Three-dimensional coherent x-ray diffraction imaging of ferroelastic domains in single CsPbBr$_3$ perovskite nanoparticles

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Abstract

Metal halide perovskites attract significant interest due to their remarkable performance in optoelectronic devices. However, the gap in understanding the relationship between their nanoscale structure and properties limits their application towards novel devices. In this work, twinned ferroelastic domains in single 500 nm CsPbBr$_3$ particles are studied with 3D Bragg coherent x-ray diffraction imaging. A preferential double-domain structure is revealed in four identical particles, with one domain oriented along the [110] and the other along the [002] direction. The particles exhibit similar scattering volume ratios of 0.12 ± 0.026 between twin phases, suggesting the possibility of a deterministic formation process. The domains exhibit a difference in lattice tilt of 0.59 degrees, in excellent agreement with calculations of the lattice mismatch at the (112) twin boundary. These results provide important insights both for the fundamental understanding of ferroelastic nanoscale materials and for the performance improvement of perovskite-based devices. Moreover, this work paves the way towards real-time imaging of the domain dynamics in ferroelastic systems.

1. Introduction

Metal halide perovskites (MHPs) have been attracting significant attention over the past few years due to their outstanding performance in photovoltaic [1], light-emitting [2], energy storage [3], and scintillation applications [4]. The crystal structure of MHPs with a common formula of ABX$_3$ allows for flexible chemical composition, which is an efficient way to tune their properties [5]. All-inorganic lead halide CsPbX$_3$ nanocrystals (NCs) are one of the promising candidates for MHP-based novel optoelectronic devices [6]. They demonstrate high efficiency as light emitters through photoluminescence (PL) across the entire visible spectral range (410–700 nm) [5, 7], where the formation of Cl/Br and Br/I solid solutions enables a highly accurate adjustment of their band gap energies.

An important aspect of MHPs is the structural phase transitions at moderate temperatures, changing from higher to lower symmetries upon cooling. Particularly, lead halide CsPbX$_3$ single crystals transition through cubic, tetragonal, and orthorhombic structures [8] and the formation of twin domains is induced [9]. This process is possible due to coordination octahedra tilting, causing fragmentation of the crystals into domains with twin boundaries [10]. If two interfacing domains have different lattice spacing, the domains will generally tilt due to the lattice mismatch at the domain boundary [9, 11]. One important question is how the twin substructures modify transport and chemical properties in the vicinity of the domain boundaries relative to the bulk. Similarly to semiconductors [12], strain engineering approaches can alter...
the properties of MHPs, including phase transition diagrams, via thermal, mechanical, and light-induced stress [13, 14]. Surface relaxation may also affect the behavior of twin walls as they intersect surfaces in three-dimensional (3D) nanostructures like nanoparticles or nanowires. Consequently, incompatibility of the two domains at the surface may lead to large strains [15]. Additionally, there is a strong debate whether MHPs can exhibit ferroelectricity similar to other well-known perovskites such as BaTiO₃ and PbTiO₃ [16–18], and which role strain and defects play in this case.

Recently, it was demonstrated that the emission characteristics of lead halide NCs also depend on their size and shape [7, 19]. However, the information on internal structure and strain remains limited. Recent studies only indirectly inferred the presence of sub-domains in CsPbBr₃ NCs with the size of several nanometers [5], which was done by evaluating powder diffraction data and constructing a model of coherent nanotwins. In the case of macroscopic scale single crystals of CsPbBr₃, (002)/(110) domains with {112} boundaries were observed directly by polarized optical microscopy and electron microscopy [8]. Overall, there is a lack of direct, decisive, and nondestructive characterization methods for imaging ferroelastic domains and their dynamics in MHP NCs at the nanoscale.

Until recently MHPs were investigated mainly by PL technique with micron-scale spatial resolution [20–23]. Transmission electron microscopy provides an ultimate spatial resolution on the atomic scale [7, 8, 18]. However, the bulk structure remains inaccessible due to the low penetration depth of electrons and related damage to the specimens [24]. X-ray diffraction, on the other hand, provides a perfect tool to probe internal nanoscale structures of MHPs crystals due to long penetration depth and reduced damage. Particularly, the development of hard x-ray synchrotron radiation sources with both high photon flux and spatial coherence provides a variety of scattering and microscopy techniques to be extended towards the research of halide perovskites [25, 26].

Direct mapping of ferroelastic domains in CsPbBr₃ nanowires was performed recently by scanning x-ray nanodiffraction [27]. However, the distribution of the domains was revealed only in 2D, with the information averaged along the third dimension. Also, the spatial resolution was limited by the size of the focal spot of the x-ray beam. Bragg coherent x-ray diffraction imaging (BCDI) is a synchrotron-based lensless technique, which is capable of reconstructing the morphology and internal structure of 3D crystalline nanomaterials [28, 29]. The spatial resolution of BCDI is not limited by the beam spot size on the sample, but by the largest scattering angle reliably recorded at the detector. The method is also very sensitive to crystal lattice strain (10⁻⁴) and tilts, providing valuable information on elastic strains and defects within the structure [30]. In a typical BCDI experiment, the 3D scattering intensity pattern is collected in the vicinity of selected Bragg peaks. The 3D complex-valued function ρ(𝑟) of the particle is reconstructed by solving the phase problem with advanced phase retrieval algorithms [28]. There is a linear relationship between the crystal displacement field 𝑢(𝑟) and the reconstructed object phase

\[ \varphi(\mathbf{r}) = -\mathbf{H}_{\mathbf{hkl}} \cdot \mathbf{u}(\mathbf{r}) \]

where \( \mathbf{H}_{\mathbf{hkl}} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \) is the reciprocal lattice vector. Any local displacement of the unit cells of the crystal parallel to \( \mathbf{H}_{\mathbf{hkl}} \) will change the relative phase of the scattering from those unit cells relative to the rest of the crystal. If this occurs in regions large enough to be resolved, the distortion can be visualized as a region or domain with a measurable phase appearing in the image.

BCDI studies of ferroelastic domains were recently reported for BaTiO₃ perovskite NCs [32, 33], but MHPs are more challenging for imaging due to their instability under hard x-rays. Here, we demonstrate that BCDI can be used to study single MHP NCs, by appropriate sample preparation and careful adjustment of coherent flux and exposure times during the measurements. We exploit the unique coherence properties of the NanoMAX beamline [34] at the diffraction-limited storage ring MAX IV to directly image ferroelastic domains of CsPbBr₃ NCs in 3D. The combination of reciprocal space analysis and BCDI is employed by considering the case of two nearby Bragg peaks, originating from different regions or domains in the same NC. Surprisingly, we find that the all four investigated particles show two domains with a similar atomic structure, size, and morphology. Our results pave the way towards rapid in situ imaging experiments. Systematic characterization of the structure–composition–property–performance relation in halide systems would boost the development of novel perovskite-based devices towards the limits of their capabilities.

2. Results and discussion

We start by describing a few essential aspects of the sample preparation and experimental method design, as they are crucial for successful application of BCDI towards complex functional materials. BCDI requires NCs smaller than the beam, a requirement that can be overcome by changing the beam size. Furthermore, the Bragg reflections from different NCs should not overlap at the detector plane, although many particles may be illuminated at once. Our CsPbBr₃ particles were synthesized by a solvent evaporation method (see appendix A for details). In the scanning electron microscopy (SEM) image, the NCs appear as almost
Figure 1. (a) Scheme of Bragg coherent diffraction imaging experiment in the sample reference frame. Coherent x-rays fully illuminate the nanocrystal and produce the Bragg peak shown in red isosurface. The 3D diffraction pattern is obtained by recording intensities at the detector plane for a set of incidence angles $\delta \theta$ in the vicinity of (002)/(110) Bragg conditions. (b) SEM image of CsPbBr$_3$ NCs, revealing their typical shapes and sizes. (c) Reconstructed morphology of the double domain structure of a single CsPbBr$_3$ nanocrystal, retrieved from the diffraction pattern in (a).

perfect cubes with no obvious signs of defects or domains (see figure 1(b)). The sample was pre-characterized by laboratory x-ray diffraction, which revealed that the NCs were preferably oriented with the $\{002\}/\{110\}$ facets parallel to the silicon nitride window as a substrate was revealed (see appendix B for details). The orientation of the particles in the plane of the window is random, which allows measurement of isolated Bragg reflections from single crystallites. The NCs of CsPbBr$_3$ are stabilized in an orthorhombic phase with lattice constants: $a = 8.207$ Å, $b = 8.255$ Å, and $c = 11.759$ Å (space group Pbnm), just like the bulk material [35].

The BCDI experiment was performed at the nanofocusing beamline NanoMAX at the 4th generation synchrotron source MAX IV (Lund, Sweden) [34]. The photon energy of incoming x-ray beam was 9 keV. The geometry of the experiment is presented in figure 1(a). For the analysis of the scattering intensities in reciprocal space, the diffraction patterns were mapped onto an orthogonal coordinate system $Q = (q_x, q_y, q_z)$, where $Q \equiv k_s - k_i$ is a wave transfer vector aligned with the $x$-axis, and $k_i$ and $k_s$ are the wave vectors of the incident and scattered beams respectively (see figure 1(a)). Reliable BCDI datasets were obtained from isolated NCs which were fully illuminated by the coherent x-ray beam. An appropriate NC size was determined by the presence of interference fringes in the diffraction pattern, which arise from the finite shape of the particle. We analyzed only the particles which are comparable to the adjusted x-ray beam size of 0.4 μm (see appendix C for details). The 3D reciprocal space maps were recorded in the vicinity of the (002)/(110) Bragg peaks of CsPbBr$_3$. Each dataset consisted of 101 diffraction patterns with 1 s exposure per frame with reduced incident photon flux of $8 \times 10^8$ ph s$^{-1}$. The exposure time was limited by x-ray beam damage to the sample. In total, more than four successful datasets were recorded during the experiment (see section 2 in supplementary material (https://stacks.iop.org/NJP/23/063035/mmedia)). We will focus on a single example in the following text. The experimental data were analyzed in two independent steps. First, we revealed the atomic structure of the NCs by evaluating positions of the Bragg peaks in reciprocal space. Second, the 3D phase retrieval was performed on the coherent diffraction data, followed by further analysis of NC morphology and internal structure.

The 3D isosurface of scattering intensity in figure 1(a) and $Q$-space projections in figure 2(a) resemble a well-known 'dog-bone' structure, observed previously, for example, in WO$_3$ [36]. It represents two separated Bragg peak intensity distributions connected through a diffuse scattering intensity or a 'ridge'. Each Bragg peak comes from distinct domains inside the particle, which are twinned and tilted with respect to each other. The weaker peak in the data corresponds to (002) reflection at $q_x = 1.068$ Å$^{-1}$. The stronger peak corresponds to (110) Bragg reflection. Using the direct beam position on the detector as a reference and the center of mass positions for each peak the lattice $d$-spacings for $\{002\}$ and $\{110\}$ sets were obtained...
to be $d_{002} = 5.882$ Å and $d_{110} = 5.824$ Å. The difference of these values $\delta d = 0.0584$ Å can be compared to the theoretical one $\delta^T = 0.059$ Å—only 1% relative difference [37].

A lattice mismatch should occur at the boundary of discovered domains within a single particle. The misfit can be accommodated through a slight tilt $\omega$ between $\{110\}$ and $\{002\}$ domains via (112)-oriented twin boundary. For reflection $\{110\}$ the spacing between the planes is $\hat{a} = \sqrt{a^2 + b^2}$ which will be matched to larger distance of $c$. A simple model of twinning at the domain boundary in orthorhombic crystal allows an estimation of the twinning angle by equation [38]

$$\omega_T = 1 - \frac{\hat{a}}{c} \approx 0.58^\circ.$$  

(1)

The tilt obtained from the Q-space analysis of the experimental data equals to $\omega = 0.59^\circ$ (see figure 2(a)). This value is remarkably close to the theoretical prediction $\omega_T$. The orientation of the domain boundary itself with respect to the $y$-axis is $\gamma = 43.59^\circ$. This value is in good agreement with an expected inclination $\gamma^T = 44.71^\circ$ of $\{112\}$-planes with respect to $\{110\}$-planes in orthorhombic CsPbBr$_3$ crystal [8]. The two peaks are connected by a ‘ridge’ of diffuse scattering arising from the presence of a sharp domain boundary between twin phases.

An important observation can be made regarding the ratio in integrated intensities of the measured Bragg peaks within the ‘dog-bone’ structures. Following [39] for crystalline particles fully illuminated by the x-ray beam we can estimate the ratio $R_{A/B}$ of scattering intensities of twinned domains $A$ and $B$ by the following expression (see appendix D for details)

$$R_{A/B} \approx \frac{I_{002}^T}{I_{110}^T} \frac{|F_{110}|^2}{|F_{002}|^2}.$$  

(2)

Here, $I_{002}^T$ and $I_{110}^T$ are total measured intensities in the vicinity of corresponding Bragg spots, and the modulus or structure factors are $|F_{110}| = 200.324$ and $|F_{002}| = 208.664$ [37]. By substituting experimentally measured intensities $I_{002}^T = 0.3256$ arb. unit and $I_{110}^T = 2.205$ arb. unit into two one obtains $R_{A/B} = 0.14$.

The same analysis routine revealed two distinct types of particles in the investigated set. Two of them had a larger volume of (002) domain and other two of (110). Strikingly, the ratios $R_{A/B}$ between scattering intensities are almost the same for similar diffraction peaks (see table 1). However, it is important to note that the integrated intensities $I_{dld}^T$ are influenced by the presence of strain. In general, smaller domains can be expected to be affected more by, for instance, surface strain than larger domains. Therefore, we will compare the values of $R_{A/B}$ with the volume ratios obtained by the BCDI reconstructions further below.
Now we may construct a description of the morphology and atomic structure of the particle, based on the \(Q\)-space analysis only. Here we assume the overall shape of the particle to be cubic as it follows from the SEM results. The model view along the \(z\)-axis is presented in figure 2(b). Domain A is oriented with \(\{002\}\) planes aligned along the \(x\)-axis. Domain B is twinned and has to be oriented with \(\{1\!\!10\}\) planes at \(\omega = 0.59^\circ\) with respect to \(\{002\}\) in domain A. The domain boundary aligns with \(\{1\!\!12\}\) crystal planes direction to accommodate the lattice mismatch. The procedure of the \(Q\)-space analysis was performed in total on four datasets presented in this work. The obtained quantities are summarized in table 1. All particles possess a very similar domain and crystalline structure. All NCSs which revealed fringes in their diffraction patterns have sizes around 500 nm and double twin domain structure. The values of \(d\)-spacing and tilt between twin domains are very similar for a set of particles under investigation.

### 2.1. Phase retrieval

BCDI reveals embedded crystalline structures not accessible by other techniques. Next, we show how inversion of the measured Bragg peaks can be used to retrieve the 3D morphology and internal structure of domains in CsPbBr\(_3\) NCs. The x-ray beam produced by the NanoMAX beamline has a high degree of spatial coherence [40]. That ensures the high contrast of interference patterns in the data from localized particles. The phases of scattering amplitudes are lost during the measurement process and the modulus can be obtained by taking a square root of recorded intensities \(A(Q) = \sqrt{I(Q)}\). It was demonstrated that standard algorithms fail to solve the ‘phase problem’ and reconstruct highly-strained nanostructures [41]. In our case a similar issue arises due to a significant split of the diffraction peaks and the lack of observed interference fringes between the Bragg peaks. Recently, this challenge was addressed by various approaches: support conservation during domain structure evolution [42], the postulation of the particle shapes indirectly [32], and separate reconstruction of the double-peak diffraction pattern in the case of ferroelastic domain wall presence [33]. In this work, we exploit the fact that the Bragg peaks from twinned domains are sufficiently split along the tilt direction to be reconstructed separately. Both intensity distributions reveal fringe patterns arising from the shape of domains. The Bragg peaks were apodized by the Tukey window function with a diameter of 72 pixels in the \(xy\)-plane, which minimized the numerical artifacts due to the \(Q\)-space truncation [43] (see section 3 in supplementary material).

The 3D complex-valued reconstruction \(\rho(r)\) is presented in figure 3, which was selected based on the lowest error-metric (see appendix E for details). The modulus \(|\rho(r)|\) represents an electron density for a given set of crystal planes, in other words, it contains information about the crystallinity and morphology of the crystal. The isosurfaces of reconstruction at 20% of the maximum amplitude value allow for surface morphology evaluation (see figure 3(a)). Both reconstructions were manually combined in 3D real-space and altogether they reveal the cubic shape of the CsPbBr\(_3\) NC as expected from the SEM overview (see figure 1(b)). The missing volumes of amplitude are attributed to the defects of the crystalline structure. The spatial resolution of the reconstruction is 58 nm, as it was estimated by evaluating line spread functions at the known edges of the particle (see section 5 in supplementary material).

Importantly, we can now compare the expected values of scattering volume ratios \(R_{A/B}^{bcdi}\) obtained through the \(Q\)-space analysis, with the volume ratios revealed by the BCDI phasing, \(R_{A/B}^{bcdi}\). We obtained the ratio \(R_{A/B}^{bcdi} = 0.36\) by dividing volumes of reconstructed modulus \(|\rho(r)|\) of the \(A\) and \(B\) domains respectively at 20% threshold. This value is larger than \(R_{A/B} = 0.14\) for the same NC. Importantly, the volume obtained by BCDI is not influenced by strain, which is ubiquitous in nanoparticles. The difference in ratios obtained by different methods highlights the strength of BCDI to correctly reconstruct the morphology of nanoscale

| Particle | I    | II   | III  | IV   |
|----------|------|------|------|------|
| \(d_{002}\) [Å] | 5.881 | 5.882 | 5.882 | 5.881 |
| \(d_{110}\) [Å] | 5.823 | 5.823 | 5.824 | 5.822 |
| \(\delta d\) [Å] | 5.84 \times 10^{-2} | 5.8 \times 10^{-2} | 5.84 \times 10^{-2} | 5.88 \times 10^{-2} |
| \(\omega\) [deg] | 0.578 | 0.574 | 0.590 | 0.585 |
| \(R_{A/B}\) | 0.14 | 0.1 | 0.14 | 0.09 |
| \(R_{bcdi}\) | 0.28 | — | 0.36 | — |
Figure 3. 3D BCDI reconstruction of CsPbBr$_3$ nanocrystal III. (a) Combined 3D isosurfaces of domains $A$-\{002\} and $B$-\{110\} at 20% of maximum amplitude value. The domains are manually aligned to form a cubic particle. (b) Local phase distribution overlaying isosurfaces of the domains from (a). (c) Plane cut through domain $B$, orthogonal to the $Q$ vector. The missing amplitude region represents the core of the phase vortex—the sign of a dislocation. The phase values in colorbars presented in (b) and (c) include both ranges for domain $A$ and $B$. The direction of the probed $Q$ vector is aligned with the positive direction of the $x$-axis.

domains. However, the similarity of the ratios of the Bragg peak intensities is still a strong indication that the domain volume ratios are also similar. This hypothesis is supported by BCDI reconstruction of another particle in the set giving $R_{bcdi}^{A/B} = 0.28$ (see section 6 in supplementary material).

The local phase distributions within each of the domains are presented in 3D in figure 3(b). They are related to atomic displacement fields and allow to reveal defects in crystalline structure of the particle. Additional ringing is observed both in amplitude and phase as stripes parallel to the domain boundary. This effect is attributed to the Gibbs phenomenon arising from the properties of the Fourier transform of truncated functions [44]. In our case, it is the truncation of the ridge intensity arising from the domain boundary (see section 7 in supplementary material). Unfortunately, this effect limits the extraction of quantitative values of phase and strain respectively. However, the 2D cuts parallel to the domain interface should provide valuable information on phase and displacement field distributions. The ringing is more pronounced in a smaller domain $A$.

A strength of BCDI is the ability to resolve crystal defects in 3D, due to the high sensitivity of atomic displacements. A dislocation was identified in domain $B$ by the presence of a characteristic phase vortex and the zero amplitude core. The corresponding cut through 3D phase distribution is shown in figures 3(c) and
Figure 4. Orthogonal cuts through 3D BCDI reconstruction of CsPbBr3 NC. The slices are grouped by amplitudes (a) and phases (b) for the domains A (1) and B (2). The Gibbs phenomenon artifacts are shown by arrows.

(b.2). We tentatively attribute this to a screw or edge dislocation, based on the angular profile of the displacement field (see section 4 in supplementary material).

2.2. Discussion
Surprisingly, we obtained four almost identical datasets, revealing similar atomic and domain structure. Based on integrated intensity around each of the peaks we could conclude on the relative scattering volume of twin domains within the NC. Two of them reveal a larger volume of (002) domain, and the other two of (110). Note that that these planes are orthogonal, so in a different scattering geometry the observed planes would be swapped. Therefore, all four particles show the same domain distribution. The ratio of the integrated intensities $R_A / B$ has similar values for each NC (see table 1) with the mean value of 0.12 and a standard deviation of 0.026. The values $R_{bcdi}^{A/B} = 0.32 \pm 0.06$ obtained from BCDI reconstructions, which is insensitive to strain, shows the actual volume ratios between the domains. It is also important to note that all particles are expected to be within a narrow range of sizes since we can analyze and reconstruct only NCs smaller than the beam size.

The observed similarities suggest the possibility of a deterministic process behind the domain structure formation in the NC for a given size and shape. The ferroic nature of lead halide perovskites allows for spontaneous structure transformations due to the flexible PbX$_6$ octahedra-based 3D framework. It is well established that due to the high surface to volume ratio for NCs contribution from surface stress can be significant in determining their domain structure in ferroelectrics [45]. We believe that fine tuning of the growth parameters allows for the predictable formation of domain structures in this class of nanomaterials that could be further exploited in novel optoelectronic devices.

The resolution in our measurements is limited by x-ray beam damage. It also limits the applicability of multi-reflection BCDI technique for full strain tensor characterization of CsPbBr$_3$ NCs [46]. We address this issue in the appendix F. The stability of MHP samples could potentially be improved by using advanced growth techniques and employing cryogenic sample environments and inert atmospheres during x-ray measurements [47]. With these opportunities, the research of MHP nanostructures with x-ray imaging...
methods will become considerably more quantitative, decisive, and effective. It also brings the possibility of operando BCDI studies to reconstruct the 3D dynamics of ferroelastic nano-domains within NCs while going through phase transitions upon heating [48].

3. Conclusion

In summary, we studied the structure and morphology of twinned domains in an important class of all-inorganic CsPbBr3 NCs by BCDI in their pristine state. We revealed a systematic formation of double domain structures inside CsPbBr3 NCs of a given size at 58 nm resolution. Coherent diffraction patterns revealed the split in scattering intensity with a connecting ridge structure arising from a sharp domain boundary. The atomistic model of the particles was constructed by Q-space analysis of the diffraction patterns. The 3D local morphology and phase was obtained by apodizing Bragg peaks and reconstructing them separately with iterative phase retrieval algorithms. We believe, that our study will pave the way towards a better understanding of MHPs’ structure and functionality at the nanoscale.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

Appendix A. Sample preparation

The CsPbBr3 NCs were synthesized by a solvent evaporation method. First, 0.008 mol l⁻¹ CsPbBr3 in anhydrous dimethylformamide (DMF, 99.8%, Sigma-Aldrich) is prepared as a precursor by mixing 17 mg of CsBr (99.9%, Sigma-Aldrich) and 29.4 mg of PbBr2 (≥ 98%, Sigma-Aldrich) into 10 ml DMF. The droplet was put on the 5 × 5 mm² Si₃N₄ window for x-ray microscopy (Silson) on a hotplate heating at 70 °C. Then 5 μl of the precursor was added by pipette on the window. The CsPbBr3 nanoparticles were grown within 5 min under heating at 70 °C. Additional heating for 15 min was done to anneal the crystals and improve their crystalline quality.

Appendix B. Sample pre-characterization

The sample was pre-characterized by laboratory source x-ray diffraction (XRD) (see figure S1 in supplementary material). The measurement was performed on the CsPbBr3 sample from the same growth batch as the one used for the synchrotron experiment. The XRD pattern is collected using STOE STADI MP diffractometer with Cu anode x-ray source (voltage of 40 kV, current with 40 mA) in reflective geometry probing crystal planes that are approximately parallel with substrate. The scanning step width is 0.2° and the counting time is 30 s per step. Typical size of the beam spot on the sample for STOE STADI MP diffractometer is 0.4 × 12 mm, therefore a considerable number of particles were illuminated to obtain their average structure and orientation. The DECTRIS MYTHEN 1K pixel detector gives a precise angular resolution of 0.03° at full width at half maximum (FWHM). The assemble averaged diffraction pattern is shown in figure S1 in supplementary material. It is important to notice that the 112 peak in the experimental data is almost two orders of magnitude weaker as compared to the theoretical prediction. The reason for this becomes clear if one assumes a preferential {002}/[110] orientation of NCs on the surface of the silicon nitride window. The {112} lattice planes are oriented about 45 degrees away from these planes and the substrate, and therefore do not contribute to the XRD signal in specular scattering geometry.

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Appendix C. Synchrotron experiment

NanoMAX employs a Kirkpatrick–Baez (KB) mirror focusing system to provide a coherent focus at the sample [40]. The size of the focal spot can be controlled by the slits opening before the KB system. The 3D beam profiles were characterized at each slit opening by transmission ptychography technique [49] (see section 1 in supplementary material). That allowed for fast switching between desired beam sizes and available coherent x-ray flux. In this work, we utilized the beam with the FWHM of $0.4 \mu m$ and flux of $8 \times 10^{8}$ ph s$^{-1}$. X-ray fluorescence detector was positioned close to the Si$_3$N$_4$ window to locate CsPbBr$_3$ particles based on the $L_\alpha$ fluorescence emission line of Cs (see supplementary material for details). A Merlin 2D detector (Quantum Detectors Ltd) was positioned at the distance $L = 1$ m downstream the sample at $2\theta_B = 13.5^\circ$ for expected (002) reflection of CsPbBr$_3$. The 3D reciprocal space maps were recorded in the vicinity of the (002)/(110) Bragg peaks of CsPbBr$_3$ [35] by rocking the sample in the range of $2^\circ$ with the step size of $\delta\theta = 0.02^\circ$.

Appendix D. Scattering volume estimation

In general case of kinematical approximation the integrated intensity in the vicinity of the Bragg point is defined by the incoming beam, the shape and volume of the scattering crystal, and by the presence of strain and defects [50]. We may employ a simplified approach to estimate the ratio of scattering volumes of the domains inside the NCs, assuming the incoming flux to be fixed for every sample and the strain effects to be similar for each NC. Following [39], when the crystal completely irradiated by the x-ray beam the total intensity $I_{T/hkl}^i$ measured by the detector is defined by the proportionality

$$I_{T/hkl}^i \propto V |F_{hkl}|^2,$$

where, $V$ is the volume of the particle, and $|F_{hkl}|$ is the structural factor of selected Bragg reflection.

Appendix E. Phase retrieval

The iterative phase retrieval was performed by employing the combination of error-reduction, hybrid input–output algorithms, and guided approach for five generations, with a population of 10 per generation [51, 52]. The selection rule for the best candidate of the complex-valued object $\rho_i(r)$ in each generation was based on the highest value of sharpness metric $S = \sum |\rho(r)|^4$ and breeding of new estimates of the object for the new generation is calculated as $\rho_i^\ast(r) = \sqrt{\rho_i(r)\rho_{best}(r)}$. The final error-metric $E = \sum_Q ||\mathcal{F}(\rho(Q))|^2 - I(Q)||$ reached the lowest value of about 2% in the case of both domains. The phase ramps were removed from the reconstructed objects. The additional phase shift due to the refraction along different propagation distances $\Delta l$ inside the CsPbBr$_3$ NC has a maximum value of $\delta \varphi = 0.088$ rad for $\Delta l = 500$ nm [53]. It is much smaller than the phase profiles induced by surface relaxation and defects.

Appendix F. Beam damage

The issue of the x-ray beam damage in the NCs was assessed by repeating the measurement twice (see section 8 in supplementary material). Most features remain unchanged in the second dataset such as the Bragg peaks positions and the ridge structure. However, the coherent fringes get distorted and the contrast of the diffraction pattern decreases. Overall, the intensity of the diffraction pattern dropped by 40% after 100 s of exposure.

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