Halide perovskites exhibit remarkably long carrier lifetimes and diffusion lengths for a highly defective, solution-processable material, allowing for the creation of solar cells with certified efficiencies of 25.2%.[1–5] Unlike in silicon which can be fabricated with defect densities better than one part per million,[6] halide perovskites have a defect-density orders of magnitude greater than silicon and exhibit ion conduction.[7,8] Despite the defect density, halide perovskites still exhibit long lifetimes and high fluorescence quantum yields,[9] which is remarkable because defective materials usually have short lifetimes and low quantum yields resulting from defect-assisted carrier recombination.[10] The dominant halide perovskite in solar energy conversion applications is methylammonium lead iodide, an organic–inorganic hybrid material where the A-site cation is the metallic ammonium (CH₃NH₃⁺) ion. The structural properties of methylammonium lead iodide have been widely studied.[11,12] However, methylammonium lead iodide and other hybrid perovskites suffer from stability problems in solar cells, which are hypothesized to be related to the volatile organic cation.[13]

Despite the tremendous interest in halide perovskite solar cells, the structural reasons that cause the all-inorganic perovskite CsPbI₃ to be unstable at room temperature remain mysterious, especially since many tolerance-factor-based approaches predict CsPbI₃ should be stable as a perovskite. Here single-crystal X-ray diffraction and X-ray pair distribution function (PDF) measurements characterize bulk perovskite CsPbI₃ from 100 to 295 K to elucidate its thermodynamic instability. While Cs occupies a single site from 100 to 150 K, it splits between two sites from 175 to 295 K with the second site having a lower effective coordination number, which, along with other structural parameters, suggests that Cs rattles in its coordination polyhedron. PDF measurements reveal that on the length scale of the unit cell, the Pb—I octahedra concurrently become greatly distorted, with one of the I—I—Pb—I angles approaching 82° compared to the ideal 90°. The rattling of Cs, low number of Cs—I contacts, and high degree of octahedral distortion cause the instability of perovskite-phase CsPbI₃. These results reveal the limitations of tolerance factors in predicting perovskite stability and provide detailed structural information that suggests methods to engineer stable CsPbI₃-based solar cells.

Understanding the Instability of the Halide Perovskite CsPbI₃ through Temperature-Dependent Structural Analysis

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Our study indicates that the rattling of the Cs cation, lower coordination of the second Cs site, and local octahedral distortion contribute to the thermodynamic instability of γ-CsPbI₃. These results explain the metastability of perovskite-type γ-CsPbI₃ and demonstrate that tolerance-factor-based approaches to predicting the formation of halide perovskites have significant limitations such that they should not be the relied on as the exclusive method to predict the formation of the perovskite structure type. The detailed structural information we provide suggests methods to stabilize the perovskite phase of CsPbI₃ and thus improve the stability of halide perovskite solar cells.

As previously reported,[16,17,19] at 295 K perovskite-type γ-CsPbI₃ displays the orthorhombic Pnma (No.62) space group. Here, we observe no change in symmetry between 100 and 295 K (Figure S1 and Tables S1–S2, Supporting Information). Figure 1A shows the pseudocubic cell constants as a function of temperature with the unit cell volume in Figure S2 in the Supporting Information. While the unit cell volume, \(V\), and \(c\) increase with temperature, \(a\) decreases to eventually become metrically equal to \(c\) upon the phase transition to tetragonal symmetry around 457 K.[19] Common to the perovskite structure type,[31] γ-CsPbI₃ becomes less distorted as the temperature increases, which can be seen through the reduction of the Glazer tilt angles \(a'\) and \(b'\) as well as the angles \(\theta, \phi,\) and \(\Phi\) defined by Zhao et al. (Figure 1B).[32,33] \(\theta\) and \(a'\) are equal. While the average thermal parameter \(U_{eq}\) of Pb varies linearly with temperature,
The thermal parameters of I are much more oblate than those of Pb (Figure 1D; Figure S3, Supporting Information), indicating that the Pb–I bond is rigid and the I atoms predominantly move orthogonally to the Pb–I bond rather than along it at all temperatures from 100 to 295 K.\[34\] Interestingly, the Pb–I bond lengths are invariant with temperature (Figure 1E). This indicates that the change in lattice parameters must come from tilting between adjacent octahedra and/or from angular changes within the octahedra themselves (Figure 1B, F).

The most noteworthy change is that as the temperature increases, Cs becomes disordered between two sites. Figure 2A shows the partial Cs density at 100 K, indicating that the Cs atom is well-behaved and a single site is occupied. As the temperature increases above 150 K, however, the Cs scattering density becomes irregular. The partial Cs density at 295 K is shown in Figure 2B and exhibits significant elongation, indicating that Cs is not well-behaved. We find the residual density is minimized by splitting the Cs occupancy between two sites that are separated by approximately 0.5 Å. We call the dominant site CsA and the other CsB. In the structure refinement, the atomic displacement parameters of CsA and CsB are constrained to be identical and the sum of the occupancies is fixed at 1. If the Cs atom is modeled without disorder, $U_{eq}$ for Cs is significantly more superlinear at temperatures $\geq$ 200 K (Figure S4, Supporting Information) and there is an unacceptable amount of superlinear parameter deviation from the average bond length within the polyhedron, $\delta l_{mean}$ = 0.08 Å. The additional regression $\delta l_{mean}$ is the unweighted average bond length within the coordination polyhedron as defined in ref. [39]. We also compute the distortion index\[39,40\] $D = \frac{1}{n} \sum_{i=1}^{n} \frac{l_i - l_{mean}}{l_{mean}}$, which quantifies the normalized deviation from the average bond length within the polyhedron, where $l_{mean}$ is the unweighted average bond length within the coordination polyhedron. We find the ECoN of CsA to be 8.1 and of CsB to be 5.9, with $D = 0.12$ and 0.099 respectively. The standard deviation $\sigma$ of Cs–I bond lengths for CsA is 0.61 Å and for CsB is 0.51 Å. In comparison, the ECoN of the Cs–I coordination polyhedron of nonperovskite $\delta$CsPbI$_3$ is larger with a value of 8.9. The polyhedron is also significantly less distorted with $D = 0.016$ and $\sigma = 0.08$ Å. The additional regularity of the Cs coordination environment in $\delta$CsPbI$_3$ can also be seen in Figure 3E, where the Cs–I contacts are all within 0.25 Å. The thermodynamic instability of $\gamma$CsPbI$_3$ is consistent with nonperovskite $\delta$CsPbI$_3$ having a significantly less distorted coordination polyhedron with an ECoN 0.8 larger than CsA and 3.0 larger than CsB. The order of magnitude higher $D$ and $\sigma$ values for both CsA and CsB in perovskite $\gamma$CsPbI$_3$ compared to stable yellow $\delta$CsPbI$_3$ further support the hypothesis that the Cs$^+$ ion rattles in its coordination polyhedron.
At temperatures $>600$ K, $\delta$-CsPbI$_3$ spontaneously converts to the cubic perovskite $\alpha$-CsPbI$_3$, where Cs is in the middle of the iodine cavity.$^{[19,41]}$ Its Cs$^+$I coordination polyhedron is shown in Figure 3D, and there are 12 identical Cs$^+$I contacts resulting in an ECoN of 12 and $\Delta$ and $\sigma$ of 0 (Figure 3E). We believe $\alpha$-CsPbI$_3$ becomes the thermodynamically stable phase at high temperature because increased thermal motion of the Cs$^+$ and I$^-$ ions allows the longer 4.45 Å Cs$^+$I contacts to be stable while also maximizing the ECoN. Changes in the Pb$^+$I bonds likely do not contribute to the stability of $\alpha$-CsPbI$_3$ at high temperatures because at 634 K, the Pb$^+$I bond length is 3.14 Å, which only differs by 0.03–0.06 Å from the Pb$^+$I bond lengths we measure in $\gamma$-CsPbI$_3$ from 100 to 295 K.$^{[41]}$

Our structural study also suggests that perovskite $\gamma$-CsPbI$_3$ may exhibit increased stability at temperatures below 175 K, where the Cs ion only occupies the Cs$_A$ site, which has a much larger ECoN than Cs$_B$. This hypothesis is supported by the observation that the Cs disorder is a thermally activated process. Using density-functional theory calculations, Marronier et al. found that $\gamma$-CsPbI$_3$ has a lower total energy than non-perovskite $\delta$-CsPbI$_3$, contrary to the experimental observation that $\delta$-CsPbI$_3$ is what forms when CsPbI$_3$ is synthesized at room temperature.$^{[19]}$ It may be possible that $\gamma$-CsPbI$_3$ is the thermodynamic product at temperatures $\leq 175$ K, where the Cs atom is well-behaved and occupies only a single site, although the ECoN at 100 K (8.0) does not significantly change from 295 K and is still smaller than the ECoN for yellow $\delta$-CsPbI$_3$ (8.9).

A major implication of our study is that CsPbI$_3$ reveals the limitations of tolerance factor approaches to predicting the formation of halide perovskites. The original tolerance factor to predict perovskite stability is attributed to Goldschmidt,$^{[23,24,42]}$ where $t = \frac{r_x + r_z}{\sqrt{2}(r_x + r_z)}$. A perovskite structure is predicted to be stable in the range of $0.8 \leq t \leq 1$, and values of $t$ near 0.8 typically result in distorted perovskite structures.$^{[42]}$ Goldschmidt’s tolerance factor has also been extended to account for non-spherical molecular cations and is widely used to predict the stability of organic–inorganic hybrid perovskites.$^{[43,44]}$ Using the ionic radii from Shannon’s table,$^{[45]}$ the Goldschmidt tolerance factor for CsPbI$_3$ is 0.851, similar to that of GdFeO$_3$ (0.848),$^{[25]}$ yet the thermodynamically stable phase of CsPbI$_3$ at room temperature is the nonperovskite $\delta$-CsPbI$_3$. If instead of Shannon’s radii we instead use a smaller ionic radius of 1.03 Å for Pb$^{2+}$ that is computed solely from lead iodide compounds,$^{[42]}$ the tolerance factor increases to 0.893, which indicates that the perovskite structure is more strongly favored than when using Shannon’s radius. Other methods that replace the Shannon radii with values that are more accurate for halide perovskites also increase the Goldschmidt tolerance factor.$^{[46]}$ Similarly, based on the observed tolerance factor defined by Sasaki et al. $\tau = \frac{(A-X)/(B-X)}{[A-X]/[B-X]}$,$^{[25]}$ where $A$—X and $B$—X refer to average bond distances within each coordination polyhedron, the value for $\gamma$-CsPbI$_3$ (0.987) is in the range of many stable oxide perovskites, such as CaTiO$_3$ (0.96) and GdFeO$_3$ (0.977). Filip and Giustino incorporate the Goldschmidt tolerance factor and the octahedral factor ($\mu = r_6/r_3$) to find a stable region for perovskites,$^{[24]}$ yet their model predicts CsPbI$_3$ to be stable as a perovskite. Bartel et al. propose a tolerance factor $\tau = \frac{r_x}{r_6} - n_\lambda \left(\frac{r_x}{r_6} - \frac{r_x}{r_6 \ln(r_x/r_6)}\right)$ where $n_\lambda$ is the oxidation state of the...
A-site cation (Cs in CsPbI$_3$), and under their model, a perovskite structure is stable for $\tau < 4.18$. Their model then correctly predicts that CsPbI$_3$ will not be a perovskite at room temperature because $\tau = 4.30$. Compared to the stable perovskite CsPbBr$_3$ with a Goldschmidt tolerance factor of 0.862 (only 0.011 larger than for CsPbI$_3$), the major structural differences in CsPbI$_3$ are larger tilt angles and a more off-center Cs position than in the Cs-X coordination polyhedron. The off-centering of Cs seems to be neglected in simple tolerance-factor-based models.

In contrast to SCXRD and conventional powder diffraction measurements, PDF measurements take the diffuse scattering into account in addition to the Bragg reflections to generate a pair distribution function $G(r)$, which quantifies the probability of finding two atoms separated by a distance $r$. A major advantage to PDF measurements is that they allow the local structure to be analyzed separately from the long-range average structure. We fit $G(r)$ with a single Cs site at all temperatures because when attempting to fit $G(r)$ with split Cs positions, the resulting structure is not physically reasonable. The inability to resolve the long-range disorder we observe in SCXRD measurements is likely due to the relative insensitivity of the PDF method to the kind of disorder we observe in the long-range structure; peaks corresponding to the two Cs sites will overlap significantly in the one-dimensional PDF dataset while the three-dimensional dataset provided by SCXRD measurements allows the two sites to be individually resolved.

Like the SCXRD data, we fit $G(r)$ using a structural model with orthorhombic symmetry in the $Pnma$ space group. Figure 4A,B shows good agreement between the long-range data ($r = 20 – 50$ Å) and the fit at both 100 and 295 K; data and fits at intermediate temperatures are shown in Figure S6 in the Supporting Information. However, the structure found

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**Figure 4.** The local crystal structure of perovskite-type $\gamma$CsPbI$_3$. A,B) $G(r)$ (blue) at 100 K (A) and 295 K (B), with fit to long-range ($r = 20 – 50$ Å) data (orange) and residual (green). C,D) $G(r)$ (blue) at 100 K (C) and 295 K (D), with fit to short-range ($r = 2.5 – 8$ Å) data (orange) and residual (green). E) Cs–I bond lengths and F) I–Pb–I angles at short range from PDF fits. Dashed lines are to guide the eye.
by fitting the long-range data does not adequately fit the local region from $r = 2.5 - 8 \, \text{Å}$, which is on the length scale of a single unit cell. Most of the poor correspondence between the long-range fit and the local $G(r)$ is for distances corresponding to Cs–I and I–I bonds.

Fitting the short-range local crystal structure separately, we find much better agreement between $G(r)$ and the fit (Figure 4C,D). At temperatures $>175 \, \text{K}$, the Cs–I bonds begin to elongate (Figure 4E) and the Pb–I octahedra become highly distorted on the length scale of the unit cell with one of the I–Pb–I angles approaching $82^\circ$ compared to the ideal $90^\circ$ (Figure 4F), contributing to the instability of perovskite-type $\gamma$CsPbI$_3$. Because these distortions greatly increase at the same temperatures that the Cs scattering density splits in SCXRD measurements, the increased local octahedral distortion found from PDF measurements and split Cs density observed in the SCXRD data are likely manifestations of the same phenomenon. While an I–Pb–I angle near $82^\circ$ is drastically different than what is observed in the SCXRD data, we note that at $295 \, \text{K}$ the equivalent isotropic thermal parameters $U_{eq}$ for I are 2–4× larger in the long-range SCXRD structures than in the local PDF structures while $U_{eq}$ for Pb only differs by $\approx 20\%$ (Figure S7, Supporting Information). This is consistent with the larger thermal parameters of I in the long-range structure reflecting the average of all orientations of the distorted local structure, while Pb remains fixed at the center of the octahedra in both the local and long-range structures so local distortions do not significantly affect its behavior.

Like what we find here for perovskite-type $\gamma$CsPbI$_3$, PDF measurements on organic–inorganic hybrid halide perovskites[31,48,51] as well as inorganic halide perovskites such as CsSnBr$_3$[52] and the high-temperature cubic perovskite $\alpha$ phase of CsPbI$_3$[34] exhibit different local and long-range structures, which different authors attribute to interactions between halides and the organic cation[48] or deformations of the metal halide octahedra.[11,51–53] In cubic Sn- and Pb-based halide perovskites, off-centering of the metal cation within the metal-halide octahedra has been observed and is attributed to the stereochemical activity of the lone pair causing instabilities under cubic symmetry.[51–53] We do not see off-centering of the metal cation in the local structure of $\gamma$CsPbI$_3$, supporting the hypothesis that such off-centering does not occur in the presence of octahedral rotations which are present under the orthorhombic symmetry of $\gamma$CsPbI$_3$[52]. Indeed, off-centering of the metal cation is prohibited in the orthorhombic $Pnma$ space group because the I–Pb–I bond angles for opposing halides in an octahedron are constrained to be $180^\circ$ by symmetry. The local distortions we observe in $\gamma$CsPbI$_3$ are unique because perovskites typically become less distorted and raise their symmetry upon warming,[12,31] whereas here we observe the emergence of major local octahedral distortions while maintaining orthorhombic $Pnma$ symmetry. It has also been hypothesized that organic–inorganic hybrid perovskites may exhibit ferroelectricity or the Rashba effect, both of which require non-centrosymmetric structures.[54–56] Here, we find that both the local and long-range structures are centrosymmetric for $\gamma$CsPbI$_3$, which rules out the existence of the static Rashba effect. In contrast, cubic perovskites that exhibit off-centering of the metal cation become locally noncentrosymmetric, allowing a conventional Rashba effect to exist.[11,51–53] It may still be possible that vibrations in $\gamma$CsPbI$_3$ can result in subtle transient local symmetry breaking, which may allow for a dynamic Rashba effect.[57]

We use SCXRD and PDF measurements to analyze the temperature-dependent structural behavior of orthorhombic perovskite $\gamma$CsPbI$_3$. We find that $\gamma$CsPbI$_3$ at ambient temperature has fewer good Cs–I contacts than nonperovskite $\delta$CsPbI$_3$, which in accordance with Goldschmidt’s principle of maximum anion contact[53] we hypothesize is one reason that yellow $\delta$CsPbI$_3$ is the thermodynamically stable product at room temperature. Furthermore, between 175 and 295 K we find that the Cs atom is split between two sites in a thermally activated process, which suggests the Cs atom rattles in its cage of I atoms and also contributes to the thermodynamic instability of perovskite-type $\gamma$CsPbI$_3$. The thermally activated Cs site has fewer anion contacts than the dominant site, which may further decrease the stability of $\gamma$CsPbI$_3$ at these temperatures. Between 100 and 150 K, the Cs atom occupies a single site with well-behaved electron density, indicating that $\gamma$CsPbI$_3$ is more stable at these temperatures. PDF measurements show that the local structure of $\gamma$CsPbI$_3$ is more distorted than the global structure between 100 and 295 K, like in other halide perovskites. The tremendous distortion of the Pb–I octahedra at short range likely also contributes to the instability of $\gamma$CsPbI$_3$. The observations of the rattling Cs cation and the extreme local distortion of the Pb–I octahedra are vital pieces of information for theoretical studies because to the best of our knowledge, the mechanism for the phase transition between $\gamma$CsPbI$_3$ and $\delta$CsPbI$_3$ as well as the reason water vapor catalyzes this transition[57] are not yet understood.

Our findings provide structural support for two routes to stabilize bulk CsPbI$_3$-based perovskite solar cells. The first route involves chemical modification of CsPbI$_3$ to reduce or eliminate the rattling of the Cs$^+$ cation. Several approaches have shown promise thus far. Incorporating excess Cs in thin films formed by evaporation of CsI and PbI$_2$ allows the perovskite phase to form at 50 °C with excellent stability under nitrogen.[22] The exact mechanism of stability is unclear, but our results herein imply that excess Cs may occupy empty spaces, reducing rattling. Other modifications have been used such as alloying Br and I to make CsPbI$_{3-x}$Br$_x$,[58–60] and adding Br likely reduces the rattling of Cs$^+$ because of the reduction in size of the Cs-X coordination polyhedron. These modifications do not seem to increase the stability to moisture, however.[22,60] If maintaining the chemical integrity of CsPbI$_3$ is desired, the rattling of Cs$^+$ cannot be suppressed and the phase transition to nonperovskite $\delta$CsPbI$_3$ must be controlled through another route, which is mechanically stabilizing $\gamma$CsPbI$_3$ through strain or epitaxy to eliminate the transition pathway to $\delta$CsPbI$_3$. Straining the substate of a CsPbI$_3$ thin film was found to increase the thermodynamic stability of the film but did not enhance the moisture stability.[60] In contrast, a recent report[61] grew epitaxial PbI$_2$(OH) layers on $\gamma$CsPbI$_3$ microcrystals that were synthesized in the presence of and stable to moisture, indicating the promise of epitaxial stabilization. We suggest the further exploration of epitaxial methods to stabilize perovskite-phase $\gamma$CsPbI$_3$ because it is impossible to substitute a larger inorganic cation given that Cs$^+$ is the largest inorganic cation, so engineering approaches...
are therefore needed to work around the destabilizing effect of the rattling Cs\(^+\) cation. Our detailed characterization of the local and long-range structures provides vital structural information that will guide theoretical and experimental studies that aim to stabilize bulk forms of perovskite-phase γCsPbI\(_3\), allowing it to be used in stable solar cells.

Experimental Section

γCsPbI\(_3\) was crystallized from the melt using a previously published procedure.[7] A stoichiometric quantity of CsI (Sigma-Aldrich, anhydrous, 99.999%) and PbI\(_2\) (Alfa-Aesar, ultrady, 99.999%) were loaded into a quartz tube in an argon-filled glove box (\(O_2\) and \(H_2O\) < 1 ppm), evacuated and flushed 3x with dry argon, and ampouled under vacuum. The ampoule was heated to 550 °C and slowly cooled to 370–400 °C at which point it was quenched in an ice-water bath and opened in an argon-filled glove box.

SCXRD data were collected on a Bruker Kappa Apex2 CCD Diffractometer using graphite-monochromated Mo-K\(\alpha\) radiation (\(\lambda = 0.71073\ \text{Å}\)). For SCXRD measurements, γCsPbI\(_3\) was placed in degassed Pararad 10312 oil while in an argon-filled glove box and transferred to the microscope for selection in a sealed vial. Crystals were selected in air with dry nitrogen flowing over the crystals. A single crystal was mounted on a Kapton microloop (MiTiGen), and extreme care was taken to place crystals on the diffractometer as quickly as possible to minimize air exposure. An Oxford Cryostream 700 cryocooler flowed dry nitrogen over the crystal the entire time it was mounted on the diffractometer. Background, polarization, Lorentz-factor, and multi-scan absorption corrections were used when processing the data. The initial structure solution was found using the intrinsic phasing method of the ShelXT program[62] and refined using the least-squares algorithm in the ShelXL program[63] using the Olex2 GUI.[64] The 295 K structure presented here is a re-refinement of data from ref. [17]. Structures were visualized using VESTA.[39] The partial Cs density (Figure 2A,B) was obtained by starting with the refined SCXRD structure, removing Cs, and running a ShelXL least squares refinement cycle with the number of least squares cycles set to 0 (L.S. 0 instruction), which computes structure factors but does not change the atomic positions or displacement parameters.[65] The partial Cs density was then found by subtracting F(calc) from F(obs).

To perform X-ray PDF measurements, γCsPbI\(_3\) was ground using a mortar and pestle in an argon-filled glove box and sifted using a 200-mesh sieve. The powder was loaded into quartz capillaries in an argon-filled glove box, which were subsequently evacuated and flushed with dry argon 3x before being sealed under high vacuum (\(\approx 10^{-4}\) torr). Data were collected at beamline 28-ID-1 at NSLS-II at Brookhaven National Laboratory in the temperature range of 100–295 K. The sample temperature was controlled using a liquid N\(_2\) cryostream. Measurements were performed at an X-ray energy of 74.69 keV (\(\lambda = 0.1660\ \text{Å}\)) using a PerkinElmer area detector (200 × 200 µm pixel size) mounted 204 mm downstream of the sample. 2D diffraction data were integrated and converted to intensity vs \(Q\) (momentum transfer) patterns using Fit2D[614] and converted to PDFs using xPDFsuite.[655] PDFs were fit using Diffrpy-CML.[66] The PDF Gaussian envelope damping parameter Qdamp and the PDF peak broadening parameter Qbroad were determined from measurements of a Ni standard and were fixed at these values for all analysis of γCsPbI\(_3\). At each temperature, the long-range structure \((r = 20 - 50\ \text{Å})\) from the PDF was fit using the SCXRD structure as the initial guess. All symmetry-allowed positions and anisotropic atomic displacement parameters as well as the dataset scale factor were varied in this fit. After the long-range structure was determined, the peak sharpening parameter \(\delta_p\) that models correlated motion and that was used in the short-range fits was determined by fixing all parameters, extending the fit-range to \(r = 2.5–50\ \text{Å}\), and fitting \(\delta_p\), which was not varied in the short-range fits. \(\delta_p\) was used to model the correlated motion because it models correlated motion above the Debye temperature and best fit the data; the Debye temperature in γCsPbI\(_3\) was calculated to be 104 K.[67] The short-range structure was fit for \(r = 2.5–8\ \text{Å}\). In the short-range fits, the dataset scale factor was fixed to the value determined from the long-range fit, and isotropic thermal parameters were used because of the low data-to-parameter ratio.

Further details of the crystal structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the deposition number CSD 1984123–1984140.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

CsPbI\(_3\), diffraction, pair distribution function, perovskites, solar cells, stability, rattling

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