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Electronic Supplementary Information

On the coexistence of ferroelectric and antiferroelectric polymorphs in $NaNbO_3$ fiber-like particles at room temperature

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1. Powder XRD diffractogram of the precursor

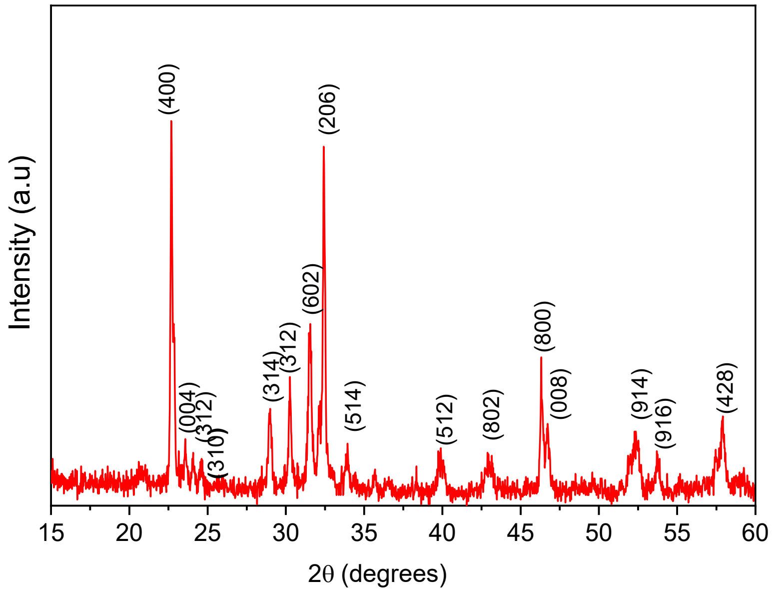

Figure S1: XRD pattern of $Na_2Nb_2O_6 \cdot H_2O$ obtained from MAHM at 160 °C for 40 minutes

2. Rietveld's refinement

Table S1: Reliability factors from the Rietveld refinement method for the $P2_1ma$ polymorph.

		This work			Ref. 61* [**CIF. N° 39624**]		
Atoms	**Wyckoff**	**x**	**y**	**z**	**x**	**y**	**z**
Na1	2a	0.27007(0.00553)	0	0.72934(0.00464)	0.2523	0	0.7392
Na2	2b	0.28	0.5	0.73768(0.00475)	0.28	0.5	0.7415
Nb1	4c	0.29122(0.00263)	0.24999(0.00102)	0.24485(0.00079)	0.2697	0.2507	0.2440
O1	2a	0.30810(0.00831)	0	0.30625(0.00481)	0.2401	0	0.3096
O2	2b	0.33483(0.00767)	0.5	0.15959(0.00563)	0.2213	0.5	0.1895
O3	4c	0.0265	0.27413(0.00379)	0.51465(0.00481)	0.0265	0.2804	0.5387
O4	4c	-0.02140(0.00339)	0.22963(0.00385)	0.03810(0.00389)	-.0459	0.2206	0.0380
		R_{wp} = 5.85 R_{exp} = 5.24 R_B = 0.39 χ^2 = 1.11 volume = 238.347 (17)Å^3 a = 5.5651(1)Å b = 7.7731 (2) Å c = 5.5098 (2)Å wt% = 87.10 (Space group $P2_1ma$) and R_B = 0.60 volume = 481.70(82) Å^3 a = 5.5147(25) Å b = 5.5809(19) Å c = 15.6511(84) Å wt% = 12.90 (Space group Pbcm)			volume = 239.38Å^3 a = 5.569 Å b = 7.790 c = 5.518		

* Reference from the principal file.

Table S2: Reliability factors from the Rietveld refinement method for the Pbcm polymorph.

		This work			Ref. 62* [**CIF. N° 23239**]		
Atoms	**Wyckoff**	**x**	**y**	**z**	**x**	**y**	**z**
Na1	4g	0.27007(0.00553)	0	0.72934(0.00464)	0.243	0.75	0
Na2	4f	0.28	0.5	0.73768(0.00475)	0.239	0.782	0.25
Nb1	4e	0.29122(0.00263)	0.24999(0.00102)	0.24485(0.00079)	0.2566	0.2722	0.1262
O1	2d	0.30810(0.00831)	0	0.30625(0.00481)	0.304	0.25	0
O2	2c	0.33483(0.00767)	0.5	0.15959(0.00563)	0.191	0.233	0.25
O3	2b	0.0265	0.27413(0.00379)	0.51465(0.00481)	0.536	0.032	0.140
O4	2a	-0.02140(0.00339)	0.22963(0.00385)	0.03810(0.00389)	0.966	0.467	0.110
		R_{wp} = 5.85 R_{exp} = 5.24 R_B = 0.39 χ^2 = 1.11 volume = 238.347 (17)Å^3 a = 5.5651(1)Å b = 7.7731 (2) Å c = 5.5098 (2)Å wt% = 87.10 (Space group $P2_1ma$) and R_B = 0.60 volume = 481.70(82) Å^3 a = 5.5147(25) Å b = 5.5809(19) Å c = 15.6511(84) Å wt% = 12.90 (Space group Pbcm)			volume = 475.632 Å^3 a = 5.506 Å, b = 5.566 Å c = 15.52 Å		

* Reference from the principal file.

3. Theoretical vibrational frequencies

Table S3. List of vibrational modes for the $P2_1ma$ polymorph using the B3LYP(D3-BJ) functional.

Mode symmetry	TO (cm^{-1})	LO (cm^{-1})	IR Active	RAMAN Active	Relative intensity**
A2	51		I	A	0.002
B2	58	890	A	A	1.000
A2	94		I	A	0.001
B2	101	92	A	A	0.131
A1	105	122	A	A	0.503
B1	108	112	A	A	0.112
B1	126	151	A	A	0.235
A1	132	134	A	A	0.003
A1	157	162	A	A	0.100
B2	166	162	A	A	0.024
A2	169		I	A	0.000
B1	181	185	A	A	0.007
A2	190		I	A	0.005
B2	196	196	A	A	0.004
B2	199	199	A	A	0.002
A1	200	206	A	A	0.061
A2	203		I	A	0.004
B1	206	206	A	A	0.000
A1	221	221	A	A	0.052
B1	225	898	A	A	0.442
A1	231	893	A	A	0.608
B1	234	232	A	A	0.061
B1	249	249	A	A	0.003
A1	250	248	A	A	0.042
A2	252		I	A	0.005
B2	259	259	A	A	0.001
A1	277	267	A	A	0.213
B1	280	280	A	A	0.000
A1	291	284	A	A	0.126
A1	312	311	A	A	0.026
A1	325	324	A	A	0.024
A2	332		I	A	0.000
B2	335	323	A	A	0.003
B1	346	331	A	A	0.015
B2	353	341	A	A	0.006
A2	365		I	A	0.005
B1	365	365	A	A	0.000
B1	393	369	A	A	0.024

A1	422	418	A	A	0.005
B1	449	445	A	A	0.000
B1	454	454	A	A	0.001
A2	458		I	A	0.001
A1	473	474	A	A	0.012
B1	483	483	A	A	0.007
A2	486		I	A	0.001
A1	519	520	A	A	0.008
B2	545	434	A	A	0.013
A2	557		I	A	0.000
B2	570	570	A	A	0.000
B1	582	470	A	A	0.180
A1	595	442	A	A	0.615
A2	603		I	A	0.011
B2	651	650	A	A	0.001
A1	682	679	A	A	0.014
B2	864	864	A	A	0.000
B1	906	906	A	A	0.000
A2	931		I	A	0.000

*I = Inactive and A = Active. **Calculated using the temperature of 295 K and without the LO-TO splitting.

Table S4. List of vibrational modes for the Pbcm polymorph using the B3LYP(D3-BJ) functional.

Mode symmetry	**TO (cm^{-1})**	**LO (cm^{-1})**	**IR Active**	**RAMAN Active**	**Relative intensity****
B1u	47	893	A	I	0.004
B3g	61		I	A	0.132
B1g	69		I	A	0.239
B1u	73	69	A	I	0.001
Ag	73		I	A	0.002
Au	76		I	I	0.027
B2g	93		I	A	0.238
B3g	95		I	A	0.001
B3u	109	121	A	I	0.065
B1g	111		I	A	0.000
Ag	114		I	A	0.001
B3g	117		I	A	0.174
B1g	119		I	A	0.002
B2g	122		I	A	0.079
B3u	132	133	A	I	0.000
B1u	138	114	A	I	0.013
B3g	140		I	A	0.004

Ag	159		I	A	0.001
B3u	160	196	A	I	0.002
B2g	162		I	A	0.289
B3u	164	164	A	I	0.000
B2u	164	190	A	I	0.214
B1u	166	162	A	I	0.019
B1g	168		I	A	0.077
Au	171		I	I	0.065
B2u	179	179	A	I	0.036
B3g	180		I	A	0.095
B1u	195	194	A	I	0.061
Au	200		I	I	0.000
B1g	202		I	A	0.471
Ag	205		I	A	0.001
B3u	205	205	A	I	0.116
B3g	205		I	A	0.154
B2g	209		I	A	0.003
B1u	210	210	A	I	0.116
B2u	212	215	A	I	0.000
Au	213		I	I	0.001
B3u	214	214	A	I	0.006
B1g	219		I	A	0.000
B2g	224		I	A	0.008
Ag	224		I	A	0.005
B2u	225	228	A	I	0.001
B3g	230		I	A	0.000
B1g	233		I	A	0.002
B2u	242	337	A	I	0.003
Ag	244		I	A	0.019
B3u	245	254	A	I	0.015
B1g	257		I	A	0.001
Ag	258		I	A	0.010
Au	260		I	I	0.000
B1u	260	260	A	I	0.188
B1g	261		I	A	0.117
B1u	268	268	A	I	0.000
Au	269		I	I	1.000
B2g	270		I	A	0.013
B3u	276	442	A	I	0.002
B2u	277	275	A	I	0.025
B3u	286	286	A	I	0.001
Ag	291		I	A	0.000
B2g	299		I	A	0.000
B2u	299	299	A	I	0.004
Ag	311		I	A	0.132

Ag	314		I	A	0.239
B3g	314		I	A	0.001
B3u	323	314	A	I	0.002
Au	324		I	I	0.027
B1g	329		I	A	0.238
B1u	334	320	A	I	0.001
B2g	335		I	A	0.065
B1g	347		I	A	0.000
B3g	352		I	A	0.001
B3u	354	345	A	I	0.174
B1u	354	343	A	I	0.002
B2u	355	367	A	I	0.079
Au	355		I	I	0.000
Au	380		I	I	0.013
B2u	389	391	A	I	0.004
B2u	405	470	A	I	0.001
B1g	412		I	A	0.002
Ag	415		I	A	0.289
B3g	420		I	A	0.000
B3u	435	435	A	I	0.214
B2g	449		I	A	0.019
B1g	449		I	A	0.077
B2u	452	452	A	I	0.065
B3g	458		I	A	0.036
Au	466		I	I	0.095
B2g	471		I	A	0.061
Ag	472		I	A	0.000
B3u	474	474	A	I	0.471
B1g	474		I	A	0.001
B2u	479	479	A	I	0.116
B3g	489		I	A	0.154
Ag	519		I	A	0.003
B1u	545	433	A	I	0.116
Au	565		I	I	0.000
B3g	570		I	A	0.001
B1g	575		I	A	0.006
B1g	586		I	A	0.000
Au	586		I	I	0.008
B2u	587	900	A	I	0.005
B2g	590		I	A	0.001
B1u	592	592	A	I	0.000
Ag	600		I	A	0.002
B3u	602	895	A	I	0.003
B3g	615		I	A	0.019
B1u	670	669	A	I	0.015

B2g	671		I	A	0.001
B3u	687	682	A	I	0.010
Ag	689		I	A	0.000
B1u	864	864	A	I	0.188
B2g	882		I	A	0.117
B3u	882	882	A	I	0.000
B2u	907	907	A	I	1.000
Au	922		I	I	0.013
B1g	923		I	A	0.002
B3g	931		I	A	0.025

*I = Inactive and A = Active. **Calculated using the temperature of 295 K and without the LO-TO splitting.

4. Simulation of the electric field on the polymorph stability

The internal static electric field in the direction *d* ($F_{0,d}$) was related to the macroscopic electric field in the same direction (F_d) using the following equation[1–4]:

$$F_d = \frac{F_{0,d}}{\varepsilon_{0,d}}, \qquad \text{Eq. S1}$$

where $\varepsilon_{0,d}$ are the static dielectric tensor components for the polymorph. Besides, the static dielectric tensor ε_0 was obtained using the Coupled Perturbed Kohn-Sham (CPKS) method [5,6], resulting in the following values:

$$\varepsilon_0^{Pbcm} = \begin{pmatrix} 44.56170 & 0 & 0 \\ 0 & 46.64046 & 0 \\ 0 & 0 & 564.08320 \end{pmatrix} \qquad \text{Eq. S2}$$

and

$$\varepsilon_0^{Pmc2_1} = \begin{pmatrix} 505.80475 & 0 & 0 \\ 0 & 61.82059 & 0 \\ 0 & 0 & 50.01120 \end{pmatrix} \qquad \text{Eq. S3}$$

Since the atomic site positions are different from the Pbcm polymorph to the Pmc2$_1$ (standard space group of the P2$_1$ma), such tensor was rotated to match such sites and orientations. Such rotation creates the relation for axis equivalence between the polymorphs as given in Table S5 (with the necessity of duplicating the new cell in the z direction to match the number of atoms in the Pbcm cell).

Table S5. Relation between the space group axis of the $NaNbO_3$ polymorphs. The last columns define the frame used for the applied electric field in the DFT simulations.

Pbcm	**$Pmc2_1$**	**$P2_1ma$**	**Direction**
a	b	c	x
b	c	a	y
c	a	b	z

This rotation results in the following tensor:

$$\left(\varepsilon_{0}^{Pmc2_1}\right)' = \begin{pmatrix} 61.80259 & 0 & 0 \\ 0 & 50.01120 & 0 \\ 0 & 0 & 505.80475 \end{pmatrix} \qquad \text{Eq. S4}$$

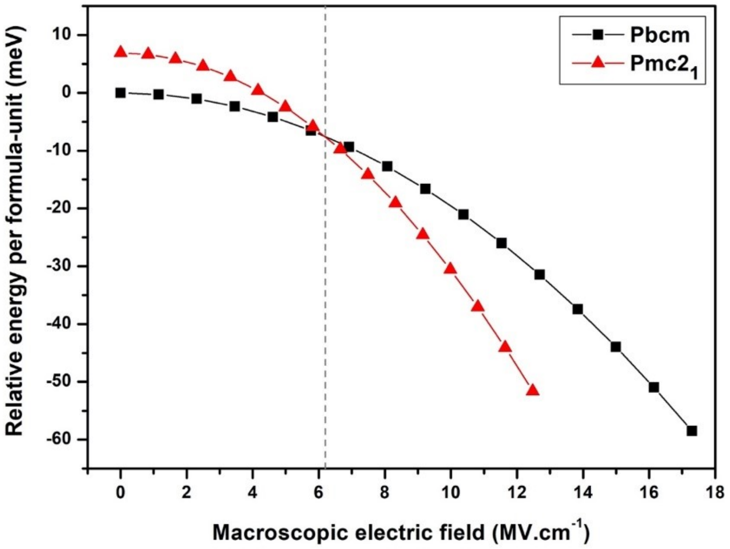

Figure S2. Macroscopic electric field effect in the x direction on the relative energy to the Pbcm polymorph under an applied electric field (see Table S5).

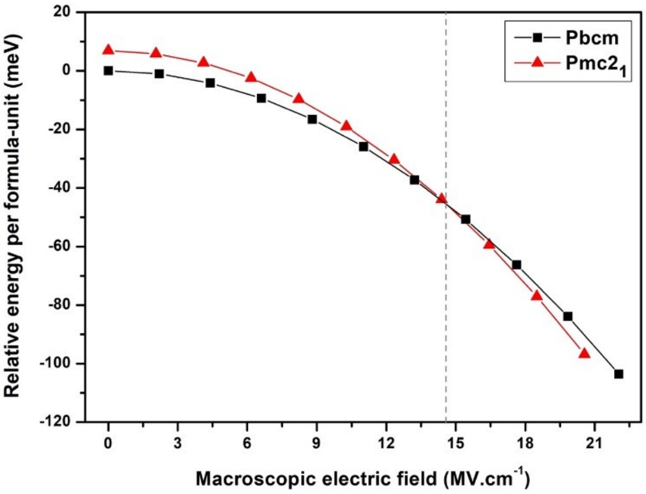

Figure S3. Macroscopic electric field effect in the y direction on the relative energy to the Pbcm polymorph under an applied electric field (see Table S5).

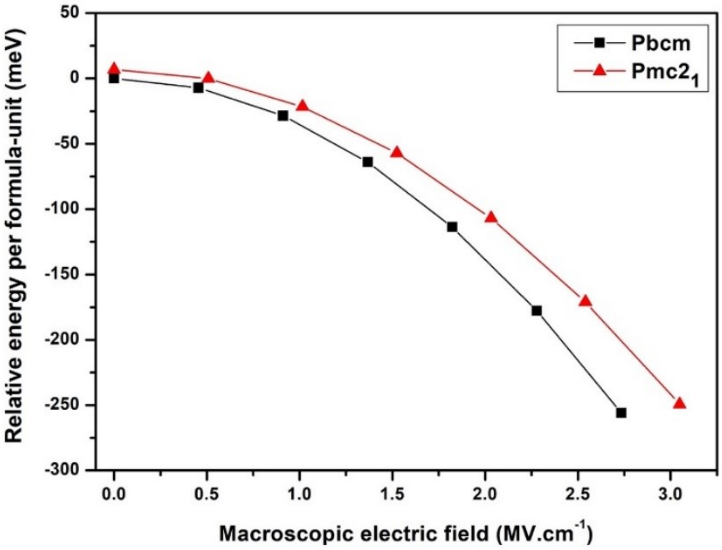

Figure S4. Macroscopic electric field effect in the z direction on the relative energy to the Pbcm polymorph under an applied electric field (see Table S5).

5. References

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