	Occ.	x	y	z	U_{iso} (Å ²)
Nb	$1b$	1	1/2	1/2	0.5215(7)	0.007
Rb	$1a$	1	0	0	0	= U_{iso} (Nb)
O1	$1c$	1	1/2	1/2	0.951(2)	= U_{iso} (Nb)
O2	$2c$	1	1/2	0	0.566(3)	= U_{iso} (Nb)

(3) At 643 K,

$R_{wp}=6.43\%$, $S=0.89$. A possible reason for S less than 1 is that the data were collected by the lab-XRD. It happens if the intensity of background is relatively high compared with data taken in the synchrotron facility.

Phase A (Tetra2), Tetragonal (Space group: $P4mm$), $a= 3.8249(12)\text{\AA}$, $c= 5.4723(19)\text{\AA}$. Fraction of phase A is 95.0(6) %, U_{eq} s were fixed roughly expected value.

Atom	site	Occ.	x	y	z	$U_{iso} (\text{\AA}^2)$
Nb	$1b$	1	1/2	1/2	0.5011(2)	0.007
Rb	$1a$	1	0	0	0	$= U_{iso}(\text{Nb})$
O1	$1c$	1	1/2	1/2	0.899(17)	$= U_{iso}(\text{Nb})$
O2	$2c$	1	1/2	0	0.541(9)	$= U_{iso}(\text{Nb})$

Phase B (Tetra1), Tetragonal (Space group: $P4mm$), $a = 4.020$ (fix) \AA , $c = 4.308$ (fix) \AA Fraction of phase B is 5.0(6) %. All parameters were fixed based on the parameters at 533 K because of the low fraction.

Atom	site	Occ.	x	y	z	$U_{iso} (\text{\AA}^2)$
Nb	$1b$	1	1/2	1/2	$z(\text{Nb}, 533\text{K})$	0.007
Rb	$1a$	1	0	0	0	$= U_{iso}(\text{Nb})$
O1	$1c$	1	1/2	1/2	$z(\text{O1}, 533\text{K})$	$= U_{iso}(\text{Nb})$
O2	$2c$	1	1/2	0	$z(\text{O2}, 533\text{K})$	$= U_{iso}(\text{Nb})$