

Supplemental Material: Microscopic picture of paraelectric perovskites from structural prototypes

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1. METHODS

Our first-principles DFT-based calculations are performed using Quantum ESPRESSO [1, 2] with the PBEsol [3] functional, RRKJ pseudopotentials [4] and wavefunction and charge-density energy cutoffs of 60 and 600 Ry, respectively.

A. Car-Parrinello Molecular Dynamics

CPMD calculations [5] are carried out using the `cp.x` code of Quantum ESPRESSO in the NVE ensemble (constant number of particles, volume and energy) on a $4 \times 4 \times 4$ supercell (320 atoms) using a Γ -only sampling, where the initial atomic positions are chosen so that, after an initial equilibration (1.5 ps), the average temperature is the one reported in the figure caption. The lattice parameter is also increased with respect to the $T = 0$ K value so as to account for the experimentally-measured thermal expansion [6]. The wavefunction and charge-density energy cutoffs is set to 40 and 320 Ry, respectively. A time step of 0.25 fs and an electron mass of $400 m_e$ are used.

B. Symmetry analysis to determine the microscopic templates

We search for all the subgroups with a desired point symmetry (here, cubic) of the high-symmetry space group with unique Wyckoff splittings in a recursive fashion. We use and compare both the ISOTROPY command-line tool [7] and the tools available on the Bilbao Crystallographic server [8, 9], in particular the CELLSUB program to obtain the list of subgroups, the conjugacy classes and the transformation matrices, then used as input to the WYCKSPLIT program [10] to get the splitting of the relevant Wyckoff positions. These two set of rules yield the same results and allow us to generate the group-subgroup relationship used to build Tables 1 (main text), S1 and S2. To confirm the space group, removing the duplicate microscopic templates, we perform a final check with `spglib` [11].

C. Density functional theory calculations to search for structural prototypes

Using a random displacement on the order of 0.05 Å for each Wyckoff-position free parameter, we construct cells for each of the 27 cubic microscopic templates associated with each unique subgroup for the cubic phase of BaTiO₃ and perform variable-cell relaxations constraining cubic point symmetry. At every ionic minimization, the forces were symmetrized, effectively enforcing symmetries detected at the onset of the calculation. This ensures that the system reaches the minimum-energy structure with the constraint of possessing the symmetry of the parent space group (e.g., a given cubic spacegroup), avoiding that the system relaxes to one of the lower-symmetry structures (e.g., the rhombohedral structure that is the ground state at $T = 0$ K for BaTiO₃). This enforces the cubic point symmetry possessed by all of the 27 microscopic templates. The calculations are managed using the AiiDA framework [12, 13], a high-throughput platform that allows to automatically launch, retrieve, parse and organize the calculations, storing the results in a database and automatically managing sequences of calculations via its workflow engine. Given a microscopic template as a starting structure, we relax both the lattice parameters and the internal coordinates with

a force tolerance of 5×10^{-5} eV/Å and an energy tolerance of 3×10^{-11} eV using a $3 \times 3 \times 3$ k -mesh in the $2 \times 2 \times 2$ supercells (and equivalent meshes in different cell sizes, e.g., $6 \times 6 \times 6$ in the 5-atom unit cell).

To calculate the potential energy landscape, we perform a nudged-elastic-band (NEB) calculation [14] using the metastable 4+4 and 2+6 structures and the undistorted structure as the constrained points. To calculate the phonon dispersion we use density functional perturbation theory (DFPT) [15, 16] as implemented in Quantum ESPRESSO with a $2 \times 2 \times 2$ q -mesh imposing the acoustic sum rule. For the phonon dispersions, 50 points are used along each segment for the Fourier interpolation. We use ISODISTORT [17, 18] from the ISOTROPY package to analyze the symmetry of the unstable modes and of the displacement patterns of the metastable lower-symmetry structures, i.e. the structural prototypes.

2. 27 DISTINCT SUBGROUPS OF SPACE GROUP 221 FOR OCCUPIED WYCKOFF POSITIONS 1A, 1B, 3C

TABLE S1. The 27 distinct cubic subgroups of parent group $\text{Pm}\bar{3}\text{m}$ (221) possessing non-trivial splittings of the 1a, 1b and 3c Wyckoff positions are reported which each correspond to a microscopic template, including the 10 subgroups reported in the main text. We list the subgroup (international short symbol and number) followed by the subgroup index (in square brackets); the transformation matrix T_x ; and the splittings of the three relevant Wyckoff positions. T_x is defined as the transformation from the primitive cell to the $2 \times 2 \times 2$ cell (with matrix equal to twice the identity), and with an origin shift (x, x, x) . In the first ten subgroups (above the dividing line), only oxygen atoms can displace from the high-symmetry structure.

Group	[Index]	T_x	1a	1b	3c
$\text{Im}\bar{3}\text{m}$ (229)	[4]	$T_{1/2}$	8c	2a 6b	12e 12d
$\text{Im}\bar{3}\text{m}$ (229)	[4]	T_0	2a 6b	8c	24h
$\text{Fm}\bar{3}\text{m}$ (225)	[2]	$T_{1/2}$	8c	4a 4b	24e
$\text{Pn}\bar{3}\text{m}$ (224)	[8]	$T_{1/2}$	2a 6d	4b 4c	24k
$\text{Pm}\bar{3}\text{n}$ (223)	[8]	T_0	2a 6b	8e	24k
P4_232 (208)	[16]	T_0	2a 6d	4c 4b	24m
$\text{Ia}\bar{3}$ (206)	[8]	T_0	8a	8b	24d
$\text{Im}\bar{3}$ (204)	[8]	T_0	2a 6b	8c	24g
$\text{Im}\bar{3}$ (204)	[8]	$T_{1/2}$	8c	2a 6b	12d 12e
$\text{Pn}\bar{3}$ (201)	[16]	$T_{1/2}$	2a 6d	4b 4c	24h
$\text{Pm}\bar{3}\text{m}$ (221)	[8]	$T_{1/2}$	8g	1a 3c 3d 1b	6e 12h 6f
$\text{Pm}\bar{3}\text{m}$ (221)	[8]	T_0	1a 3d 3c 1b	8g	12i 12j
$\text{P4}_3\text{n}$ (218)	[16]	T_0	2a 6b	8e	24i
$\text{I}\bar{4}3\text{m}$ (217)	[8]	T_0	2a 6b	8c	24g
$\text{I}\bar{4}3\text{m}$ (217)	[8]	$T_{1/2}$	8c	2a 6b	12e 12d
$\text{P}\bar{4}3\text{m}$ (215)	[16]	$T_{1/2}$	4e 4e	1a 3c 3d 1b	6f 12h 6g
$\text{P}\bar{4}3\text{m}$ (215)	[16]	T_0	1b 3c 3d 1a	4e 4e	12i 12i
$\text{Pa}\bar{3}$ (205)	[16]	$T_{1/2}$	8c	4a 4b	24d
$\text{Pa}\bar{3}$ (205)	[16]	T_0	4a 4b	8c	24d
$\text{Pm}\bar{3}$ (200)	[16]	$T_{1/2}$	8i	1a 3c 3d 1b	6e 6g 6f 6h
$\text{Pm}\bar{3}$ (200)	[16]	T_0	1a 3d 3c 1b	8i	12j 12k
I2_13 (199)	[16]	T_0	8a	8a	12b 12b
P2_13 (198)	[32]	T_0	4a 4a	4a 4a	12b 12b
I23 (197)	[16]	T_0	2a 6b	8c	24f
I23 (197)	[16]	$T_{1/2}$	8c	2a 6b	12d 12e
P23 (195)	[32]	$T_{1/2}$	4e 4e	1a 3c 3d 1b	6f 6h 6g 6i
P23 (195)	[32]	T_0	1a 3d 3c 1b	4e 4e	12j 12j

3. DUPLICATE AND TRIVIAL SUBGROUPS OF SPACE GROUP 221 FOR OCCUPIED WYCKOFF POSITIONS 1A, 1B, 3C

TABLE S2. In addition to the 27 cubic subgroups of parent group $\text{Pm}\bar{3}\text{m}$ (221) reported in the main text, there are 10 cubic subgroups with trivial splittings of the 1a, 1b and 3c Wyckoff positions and 15 duplicate subgroups. In the trivial subgroups, the resulting split Wyckoff positions have no degrees of freedom. The cell of the representation of the first four subgroups is the primitive cell and of the remaining six is the $2 \times 2 \times 2$ cell. The duplicate subgroups, identified using spglib [11], when only the Wyckoff positions originating from the 1a, 1b and 3c positions in the parent group are occupied, actually have higher symmetry and fall back in one of the subgroups of Table S1, reported in the right-most columns. For these duplicate subgroups, there are 12 in which only the oxygens have degrees of freedom, and 3 in which the A and/or B sites have degrees of freedom. We report the subgroup using the international short symbol; the subgroup number followed by the subgroup index (in square brackets); the transformation matrix T_x ; and the splittings of the three relevant Wyckoff positions. T_x is defined as the transformation from the primitive cell to the $2 \times 2 \times 2$ cell (with matrix equal to twice the identity), and with an origin shift (x, x, x) . For the four subgroups with primitive cell representations, the transformation matrix is trivial. The reported subgroup index and transformation matrix, in all cases, is given with respect to the parent group $\text{Pm}\bar{3}\text{m}$ (221) with the 1a, 1b, and 3c positions occupied.

Group	[Index]	T_x	1a	1b	3c	Equivalent group	[Index]	T_x
Trivial subgroups								
$\text{P}\bar{4}3\text{m}$	(215)	[2]	1a	1b	3c	$\text{Pm}\bar{3}\text{m}$	(221)	[1]
$\text{P}432$	(207)	[2]	1a	1b	3c	$\text{Pm}\bar{3}\text{m}$	(221)	[1]
$\text{Pm}\bar{3}$	(200)	[2]	1a	1b	3c	$\text{Pm}\bar{3}\text{m}$	(221)	[1]
$\text{P}23$	(195)	[4]	1a	1b	3c	$\text{Pm}\bar{3}\text{m}$	(221)	[1]
$\text{Fm}\bar{3}\text{c}$	(226)	[2]	T_0 8a	8b	24d	$\text{Pm}\bar{3}\text{m}$	(221)	[1]
$\text{Fm}\bar{3}\text{c}$	(226)	[2]	$T_{1/2}$ 8b	8a	24c	$\text{Pm}\bar{3}\text{m}$	(221)	[1]
$\text{Fm}\bar{3}\text{m}$	(225)	[2]	T_0 4a 4b	8c	24d	$\text{Pm}\bar{3}\text{m}$	(221)	[1]
$\text{F}\bar{4}3\text{c}$	(219)	[4]	T_0 8a	8b	24c	$\text{Pm}\bar{3}\text{m}$	(221)	[1]
$\text{F}432$	(209)	[4]	T_0 4a 4b	8c	24d	$\text{Pm}\bar{3}\text{m}$	(221)	[1]
$\text{Fm}\bar{3}$	(202)	[4]	T_0 4a 4b	3c	24d	$\text{Pm}\bar{3}\text{m}$	(221)	[1]
Duplicate subgroups, only oxygen degrees of freedom								
$\text{Pn}\bar{3}\text{m}$	(224)	[8]	$T_{1/2}$ 4b 4c	2a 6b	12g 12h	$\text{Im}\bar{3}\text{m}$	(229)	[4] $T_{1/2}$
$\text{Pm}\bar{3}\text{n}$	(223)	[8]	$T_{1/2}$ 8e	2a 6b	6c 6d 12f	$\text{Im}\bar{3}\text{m}$	(229)	[4] $T_{1/2}$
$\text{Pn}\bar{3}\text{n}$	(222)	[8]	T_0 8c	2a 6b	12e 12d	$\text{Im}\bar{3}\text{m}$	(229)	[4] $T_{1/2}$
$\text{Pn}\bar{3}\text{n}$	(222)	[8]	$T_{1/2}$ 2a 6b	8c	12e 12d	$\text{Im}\bar{3}\text{m}$	(229)	[4] T_0
$\text{F}\bar{4}3\text{m}$	(216)	[4]	T_0 4a 4b	4c 4d	24g	$\text{Fm}\bar{3}\text{m}$	(225)	[2] $T_{1/2}$
$\text{I}432$	(211)	[8]	$T_{1/2}$ 8c	2a 6b	12e 12d	$\text{Im}\bar{3}\text{m}$	(229)	[4] T_0
$\text{I}432$	(211)	[8]	T_0 2a 6b	8c	24h	$\text{Im}\bar{3}\text{m}$	(229)	[4] $T_{1/2}$
$\text{F}432$	(209)	[4]	T_0 2a 6b	8c	24e	$\text{Fm}\bar{3}\text{m}$	(225)	[2] $T_{1/2}$
$\text{P}4_232$	(208)	[16]	$T_{1/2}$ 4b 4c	2a 6d	6e 6f 12d	$\text{Im}\bar{3}\text{m}$	(229)	[4] $T_{1/2}$
$\text{Fm}\bar{3}$	(202)	[4]	$T_{1/2}$ 8c	4a 4b	24e	$\text{Fm}\bar{3}\text{m}$	(225)	[2] $T_{1/2}$
$\text{Pn}\bar{3}$	(201)	[16]	T_0 4b 4c	2a 6d	12f 12g	$\text{Im}\bar{3}$	(204)	[8] $T_{1/2}$
$\text{F}23$	(196)	[8]	T_0 4a 4b	4c 4d	24g	$\text{Fm}\bar{3}\text{m}$	(225)	[2] $T_{1/2}$
Duplicate subgroups, A and/or B site degrees of freedom								
$\text{P}\bar{4}3\text{n}$	(218)	[16]	$T_{1/2}$ 8e	2a 6b	6c 6d 12f	$\text{I}\bar{4}3\text{m}$	(217)	[8] $T_{1/2}$
$\text{P}432$	(207)	[16]	$T_{1/2}$ 8g	1a 1b 3c 3d	6e 6f 12h	$\text{Pm}\bar{3}\text{m}$	(221)	[8] $T_{1/2}$
$\text{P}432$	(207)	[16]	T_0 1a 1b 3c 3d	8g	12i 12j	$\text{Pm}\bar{3}\text{m}$	(221)	[8] T_0

4. ENERGY BARRIERS

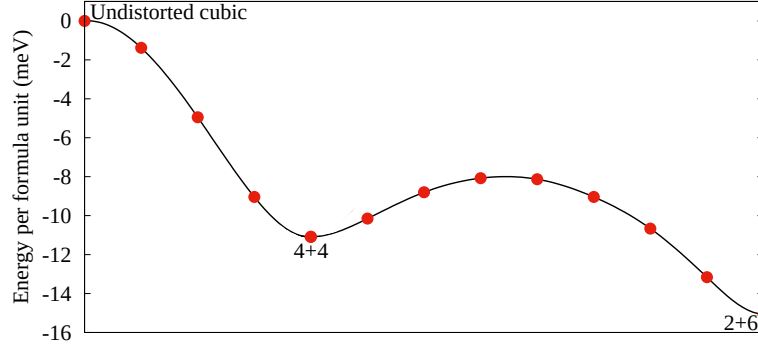


FIG. S1. Potential energy landscape calculated via two nudged-elastic-band calculations between the undistorted cubic BaTiO_3 (used as the reference energy) and the relaxed 4+4 structure, and between the relaxed 4+4 and 2+6 structures. The calculations show that the barrier between the 4+4 and 2+6 structures is lower than the energy difference with respect to the undistorted cubic BaTiO_3 . We note that the non-centrosymmetric lower-temperature phases of BaTiO_3 , associated with the polar instability Γ_4^- are lower in energy than the 4+4 and 2+6 structural prototypes.

5. UNSTABLE BaTiO_3 MODES AND DECOMPOSITION OF THE STABLE PROTOTYPES

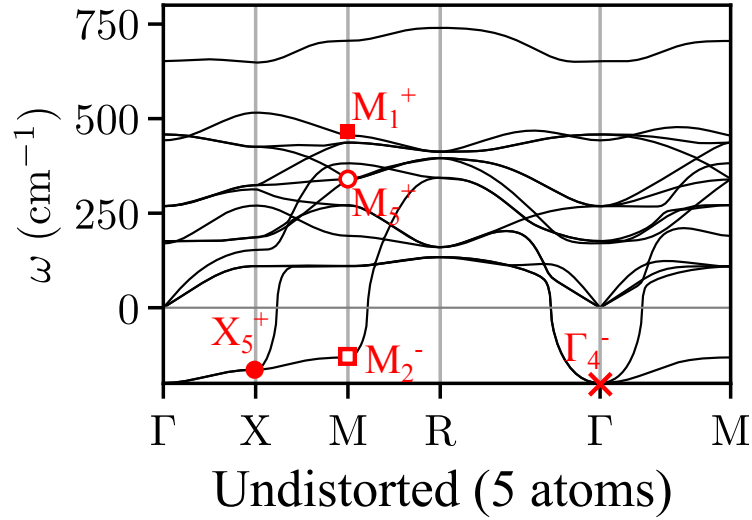


FIG. S2. Phonon dispersion of the 5-atom primitive cubic cell, displaying unstable phonon modes. The high-symmetry Γ_4^- , X_5^+ and M_2^- instabilities are marked in red with a cross, a filled circle and an empty square, respectively. Furthermore the M_1^+ and M_5^+ modes which occur in the 4+4 and 2+6 stable prototypes, respectively, are marked with a red filled square and an open circle.

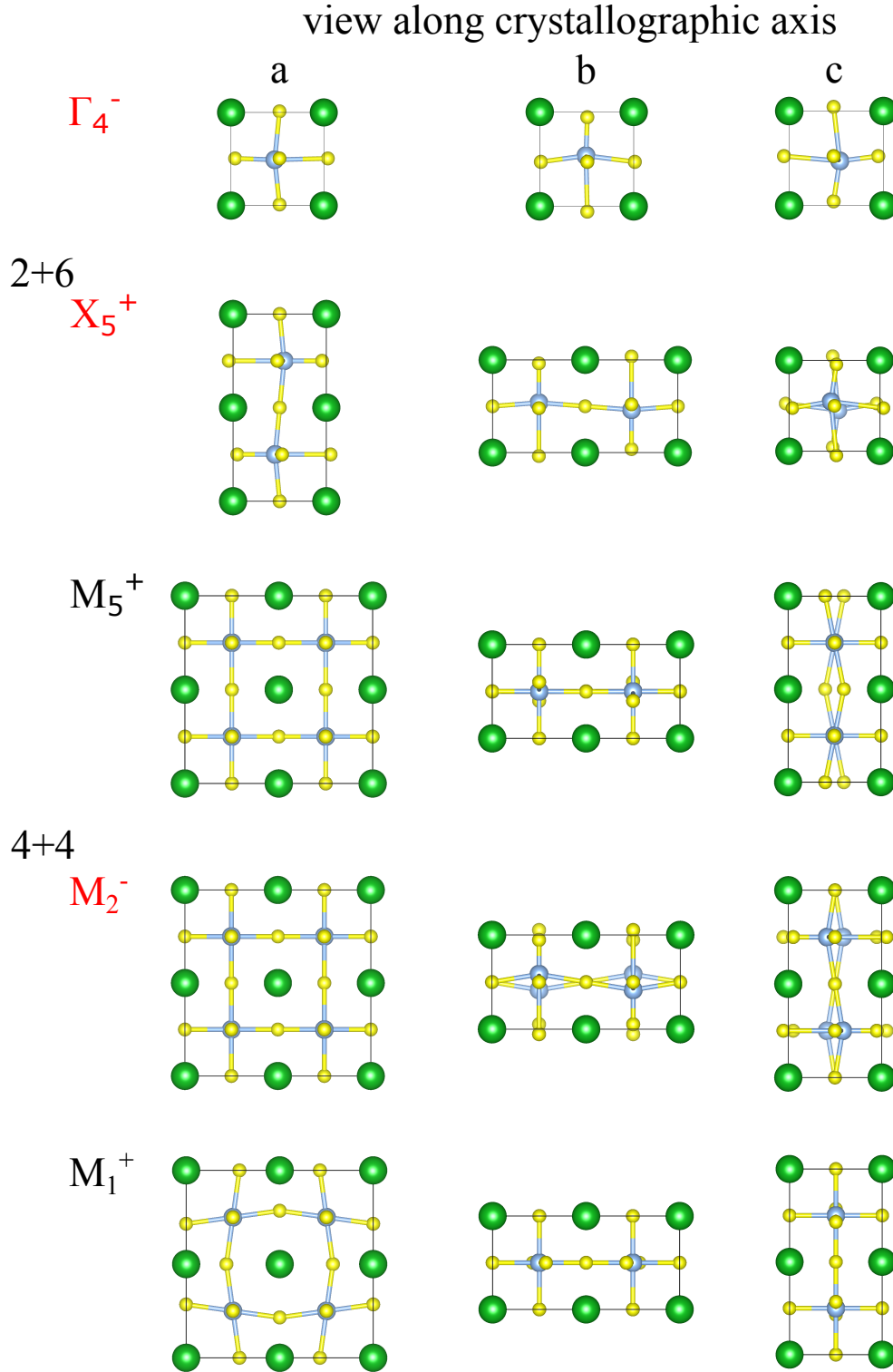


FIG. S3. The displacement patterns associated with the unstable Γ_4^- , M_2^- , and X_5^+ modes (labelled in red) as well as the M_1^+ and M_5^+ modes which occur in the 4+4 and 2+6 stable prototypes, respectively - each labelled in the preceding figure. Each mode is shown in its own primitive cell. We note that the Γ_4^- , X_5^+ , and M_5^+ modes are all two-fold degenerate. All data (inputs and outputs) from our self-consistent DFT calculations as well as the DFPT phonon calculations are available in a Materials Cloud Archive entry at the following DOI: <https://doi.org/10.24435/materialscloud:pg-50>, within the file `materials_5atom_phonon.zip` file, in the directory `materials_5atom_phonon/BaTiO3/3.98`; the displacement patterns associated with these phonon modes can be visualized in an interactive manner, using the “Interactive phonon visualizer” tool on the Materials Cloud, available at the following address: <https://www.materialscloud.org/work/tools/interactivephonon>.

6. DOUBLE-WELL MODEL FOR DISPLACEMENT PATTERN ONSET IN BARIUM TITANATE

Using a simple double-well model we can fit the Ti displacement as a function of volume. Assuming a simple double-well potential where the central point is the undistorted cubic structure and the minima of the wells correspond to the 4+4 (or 2+6) metastable structure, we define

$$E(x) = A(V)x^2 + B(V)x^4, \quad (1)$$

where E is the total energy (with the zero set at the energy of the undistorted structure), x is the set of coordinates that takes the undistorted structure to the metastable state (we will use here the magnitude of Ti displacements), and the coefficients A and B depend on the volume of the system. Solving for the stationary points of Eq. (1), we can find the minima at $(\tilde{x}(V), \tilde{E}(V))$, and then invert the solutions to obtain:

$$A(V) = 2\tilde{E}/\tilde{x}^2, \quad B(V) = -\tilde{E}/\tilde{x}^4. \quad (2)$$

From our DFT results of the relaxed displacement patterns as a function of lattice parameter (or, equivalently, volume) we can extract values for $\tilde{x}(V)$, and the corresponding total energy $\tilde{E}(V)$, and thus obtain data points for $A(V)$ and $B(V)$ as a function of the volume from Eq. (2). These are reported in Fig. S4a,b (Fig. S5a,b) for the 4+4 (2+6) displacement pattern. Because of the dependence of the data points, we fit them with the following functional forms: $A(V) = A_0 \cdot (V - V_0)$ (with A_0 and V_0 two constants) and $B(V)$ with a constant B_0 ; the resulting fits are reported in the plots (as well as $a_0 = \sqrt[3]{V_0}$, for convenience). In Fig. S4c (Fig. S5c) we then report the data for $\tilde{x}$ as a function of $\tilde{V}$ for the 4+4 (2+6) pattern, where the solid line is the analytical expression for $\tilde{x}(V) = \sqrt{A_0(V - V_0)/2B_0}$ (for $V > V_0$), obtained using the fitted values for A_0 , V_0 and B_0 in panels a and b, that reproduces very well the DFT data points. Similarly, in Fig. S4d (Fig. S5d) we plot the energy difference $\tilde{E}$ of the 4+4 (2+6) pattern with respect to the undistorted structure, and the corresponding analytical curve $\tilde{E} = -A_0^2(V - V_0)^2/4B_0$ (for $V > V_0$).

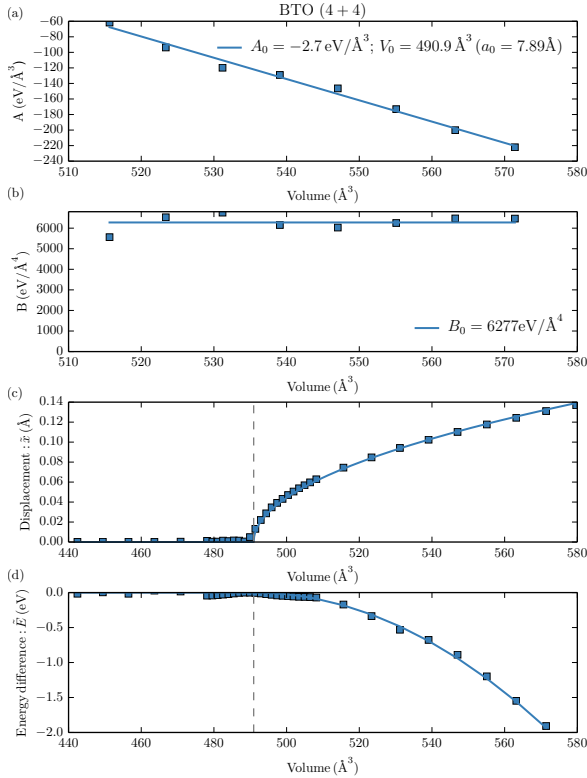


FIG. S4. Double-well model for the 4+4 displacement pattern. (a) Fit of $A(V) = A_0 \cdot (V - V_0)$; (b) fit of $B(V) = B_0$; (c) displacement $\tilde{x}(V)$ and analytical expression using the fit parameters from panels a and b; and, (d) energy difference $\tilde{E}(V)$ of the relaxed displacement patterns w.r.t. the undistorted structure.

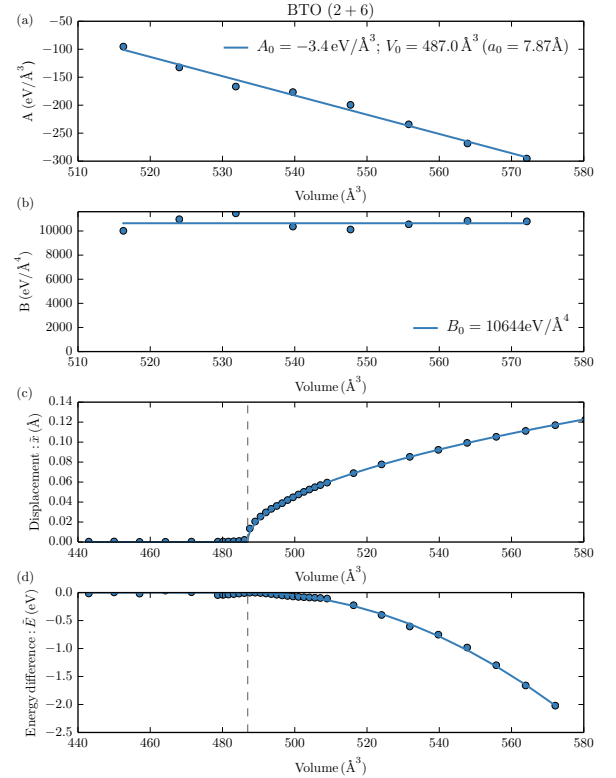


FIG. S5. Double-well model for the 2+6 displacement pattern. (a) Fit of $A(V) = A_0 \cdot (V - V_0)$; (b) fit of $B(V) = B_0$; (c) displacement $\tilde{x}(V)$ and analytical expression using the fit parameters from panels a and b; and, (d) energy difference $\tilde{E}(V)$ of the relaxed displacement patterns w.r.t. the undistorted structure.

7. TITANIUM DISPLACEMENT ACROSS THE TITANATE FAMILY, AND RELATION TO THE PHONON MODE INSTABILITIES

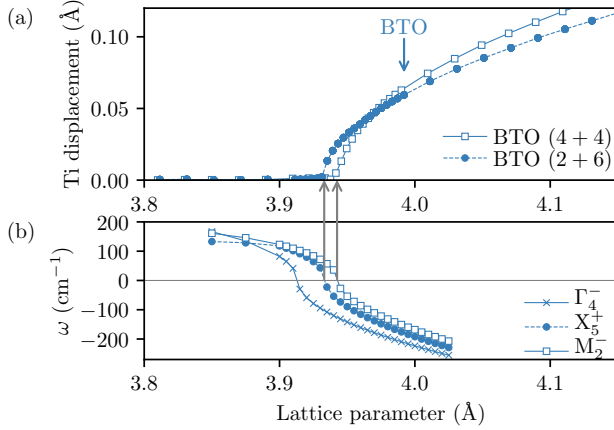


FIG. S6. Same as Fig. 3 in the main text. (a) Magnitude of the displacement of the Ti atoms along one Cartesian coordinate for the 4+4 and 2+6 displacement patterns in BaTiO₃. (b) Plot of the unstable phonon modes of BaTiO₃ with irreducible representation (irrep) Γ_4^- , X_5^+ and M_2^- in the 5-atom undistorted cubic cell as a function of the lattice parameter.

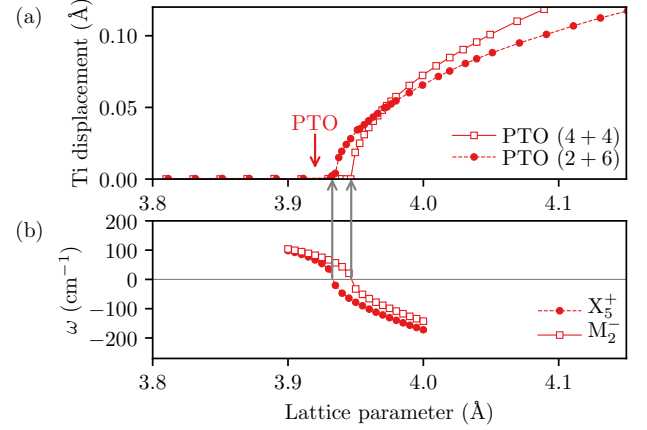


FIG. S7. Same analysis for PbTiO₃ as in Fig. S6: (a) Magnitude of the displacement of the Ti atoms along one Cartesian coordinate for the 4+4 and 2+6 displacement patterns in PbTiO₃. (b) Plot of the unstable phonon modes of PbTiO₃ with irrep X_5^+ and M_2^- in the 5-atom undistorted cubic cell as a function of the lattice parameter.

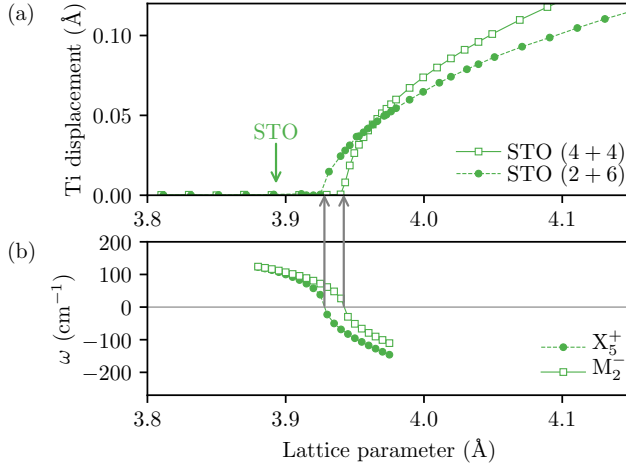


FIG. S8. Same analysis for SrTiO₃ as in Fig. S6: (a) Magnitude of the displacement of the Ti atoms along one Cartesian coordinate for the 4+4 and 2+6 displacement patterns in SrTiO₃. (b) Plot of the unstable phonon modes of SrTiO₃ with irrep X_5^+ and M_2^- in the 5-atom undistorted cubic cell as a function of the lattice parameter.

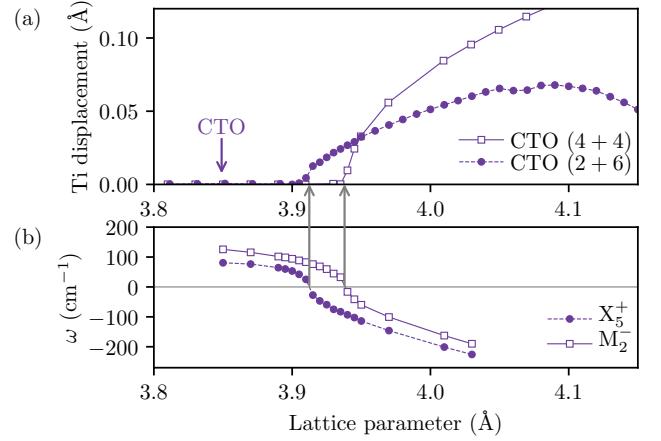


FIG. S9. Same analysis for CaTiO₃ as in Fig. S6: (a) Magnitude of the displacement of the Ti atoms along one Cartesian coordinate for the 4+4 and 2+6 displacement patterns in CaTiO₃. (b) Plot of the unstable phonon modes of CaTiO₃ with irrep X_5^+ and M_2^- in the 5-atom undistorted cubic cell as a function of the lattice parameter. The non-monotonicity of the Ti displacement for the 2+6 ordering is discussed in Fig. S10.

We explore the stability of the 4+4 and 2+6 displacement patterns for other perovskite oxides of the titanate family, namely PbTiO₃, SrTiO₃, and CaTiO₃. For the sake of completeness, we include here also Fig. S6 with the results for BaTiO₃, i.e., the same as Fig. 3 of the main text. These figures show that the 4+4 (2+6) displacement pattern onset coincides with the lattice parameter at which the M_2^- (X_5^+) irrep of the 5-atom undistorted cubic cell becomes unstable, indicated by the gray arrows. For clarity, these figures do not include other zone-boundary phonon modes that are unstable within this range of lattice parameters; however, they are discussed in the material-specific sections

below. The Γ_4^- irrep does not have any cubic subgroups and, therefore, does not correspond to a metastable cubic structure, so we omit it from the other plots.

A. Lead titanate

At the equilibrium lattice constant of cubic PbTiO_3 computed with PBEsol (3.93Å), we find unstable zone-boundary phonons at $q = \text{M}$ and R as well as an unstable zone-center mode. These modes, omitted from Fig. S7 as they are not involved in the 4+4 or 2+6 displacement patterns, transform with the symmetry of irreps M_2^+ , R_5^- , and Γ_4^- , respectively. The irreps at R and Γ have no cubic subgroups, and the mode that transforms as M_2^+ is dominated by oxygen. Using instead a lattice constant of 3.97Å (the experimental cubic lattice parameter for the cubic phase, stable at temperatures higher than 763K [19]), we find additional unstable phonons at $q = \text{X}$ and M that transform like X_5^+ and M_2^- , respectively (like for BaTiO_3). These are the modes that are present in the 2+6 and 4+4 displacement patterns, respectively. As for BaTiO_3 , the Ti displacement onset for the 2+6 (4+4) displacement patterns correlates with the X_5^+ (M_2^-) mode becoming unstable, see arrows in Fig. S7. The stability of the 4+4 and 2+6 displacement patterns at the experimental lattice parameter of cubic PbTiO_3 suggests that the Ti atoms will displace along the $\langle 111 \rangle$ directions and is consistent with the non-negligible degree of order-disorder that has been observed experimentally [20–24]. As we continue to increase the lattice constant we find that additional modes become unstable, in particular the ones transforming like M_5^- (at $\sim 3.975\text{\AA}$) and like X_5^- (at $\sim 4.00\text{\AA}$).

B. Strontium titanate

At the equilibrium lattice constant of cubic SrTiO_3 computed with PBEsol (3.89Å), we find unstable zone-boundary phonons at $q = \text{M}$ and R as well as an unstable zone-center mode. These modes, again omitted from Fig. S8 as they are not involved in the 4+4 or 2+6 displacement patterns, transform with the symmetry of irreps M_2^+ , R_5^- , and Γ_4^- respectively. Again we show that the Ti displacement onset for the 2+6 (4+4) displacement patterns correlates with the X_5^+ (M_2^-) mode becoming unstable, see arrows in Fig. S8.

C. Calcium titanate

At the equilibrium lattice constant of cubic CaTiO_3 computed with PBEsol (3.85Å), we find unstable zone-boundary phonons at $q = \text{M}$ and R as well as an unstable zone-center mode. These modes, again omitted from Fig. S9 as they are not involved in the 4+4 or 2+6 displacement patterns, transform with the symmetry of irreps M_2^+ , M_5^- , R_5^- , and Γ_4^- respectively. The displacement pattern associated with R_5^- has no cubic subgroups, while the unstable M modes do correspond with cubic subgroups. The displacement pattern associated with M_2^+ only involves motion of the oxygen atoms; the displacement pattern associated with M_5^- involves all of the atoms; however, the displacements of the calcium and oxygen are more pronounced than the displacement of the titanium. This implies that, in the paraelectric phase, displacements from the high-symmetry structure would be dominated by the oxygen and calcium with only a small contribution from the titanium. This is not surprising as the tolerance factor of CaTiO_3 is well below 1 and has a well-known $Pbnm$ (spacegroup 62) orthorhombic phase that can be constructed through a linear combination of the M_2^+ and R_5^- modes. It is worth noting that, according to the M_5^- mode, the titanium atoms are still restricted by symmetry to displace along the local $\langle 111 \rangle$ directions. Again we show that the Ti displacement onset for the 2+6 (4+4) displacement patterns correlates with the X_5^+ (M_2^-) mode becoming unstable, see arrows in Fig. S9. However, we see that the onset for the 2+6 pattern occurs at a smaller lattice parameter than the other titanates. Moreover, we see that as the lattice parameter increases, the titanium displacement reaches a maximum and then decreases, unlike all the other titanium displacement curves of the other titanates.

In contrast to the behavior of the Ti displacement as a function of the lattice parameter, the X_5^+ mode of the 5-atom primitive cell continues to soften monotonically, while at the same time, the other mode present in the structure (M_5^+ , which only displaces oxygen atoms), remains stable. Using ISODISTORT to analyze the symmetry of the distortion present in the 2+6 displacement patterns under larger tensile strain, we find that the displacement associated with the X_5^+ irrep (a six-dimensional irrep) becomes dominated by oxygen. In Fig. S10 we plot the supercell mode amplitude as a function of lattice parameter for the X_5^+ irrep present in the 2+6 (40-atom) structures. In green are the supercell mode amplitudes associated with the oxygen displacements that transform according to the A_{2u} (solid circles) and E_u (open squares) irreps of the point-group and in purple is the supercell mode amplitude associated with the titanium displacement. The total supercell X_5^+ mode amplitude, in blue, is the norm of the three components, i.e., the square root of the sum of each component squared. To convert from supercell mode amplitude $A_{s,\text{Ti}}$ plotted in Fig. S10 (as defined within the ISODISTORT [17, 18] program) to the titanium displacement Δx_{Ti} of Fig. S9 (the displacement

in Å from the cubic high-symmetry position along one coordinate), the following prescription is used:

$$\Delta x_{\text{Ti}} = A_{s,\text{Ti}} \cdot a_s \cdot n = A_{s,\text{Ti}} / \sqrt{m},$$

$$n = 1 / \sqrt{m \cdot a_s^2},$$

where a_s is the supercell lattice parameter (*i.e.*, the lattice parameter of the $2 \times 2 \times 2$ supercell), n is a normalization factor, and m is the number of components of the displacement pattern associated with the irrep. Here, the number components for the titanium displacements is 24: the 8 Ti atoms displace along all three components, so we have $m = 8 \cdot 3 = 24$.

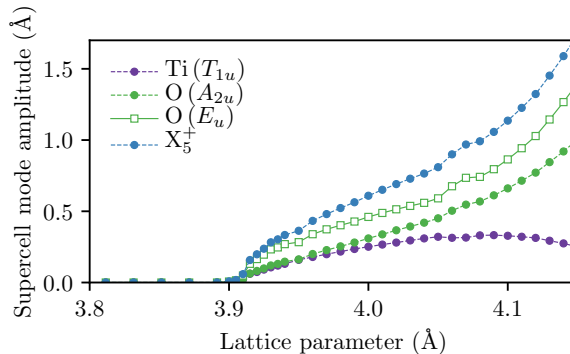


FIG. S10. The supercell mode amplitude for the X_5^+ irrep and its Ti and O components present in the 2+6 (40-atom) structures.

8. STABILITY OF THE 4+4 AND 2+6 MICROSCOPIC TEMPLATES ACROSS A FAMILY OF 49 PEROVSKITES AT RELAXED VOLUME

To investigate the universality of the paraelectric phases in other cubic perovskites, we explore the stability of the 4+4 and 2+6 orderings for the entire set of perovskites in the work of Armiento *et al.* [25]. The Goldschmidt tolerance factor t [19, 26], defined as

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)},$$

where r_i are the atomic radii of the A-site cation, the B-site cation or the oxygen anion. We calculate the tolerance factor using the ionic radii from Ref. 27 taken from the database hosted on Ref. 28. In cases where the ionic radii for the relevant oxidation state or coordination number was not available, we used the closest one.

In materials where the 4+4 and 2+6 prototypes are significantly lower in energy, the tolerance factor is $t \gtrsim 1.1$, and in materials where only the 2+6 prototype significantly lowers the energy, the tolerance factor is $t \lesssim 0.9$ (Fig. S11). Specifically, Cs-based compounds have $t > 1.1$; Rb-based compounds have $t \approx 1.1$; Ca-based compounds have $t \approx 0.84 - 0.9$; Li-based compounds have $t \approx 0.8$; Cu-based compounds have $t < 0.8$; and BiScO_3 has $t \approx 0.7$. Note that a number of compounds stabilize the 2+6 and 4+4 prototypes, but the energy gain is quite modest, such as BaTiO_3 or KNbO_3 . In these cases we do not find a general trend of the tolerance factors. Moreover, many of the silicates, that have a tolerance factor less than 0.9 or greater than 1.1, do not stabilize neither the 4+4 nor the 2+6 orderings further supporting the fact that we cannot predict what prototypes will be stable or not from the tolerance factor alone.

We find that these large energy gains correlate with the change in lattice parameter between the cubic cell without displacements and the one with displacements; however, the energy gain is not due to the change in lattice parameter alone, and a significant energy gain occurs even when the total volume is kept fixed. A better understanding of the behavior of these systems can be obtained by investigating the occurrence of stable displacements as a function of the system volume, see Fig. S12.

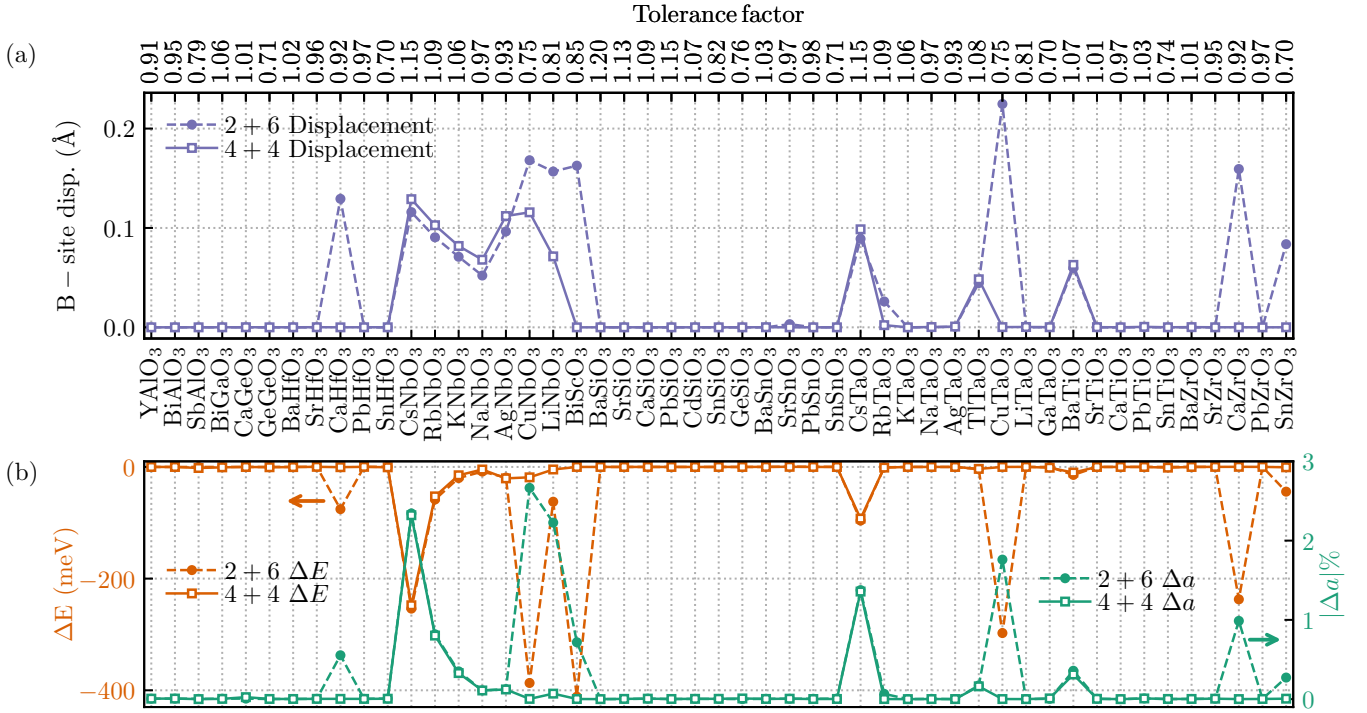


FIG. S11. Occurrence of cubic-symmetry displacement patterns in $2 \times 2 \times 2$ supercells for the family of 49 perovskites from Armiento *et al.* [25]. Solid line: 4+4 displacement pattern; dashed line: 2+6 displacement pattern. The lattice parameter is fixed to that of the relaxed 5-atom cubic structure. The tolerance factor is given along the top axis (a) Off-site displacement of the B-site cation. (b) Energy difference per formula unit ΔE and relative lattice parameter change $|\Delta a|$, both with respect to the cubic cell without displacements.

9. STABILITY OF 4+4 AND 2+6 ORDERINGS IN THE NIOBATES, TITANATES AND ZIRCONATES AS A FUNCTION OF VOLUME

We investigate 12 different perovskites as a function of volume, focusing only on the 4+4 and 2+6 displacement patterns, to demonstrate the generality of the occurrence of local displacements in different perovskite families. The results are shown in Fig. S12

The phonon dispersion of cubic 5-atom KNbO_3 , which also stabilizes the 4+4 and 2+6 displacement patterns, has the same zone-center and zone-boundary instabilities [29] as BaTiO_3 at the equilibrium volume; however, the Nb off-centering as a function of volume does not match that of the titanates. In particular, for all niobates that we investigate here, also a volume compression can trigger the occurrence of local displacements, and there is a very narrow lattice parameter range (or even no range at all) in which displacements do not occur. This occurs as additional phonons become unstable under compression. We also present four zirconates, which have a different B-site displacement vs. volume relationship, where instead a compressive strain is needed to stabilize these two patterns, and at relaxed volume no displacements are stabilized (except for CaZrO_3 in the 2+6 pattern, where also an increasing volume stabilizes them, including at the relaxed volume). In all cases, we confirm that the volume dependence and stability of the structural prototypes in a given material cannot be inferred from equilibrium properties alone (like in Fig. S11), but a detailed understanding requires an analysis as a function of the system volume.

10. TITANIUM-DISPLACEMENT DEPENDENCE ON DFT FUNCTIONAL

The choice of the DFT functional essentially does not affect the magnitude of Ti displacements, as well as the onset as a function of the lattice parameter, for both the 4+4 and 2+6 displacement patterns; however, it does change the predicted equilibrium lattice constant (indicated by vertical arrows). In the figure we compare the PBEsol [3], PBE [30, 31], and LDA [32] functionals. The PBEsol equilibrium lattice parameter (at $T = 0$ K) is the closest to the experimental lattice constant (at finite temperature) of $\sim 4.01 \text{ \AA}$ [6, 19] of cubic BaTiO_3 (stable above ~ 390 K).

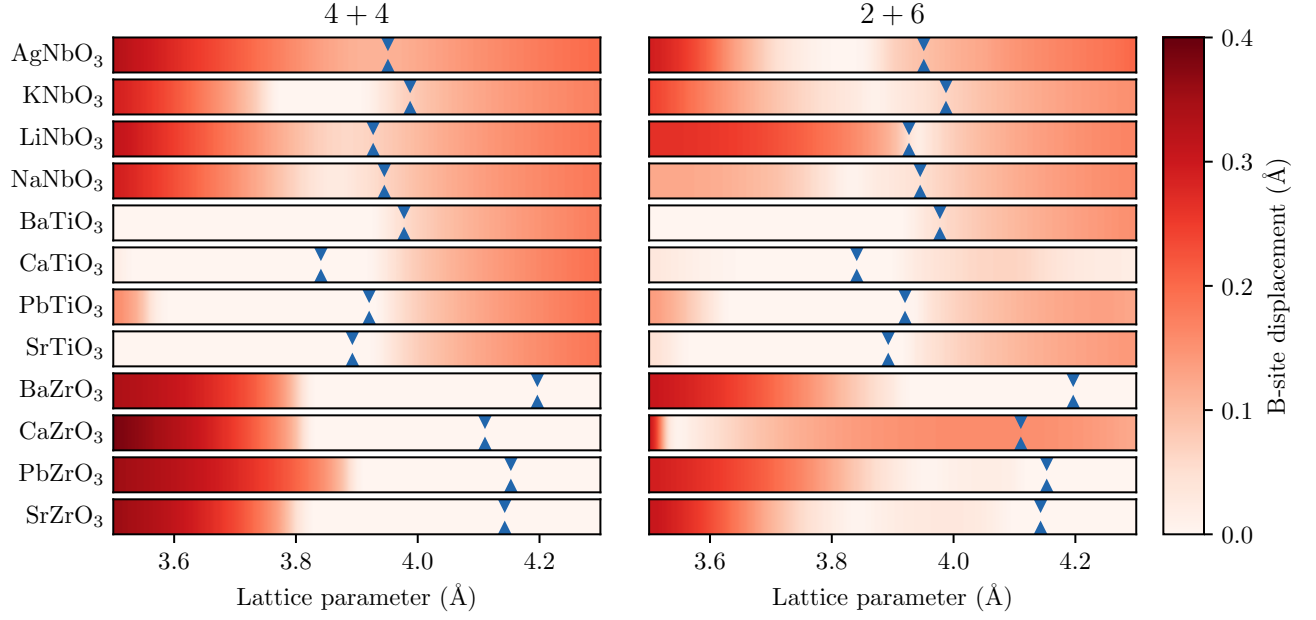


FIG. S12. The B-site displacement for the 4+4 and 2+6 displacement patterns for selected members of the niobates, titanates and zirconates as a function of the lattice parameter. The titanates are included here as well for comparison (same results reported earlier in Sec. 7, here with a different graphical representation). The equilibrium lattice parameter (calculated with PBEsol) is indicated by the blue markers.

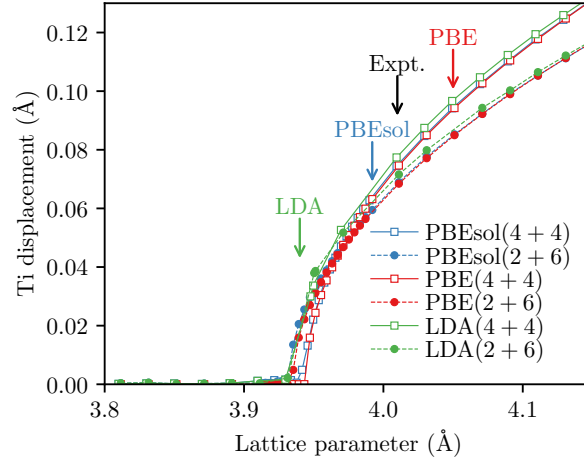


FIG. S13. Onset of the cubic-phase instabilities as a function of the lattice parameter for the 4+4 and 2+6 structures of BaTiO₃ using the PBEsol, PBE and LDA functionals. The relaxed lattice parameter for each functional in its lowest-energy cubic configuration is indicated by an arrow.

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