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Depressed Phase Transitions and Thermally Persistent Local Distortions in CsPbBr₃ Quantum Dots

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ABSTRACT: The optoelectronic properties of $CsPbX_3$ quantum dots (where X = Cl, Br, or I) are influenced by both their local and average structures. Variable-temperature synchrotron X-ray diffraction measurements of CsPbBr₃ quantum dots show that the temperatures for both the orthorhombic-to-tetragonal (50 °C < $T_{\gamma-\beta}$ < 59 °C) and tetragonal-tocubic (108 °C < $T_{\beta-\alpha}$ < 117 °C) phase transitions of the average structure are depressed relative to their temperatures in bulk CsPbBr₃. Simultaneously, pair distribution function (PDF) analysis of synchrotron X-ray total scattering measurements indicate that the local crystal structure of the quantum dots is best described as orthorhombically distorted over the temperature range of 22 $^{\circ}C < T < 160 ^{\circ}C$, with only small changes in the magnitude of the distortion occurring during the observed changes in the average structure. Taken together, these results suggest that phase transitions in CsPbBr₃ quantum dots are order-disorder, involving the gradual ordering of individually coherent domains that cannot be attributed to changes in the surface area or to ferroelectric phenomena.

INTRODUCTION

Following the publication of a facile hot-injection synthesis for producing monodisperse halide perovskite quantum dots (QDs) of CsPbX₃ (where X = Cl, Br, I),¹ these colloidal materials have been the subject of intense research interest. Halide perovskite QDs feature high photoluminescence quantum yields and narrow emission line widths, suppressed photoluminescence blinking, long carrier lifetimes, and band gaps that are tunable throughout the visible spectrum, making them particularly attractive for next-generation optoelectronic applications such as lasers, LEDS, and solar cells.² The attractive optoelectronic properties that these materials possess are strongly dependent on variations in both the long-range (nm-scale), average crystal structure and the local (Å-scale) structure. For example, rapidly fluctuating polar distortions have been implicated in anomalous trends of optical properties vs. temperature in bulk CH₃NH₃PbI₃ and CH₃NH₃PbI₃ thin films.^{3,4} Other results show that large changes in the photoluminescence intensity and lifetime of CsPbBr₃ QDs occur within a $\Delta T = 50$ K window spanning the temperatures at which symmetry-lowering phase transitions occur in bulk CsPbBr₃, suggesting that distortions play an important role in determining these properties.5,6

The sequence of phase transitions in bulk CsPbBr₃ is well understood. At high temperatures, bulk CsPbBr₃ possesses the cubic α -perovskite structure ($Pm \overline{3}m; a =$ 5.86 Å). As bulk CsPbBr₃ is cooled through $T_{\beta-\alpha} = 130$ °C, it undergoes a first-order phase transition involving rotations of the PbBr₆ octahedra in the *ab* plane to generate the tetragonal β -perovskite structure (*P*4/*mbm*; a = 8.26 Å, c = 5.89 Å). Finally, upon cooling through T_{γ} - $\beta = 88$ °C, the PbBr₆ octahedra tilt away from the *c* axis in order to generate the orthorhombic y-perovskite structure (*Pbnm*; a = 8.20 Å, b = 8.26 Å, c = 11.78 Å, more ACS Paragon Plus Environment

commonly presented in the Pnma setting in which a = 8.26 Å, b = 11.78 Å, c = 8.20).⁷ CsPbBr₃ QDs were originally reported to possess the cubic, α -perovskite structure at room temperature based on laboratory X-ray diffraction; however, subsequent, higher-resolution studies using synchrotron X-ray total scattering revealed that the QDs possess the orthorhombic, γ -perovskite structure at room temperature.8

The temperatures at which phase transitions occur in nanomaterials are often substantially reduced versus those in the analogous bulk materials.9-13 Differential scanning calorimetry measurements of colloidal CsPbBr₃ QDs unexpectedly show a small increase in the temperature of the orthorhombic-tetragonal phase transition relative to bulk.14 Recent studies using X-ray total scattering have suggested that phase transitions in CsPbBr₃ QDs proceed through the formation of twin boundaries and that orthorhombic distortions persist on the local scale near the temperature at which the average structure of the bulk material is cubic.15

Given that the technological applications of CsPbX₃ QDs involve heating of the optical medium during processing (e.g., lithography resist annealing) and/or in operando (i.e., Joule effect), it is of fundamental importance to understand in detail the sequence of structural changes that occurs in these materials, on both the average and local length scales. In this work, we use a combination of Rietveld refinements of synchrotron Xray diffraction data and pair distribution function (PDF) analysis of synchrotron X-ray total scattering data to observe the evolution with temperature of the crystal structure for CsPbBr₃ QDs, which is perhaps the most widely studied composition for perovskite QDs.

RESULTS AND DISCUSSION

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59 60 Colloidal CsPbBr₃ QDs used for these measurements were prepared according to the prototypical hotinjection method of Protesescu et al.¹ The QDs were characterized by transmission electron microscopy (TEM, Figure S1) and were found to consist of welldefined cuboidal particles with an average edge length of ca. 9 nm. Steady-state photoluminescence measurements of the CsPbBr₃ QDs show a narrow, band-edge emission peak at 2.39 eV that is consistent with the optical absorption edge measured by UV-vis spectroscopy (Figure S2), and with published band gap-size trends for CsPbBr₃ QDs.¹

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Synchrotron X-ray diffraction of CsPbBr₃ QDs. High-resolution synchrotron X-ray diffraction data were collected on the CsPbBr₃ QDs at six temperatures spanning the phase transitions of the bulk analog (i.e., T = 22, 70, 90, 120, 140, and 160 °C) using the 11-BM instrument at the Advanced Photon Source (APS) at Argonne National Laboratory with a photon wavelength of λ = 0.457 Å and a step size of 0.001° 2θ . Data were re-binned with a coarser spacing of 0.005° 2θ in order to facilitate convergence. All fits were performed in the range of 6° < $2\theta < 25^{\circ}$ to avoid the large background signal contributed by organic ligands and residual solvent.8,16 Rietveld refinements of the cubic, tetragonal, and orthorhombic structures to the diffraction data were performed for the data at each temperature. Refinements of the cubic structure converged at all temperatures, whereas refinements to the tetragonal structure converged only for T =22, 70, and 90 °C and refinements to the orthorhombic structure converged only for T = 22 °C. Refined lattice parameters and quality-of-fit values are given in Table 1. Full refinement results, including atomic positions and $U_{\rm iso}$ values, are given in Table S1.

Table 1. Refined lattice parameters and quality-of-fit values for Rietveld refinements of the cubic, tetragonal, and orthorhombic structures of CsPbBr₃ QDs to synchrotron X-ray diffraction data.

| | ~ | | | | | | | | |
|---------------|--------------------|--------------|----------------|-----------------|---------|----------|----------------|--|--|
| | | cul | bic, <i>Pm</i> | $\overline{3}m$ | | | | | |
| <i>T</i> (°C) | a (Å) | | | R_{wp} | | | χ^2 | | |
| 22 | 5.84979(21) | | | 8.87 | | | 3.880 | | |
| 70 | 5.86029 | 9(18) | | 8.03 | | | 3.127 | | |
| 90 | 5.8638 | 1(18) | | 8.08 | | | 2.747 | | |
| 120 | 5.86877(18) | | | 8.33 | | 2.945 | | | |
| 140 | 5.87173(20) | | | 8.70 | | 3.120 | | | |
| 160 | 5.87483(20) | | | 8.32 | | 2.840 | | | |
| | tetragonal, P4/mbm | | | | | | | | |
| T | a (Å) | | c (Å) | | R_{i} | vp | χ^2 | | |
| (°C) | | | | | | | | | |
| 22 | 8.2452(4) | | 5.8879(6) | | 6. | 4 | 2.020 | | |
| 70 | 8.26618(3 | | 5.8974(6) | | 5. | 9 | 1.723 | | |
| | 3) | | | | | | | | |
| 90 | 8.2731(5) | | 5.8942(8 | | 7. 2 | 0 | 2.077 | | |
| | 0 | rthor | hombie | Pnm | | | | | |
| | | | | | | | | | |
| T (°C) | a (A) | <i>b</i> (A) | | <i>c</i> (A) | | K_{wp} | χ ² | | |
| 22 | 8.2676(| 11.7744(9 | | 8.2210(1 | | 5.12 | 1.29 | | |
| | | • | | | | | | | |

| 9) |) | 0) | 3 |
|----|---|----|---|
|----|---|----|---|

At T = 22 °C, refinement of the orthorhombic structure provides a quantitatively superior fit to the data, giving χ^2 = 1.293, compared to χ^2 = 2.020 and χ^2 = 3.880 for the refined tetragonal and cubic structures, respectively. Figure 1a shows the T = 22 °C diffraction pattern and the results of the refinements of each structure to the data. The orthorhombic structure provides a particularly superior fit for the distinct and informative quartet of diffraction peaks in the region $6.9^{\circ} < 2\theta < 8.9^{\circ}$. Three diffraction peaks within this region, centered at $2\theta = 7.1, 7.45$, and 8.4°, are not indexed at all by the cubic structure. In the orthorhombic fit, these diffraction peaks are created by the superposition of several reflections that are generated by the expansion of cubic unit cell to the orthorhombic unit cell: (201) and (102) for $2\theta = 7.1^{\circ}$, (031), (211), and (112) for $2\theta = 7.45^{\circ}$, and (221) and (122) for 2θ = 8.4°. All but the peak at 2θ = 7.45° are also fit by the tetragonal structure.



Figure 1. Synchrotron X-ray diffraction patterns and Rietveld refinements to the cubic $Pm\bar{3}m$ (red), tetragonal P4/mbm (green), and orthorhombic Pnma (blue) structures collected at (a) T = 22 °C, (b) T = 70 °C, and (c) T = 120 °C, and the residuals of those fits. $\lambda = 0.457$ Å for all experiments.

The refinements to the T = 22 °C data are consistent with the results of previous synchrotron X-ray studies which show that, at room temperature, the CsPbBr₃ QDs contain orthorhombic domains that are coherent over sufficiently long scales to generate the observed orthorhombic-only reflections.^{8,16} Recent work using Debye scattering equation (DSE) analysis of synchrotron X-ray total scattering data has further elaborated that CsPbBr₃ QDs contain multiple orthorhombic domains within the Br sublattice that are twinned at dynamic grain boundaries, whereas the Pb sublattice consists of a single domain comprising the nanocrystal.¹⁵ Although our diffraction data are unable to discriminate the domain structure in these CsPbBr₃ QDs, they are not inconsistent with the existence of twinned sublattice domains.

The reflection at $2\theta = 7.45^{\circ}$ is absent from the diffraction pattern collected at $T = 70^{\circ}$ C, shown in Figure 1b. All existing peaks in this pattern are satisfactorily fit by tetragonal structure, with $\chi^2 = 1.723$ compared to $\chi^2 = 3.127$ for the cubic structure. The absence of the (031), (211), and (112) reflections from the $T = 70^{\circ}$ C data suggests that the average structure has become tetragonal at this temperature. The remaining diffraction peaks that are not indexed by the cubic structure are absent from the diffraction pattern at $T = 120^{\circ}$ C, as shown in Figure 1c. At this temperature, the cubic structure gives a qualitatively satisfactory fit with $\chi^2 = 2.945$.



Figure 2. PDFs extracted from data collected at (a) T = 22 °C and (b) T = 160 °C along with fits to the cubic, tetragonal, and orthorhombic models using 2 Å $\leq r \leq 20$ Å. Colored lines below the data represent residuals. The orthorhombic model provides a quantitatively superior fit at all temperatures.

This evolution of the Bragg diffraction in the $6.9^{\circ} < 2\theta < 8.9^{\circ}$ range suggests that the temperatures for the ortho-

rhombic-to-tetragonal and tetragonal-to-cubic phase transitions are substantially depressed compared to their corresponding values in bulk CsPbBr₃. Variabletemperature laboratory X-ray diffraction ($\lambda = 1.542$ Å) in this angular range was collected at finely spaced temperatures to determine more exact bounds for the orthorhombic-to-tetragonal and tetragonal-to-cubic phase transition temperatures (Figure S3). Qualitative examination of the evolution of the peaks exclusive to the orthorhombic and tetragonal phases as a function of temperature suggests that the orthorhombic-to-tetragonal phase transition in these CsPbBr₃ QDs occurs at 50 °C < $T_{\gamma-\beta} < 59$ °C, compared $T_{\gamma-\beta} = 88$ °C for bulk CsPbBr₃. The tetragonal-to-cubic phase transition occurs at 108 °C < $T_{\beta-\alpha}$ < 117 °C in these CsPbBr₃ QDs, compared with $T_{\beta-\alpha} = 130$ °C for the bulk material. Variabletemperature laboratory X-ray diffraction was also collected on bulk polycrystalline CsPbBr₃ to confirm the reported sequence of phase transitions (Figure S4). All variable-temperature laboratory X-ray diffraction measurements were performed on warming, so any errors introduced by insufficient equilibration of the sample and stage will tend to increase the observed transition temperatures relative to their actual values.

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The transition temperatures of the orthorhombic-totetragonal and tetragonal-to-cubic phase transitions are depressed by at least 29 and 13 °C, respectively, relative to their values in the bulk material. The observed depression of transition temperatures of both liquid-solid and solid-solid phase transitions in nanocrystals has been explained in terms of a competition between the lattice energy and surface energy. As crystallites become smaller, the ratio of surface area to volume is increased, and phase transitions that reduce the surface energy (e.g., by

increasing the density of crystallites) become more favorable.9,17 An analogous phenomenon occurs with regards to pressure-induced phase transitions in some materials, although the effect of dimensional reduction in CsPbBr₃ is to stabilize the γ -phase vs. a highly-distorted high-pressure phase.¹⁸⁻²⁰ Depression of the Curie temperature (i.e., the temperature of the transition from an ordered, ferroelectric state to a disordered, paraelectric state) is also observed for nanocrystals of the ferroelectric perovskites PbTiO₃, BaTiO₃, and CH₃NH₃PbI₃, as well as for GeTe.²¹⁻²⁶ The transition temperature depression observed in CsPbBr₃ QDs is remarkable because CsPbBr₃ is centrosymmetric (i.e., non-ferroelectric) in each of its phases, and there is minimal difference in volume per formula unit across either of the two-phase solid-solid transitions.

PDF analysis of synchrotron X-ray total scattering of CsPbBr₃ QDs. To investigate the atomistic nature of changes occurring in the vicinity of the phase transitions observed in the average Bragg structure, synchrotron X-ray total scattering data were collected on the CsPbBr₃ QDs at a series of temperatures using the beamline 11-ID-B at the APS. Data were collected with $\lambda =$ 0.143 Å up to $Q_{max} = 27$ Å⁻¹ at 35 temperature points from 22 °C $\leq T \leq$ 160 °C. Fits to the PDFs extracted from data collected at T = 22 °C and T = 160 °C are given in Figures 2a and b, respectively.

At both 22 and 160 °C, the orthorhombic structure provides a qualitatively and statistically superior fit compared with the tetragonal and cubic structures. Complete fitting results, including lattice parameters, atomic positions, thermal parameters and quality-of-fit values are given in Table S2.



Figure 3. (a) The difference in the quality-of-fit value R_w between the cubic and orthorhombic PDF models for two different r ranges over the temperatures 22 °C \leq *T* \leq 160 °C. (b) Graphic representation of sampling of twinned domains by two different r-space fitting ranges. (c) Evolution of the lattice parameters of the cubic, orthorhombic, and tetragonal fits as a function of temperature. Orthorhombic and tetragonal lattice parameters are normalized for comparison to the cubic lattice parameter a. The lattice parameters shown are taken from fits over 2 $\dot{A} \le r \le 20$ Å.

The improved quality-of-fit provided by the orthorhombic model is robust to the choice of fitting range. Figure 3a shows the difference in R_w for the cubic and orthorhombic models over the ranges 2 Å $\leq r \leq$ 20 Å and 20 Å $\leq r \leq$ 40 Å. The maximum value of r used was 40 Å because the intensity of the PDF attenuates rapidly beyond this value (Figure S5). This attenuation is common to all PDFs generated from data collected using the ultrafast mode of beamline 11-ID-B and is an artifact of pixel binning.²⁷ While the orthorhombic model provides a superior fit over both ranges, the difference is less for the higher-r range. This discrepancy is consistent with the twinning model described by Bertolotti *et al.*, for reasons depicted in Figure 3b. The PDF represents the statistical density of atom pairs possessing an interatomic distance r. In a crystallite with twinned domains, atom pairs existing at short interatomic distances are more likely to reside within a single, coherent domain than atom pairs with large interatomic distances. As r increases, an increasing fraction of pairs reside in separate domains. These pairs will not sit at the interatomic distances predicted by a regular orthorhombic structure, leading to a decrease in R_W . ΔR_W is shown in Figure 3a rather than R_W of the orthorhombic model in order to account for changes in the resolution and quality of the data with changing r. The decrease in ΔR_W with temperature in

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both ranges is consistent with the progressive introduction of additional twin boundaries described in the twinning model. The resulting reduction in the size of individual orthorhombic domains explains the apparent elimination of reflections in the diffraction pattern due to Scherrer broadening.

The influence of temperature on the magnitude of the 6 orthorhombic distortion can be assessed through the 7 evolution of the lattice parameters, which are plotted in 8 Figure 3c. For each of the structural models, the lattice 9 parameters vary approximately linearly with tempera-10 ture with no indication of convergence between the val-11 ues for different models as temperature increases. These 12 results show the preservation of orthorhombicity well 13 above the phase transition. This observation is consistent with the twinning model of phase transitions in CsPbBr₃ 14 ODs and with lattice dynamics calculations²⁸ suggesting 15 that local distortions involving tilting of PbBr₆ octahedra 16 are energetically favorable in the high-temperature cubic 17 phase for bulk CsPbBr₃. Furthermore, it appears that the 18 magnitude of the local distortion is weakly dependent on 19 temperature for temperatures less than T = 160 °C. This 20 weak dependence is consistent with the phase transitions 21 in CsPbBr₃ QDs proceeding through an order-disorder 22 process such as the formation of twin boundaries, rather 23 than a displacive mechanism. The evolution of R_W , the lattice parameters, and atomic positions of Br (shown in 24 Figure S6) are all smooth in the vicinity of the phase 25 transitions in the average structure. This suggests that 26 the reorientation of tilting patterns to form twinned do-27 mains may occur in a gradual, rather than stepwise 28 manner. 29

CONCLUSIONS

We confirm that the orthorhombic-to-tetragonal and cubic-to-tetragonal phase transitions in CsPbBr₃ QDs proceed through an order-disorder mechanism involving the coherence of rotation patterns between locally ordered orthorhombic domains. In contrast to other reports, we find that in these phase transitions occur at 50 °C < $T_{\gamma-\beta}$ < 59 °C and 108 °C < $T_{\beta-\alpha}$ < 117 °C. These temperatures are depressed by at least 29 °C and 13 °C, respectively, compared with the bulk material. The origin of transition temperature depression for a transition of this type is not apparent according to conventional explanations of transition temperature depression in nanomaterials and presents an intriguing avenue for future research. We find that local orthorhombic domains persist as high as T = 160 °C with no decrease in the magnitude of the orthorhombic distortion.

EXPERIMENTAL SECTION

Synthesis Methods. Cs_2CO_3 (0.814 g, Alfa Aesar, 99%) was combined with 1-octadecene (40 mL, Aldrich, 90%) and oleic acid (2.5 mL, Sigma-Aldrich, 90%) in a 100-mL three-neck flask and heated to 120 °C under vacuum with stirring and held at that temperature for 1 h. The suspension was heated to 150 °C under vacuum until all Cs_2CO_3 appeared dissolved by visual inspection. The solution was allowed to cool, upon which it formed an opaque, off-white gel. The gel was later liquified by reheating to 100 °C before use. PbBr₂ (69.0 mg, Alfa Aesar, 99.999%) and 1-octadecene (5 mL) were combined in a 25-mL 3-neck flask and heated to 120 °C under vacuum with stirring and held at that temperature for 1 h. Dried oleic acid (0.5 mL) and olevlamine (0.5 mL, Sigma, 70%) were injected under flowing nitrogen. After dissolution of all PbBr₂, the temperature of the solution was raised to 180 °C. In order to precipitate QDs, 0.4 mL of the preheated Cs(oleate) solution was injected, and after 5 s, the flask was submersed in an ice bath while 10 mL of cold 1octadecene was simultaneously injected in order to provide rapid and homogenous cooling. The resulting product was centrifuged for 5 min at 6000 RPM and the precipitated QDs were resuspended in hexanes. For bulk CsPbBr₃, CsBr (11.0 mg, Aldrich, 99.999%) and PbBr₂ (19.0 mg, Alfa Aesar, 99.999%) were co-dissolved in 2 mL of DMF by sonication. The resulting solution was added dropwise to 5 mL of toluene, resulting in the precipitation of yellow-orange CsPbBr₃ microcrystals. The crystals were dried under flowing nitrogen at room temperature.

Laboratory Characterization Methods. UV-vis absorbance spectra for suspensions of CsPbBr₃ QDs in hexanes were collected in transmission mode using a Shimadzu UV-1800 spectrometer. Emission spectra of CsPbBr₃ QDs suspended in hexanes were collected using a Horiba Nanolog spectrofluorometer equipped with a monochromated 450 W Xe lamp as the excitation source and a photomultiplier tube detector. TEM images of CsPbBr₃ ODs were collected using a JEOL JEM2100F (JEOL Ltd.) electron microscope operating with an accelerating voltage of 200 kV. Dilute suspensions of QDs in hexanes were deposited onto 200 mesh copper grids coated with a lacey carbon film (Ted Pella, Inc.) for imaging. Laboratory variable-temperature X-ray diffraction data were collected using a Bruker D8 Advance diffractometer with a copper target and an Anton Parr HTK 16 high-temperature stage. Bulk samples were tamped onto the stage in order to ensure good thermal contact. CsPbBr₃ QDs suspended in hexanes were added dropwise to the stage and allowed to dry before measurement.

Synchrotron X-ray Diffraction. Suspensions of $CsPbBr_3$ QDs in hexanes were initially partially dried by adding them dropwise to glass slides at room temperature. The samples were subsequently further dried by heating at 70 °C in a vacuum oven for 3 h. The dried samples were scraped with a razor blade and loaded into Kapton tubes, which were then sealed with epoxy.

High-resolution synchrotron X-ray diffraction (SXRD) data were collected at T = 22, 70, 90, 120, 140, and 160 °C on beam-line 11-BM at the Advanced Photon Source (APS) at Argonne National Laboratory with a photon wavelength of $\lambda = 0.4576$ Å and a binning of $0.001^{\circ} 2\theta$. Data were subsequently re-binned with a coarser spacing of $0.005^{\circ} 2\theta$ in order to facilitate the convergence of Rietveld refinements. Rietveld refinements to the SXRD data were made using the GSAS/EXPGUI package.^{30,31}

Synchrotron X-ray total scattering. Samples were prepared as in the previous section. X-ray total scattering data were collected at 35 temperatures from 22 °C < *T* < 160 °C using the 11-ID-B beamline at the Advanced Photon Source with a photon wavelength of λ = 0.143 Å. A reduced scattering structure function, S(Q), with the appropriate corrections for multiple scattering, sample absorption, X-ray polarization, and Compton scattering was obtained from the data using the program PDFgetX3.³² A pair distribution function (PDF), G(r),

was obtained by direct Fourier transformation of S(Q) with a $Q_{max} = 27 \text{ Å}^{-1}$. X-ray PDFs were analyzed using the program PDFGUI.³³ Parameters for scale and the quadratic atomic correlation factor were allowed to refine. Values of the instrumental variables Q_{damp} and Q_{broad} were determined from data collected on a CeO₂ standard.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

TEM image; UV-vis and PL spectra; variable temperature laboratory diffraction data; structural parameters of Rietveld refinements; parameters for PDF analysis; room temperature PDF G(r); PDF quality of fits as a function of temperature (PDF)

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