Semiconductor Nanocrystals



Low-Temperature Absorption, Photoluminescence, and Lifetime of $CsPbX_3$ (X = Cl, Br, I) Nanocrystals

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The absorption and photoluminescence, both steady-state and timeresolved, of CsPbX₃ (X = Cl, Br, I) nanocrystals are reported at temperatures ranging from 3 to 300 K. These measurements offer a unique window into the fundamental properties of this class of materials which is considered promising for light-emitting and detection devices. The bandgaps are shown to increase from low to high temperature, and none of the examined cesium-based perovskite nanocrystals exhibit a bandgap discontinuity in this temperature range suggesting constant crystal phase. Time-resolved measurements show that the radiative lifetime of the band-edge emission depends strongly on the halide ion and increases with heating. The increasing lifetime at higher temperatures is attributed primarily to free carriers produced from exciton fission, corroborated by the prevalence of excitonic character in absorption. The results particularly highlight many of the similarities in physical properties, such as low exciton binding energy and long lifetime, between CsPbl₃ and hybrid organic-inorganic plumbotrihalide perovskites.

1. Introduction

The tremendous and rapid success of plumbotrihalide perovskite materials as single crystals, thin films, and nanocrystals (NCs) in solid-state devices including solar cells,^[1–4] light-emitting diodes (LEDs),^[5–7] detectors,^[8,9] and lasers^[10–12] has led to great interest in their fundamental properties. The successful implementation of methylammonium (MA) and formadinium (FA) lead iodide in solution-processes solar cells inspired renewed interest in the long-known cesium analogs,^[13] which share many of the advantageous optoelectronic properties of organolead trihalides. The synthesis of both single-crystal and

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NC of CsPbX₃ (X = Cl, Br, or I) has developed rapidly both as a potentially more chemically or thermally stable alternative material for solar cells,^[3,14,15] or others uses to which the material well-suited, like high-energy detection^[8] or light-emitting devices.^[12,16] Although most work with these materials is focused on roomtemperature behavior, low-temperature measurements offer the opportunity to answer fundamental questions about CsPbX₃ materials, including changes in the bandgap, exciton binding energy, and electronic structure.

In this work, we examine the optical properties of pure $CsPbX_3$ (X = Cl, Br, or I) NCs from 3 to 300 K, using absorption, photoluminescence (PL), and time-resolved PL (trPL) measurements. Similar to earlier reports on selected NCs and single-crystal samples, both absorption and PL measurements reveal that the

bandgap of CsPbX₃ NCs increases upon heating from 3 K, although the magnitude of the wavelength shift in CsPbCl₃ is very small. Unlike bulk materials,^[13] no phase transition from the orthorhombic phase stable at room temperature is observed optically from 3 to 300 K in this work, or even to 500 K in earlier work.^[17] This is confirmed by X-ray diffraction over a more limited number of temperatures. Absorption measurements at low temperature reveal a clear bound excitonic feature which decreases in strength with increasing temperature, permitting an estimate of the exciton binding energy. Time-resolved PL data show that the radiative rate of CsPbX₃ species is fastest at low temperature, reaching a decay lifetime of just 30 ps for CsPbCl₃ NCs, confirming that the lowest excitonic state is optically allowed. This is distinct from the apparent excitonic structure of both FAPbI3 and MAPbI3 NCs, which show long PL lifetimes at low temperatures.^[18,19] Several potential mechanisms to explain this behavior are discussed and compared with experimental data. The temperature-dependent changes in lifetime of the CsPbX₃ NCs are best explained as a combination including exciton fission and additional thermally induced changes in the radiative rate, which is particularly important for CsPbI₃.

2. Results and Discussion

At least one aspect of the appeal of plumbotrihalide perovskites is that changing the halide composition permits a change in







Figure 1. a) Absorption and photoluminescence spectra of solution of CsPbX₃ nanocrystals. TEM images of the b) CsPbI₃, c) CsPbBr₃, and d) CsPbCl₃ NC samples.

the bandgap energy through the visible spectrum. In this work, pure-halide compositions were synthesized as NCs following literature recipes for hot injection synthesis.^[20] Special care was

taken to isolate NCs without antisolvent precipitation of any kind, since common polar solvents readily dissolve the polar halide perovskite compounds.^[3] Typical optical spectra of the CsPbX₃ NCs are shown in Figure 1a with accompanying transmission electron microscopy (TEM) images in Figure 1b-d. The absorption edges and PL spectra span the visible spectrum as the halide composition is changed. This size of the approximately cubic NCs used in this study is 9.1 nm for CsPbCl₃, 15.0 nm for CsPbBr₃, and 16.6 nm for CsPbI₃, which is above the estimated Bohr radii for the chloride (5 nm), bromide (7 nm), and iodide (12 nm).^[20] Thus, quantum confinement is not anticipated to play a significant role in the observed optical properties. Multiple samples were examined for each composition to confirm the same observed trends, indicating relative insensitivity to small changes in size. As the cubic perovskite "black" phase of CsPbI₃ is metastable and the family of CsPbX₃ is known to be quite sensitive to air, all samples were measured soon after purification (<24 h) under high-vacuum conditions ($\approx 10^{-7}$ Torr). The use of NCs, which present distinct phase stability from bulk materials,^[3] enables the study of the metastable CsPbI₃ perovskite phase in a manner which has proven difficult to achieve with single crystals or thin films; this study represents, to our knowledge, the first examination of absorption and PL of cubic $CsPbI_3 < 80$ K.

Temperature-dependent PL and absorption collected from 3 to 300 K for the CsPbX₃ samples are shown in **Figure 2**. Both PL and absorption data show that bandgap increases with temperature, which is atypical for most semiconductors but widely reported for plumbotrihalides. Similar results have



Figure 2. Normalized steady-state PL of a) CsPbI₃, b) CsPbBr₃, and c) CsPbCl₃ NC samples collected from 3 to 300 K. Absorption measurements of d) CsPbI₃, e) CsPbBr₃, and f) CsPbCl₃ NC samples collected over the same temperature range.







Figure 3. a) Temperature dependence of the bandgap of CsPbX₃ NCs based upon measurements of absorption (solid circles), derived from Tauc plots, PL (solid diamonds), derived from the center wavelength of the emission, and excitonic absorption maximum (open circles), derived from second derivative analysis of the absorption. Solid lines represent Varshni fits to the data. b) Temperature dependence of the PL linewidth for CsPbX₃ NCs (open symbols) fitted in solid lines with a model for thermal broadening. c) Temperature dependence of the relative oscillator strength of the excitonic absorption feature for the CsPbX₃ NC samples. Solid fit lines represent a function of the form $I(T) = I_0(1 + Ae^{E_b/kT})^{-1}$.

been observed previously in low-temperature measurements of selected plumbotrihalide perovskites.^[16,21–23] The magnitude of increase follows the trend of CsPbCl₃ < CsPbBr₃ < CsPbI₃. As expected, the samples display thermal broadening of PL at higher temperatures. Unlike the same bulk materials,^[13] no phase transition is apparent in the optical data collected here or in measurements up to 500 K.^[17] Consistent with these optical observations, a more limited sampling of temperature-dependent X-ray measurements, presented in Figure S1 (Supporting Information) as well as in prior literature,^[24] shows no change in the crystal structure with temperature, as is expected for most materials.

The trends in bandgap and spectral broadening are tracked quantitatively in **Figure 3**. Figure 3a relates three measures of the semiconductor bandgap as a function of temperature: measured from fitted center of PL energy (open circles), second derivative minima representing the energy of the excitonic absorption (triangles), and Tauc plot measurement extrapolations (solid circles). With the exception of the PL energy of the CsPbCl₃ NC sample at temperatures > 250 K, the bandgaps increase with increasing temperature. This small blueshift followed by a small redshift with increasing temperature for CsPbCl₃ was reproducible for NCs synthesized in several batches. Thermal changes in bandgap determined by each method for each composition were fitted using the empirical Varshni relation, which describes the temperature-dependent bandgap of semiconductors according to Equation (1)

$$E_{\rm gap} = E_{\rm gap, 0K} - \alpha T^2 / (\beta + T) \tag{1}$$

in which α is the coefficient of change and β is the Debye temperature for the material.^[25] The plots of the bandgap change for each of the materials are close to linear, with fitted β values from the Varshni relation close to zero, suggestive of low Debye temperatures. α values for all the samples are negative, but increase in absolute magnitude from chloride to bromide to iodide. These values range from -0.5×10^{-5} K⁻² for CsPbCl₃, $-(1.3 \text{ to } 1.9) \times 10^{-4}$ K⁻² for CsPbBr₃, and $-(2.0 \text{ to } 2.6) \times 10^{-4}$ K⁻² for CsPbI₃ (see Table S1, Supporting Information). Thermal changes in bandgap are opposite in sign and smaller in magnitude than most semiconductors (e.g., α is 7.0 $\times 10^{-4}$ K⁻²

for Si and 8.9 \times 10⁻⁴ K⁻² for GaAs),^[25] with especially small thermal bandgap changes for CsPbCl₃.^[25] This indicates that thermo-optic changes in PL color are a significantly smaller factor in light-emitting technology that operates at elevated temperatures.

PL broadening arises from intrinsic inhomogeneity (Γ_{inh}), contributions of exciton–acoustic phonon coupling (Γ_{ac}), and exciton-longitudinal optical (LO) phonon coupling (Γ_{LO} at E_{LO})

$$\Gamma(T) = \Gamma_{\rm inh} + \Gamma_{\rm AC}T + \Gamma_{\rm LO} \left(e^{E_{\rm LO}/kT} - 1\right)^{-1}$$
(2)

Unlike single crystals, NCs may show an inhomogeneous linewidth due to variable environments (frequently observed as spectral diffusion in single particle measurements) and size dispersion, arising from quantum confinement effects, although these are expected to be weak for the NCs measured here.^[20] We do not observe any clear secondary features or shoulder of the PL at any temperature, despite earlier reports.^[26,27] Thermal broadening of PL at higher temperatures, plotted in Figure 3b, is accounted for using a Voight fit. Raman measurements of LO phonon energies ($E_{\rm LO}$) are 46 meV for CsPbCl₃,^[28] 16^[29] or 19 meV^[30] for CsPbBr₃, and values for CsPbI₃ are not reported, but the value obtained by fitting the PL line broadening here is 16 meV.

The most noteworthy change observed in the absorption profile is the increasing prominence, at low temperature, of distinctive excitonic absorption features in the samples. These absorption features are associated with bound excitonic states in the materials and have also been identified at low temperature in bulk films for CsPbBr₃^[31,32] and stand in stark contrast to our previous measurements of the absorption spectrum of MAPbI3 and FAPbI3 NCs, which show very weak excitonic absorption.^[19] These results are at least qualitatively consistent with earlier work that has described the exciton binding energy, based upon modeling of relative PL intensity versus temperature, to be 20 meV for CsPbI₃,^[20] 37-44 meV CsPbBr₃,^[16,20,33] and 57-75 meV for CsPbCl₃.^[20,33,34] Calculations based upon a hydrogenic Wannier-Mott model place the exciton binding energy between 50 and 80 meV for CsPbX₃, but also claim that predicted exciton binding energies follow the trend of I < Cl < Br for CsPbX₃ in contradistinction to other trihalide perovskites.^[35] Our absorption data allow a direct experimental

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estimation of the exciton binding energy, which is a critical parameter which underlies performance of optoelectronic devices. This methodology also improves on other indirect methods for estimating exciton binding energy, which are particularly fraught in nanomaterials.

Exciton binding energy estimates using temperature-dependent PL intensity measurements, which typically show thermally activated quenching of PL,^[16,34] assume that exciton fission must result in nonradiative recombination. It is far from clear that exciton fission should have a similar impact on NCs as on single crystals; in some cases many thermally activated processes can occur simultaneously to quench PL;^[34] and sample preparation may yield distinct thermal stability.^[16,17,34] Here, we modify this procedure by observing the *absorption* spectrum directly as a function of temperature and estimating the exciton binding energy by fitting the temperature dependence of the intensity (1) of the bound excitonic absorption of CsPbX₃ samples normalized to the higher-energy continuum absorption, which corrects for any changes in the scale of absorption from sample heterogeneity. Because absorption is less sensitive to impurities than PL and represents a direct measure of oscillator strength of various transitions, this measurement offers a more reliable measure

of exciton binding energy. The exciton binding energy, $E_{\rm b}$, is obtained according to $I(T) = I_0 (1 + Ae^{E_b/kT})^{-1,[16,34]}$ in which A is a scaling factor. Although exciton binding energies may change with temperature, the CsPbX₃ samples do not undergo a phase transition and therefore the assumption of comparable $E_{\rm b}$ over the experimental temperature range is less problematic than for the organolead halide perovskites.^[36,37] The result, plotted in Figure 3a, yields values of 67 meV for CsPbCl₃, 47 meV for CsPbBr₃, and 25 meV for CsPbI₃, close to most predicted theoretical values. Compared to organolead trihalides, the estimated exciton binding energies of the CsPbX₃ samples are larger as these materials cannot demonstrate the same plastic crystal properties associated with free cation rotation.^[36,38] Although the excitonic absorption of CsPbI3 is weaker at room temperature (and above) than in the chloride and bromide samples, second derivative analysis still reveals a small excitonic contribution to the band-edge absorption (Figures S2 and S3, Supporting Information). As has already been demonstrated,^[3] these results confirm that the "black" CsPbI₃ phase is a more promising solar cell material because it not only has a more ideal bandgap, but also that absorption leads to a substantially larger fraction of free carriers and performance is unconstrained by excitonic effects that may reduce carrier lifetime, as contemplated in the following section.^[39,40]

Figure 4 shows time-resolved photoluminescence measurements collected for the CsPbX₃ NC samples with the fitted exponential lifetimes plotted in Figure 4d. As found previously, the



Figure 4. Normalized trPL data for a) CsPbCl₃, b) CsPbBr₃, and c) CsPbI₃ samples collected from 2.7 to 300 K. d) Lifetimes obtained from fits to the experimental trPL data.

halide composition is strongly predictive of the lifetime, with Cl < Br < I.^[20,41] In particular, the radiative rate at 2.7 K is dictated by recombination of bound excitons, which in turn depends strongly on the dielectric screening of the different materials.^[42] This relationship holds at all temperatures, with a change in halide composition increasing the lifetime by a factor of 3-10 from CsPbCl₃ to CsPbBr₃ and from CsPbBr₃ to CsPbI₃. For the CsPbCl₃ sample, a more clearly biexponential decay is observed beginning at 120 K. It is not clear if this is trap-related recombination, as it appeared in all NC samples measured and also appears in single crystals.^[34] As highlighted in previous work, bromide and iodide samples showed substantially maintained integrated PL intensity upon cooling from room temperature, while chloride samples brighten significantly.^[17] This is also reflected in the biexponential character of PL decay in the chloride sample in Figure 4c. Consequently, the CsPbCl₃ NC data were fitted with a biexponential decay at higher temperatures (plotting the averaged lifetime),^[43] but the CsPbBr₃ and CsPbI₃ samples exhibited trPL dominated by single-exponential decays at all temperatures. The trPL measurements at 2.7 K confirm that the lowest energy states of all CsPbX₃ samples are bright and well-described by a single exponential decay, with lifetimes of 30 ps (CsPbCl₃), 120 ps (CsPbBr₃), and 2.0 ns (CsPbI₃).

As shown in Figure 4d, the fitted lifetimes of the samples increase from 3 to 300 K. An increase in lifetime with temperature elevation has been observed in other measurements of trihalide perovskites.^[17,21–23,44–46] Importantly, the CsPbI₃







Figure 5. Superimposed average lifetime data (closed circles) with the excitonic absorption feature (open circles) for a) $CsPbBr_3$, b) $CsPbBr_3$, and c) $CsPbCl_3$.

NC trPL lifetime at room temperature is comparable to FAPbI₃ and MAPbI₃ NCs of similar size, underlining that the organic cation of hybrid perovskites is not essential for longer carrier lifetimes.^[40] The extensive literature on cesium- and organolead halide perovskites provides several, sometimes contradictory, mechanisms for the observed behavior. Primarily, the focus of literature on perovskites has been to explain long room-temperature lifetime which is advantageous in many optoelectronic devices, but these data show that these materials may also have relatively short PL decay times at lower temperature. Several mechanisms to explain temperature-dependent lifetime behavior include (i) dark-state occupation, (ii) direct-to-indirect bandgap through Rashba splitting, and (iii) exciton fission, with the most evidence supporting the last of these.

Combined with previous studies, our data argue strongly against dark states, direct-to-indirect bandgaps, and changes in oscillator strength for NC forms of these materials. Temperature-dependent occupation of singlet and triplet character of PL is observed in several inorganic and organic/biological systems.^[47,48] However, single NC magneto-optical measurements demonstrate multiple closely spaced (<5 meV) bright states at 2 K, but no clear evidence of singlet-triplet mixing (i.e., dark states) in the spectrally resolved or time-resolved data under strong magnetic fields.^[49] These measurements suggest that if dark excitonic states exist above a bright ground state, they remain inaccessible with a high magnetic field (7 T) and therefore are unlikely to influence dynamics < 100 K. Several works have explained the comparatively long lifetime and enhanced photovoltaic performance for organolead trihalide perovskites as attributable to an indirect bandgap transition as the lowest energy state.^[50,51] Band-edge Rashba splitting has been determined computationally in methylammonium lead iodide (MAPbI₃)^[51–54] and CsPbI₃.^[55] But the application of this theory to the family of CsPbX₃ materials is less clear, as these samples can exhibit very short lifetimes (particularly in the case of CsPbCl₃ and CsPbBr₃ at cryogenic temperatures) and small Stokes shifts which are uncorrelated with PL lifetime, which make this unlikely (see Figure S9, Supporting Information).

Absorption data in Figure 2 showing relatively small increases (up to a factor of 2) in the sample extinction suggest that gross changes in oscillator strength of CsPbX₃ at low temperature do not explain the observed lifetime trend. However, as described above, the band edge absorption feature, which reflects bound excitons, changes more significantly than absorption into continuum states. Previously, the increased lifetime of

plumbotrihalide perovskites has been described as originating from exciton fission.^[16,36,37] Under this explanation, exciton fission would be expected to slow electron-hole recombination. Consistent with this picture, as the size of CsPbBr3 NCs is increased, and compared with a single crystal (see Figure S4, Supporting Information), lifetime also increases, which suggests that the spatial extent of delocalization controlled by the crystal size can play a role in dictating the radiative rate in NCs. Qualitatively, an exciton fission model is consistent with decreasing excitonic absorption features, such as in Figure 2d-f as well as the absolute lifetimes of the CsPbX₃ samples and the fitted exciton binding energies. Comparison of lifetime and excitonic absorption data in Figure 5 for the CsPbX₃ samples show that although the temperature dependence of both parameters is similar for the chloride and bromide samples, CsPbI₃ shows divergent behavior of the lifetime and excitonic absorption. The CsPbI₃ sample does present a significant increase in lifetime as thermal energy enables exciton fission to free carriers, but an even larger increase at higher temperatures > 200 K where excitons are comparatively rare. In this regard. CsPbI₂ is similar to organic-inorganic hybrid perovskites, which show that the lifetime of PL continues to increase without significant bound exciton populations.^[17,23] Although long lifetime in organolead halide perovskites has been attributed by others to free rotation of the organic cation which raises the dielectric function and enhances charge screening, this has more recently been demonstrated to be nonessential, as CsPbI₃ can also exhibit long lifetimes in the bulk.^[40] Another specific example of thermally activated process which may explain the continued elongation of PL lifetimes above which exciton fission can occur is the formation of polar domains,^[56] which are more prominent at higher temperature. Diffraction measurements^[24] and low-dose TEM imaging^[57] have each found evidence of polytypism within individual NCs, although without explicit reference to polar domains, which may also result in slower recombination.

3. Conclusion

In conclusion, we have presented the temperature-dependent absorption, PL, and PL lifetime of colloidal CsPbX₃ NCs. Combined with previous work at high temperature, these measurements show the distinct phase stability of NCs versus bulk materials, particularly in the stability of "black" CsPbI₃, with





no phase change detected in optical measurements from 2.7 to 500 K. Absorption and PL measurements confirm the unusual bandgap blueshift with increasing temperature which has also been observed in other plumbotrihalides. Low-temperature absorption measurements enable a direct estimation of the exciton binding energy from the temperature-dependent behavior of the bound excitonic absorption feature, in contrast to previous indirect measurements based upon temperature-dependent PL intensity. The decrease in the exciton binding energy which results from heavier halides in the crystal, related to the concomitant change in the dielectric function of CsPbX₃, translates into large changes in the temperature-dependent PL lifetime dictated primarily by exciton fission with increasing temperature.

4. Experimental Section

Materials: Oleic acid (90%), oleylamine (70%), octadecene (ODE, 90%), tricotylphosphine (97%), lead bromide (>98%), lead iodide (99%), cesium carbonate (99.9%), and polybutylmethacrylate-*co*-polyisobutylmethacrylate (354 kDa) were purchased from Sigma-Aldrich. Oleic acid and oleylamine were dried and stored in a nitrogen filled glove box. All solvents were ACS grade or higher.

Synthesis: Synthesis of perovskite NCs followed the procedure of Protesescu et al.^[20] Typically, a reaction flask containing 4 mL ODE and 0.19 mmol PbX₂ was heated to 120 °C under vacuum and held 1 h. Once the reaction flask was under vacuum 1 h, it was flushed with nitrogen and 0.5 mL of dry and degassed oleylamine and oleic acid were added. The temperature was maintained until the reaction flask contained a homogeneous solution. To synthesize CsPbCl₃, an additional 1 mL of trioctylphosphine was added. The flask was then heated under nitrogen flow to 160 °C for synthesis of CsPbI3 and 180 °C for CsPbCl3 and CsPbBr₃. Separately, to prepare the Cs-oleate precursor, 407 mg Cs₂CO₃, 1.25 mL oleic acid, and 20 mL ODE were heated under vacuum to 120 °C and held 1 h, then heated under nitrogen to 150 °C and held until the Cs₂CO₃ completely dissolved. The Cs-oleate precursor was maintained as a homogeneous clear solution by heating prior to injection. Once the flask reached the set-point temperature, 0.4 mL of hot Cs-oleate solution was rapidly injected, the reaction proceeded for 5 s, then was cooled using a water bath. Samples were isolated by centrifugation of the reaction media at 15 000 rpm for 15 min.

Optical Measurements: Steadv-State Steady-state absorption measurements were collected using a white light source focused on to the sample within a Janis helium cryostat to a spot size of \approx 0.5 mm. The transmitted light was collected into a fiber and directed into a calibrated Ocean Optics spectrometer. Steady-state PL measurements were performed by exciting the samples with either a 350 nm 2 kHz source (CsPbCl₃ and CsPbBr₃) generated by an OPA driven by a Spectra-Physics Ti: sapphire laser or a 100 kHz PicoQuant 405 nm diode laser (CsPbI₃). The choice was driven both by wavelength considerations for absorption and ability to synchronize the laser outputs with appropriate time-resolved detection (Hamamatsu streak camera for CsPbCl₃ and CsPbBr₃; PicoQuant avalanche photodiode for CsPbI3). To ensure that the results reflect low-fluence single-exciton regime behavior, the laser was not focused and power dependence was measured in time-resolved experiments, which showed power-independent dynamics. PL was collected on the opposite sample side of excitation and fiber coupled through a Princeton Instruments spectrometer to a Princeton Instruments CCD.

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.

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