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HF-Free Synthesis of Colloidal Cs₂ZrF₆ and (NH₄)₂ZrF₆ Nanocrystals

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A solution-phase hot-injection synthesis of colloidally stable A_2BF_6 nanocrystals is reported for the first time, focusing on $A = Cs^+$, NH_4^+ and $B = Zr^{4+}$. Handling hypertoxic HF is avoided by using NH_4F dissolved in a low-boiling-point alcohol, representing the first synthesis of any A_2BF_6 nanocrystals without HF addition. The chemical incompatability of Zr^{4+} with other common fluoride sources is discussed.

Colloidal fluoride nanocrystals (NCs) of lattices involving trivalent cations, such as NaYF₄, LaF₃, and LiLuF₄, have been extensively studied for uses in bioimaging, optoelectronics, Xray scintillation, laser cooling, optical thermometry, anticounterfeiting, and lighting, among others.¹⁻³ These lattices offer high optical transparency and chemical stability, and their optical functionality can be tailored via facile doping with trivalent lanthanide ions.⁴ These lattices provide reasonably phonon energies that favour high lanthanide low photoluminescence quantum yields (PLQYs). Isovalent substitution by trivalent lanthanides also supports site homogeneity and consequently narrow emission lines and low trap densities. Fluoride NCs based on divalent (e.g., SrF₂, FeF₂, MnF₂) and monovalent (e.g., NaF, LiF) cations have also been widely investigated.⁵⁻⁸ Despite the tremendous popularity of colloidal fluoride NCs, however, those involving tetravalent cations (such as A_2BF_6 , $A^+ = K^+$, Na^+ , Cs^+ ; $B^{4+} = Zr^{4+}$, Si^{4+} , Ti^{4+} , Ge⁴⁺, Sn⁴⁺) remain almost completely unexplored. In bulk, A_2BF_6 lattices doped with Mn^{4+} ions are leading candidates for next-generation narrow-line red emitters in display and lighting technologies,^{9,10} and those doped with Re⁴⁺ show very efficient upconversion.¹¹ The host A- and B-site cations also affect the B-site's local symmetry, which allows fine-tuning of dopant spectral linewidths, peak positions, and lifetimes.^{12,13} Access to these materials as colloidal NCs could reduce light scattering in conventional optoelectronics applications, facilitate surface functionalization to access new chemistries or photosensitization schemes, and enable entirely unprecedented opportunities in solution-phase processing, such as electrohydrodynamic ink-jet printing.^{14,15} Here, we report the first hot-injection synthesis of colloidally stable A_2BF_6 NCs, Cs_2ZrF_6 and $(NH_4)_2ZrF_6$.

Hydrofluoric acid (HF) has been inextricably linked to the syntheses of A_2BF_6 crystals for decades.¹⁶⁻¹⁸ Although a very effective fluoride source, the inherent chemical and environmental hazards of handling HF, and the accompanying safety-engineering costs, make syntheses requiring HF handling difficult to justify or scale up and potentially hinder commercialization of many promising fluoride materials. Consequently, there is growing interest in the development of A₂BF₆ syntheses that do not require addition of HF. Polycrystalline A_2BF_6 powders have now been successfully prepared without this precursor, ^{19,20} but colloidal NCs have not. Until very recently, in fact, there were no reports of any type of colloidal A₂BF₆ NCs, made with or without addition of HF. The sole report²¹ of colloidal A₂BF₆ NCs to date describes the syntheses of Cs₂SnF₆, Cs₂SiF₆, and K₂SiF₆ NCs via a coprecipitation method in which crystalline powders of the preformed fluoride lattices were dissolved in concentrated HF (40%, aqueous), and these HF solutions were injected into solutions of organic ligands in polar solvent at room temperature. Mn⁴⁺ doping was achieved by co-dissolution of bulk A2MnF6 in the HF solution. The use of HF in such syntheses is undesirable for health and environmental reasons, and as a result there is a need for alternative syntheses using fluoride sources with comparable reactivity.

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COMMUNICATION

Recent works have successfully prepared mixed-metal fluoride bulk powders of A_2MnF_4 (A = K⁺, Rb⁺, Cs⁺) and RbMF₃ $(M = Mg^{2+}, Ca^{2+})$ using metal-trifluoroacetates $(M(tfa)_n)$ as a safer single-source fluoride precursor via both solid-state and solution-phase syntheses.^{22,23} Trifluoroacetic acid (TFA) has also been used as a fluoride source in preparing a variety of colloidal fluoride NCs (*e.g.*, NaYF₄, LaF₃, FeF₃).^{5,24,25} TFA (or tfa) does not liberate fluoride anions until its decomposition between 250 and 300 $^\circ\!\text{C}\textsc{,}$ creating a controlled and tuneable release of reactive F ions into solution. We therefore attempted to adapt an attractive solution-phase synthesis²⁴ of NaYF₄ NCs using TFA for the synthesis of Cs₂ZrF₆ NCs. Our attempts did not yield any discernible crystalline fluoride products (Fig. S1). Further investigation suggested that TFA is chemically incompatible with the oxophilic tetravalent B-site cations at the elevated temperatures necessary to release fluoride anions under our conditions. Indeed, related attempts to prepare bulk metal-fluorides by calcination of TFA complexes of various cations (e.g., Li⁺, Na⁺, Pb²⁺, Y³⁺, Ti⁴⁺, Zr⁴⁺) yielded the desired fluoride salts in every case except the two 4+ cations $(Zr^{4+} \text{ and } Ti^{4+})$, which instead yielded metaloxyfluoride products.²⁶ Release of gaseous oxygen-based byproducts during decomposition of $M(tfa)_n$ precursors at $T \ge 1$ 300 °C has been observed in syntheses of mono-, di-, and trivalent metal-fluorides, 27,28 and such species may interfere with formation of the target Cs₂ZrF₆ lattice by binding to the highly oxophilic B⁴⁺ ions. Alternatively, we do note a promising recent demonstration that solid-state thermolysis of the alkali trifluoroacetates KH(tfa)₂ and CsH(tfa)₂ will fluorinate a-SiO₂ to form crystalline K_2SiF_6 and $Cs_2SiF_{67}^{29}$ albeit under conditions very different from those required to form colloidal NCs.

The unsuitability of TFA as a F⁻ precursor for A_2BF_6 NC synthesis led us to consider less common alternative fluoride sources that offer greater reactivity at lower temperatures. Anhydrous fluoride salts such as tetramethylammonium fluoride (TMAF) have been shown to replace the chloride and tosylate groups of organic complexes in polar solvents at room temperature,³⁰ and we hypothesized that these high-reactivity oxygen-free fluoride sources may also circumvent the B⁴⁺-oxo impasse encountered with TFA. Critically, handling these solid fluoride precursors rather than liquid HF vastly reduces the risk of accident and is thus highly advantageous from a safety standpoint. We decided to investigate NH₄F as a fluoride source for the synthesis of A_2BF_6 NCs.

A recent report identified that solvent polarizability has a prodigious impact on the reactivity of ammonium-based fluoride salts.³¹ Non-polar solvents cause the formation of low-reactivity salt aggregates, whereas polar solvents favour highly reactive free fluoride ions. We therefore decided to dissolve NH₄F in methanol (MeOH) to generate precursor solutions of active F⁻ ions. This fluoride precursor could then be added into non-polar solutions of Zr-oleate for crystal nucleation and growth. The high volatility of MeOH ensures that it can be swiftly pulled off under vacuum after mixing, without further chemical consequence. NH₄F in MeOH has been used in the solution-phase syntheses of other fluoride NCS (*e.g.*, core-shell doped NaGdF₄ and Yb,Er/Tm-doped NaYF₄), with promising

Page 2 of 4



Fig. 1 (a) TEM image and (b) pXRD data of Cs_2ZrF_6 microcrystals via one-stepaddition synthesis. (c) TEM image and (d) pXRD data of hollow Cs_2ZrF_6 nanocrystals after 10-min reaction time. pXRD data are compared to Cs_2ZrF_6 (trigonal, ICSD Coll. Code 25598) reference.

results.^{32,33} Most encouragingly, NH₄F in MeOH has also been used to prepare Yb,Er-doped Na_3ZrF_7 NCs, involving the tetravalent Zr^{4+} cation.³⁴

In an initial synthetic attempt at preparing Cs_2ZrF_6 crystals, MeOH, NH₄F, and CsOH were added to a room-temperature solution of Zr-oleate in 1-octadecene. MeOH was pulled off under vacuum, and the remaining solution was heated to and kept at 250 °C for 10 min before cooling (experimental details in SI). Fig. 1a shows a transmission electron microscope (TEM) image of the resulting product of this synthesis, revealing microcrystals of various sizes and morphologies. Fig. 1b shows the corresponding powder X-ray diffraction (pXRD) data. The only crystalline product detected is trigonal-phase Cs_2ZrF_6 . The lack of control over nucleation and growth in this reaction likely causes the wide distribution of crystallite sizes observed in Fig. 1a. Nonetheless, these data demonstrate that NH₄F can be used as a fluoride precursor for the synthesis of Cs_2ZrF_6 under these conditions.

The successful preparation of A_2BF_6 crystallites using NH_4F at 250 °C indicates that this chemistry is not impeded by the same kind of B^{4+} -oxo bond formation encountered during use of TFA. A major difference between the two fluoride sources is that NH_4F in MeOH offers a high F⁻ chemical potential already at room temperature, whereas TFA requires high temperatures to liberate any F⁻ and it likely never generates an equivalent F⁻ chemical potential under experimentally accessible conditions.

To better control crystal nucleation, the above synthesis of



Fig. 2 Low-temperature (T_{rxn} = 180 °C) Schlenk-line synthesis of colloidal Cs_2ZrF_6 nanocrystals.

Journal Name



Fig. 3 (a,b) TEM images of Cs_2ZrF_6 nanocrystals. (c) pXRD data of Cs_2ZrF_6 nanocrystals. A minor CsF impurity is observed. For comparison, Cs_2ZrF_6 (trigonal, ICSD Coll. Code 25598) and CsF (cubic, ICSD Coll. Code 61563) references are given. (d) Cs_2ZrF_6 nanocrystal colloids suspended in hexane.

Cs₂ZrF₆ was restructured to now involve injection of Cs-oleate into a reaction pot containing the Zr⁴⁺ and F⁻ precursors, held at 250 °C. Aliquots of the reaction solution were taken at various time points between 1 and 55 min (Fig. S2). Fig. 1c,d show a TEM image and pXRD data for the 10-min reaction product. The pXRD data again show only trigonal-phase crystalline Cs₂ZrF₆, with no detectable crystalline impurities. The TEM image shows that this procedure now yields NCs instead of microcrystals. Scherrer analysis of the pXRD linewidths indicates an estimated lattice coherence length of ~20 nm. Interestingly, the TEM data also show that many of the Cs₂ZrF₆ NCs are hollow, validated by high-angle dark field scanning transmission electron microscopy (Fig. S12).

Hollowing has been observed in a variety of fluoride NCs,^{35,36} and in some cases its sensitivity to surfactants has been demonstrated.³⁷ We thus hypothesized that altering the surface chemistry may affect NC hollowing. Following the same hot-injection procedure described above, capping ligands trioctylphosphine and oleylamine were now introduced to the reaction solution, in addition to oleic acid. Aliquots were collected 1 and 3 min after hot-injection. Unfortunately, the additional surfactants did not affect hollowing at either time point, as observed via TEM (Fig. S3). Instead, this synthesis again produced non-uniform hollow nanoparticles. We then looked to alter the reaction temperature. We found that reaction temperatures (T_{rxn}) above 200 °C consistently yielded inhomogeneous and hollow Cs_2ZrF_6 NCs (Fig. S4). At T_{rxn} = 180 °C, though, solid Cs₂ZrF₆ NCs were successfully formed. This 180 °C synthesis is summarized schematically in Fig. 2.

Fig. 3a,b shows TEM images of representative Cs_2ZrF_6 NCs prepared by this method, quenched 1 min after hot-injection. These images show hexagonally shaped NCs with a narrow size distribution ($d = 26.5 \pm 2.0$ nm). This result is consistent with



Fig. 4 Mechanisms of Cs₂ZrF₆ nanocrystal formation at 180 °C (left) and >200 °C

Fig. 4 Mechanisms of Cs₂zrF₆ nanocrystal formation at 180 °C (left) and >200 °C (right). At both temperatures, precursor heating before Cs⁺ injection forms similar hexagonal (NH₄)ZrF₆ nanocrystals. Injection of Cs-oleate at 180 °C yields solid hexagonal Cs₂ZrF₆ nanocrystals *via* balanced A-site cation exchange, but at >200 °C yields hollow Cs₂ZrF₆ nanocrystals *via* a nanoscale Kirkendall effect caused by imbalanced NH₄⁺ and Cs⁺ diffusion rates during the cation exchange.

the Cs₂ZrF₆ crystalline domain size of ~26 nm estimated using Scherrer analysis of pXRD linewidths. Note that minor holing is observed in the TEM images of some Cs₂ZrF₆ nanocrystals prepared by this route; TEM measurements as a function of electron-beam exposure show that this holing is caused by beam damage during TEM imaging, and that it is therefore clearly distinct from the high-temperature hollowing discussed above (see SI). Fig. 3c plots pXRD data of the washed reaction precipitate. These data again show trigonal-phase Cs₂ZrF₆, but now also show a minor impurity identified as cubic CsF. The CsF grain size was estimated to be >~50 nm from Scherrer analysis of its pXRD linewidths, but TEM reveals that these CsF particles actually aggregate into large clusters (>>100 nm, see SI Fig. S8 and discussion for further details). Because of its large size, the CsF impurity is easily separated from the Cs₂ZrF₆ NC solution by simple centrifugation, as confirmed using electron diffractometry of the collected supernatant (Fig. S6). Fig. 3d shows a photograph of the final colloidal Cs₂ZrF₆ NCs in hexane solution, highlighting the first colloidal Cs₂ZrF₆ NCs, and the first colloidal A₂BF₆ NCs of any composition prepared without handling HF.

To understand the mechanism by which Cs₂ZrF₆ NCs form,

COMMUNICATION

and the hollowing observed at elevated temperatures, aliquots taken from heated reaction mixtures prior to Cs-oleate injection were investigated by XRD and TEM. Remarkably, hexagonal (NH₄)₂ZrF₆ NCs were found in these precursor solutions at all temperatures between 180 and 250 °C (Fig. 4 and S9). (NH₄)₂ZrF₆ NCs thus form during precursor heating and are already present prior to Cs-oleate injection. Injection of Cs-oleate then converts these NCs into Cs₂ZrF₆ NCs by rapid A-site cation exchange. Whereas cation exchange at 180 °C yields isomorphic hexagonal Cs₂ZrF₆ NCs, the observation of hollow Cs₂ZrF₆ NCs at temperatures above 200 °C suggests faster outward diffusion of NH_4^+ from within the $(NH_4)_2 ZrF_6$ lattice than inward diffusion of Cs⁺, *i.e.*, a nanoscale Kirkendall effect.³⁸ These findings are summarized in Fig. 4. The formation of large CsF crystallites as a byproduct at 180 °C is likely caused by the excess $\mathsf{Cs}^{\scriptscriptstyle +}$ and $\mathsf{F}^{\scriptscriptstyle -}$ ions in solution prior to cation exchange, but over time this CsF redissolves and contributes to growth of the Cs₂ZrF₆ NCs (Fig. S5). Additional control experiments in which Zr⁴⁺ was omitted but other parameters were held constant failed to yield Cs₂ZrF₆, ruling out CsF as a viable intermediate in the direct pathway to the isolated Cs₂ZrF₆ NCs (Fig. S12).

In summary, a unique hot-injection synthesis of hexagonal Cs₂ZrF₆ NC colloids that avoids the handling of toxic HF has been developed. The incompatibility between the tetravalent Zr⁴⁺ and TFA, a common HF alternative used in many NC syntheses, led to identification of NH₄F solubilized in MeOH as an attractive and potent fluoride precursor for A2BF6 NC syntheses. Analysis of this synthesis revealed formation of hexagonal $(NH_4)_2 ZrF_6$ NCs as a reaction intermediate that can be isolated when Cs^{+} is omitted entirely. These $(NH_4)_2 ZrF_6 NCs$ are converted into Cs₂ZrF₆ NCs via cation exchange, representing the first A-site cation exchange reported for any A₂BF₆ NCs. Cs₂ZrF₆ NC hollowing was observed at temperatures above 200 °C, attributed to an imbalance in NH_4^+ and Cs^+ diffusion rates under these conditions, i.e., a nanoscale Kirkendall effect. Hollowing is suppressed by lowering the temperature to 180 °C, ultimately yielding nearly uniform hexagonal Cs_2ZrF_6 NCs. The identification of NH_4F in MeOH as a relatively safe, versatile, and effective fluoride precursor for A₂BF₆ NC syntheses and of A-site cation exchange as an effective tool for composition control are anticipated to enable new chemical approaches to A₂BF₆ NCs with rich compositions and desirable physical properties.

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