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Permalink
https://escholarship.org/uc/item/5jp0f4h1

Journal
Chemistry of Materials, 31(9)

ISSN
0897-4756

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Publication Date
2019-05-14

DOI
10.1021/acs.chemmater.8b04202

Peer reviewed
Probing the Stability and Band Gaps of Cs₂AgInCl₆ and Cs₂AgSbCl₆ Lead-Free Double Perovskite Nanocrystals

Jakob C. Dahl, Wojciech T. Osowiecki, Yao Cai, Joseph K. Swabeck, Yehonadav Bekenstein, Mark Asta, Emory M. Chan, and A. Paul Alivisatos

INTRODUCTION

Metal halide nanocrystals¹,² are a class of material for which it is possible to create and explore a wide variety of compositions. The prototypical lead system is well studied because of the attractive optoelectronic properties, which include high photoluminescence (PL) quantum yield³,⁴ and high tolerance to defects.⁵,⁶ Recent synthetic advances have demonstrated the ability to precisely control the size,⁷ shape,⁸ cation⁹,¹⁰ and anion¹¹–¹⁵ compositions of the nanocrystals to fine tune the respective band gaps and optical properties.⁹,¹⁰ Of particular interest from the point of view of solid-state chemistry and nanochemistry is isostructural nanocrystal systems¹⁴,¹⁵ in which the doubly charged Pb²⁺ ions are replaced by alternating singly and triply charged cations, a crystal structure referred to as double perovskite or elpasolite. Exploration of these systems, and their relative stabilities, offers rich opportunities for learning more about the chemical and physical principles that influence material properties and stability in metal halides.

The investigation of these questions is all of the more timely, since the practical application of lead halide perovskite nanocrystals is severely limited by their long-term instability¹⁶ and regulations restricting the use of lead in devices¹⁷. Identifying environmentally stable, synthetically accessible metal halide nanocrystals that avoid the use of lead while retaining the physical properties of lead halide perovskite archetypes might allow the realization of the many proof-of-concept solar and device applications in development.¹⁸

Several groups of related materials that substitute lead with other metals have been explored in the recent literature.¹⁹–²¹ In principle, 3d- or 4th-row p-block metal halides should have similar electronic structures, due to a potential defect tolerant band structure arising from the Fermi level lying between two antibonding orbitals (mostly composed of metal ns² and np⁰) and strong spin-orbit coupling.²² Tin halide and germanium halide perovskites are the closest structural and electronic analogs to lead halide perovskites and are predicted to

Received: October 3, 2018
Revised: April 12, 2019
Published: April 24, 2019
demonstrate efficient absorption and emission as well as defect tolerance.22,23 Unfortunately, these materials are even less stable to light, heat, and moisture than lead halide perovskites.23−26 Cs2M2X6 (M = Sb, Bi) and Cs2M3X8 (M = Bi, Sb, Te) structures are ternary metal halide structures that can accommodate p-block metals, and several interesting examples, including Cs2SnI6−30 Cs2BiI6−31,32 and Cs2SbI6−33,34 have been synthesized successfully both in bulk and at the nanoscale. The lower level of structural connectivity of the metal halide octahedra in these structure types reduces conductivity and exciton radii, which may limit their utility in electrical devices. Cs2AgMX6 (M = Bi, Sb, In) is a promising structure for lead-free halide perovskites since the metal halide octahedra are connected across all three dimensions.19 This 3D connectivity may explain why photovoltaic devices made from these materials have exhibited some of the highest power conversion efficiencies reported for lead-free halide materials despite the indirect nature of their band gaps.32,33

Recently, several groups have reported syntheses of Cs2AgBiX6 (X = Br, Cl) nanocrystals.1,4,15,34,35 There are discrepancies in reports of optical spectra between nanocrystal and bulk measurements such as the peak at 430 nm for Cs2AgBiBr6, which could lead to the interpretation that there is significant quantum confinement in these systems. However, we proposed that these discrepancies arise from differences in measurement technique (transmission vs reflection) and concentration of the sample instead of from the underlying optical response.15 This hypothesis received further support from thin film transmission measurements of single-crystalline Cs2AgBiBr6, which shows very similar optical signals to the nanocrystal solutions. In this work, we further elaborate on how these discrepancies may arise and how to eliminate them to ensure comparability between optical absorption measurements from the nanocrystal and solid-state chemistry fields. Besides Cs2AgBiX6, two other silver-containing double perovskite crystal structures have recently been reported in bulk: Cs2AgSbCl6 and Cs2AgInCl6.37−39 Although neither of these materials is well suited for photovoltaic applications due to their large band gaps, they may have applications in optoelectronic technologies such as the low-noise UV photodetectors recently demonstrated for Cs2AgInCl6.40 Here, we report the successful synthesis of Cs2AgSbCl6 and Cs2AgInCl6 nanocrystals and investigate their structure, absorption, and emission properties. In contrast to a recent report on Cs2AgInCl6 nanocrystals,32 we demonstrate that the optical properties of these nanomaterials are mostly unchanged from bulk.

Concerning the understanding of stability, most work has been predicated on the idea that the Goldschmidt tolerance factor can be used as a first guide to predict not only whether a material will form but also what the stability will be. In recent publications, both thermodynamic measurements and more extensive theoretical calculations or literature comparisons support the idea that the intrinsic stability of these halide systems does indeed correlate well with the Goldschmidt tolerance factor.41 However, this does not take into account the relative propensity to decompose according to specific pathways. When a perovskite decomposition product consists of metal−ligand complexes or other molecular species with varied bonding arrangements, the stability of those products can also vary widely across a series of metals, and it is the net reaction thermodynamics that is most relevant. The instability of many members of this class of compounds in the presence of water is of particular practical concern. Even slight exposure to humidity is sufficient to decompose materials such as CsPbI3.46 Many reports include discussions of stability by documenting X-ray diffraction (XRD) data after a period of storage or immersion of the material in water, ethanol, or another solvent.47,48 In this work, we develop an assay based on an amine degradation reaction observed previously in CsPbBr3 nanocrystals to quantitatively evaluate the stability of Cs2AgInCl6 and Cs2AgSbCl6 nanocrystals relative to Cs2AgBiCl6 and CsPbCl6. We demonstrate that Cs2AgSbCl6 decomposes with a 1000-fold lower amine concentration than Cs2AgInCl6 and extract both equilibrium constants and free reaction energies from an equilibrium model of the data.

## EXPERIMENTAL METHODS

### Materials

Acetone (99.9%, Fischer Scientific), antimony(III) acetate (99.99%, Aldrich), benzyl chloride (99%, VWR), bismuth(III) acetate (99.99%, Aldrich), cesium Acetate (99.9%, Aldrich), cesium standard for ICP (1000 ppm in 2% aqueous nitric acid, Aldrich, TraceCert Lot: BCBKB9483V), 2% aqueous nitric acid (99.99%), 2-ethylhexanol chloride (98%, Aldrich), hexanes (mixture of isomers 99.99%, Fisher Scientific), Indium(III) acetate (99.99%, Aldrich), lead(II) acetate hydrate (99.99%, Aldrich), oleic acid (90%, Aldrich), oleylamine (70%, Aldrich), silver acetate (99.99%, Aldrich), and m-xylene (99.8%, Fisher Scientific). All chemicals were used as purchased without further purification.

### Synthesis of Cs2AgInCl6 Nanocrystals

In a typical synthesis, 5 mg (0.025 mmol) of cesium acetate, 8 mg (0.05 mmol) of silver acetate, and 16 mg (0.05 mmol) of indium(III) acetate were placed into a 4 mL glass vial with a stir bar. Xylene (1 mL), oleic acid (0.25 mL, 0.8 mmol), and oleylamine (0.075 mL, 0.2 mmol) were added, and the vial heated to 100 °C for 10 min in an oil bath. Benzoyl chloride (0.040 mL, 0.3 mmol) was injected quickly. Then, the vials were taken out of the oil bath and left to cool to room temperature. The cooling rate and precise time of removal after injection did not appear to have any major effects on the result of this synthesis. For routine measurements, the nanocrystal reaction mixture was precipitated by centrifugation at 14,000 rpm for 5 min, and the resulting pellet was dispersed in hexanes.

### Synthesis of Cs2AgSbCl6 Nanocrystals

A typical synthesis of Cs2AgSbCl6 nanocrystals started with 5 mg (0.025 mmol) of cesium acetate, 3 mg (0.02 mmol) of silver acetate, and 17 mg (0.05 mmol) of antimony(III) acetate in a 4 mL glass vial with a stir bar. Liquid reagents, including xylene (1 mL), oleic acid (0.1 mL, 1.3 mmol), and oleylamine (0.075 mL, 0.2 mmol), were added next, then the vial was plunged into an oil bath at 100°C for 1 min. An acyl chloride, 2-ethyl-2-hexanoyl chloride (0.100 mL, 0.6 mmol) was injected quickly, and the vials were taken out of the oil bath and left to cool to room temperature and worked up in the same way as the Cs2AgInCl6 nanocrystal mixture. Cs2AgSbCl6 metal halide and surfactant precursor mixtures that were heated for more than a minute or left stirring under argon at room temperature for an prolonged period of time developed a reddish-brown tint and did not yield nanocrystals.

Procedures for CsPbCl3 and Cs2AgBiCl6 nanocrystals are similar to the procedure for Cs2AgInCl6 nanocrystals and can be found in the Supporting Information (SI).

### Absorption Measurements

For dilute absorption measurements, approximately 10−100 μL of nanocrystal solution was added to a quartz cuvette containing 3 mL of hexanes and measured in a Shimadzu UV-3600 UV−vis−NIR spectrophotometer. To measure the band edge, the entire concentrated nanocrystal solution was placed in a quartz cuvette and measured in the same spectrophotometer. Then, the absorbance was converted to absorption, and either the square root (for indirect band gaps in Cs2AgSbCl6) or the square (for direct band gaps in Cs2AgInCl6) of this value was plotted against energy. A straight line was fit to the linear part of this function, and the x-axis intercept was reported as the band gap. The
errors of the band gap were propagated from the fitting errors in the parameters of the line equation.

Photoluminescence and Photoluminescence Excitation (PLE) Measurements. A concentrated nanocrystal solution was placed in a quartz cuvette, and spectral photoluminescence and photoluminescence excitation measurements were taken on an Edinburgh FL5 980 Spectrometer. The photoluminescence quantum yield of Cs$_2$AgInCl$_6$ was measured at an excitation of 300 nm wavelength in an Edinburgh spectrometer equipped with an integrating sphere. The light out of the integrating sphere was integrated between 480 and 840 nm for emission and between 275 and 325 nm for absorption.

Transmission Electron Microscopy (TEM). One drop of dilute nanocrystal solution (prepared for optical measurements, 1:30 dilution) was cast onto a TEM grid (EMS, CF400-Cu). The samples were observed with a 200 kV Tecnai G2 T20 S-TWIN with a Gatan SC200 CCD camera.

X-ray Diffraction. The nanocrystal solution in hexanes was further concentrated by evaporating with a flow of nitrogen. This concentrate was drop-cast onto a low-background substrate, and the X-ray beam focused on the resulting film. Measurements were taken using a GADDS D-8 Series 1 Difractometer equipped with a Vantec 500 detector and on a D2 Phaser equipped with a Silicon SSD 160 detector.

Scanning Transmission Electron Microscopy and Energy Dispersive X-ray Spectroscopy (STEM—EDS). Samples were investigated with FEI TitanX operating at 120 kV, using a Fischione high-angle annular dark-field detector with an inner semiangle, $\beta$, of 63 mrad. The STEM—EDS measurement was then initiated and averaged over $3\sim4$ min for every image, and the characteristic X-ray fluorescence of each material analyzed using modified Cliff—Lorimer Factors in the Bruker Esprit program (details in SI).

Cs GF-AAS Concentration Measurements. About 1 mL of each nanocrystal stock solution was dried in a vial. High-purity aqueous nitric acid (2%) was added, and the vial sonicated for 20 min. The resulting solutions were weighed and diluted 20,000 times in 2% nitric acid. A 1000 ppm Cs standard solution was diluted 20,000, 50,000, and 200,000 times. These dilutions were used to create a calibration curve, against which the other samples were measured. The solutions had Cs concentrations of 6.194, 6.316, 18.03, and 13.37 ppb for curve, against which the other samples were measured. The samples were observed with a 200 kV Tecnai G2 T20 S-TWIN with a Gatan SC200 CCD camera.

Amine Degradation Assay. Diluted solutions of amines (0.00001–0.1 M in dodecane) were added to nanocrystal solutions (0.3 mM in dodecane). The absorption was monitored with a Biotek 3136 Chem. Mater. 2019, 31, 3134–3143

Figure 1. Reaction scheme for the synthesis of double perovskite nanocrystals. A solution of metal acetates (cesium, silver and indium, antimony or bismuth) in xylene with oleic acid and oleylamine is heated to 100 °C, then an acyl chloride precursor is injected to form nanocrystals of the corresponding Cs$_2$AgMCl$_6$ (M = In, Sb, Bi) double perovskite. The reactivity of the acyl chloride precursor is an important factor for tuning nanocrystal formation.

This substitutes the water- and air-sensitive antimony(III) chloride with the more stable antimony(III) acetate as a precursor and provides more tunability over the reaction by enabling the change of type or concentration of acyl halide.

To synthesize Cs$_2$AgSbCl$_6$ and Cs$_2$AgInCl$_6$ nanocrystals, we adapt a recent method employing an injection of acyl halides into a solution of metal acetate precursors rather than adding cesium oleate to a solution of metal halides. Briefly, in an open vial under atmospheric conditions, metal acetates are added to a solution of xylene, oleic acid, and oleylamine, heated to 100 °C, then an acyl halide is injected (Figure 1).

The effective mass was calculated using VASP and the methodology implemented in the BoltzTrap code (details in SI).

RESULTS AND DISCUSSION

To synthesize Cs$_2$AgSbCl$_6$ and Cs$_2$AgInCl$_6$ nanocrystals, we adapt a recent method employing an injection of acyl halides into a solution of metal acetate precursors rather than adding cesium oleate to a solution of metal halides. Briefly, in an open vial under atmospheric conditions, metal acetates are added to a solution of xylene, oleic acid, and oleylamine, heated to 100 °C, then an acyl halide is injected (Figure 1).

This substitutes the water- and air-sensitive antimony(III) chloride with the more stable antimony(III) acetate as a precursor and provides more tunability over the reaction by enabling the change of type or concentration of acyl halide.

The reaction reaches completion after less than 1 min, and nanocrystals are separated from the reaction solution through centrifugation and redispersal. To showcase the broad utility of this synthesis, we also make Cs$_2$AgBiCl$_6$ and Cs$_2$PbCl$_6$ using the same method, which show similar properties as previously reported nanocrystals (Figure S9).

For the synthesis of Cs$_2$AgSbCl$_6$ the control afforded by acyl halide injection is crucial: the addition of an equimolar amount of benzoyl chloride leads to the formation of lamellar structures or stacks of small plates, whereas two equivalents produce a mixture of nanoplatelets and nanocubes; when a more reactive precursor, 2-ethylhexanoyl chloride, is added instead, nanocubes form (Figure S10). This behavior bears some resemblance to the influence of the temperature on the synthesis of Cs$_2$PbBr$_4$ nanocrystals, with similar lamellar structures found at very low temperatures, which then transition to plates and cubes as the temperature rises. It is possible that the decomposition kinetics of the acyl halide precursor could control the shape of the crystal through a growth instability arising from the competition of nucleation islands on facets of different size, similar to recent reports on the synthesis of CdSe nanoplatelets. Slower kinetics may allow the formation of plates or even lamellar structures when the difference in activation barrier to form a new layer on a smaller crystal facet instead of a larger crystal facet is a significant part of the overall energetic process; faster kinetics
may overwhelm this difference in activation energy, causing isotropic shapes at higher temperatures, higher concentrations of the halide species or with a more reactive halide precursor.

Structurally, both Cs₂AgInCl₆ and Cs₂AgSbCl₆ nanocrystals appear to exhibit only the elpasolite or double perovskite Fm$\overline{3}$m structure in powder X-ray diffraction measurements of nanocrystal thin films, as determined by comparing the peak positions to the bulk Fm$\overline{3}$m phase of Cs₂AgInCl₆ and Cs₂AgSbCl₆ (Figure 2). Orientation effects appear to change the relative peak intensities in the nanocrystal thin films we measure compared to the bulk phase. Under some synthesis conditions, we observe AgCl impurities, which can be removed following synthesis through careful centrifugation and redissolution of the nanocrystals in the case of Cs₂AgInCl₆ but not for Cs₂AgSbCl₆. We eliminated impurities in Cs₂AgSbCl₆ by changing the ratio of M(III) to Ag(I) precursor (Figure S2). Due to the negligible optical response in the region important for Cs₂AgSbCl₆, we measure the properties of Cs₂AgSbCl₆ nanocrystals without interference in a mixed sample of AgCl and Cs₂AgSbCl₆ nanocrystals (see SI for a more thorough discussion of the AgCl impurity).

In transmission electron microscopy (TEM) images, we observe cubic nanocrystals with edges approximately 10 nm in length and a size dispersion of about 15%. There is close agreement between sizes determined by TEM (Figure S11) and from Scherrer analysis of X-ray diffraction (XRD) patterns (Figure S12 and Table S1) for Cs₂AgInCl₆ crystals (Figure 2) and for Cs₂AgSbCl₆ crystals with AgCl impurity (Figure S2) synthesized under similar conditions as the Cs₂AgInCl₆ crystals. Cs₂AgSbCl₆ nanocrystals synthesized in a phase pure manner were larger and less monodisperse (Figure 2).

High-resolution TEM images of Cs₂AgInCl₆ nanocrystals display a lattice spacing of 0.37 nm corresponding to a [220] plane. For Cs₂AgSbCl₆ nanocrystals, we observe 0.38 and 0.45 nm lattice spacings that correspond well to [220] and [200] planes. The correspondence of the lattice spacings throughout the crystal to high-reflection, low-index planes supports the claim that these nanocrystals are phase pure and single crystalline. The orientation of these planes relative to the edges further suggests that the cubes are terminated by [200] facets, similar to reports on lead halide perovskites as well as our recent results on Cs₂AgBiX₆ double perovskites. The elemental ratios from scanning transmission electron microscopy energy dispersed X-ray spectroscopy (STEM−EDS) measurements are consistent with expected values (Figure S13), and the ions appear co-localized in the material. We also observe small Ag(0) nanocrystallites decorating the cubes, which suggests similarities in the degradation process of silver-containing double perovskites. In our previous work with Cs₂AgBiBr₆, we demonstrated that these smaller silver nanocrystallites grow during the growth reaction itself and not subsequently during analysis through an interaction with the TEM beam. Likewise, in these materials, we do not observe a significant growth of the nanocrystallites during 5 min STEM−EDS mapping experiments (300 pA/nm exposure), though some migration and coalescence do occur (Figure S14). From structural characterization, we conclude that the synthesized particles are single-crystalline, cubic double perovskite nanocrystals around 10 nm in size, terminated by [200] facets and decorated with Ag(0) nanocrystallites.

Having ascertained the nature of the double perovskite nanocrystals, we investigate their optical properties, which

Figure 2. Structural characterization of Cs₂AgSbCl₆ (A−D) and Cs₂AgInCl₆ nanocrystals (E−H). (A) XRD pattern of nanocrystals measured with a Co source ($\lambda = 1.7789$ Å) with references COD 1546185 (Cs₂AgSbCl₆), (B) TEM image showing cubic nanocrystals, (C) high-resolution transmission electron microscopy (HR-TEM) image of a nanocube on a [100] zone axis showing 0.45 nm ([220]) lattice planes parallel to the edge of the cube and 0.38 nm ([200]) planes diagonal to the edge of the cube, and (D) STEM−EDS map of Cs₂AgSbCl₆ showing co-localization of cations. (E) XRD pattern of nanocrystals measured with a Co source ($\lambda = 1.7789$ Å) with reference COD 1546186 (Cs₂AgInCl₆). (F) TEM image showing cubic nanocrystals. (G) HR-TEM image of a nanocube on a [100] zone axis showing 0.37 nm ([220]) lattice planes diagonal to the edge of the cube and (H) STEM−EDS map of Cs₂AgInCl₆ showing co-localization of cations as well as silver spots.
serve as a probe of the degree of quantum confinement. We observe that the absorption spectra of the nanocrystal solutions have a rising shoulder from 310 to 290 nm for Cs₂AgInCl₆ nanocrystals (Figure 3) as reported previously⁴ and peaks at 360 and 300 nm for Cs₂AgSbCl₆ nanocrystals, which are both significantly removed from the reported bulk band edge.⁷ The dual absorption peaks for Cs₂AgSbCl₆ nanocrystals are similar to the shape of reflectometry peaks found in bulk samples.³⁹ A Tauc analysis⁵⁰ on absorption spectra of dilute solutions of Cs₂AgSbCl₆ and Cs₂AgInCl₆ nanocrystals indicates band gaps of 2.83 ± 0.02 and 4.15 ± 0.05 eV, respectively (Figure S16). This is a significant blue-shift from the reported bulk band gaps of 2.5 and 3.5 eV,⁵⁰ which at first glance would lead to the conclusion that both nanocrystals show significant quantum confinement. However, we do not observe a corresponding blue-shift of the broad emission of Cs₂AgInCl₆ (<0.1 eV) compared to the emission in bulk.⁵ⁱ The photoluminescence quantum yield of Cs₂AgInCl₆ nanocrystals was measured to be 6%, which is within measurement error of the quantum yield reported previously.⁴ In addition, confined structures of Cs₂AgSbCl₆, such as the small nanoplates in Figure S10, do not show a blue-shift of either the shoulder at 360 nm or the peak at 300 nm, as would be characteristic for a quantum confined exciton peak. The excitation spectrum of this emission decays into the background at approximately 350 nm or 3.5 eV. This band edge is 0.7 eV lower than the calculated band gap from absorption measurements but nearly identical to the bulk band gap. These different optical measurements do not agree with each other, with absorption spectra suggesting confinement energies of 0.7 eV for Cs₂AgInCl₆ and 0.3 eV for Cs₂AgSbCl₆, whereas emission and excitation spectra of Cs₂AgInCl₆ suggest less than 0.1 eV of confinement. Turning to density functional theory to investigate which level of confinement one should expect in the different double perovskites, we calculate the effective electron and hole masses and dielectric constants (Table S2). The resulting exciton Bohr radii, 1.02 nm for Cs₂AgSbCl₆ and 0.82 nm for Cs₂AgInCl₆ are an order of magnitude smaller than the size of the crystals, strongly suggesting that quantum confinement should be minimal in both materials.

Since the absorption spectra are the only measurements supporting the interpretation of strong quantum confinement, we considered the differences in measurement conditions between bulk and nanocrystal to enable a more confident measurement and analysis of band gaps in nanocrystals in the cases where there is no emission and excitation data, such as in Cs₂AgSbCl₆. Band gaps of bulk materials are commonly calculated from Tauc plots made with data obtained by reflection measurements of pure powders, whereas colloidal nanocrystals are measured in dilute solutions in transmission mode and have historically not been analyzed with Tauc plots. The difference in concentration is large, changing from pure material in bulk to an optically dilute sample for nanocrystals, a range of 3 orders of magnitude in the number of unit cells sampled. Preparation of nanocrystal solution samples is usually quite dilute to enable peak analysis in the most strongly absorbing species. As the variation in peak extinction coefficients of transition metal complexes (up to 7 orders of magnitude)⁵⁸ exceeds the dynamic range of most absorption spectrometers (0.001–4 absorbance units in the instrument we utilize), it stands to reason that spectra optimized for observing the strongest absorption peaks in nanocrystals may have insufficient signal to accurately measure the absorption at the band edges for weakly absorbing bands. In this particular case, the band edge absorption features are indeed expected to be weak since the transitions close to the band edge should be Laporte forbidden for Cs₂AgInCl₆ due to the 4d→5s transition at the band edge⁴⁰ and momentum forbidden for Cs₂AgSbCl₆ due to the indirect band gap.⁹⁰

To overcome these problems and more accurately measure the absorption at the band edges of Cs₂AgInCl₆ and Cs₂AgSbCl₆ nanocrystals, we perform Tauc analysis using absorption spectra of nanocrystal solutions that are 300 times more concentrated than those used to observe the absorption maxima. Although these spectra do not provide information on transitions that lie higher in energy due to the noise limit of the detector, this scheme is necessary to obtain precise linear fits of the absorbance spectra at the weakly absorbing band edges. The Tauc analysis of concentrated nanocrystal absorption spectra results in band gaps consistent with those measured for bulk samples,⁴⁶,⁴⁸ with an indirect gap of 2.57 ± 0.05 eV for Cs₂AgSbCl₆ and a direct gap of 3.57 ± 0.03 eV for Cs₂AgInCl₆.

One possible concern when using concentrated colloidal solutions for Tauc analysis is that lower-band gap impurities may confound the measurement. However, since the Tauc plot is designed to ignore low probability contributions at lower
energies, such as the Urbach tail, it is also insensitive to contamination by lower-band gap impurities, since the slope of any impurity absorptions that are not at their band edge in Tauc plots is significantly different than the slope for the band edge. A good test case is the analysis of Cs₂AgSbCl₆ (Figure 3C). There is a small-band gap impurity of unknown origin in the Cs₂AgSbCl₆ spectrum, visible in the deviation of the spectrum from the baseline below the band gap of Cs₂AgSbCl₆. Despite the evident impurity, it is possible to assign the slopes to different materials, allowing for an unambiguous identification of the band gap. We, therefore, confirm that Tauc analysis can be a valuable tool in analyzing energies of band gaps in nanocrystals, if appropriate measurement conditions are chosen. From our optical and theoretical analyses, we further conclude that both Cs₂AgInCl₆ and Cs₂AgSbCl₆ have close to no quantum confinement at the length scale synthesized and are unlikely to exhibit much confinement unless the size is drastically decreased.

The instability of metal halide nanocrystals in the presence of polar molecules has been widely acknowledged as a significant obstacle to many applications. Despite this recognition, there are few methods to measure and compare the relative stability of metal halide nanocrystals. We sought a robust and quantitative measure of perovskite nanocrystal stability, so we developed a decomposition titration assay in which Cs₂AgSbCl₆, Cs₂AgInCl₆, Cs₂AgBiCl₆, and CsPbCl₃ nanocrystals are titrated with amines. This assay is based on decomposition reactions of halide perovskites with amines previously observed in the case of CsPbBr₃ and Cs₂AgBiBr₆. Reactions with amines serve as a more reproducible proxy for the stability of perovskite nanocrystals than direct exposure to water, since amines and water are similar in hardness, but amines are miscible with nonpolar colloidal solutions of halide nanocrystals. In the decomposition reaction of CsPbBr₃ to CsPbBr₂, it has been proposed that three units of PbBr₂ from every four unit cells react with amines to form a complex in solution, leaving behind lead-depleted nanocrystals. For the double perovskites, STEM–EDS analysis of the depleted products after amine degradation reveals trace amounts of Sb, Bi, or In, leaving large aggregates containing Cs₂Ag and Cl (Figures S11–S13). The concentration of double perovskite unit cells converges to a fixed nonzero value after being exposed to an excess of amine-containing solutions during the time scale of the reaction. This suggests the possibility that the metal–ligand complexes and other molecular species reach a quasi-equilibrium with the nanocrystals in solution. The degradation process is a complex process on the individual nanocrystal level, and nanocrystals of both double perovskite and perovskite compositions appear to etch, grow, and fuse at the same time (Figure S23). Nevertheless, on the macroscopic level, this process appears reversible, as demonstrated previously for CsPbBr₃ nanocrystals through heat or addition of oleic acid. Since we cannot remove amines or nanocrystals from the solution without substantially altering the reaction, we reduce the number of amines available chemically. By protonating the amine by adding oleic acid in excess of that already present as surfactant in the nanocrystal solution, we couple the equilibrium of nanocrystals with amine to an acid-base equilibrium of the amine with oleic acid. This allows us to reverse some of the degradations of double perovskite nanocrystals and suggests reversibility of the nanocrystal degradation reaction at room temperature (Figure S28).

We, therefore, propose the following reaction with amines for all double perovskites (M = Sb, In, Bi):

$$\text{Cs}_2\text{AgMCl}_6 + \text{RNH}_2 \leftrightarrow \text{MCl}_x\text{RNH}_2 + \text{Cs}_2\text{AgCl}_3$$  

To measure the degradation behavior of the above reaction, amines are titrated into solutions of nanocrystals in dodecane, and the change in absorption from the original solution is measured. For the materials examined here, Cs₂AgSbCl₆ dissolves in the presence of the lowest concentrations of octylamine (0.01–0.1 mM), whereas Cs₂AgBiCl₆ dissolves at a higher concentration (~1 mM) and Cs₂AgInCl₆ and CsPbCl₃ require still higher concentrations (~10–100 mM) (Figure 4).

These materials can be characterized and compared by the concentration of amine required to degrade a defined fraction of the sample. This point is defined as the 1/e point in our analysis (see Table 1). Based on some of our observations as well as prior publications on CsPbBr₃, we postulate that this reaction is in quasi-equilibrium. Under this assumption, we developed a simplified equilibrium model, which we use to fit the data to a model equilibrium constant. The decomposition of several different materials can be well fit with this simplified equilibrium equation, lending additional support to the idea that an equilibrium reaction is occurring. Based on the

![Figure 4. Stability analyses of Cs₂AgSbCl₆, Cs₂AgBiCl₆, Cs₂AgInCl₆, and CsPbCl₃ nanocrystals. Individual points represent the fraction of initial absorption remaining after 4 h as a function of the different concentrations of octylamine that the nanocrystal solutions were exposed to. The solid lines are fits of the data points to an equilibrium equation (eq 2), whereas the shaded regions represent 1σ confidence intervals for those fits.](image-url)

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"Equilibrium constants are based on fits to optical absorption data of the degradation reaction (Figure 4). We calculate the equilibrium constant based on the assumption that all activity coefficients are equal to 1. The number reported here is technologically not an equilibrium constant but rather a concentration ratio with units of M⁻¹. Standard Gibbs enthalpies of reaction are calculated based on the equilibrium constants. The 1/e point is the characteristic point at which 1/e of the initial concentration of unit cells remains. It is calculated based on the linear fit in the log–log plot (Figure S27) and does not rely on the equilibrium model."
AgCl from Cs2AgSbCl6 might also arise in part from the outside of the crystals (Figure S31). The diaccumulation of amorphous Sb-containing agglomerations of Sb content in the crystals, with a corresponding also exposed to air for more than an hour show a significant degradation to AgCl during puriﬁcation. We anticipate that the method presented here could aid in the quantiﬁcation of the stability of metal halide materials.

**CONCLUSIONS**

In this report, we demonstrate a colloidal synthesis of nanocrystals of Cs2AgInCl6 and Cs2AgSbCl6 using a robust, tunable method of injecting acyl halides under atmospheric conditions and relatively mild temperatures. We identify the type and concentration of acyl halide as an easily tunable variable that profoundly affects the synthetic outcome. The particles synthesized are crystalline nanocubes of 10 nm edge length terminated with [200] facets and decorated with silver particles. We show that the optical properties remain unchanged from bulk despite the appearance of dilute absorbance spectra and discuss the need to prepare concentrated optical samples for accurate Tauc analysis of nanocrystals. We develop a degradation assay for the nanocrystals and show a decrease in chemical stability from Cs2AgInCl6 over Cs2AgBiCl6 to Cs2AgSbCl6. This ability to quantitatively measure perovskite environmental stability can enhance the understanding of metal halide materials, accelerate the identification of more stable perovskite analogs, and enable the elucidation of design rules for the environmental stability of a broad range of metal halide semiconductor nanocrystals.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.8b04202.

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ACKNOWLEDGMENTS

All experimental work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, under Contract No. DE-AC02-05-CH11231 within the Physical Chemistry of Inorganic Nanostructures Program (KC3103). The STEM−EDS and amine degradation measurement work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05-CH11231. All theory calculations were supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under Contract No. DE-AC02-05-CH11231 within the Materials Project program (KC233MP). J.C.D. acknowledges support by the National Science Foundation Graduate Research Fellowship under DGE 1752814. Y.C. was funded by the National Research Foundation (NRF), Singapore (CRP NRF2014-NRF-CRP002-036), and the Singapore-Berkeley Research Initiative for Sustainable Energy (SinBeRISE) CREATE program. The authors acknowledge QinQin Yu, Brent Koshier, Arunima Banal, Justin Ondry, Dante Valdez, Dr. Karen Bustillo, Dr. Assaf Ben Moshe, Dr. Ayelet Teitelboim, and Dr. Myoungwhan Oh for fruitful discussions.

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