

Spontaneous Octahedral Tilting in the Cubic Inorganic Cesium Halide Perovskites CsSnX_3 and CsPbX_3 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$)

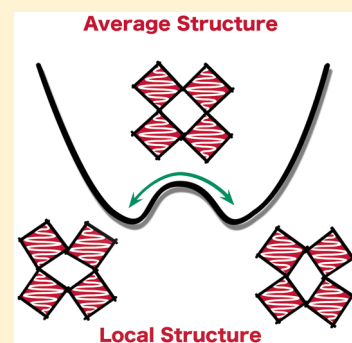
Ruo Xi Yang,^{†,‡} Jonathan M. Skelton,^{†,§} E. Lora da Silva,[†] Jarvist M. Frost,^{†,‡} and Aron Walsh^{*,‡,§,ⓓ}

[†]Department of Chemistry, University of Bath, Claverton Down BA2 7AY, United Kingdom

[‡]Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, United Kingdom

[§]Department of Materials Science and Engineering, Yonsei University, Seoul 03722, Korea

ABSTRACT: The local crystal structures of many perovskite-structured materials deviate from the average space-group symmetry. We demonstrate, from lattice-dynamics calculations based on quantum chemical force constants, that all of the cesium–lead and cesium–tin halide perovskites exhibit vibrational instabilities associated with octahedral tilting in their high-temperature cubic phase. Anharmonic double-well potentials are found for zone-boundary phonon modes in all compounds with barriers ranging from 108 to 512 meV. The well depth is correlated with the tolerance factor and the chemistry of the composition, but is not proportional to the imaginary harmonic phonon frequency. We provide quantitative insights into the thermodynamic driving forces and distinguish between dynamic and static disorder based on the potential-energy landscape. A positive band gap deformation (spectral blue shift) accompanies the structural distortion, with implications for understanding the performance of these materials in applications areas including solar cells and light-emitting diodes.



Since the discovery of photoconductivity in the cesium–lead halides (CsPbX_3 ; $\text{X} = \text{Cl}, \text{Br}, \text{I}$),¹ the semiconducting properties of halide perovskites have attracted significant research attention, including analogous compounds based on tin.^{2,3} Interest has since expanded to the hybrid organic–inorganic perovskites, with applications ranging from field-effect transistors⁴ to photovoltaics^{5,6} and light-emitting diodes.⁷ This family of materials displays a unique combination of physical and chemical properties, including fast ion and electron transport, long minority-carrier diffusion lengths, and high quantum efficiencies.

The crystallography of halide perovskites dates back to the 1950s, where the high-temperature crystal structures of the CsPbX_3 series were determined to be the prototypical cubic perovskite structure (space group $Pm\bar{3}m$).¹ The crystal structure consists of Cs in a cuboctahedral cavity at the center of a corner-sharing lead halide octahedral network. The same high-temperature cubic structure was also reported for the organic–inorganic $\text{CH}_3\text{NH}_3\text{PbX}_3$ series.⁸ In all cases, phase transitions to lower symmetry perovskite phases are observed at lower temperatures; for example, in CsPbCl_3 there is a transition to a tetragonal phase at 320 K, an orthorhombic phase at 316 K, and a monoclinic phase at 310 K.⁹

In the 1970s, Poulsen et al. determined the room-temperature structure of CsSnCl_3 to be monoclinic ($P2_1/n$ type) and identified a phase transition to a higher-symmetry structure at 393 K.¹⁰ An X-ray diffraction (XRD) study of CsSnBr_3 determined the structure to be cubic at room temperature, but symmetry lowering was observed as the temperature was reduced.¹¹ More recently, temperature-dependent synchrotron XRD experiments determined CsSnI_3

to be cubic at 500 K, with tetragonal and orthorhombic phases observed at lower temperatures.³ It was suggested that the phase transitions are associated with the $5s^2$ lone electron pair of Sn and the consequential distortion of the corner-sharing octahedral metal halide framework.

Despite numerous crystallographic studies on lead- and tin-based perovskites, the nature of the high-temperature cubic phases of these compounds has received less attention. Analysis of the X-ray pair distribution functions of $\text{CH}_3\text{NH}_3\text{SnBr}_3$ suggested that the local cubic symmetry was broken, with significant distortions of the octahedral network.¹² It was recently confirmed from both inelastic X-ray scattering and neutron total scattering that the cubic phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$ is also symmetry-broken.^{13,14} These observations have been associated with the rotational disorder of the molecular CH_3NH_3^+ cation. For inorganic halide perovskites, this molecular disorder is absent, and instead the disorder in the cubic inorganic halide perovskites should be due solely to the flexibility associated with the inorganic octahedral network.

It is also interesting to note that many quantum dots and nanoparticles of halide perovskites have been reported to adopt a cubic structure at room temperature.^{15,16} It was unclear initially whether the stability of the cubic phase was due to surface effects, lattice strain, or phonon confinement. However, a recent X-ray total scattering study of colloidal CsPbX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) nanocrystals provided the first evidence that the local

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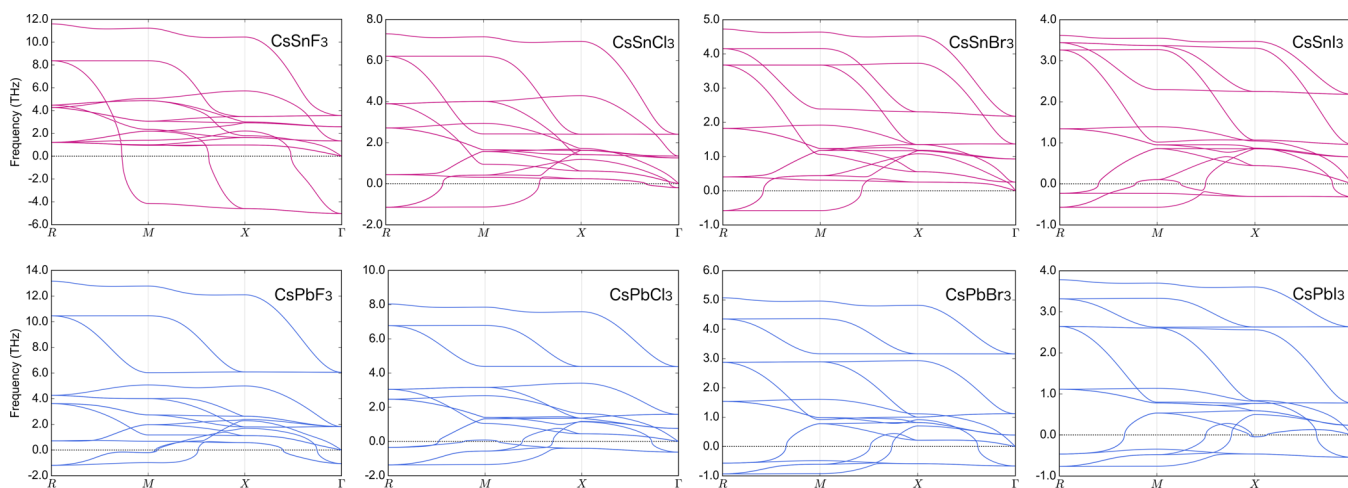
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Table 1. Comparison of Known Inorganic Halide Perovskite Phases and the Temperature at Which the Phases Are Observed for Each Composition

	cubic ($Pm\bar{3}m$) (K)	tetragonal ($P4/mbm$)	orthorhombic ($Pnma$) (K)	monoclinic ($P2_1/n$) (K)
CsSnF ₃				
CsSnCl ₃	293 ¹¹			<293 ¹¹
CsSnBr ₃	292, ²⁸ 300 ³¹	270 ³¹	100 ³¹	<292 ²⁸
CsSnI ₃	500, ³ 446 ³²	380, ³ 373 ³²	300 ^{3,32}	
CsPbF ₃	186 ²⁹			
CsPbCl ₃	320 ⁹	315 ⁹	310 ⁹	<310 ⁹
CsPbBr ₃	403 ³³	361 ³³	<361 ³³	
CsPbI ₃	634 ²⁷		298 ²⁷	

**Figure 1.** Harmonic phonon dispersion of ABX₃ compounds in the cubic perovskite structure. The labels correspond to special points in the vibrational Brillouin zone: Γ (0, 0, 0), $X(\frac{1}{2}, 0, 0)$, $M(\frac{1}{2}, \frac{1}{2}, 0)$, and $R(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Imaginary frequencies are represented by negative numbers on the y axis for convenience of plotting.

structure is not cubic but consists of domains with orthorhombic tilting.¹⁷

In this Letter, we demonstrate that spontaneous octahedral tilting is common to cesium–lead and cesium–tin halide perovskites. Through first-principles lattice-dynamics calculations, we assess the chemical and thermodynamic driving forces for these instabilities. Double-well potentials are found for “soft” phonon modes in all cases, with barrier heights ranging from 108 to 512 meV. We also show that octahedral tilting results in a positive band gap deformation, indicating that local symmetry breaking would lead to a larger band gap than anticipated from the regular cubic perovskite structure.

Octahedral Tilting in Perovskites. The aristotype cubic ABX₃ perovskite structure is usually only observed at high temperature, while at lower temperatures a group of lower symmetry phases, including tetragonal, orthorhombic, monoclinic, and rhombohedral, is found. With reference to the cubic phase, the associated phase transitions are driven by a range of symmetry-breaking lattice distortions. The phase diversity of perovskites can be qualitatively explained using the concept of the tolerance factor introduced by Goldschmidt,¹⁸ where

$$\alpha = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (1)$$

with r_A , r_B , and r_X are the ionic radii for the A, B, and X atoms, respectively. Values of $\alpha < 1$ are usually associated with octahedral tilting due to the A cation being smaller than is optimal for bonding with the BX₃ framework. This is the case

for the majority of compounds considered here, which explains the experimentally observed orthorhombic ($Pnma$) ground-state structures of CsPbCl₃ and CsSnI₃.^{3,19}

Glazer developed a simple classification system to describe the octahedral tilting in perovskites and to relate it to phase transitions.²⁰ In the Glazer notation, octahedral tilting is described as a linear combination of in-phase and out-of-phase rotations along the three crystallographic axes. For example, the notation $a^0b^-c^-$ indicates two out-of-phase tilts along the [010] and [001] directions (b and c axes) with distinct tilt angles. Stokes et al. provided a group-theoretical description of the relationships between different tilt systems and also considered B cation displacements within the octahedra,^{21,22} where the distortion is expressed with irreducible representations such as M_3^+ or R_4^+ . For example, the cubic ($Pm\bar{3}m$) to tetragonal ($P4/mbm$) phase transition of CsPbCl₃ can be described as $a^0a^0a^0 \rightarrow a^0a^0c^+$ tilting or, equivalently, as the condensation of an M_3^+ phonon mode.⁸ Woodward further provided insights into the stabilizing chemical forces based on the bonding environment and crystal structure (tolerance factor) of specific oxide compounds.^{23,24}

A search of the Inorganic Crystal Structure Database (ICSD),²⁵ summarized in Table 1, reveals that CsPbCl₃, CsPbBr₃, CsPbI₃, and CsSnI₃ adopt cubic phases (space group $Pm\bar{3}m$) above room temperature,^{3,19,26,27} while CsSnBr₃ and CsSnCl₃ have been reported to be cubic at room temperature (from XRD) and CsPbF₃ at 187 K (from neutron diffraction).^{11,28,29} Recently, low-frequency Raman spectroscopy has shown that the cubic phase of CsPbBr₃ determined by

XRD fluctuates on a short time scale between different lower symmetry phases, but appears to be cubic on average due to the dynamic structural flexibility, a phenomenon that could be present in other halide perovskites.³⁰

Harmonic Lattice Dynamics. We start by computing the harmonic phonon frequencies and dispersions for eight inorganic halide compounds ABX_3 ($A = \text{Cs}$; $B = \text{Sn, Pb}$; $X = \text{F, Cl, Br, I}$) in the cubic perovskite structure. Lattice dynamic calculations were performed using the open-source PHONO-PY³⁴ package with forces calculated within the Kohn–Sham density functional theory (DFT) formalism, as implemented in the VASP code.^{35,36} Particular attention was given to the convergence of the energy and forces, 1×10^{-8} eV and 1×10^{-3} eV/Å, respectively. Production calculations were performed with the exchange-correlation functional PBEsol^{37,38} using an $8 \times 8 \times 8$ sampling of the electronic Brillouin zone and a plane-wave cutoff of 800 eV. Projector augmented wave³⁹ core potentials (reciprocal space projection) were used with valence $4d^{10}5s^25p^2$ electrons on Sn, $6s^26p^2$ electrons on Pb, $5s^25p^66s^1$ electrons on Cs, and outmost ns^2np^5 electrons on halogen atoms (X). Input structures were built in the cubic perovskite structure $Pm\bar{3}m$ and the lattice volume was fully relaxed with fixed symmetry. The phonon frequencies and eigenvectors were determined by finite-displacement calculations with a step size of 0.01 Å, performed in $2 \times 2 \times 2$ supercell expansion of the cubic unit cell. An imaginary phonon frequency, demonstrated as negative frequency in the phonon band structure, indicates the presence of a structural instability; that is, the phase is not a true local minimum on the potential energy surface. The structure can distort along the pathway determined by the phonon eigenvector to lower the internal energy of the system. The energy landscape as a function of phonon distortion amplitude is obtained by the code ModeMap.^{40,41}

The phonon dispersion of all eight compositions displays imaginary frequencies (lattice instabilities) in the phonon Brillouin zones (Figure 1). Instabilities associated with tilting of the octahedra can be found at the Brillouin zone boundary (X , R , M special points). All compounds exhibit M -point instabilities. Excluding CsSnF_3 , all compounds also exhibit R -point instabilities, and five of the eight systems exhibit X -point instabilities, viz. CsSnF_3 , CsSnI_3 , CsPbCl_3 , CsPbBr_3 , and CsPbI_3 . These zone boundary distortions are by definition antiferroelectric in nature; that is, opposing polarization induced in neighboring unit cells cancels and no long-range spontaneous polarization is formed. In addition, all compounds excluding CsSnBr_3 (Figure 1c) exhibit Γ -point instabilities, which is a ferroelectric distortion that will not be considered further here.

The presence of vibrational instabilities across all compositions is consistent with the scarcity of experimentally observed cubic phases at low temperature (Table 1), as anharmonic processes at high temperature are required for dynamic stabilization of the phase. It is worth noting that from the present calculations, cubic CsSnBr_3 , which adopts a cubic structure close to room temperature, displays the smallest number of phonon instabilities among all of the considered compositions. However, the number of imaginary modes is not necessarily related to the energetic barriers associated with the phase transition, which is the subject of the following section.

Anharmonic Potential Energy Surface. By distorting the crystal structure along a phonon eigenmode, the change in potential energy as a function of distortion amplitude (Q) can be

obtained. For a harmonic phonon mode in an equilibrium structure, the change in energy with mode amplitude should be parabolic with the minimum at $Q = 0$. Double-well potential-energy surfaces are observed in each of the cubic perovskites studied here, which is consistent with anharmonic behavior that can be described within Landau's theory of phase transitions.⁴² The potential energy surface is well-fitted by a function of the form

$$E(Q) = aQ^2 + bQ^4 + O(Q^6) \quad (2)$$

where a and b are fitted coefficients, and the former corresponds to the square of the harmonic phonon frequency. For imaginary modes, representing structural instabilities, a will be negative as the energy surface forms a double well with $Q = 0$ as a saddle point.

Mapping and fitting the anharmonic potential energy surfaces provides access to a number of quantities, including the depth of the well (ΔE), the normal-mode coordinate of the local minima (ΔQ), and the curvature of the potential energy about $Q = 0$. The well depth ΔE determines the energy difference between the cubic and lower-symmetry structures represented by the distortion, and further dictates an upper limit to the transition rate between equivalent symmetry-broken distorted structures. ΔQ determines the degree of distortion that minimizes the potential energy. There are some caveats to this approach, as follows. The phonon eigenvector represents atomic motion by a three-component vector of orthogonal displacements, which cannot fully describe rotational motion. For soft modes involving octahedral tilting, at large Q , the mode eigenvector may no longer accurately reflect the atomic displacements. In practice, this means that a structure at the local minimum along the mode potential may undergo further relaxation if allowed to optimize freely, which would produce a larger energy barrier. Second, in the case of degeneracy, linear combinations of the eigenvectors are valid solutions to the harmonic problem, and so the mode eigenvectors are not uniquely defined. The “true” energy minimum may lie at a combination of the two. In high-symmetry structures, however, the displacement pathways may be fixed by crystal symmetry.

As all eight halide-perovskite compositions studied here exhibit singly degenerate soft modes at the M -point, we take this as a representative instability and investigate these imaginary modes further. The soft-mode potential wells of the eight compounds are plotted in Figure 2. To enable a direct comparison, the energy is calculated as a function of a normalized mode amplitude Q , such that the energy minima for each compound lie at $Q = \pm 1$. Across the CsPbX_3 series, the well depth increases (i.e., the distorted structure lowers in energy relative to the cubic phase) systematically from F to I, with the Cl and Br perovskites having similar depths. The same trends are evident in the CsSnX_3 family from Cl to I, while CsSnF_3 marks a notable exception, with a well depth comparable to those of the Cl and Br perovskites. In addition, CsPbX_3 appears to have deeper minima than CsSnX_3 in general (excluding the anomaly CsSnF_3).

Static or Dynamic Disorder. The rate of hopping between the symmetry equivalent local minima in the potential energy surface can be estimated in several ways. First, we consider a classical kinetic model to compute a hopping rate (Γ) for the structural transition

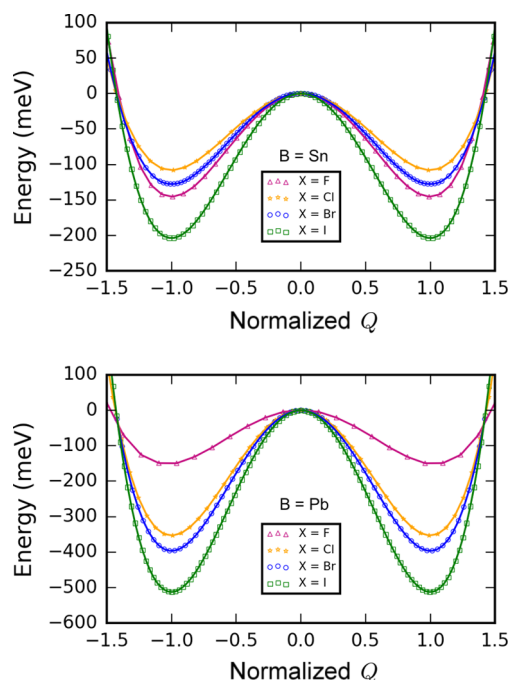


Figure 2. Double-well potential energy surface associated with the soft M -point modes in CsSnX_3 (top) and CsPbX_3 (bottom) from frozen-phonon calculations. The energy surface is calculated from DFT-PBEsol ($2 \times 2 \times 2$ supercell) and Q is the distortion amplitude. The energy zero refers to the undistorted structure. The high-symmetry cubic phase lies at $Q = 0$, and the distortion amplitude has been normalized so that the energetic minima lie at $Q = \pm 1$. The legend indicates the halide X in each composition.

$$\Gamma = \nu \exp\left(\frac{-\Delta E}{k_B T}\right) \quad (3)$$

where ν is the attempt frequency that is equivalent around the curvature of the double-well minima, k_B is the Boltzmann constant, and T is temperature. Alternatively, we can solve a Schrödinger equation for the double-well potential and define an effective harmonic frequency that reproduces the partition function of the anharmonic system. Here we follow the procedure of Skelton et al. that has previously been applied to SnSe .^{40,43} The temperature dependence of the renormalized harmonic frequency is shown for CsPbI_3 in Figure 3a. It is found that the frequencies calculated using the (athermal) classical and (finite temperature) quantum approaches are in good agreement subject to a scaling factor (shown in Figure 3b). At $T = 300$ K, the renormalization factor is 0.34, and the quantum solutions suggest a characteristic vibration of 0.5–3 THz depending on the chemical composition. The associated hopping rate for each compound is summarized in Table 2. We note that rates are based on a single anharmonic mode and neglect phonon–phonon interactions that could be considered using a higher level of theory, for example, a self-consistent phonon procedure.^{44–46}

For deeper wells, the transition between equivalent symmetry-broken local minima becomes less probable at a given temperature, giving rise to a slower hopping rate. Diffraction samples long-range order, within the penetration depth of the coherent beam. We assume that only if the transition rate between structures is < 1 Hz would the material phase segregate into macroscopically ordered domains. Such slow transitions are predicted for CsPbCl_3 , CsPbBr_3 , and

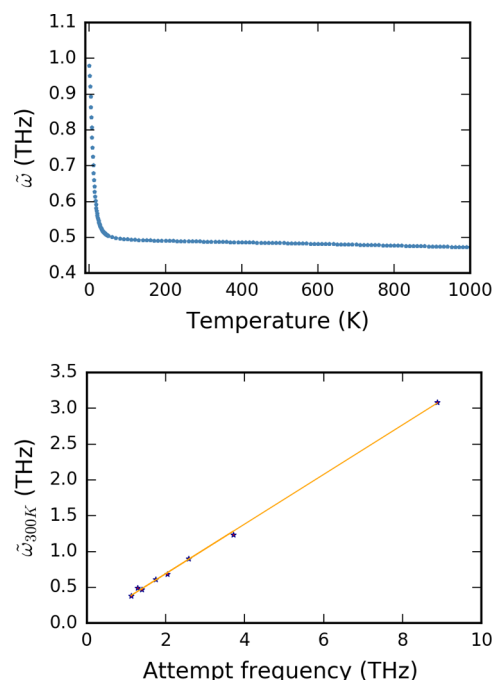


Figure 3. (top) Renormalized phonon frequency ($\tilde{\omega}$) for the M mode instability in CsPbI_3 from a solution of the 1D Schrödinger equation with the well depth of 512.3 meV. (bottom) Comparison of the renormalized effective phonon frequency ($\tilde{\omega}_{300\text{K}}$) and the classical well curvature (attempt frequency) for the M mode instability of all inorganic halide perovskites considered at $T = 300$ K.

CsPbI_3 at 150 K. We thus conclude that this dynamic disorder would not be observed with X-ray diffraction at room temperature. The random (non-correlated) local orientations give rise to the observed higher symmetry space group.⁴²

Optoelectronic processes such as light absorption (fs), carrier thermalization (fs), carrier scattering (sub ps), and recombination (ns) are all relatively fast. An adiabatic approximation can therefore be made. From the perspective of electrons, the potential energy surface is stationary, with fixed distortions randomly orientated throughout the bulk. Electronic and optical processes sample the local symmetry broken structure, and thus its influence should be included in quantitative models of transport and device operation. The classification between static and dynamic disorder depends on the time scale of the interactions. In the limit of very high temperatures (i.e., $k_B T \gg \Delta E$), all of the halide perovskites would revert to dynamic disorder, although for the systems with large ΔE , this limit would be much higher than the typical operating temperatures of semiconductor devices.

Interestingly, we found that the local minima for CsSnF_3 occurred at relatively small absolute values of Q , suggesting that this perovskite might undergo a different type of M -point distortion to the other compounds. On examining the phonon eigenvectors, we verified that this is indeed the case. The M -point soft mode in CsSnF_3 is an M_2^- distortion, while those in other compositions correspond to M_3^+ tilts. The M_2^- mode is related to a second-order Jahn–Teller distortion where B–X bonds shorten and lengthen, whereas the M_3^+ mode represents rigid in-phase octahedral tilting. This can be explained by orbital mixing between the Sn 5s and F 2p orbitals, which produces the asymmetric electron density around the B-site that is required to support a Jahn–Teller distortion.⁴⁷

Table 2. Calculated Transition Rate (Γ) Across the Double-Well Potential (values in Hz)^a

	ΔE (meV)	ν (THz)	Γ at 150 K (Hz)	Γ at 298 K (Hz)	Γ at 500 K (Hz)
CsSnF ₃	144.7	8.87	1.19×10^8	3.18×10^{10}	3.09×10^{11}
CsSnCl ₃	108.1	2.04	4.69×10^8	3.05×10^{10}	1.66×10^{11}
CsSnBr ₃	127.7	1.28	6.45×10^7	8.93×10^9	6.64×10^{10}
CsSnI ₃	203.7	1.12	1.55×10^5	4.04×10^8	9.90×10^9
CsPbF ₃	151.8	3.71	2.88×10^7	1.01×10^{10}	1.10×10^{11}
CsPbCl ₃	353.4	2.58	3.27	2.76×10^6	7.10×10^8
CsPbBr ₃	396.5	1.74	7.81×10^{-2}	3.48×10^5	1.76×10^8
CsPbI ₃	512.3	1.40	7.91×10^{-6}	3.08×10^3	9.62×10^6

^aAs the temperature increases, the hopping rate increases, but the absolute value also depends on the attempt frequency (ν). Contributions from quantum mechanical tunnelling are not considered. Note that the time scale of typical diffraction experiments is seconds, while electronic processes (carrier transport and recombination) can occur on time scales of 10^{-15} to 10^{-9} seconds.

Correlation between the Harmonic Frequency and ΔE . The imaginary harmonic phonon frequency (at the saddle point) has been assumed to be indicative of the energetic driving force for distortions in perovskites.^{48,49} To assess the correlation between the frequency and the depth of the minima, we plotted the well depths of the *M*-point soft modes obtained by the potential-energy mapping against the squared harmonic frequency ω^2 (Figure 4). From this analysis, we see that

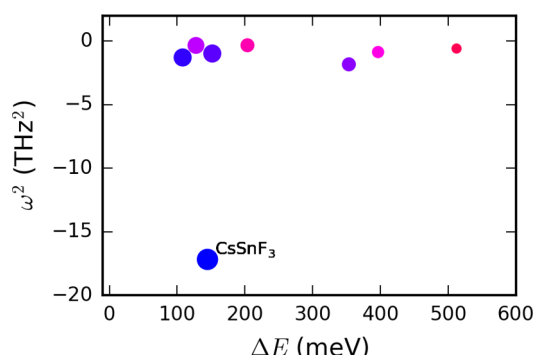


Figure 4. Squared imaginary harmonic phonon frequencies, ω^2 (THz²) for the *M*-point soft modes against the well depth (meV). The size of the markers is proportional to the structural tolerance factors α , which range from 0.93 (CsSnF₃) to 0.85 (CsPbI₃). The colors correspond to the overall mass of the unit cell, with the heaviest being the “warmest” (CsPbI₃; red) and the lightest the “coolest” (CsSnF₃; blue).

there is little correlation between the two. Excluding the outlier CsSnF₃, the well depths span a 400 meV range, with a spread in ω^2 of 1.5 THz². The data are scattered across the energy range, with no clearly evident patterns of frequency distribution, indicating that the imaginary harmonic frequencies may be a poor proxy for the well depths. This can be understood from the fact that the harmonic frequency reflects the curvature of the potential-energy surface at the average structure ($Q = 0$), which does not contain sufficient information to extrapolate to the anharmonic region of the soft-mode potential.

Analysis of Figure 4 does, however, reveal a correlation between the well depth and the tolerance factor, namely, that compounds with larger tolerance factors tend to produce shallower minima (i.e., the distorted structures are closer in energy to the cubic average structure). This supports the established simple relationship between chemical composition and structural instability. The closer the tolerance factor to unity, the more “cubic” a structure is expected to be. Our data show that lower-symmetry configurations are indeed more

energetically favorable for compositions with smaller tolerance factors.

For the CsPbX₃ series, when X increases from F to I the tolerance factor decreases from 0.90 to 0.85, and the temperature of the cubic phase transition increases from 187 to 328, 413, and 634 K.^{1,27,29,50} This indicates that for compounds with smaller tolerance factors more thermal energy is required to lift the symmetry to cubic phase, which is in agreement with our calculations. Structurally, when $\alpha < 1$, the A–X bonding is undercoordinated, and octahedral tilting is required to optimize the chemical bonding environments. If we explicitly plot the well depth as a function of tolerance factor (shown in Figure 5a), then this trend becomes apparent. There is also a correlation between tolerance factor and the distortion amplitude that minimizes the energy (ΔQ), shown in Figure

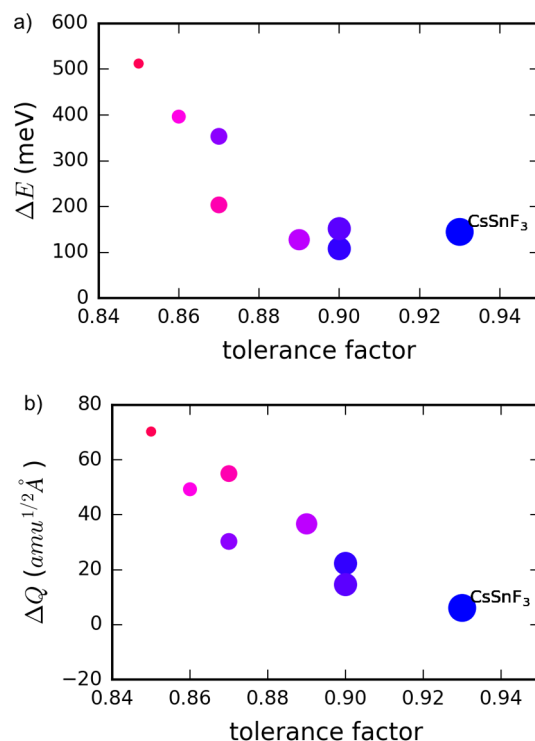


Figure 5. Double well depths and distortion amplitudes along the *M*-point soft phonon modes as a function of tolerance factor. The ionic radii used for each of the elements are Cs: 1.88 Å; F: 1.33 Å; Cl: 1.81 Å; Br: 1.96 Å; I: 2.20 Å; Pb: 1.19 Å;⁵¹ and Sn: 1.10 Å.⁵² The size and the color of the circles represent the tolerance factor and relative formula mass, as in Figure 4.

5b. Compositions with small α require a larger distortion to the local minimum to optimize the cation-bonding environment due to the undercoordination.

Electronic Structure Effects. We further assess the effect of the M -point tilting distortions on the electronic structure by calculating the change in the band gap along the normal-mode coordinate Q . The band gap for all eight compounds increases to different extents when distorting along the soft modes (Figure 6). This indicates that distortions from average cubic

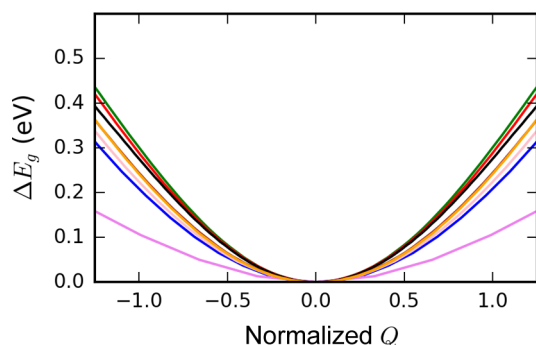


Figure 6. Change in band gap ΔE_g (eV) relative to the cubic structure for each compound as a function of normalized soft mode amplitude Q . The average cubic structure lies at $Q = 0$, while the lowest energy distorted structure lies at $Q = 1$. The pink line, showing least change in E_g , corresponds to CsPbF_3 , and green line, showing most change, corresponds to CsPbCl_3 .

symmetry will lead to a band gap increase in these perovskites. Although the semilocal exchange-correlation functional (PBEsol) used to estimate the band gap underestimates the absolute value, the relative shifts should be reliable. Because of the fact that the upper valence band consists of strong Sn/Pb s and X p antibonding character, upon tilting, the overlap of the orbitals decreases and results in a lower energy valence-band maximum and thus an increase in the gap.^{2,24,33} The ultimate effect of such distortions on the band gap will also depend on the type of disorder. Static disorder would lead to a more pronounced widening of the band gap, whereas dynamic disorder would produce a less-pronounced time-averaged effect. A more quantitative description will require the development and application of more sophisticated theories for anharmonic electron–phonon coupling.

In summary, we have performed a comprehensive investigation of the phonon stabilities in the cubic CsSnX_3 and CsPbX_3 halide perovskites ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$). Our results show that all eight compounds exhibit phonon soft-mode instabilities in the cubic phase. Examining the potential energy surface along a representative soft-mode structural distortion reveals a correlation between the chemical composition and structural tolerance factor and the energetic barrier to accessing the high-symmetry structure. We also found that the nature of the distortions differ depending on the chemistry, with CsSnF_3 showing a fundamentally different M -point distortion to the other seven halide perovskites. The hopping rate of the structural transition between two local minima is calculated, which relates to the time scale of diffraction measurements. Finally, we have also studied the effect of the distortion from cubic symmetry on the electronic structure and find that, in all cases, distortion along the M -point soft modes leads to a widening of the band gap. There are implications on future electronic-structure studies and assessment of the role of local

symmetry breaking and electrostatic (band gap) fluctuations on the performance of perovskite optoelectronic devices.

AUTHOR INFORMATION

Corresponding Author

*E-mail: a.walsh@imperial.ac.uk.

ORCID

Jonathan M. Skelton: 0000-0002-0395-1202

Aron Walsh: 0000-0001-5460-7033

Notes

The authors declare no competing financial interest.

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