Defect-Triggered Phase Transition in Cesium Lead Halide Perovskite Nanocrystals

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Supporting Information

ABSTRACT: All-inorganic perovskite nanocrystals (NCs) have emerged as a class of low-cost and high-efficiency light-emitting materials. However, the structure and phase transition behavior of these NCs remain poorly understood. Here, we provide unambiguous evidence that all these properties are associated with structural defects in NCs. Using CsPbCl₃ NCs as a model system, we find that the cubic subdomains in highly defective NCs gradually convert to the orthorhombic upon cooling room-temperature quasi-cubic NCs, whereas high-quality cousins, with mixed cubic and orthorhombic subdomains at room temperature, exhibit a significant resistance for such a phase transition. Car-Parrinello molecular dynamics simulations unveil the important role of point defects in triggering a stepwise, reversible phase transition of CsPbCl₃ NCs. Importantly, we show that the defect-triggered phase transition also exists in other all-inorganic perovskite NCs. Our findings provide new insight into the structure and phase transition of CsPbX₃ NCs and highlight the important role of defects in impacting these properties.

Lead halide perovskites such as methylammonium lead iodide (CH₃NH₃PbI₃ or MAPbI₃) have received wide-ranging attention owing to their outstanding optoelectronic properties, which lend them to application in high-efficiency solar cells, light-emitting devices, and detectors.^{1–6} The optoelectronic properties of lead halide perovskites are typically tailored by modifying the chemical compositions (e.g., partial replacement of cationic or anionic ions by other elements that can retain the perovskite structure).^{7–12} Besides, tuning temperature, one of the most accessible strategies, has been gradually recognized as a useful knob for increasing the tunability of perovskite's properties by virtue of the phase transition.^{13–20} For instance, MAPbI₃ is cubic at temperatures above 330 K, tetragonal between 330 K and ~160 K, and finally transforms to a low-symmetry orthorhombic crystal structure below ~160 K.¹³ Interestingly, recent studies have shown that the temperature of the tetragonal-to-orthorhombic phase transition of MAPbI₃ is intimately associated with structural defects,¹⁹ which leads to the coexistence of tetragonal and orthorhombic phases at low temperatures.

The great benefit of dual-phase coexistence lies in drastically enhanced emission quantum yields,²¹ which result in the first demonstration of continuous-wave lead halide perovskite lasers.²² Interestingly, the phase transition of defect-bearing MAPbI₃ is not totally reversible at around the phase transition temperature, as reflected by the temperature hysteresis.¹⁹

To overcome the instability issue of hybrid perovskites, recent efforts have been devoted to cesium lead halide perovskite (CsPbX₃, X = halide ions) nanocrystals (NCs) due to their good stability, unique optical versatility, high luminescence quantum yields, and facile synthesis.^{23–33} However, in contrast to well-studied bulk CsPbX₃,^{34–39} the phase transition behavior and photophysical properties of CsPbX₃ NCs have yet to be dissected fully. Until now, only a few studies of the phase transition have been conducted on

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Figure 1. (a) Temperature-dependent XRD patterns of highly defective CsPbCl_3 NCs during the cooling and heating cycle; the NCs were first cooled from 290 to 100 K and then heated from 100 to 290 K with a rate of 10 K/min. (b, c) Temperature-dependent XRD patterns of NCs in the ranges of 4° – 8° (b) and 13° – 15° (c) upon cooling from 290 to 100 K.

such material systems.^{40–43} For instance, Bertolotti and coworkers investigated the structures of CsPbX_3 NCs and suggested that the local structure of these NCs always exhibits orthorhombic tilting of PbX_6 octahedra within locally ordered subdomains that are hinged through a two-/three-dimensional network of twin boundaries.⁴⁰ However, no obvious phase transition for CsPbCl_3 NCs has been observed at low temperatures, as signified by the absence of superstructure diffraction peaks of the orthorhombic phase. Furthermore, the full details of the phase transition and the nature of the mechanism for the formation of multi-subdomains in individual CsPbX_3 NCs remain essentially unexplored. Previous works have revealed that CsPbX_3 NCs, similar to their hybrid counterparts, are highly defective.^{23,44,45} Nevertheless, to date, there exists no convincing prior identification of how defects influence the phase transition of CsPbX_3 NCs. We took the view that understanding these challenging scientific issues could provide insight into unconventional optoelectronic properties observed in CsPbX_3 NCs.^{46,47}

Here, we present an in-depth investigation of the phase transition of CsPbX_3 NCs across a wide temperature range by a combination of experimental characterizations and molecular dynamics simulations. We discover that the reversible phase transition behavior of CsPbCl_3 NCs is intimately linked with structural defects. Highly defective CsPbCl_3 NCs are quasi-cubic at room temperature (RT), in which the cubic subdomains gradually convert to the orthorhombic phase upon cooling. By contrast, high-quality CsPbCl_3 NCs show a greatly retarded phase transition from RT mixed cubic and orthorhombic subdomains. Molecular dynamics simulations demonstrate that point defects such as chloride vacancies play a pivotal role in triggering the phase transition of CsPbCl_3 NCs. We also discuss the generality of our findings in other CsPbX_3 NCs. Our work offers new insight into the structure

and phase transition of CsPbX_3 NCs and emphasizes the important role of defects in impacting their structures.

The CsPbCl_3 NCs were synthesized by a hot-injection method as first reported by Protesescu and coworkers.²³ The average edge length of CsPbCl_3 NCs is 10.9 nm (Figure S1). These NCs show an exciton absorption band at 397 nm and band-edge emission at 405 nm with a photoluminescence quantum yield (PLQY) of 1.2%, consistent with previous results.^{23,48} Such a low PLQY indicates a highly defective lattice that contains chlorine and/or chlorine-related defects.^{44,48} To avoid any possible adverse effect of water molecules on the structure, the as-synthesized NCs were stored in a N_2 -filled glovebox for the following measurements. The preliminary structural characterization based on laboratory X-ray diffraction (XRD) suggests the formation of cubic CsPbCl_3 at RT (Figure S2). We then performed the temperature-dependent synchrotron XRD measurements at the BL02B2 beamline of SPRING-8, using a MYTHEN detector system,⁴⁹ to examine the phase transition behavior. The NCs sealed in a capillary were first cooled from 290 to 100 K and then heated to 290 K, with a same cooling/heating rate of 10 K/min. As illustrated in Figure 1a, it is apparent that the phase transition of CsPbCl_3 NCs is reversible, indicating that, different from some hybrid cousins,¹⁹ the long-range order of the CsPbCl_3 NCs is well retained after undergoing phase transition, although they are defective. We stress that the reversible phase transition behavior of CsPbCl_3 NCs has not been reported so far. We note, upon cooling, a superstructure peak at 7.07° develops at ~ 270 K (Figure 1b), which can be assigned to the orthorhombic CsPbCl_3 . Further decreasing the temperature leads to the appearance of more superstructure peaks at $\sim 4.77^\circ$, 6.76° , 7.67° , and 7.99° . Interestingly, we find that as the temperature decreases, the peak corresponding to the (222) plane of the RT cubic CsPbCl_3 is gradually

Figure 2. (a) Rietveld refinement of the high-resolution synchrotron XRD patterns at 290, 200, and 100 K for highly defective CsPbCl₃ NCs. The insets show the enlarged patterns corresponding to the peaks of the orthorhombic phase. The red lines and overlying crosses show the calculated and observed intensities, respectively. The pink and green lines indicate the positions of the calculated Bragg reflections of orthorhombic and cubic CsPbCl₃, respectively. The difference between the observed and calculated profiles is plotted in blue. (b, c) Percentages (b) and cell volumes (c) of the cubic and orthorhombic phases in highly defective CsPbCl₃ NCs at different temperatures.

broadened, accompanied by weakened intensity and notable peak splitting at 100 K (Figure 1c and Figure S3). These observations unambiguously provide fingerprints of [PbCl₆] octahedral tilts taking place at 270 K and of a stepwise phase transition occurring over an extremely broad temperature window (100–270 K).

To gain deep insight into this unconventional, stepwise phase transition, we next took high-resolution synchrotron XRD patterns of CsPbCl₃ NCs at different temperatures, which have been used for Rietveld refinement. Three representative synchrotron XRD spectra are shown in Figure 2a. All diffraction peaks of CsPbCl₃ NCs at 290 K match the Bragg positions of the cubic CsPbCl₃, and no impurities exist in the product. Assuming a cubic lattice, Rietveld refinement of the data can be performed quite adequately (Figure 2a and Table S1). In the refinement, the isotropic atomic displacement parameters (ADPs), not the anisotropic ADPs, which were considered as diffraction data from nanosized materials cannot provide robust information.⁴⁰ Owing to the appearance of superstructure peaks that can be assigned to the orthorhombic CsPbCl₃ for the pattern at 200 K, we refined this data using a two-phase model because merely refining it using an orthorhombic model shows notable deviation from the experimental data (Figure S4). We find that the weight ratio of the orthorhombic phase in NCs is 69.4% (Figure 2a and Table S2). Compared with this, refinement of the two-phase model against the data taken at 100 K gives a ratio of 96.2%, signifying that the dominant phase is orthorhombic (Figure 2a and Table S3). We also refined the high-resolution patterns taken at other temperatures, from which we obtain the change in the ratio of the orthorhombic phase in NCs (Figure 2b, Figures S5–S10 and Tables S4–S9). Notably, the amount of the orthorhombic phase gradually increases from 7.7% at 270 K to 96.2% at 100 K. As expected, both the lattices of the

cubic and orthorhombic phases contract upon decreasing the temperature (Figure 2c). The volume of the unit cell for the cubic phase decreases from 175.980(4) Å³ at 290 K to 169.07(19) Å³ at 100 K, while that of the orthorhombic decreases from 709.4(5) Å³ at 270 K to 678.40(5) Å³ at 100 K.

To examine the influence of defects on the phase transition behavior, we next prepared high-quality CsPbCl₃ NCs by a modified hot-injection method. We used benzoyl chloride as an additional chloride source to create Cl-rich growth conditions,³² which favors the suppression of the formation of Cl vacancies as we previously revealed.⁴⁴ The resulting NCs, with an edge length of 10.1 nm, display similar absorption and emission bands to their highly defective analogues but exhibit a high PLQY of 78.8% (Figure S11). Previous work revealed that, different from Pb and Cs vacancies, Cl vacancies can introduce deep in-gap defect levels, which function as charge carrier traps and result in low-efficiency band-edge emission.⁴⁴ We thus conclude that the concentration of Cl vacancies and/or Cl-vacancy-related defects in high-quality CsPbCl₃ NCs should be much smaller than that in highly defective cousins. As shown in Figure 3a, these high-quality NCs also demonstrate reversible phase transition in the range of 100–290 K. However, careful inspection of the high-resolution synchrotron XRD patterns suggests that the structure and phase transition behavior of these NCs are different from those of highly defective cousins. Notably, comparison of the RT diffraction patterns of these two kinds of NCs shows that high-quality NCs exhibit relatively broad, asymmetric peaks (Figure S12), implying the intrinsic difference in their structures. We further attempt to refine the experimental data using the models of different polymorphs, and the results suggest that the high-quality NCs consist of mixed phases of cubic and orthorhombic at RT (Figure S13). We then carried out Rietveld refinement of the synchrotron XRD data at different

Figure 3. (a) Temperature-dependent XRD patterns of high-quality CsPbCl_3 NCs during the cooling and heating cycle; the NCs were first cooled from 290 to 100 K and then heated from 100 to 290 K with a rate of 10 K/min. (b) Rietveld refinement of high-resolution synchrotron XRD patterns at 290, 200, and 100 K. Insets show the enlarged patterns corresponding to the peaks of the orthorhombic phase. The red lines and overlying crosses show the calculated and observed intensities, respectively. The pink and green lines indicate the positions of the calculated Bragg reflections of orthorhombic and cubic CsPbCl_3 , respectively. The difference between the observed and calculated profiles is plotted in blue. (c, d) Percentages (c) and cell volumes (d) of the cubic and orthorhombic phases in high-quality CsPbCl_3 NCs at different temperatures.

temperatures by using a two-phase model (Figure 3b, Figures S14 and S15, and Tables S10–S14). As shown in Figure 3c, the ratio of the orthorhombic polymorph in NCs at RT is 48.4%, which increases upon cooling, corresponding to a ratio of 75.3% at 100 K. This is in sharp contrast with the highly defective NCs, suggesting that a lower concentration of defects causes a greatly retarded conversion of the cubic polymorph to the orthorhombic. Beyond this, we also find that the high-quality NCs show a smaller variation in the volume of the unit cell for both the cubic and orthorhombic phases than the highly defective cousins (Figure 3d), meaning that lower-concentration defects favor resistance of lattice contraction upon cooling (i.e., lower-concentration defects result in a robust lattice). Collectively, our results unambiguously indicate that, similar to the hybrid cousins,¹⁹ the phase transition behavior of CsPbCl_3 NCs is defect-correlated and that the concentration of certain defects (e.g., Cl vacancies and/or Cl-

vacancy-related defect complexes) not only govern the RT structure but also the phase transition behavior over an extremely large temperature interval (100–290 K).

Our experimental measurements reveal that the low PLQY of CsPbCl_3 NCs at RT can be attributed to the nonradiative trap centers induced by the Cl vacancies. To gain deep insights into the crystal structure and vacancy-related phase transition behavior as observed in CsPbCl_3 NCs, we performed the Car-Parrinello molecular dynamics (CPMD) calculations on the $3 \times 3 \times 3$ CsPbCl_3 supercells without and with a Cl vacancy (Figure 4). Overall, starting from experimental crystal structures, CsPbCl_3 experiences a strong thermal fluctuation and would not retain the perfect cubic phase after 2 ps. As illustrated in Figure 4c,d, in comparison with the perfect case, the Pb–Cl–Pb bonds in the defective crystal undergo a large fluctuation with an average tilting angle between 155° and 167° at 290 K because the Cl vacancy leads to a strong lattice

Figure 4. CPMD simulations. (a, b) Illustrations of the four Pb–Cl–Pb band angles taken from $3 \times 3 \times 3$ CsPbCl₃ supercells. The Pb–Cl–Pb bond angle evolution starting from initial cubic-phase CsPbCl₃ at 290 K (c, d), 200 K (e, f), and 100 K (g, h) with and without Cl vacancy and the corresponding snapshots obtained from CPMD calculations.

distortion (i.e., octahedral tilting) surrounding this vacancy. Such local structural deformation can release the lattice strain, resulting in less Pb–Cl–Pb tilting away from the Cl vacancy center (see the plots of Pb–Cl–Pb bond angles in Figure S16). Interestingly, reducing the temperature from 290 to 100 K inhibits the Pb–Cl–Pb tilting around the Cl vacancy of CsPbCl₃ supercell (Figure 4c,e,g), but promotes the Pb–Cl–Pb tilting away from the Cl vacancy, i.e., the average Pb–Cl–Pb bond angle around a Cl vacancy increases (between 165° and 175°) and it decreases away from a Cl vacancy (between 145° and 155°, see Figure S16c,d). This indicates the contraction of the resulting CsPbCl₃ crystal with a Cl vacancy at low temperatures, making it closer to the typical orthorhombic phase with the Pb–Cl–Pb tilting angle of 150–155°. In a sharp contrast, the perfect CsPbCl₃ crystal inclines to keep the orthorhombic phase with the average Pb–

Cl–Pb bond angle of $\sim 157^\circ$, as no lattice relaxation occurs for the phase change (Figure 4d,f,h). It is worth noting that the high-quality CsPbCl₃ NCs are not perfect but contain a small amount of Cl vacancies, which gives rise to the mixed cubic/orthorhombic phase as observed in our experiments. Collectively, our CPMD calculations support that the Cl vacancy can trigger the phase change of CsPbCl₃ NCs: (i) the Cl vacancy induces a strong local lattice deformation at RT (that results in the occurrence of quasi-cubic phase way from the vacancy) in highly defective CsPbCl₃ NCs as well as a large Pb–Cl–Pb tilting at low temperatures far from the vacancy (that results in the contraction of the lattice); (ii) for the high-quality CsPbCl₃ NCs, the less Pb–Cl–Pb tilting releases lattice strain, which can suppress the phase transition from quasi-cubic to orthorhombic. We underscore that in the CsPbCl₃ NCs, the appearance of other defects, such as the

Cs⁺–Cl[–] vacancy complex, can further promote crystal lattice deformations and impact the phase transition, which is more complicated than our used model containing one Cl vacancy.

We next examined whether other CsPbX₃ NCs demonstrate a similar phenomenon as observed in CsPbCl₃ NCs. For this purpose, we prepared defective and high-quality CsPbBr₃ NCs with PLQYs of 43.8% and 97.0%, respectively. The average size of both defective and high-quality CsPbBr₃ NCs is 8.6 nm (Figure S17). It is also noted that both NCs are capped with the same class of ligands. These facts indicate that the ligand and NC's size have a negligible effect on the structure of CsPbBr₃ NCs, which is similar to the case of CsPbCl₃ NCs. As shown in Figure S18, defective and high-quality CsPbBr₃ NCs exhibit a reversible phase transition across a wide temperature interval. However, close examination of the diffraction patterns (e.g., those at 103 K) obviously evidence that defects can also trigger the phase transition behavior of CsPbBr₃ NCs.

In conclusion, we have revealed that structural defects dictate the structure and phase transition behaviors of all-inorganic perovskite NCs across wide temperature intervals. We found that the cubic subdomains in highly defective CsPbCl₃ NCs gradually convert to the orthorhombic upon cooling the RT quasi-cubic NCs, while high-quality cousins exhibit a significantly retarded phase transition from RT mixed cubic and orthorhombic subdomains. Importantly, we found that the defect-triggered phase transition also exists in other all-inorganic halide perovskite NCs. Our work highlights the intrinsic complexity of a seemingly simple CsPbX₃ perovskite structure when downsizing and structural defects meet together and sheds new light on the important role of defects in impacting the structures of perovskite NCs.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmaterialslett.9b00128.

Experimental methods, TEM images, additional XRD patterns, absorption and PL spectra, additional CPMD simulation results, and supplementary tables of Rietveld refinement results (PDF)

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Notes

The authors declare no competing financial interest.

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