Colloidal Synthesis and Optical Properties of Perovskite-Inspired Cesium Zirconium Halide Nanocrystals

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ABSTRACT: Optoelectronic devices based on lead halide perovskites are processed in facile ways, yet are remarkably efficient. There are extensive research efforts investigating lead-free perovskite and perovskite-related compounds, yet there are challenges to synthesize these materials in forms that can be directly integrated into thin film devices rather than as bulk powders. Here, we report on the colloidal synthesis and characterization of lead-free, antifluorite Cs$_2$ZrX$_6$ (X = Cl, Br) nanocrystals that are readily processed into thin films. We use transmission electron microscopy and powder X-ray diffraction measurements to determine their size and structural properties, and solid-state nuclear magnetic resonance measurements reveal the presence of oleate ligand, together with a disordered distribution of Cs surface sites. Density functional theory calculations reveal the band structure and fundamental band gaps of 5.06 and 3.91 eV for Cs$_2$ZrCl$_6$ and Cs$_2$ZrBr$_6$, respectively, consistent with experimental values. Finally, we demonstrate that the Cs$_2$ZrCl$_6$ and Cs$_2$ZrBr$_6$ nanocrystal thin films exhibit tunable, broad white photoluminescence with quantum yields of 45% for the latter, with respective peaks in the blue and green spectral regions and mixed systems exhibiting properties between them. Our work represents a critical step toward the application of lead-free Cs$_2$ZrX$_6$ nanocrystal thin films into next-generation light-emitting applications.
integration required for device applications. So far, thin films of A2BX6 materials, for example, have been fabricated for Cs3PdBr6, Cs3TiBr6, and Cs3SnI6, but this is only a small subset of all experimentally known A2BX6 materials; this small sample space limits us from exploiting the full family of these materials for optoelectronic device application. One approach to fabricate thin films with excellent optoelectronic properties is through deposition of colloidal suspensions of nanocrystals (NCs), yet only Sn4+- or Pd4+-based A2BX6 NC systems have been reported to date.

Here, we report the novel synthesis and characterization of colloidal, antifluorite cesium hexachlorozirconate(IV) and cesium hexabromozirconate(IV) NCs, thereby opening up the range of tunable antifluorite NC compositions. Powder X-ray diffraction (XRD) measurements show that the Cs2ZrX6 (X = Cl, Br) NCs crystallize into the antifluorite structure. Solid-state nuclear magnetic resonance (NMR) experiments validate that the surfaces of Cs2ZrCl6 NCs are capped with oleate ligands and a disordered distribution of Cs sites. Using density functional theory (DFT), we calculate fundamental band gaps of 5.06 eV for Cs2ZrCl6 and 3.91 eV for Cs2ZrBr6, which is consistent with the experimentally measured values and band structure. Thin films of Cs2ZrCl6 and Cs2ZrBr6 NCs show broad photoluminescence (PL) peaking at ~450 nm (blue-white) and ~528 nm (green-white), respectively, with the bromide system exhibiting a photoluminescence quantum yield (PLQY) of 45%. By mixing the colloidal suspensions of Cs2ZrCl6 and Cs2ZrBr6 NCs and depositing films, we demonstrate tunable white emission, which is not limited by anion exchange reactions, as is otherwise the case for lead-based CsPbX3 NC systems. These results reveal that halide engineering is a viable strategy for tuning the optical properties of Cs2ZrX6 NC thin films, and that they will be particularly interesting for light-emission applications requiring optically homogeneous thin films such as light-emitting diodes and scintillators.

Using strict air-free Schlenk line techniques, in conjunction with a hot-injection approach, we fabricate colloidal suspensions of Cs2ZrCl6 NCs. Specifically, we rapidly inject benzoyl chloride diluted in dried 1-octadecene (ODE) into a solution of stoichiometric quantities of cesium and zirconium precursors in a mixture of oleylamine (OLA) and oleic acid which is consistent with the experimentally measured values and band structure. Thin films of Cs2ZrCl6 and Cs2ZrBr6 NCs show broad photoluminescence (PL) peaking at ~450 nm (blue-white) and ~528 nm (green-white), respectively, with the bromide system exhibiting a photoluminescence quantum yield (PLQY) of 45%. By mixing the colloidal suspensions of Cs2ZrCl6 and Cs2ZrBr6 NCs and depositing films, we demonstrate tunable white emission, which is not limited by anion exchange reactions, as is otherwise the case for lead-based CsPbX3 NC systems. These results reveal that halide engineering is a viable strategy for tuning the optical properties of Cs2ZrX6 NC thin films, and that they will be particularly interesting for light-emission applications requiring optically homogeneous thin films such as light-emitting diodes and scintillators.

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OA) in ODE at 185 °C, then isolate and redisperse the NCs in toluene, following previous reports on the synthesis of halide perovskite NCs17,18 (see Supporting Information (SI) for details). We also fabricated Cs2ZrBr6 NCs using a similar method but without addition of OLA; we found that omission of OLA also leads to more reliable and reproducible syntheses of the Cs2ZrCl6 NCs (see the SI and NMR section below).

The synthesis of bulk Cs2ZrCl6 and Cs2ZrBr6 reference powders follows a published method with slight modifications19 (see the SI for details).

Figures 1a and 1b show the XRD patterns of bulk powder and NC samples of Cs2ZrCl6 and Cs2ZrBr6, respectively, measured under air-free conditions using an air-free sample holder. Here, we prepared the NC thin film samples by depositing the colloidal suspensions of Cs2ZrCl6 NCs on a Si substrate and of Cs2ZrBr6 NCs on a glass substrate. The patterns in Figure 1a match the reference XRD pattern of Cs2ZrCl6 (Joint Committee on Powder Diffraction Standards (JCPDS) File No. 01-074-1001, space group Fm3m, a = 10.407 Å).20 suggesting that the samples are phase-pure with any phase impurities at concentrations below the detection limit or amorphous in nature. The corresponding pure Cs2ZrBr6 reference XRD pattern is not available from the literature; therefore, we calculated a crystallographic information file (CIF) for Cs2ZrBr6 by replacing Cl with Br in the structure of Cs2ZrCl6 and performed a full hybrid DFT geometry optimization, allowing all lattice parameters to change (see the SI for details and CIF file). We then used the program VESTA21 to simulate the reference XRD pattern for Cs2ZrBr6, as shown in Figure 1b, with the computed unit-cell parameter reduced from 11.16 Å to 10.89 Å, to better match the experimental XRD data. From these XRD measurements (Figure 1b), we find that the NC thin film sample is also phase-pure Cs2ZrBr6, although the bulk powder contains CsBr impurities (see CsBr reference JCPDS File No. 00-005-0588, shown in orange in figure).22 We note that extended exposure of the Cl- and Br-containing compositions to ambient air conditions can lead to the formation of various impurity phases including (but not limited to) CsCl and CsBr, respectively, in both NC thin film and bulk powder form (see Figure S1 in the SI for examples), which we attribute to the hygroscopic nature of these compounds.23−25 The insets of Figure 1a and 1b compare XRD peaks of the Cs2ZrCl6 (220) and Cs2ZrBr6 (222) bulk powder and NC thin film, respectively. The peak widths are narrower for the bulk powder, which implies larger crystallite sizes, compared to those in the NC thin film samples.

Figures 1c and 1d show transmission electron microscopy (TEM) images for Cs2ZrCl6 and Cs2ZrBr6 NCs, respectively. In the high-resolution TEM (HR-TEM) image of a Cs2ZrCl6 NC (inset of Figure 1c), we observe lattice fringes with ∼3.7 Å separation, which we index as the (220) plane of Cs2ZrCl6. We corroborate this assignment by performing a fast Fourier transform (FFT) analysis of the HR-TEM image (see Figure S2), which confirms the structure of Cs2ZrCl6 and reveals that the analyzed Cs2ZrCl6 NC is oriented along the [114] zone axis in the real-space image. In the HR-TEM image of a Cs2ZrBr6 NC (inset of Figure 1d), we observe lattice fringes...
with ~3.9 Å separation that index as the (220) plane of Cs$_2$ZrBr$_6$. FFT analysis of the HR-TEM image (see Figure S3) confirms the structure of Cs$_2$ZrBr$_6$ and shows that the analyzed Cs$_2$ZrBr$_6$ NC is oriented along the $[111]$ zone axis. We note that the NCs of both halide compositions appear slightly aggregated and, therefore, do not exhibit well-defined shapes, even when washed multiple times (see Figure S4 in the SI), although we attribute this in part to the drop-casting deposition method employed that leads to heterogeneous drying of the solvent on the TEM grid; the NCs are colloidaly stable in suspension with slow precipitation occurring over a period of weeks to months that can be easily redispersed by agitating the suspension. Further work would be required to achieve well-dispersed particles upon deposition.

To study the atomic-level microstructure of Cs$_2$ZrCl$_6$ bulk powders and dried Cs$_2$ZrCl$_6$ NCs, as well as the surface ligands of the dried NCs, we use solid-state magic angle spinning (MAS) NMR spectroscopy and surface-enhanced dynamic nuclear polarization (DNP SENS) solid-state MAS NMR. DNP SENS has emerged as a powerful extension of solid-state NMR for studying dilute surface species and nanoparticles by providing signal enhancements that, compared to conventional NMR, can reach a factor of 660 for protons.26–30 Figure 2a shows the $^{133}$Cs MAS NMR spectrum of Cs$_2$ZrCl$_6$ bulk powder and dried Cs$_2$ZrCl$_6$ NCs (see the SI for details). The spectrum of Cs$_2$ZrCl$_6$ bulk powder has a single peak (shift $\delta = 86$ ppm, full width at half maximum (FWHM) = 106 ± 1 Hz), consistent with the presence of a single Cs site in the crystal structure of Cs$_2$ZrCl$_6$. The spectrum of dried Cs$_2$ZrCl$_6$ NCs yields a signal at the same $^{133}$Cs shift ($\delta = 86$ ppm) but is considerably broader (FWHM = 474 ± 3 Hz), because of the presence of a wider distribution of local cesium environments in the NCs than in the bulk powder sample. In addition, we observe a very broad signal spanning ~80 ppm visible on the vertical zoom ($\times8$) of the NC signal, which we attribute to the presence of a particularly large distribution of environments for the surface layer of Cs$^+$ ions, because of the intrinsically disordered nature of surfaces,29 which are dominant in NC samples (because of the large surface-area-to-volume ratios).

For DNP SENS NMR experiments (see the SI for details), we mix the colloidal suspension of Cs$_2$ZrCl$_6$ NCs with hexagonal boron nitride (h-BN), dry the mixture at ~50 °C in the glovebox, dope it with a stable binitrooxide radical (here, TEKPol)$^{31}$ in an inert solvent (1,1,2,2-tetrachloroethane, TCE) and irradiate with continuous wave high power and high-frequency microwaves, which drive the polarization transfer from the radicals to the solvent protons.32 This subsequently transfers the increased Boltzmann polarization of the solvent protons to the protons in the surface ligands of the Cs$_2$ZrCl$_6$ NCs through spin diffusion and can transfer to $^{133}$Cs of Cs$_2$ZrCl$_6$ through $^1$H–$^{133}$Cs cross-polarization (CP)$^{33,34}$. The purpose of mixing the Cs$_2$ZrCl$_6$ NCs with microwcrystalline dielectric particles (here, h-BN) is to further boost the DNP enhancement by improving the homogeneity of the microwave field inside the sample.35,36

The DNP surface-enhanced $^1$H–$^{133}$Cs spectrum of Cs$_2$ZrCl$_6$ NCs (see Figure S5 in the SI, top) shows a broad distribution of shifts, which is comparable to that recorded using conventional MAS NMR at room temperature (RT; cf. Figure 2a) and further corroborates our earlier assignment of surface Cs$^+$ environments. Despite its large line width, the DNP-enhanced $^{133}$Cs spectrum does resolve at least two distinct local surface Cs environments (at 104 and 124 ppm). While their unambiguous assignment to specific surface sites is beyond the scope of the present work, we note that similar complexity of surface signals has been previously seen in semiconducting ZnSe NCs of various shapes and surface-to-volume ratios,37 as well as in CsPbBr$_3$ nanocuboids$^{38}$ and nanoplatelets.$^{39}$ We also detect the NC core signal with an echo sequence without microwave irradiation (see Figure S5, bottom). The signal is broader than at RT ($\delta = 104$ ppm, FWHM = 874 ± 18 Hz), suggesting that the crystal structure undergoes slight lattice parameter changes upon going from RT to 100 K. Both the core and surface signals are slightly shifted to higher frequencies at 100 K, with respect to RT, which we also attribute to temperature-induced structural changes.

In turn, we use DNP SENS to probe the surface ligands of Cs$_2$ZrCl$_6$ NCs. The $^1$H–$^{13}$C spectrum (Figure 2b) yields enhancement factors of 42 and 15 for the TCE solvent and $–\text{CH}_2–$ signals, respectively, and evidences the presence of aliphatic chains, $\text{–C=C–}$ moieties, as well as carbonyl (C–O) groups, consistent with the presence of oleate (OA)$^+$ as a surface ligand. In particular, the C–O signal spans 20 ppm and has a non-Gaussian envelope, which is indicative of highly disordered C–O groups that may originate from OA$^+$ species bound to the surface of the NCs. The $^1$H–$^{15}$N CP spectrum recorded under DNP SENS conditions (Figure 2c) contains a single peak ($\delta = 126$ ppm, FWHM = 1343 ± 28 Hz), which we attribute to the $–\text{NH}_2$ group of oleylammonium (OLA)$^+$. The large FWHM of this peak suggests the presence of highly disordered OLA$^+$ environments that may arise from surface-bound molecules. The presence of OA$^+$ and OLA$^+$ as capping agents for these systems is analogous to those seen in lead halide perovskite NCs.40–46 We note that the $^1$H–$^{13}$C spectrum (Figure 2b) also contains $–\text{C=C–}$ moieties belonging to ODE used as solvent in the synthesis. This suggests that the post-synthetic workup used here yields a material that may contain traces of the unreacted precursors, which we may have not detected with XRD if they are amorphous in nature or their concentrations are below the XRD detection limit. While the large FWHM of the peak in the $^1$H–$^{15}$N spectrum suggests the presence of OLA$^+$ on the surface, we cannot exclude that it originates from free residual OLA$^+$ in the frozen sample. Nevertheless, we show that OLA is not necessarily required for the formation of phase-pure Cs$_2$ZrCl$_6$ NCs by performing a control experiment in which we use OA as the sole ligand precursor. The colloidal stability of these OA-only NCs suggests successful OA$^+$-capping and, as previously mentioned, this synthesis approach shows even better reproducibility than the method that also involves OLA.

Figure S4 shows the TEM and HR-TEM images of OA$^+$-capped Cs$_2$ZrCl$_6$ NCs, which are very similar in size and shape to the NCs synthesized using both OLA and OA. Hence, we conclude that OA$^+$ is the predominant ligand on Cs$_2$ZrCl$_6$ NCs regardless of the presence/absence of OLA during synthesis. Figure 2d summarizes our conclusions on the form of the NC surfaces from our combined conventional MAS and DNP SENS NMR studies.

We now assess the optical properties of the samples. Figure 3a shows the ultraviolet-visible (UV-Vis) absorption and PL spectra of Cs$_2$ZrCl$_6$ and Cs$_2$ZrBr$_6$ NC thin films deposited by drop-casting the colloidal suspensions on fused silica substrates and encapsulated by a fused silica substrate in an argon glovebox. We observe a strong absorption onset at ~260 nm for Cs$_2$ZrCl$_6$, consistent with photoluminescence excitation...
Stokes shift of photographs of the NC suspension in toluene. We determine the diﬀerence in emission color (see Figure S6 in the SI) and absorption peaks between this onset and 528 nm, respectively. The spectra show broad, asymmetric PL features suggest the original PL peaks of pure Cs2ZrCl6 and Cs2ZrBr6 NC thin films (Figure 3a); selective PLE measurements conﬁrm the simultaneous presence of Cs2ZrCl6 and Cs2ZrBr6 NCs in the mixed sample, allowing us to tune the broad, white emission without being limited by fast anion exchange reactions that hinder such tunability in conventional lead-based CsPbX3 NCs.13,14 Although further work will be required to ascertain the exact reason for the stability of the mixed-anion Cs2ZrX6 NC sample in comparison to the lead-based mixed-anion perovskites, we speculate that it could be due to a lack of interstitial sites in the crystal structure of Cs2ZrX6 because of its structurally isolated ZrX6- octahedra.

Time-resolved PL measurements of an encapsulated Cs2ZrBr6 NC thin film (see Figure S8 in the SI) reveal a long-lived component that we ﬁt with a double-exponential decay yielding decay constants of τ1 = 780 ± 40 ns and τ2 = 4500 ± 100 ns of comparable amplitude contribution, in good agreement with the values extracted from scintillation decay measurements on Cs2ZrBr6 bulk crystals.55 Furthermore, the PLQY of the Cs2ZrBr6 NC thin ﬁlm is 45% without considering emitted photons lost to thin ﬁlm waveguiding (see the Characterization section in the SI), with the PLE spectrum closely matching the absorption spectrum (Figure 3a). These results match well with the PLYQ of the Cs2ZrBr6 NC suspension (∼40%) and powder (∼44%), demonstrating that we can eﬀectively translate the solution or powder properties to thin ﬁlm forms required for device applications. Such PLQY values are obtained even after depositing ﬁlms from solutions stored under inert glovebox conditions for several months, indicating the encouraging stability of these materials. We note that instrumental limitations inhibit similar quantitative or time-resolved analyses of the Cs2ZrCl6 NCs, which requires deeper UV excitation. The combination of large Stokes shifts and broad, asymmetric PL features suggests radiative recombination may originate from self-trapped excitons,49 which has been reported for similar compounds such as Cs2HCl4p50–52. The lack of subgap contribution to the PLE spectrum of the Cs2ZrBr6 NC thin ﬁlms also indicates that radiative recombination is not due to permanent defect states.53 The similar PLQY values of the bulk powder, NC suspensions, and NC thin ﬁlms support the hypothesis that (i) the self-trapped exciton emission is intrinsic, related to the bulk, and (ii) the emission, consequently, is not strongly dependent on the crystalline size for the sizes studied here nor on its surface/volume ratio. Although further work will be required to elucidate all of the recombination processes in these Cs2ZrX6 NC thin ﬁlms, these results reveal very eﬃcient and tunable radiative recombination.

In order to support our collective experimental ﬁndings, we perform electronic structure and optical property calculations on Cs2ZrCl6. We performed all periodic DFT calculations within the Vienna Ab Initio Simulation Package (VASP);14–17 further computational details are found in the SI. Relaxation of the crystal structure of Cs2ZrCl6 with HSE06 (the Heyd–

**Figure 3.** Optical characterization of Cs2ZrX6 NC thin ﬁlms. (a) Blue curves represent UV-Vis absorption and PL spectrum (excitation: 250 nm) of encapsulated Cs2ZrCl6 NC thin ﬁlm. Green curves represent UV-Vis absorption, PLE (dotted line; emission: 519 nm) and PL spectrum (excitation: 300 nm) of encapsulated Cs2ZrBr6 NC thin ﬁlm. The black curve represents PL spectrum (excitation: 250 nm) of encapsulated, mixed Cs2ZrCl6 and Cs2ZrBr6 NC thin ﬁlm. The UV-Vis absorption and PL spectra are normalized to the respective maximum intensity of the scan. The UV-Vis absorption spectrum of the Cs2ZrBr6 NC thin ﬁlm shows a broad background that we attribute to scattering. (b, c) Photographs of emission from a Cs2ZrCl6 NC thin ﬁlm (panel (b)) and a Cs2ZrBr6 NC thin ﬁlm (panel (c)) on fused silica substrates, respectively, irradiated with 254 nm light from a UV lamp. The PL arises from the NC thin ﬁlms.
Scuseria–Ernzerhof exchange-correlation functional) results in an optimized lattice parameter of 10.67 Å, overestimated by ~3%, with respect to the RT experimental lattice parameter of 10.407 Å (cf. JCPDS File No. 01-074-1001). The band structure of Cs₂ZrCl₆ (Figure 4a), calculated using HSE06 with the addition of spin-orbit coupling (SOC), demonstrates a localized nature of both valence and conduction bands, with very low dispersion in both. The valence band maximum (VBM) is set to 0 eV. (b) Calculated absorption coefficient spectrum of Cs₂ZrCl₆. For comparison to the photoionization cross-section weighted DOS in the regions around valence and conduction bands. (d) XPS valence band spectrum of a Cs₂ZrCl₆ NC sample (orange dots). Here, for Cs₂ZrCl₆, the weighted HSE06 DOS accurately reproduces the primary features of the valence band determined from XPS measurements and, other than a shift of the Cs p states, split by SOC, the corresponding occupied states lying lower in the valence band (~3 eV).

After weighting each orbital by its photoionization cross section and convolving with Gaussian and Lorentzian curves of suitable width to simulate experimental broadening, we compare the calculated electronic DOS directly with X-ray photoelectron spectroscopy (XPS) valence band spectra measured on a Cs₂ZrCl₆ NC thin film sample (Figure 4d, orange dots). Here, for Cs₂ZrCl₆, the weighted HSE06 DOS accurately reproduces the primary features of the valence band determined from XPS measurements and, other than a shift of the Cs p states, split by SOC, toward lower binding energies by 0.2 eV, presents strong agreement with experiment. Such agreement between peak positions and intensities predicted by hybrid DFT with XPS is similar to previous reports in a variety of d-block materials in the absence of plasmon features.

In summary, we have reported the colloidal synthesis of antifluorite Cs₂ZrCl₆ and Cs₂ZrBr₆ NC samples that can be processed into thin films. We used XRD and conventional and surface-enhanced solid-state NMR measurements to confirm the structural and compositional properties of the products, validating that the surfaces are primarily capped by olate ligands and a distribution of disordered Cs configurations. Thin films of the Cs₂ZrCl₆ and Cs₂ZrBr₆ NCs exhibit broad blue-white and green-white PL, respectively, with a large Stokes shift. In addition, we measured a PLQY of 45% for a Cs₂ZrBr₆ NC thin film. The white emission color is tunable by modular mixing of the Cs₂ZrCl₆ and Cs₂ZrBr₆ NC components, revealing that anion exchange does not limit color tunability in the same way as that observed for lead halide perovskites. We present band structure calculations, which, in turn, provide strong support for our chemical and optical experimental results. These results provide an important step toward opening up a new family of tunable lead-free emitting materials for emerging thin film optoelectronic applications, including use as light-converting phosphors and electroluminescent light-emitting diodes.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmaterialslett.0c00393. Additional experimental details; details on sample characterization with XRD, TEM, NMR spectroscopy, UV-Vis absorption, PL, PLE and time-resolved PL spectoscopy, PLQY measurements, and XPS; computational details on DFT calculations; XRD data on sample...
degradation in air; FFT analysis on HR-TEM images of Cs$_2$ZrX$_6$ NCs; additional NMR, TEM, UV-Vis absorption, PL, PL decay, PLE and XPS data; results on electronic and optical property calculations on Cs$_2$ZrBr$_6$ (PDF)

CIF of Cs$_2$ZrBr$_6$ (CIF)

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Notes
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