Facile Synthesis of Lead-Free Mixed Halide Double Perovskite Cs_2AgBiX_6 (X = Br, I) Nanocrystals (NCs) for Photovoltaics Applications

Mohammad Salman Khan, Mohd. Bilal Khan, Sultan Ahmad, Hasan Abbas, Asim Khan, Ankur Mishra, Reeba Marry Thomas, and Zishan Husain Khan

Abstract Cesium-based lead-free perovskites are promising alternatives to the organic–inorganic lead perovskites due to lead toxicity and moisture/oxygen sensitivity of the latter. Perovskites can be synthesized in the form of single perovskite structures having the general formula (ABX_3) as well as double perovskite structures with the formula ($A_2B^IB^{III}X_6$). Double perovskites structures have several advantages over single perovskite structures in terms of phase stability. Ag and Bi-based Cs halide double perovskites (Cs_2AgBiX_6) are significantly promising among different double perovskite structures. The theoretical predictions have shown that the Cs_2AgBiI_6 has the most suitable optoelectronic characteristics among their bromide and chloride counterparts. Experimentally, the synthesis of Cs_2AgBiI_6 is challenging due to the formation of thermodynamically more stable $Cs_2Bi_2I_9$. On the other hand, $Cs_2AgBiBr_6$ is a stable composition, but it is undesirable in solar cell applications due to its larger bandgap. In the present work, we report the facile synthesis and characterization of stable mixed halide Cs_2AgBiX_6 (X = Br, I) nanocrystals which show better stability than Cs_2AgBiI_6 and have smaller band gap in comparison with that of $Cs_2AgBiBr_6$.

Keywords Double perovskite · Mixed-halide · Lead-free · Nanocrystals (NCs) · Phase stability · Photovoltaics

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1 Introduction

Lead (Pb) halide perovskites, with the generic chemical formula ABX_3, have received a lot of attention from both the scientific and industrial communities. Here, A is a $CH_3NH_3^+$ (MA^+), $CH(NH_2)_2^+$ (FA^+), or Cs^+ cation, B is a Pb^{2+} cation, and X is a Cl^-, Br^-, or I^- anion [1, 2].The remarkable 3D perovskite structure that includes a ns^2 electronic structure at the outermost orbital and higher-quality charge carrier characteristics such as better carrier mobility and relaxed carrier without traps, accounts for the excellent optical features of the lead-based perovskite NCs. However, Pb toxicity is frequently seen as a drawback, which motivates researchers to identify alternative substitutes. Recently, lead-free perovskite NCs have been reported by using non-hazardous metal ions in place of Pb^{2+} in the perovskite structures [3]. The 3D double perovskites $AB^{I}B^{III}X_6$ (A: Cs, CH3NH3; B^I: Ag, Au; B^{III}: Bi, In; X: Cl, Br, I) have been shown to be synthesized by substitution of one monovalent B^+ and one trivalent B^{3+} cation for the Pb^{2+} cation. Lead-free double perovskites exhibit attractive optical and electrical characteristics, such $Cs_2AgBiBr_6$ [4]. The key factor limiting $Cs_2AgBiBr_6$ photovoltaic performance is its large band gap. On the other hand, $Cs_2AgBiIr_6$ shows suitable bandgap but lacks stability [4]. It is highly desirable to develop effective approaches to synthesize the stable lead-free double perovskite compositions having suitable bandgap for solar cell applications. In this direction, several efforts have been made to modify the structure and to improve the photovoltaic characteristics. For instance, the bandgap of $Cs_2AgBiBr_6$ has been successfully reduced from 2.12 to 1.86 eV via Sb impurity doping which has been attributed to the upshifting of valence band maximum resulting in the narrowing of bandgap due to higher energy levels of Sb 5 s states when compared with those of 6 s states [5, 6]. Synthesis of mixed halide compositions is another strategy which can be used to obtain stable Pb-free double perovskite compositions by suitably optimizing the ratio of halide ions in the compositions [5–7]. Traditionally, mixed halide compositions are synthesized using ion exchange method which is a complex multistep method not suitable for bulk synthesis [6, 7]. Herein, we report the facile one step synthesis and characterization of mixed halide (I/Br) double perovskite (Cs_2AgBiX_6: X = Br, I) nanocrystals.

2 Materials and Methods

2.1 Materials

All the chemicals used in the synthesis process, namely Cs_2CO_3 (99% purity cesium carbonate), AgBr (99% purity silver(I) bromide), BiI_3 (99% purity bismuth(III) iodide), mineral oil (light), oleic acid (90%, technical grade), oleylamine (70%, technical grade), and hexane ($\geq$ 97.0% purity HPLC grade, GC), were procured from Thermo-Fisher Scientific and handled without going through extra purifying procedures.

2.2 *Facile Synthesis of Mixed Halide Double Perovskite Nanocrystals (DPNCs)*

The production of double perovskite nanocrystals (DPNCs) was made possible by the use of a facile synthesis approach. For the synthesis of Cs_2AgBiX_6 (X = Br, I), mixed halide DPNCs 0.1 mmol of Cs_2CO_3, 0.1 mmol of AgBr, and 0.4/0.5 mmol (for two different compositions) of BiI_3 were mixed with 500 μL of oleic acid, 500 μL of oleyl amine and 10 ml of mineral oil and subjected to using probe sonication at the power of 60-W for 12 min until the initially colorless solution turned into red colored. At this stage the reaction flask was rapidly cooled down in an ice bath. The as-synthesized crude solution was centrifuged at 8000 rpm for 10 min to eliminate the impurities, followed by redispersion of the precipitates in 5 ml of hexane using mild sonication. Further centrifugation at 2000 rpm was used to eliminate any large crystals resulting and to achieve supernatant having well dispersed double perovskite nanocrystals.

2.3 *Characterization*

To study the structural and optical properties of the as-synthesized double perovskite nanocrystals (DPNCs), various characterization techniques were employed. The morphology of the DPNCs was analyzed using TEM (Technai, F30 S-Twin). The x-ray diffraction pattern of the DNCs thin film was obtained at room temperature using x-ray diffractometer (Rigaku Smart-Lab). Optical absorption and photoluminescence studies of DPNCs were conducted using UV–visible spectroscopy (Perkin Elmer-Lambda 365^+) and photoluminescence spectrophotometry (Shimadzu-RF-5301PC), respectively.

3 Results and Discussion

Figure 1a depicts a typical low magnification TEM image of pure double perovskite nanocrystals (DPNCs). It shows a narrow size distribution within the range of 15–30 nm. The well-dispersed DPNCs without any indication of aggregation are clearly apparent in the high magnification TEM image (Fig. 1b).

X-ray diffraction pattern of as-synthesized mixed halide double perovskite nanocrystal sample are shown in Fig. 2. In this double perovskite structure $AgBr(I)_6$,

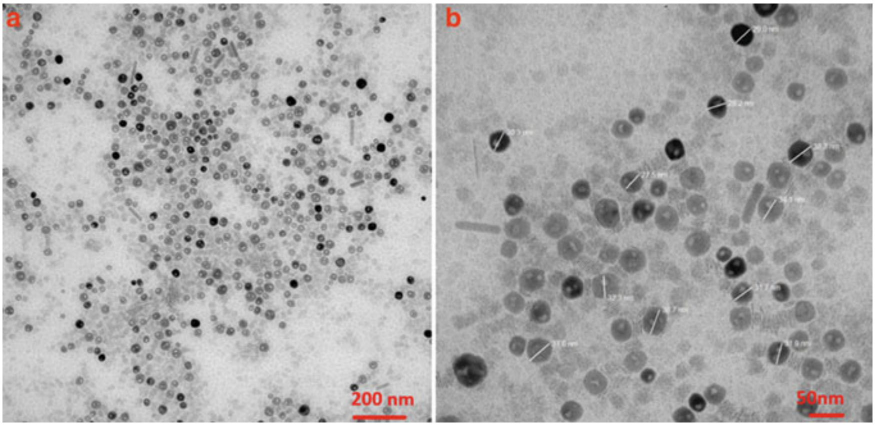

Fig. 1 TEM micrograph of purified DPNCs **a** Low-magnification **b** High-magnification TEM micrograph shows cubic shapes of NCs

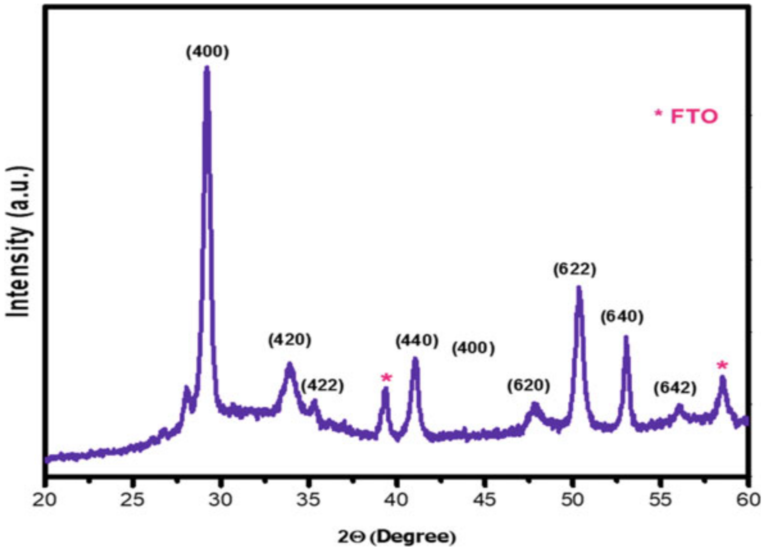

Fig. 2 XRD pattern of Cs_2AgBiX_6 (X = Br, I) mixed halide double perovskite nanocrystals

$BiBr(I)_6$ octahedrons are alternatively connected by sharing bridged $Br^-(I^-)$ ions. The XRD pattern of Cs_2AgBiX_6 (X = Br, I) depicts the peaks located at 2θ values of 29.24°, 33.92°, 35.26°, 40.94°, 47.82°, 50.38°, 53.06°, and 58.52°, which can be indexed to (400), (420), (422), (440), (620), (622), (640), and (642) planes, respectively [7]. All the members of the compositional family Cs_2AgBiX_6 show XRD peak positions very close to each other. However, these peak positions shift toward lower 2-theta values when one moves from Cl^- containing compositions to I^- containing

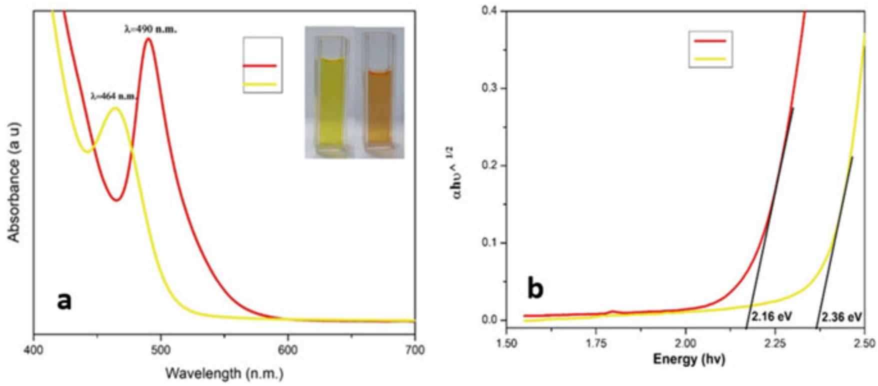

Fig. 3 **a** UV–vis. absorption spectra. **b** Tau's plot (indirect bandgap) of DPNCs

compositions due to increase in the size of halogen ions [8]. For instance, diffraction peak corresponding to (400) plane of $Cs_2AgBiBr_6$ occurs at 31.14°, while for Cs_2AgBiI_6 it occurs at 29.15° [7]. In the present structure XRD peak for (400) plane appears at 29.24°, which is a clear indication of the successful synthesis of mixed halide Cs_2AgBiX_6 nanocrystals containing I^- and Br^- ions.

Figure 3a shows the UV–vis absorption spectra of as-synthesized Cs_2AgBiX_6 nanocrystals having different I^- content. With the increase in the amount of iodine ions, the UV–vis absorption spectra of double perovskite nanocrystal structure bathochromically shifts from 464 to 490 nm (Fig. 3a) and the optical bandgap is reduced from 2.36 to 2.16 eV. The decrease in optical bandgap on the increase in iodine ions may be due to smaller gap between the bonding and antibonding states of Pb^{2+}–I^- hybridized orbitals in comparison with that of Pb^{2+}–Br^- hybridized orbitals [7, 8].

PL spectra have been used to evaluate the effect of increase in the iodine content on the luminescent properties of lead-free mixed halide double perovskite nanocrystals (Fig. 4) which shows that the lead-free mixed halide DPNCs Cs_2AgBiX_6 (X = Br, I) has relatively broad emission in comparison with the reference material Cs_2AgBiX_6 NCs. With increase in iodine contents, the PL emission is red shift from 523 to 552 nm. This result is consistent with the results of the UV–visible spectra and can be seen as the result of bandgap narrowing on increase of the iodine content [8].

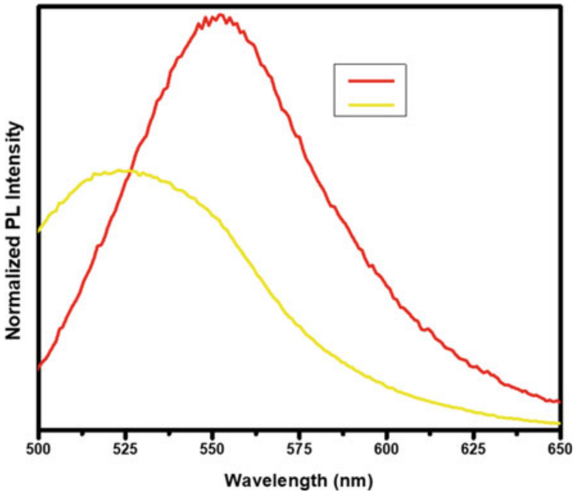

Fig. 4 Normalized photoluminescence (PL) spectra of DPNCs

4 Conclusion

We demonstrated the facile synthesis of lead-free mixed halide DPNCs with enhanced chemical and colloidal stability. The optical bandgap of these DPNCs was found to decrease when compared with that reference Cs_2AgBiX_6 NCs, which may be due to the introduction of iodine ions in the lattice as confirmed by UV–vis absorption spectra. PL emission spectra showed red-shifted broad emission. We believe that the protocols used in this work may further be extended to other double perovskite compositions to achieve higher chemical stability toward the development of high performing lead hazard-free perovskite solar cells.

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Conflict of Interest The authors declare that they have no conflict of interest.

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