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Electronic Supplementary Information

On the Crystal Structure of Colloidally Prepared $CsPbBr_3$ Quantum Dots

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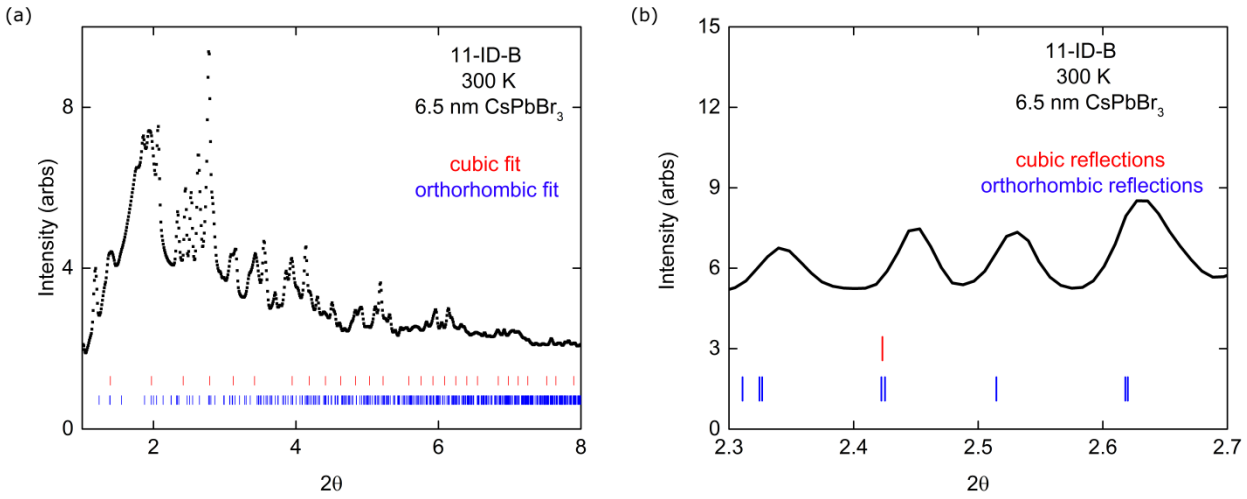

Fig. 1 Synchrotron X-ray diffraction pattern of 6.5 nm $CsPbBr_3$ QDs over the ranges **(a)** $1 < 2\theta < 8$ and **(b)** $2.3 < 2\theta < 2.7$. The red and blue tic marks indicate the positions of Bragg reflections in refinements of the cubic and orthorhombic structures, respectively, to the diffraction pattern of 12.5 nm $CsPbBr_3$ QDs.

Bulk CsPbBr3	$Pm\bar{3}m$	T = 300 K	a = 5.84451(3) Å	V = 199.638(3) Å^3		
Atom	Site	x	y	z	occ.	U_{iso} (Å^2)
Cs	1*a*	0	0	0	1	0.0954(4)
Pb	1*b*	0.5	0.5	0.5	1	0.0333(2)
Br	3*c*	0.5	0.5	0	1	0.159(5)

Bulk CsPbBr3	*Pnma*	T = 300 K	a = 8.2609(1) Å;	b = 11.7652(5) Å	c = 8.2124(1) Å	V (Å^3) = 798.16(4)
Atom	Site	x	y	z	occ.	U_{iso} (Å^2)
Cs	4*c*	-0.4708(6)	0.25	0.0085(9)	1	0.0636(3)
Pb	4*a*	0	0.5	0	1	0.0248(5)
Br1	8*d*	0.2961(8)	0.4749(4)	0.2064(8)	1	0.0394(2)
Br2	4*c*	0.005(1)	0.75	0.0445(8)	1	0.0474(3)

12.5 nm CsPbBr3	$Pm\bar{3}m$	T = 300 K	a = 5.8570(4) Å	V = 200.92(4) Å^3		
Atom	Site	x	Y	z	occ.	U_{iso} (Å^2)
Cs	1*a*	0	0	0	1	0.1055(3)
Pb	1*b*	0.5	0.5	0.5	1	0.0222(2)
Br	3*c*	0.5	0.5	0	1	0.1263(4)

12.5 nm CsPbBr3 QD	*Pnma*	T = 300 K	a = 8.264(4) Å;	b = 11.781(4) Å	c = 8.2492(3) Å	V = 803.12(2) Å^3
Atom	Site	x	Y	z	occ.	U_{iso} (Å^2)
Cs	4*c*	-0.5019(2)	0.25	0.004(4)	1	0.0868(2)
Pb	4*a*	0	0.5	0	1	0.0178(1)
Br1	8*d*	0.2885(2)	0.4768(9)	0.2104(2)	1	0.0356(3)
Br2	4*c*	0.0447(3)	0.75	0.0288(2)	1	0.007(4)

Table S2. Structural parameters determined from Rietveld refinements of cubic ($Pm\bar{3}m$) and orthorhombic (*Pnma*) structures to synchrotron X-ray diffraction data collected on bulk $CsPbBr_3$ and 12.5 nm $CsPbBr_3$ QDs.

Bulk CsPbBr3	$Pm\bar{3}m$	T = 300 K	a = 5.85 Å	V = 200 ´ 3		
Atom	Site	x	y	z	occ.	U_{iso} (Å^2)
Cs	1*a*	0	0	0	1	0.115
Pb	1*b*	0.5	0.5	0.5	1	0.0282
Br	3*c*	0.5	0.5	0	1	0.263

Bulk CsPbBr3	*Pnma*	T = 300 K	a = 8.43 Å;	b = 11.7 Å	c = 8.17 Å	V = 804 ´ 3
Atom	Site	x	y	z	occ.	U_{iso} (Å^2)
Cs	4*c*	-0.473	0.25	0.027	1	0.0962
Pb	4*a*	0	0.5	0	1	0.0248
Br1	8*d*	0.276	0.476	0.206	1	0.0632
Br2	4*c*	0.044	0.75	0.081	1	0.0463

12.5 nm CsPbBr3	$Pm\bar{3}m$	T = 300 K	a = 5.86 Å	V = 201 ´ 3		
Atom	Site	x	y	z	occ.	U_{iso} (Å^2)
Cs	1*a*	0	0	0	1	0.141
Pb	1*b*	0.5	0.5	0.5	1	0.0338
Br	3*c*	0.5	0.5	0	1	0.230

12.5 nm CsPbBr3 QD	*Pnma*	T = 300 K	a = 8.49 Å;	b = 11.6 Å	c = 8.15 Å	V (´ 3) = 798
Atom	Site	x	y	z	occ.	U_{iso} (Å^2)
Cs	4*c*	-0.469	0.25	0.0261	1	0.117
Pb	4*a*	0	0.5	0	1	0.0258
Br1	8*d*	0.270	0.476	0.213	1	0.0600
Br2	4*c*	0.045	0.75	0.080	1	0.0519

Table S3. Parameters determined from fits of cubic ($Pm\bar{3}m$) and orthorhombic (*Pnma*) structural models to PDFs extracted from synchrotron X-ray total scattering data collected on bulk $CsPbBr_3$ and 12.5 nm $CsPbBr_3$ QDs.

Synthesis Methods

Preparation of Cs(oleate): Cs_2CO_3 (0.814 g, Alfa Aesar, 99%) was combined with octadecence (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 flowing vacuum until all Cs_2CO_3 appeared dissolved by visual inspection. The solution was allowed to cool, upon which it formed an opaque gel. The gel was later re-dissolved by reheating to 100 °C before use.

Synthesis of $CsPbBr_3$ QDs: $PbBr_2$ (69.0 mg, Alfa Aesar, 99.999%) and ODE (5 mL) we combined in a 25 mL 3-neck flask and heated to 120 °C under vacuum with stirring and held at that temperature for 1 hour. Dried oleic acid (0.5 mL) and oleylamine (0.5 mL, Sigma, 70%) were injected under flowing nitrogen. After dissolution of all $PbBr_2$, the temperature of the solution was raised to either 130 °C or 200 °C. In order to precipitate QDs, 0.4 mL of the pre-heated Cs(oleate) solution was injected and after 5 s, the flask was submersed in an ice bath while 10 mL of cold octadecene 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.

Synthesis of bulk $CsPbBr_3$: CsBr (11.0 mg, Aldrich, 99.999%) and $PbBr_2$ (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 $CsPbBr_3$ microcrystals. The crystals were dried under flowing nitrogen at room temperature.

Characterization Methods

Absorbance: UV-vis absorbance spectra for suspensions of $CsPbBr_3$ QDs in hexanes were collected in transmission mode using a Shimadzu UV-1800 spectrometer. The absorbance spectrum of bulk $CsPbBr_3$ was determined from diffuse reflectance. Diffuse reflectance measurements were performed using a Perkin-Elmer Lambda 950 spectrophotometer on a sample containing 3 mg of bulk $CsPbBr_3$ intimately mixed with 200 mg of MgO (99.5%, Alfa Aesar).

Steady-State Photoluminescence (PL): Emission spectra of $CsPbBr_3$ 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.

Transmission Electron Microscopy (TEM): TEM images of $CsPbBr_3$ QDs were collected using a JEOL JEM2100F (JEOL Ltd.) electron microscope operating with an accelerating voltage of 200 kV. Suspensions of QDs in hexanes were deposited onto 200 mesh copper grids coated with a lacey carbon film (Ted Pella, Inc.) for imaging.

Scanning Electron Microscopy (SEM): SEM images of bulk $CsPbBr_3$ were collected using at JEOL JSM-7001F (JEOL Ltd.) instrument operating with an accelerating voltage of 20 kV.

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 50 °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. Bulk $CsPbBr_3$ samples were directly loaded into Kapton tubes without additional drying. High-resolution synchrotron X-ray diffraction (SXRD) data were collected at room temperature on beam-line 11-ID-B at the Advanced Photon Source (APS) at Argonne National Laboratory with a photon wavelength of λ = 0.143 Å. Rietveld refinements to the SXRD data were made using the GSAS/EXPGUI package.[1,2]

X-ray total scattering:

X-ray total scattering data were collected at room temperature 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 PDFgetX2.[3] A pair distribution function (PDF), G(r), was obtained by direct Fourier transformation of S(Q) with a Q_{max} = 37 $Å^{-1}$. X-ray PDFs were analyzed using the program PDFGUI.[4]

Supporting References

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