Cesium lead halide perovskite nanostructures: tunable morphology and halide composition

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Abstract: Inorganic halide perovskite (CsPbX_3) nanostructures have gained considerable interest in recent years owing to their enhanced stability and optoelectronic application. Recent developments in the synthesis of nanostructures are reviewed. The impact of the precursor and ligand nature, temperature and growth time on the morphology and shape tuning of CsPbX_3 nanostructures is described in relation to their optical properties. The presynthetic and postsynthetic anion exchange strategies to retain pre-existing crystal phase and shape are discussed in this minireview.

1. Introduction

Recently, hybrid metal halide perovskites have emerged as potential materials for the photovoltaic application, showing an improvement in solar energy conversion efficiency from 3.81 % to 21% since 2009.^[1] Besides the solar cell application which was explored in detail, scientist found this class of materials useful in other applications including light emitting diodes,^[2] lasers,^[3] sensors^[4] and field effect transistors.^[5] Despite of these outstanding prosperity, hybrid metal halide perovskites were found to be highly sensitive to oxygen and moisture, which make them unstable, therefore requiring a critical environment for processing and storage. In addition, thermal and photo stability issues were also identified as due to organic cations.^[6] Most attention is currently given to the resolution of stability issues, which include by treating surface with surface tolerant molecules, polymers and by replacing organic carrier transport molecules with inorganic oxides. However, this intrinsic instability due to organic cation impeded the commercial applications of hybrid metal halide perovskite. One of the possible stratagem was to replace the organic cation in halide perovskites with inorganic cation while maintaining the electrical and optical properties. In 2015, all-inorganic CsPbX_3 nanocrystals were synthesized which shows high stability making them an alternate to hybrid metal halide perovskites.^[7] Colloidal nanocrystalline inorganic lead halide perovskite nanomaterial^[8] possess sharp, high quantum yield (30-90%) emission with entire visible range tunability.^[8c, 9] Owing to exceptional photophysical properties, CsPbX_3 inorganic perovskites has grabbed the attention of the scientific world to be explored in terms of controlled nanometric dimensions. Unlike, Cd-chalcogenides,^[10] CsPbX_3 nanocrystals have an advantage to tune photoluminescence with high precision both by anionic compositional controlled synthesis and

quantum sized engineering.^[11] Similarly, these inorganic perovskite nanocrystals show high tolerance of their band structure. Therefore, low cost and simple synthetic procedure is used for CsPbX_3 nanocrystals as no electronic passivation is required for the realization of high PL quantum yields.^[11]

Although, these inorganic perovskites have been studied from last 60 years, most of the work was to explore their structural features and optical properties.^[12] However, there was no report of their practical applications due to which this material could not gain much attention and remained quite anonymous. With the success of hybrid halide perovskites, the all inorganic CsPbX_3 perovskite re-entered as potential candidate for optoelectronic applications.^[13] However, extensive investigation is still lacking. From last two years, around 100 research articles have been published on CsPbX_3 perovskites. Many synthetic methods have been adopted to develop scalable synthetic methods and to control the materials morphology with tunable dimensions.^[14] Therefore, in this minireview article, we summarize recent developments in the synthesis of nanostructures of all inorganic cesium lead halide perovskites. The synthetic routes for all type of morphology and size tuned nanostructures of CsPbX_3 are discussed. In addition, this review includes pre-synthetic and post synthetic halide exchange methodologies to retain the shape and crystal structure to tune optical properties of CsPbX_3 .

1.1. Synthesis of CsPbX_3 nanoparticles with controlled morphology and size

Inorganic lead halide perovskite nanoparticles have been synthesized in various morphologies and sizes by varying different conditions including temperature, time, and nature of capping agents by using wet chemical method. Among the CsPbX_3 derivatives, the direct synthesis of CsPbBr_3 gained more attention due to its phase stability,^[8b, 15] and interesting optical and electronic properties.^[15a] Inorganic cesium lead halide perovskites crystalizes in orthorhombic, tetragonal and cubic phase depends upon reaction temperature.^[16] The difference in crystal geometries effects the properties of materials.^[17] The CsPbI_3 nanoparticles show one phase transition between cubic to orthorhombic phase at 328 °C, while CsPbBr_3 exhibits two phase transitions, cubic-tetragonal at 130 °C and tetragonal to orthorhombic at 88 °C. On the other hand CsPbCl_3 displays three successive phase transitions including cubic-tetragonal (47 °C), tetragonal-orthorhombic (42 °C) and orthorhombic to monoclinic at 37 °C.^[16b, 18] The cubic phase of CsPbI_3 is unstable and converted to orthorhombic phase upon storage for months, whereas, all other CsPbX_3 are stable in cubic phase.

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Within the class of perovskite materials, Protesescu et al.^[8b] have turned the attention to explore the all inorganic cesium lead halide perovskite as nanomaterial by hot injection method. In detail, the colloidal monodispersed nanocrystals have been synthesized, using Cs-oleate, lead halide precursors in high boiling solvent. The role of capping agents is to stabilize nanoparticles as well as to solubilize lead halide salts. Whereas, the use of Cs-oleate precursor rather than CsX (Cl, Br, I) is due to the less solubility of heavy metal halides in common solvents. The preheated Cs-oleate in 1:1 mixture of oleic acid and

of CsPbX₃ nanostructures preparation must be quenched and brought to room temperature immediately after the addition of Cs-oleate due to rapid crystallization of CsPbX₃ nanocrystals. The fast reaction kinetics limits the size tuning by reaction time. These CsPbX₃ nanocrystals show high photoluminescence (PL) quantum yield of 50-90% and narrow emission line widths of 12-42 nm.^[8b] De Roo et al.^[19] explored the dynamics of ligand binding and surface chemistry of inorganic perovskite nanostructures. The surface composition and reactivity of inorganic perovskite nanostructure were studied and gave an

Figure 1. The reaction temperature and growth time effect the size and shape of nanoparticles. The amount of additives (HBr) in the reaction mixture decreases the thickness of nanoplates.

oleylamine having PbX₂ in octadecene at 150-200 °C produces the cubic shape monodispersed CsPbX₃ nanoparticles. The mixture of oleylamine and oleic acid helps to purify and maintain the photoluminescence properties of CsPbX₃ nanostructures,^[19] particularly, oleic acid provides stability to colloidal form whereas, oleylamine plays a role to solubilize the PbX₂ salts in octadecene.^[20] Unlike chalcogenide nanoparticles, the reaction

idea of purification process of perovskites in which minimal excess of organic compounds is required. Bekenstein et al.^[15a] use the similar precursors for the synthesis of nanoplates and explore the temperature influence on the symmetry of the nanostructures. The low temperature reaction favours the

formation of thin nanoplates. The thickness and lateral dimension of nanoplates were found to be strongly dependent on temperature variation. However, high temperature yields big nanocubes which are converted to nanowires on prolonged time.^[15a]

On contrary, the controlled reaction parameters including temperature, reaction time and molar ratio of precursors were efficiently studied by Lignos et al. to yield an efficient reaction that requires small amounts of reagent and few hours of reaction.

small cubes which are due to temperature dependent surface ligand interaction. On the other hand, small amines which can diffuse faster into the structure lead to thinner structures whereas the weakening of amine-surface interaction leads to thicker nanostructures.

Shamsi et al.^[22] have made two major changes in the reaction strategy to find out the effect of solvent and nature of capping agent on the morphology. The nanoplates with no nanocube byproduct over a wide temperature range were obtained when

Figure 2. Effect of capping agents on the morphology of CsPbX_3 nanoparticles.

The effect of these parameters was monitored effectively by measuring in-situ optical properties. This study reveals that reaction kinetics is very fast at all temperature and precursor concentrations, therefore, time do not much affect the size of these nanostructures. This strategy has saved time and chemicals.^[11]

To explore the role of organic base, acid and precursor to control the morphology of inorganic perovskite, Pan et al.^[21] have performed an extensive experimentation, in which injection time and length of surfactant were studied. Short chain amine leads to thinner plates while low temperature gave 2D structures. However, acid chain length does not affect the thickness at low temperature. At Increased temperature, long chain acids gave

Cs-oleate dissolved in oleic acid is used rather than Cs-oleate dissolved in octadecene. This temperature range was more than reported by Bekenstein et al.^[15a] However, it was found that the increase in time increases the lateral size as well as thickness of nanoplates.

The second strategy was found to control the lateral size of nanoplates. In this study, the short chain ligands like octanoic acid and octylamine were introduced during the synthesis of nanoplates. By varying the ratio of these ligands, the thickness of nanoplates remained constant whereas the lateral size of particles tuned from 300nm to 5 μm . The combination of octanoic acid and octylamine was found necessary to control the shape and purity of nanoplates. Additionally, temperature and

time are also the important factors to control the shape and thickness of nanoplates. The optimum temperature for growth of large sized nanoplates was 145–155 °C, above and below this temperature range, shape and purity of these nanoplates were mainly affected. On the other hand, the optimum growth time of nanoplates was 5 minutes, prolonged time lead to aggregation of nanoplates.^[22]

Besides, Longfei et al.^[23] have dissolved the Cs-oleate in oleylamine which remained stable in liquid form for months in glove box and like oleic acid Cs-oleate mixture favours the lateral growth of CsPbX₃ nanocrystals. However, the nanoplates appeared with some nanocrystals as by product in the beginning. The prolonged reaction time leads to pure nanoplates with increased thickness and lateral growth. This increase in lateral growth using liquid Cs-oleate precursor was found larger than previous reports.^[15a, 22, 24] However, particularly during the synthesis of CsPbI₃, the amount of oleylamine and oleic acid was reduced to get pure nanosheets otherwise large amount of nanocube byproduct were produced along with nanosheets. The liquid Cs-oleate precursor not only effects the lateral growth of nanosheets but also has influenced the crystal structure of CsPbBr₃. The CsPbBr₃ nanosheets were crystallized in orthorhombic phase, whereas CsPbCl₃ and CsPbI₃ nanosheets appeared in tetragonal crystalline phase. However, in the previous reports,^[8b, 22, 24b, 25] the CsPbX₃ nanosheets exhibit cubic crystalline phase under similar condition, except the state of Cs-oleate precursor.

The impact of kinetics on the size distribution of all inorganic perovskites (CsPbX₃) nanoparticles was broadly studied by Koolyk et al.^[26] using focusing and defocusing of size distribution. It was found that the size distribution at growth duration of 1 s, 4 s, 20 sand 40 s have followed the divisibility. In the case of CsPbBr₃ nanoparticles, defocusing appears in the beginning, while the size distribution of CsPbI₃ nanoparticles exhibits focusing upto 20 s, followed by defocusing. The bromine based monomers have high diffusion rate which does not allow particles of CsPbBr₃ to reaches the critical radius of nucleation, therefore, broadening of size distribution takes place.

Along with nanocubes and nanoplates, one dimensional nanowire have gained interest due to their interesting physical and optical properties being used in wide applications including electronics, optoelectronics, sensing and energy harvesting.^[27] However, the synthesis of CsPbX₃ nanowires with controlled size, composition and properties is a challenge for the scientific community. Zhang et al.^[15b] have reported the synthesis of CsPbBr₃ nanowires using oleylamine and oleic acid capping agent and Cs-oleate precursor in octadecene at high temperature. The nanowires were obtained by keeping reaction time more than 10 minutes with some other morphology as byproduct. However, after 40–60 minutes, other morphologies disappeared and pure nanowires with 12 nm diameter and length upto 5 µm were produced. Further increase in time converts the nanowires into large crystals. On the other hand, the synthesis of CsPbI₃ and CsPbCl₃ nanowires using same methodology showed low yield, reduced diameter control and unattractive optical properties.^[15b, 28]

Similarly, The CsPbBr₃ nanowires of 10 ± 2 nm width and few microns long with 90% purity were successfully synthesized with slight modification in reaction as compared to previous reports.^[8b] The replacement of oleic acid capping agent with octylamine gave nano wires with improved yield.^[28] The variation in ratio of octylamine and oleylamine ligands increases the width of nanowires with improved yield and purity. However, if oleic acid is replaced with shorter alkyl chain carboxylic acid (octanoic acid or Hexanoic acid), the thinner nanowires were produced. The increasing concentration of shorter alkyl carboxylic acid over oleylamine, the width of nanowires of CsPbBr₃ can be tuned from 10±1 to 3.4±0.5 nm. In addition to capping agent and growth time, temperature also affects the width of nanowires. The optimum temperature to attain width ≥ 10 nm was 120–130°C. At the same temperature nanowires with width ≤10 nm can be produced but some byproducts also appeared. However, the reaction temperature below 70 °C delivers pure nanowires.^[29] Zhang et al.^[30] have reported the highly uniform ultrathin CsPbBr₃ nanowires with diameter of 2.2 ± 0.2 nm and length up to several microns. These nanowires were purified by stepwise purification and show 30–80% PLQY after surface treatment.

Aside from the success of hot injection wet chemical method to control the morphology and shape of CsPbX₃ nanostructure, the method is tedious, requires inert conditions and could only been used to control the thickness of CsPbBr₃ perovskites. Undeniably, it is required to carry out post synthetic halide exchange reaction to prepare nanoplates of CsPbCl₃ and CsPbI₃ perovskites.^[9a] Although, room temperature synthesis of CsPbBr₃ nanocrystals was performed, but leads to relatively low PL quantum yield.^[31] Tong et al.^[32] have adopted a versatile, polar solvent free, single step scalable approach to prepare highly luminescent (75% PL quantum yield) CsPbX₃ nanocrystals and nanoplates. In this study, the halide and thickness of nanoplates was tuned by direct ultrasonication of precursors (Cs₂CO₃, PbX₂) in the presence of ligands (oleylamine, oleic acid) at ambient conditions. The nanocrystals of 10–15nm and 8–12nm were obtained for CsPbBr₃ and CsPbI₃ respectively. Furthermore, it was observed that a reduced amount of cesium precursor favors the 2D growth to produce nanoplates.

As the morphology and size of inorganic CsPbX₃ nanocrystals plays a critical role in determining the physical, optical and electronic properties due to variation in band structures.^[33] Sun and coworkers^[31] have reported the effect of nature of ligand and ratio of amount to control the shape of CsPbX₃ nanocrystals by using reprecipitation strategy in which the precursors including capping agents were dissolved in good solvent like DMF, DMSO or THF and then into poor solvent like acetone at room temperature. The mixture of Cs-oleate and PbX₂ in hexanoic acid, octylamine capping agents produces the CsPbBr₃ spherical quantum dots. By replacing hexanoic acid with oleic acid and octylamine by dodecylamine, morphology changes to nanocubes. On the other hand, when oleic acid was replaced with acetic acid and octylamine with dodecylamine capping agents, CsPbBr₃ nanorods were produced. These obtained nanorods have typical length of 200 nm and diameter of 10 nm. However, oleic acid and octylamine combination gave 5.2 nm

± 1.3 nm thick nanoplates of typical edge length of 100 nm.^[31] However, it was found that by adjusting the ratio of oleic acid and oleylamine, the shape of CsPbBr₃ nanoparticles can also be tailored to quantum dots, face to face stacking nanoplates and two dimensioned flat-lying nanosheets. For example, direct addition of 0.6 mL of oleic acid and 0.3 mL of oleylamine in PbBr₂, Cs-oleate mixture gave spherical quantum dots with an average diameter of 2.4 nm. Whereas, 0.3 mL of Oleic acid and 0.7 mL of Oleylamine, produces lamellar structures with 400 nm average length. The combination of 0.8 mL of oleic acid and 0.2 mL of oleylamine can be used to engineering the flat-lying nanosheets with an average lateral dimension of 75 nm.^[8d]

Akkerman et al.^[24a] have controlled the thickness of CsPbBr₃ nanoplates differently from previous reports.^[8b, 15a, 22] The HBr was added during synthesis at room temperature. The thickness of CsPbBr₃ nanoplates was controlled by the amount of HBr without changing temperature. The thickness of nanoplates decreases with increasing amount of HBr added. The HBr protonates the oleylamine capping agent which compete Cs⁺ ion on the surface of nanoplates leads to slowing down the growth in vertical dimension. Similar, approach was also adopted for the formation of nanosheets of hybrid perovskites.^[24b]

Table 1. Effect of capping agents, temperature and reaction time on width and length of nanowires.

Capping Agent	Temperature (°C)	Reaction Time (Minutes)	Width (Nanowires)	Length (Nanowires)
Oleic acid, Oleylamine	150	40-60	12 nm	5 μ m
Oleylamine Octylamine	120 – 130	30-50	10-20nm	Few μ m
Oleylamine Octylamine Hexanoic acid / octanoic acid	< 70	50	< 10nm	Few μ m

1.2. Anion exchange in nanostructures of CsPbX₃

Inorganic metal halides (CsPbX₃) nanocrystals have gained potential interest as by tailoring the halide ion composition, the optical properties of these compounds can be tuned efficiently to cover the visible range.^[8b, 8c, 9a, 34] Although, several attempts have been made to exchange Cs⁺ and Pb²⁺ in CsPbX₃ nanostructures, however, the parent CsPbX₃ nanocrystals decomposed.^[9a] CsPbX₃ perovskites exhibit halide ion conductivity^[35] which explains the ease of replacement of halide ion in the perovskite lattices. In contrast to cation exchange in the perovskite lattice, low temperature, partial or complete anion exchange can easily be performed by homogeneous solid solution.^[8c, 9a] The production of mixed halides (CsPbX₃) perovskite derivatives using halide exchange reactions were performed by two ways, pre-synthetic and post-synthetic anion exchange reactions.

In the pre-synthetic halide ion exchange reactions, the PbX₂ slats were only used to prepare mixed halide perovskites derivatives.^[15a, 30, 36] However, this method has limitation, as the highly luminescent cubic phase is converted to orthorhombic phase in CsPbI₃ nanostructures, whereas, CsPbCl₃ in tetragonal phase.^[9b, 16] Currently, reported methods were applied to control

the thickness of CsPbBr₃ nanostructures due to their stability and enhanced photoluminescence.^[8c] however, halide ion exchange reaction is necessary to perform phase and shape controlled synthesis of CsPbI₃ and CsPbCl₃ nanostructures.^[8c, 9a]

Nedelcu et al.^[9a] have reported the post synthetic fast anion exchange in luminescent nanocrystals of cesium lead halide perovskites at 40 °C. Grignard reagents (MeMgX), oleylammonium halides (OAmX) and PbX₂ salts were used as halide ion sources were dispersed in toluene to perform the exchange reaction.^[9a] However, the direct synthesis of CsPbX₃ mixed halide perovskites at such a low temperature yields large and polydispersed crystallites with wider band gap and orthorhombic phase or even non-crystalline product. Among the crystalline phases of perovskites, the cubic phase is highly luminescent but is less stable in the case of CsPbI₃ which converted to yellow nonluminescent orthorhombic phase.^[9b, 16] However, Cl/I perovskites cannot be produced due to the large ionic size difference which is in good agreement with bulk materials.^[8b, 11, 15a, 23, 36-37] This approach of anion exchange was not found to affect the cationic sub lattice and the cubic phase perovskite structure. In addition, the size and shape of parent perovskites nanoparticles were also well-preserved during the anion exchange reaction.^[9a] However, the CsPbX₃ nanocrystals are unstable in polar solvent which restrict to use a nonpolar solvent (Toluene) as dispersion medium.^[8c, 38] On the other hand, Trioctylphosphine oxide (TOP) was added to solubilize PbCl₂ halide ion source. Where, low temperature is required to inject MeMgX anion source.^[9a] It is well known that the halide exchange is a fast process due to the ionic property of metal halide perovskites in the absence of halide ion sources^[35], therefore, perovskite nanocrystals themselves can also act as halide ion source for each other,^[8c] for example, the addition of CsPbI₃ in CsPbBr₃ produces the CsPb(Br/I)₃ mixed perovskites.^[8c, 9a]

On the other hand, Akkerman and coworkers have studied the post synthetic anion exchange by using variety of halide ion sources that includes lead halides, methylammonium halide, octadecylammonium halides, oleylammonium halides and tetrabutylammonium halides.^[8c] the reaction was performed at room temperature by injecting halide precursor solutions in the well dispersed toluene solution of perovskites nanocrystals. The exchange of halide ions does not affect the cubic phase in CsPbBr₃ nanocrystals but it affects the size of nanocrystals. During exchange with Chloride ion (Cl⁻) the size of nanocrystals decreases slightly whereas increase in size was observed in iodide ion (I⁻) exchange reaction^[8c] which may be due to anionic sizes. However, this approach has some limitations. For example, the possibility of methylammonium halides exchange with Cs⁺ ion limits its utility as halide ion source. While, the halide exchanges using tetrabutylammonium halides source were restricted to specific directions.^[8c] The reverse routes from Br⁻ to Cl⁻ and I⁻ to Br⁻ did not work due to soft/hard acid-base reactions.

2. Conclusions

We have summarized the contribution to the CsPbX₃ inorganic perovskite based nanostructures. This material has been recently reported and gained boosted interest due to its tunable optical and electronic properties suitable for potential applications. We have discussed the synthetic routes to tune the morphology and shape of CsPbX₃ nanostructures. In addition, the halide ion exchange reaction strategies were also summarized. Importantly, it was found that the state of precursor, nature and ratio of ligands, temperature and reaction time affects the shape of inorganic CsPbX₃ perovskite nanostructures. Furthermore, the post-synthetic halide exchange reactions retained the morphology and size of perovskite nanostructures. Looking forward, there are still many questions related to the synthesis of inorganic perovskite nanostructures that have not yet been explored. Herein, we discussed some issues that need to be explored. The improvements in the synthetic strategies were required to synthesize pure nanostructures. In addition, the amine and acidic ligands were reported in the synthesis of perovskite structures. However, ligands other than amine and acidic nature can be used to synthesize the new shapes of perovskites. The synthesis of stable cubic phase CsPbI₃ nanostructure is a challenge to be sightseen. Furthermore, the halide exchange reactions using inorganic salts as ion source can also be used.

Acknowledgements

MA would like to thanks higher education commission (HEC) of Pakistan for IRSIP funding.

Keywords: keyword 1 • keyword 2 • keyword 3 • keyword 4 • keyword 5

- [1] aA. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.* **2009**, *131*, 6050-6051; bN. J. Jeon, J. H. Noh, W. S. Yang, Y. C. Kim, S. Ryu, J. Seo, S. I. Seok, *Nature* **2015**, *517*, 476-480; cK.-G. Lim, S. Ahn, Y.-H. Kim, Y. Qi, T.-W. Lee, *Energy Environ. Sci.* **2016**, *9*, 932-939.
- [2] J. Byun, H. Cho, C. Wolf, M. Jang, A. Sadhanala, R. H. Friend, H. Yang, T. W. Lee, *Adv. Mater.* **2016**, *28*, 7515-7520.
- [3] G. Xing, N. Mathews, S. S. Lim, N. Yantara, X. Liu, D. Sabba, M. Grätzel, S. Mhaisalkar, T. C. Sum, *Nat. Mater.* **2014**, *13*, 476-480.
- [4] aM. Aamir, M. Sher, M. A. Malik, J. Akhtar, N. Revaprasadu, *N. J. Chem.* **2016**, *40*, 9719-9724; bM. Aamir, M. Sher, M. A. Malik, N. Revaprasadu, J. Akhtar, *Mater. Lett.* **2016**, *183*, 135-138.
- [5] G. Lin, Y. Lin, R. Cui, H. Huang, X. Guo, C. Li, J. Dong, X. Guo, B. Sun, *J. Mater. Chem. C* **2015**, *3*, 10793-10798.
- [6] aW. Nie, J.-C. Blancon, A. J. Neukirch, K. Appavoo, H. Tsai, M. Chhowalla, M. A. Alam, M. Y. Sfeir, C. Katan, J. Even, *Nat. Commun.* **2016**, *7*; bG. Divitini, S. Cacovich, F. Matteocci, L. Cina, A. Di Carlo, C. Ducati, *Nat. Energy* **2016**, *1*, 15012.
- [7] M. Kulbak, S. Gupta, N. Kedem, I. Levine, T. Bendikov, G. Hodes, D. Cahen, *J. Phys. Chem. Lett.* **2015**, *7*, 167-172.
- [8] aM. F. Aygüler, M. D. Weber, B. M. Puscher, D. D. Medina, P. Docampo, R. n. D. Costa, *J. Phys. Chem. C* **2015**, *119*, 12047-12054; bL. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh, M. V. Kovalenko, *Nano Lett.* **2015**, *15*, 3692-3696; cQ. A. Akkerman, V. D'Innocenzo, S. Accornero, A. Scarpellini, A. Petrozza, M. Prato, L. Manna, *J. Am. Chem. Soc.* **2015**, *137*, 10276-10281; dZ. Liang, S. Zhao, Z. Xu, B. Qiao, P. Song, D. Gao, X. Xu, *ACS App. Mater. Interfaces* **2016**.
- [9] aG. Nedelcu, L. Protesescu, S. Yakunin, M. I. Bodnarchuk, M. J. Grotevent, M. V. Kovalenko, *Nano Lett.* **2015**, *15*, 5635-5640; bV. Babin, P. Fabeni, M. Nikl, K. Nitsch, G. Pazzi, S. Zazubovich, *phys. status solidi. (b)* **2001**, *226*, 419-428.
- [10] aA. Priyam, A. Chatterjee, S. C. Bhattacharya, A. Saha, *J. Cryst. Growth* **2007**, *304*, 416-424; bZ. A. Peng, X. Peng, *J. Am. Chem. Soc.* **2001**, *123*, 183-184; cY. Wang, K. S. Leck, V. D. Ta, R. Chen, V. Nalla, Y. Gao, T. He, H. V. Demir, H. Sun, *Adv. Mater.* **2015**, *27*, 169-175; dC. Dang, J. Lee, C. Breen, J. S. Steckel, S. Coe-Sullivan, A. Nurmikko, *Nat. Nanotechnol.* **2012**, *7*, 335-339; eC. Dang, A. Nurmikko, *MRS Bulletin* **2013**, *38*, 737-742; fO. Chen, J. Zhao, V. P. Chauhan, J. Cui, C. Wong, D. K. Harris, H. Wei, H.-S. Han, D. Fukumura, R. K. Jain, *Nat. Mater.* **2013**, *12*, 445-451.
- [11] I. Lignos, S. Stavakis, G. Nedelcu, L. Protesescu, A. J. deMello, M. V. Kovalenko, *Nano Lett.* **2016**, *16*, 1869-1877.
- [12] aC. K. MØLLER, *Nature* **1958**, *182*, 1436-1436; bI. Y. Zaitseva, I. Kovaleva, V. Fedorov, *Russ. J. Inorg. Chem.* **2006**, *51*, 619-623; cR. L. Narayan, M. Sarma, S. Suryanarayana, *J. Mater. Sci. Lett.* **1987**, *6*, 93-94.
- [13] C. de Weerd, L. Gomez, H. Zhang, W. J. Buma, G. Nedelcu, M. V. Kovalenko, T. Gregorkiewicz, *J. Phys. Chem. C* **2016**, *120*, 13310-13315.
- [14] M. Aamir, M. Sher, M. D. Khan, M. A. Malik, J. Akhtar, N. Revaprasadu, *Mater. Lett.* **2017**, *190*, 244-247.
- [15] aY. Bekenstein, B. A. Koscher, S. W. Eaton, P. Yang, A. P. Alivisatos, *J. Am. Chem. Soc.* **2015**, *137*, 16008-16011; bD. Zhang, S. W. Eaton, Y. Yu, L. Dou, P. Yang, *J. Am. Chem. Soc.* **2015**, *137*, 9230-9233.
- [16] aS. Sharma, N. Weiden, A. Weiss, *Z. Phys. Chem.* **1992**, *175*, 63-80; bD. Trots, S. Myagkota, *J. Phys. Chem. Solid.* **2008**, *69*, 2520-2526; cC. C. Stoumpos, C. D. Malliakas, M. G. Kanatzidis, *Inorg. Chem.* **2013**, *52*, 9019-9038.
- [17] aC. C. Stoumpos, C. D. Malliakas, J. A. Peters, Z. Liu, M. Sebastian, J. Im, T. C. Chasapis, A. C. Wibowo, D. Y. Chung, A. J. Freeman, *Crys. Growth Des.* **2013**, *13*, 2722-2727; bS. Kondo, K. Suzuki, T. Saito, H. Asada, H. Nakagawa, *Phys. Rev. B* **2004**, *70*, 205322.
- [18] aC. K. MØLLER, **1958**; bY. Fujii, S. Hoshino, Y. Yamada, G. Shirane, *Phys. Rev. B* **1974**, *9*, 4549.
- [19] J. De Roo, M. Ibanez, P. Geiregat, G. Nedelcu, W. Walravens, J. Maes, J. C. Martins, I. Van Driessche, M. V. Kovalenko, Z. Hens, *ACS Nano* **2016**, *10*, 2071-2081.
- [20] Y. Kim, E. Yassitepe, O. Voznyy, R. Comin, G. Walters, X. Gong, P. Kanjanaboos, A. F. Nogueira, E. H. Sargent, *ACS App. Mater. Interfaces* **2015**, *7*, 25007-25013.
- [21] A. Pan, B. He, X. Fan, Z. Liu, J. J. Urban, A. P. Alivisatos, L. He, Y. Liu, *ACS Nano* **2016**, *10*, 7943-7954.
- [22] J. Shamsi, Z. Dang, P. Bianchini, C. Canale, F. Di Stasio, R. Brescia, M. Prato, L. Manna, *J. Am. Chem. Soc.* **2016**.
- [23] L. Lv, Y. Xu, H. Fang, W. Luo, F. Xu, L. Liu, B. Wang, X. Zhang, D. Yang, W. Hu, *Nanoscale* **2016**, *8*, 13589-13596.
- [24] aQ. A. Akkerman, S. G. Motti, A. R. S. Kandada, E. Mosconi, V. D'Innocenzo, G. Bertoni, S. Marras, B. A. Kamino, L. Miranda, F. De Angelis, *J. Am. Chem. Soc.* **2016**, *138*, 1010-1016; bZ. Yuan, Y. Shu, Y. Tian, Y. Xin, B. Ma, *Chem. Commun.* **2015**, *51*, 16385-16388.
- [25] Q. A. Akkerman, S. G. Motti, A. R. Srimath Kandada, E. Mosconi, V. D'Innocenzo, G. Bertoni, S. Marras, B. A. Kamino, L. Miranda, F. De Angelis, *J. Am. Chem. Soc.* **2016**.
- [26] M. Koolyk, D. Amgar, S. Aharon, L. Etgar, *Nanoscale* **2016**, *8*, 6403-6409.
- [27] aW. Lu, C. M. Lieber, *Nat. Mater.* **2007**, *6*, 841-850; bR. Yan, D. Gargas, P. Yang, *Nat. Photon.* **2009**, *3*, 569-576; cF. Patolsky, C. M. Lieber, *Mater. Today* **2005**, *8*, 20-28; dZ. L. Wang, J. Song, *Science* **2006**, *312*, 242-246.
- [28] D. Zhang, Y. Yang, Y. Bekenstein, Y. Yu, N. A. Gibson, A. B. Wong, S. W. Eaton, N. Kornienko, Q. Kong, M. Lai, *J. Am. Chem. Soc.* **2016**.
- [29] M. Imran, F. Di Stasio, Z. Dang, C. Canale, A. H. Khan, J. Shamsi, R. Brescia, M. Prato, L. Manna, *Chem. Mater.* **2016**.
- [30] D. Zhang, Y. Yu, Y. Bekenstein, A. B. Wong, A. P. Alivisatos, P. Yang, *J. Am. Chem. Soc.* **2016**.

- [31] S. Sun, D. Yuan, Y. Xu, A. Wang, Z. Deng, *ACS Nano* **2016**, *10*, 3648-3657.
- [32] Y. Tong, E. Bladt, M. F. Aygüler, A. Manzi, K. Z. Milowska, V. A. Hintermayr, P. Docampo, S. Bals, A. S. Urban, L. Polavarapu, *Angew. Chem. Int. Ed.* **2016**, *55*, 13887-13892.
- [33] J. Q. Grim, L. Manna, I. Moreels, *Chem. Soc. Rev.* **2015**, *44*, 5897-5914.
- [34] J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal, S. I. Seok, *Nano Lett.* **2013**, *13*, 1764-1769.
- [35] J. Mizusaki, K. Arai, K. Fueki, *Solid State Ion.* **1983**, *11*, 203-211.
- [36] J. B. Hoffman, A. L. Schleper, P. V. Kamat, *J. Am. Chem. Soc.* **2016**, *138*, 8603-8611.
- [37] B. A. Koscher, N. D. Bronstein, J. H. Olshansky, Y. Bekenstein, A. P. Alivisatos, *J. Am. Chem. Soc.* **2016**.
- [38] L. C. Schmidt, A. Pertegás, S. González-Carrero, O. Malinkiewicz, S. Agouram, G. Minguez Espallargas, H. J. Bolink, R. E. Galian, J. Pérez-Prieto, *J. Am. Chem. Soc.* **2014**, *136*, 850-853.