Broadband emission in new lead free all-inorganic 3D CsZnCl₂I perovskite

DOI:

[10.1039/C8NJ04404J](https://doi.org/10.1039/C8NJ04404J)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Aamir, M., Khan, M. D., Sher, M., Malik, M. A., Revaprasadu, N., & Akhtar, J. (2018). Broadband emission in new lead free all-inorganic 3D CsZnCl₂I perovskite. *New Journal of Chemistry*. <https://doi.org/10.1039/C8NJ04404J>

Published in:

New Journal of Chemistry

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Broadband emission in new lead free all-inorganic 3D CsZnCl₂I perovskiteReceived 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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This contribution reports the deposition of new zinc based lead free all inorganic 3D CsZnCl₂I perovskite thin films using aerosol assisted chemical vapour deposition (AACVD) at 100 °C. Room temperature optical measurements performed on as-deposited thin films shown two absorption peaks. Upon 325 nm excitation, CsZnCl₂I perovskite thin film showed broad band white light emission having two peaks, which cover the entire visible range of the spectrum. This is the first example of white light emission from 3D all-inorganic lead free mixed halide CsZnCl₂I perovskites.

All inorganic lead halide perovskites have attracted considerable attention due to their remarkable properties including narrow band emission, tunable band gap and high photoluminescence quantum yield.¹⁻³ Owing to these merits, they have shown huge potential in the fields of photovoltaics,⁴ fluorescent sensing,⁵⁻⁷ photocatalysis,⁸ solid state displays and lighting.^{9, 10} Conventionally, the white light emitting devices of perovskite materials suffer from a drawback of non-stoichiometric compositions due to anion exchange during fabrication process.^{11, 12} Furthermore, red light emitting, CsPbI₃ and CsPb(Br/I)₃ were found to be unstable at ambient conditions due to the phase transition and phase separation phenomenon.¹³

Amongst the lead halide perovskites, white light emitting 2D hybrid perovskite materials have gained enormous attention due to their potential applications in optoelectronics.¹⁴ These hybrid 2D lead based materials have high color stability and tunability compared to 3D lead halide perovskites.¹⁵ On the other hand, recently, 3D all inorganic CsPbCl₃ perovskite has

been co-doped with Bi³⁺ and Mn²⁺ to obtained white light emission.¹⁶ A major concern with lead based perovskite materials is toxicity, which impedes their commercial applications. As an alternative, divalent Sn and Ge have been used in perovskite materials, but, chemical instability related to these metal cations faded the charm.¹⁷

Transition metals such as Cu, Zn etc. have stable oxidation state and their high absorption coefficient making them suitable candidates for metal halide perovskite materials.^{5, 6} Furthermore, the mixed halides in perovskite have distorted inorganic network that could be interesting to attain broadband white light emission.¹⁸

Herein, we report the deposition of new all inorganic lead free mixed halide CsZnCl₂I perovskite thin films via AACVD at 100 °C from CsI and ZnCl₂. The as-deposited 3D lead free CsZnCl₂I perovskite thin films were characterized by powdered X-ray diffraction spectroscopy (p-XRD), field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDX), UV-Visible (UV-Vis), and photoluminescence spectrophotometry (PL). Two distinct absorption bands and broadband emission due to the self-trapped excited states in the mixed halide inorganic perovskite was observed.

The crystallinity of as-deposited thin film was determined by p-XRD. The diffraction peaks at 2θ = 22.63°, 27.02°, 28.41°, 31.52°, 36.24°, 38.66°, 43.17°, 51.93°, and 60.82° confirm the formation of the desired CsZnCl₂I perovskite as shown in figure 1. The p-XRD analysis of CsI and ZnCl₂ (starting materials) was also measured. It can be observed that no diffraction peak of CsZnCl₂I matches with CsI or ZnCl₂, which confirms the formation of the deposited CsZnCl₂I perovskite material.

Morphology of as-deposited thin films was explored by using field emission scanning electron microscopy (FESEM). The mixed morphologies including tetragonal and some irregularly shaped clusters of plates like structures were formed by CsZnCl₂I perovskite as shown in figure 2(a-b). The substrate was uniformly covered with the deposited material. To confirm the presence of Cs, Zn, Cl, and I in the as-deposited thin films,

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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Journal Name

EDX elemental mapping was performed. The uniform distribution of Cs, Zn, Cl and I in the as-deposited film validates the formation of CsZnCl₂I perovskite as shown in figure 2 (c-f). The optical properties of the as-deposited films were determined by UV-Vis and photoluminescence spectroscopy. Room temperature absorption spectra of thin films of all-inorganic mixed halide CsZnCl₂I perovskite show two absorption peaks located at 2.67 eV (4.65 nm) and 3.45 eV (360 nm) as presented in Figure 3(a). These absorption peaks assigned to the exciton confined into the [ZnCl₂I]⁻¹ inorganic part and attributed to the electronic transition from the top of valence band including Cl(3p) and I (5p) orbitals to the bottom of the conduction band of the Zn(4s) orbital. The appearance of two peaks may be due to the energy level difference between Cl(3p) and I(5p) orbitals.¹⁹ Furthermore, the presence of excitonic absorption peak (3.45 eV) at room temperature indicates a larger exciton binding energy.¹⁹ PL spectrum of the as-deposited thin films of CsZnCl₂I was measured at room temperature at 325 nm (3.815 eV) excitation frequency. As shown in Figure 3b, very broadband white light (WL) emission which covers almost whole visible spectrum (370 nm to 630 nm) consisting of two bands positioned at 2.28 eV and 2.87 eV, respectively. We assigned high energy broad PL (2.87 eV) peak related to the exciton absorption located at 3.45 eV. This broad PL emission show large stoke shift of 390 meV. On the other hand, the peak (2.67 eV) belongs to the broader exciton absorption peak located at 2.67 eV with stoke shift of 450 meV.

These two peaks together form a very broadband emission with maximum intensity at 2.87 eV, and a full width half maximum (FWHM) of 1.12 eV (Figure 3b). This type of broadband WL emission was reported for low dimensional hybrid perovskite materials.²⁰⁻²² Recently, two dimensional (C₆H₁₁NH₃)₂CdBr₄ hybrid perovskite show similar broadband emission.²³ Dohner *et al.*¹⁴ have reported three single crystals of [2,2'-(ethylenedioxy)bis(ethylammonium)][PbX₄] (X=Cl, Br, I) which also show comparable broad band emission with FWHM of 0.95 eV, 0.80 eV and 0.32 eV. However, present work represents first 3D all-inorganic lead free mixed halide CsZnCl₂I perovskite with broadband emission. The origin of this broadband emission may be due to the distortion originated from the mixed halide ions with orbitals of different energies in the all-inorganic CsZnCl₂I perovskite structure. The lead-free nature and broadband emission make this material an exciting candidate for optoelectronic applications.

In summary, we reported the deposition of new lead free all inorganic 3D mix halide CsZnCl₂I perovskite thin films using AACVD at 100 °C for 30 minutes. The as-deposited thin films were characterized by p-XRD, SEM and EDX. The CsZnCl₂I thin films have shown two absorption peaks and broadband PL emission with FWHM of 1.12 eV, which is larger or equal to reported emission shown by 2D hybrid perovskites.²³ As far as we know this is the first example of all-inorganic lead free mixed halide perovskite showing broad white light emission. This study can open up a new venue for 3D all inorganic perovskites to be explored as white light emitters. The

optoelectronic device application is under progress and will be produced shortly.

Experimental section

Deposition of thin films by AACVD

CsZnCl₂I thin films were deposited on glass substrates consuming stoichiometric ratio of precursors zinc chloride and cesium iodide via AACVD at 100 °C using our previously reported method.^{24, 25}

Materials & Characterization

Cesium iodide (CsI), Zinc chloride (ZnCl₂), and anhydrous DMF were purchased from Sigma-Aldrich and used without further purification. p-XRD measurements were performed using a Bruker aXS D8 advanced diffractometer with Cu-K α radiation (λ = 1.5406 Å) operated at 40 kV and 40 mA. Field emission scanning electron microscopy (SEM) was carried out using a Philips XL30 FEG SEM. Energy-dispersive analysis of X-rays (EDX) spectroscopy was performed using a DX4 detector. All samples were carbon coated using Edwards coating system E306A prior to SEM analysis. A Perkin-Elmer Lamda 20 UV-vis spectrophotometer was used to carry out optical measurements in the 200-1100 nm wavelength range at room temperature. Samples were placed in quartz cuvettes (1 cm path length) and the absorbance was recorded. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 luminescence spectrometer with xenon lamp over range of 200-800 nm.

Acknowledgements

JA thanks to ORIC, Mirpur University of Science and Technology (MUST) for funding (ORIC/381/2018).

Conflicts of interest

There are no conflicts to declare.

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Figure 1. Comparative pXRD spectra of as-deposited CsZnCl_2I perovskite thin film, CsI and ZnCl_2 .

Figure 3. (a) UV-Vis absorption spectra and (b) comparative PL and UV-Vis spectra of as-deposited thin films of CsZnCl₂I.

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The Broadband emission was observed in new lead free all-inorganic 3D CsZnCl₂I perovskite thin films deposited by AACVD.