S1. PHASE TRANSITIONS DRIVEN BY SOFT PHONON MODES

Harmonic phonon dispersion calculations have been carried out to determine the phonon eigendisplacement vectors with a set of atomic displacements while considering the related symmetries of the crystal structures containing the displaced atoms. Note that the imaginary frequencies in the phonon dispersion curve are indicative of soft phonon modes (in the first Brillouin zone) that drives the specific phase transition, namely at the $\Gamma (0,0,0)$, $X (\frac{1}{2}, 0, 0)$, $M (\frac{1}{2}, \frac{1}{2}, 0)$, and $R (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ $q$-points. At the $\Gamma$ $q$-point, only one soft phonon mode ($\Gamma_4^-$) appears at 5.103i THz with a three-fold degeneracy. At the $M$ $q$-point, there are two non-degenerate soft phonon modes shown at 3.516i THz and 1.655i THz, which correspond to the $M_2^+$ and $M_2^-$ mode, respectively. At the $R$ $q$-point, there is one three-fold degenerated soft phonon mode ($R_5^-$) at 3.838i THz, while at the $X$ $q$-point, one soft phonon mode ($X_5^+$) is located at 2.931i THz with a two-fold degeneracy.
Figure S1. DFT-PBEsol phonon band structure for the aristotype cubic NaNbO$_3$ (U phase; $Pm\bar{3}m$) – (a) without and (b) with the non-analytical-term correction (NAC) [1] applied to dynamical matrix, respectively.
Table S1. DFT-PBEsol (imaginary) phonon frequencies (in THz) and their degeneracies, irreducible representations (IR with modes labelled), directions of the order parameter, crystal symmetries of the relaxed structure, the number of atoms per cell, and their calculated relative energies (in meV/formula-unit) with respect to the cubic $Pm\bar{3}m (U)$ NaNbO$_3$ phase.

<table>
<thead>
<tr>
<th>$\omega$ (THz)</th>
<th>Degeneracy</th>
<th>Mode</th>
<th>Direction</th>
<th>Symmetry</th>
<th>No. of atoms</th>
<th>$\Delta E$ (meV/f.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.103i</td>
<td>3</td>
<td>$\Gamma_4^-$</td>
<td>(a, 0, 0)</td>
<td>$P4mm$</td>
<td>5</td>
<td>-30.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(a, a, 0)</td>
<td>$Amm2$</td>
<td>10</td>
<td>-32.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(a, a, a)</td>
<td>$R3m$</td>
<td>15</td>
<td>-31.8</td>
</tr>
<tr>
<td>3.838i</td>
<td>3</td>
<td>$R_5^-$</td>
<td>(a, 0, 0)</td>
<td>$I4/mcm$</td>
<td>20</td>
<td>-70.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(a, a, 0)</td>
<td>$Imma$</td>
<td>20</td>
<td>-81.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(a, a, a)</td>
<td>$R3c$</td>
<td>30</td>
<td>-79.2</td>
</tr>
<tr>
<td>3.516i</td>
<td>1</td>
<td>$M_2^+$</td>
<td>(a; 0; 0)</td>
<td>$P4/mmb$</td>
<td>10</td>
<td>-66.2</td>
</tr>
<tr>
<td>2.931i</td>
<td>2</td>
<td>$X_5^+$</td>
<td>(0; a; 0; 0; 0)</td>
<td>$Pmna$</td>
<td>10</td>
<td>-4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(a, a; 0; 0; 0)</td>
<td>$Cmcm$</td>
<td>20</td>
<td>-4.1</td>
</tr>
<tr>
<td>1.655i</td>
<td>1</td>
<td>$M_2^-$</td>
<td>(a; 0; 0)</td>
<td>$P4/nmm$</td>
<td>10</td>
<td>-2.8</td>
</tr>
</tbody>
</table>
Table S2. DFT-PBEsol optimized crystal phases of NaNbO$_3$ known from experiments: Crystal symmetries of the relaxed structure, irreducible representations (IR with modes labelled), directions of the order parameter, basis vectors, the number of atoms per cell, and their calculated relative energies (in meV/formula-unit) with respect to the cubic $Pm3m$ ($U$) NaNbO$_3$ phase.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Mode(s)</th>
<th>Direction(s)</th>
<th>Basis vector</th>
<th>No. of atoms</th>
<th>$\Delta E$ (meV/f.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Pm3m$ ($U$)</td>
<td>-</td>
<td>-</td>
<td>(1, 1, 1)</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>$P4mm$</td>
<td>$\Gamma_4^-$</td>
<td>(a, 0, 0)</td>
<td>(1, 1, 1)</td>
<td>5</td>
<td>-31.8</td>
</tr>
<tr>
<td>$R3m$</td>
<td>$\Gamma_4^-$</td>
<td>(a, a, a)</td>
<td>($\sqrt{2}, \sqrt{2}, \sqrt{3}$)</td>
<td>15</td>
<td>-32.8</td>
</tr>
<tr>
<td>$Amm2$</td>
<td>$\Gamma_4^-$</td>
<td>(a, a, 0)</td>
<td>($\sqrt{2}, \sqrt{2}, 1$)</td>
<td>10</td>
<td>-33.7</td>
</tr>
<tr>
<td>$P4/mmb$ ($T_2$)</td>
<td>$M_2^+$</td>
<td>(a; 0; 0)</td>
<td>($\sqrt{2}, \sqrt{2}, 1$)</td>
<td>10</td>
<td>-66.2</td>
</tr>
<tr>
<td>$I4/mcm$</td>
<td>$T_2$</td>
<td>(a, 0; 0, 0; 0, 0)</td>
<td>($\sqrt{2}, \sqrt{2}, 4$)</td>
<td>40</td>
<td>-68.5</td>
</tr>
<tr>
<td>$P4/mmb$</td>
<td>$M_2^+$, $T_2$</td>
<td>(a, 0, 0), (a, 0, 0; 0, 0)</td>
<td>($\sqrt{2}, \sqrt{2}, 3$)</td>
<td>30</td>
<td>-69.3</td>
</tr>
<tr>
<td>$I4/mcm$</td>
<td>$R_5^-$</td>
<td>(a, 0, 0)</td>
<td>($\sqrt{2}, \sqrt{2}, 4$)</td>
<td>20</td>
<td>-70.8</td>
</tr>
<tr>
<td>$R3c$</td>
<td>$R_5^-$</td>
<td>(a, a, a)</td>
<td>($\sqrt{2}, \sqrt{2}, 2\sqrt{3}$)</td>
<td>30</td>
<td>-79.2</td>
</tr>
<tr>
<td>$Imma$</td>
<td>$R_5^-$</td>
<td>(0, a, −a)</td>
<td>($\sqrt{2}, 2, \sqrt{2}$)</td>
<td>20</td>
<td>-81.9</td>
</tr>
<tr>
<td>$Cmcm$ ($T_1$)</td>
<td>$M_2^+$, $R_5^-$</td>
<td>(a; 0; 0), (0, 0, a)</td>
<td>(2, 2, 2)</td>
<td>40</td>
<td>-84.8</td>
</tr>
<tr>
<td>$Pmmm$ ($S$)</td>
<td>$M_2^+$, $R_5^-$</td>
<td>(a; b; 0), (0, 0, a)</td>
<td>(2, 2, 4)</td>
<td>80</td>
<td>-87.3</td>
</tr>
<tr>
<td>$Pnma$</td>
<td>$M_2^+$, $R_5^-$</td>
<td>(a; 0; 0), (0, a, a)</td>
<td>(2, 2, 2)</td>
<td>20</td>
<td>-92.9</td>
</tr>
<tr>
<td>$Pmmm$ ($R$)</td>
<td>$M_2^+$, $R_5^-$, $T_2$</td>
<td>(0; a; b), (a, 0, 0), (0, 0; a, 0, 0)</td>
<td>(2, 6, 2)</td>
<td>120</td>
<td>-101.4</td>
</tr>
<tr>
<td>$Pnma$ ($R$)</td>
<td>$M_2^+$, $R_5^-$, $T_2$</td>
<td>(0; 0; a), (0, a, 0), (0, a, 0, 0)</td>
<td>(2, 2, 6)</td>
<td>120</td>
<td>-102.0</td>
</tr>
<tr>
<td>$Pmc2_1$ ($Q$)</td>
<td>$M_2^+$, $R_5^-$, $\Gamma_4^-$</td>
<td>(a; 0; 0), (0, a, a), (a, a, 0)</td>
<td>(2, $\sqrt{2}$, $\sqrt{2}$)</td>
<td>20</td>
<td>-109.8</td>
</tr>
<tr>
<td>$Pbcm$ ($P$)</td>
<td>$R_5^-$, $T_2$</td>
<td>(0, a, a), (a, 0, 0; 0, 0)</td>
<td>($\sqrt{2}, \sqrt{2}, 4$)</td>
<td>40</td>
<td>-110.0</td>
</tr>
<tr>
<td>$R3c$ ($N$)</td>
<td>$R_5^-$, $\Gamma_4^-$</td>
<td>(a, a, a), (a, a, a)</td>
<td>($\sqrt{2}, \sqrt{2}, 2\sqrt{3}$)</td>
<td>30</td>
<td>-112.0</td>
</tr>
</tbody>
</table>
S2. RATIONALIZATION OF POTENTIAL ENERGY SURFACES (PES) BY SYMMETRY-ADAPTED MODE ANALYSIS

Potential energy surfaces (PES) are graphed based on the symmetry-adapted modes with diverse and feasible combinations of any two major modes with considering both competitive and cooperative relations between the modes in lowering the overall energy of the crystal during a phase transition. The phonon mode amplitudes, Q (in Å) of the $R_5^-$, $\Delta_5$, and $T_2$ modes are normalized to match the Q values in the $P$ phase while the corresponding Q values for $\Gamma_4^-$ and $M_2^+$ are also normalized for the $Q$ phase in a similar fashion. To paint a simple picture of this competitive or/and cooperative relationship between the major phonon modes, the PES for different sets of combinatorial modes can be found in Figures S2 and S3 (competitive relations) and Figures S4 and S5 (cooperative relations).
Figure S2. (Left column) Potential energy surface (PES) constructed via the anti-polar $\Delta_5$ mode versus the polar $\Gamma_4^-$ mode, where all other modes are not included, i.e., $Q_{T_2}$, $Q_{M_2^+}$, and $Q_{R_5^-} = 0$. (Middle column; From top to bottom) PES now constructed by including only one other mode: $Q_{T_2} = 1$, $Q_{R_5^-} = 1$, and $Q_{M_2^+} = 1$ (in addition to $\Delta_5$ and $\Gamma_4^-$), respectively. (Right column; From top to bottom) PES now includes the additional consideration of two other modes (other than $\Delta_5$ and $\Gamma_4^-$): $Q_{T_2}Q_{R_5^-} = 1$ and $Q_{M_2^+}Q_{R_5^-} = 1$, respectively.
Figure S3. (Left column) Potential energy surface (PES) constructed via the in-phase/out-of-phase (a₀a₀a⁺/a₀a₀a⁻) rotation T₂ mode versus the in-phase (a₀a⁺) rotation M⁺₂ mode, where all other modes are not included, i.e., Q₅, Q₄⁻, and Q₅⁻ = 0. (Middle column; From top to bottom) PES now constructed by including only one other mode: Q₅ = 1, Q₅⁻ = 1, and Q₄⁻ = 1 (in addition to T₂ and M⁺₂), respectively. (Right column; From top to bottom) PES now includes the additional consideration of two other modes (other than T₂ and M⁺₂): Q₅Q₅⁻ = 1 and Q₄⁻Q₅⁻ = 1, respectively.
Figure S4. (Left) Potential energy surface (PES) constructed via the in-phase/out-of-phase $(a^0a^0a^+/a^0a^0a^-)$ rotation $T_2$ mode versus the out-of-phase $(a^-a^-a^0)$ tilting $R_5^-$ mode, where all other modes are not included, i.e., $Q_{\Delta_5}$, $Q_{\Gamma_4}$, and $Q_{M_4^+} = 0$. (Right) PES constructed via the in-phase $(a^0a^0a^+)$ rotation $M_2^+$ mode versus the out-of-phase tilting $R_5^-$ mode, where all other modes are not included, i.e., $Q_{\Delta_5}$, $Q_{\Gamma_4}$, and $Q_{\Gamma_2} = 0$. 
Figure S5. Similar to Figures S2 to S4, moving to left to right for each row, the interplay of two selected modes are chosen, firstly with all other modes set to zero, and with the inclusion of one more specific mode, and then the inclusion of two more modes.