

Perovskite Phases

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Reentrant Structural and Optical Properties and Large Positive Thermal Expansion in Perovskite Formamidinium Lead Iodide

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Dedicated to Professor Anthony K. Cheetham, FRS on the occasion of his 70th birthday

Abstract: The structure of the hybrid perovskite $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ (formamidinium lead iodide) reflects competing interactions associated with molecular motion, hydrogen bonding tendencies, thermally activated soft octahedral rotations, and the propensity for the Pb^{2+} lone pair to express its stereochemistry. High-resolution synchrotron X-ray powder diffraction reveals a continuous transition from the cubic α -phase ($\text{Pm}\bar{3}\text{m}$, #221) to a tetragonal β -phase ($\text{P4}/\text{mbm}$, #127) at around 285 K, followed by a first-order transition to a tetragonal γ -phase (retaining $\text{P4}/\text{mbm}$, #127) at 140 K. An unusual reentrant pseudosymmetry in the β -to- γ phase transition is seen that is also reflected in the photoluminescence. Around room temperature, the coefficient of volumetric thermal expansion is among the largest for any extended crystalline solid.

Photovoltaic absorbers based on the hybrid perovskite $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ (formamidinium lead iodide) and its alloys exhibit impressive performance,^[1] but the description of the crystal structure of this material is incomplete. In addition to this technological motivation,^[2] dense hybrid materials with 3D inorganic connectivity and isolated organic molecular ions combine features of traditional inorganic solids and open-framework materials, and their composition–structure relations are of fundamental interest.

The initial report of the preparation and characterization of $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ proposed perovskite structures of trigonal

symmetry for the α - and β -phases on the basis of laboratory single-crystal X-ray diffraction,^[3] while a subsequent report assigned the structure of the cubic perovskite aristotype for the α -phase from neutron powder diffraction.^[4] The structure of the γ -phase has not been reported.

The disordered molecular cation, challenges associated with twinning in single crystals, and issues of pseudosymmetry led us to employ high-resolution synchrotron X-ray powder diffraction to follow the structure evolution of $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ between 90 K and 490 K. The temperature-dependent scattering intensity around instructive low-angle Bragg peaks is given in Figure 1. The continuous α – β phase transition around 285 K is evident in the emergence of the 211 tetragonal peak and the splitting of the 200 cubic peak into the 002 and 220 tetragonal peaks on cooling. The first-order β – γ transition can be seen in the abrupt change in intensities and peak positions at 140 K (transition temperature from reported scanning

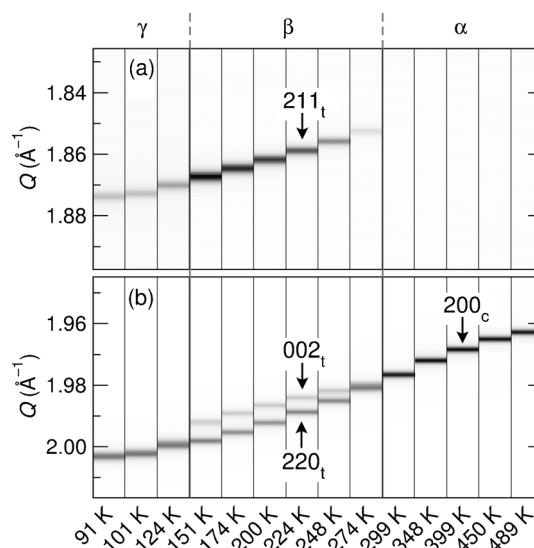


Figure 1. X-ray scattering intensity from $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ around selected low-angle Bragg peaks between 90 K and 490 K, normalized to maximum peak intensity. a) The 211_t tetragonal Bragg peak emerges upon cooling through a continuous phase transition around 285 K from the cubic α -phase to the tetragonal β -phase. b) The 200_c cubic Bragg peak splits continuously on cooling due to the emergent tetragonality. A first-order transition to the pseudo-cubic γ -phase with tetragonal symmetry occurs at 140 K.^[5] The 002_t and 220_t tetragonal peaks “fuse” across the β – γ transition while the 211_t tetragonal peak remains.

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calorimetry, which confirms the order of the transitions).^[5] Remarkably, the 002 and 220 tetragonal peaks “fuse” in the γ -phase, while the 211 tetragonal peak remains, suggesting the possibility of a tetragonal phase with cubic pseudosymmetry.

Le Bail and Rietveld analyses of diffraction data confirm this hypothesis. In agreement with the results of Weller et al.,^[4] the α -phase is well described by the cubic $Pm\bar{3}m$ aristotype ($a = 6.35788$ Å at 299 K), as shown in Figure 2a. For all phases, the A-site $[\text{HC}(\text{NH}_2)_2]^+$ cation has been modeled as a pseudo-atom with equivalent scattering power due to the dynamic disorder (see below) and limited sensitivity in the X-ray experiment.

The structure of the β -phase is that of $P4/mbm$ symmetry, with $a^0a^0c^+$ tilts in Glazer notation^[6] (temperature-dependent structure parameters for all phases are provided in the Supporting Information). This in-phase uniaxial tilt pattern (Figure 2b) is in line with computational predictions of the preferred tilts for tetragonal perovskite iodides^[7] and contrasts with the out-of-phase tilts observed in the tetragonal phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$ ^[8] and many oxides. The anisotropy of the A-site atomic displacement parameters (ADPs) suggests

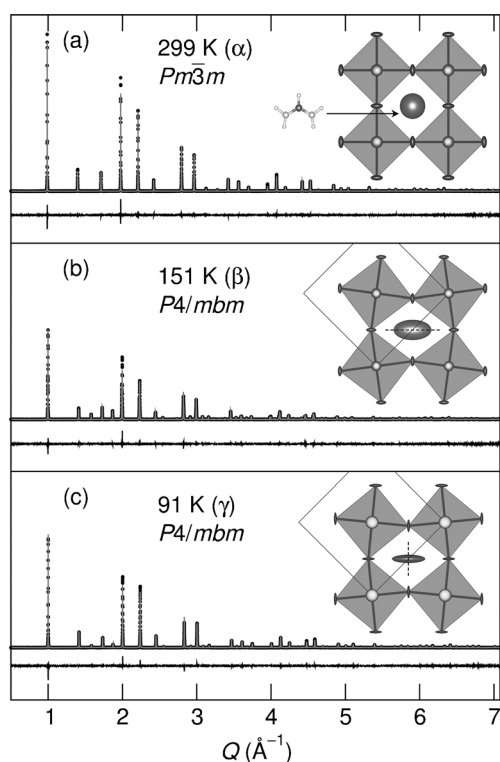


Figure 2. Rietveld refinement of X-ray powder diffraction and resulting crystal structures of the phases of $\text{HC}(\text{NH}_2)_2\text{PbI}_3$. Recorded scattering intensities are indicated by black dots, modelled intensities by gray lines, and difference curves are offset below. The A-site $[\text{HC}(\text{NH}_2)_2]^+$ cation is modelled as a pseudo-atom with the same form factor due to disorder and limited sensitivity in the X-ray experiment, and atomic displacement parameter (ADP) ellipsoids are visualized at the 50% level. a) Cubic α -phase ($Pm\bar{3}m$, #221) at 299 K, $R_w = 12.4\%$. The formamidinium cation, $[\text{HC}(\text{NH}_2)_2]^+$ is illustrated. b) Tetragonal β -phase ($P4/mbm$, #127) at 151 K, $R_w = 15.1\%$, viewed down the c -axis. c) Tetragonal γ -phase ($P4/mbm$, #127) at 91 K, $R_w = 16.1\%$, viewed down the c -axis. Dashed lines in (b,c) indicate the unique axis of the A-site ADP ellipsoid.

preferential orientations for the molecular cation due to the tilting of the octahedra.

Remarkably, the structure of the γ -phase is also that of $a^0a^0c^+$ tilts with $P4/mbm$ symmetry, as shown in Figure 2c, though there are discontinuous changes in many structure parameters (see below) as required for such a first-order transition. Alternative structures exhibiting simple tilts that maintain 3D octahedral connectivity^[9] and that allow ferroic Pb^{2+} displacements^[10] were screened and rejected based on unindexed peaks, absences of expected peaks, or both (details given in the Supporting Information).

Given this highly unusual phase evolution, we examined the temperature dependence of structure parameters from Rietveld refinement of diffraction data across the temperature range of 90 K to 490 K, as well as temperature-dependent optical and dielectric properties. The tetragonal lattice parameter ratio is given in Figure 3a, and reflects the continuous emergence of tetragonality on cooling into the β -phase, as well as the reentrant cubic pseudosymmetry in the γ -phase.

The photoluminescence (PL) emission peak energy, E_{PL} , is given in Figure 3b. E_{PL} blue-shifts with temperature in the α - and β -phases, consistent with the effects of thermal expansion on the unusual electronic structure as well as possible dynamic Pb^{2+} displacements.^[11] E_{PL} plateaus above 370 K, a range which was not accessed in previous studies. On

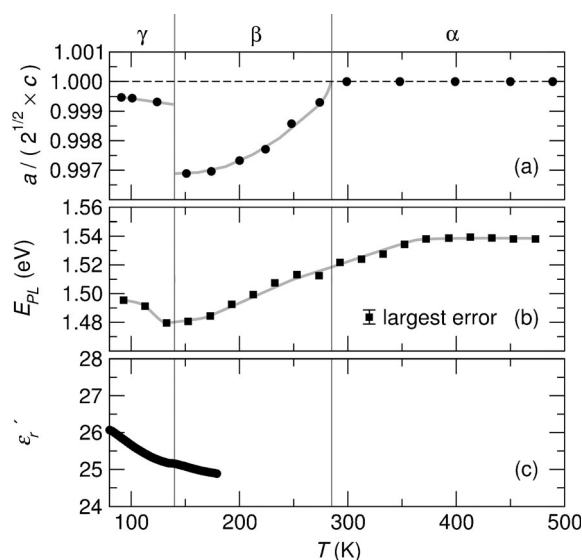


Figure 3. Tetragonal lattice parameter ratio, photoluminescence peak energy, and static dielectric permittivity of $\text{HC}(\text{NH}_2)_2\text{PbI}_3$. a) The tetragonal lattice parameter ratio reflects the continuous α - β transition on cooling, as well as the reentrant cubic pseudosymmetry in the γ -phase. Error bars are smaller than the markers and are omitted. b) The photoluminescence (PL) emission peak energy, E_{PL} , red-shifts on warming through the γ - β transition. In the β - and α -phases, E_{PL} blue-shifts with temperature, consistent with the effects of lattice expansion^[11] on the unusual electronic structure of the main-group halide perovskites, and subsequently plateaus above 370 K. c) Static dielectric permittivity, ϵ' , extracted from capacitance-loss measurements at 20 kHz. Despite a slight kink at the β - γ transition, ϵ' declines substantially with temperature in both phases, suggesting reorientation of the dipolar axis of the A-site cation is minimally inhibited even at these temperatures.

cooling through the β - γ transition, E_{PL} blue-shifts substantially, in agreement with existing reports.^[12,13] This is similar to the observed behavior at the tetragonal-orthorhombic transition in $\text{CH}_3\text{NH}_3\text{PbI}_3$,^[13] where the blue-shift arises from reduced Pb-I orbital overlap due to the lowered symmetry, though in $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ the blue-shift despite reduced tilting suggests crystallographically hidden disorder of the Pb-I network, though no disorder-induced emission broadening is apparent.

The static dielectric permittivity, ϵ_r' , indirectly probes the rotational freedom of the polar axis of the molecular cation.^[14] For the well-studied $\text{CH}_3\text{NH}_3\text{PbI}_3$, ϵ_r' rises on cooling in the tetragonal phase and drops abruptly through the tetragonal-orthorhombic phase transition,^[15] as the severe tilting of the octahedra constrains the reorientation of the C-N axis. In contrast, ϵ_r' for $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ has no discontinuity and continues to rise on cooling in the γ -phase (Figure 3c), suggesting minimally inhibited reorientation of the polar axis. The smaller value and reduced temperature dependence of ϵ_r' compared to that for $\text{CH}_3\text{NH}_3\text{PbI}_3$ are consistent with the smaller dipole moment for $[\text{HC}(\text{NH}_2)_2]^+$. The persistence of considerable cation motion in the γ -phase is in line with our previous observation of a glassy slowing of dynamics below 100 K in $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{HC}(\text{NH}_2)_2\text{PbI}_3$, with $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ exhibiting greater glass fragility.^[5]

The unit cell volume per formula unit, V , is given in Figure 4a. A comparison of the volumetric thermal expansion

Table 1: Volumetric thermal expansion coefficients, α_v , of $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ and selected other compounds near room temperature.

Composition	Phase	T [K]	α_v [10^{-6} K^{-1}]	Reference
$\text{HC}(\text{NH}_2)_2\text{PbI}_3$	β (solid)	200–299	206–202	This work
$\text{HC}(\text{NH}_2)_2\text{PbI}_3$	α (solid)	348–489	100–98.6	This work
$\text{CH}_3\text{NH}_3\text{PbI}_3$	β (solid)	280	132	[19,20]
CsSnI_3	γ (solid)	298	126	[21]
$\text{Ag}_3[\text{Co}(\text{CN})_6]$	solid	276	121	[22]
Hg	liquid	293	182	[21]

coefficient, α_v , with those of other main-group halides and selected framework materials and liquids is given in Table 1. Fit over a temperature range of 200 K to 299 K, α_v is greater than $200 \times 10^{-6} \text{ K}^{-1}$ ($R^2 = 99.8\%$). Thus, α_v for the β -phase is larger than that for liquid mercury^[21] and appears to be nearly the largest for any extended crystalline solid near ambient temperature. It was recently reported that $\alpha_v = 220 \times 10^{-6} \text{ K}^{-1}$ for the mixed A-site $[\text{CH}_3\text{NH}_3]_{0.5}[\text{HC}(\text{NH}_2)_2]_{0.5}\text{PbI}_3$, though the precise temperature and fitting range are unspecified.^[23] In the β -phase, linear thermal expansion is ca. 60 % greater in the ab -plane ($\alpha_a = 7.7 \times 10^{-5} \text{ K}^{-1}$) than in the c -direction ($\alpha_c = 4.9 \times 10^{-5} \text{ K}^{-1}$), suggesting anisotropic mechanical properties. While still large, α_v is substantially reduced in the cubic α -phase, consistent with a negative contribution from large amplitude dynamic octahedral tilts as in A-site vacant ReO_3 ^[16,17] and ScF_3 .^[18]

The isotropic ADP for Pb, U_{iso} , is given in Figure 4b, and increases monotonically with temperature. While the value is significantly elevated relative to typical values in oxides (partially a consequence of $6s^2$ lone pair-induced anharmonicity),^[11] there are no discontinuities that would suggest crystallographic Pb^{2+} displacements that are not captured in our structure models for the low temperature phases.

The Pb-I-Pb octahedral tilt angle is given in Figure 4c, and reflects the continuous α - β transition. In the γ -phase, the tilt angle jumps closer to linear, underscoring the unusual nature of this transition.

Iodine ADPs in the directions orthogonal to the Pb-I bonds, U_{\perp} , are given in Figure 4d. Consistent with thermally-activated dynamic octahedral tilts, the values of U_{\perp} decrease monotonically on cooling in the α - and β -phases. However, they increase significantly in the γ -phase, again consistent with disorder that is not captured by this crystallographic model. The discrepancy between ADPs for the two distinct I sites in the γ -phase reflects parameter correlations that arise from Bragg peak overlap.

Together, the photoluminescence, iodine ADPs, and persistence of molecular motion in the γ -phase suggest complex (possibly modulated) disorder in this regime. This is supported by the observation of weak (intensity $< 0.5\%$ that of the strongest Bragg peak) diffuse scattering features between $Q = 1.55 \text{ \AA}^{-1}$ and $Q = 2.00 \text{ \AA}^{-1}$ that are not indexed by any plausible space group symmetry.^[9,10] Nonetheless, the pseudo-cubic unit cell is unambiguous, and underscores the different N-H...I interactions between $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{HC}(\text{NH}_2)_2\text{PbI}_3$, where the diamine may hydrogen-bond to halogens on both sides of the cage.

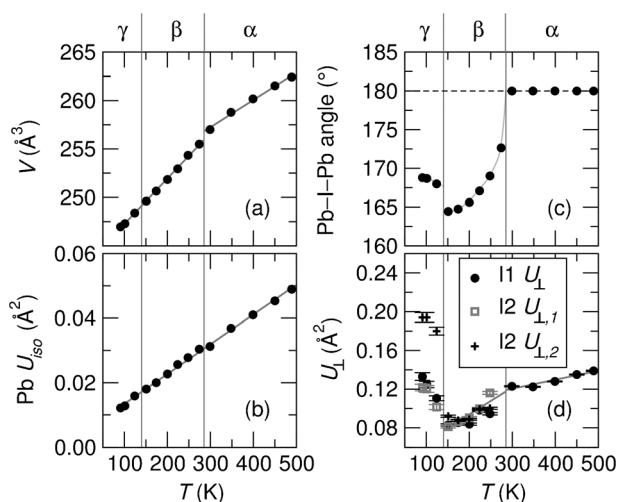


Figure 4. Selected crystallographic parameters for $\text{HC}(\text{NH}_2)_2\text{PbI}_3$. Error bars for (a)–(c) are smaller than the markers and are omitted. a) The unit cell volume per formula unit, V , reveals unusually large volumetric thermal expansion coefficients ($\alpha_v = 203 \times 10^{-6} \text{ K}^{-1}$ at 274 K). α_v is reduced in the cubic phase, consistent with a negative contribution from large amplitude dynamic octahedral tilts.^[16–18] b) The isotropic ADP for Pb, U_{iso} , is large compared to typical values in oxides but reveals no discontinuities associated with masked displacements in the tetragonal phases. c) The Pb-I-Pb octahedral tilt angle reflects the continuous α - β transition, and jumps back toward linear through the unusual β - γ transition. d) The ADPs for I in the directions orthogonal to the Pb-I bonds, U_{\perp} , decline monotonically with cooling in the α - and β -phases, consistent with reduced dynamic octahedral tilting. The increased values of the U_{\perp} ADPs on cooling to the γ -phase suggest disorder that is not fully captured by this crystallographic model.

In summary, we find that this class of materials, already so fascinating on account of their outstanding functionality in photovoltaic devices, display fundamental properties that are surprising and even counterintuitive. The implications for technological applications are profound. For example, the very large volumetric thermal expansion creates substantial challenges in device applications. The atomistic origins of the reentrant structural and optical behavior deserve further scrutiny.

Experimental Section

$\text{HC}(\text{NH}_2)_2\text{PbI}_3$ was prepared following a modification of the previously reported procedure.^[3] 4.46 g (20 mmol) of PbO was dissolved in 15 mL of concentrated aqueous HI (57 % w/w) and the solution temperature was raised and held to boiling (ca. 130 °C). In a separate beaker, 2.08 g (20 mmol) of $\text{HC}(\text{NH}_2)_2(\text{O}_2\text{CCH}_3)$ or 1.61 g (20 mmol) of freshly prepared $\text{HC}(\text{NH}_2)_2\text{Cl}$ (prepared from $\text{HC}(\text{NH}_2)_2(\text{O}_2\text{CCH}_3)$ and concentrated HCl (37 % w/w), followed by copious washing with toluene to remove excess acetic acid)^[4] were dissolved in 5 mL of concentrated aqueous HI (57 % w/w). The latter step was found to be necessary since commercially available $\text{HC}(\text{NH}_2)_2\text{Cl}$ is extremely hygroscopic and contains hydrolysis products. Addition of the $\text{HC}(\text{NH}_2)_2\text{I}$ solution to the PbI_2 solution resulted immediately in a fine black precipitate. The reaction was stopped after 5 min and the solution was filtered hot under vacuum to avoid co-precipitation of hydrated phases obtained for the cooled solution. During filtration, the black solid turns to yellow, completely converting over a period of 5 to 10 min. The yellow solid was transferred in a vacuum oven and heated at 120 °C overnight, yielding a black solid that is stable for a period of 20 to 30 days before converting back to the yellow phase. Note that if the latter step is performed in an evacuated ampule under static vacuum, the black phase converts to the yellow one within 5 to 10 min. The obtained black material consists of the crystallographically pure α -phase of $\text{HC}(\text{NH}_2)_2\text{PbI}_3$. Yield: 9 to 10 g (70 % to 80 %).

High resolution synchrotron X-ray powder diffraction data were collected using beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory at a wavelength of 0.459200 Å. 50 mg of ground, yellow $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ was packed and sealed into a 0.5 mm OD Kapton capillary. Complete conversion to the black perovskite phase was achieved in situ by heating initially to 490 K during data acquisition.

Candidate crystal structures for the phases of $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ were generated using ISODISTORT (ISOTROPY Software Suite, iso.byu.edu). Le Bail and Rietveld analyses were performed using the GSAS software suite^[24] with the EXPGUI interface.^[25]

Photoluminescence measurements were performed on a Renishaw Invia spectrometer analyzing the backscattered filtered light emitted by a laser excitation at 785 nm. The samples were loaded into a THMS600PS Linkam optical cell under an inert Ar atmosphere. The incident beam was focused on spots of $5\text{ }\mu\text{m}^2$. Power density was on the order of $\mu\text{W}\mu\text{m}^{-2}$, except above 433 K where the PL signal is very low and the incident power was raised to $0.12\text{ mW}\mu\text{m}^{-2}$. PL spectra were recorded and averaged from five different spots at each temperature. The spectra from different spots have similar spectral characteristics but different absolute intensities, and spatial variation of peak position is only 1 to 2 nm.

A flat plate capacitor was prepared by grinding black $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ and cold-pressing to 3 tons in a 6 mm diameter cylindrical die (pellet thickness 2.54 mm) and applying indium contacts via low temperature soldering. Capacitance-loss measurements were performed in a Quantum Design PPMS DynaCool using an Andeen-Hagerling AH 2700A Ultra-precision Capacitance Bridge over the frequency range 100 Hz to 20 kHz.

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- [1] M. Saliba, T. Matsui, J.-Y. Seo, K. Domanski, J.-P. Correa-Baena, M. K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt, M. Grätzel, *Energy Environ. Sci.* **2016**, 9, 1989–1997.
- [2] B. V. Lotsch, *Angew. Chem. Int. Ed.* **2014**, 53, 635–637; *Angew. Chem.* **2014**, 126, 647–649.
- [3] C. C. Stoumpos, C. D. Malliakas, M. G. Kanatzidis, *Inorg. Chem.* **2013**, 52, 9019–9038.
- [4] M. T. Weller, O. J. Weber, J. M. Frost, A. Walsh, *J. Phys. Chem. Lett.* **2015**, 6, 3209–3212.
- [5] D. H. Fabini, T. Hogan, H. A. Evans, C. C. Stoumpos, M. G. Kanatzidis, R. Seshadri, *J. Phys. Chem. Lett.* **2016**, 7, 376–381.
- [6] A. M. Glazer, *Acta Crystallogr. Sect. B* **1972**, 28, 3384–3392.
- [7] J. Young, J. M. Rondinelli, *J. Phys. Chem. Lett.* **2016**, 7, 918–922.
- [8] M. T. Weller, O. J. Weber, P. F. Henry, A. M. Di Pumpo, T. C. Hansen, *Chem. Commun.* **2015**, 51, 4180–4183.
- [9] C. J. Howard, H. T. Stokes, *Acta Crystallogr. Sect. B* **1998**, 54, 782–789.
- [10] H. T. Stokes, E. H. Kisi, D. M. Hatch, C. J. Howard, *Acta Crystallogr. Sect. B* **2002**, 58, 934–938.
- [11] D. H. Fabini, G. Laurita, J. S. Bechtel, C. C. Stoumpos, H. A. Evans, A. G. Kontos, Y. S. Raptis, P. Falaras, A. Van der Ven, M. G. Kanatzidis, R. Seshadri, *J. Am. Chem. Soc.* **2016**, 138, 11820–11832.
- [12] H.-H. Fang, F. Wang, S. Adjokatse, N. Zhao, J. Even, M. A. Loi, *Light Sci. Appl.* **2016**, 5, e16056.
- [13] A. D. Wright, C. Verdi, R. L. Milot, G. E. Eperon, M. A. Pérez-Osorio, H. J. Snaith, F. Giustino, M. B. Johnston, L. M. Herz, *Nat. Commun.* **2016**, 7, 11755.
- [14] W. Zhang, Y. Cai, R.-G. Xiong, H. Yoshikawa, K. Awaga, *Angew. Chem. Int. Ed.* **2010**, 49, 6608–6610; *Angew. Chem.* **2010**, 122, 6758–6760.
- [15] N. Onoda-Yamamuro, T. Matsuo, H. Suga, *J. Phys. Chem. Solids* **1992**, 53, 935–939.
- [16] T. Chatterji, P. F. Henry, R. Mittal, S. L. Chaplot, *Phys. Rev. B* **2008**, 78, 134105.
- [17] E. E. Rodriguez, A. Llobet, T. Proffen, B. C. Melot, R. Seshadri, P. B. Littlewood, A. K. Cheetham, *J. Appl. Phys.* **2009**, 105, 114901.

- [18] B. K. Greve, K. L. Martin, P. L. Lee, P. J. Chupas, K. W. Chapman, A. P. Wilkinson, *J. Am. Chem. Soc.* **2010**, *132*, 15496–15498.
- [19] Y. Kawamura, H. Mashiyama, K. Hasebe, *J. Phys. Soc. Jpn.* **2002**, *71*, 1694–1697.
- [20] Y. Rakita, S. R. Cohen, N. K. Kedem, G. Hodes, D. Cahen, *MRS Commun.* **2015**, *5*, 623–629.
- [21] I. Chung, J.-H. Song, J. Im, J. Androulakis, C. D. Malliakas, H. Li, A. J. Freeman, J. T. Kenney, M. G. Kanatzidis, *J. Am. Chem. Soc.* **2012**, *134*, 8579–8587.
- [22] A. L. Goodwin, M. Calleja, M. J. Conterio, M. T. Dove, J. S. O. Evans, D. A. Keen, L. Peters, M. G. Tucker, *Science* **2008**, *319*, 794–797.
- [23] O. J. Weber, B. Charles, M. T. Weller, *J. Mater. Chem. A* **2016**, *4*, 15375–15382.
- [24] A. C. Larson, R. B. Von Dreele, *General Structure Analysis System*; Technical Report no. 86-748; Los Alamos National Laboratory: Los Alamos, NM, **2000**.
- [25] B. H. Toby, *J. Appl. Crystallogr.* **2001**, *34*, 210–213.

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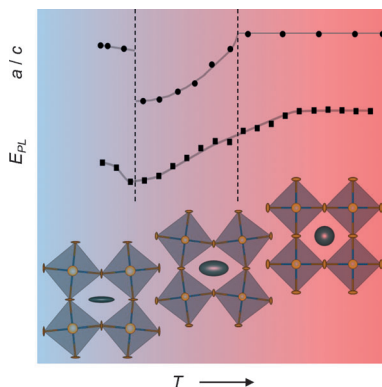
Communications



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Reentrant Structural and Optical
Properties and Large Positive Thermal
Expansion in Perovskite Formamidinium
Lead Iodide



Extraordinary phase evolution: The hybrid perovskite formamidinium lead iodide undergoes two structural transitions in the 90 K to 490 K range. Deciphering these transitions points to unusually large thermal expansion in the tetragonal phases, and strong coupling between the reentrant lower temperature structural transition and the optical band gap.