Low-dimensional metal halide perovskite phosphors for solid-state lighting

Krishnamoorthy, Thirumal

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**Low-dimensional Metal Halide Perovskite Phosphors for Solid-
State Lighting**

Krishnamoorthy Thirumal

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2019

Low-dimensional Metal Halide Perovskite Phosphors for Solid-State Lighting

Krishnamoorthy Thirumal

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for the
degree of Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research done by me except where otherwise stated in this thesis. The thesis work has not been submitted for a degree or professional qualification to any other university or institution. I declare that this thesis is written by myself and is free of plagiarism and of sufficient grammatical clarity to be examined. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Professor Subodh Mhaisalkar

Authorship Attribution Statement

This thesis contains material from one paper published in the following peer-reviewed journal where I was the first author.

Chapter 2 is published as Thirumal. K, Chong. W. K, Xie. W, Ganguly. R, Muduli. S. K, Sherburne. M, Asta. M, Mhaisalkar. S, Sum. T. C, Soo. H. S, Mathew. N. Morphology-Independent Stable White-Light Emission from Self-Assembled Two-Dimensional Perovskites Driven by Strong Exciton-Phonon Coupling to the Organic Framework. *Chem. Mater* 29, 3947-3953 (2017). DOI: 10.1021/acs.chemmater.7b00073.

The contributions of the co-authors are as follows:

- A/Prof Nripan M., A/Prof Sum. T. C, and A/Prof Soo. H. S provided the initial project direction and edited the manuscript drafts.
- Chong. W. K and I prepared the manuscript drafts. The manuscript was revised by A/Prof Mathew. N, A/Prof Sum. T. C, A/Prof Soo. H. S, and Prof Mhaisalkar. S.
- I co-designed the study with A/Prof Nripan. M, and A/Prof Soo. H. S and performed all the laboratory work at the Energy Research Institute@NTU (ERI@N) and at Chemistry and Biological Chemistry, School of Physical and Mathematical Science. I also analyzed the data.
- Sample preparation and structural characterizations were done by me at ERI@N and CBC. Photophysical characterizations were done by Chong. W. K at PAP.
- Dr Ganguly. R assisted in the collection of single-crystal X-ray diffraction data.
- Dr Muduli. S assisted in the collection of data of the transmission electron microscopy.
- DFT calculations were done and interpreted by Dr Xie. W, Dr Sherburne. M, and Prof Asta. M.

16 August 2019

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Date

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Krishnamoorthy Thirumal

Abstract

Artificial lighting accounts for close to 20% of the electricity used world-wide and solid-state light emitting diodes (LEDs) have the potential to reduce this usage by up to 80%. While inorganic phosphors have been widely used to enable white light emission, new class of materials that could be inexpensive, made from earth-abundant materials, processed at low temperatures, and solution deposited is of great interest. Metal-halide perovskite have taken the optoelectronics community by storm by delivering more than 25.2% solar cell efficiencies and external quantum efficiencies in excess of 20% in light emitting diodes. Early reports have also indicated the applicability of perovskites as broad band emitting phosphors, however to-date, perovskite phosphors have seen very limited research breadth and the understanding of the broad band emissions emanating from these phosphors is much limited. In addition to the promise of perovskites as exceptional semiconducting materials, the compositional and structural variability of these materials suggests upto 10^2 to 10^6 variants in is archetypal 3D perovskite, ABX_3 , with organic cations (CH_3NH_3), divalent metals (Pb, Sn, Ge), and halides corresponding to the A, B, X sites respectively. By the choice of the organic cation, perovskites can be synthesized with layered (2D) or molecularly lower dimensionalities (e.g. 1D, 0D); with the lower dimensionalities resulting in a more deformable structure and larger binding energies; potential more amenable to broad band emissions.

While uncovering the fundamental reasons for broad band emission, this thesis undertook a comparative study of lower dimensional perovskites by exploring substituents of the A-site cation to yield 2D, 1D, and 0D structures, metal substituents to explore both lead and lead-free systems, and halide substitutions to understand the role of composition on structure as well as on emission properties.

In the first study, a 2D lead chloride perovskite was prepared using a phenethylammonium (PEA) cation. The single crystal X-ray diffraction data, time-resolved photophysical measurements, temperature-dependent photoluminescence measurements, and density functional theory (DFT) calculations were used to demonstrate that broad band emission is arising from strong exciton-phonon coupling with the organic lattice, which is independent of the morphology of the perovskite. The phenethylammonium lead chloride (PEPC) perovskite exhibited broad band emission that closely mimicked artificial lighting from cool white light

LEDs, and thermal & photo stability showing suitability for phosphor applications. However, photoluminescence quantum yields (PLQY) were less than 1% and lower dimensional perovskites were subsequently explored.

Substituting the A-site cations by a larger m-xylylenediammonium (m-XDA) ion enabled formation of 0D perovskites with lead bromide (m-XDALB) or chloride (m-XDALC) octahedra separated by these organic moieties. These exhibited metal-centered s-p transitions along with structural deformations of the metal halide octahedra at low temperatures, although they are not emissive at room temperature. Addition of excess PbBr₂, of up to one mole, resulted in 1D perovskites with broad band, white light emission matching that of cool white light emission.

Tin substituted (m-XDATB) perovskite showed strongly Stokes-shifted broadband emission, from 400 to 650 nm, with a peak maximum at 505 nm, a full-width at half-maximum (FWHM) of 95 nm, and a high PLQY of 60%. White-light-emitting devices could be fabricated using this cyanm-XDATB emitter with a sulfoselenide phosphor. Germanium substituted, m-XDAGB, showed yellow emission (450 – 700 nm), with PLQY of 20%. White-light-emitting devices fabricated using yellow-emitting m-XDAGB with a barium aluminate phosphor displayed emission suitable for daytime white light applications. Several other materials were also explored with alkyl chains (e.g. octyl and butylammonium, OA and BA respectively) for A-site cations and some of them showed promising applications for light emission; but also, for down conversion phosphors, luminescent solar cell collectors, and for UV radiation harvesting solar cells.

Typically, 3D perovskites show very narrow emissions due to weak exciton-phonon couplings associated with large deformation energies of the metal halide octahedra. This thesis has shown that reducing the dimensionality of hybrid organic-inorganic perovskites from 3D interconnected polyanionic inorganic networks into lower-dimensional 2D, 1D, or molecular 0D octahedra results in localized electronic states, narrower conduction and valence bands. Reducing the dimensionality of perovskites localizes the charge carriers which leads to short-range lattice deformations which results in self-trapping of excitons as well as enhanced broadband emission. Using transient absorption and transient photoluminescence (TRPL) studies, and Raman spectroscopy, the broad band emission observed from films and also nanoparticles of PEPC were shown to originate from self-trapped excitons predominantly in the organic lattice. This contrasts with the commonly attributed origins of self-trapped excitons

only in the inorganic metal halide lattice. These findings highlight the importance of rational selection of both the organic and inorganic components in 2D perovskites for white-light emission.

Molecular zero-dimensional (0D) perovskites could be fabricated using newly synthesized m-XDA organic cations, where the metal halide octahedral anions were separated by the large m-XDA cationic matrix. PLQY trend observed was m-XDATB > m-XDAGB > m-XDALB; with highest PLQY of 60% seen in Sn; but the highest Stokes shift observed in Ge perovskites. These differences are yet to be fully understood; however mechanistic as well as theoretical analysis pointed to the broadband emissions attributable to exciton self-trapping. Replacing the m-XDA organic cations with alkylammonium (BA and OA) results in larger Stokes shift and much higher PL quantum yield, where the OATB could reach almost 100 % PLQY.

The exciton couples strongly to the lattice and generates lattice distortions that can be defined as “excited-state defects”. These structural deformations would be able to stabilize the exciton, allowing significant broadband emission with large Stokes shift. Low-dimensional perovskites could show strong exciton-phonon couplings as the deformation energies of the metal halide octahedra decrease with reduction of the dimensionality of the perovskite. Additionally, phosphors (e.g. m-XDATB, m-XDALB) based on metal ions with s-p electronic transition are less explored compared to phosphors with other electronic transitions like d-d, f-d, and f-f transitions. Study of the transition from the excited singlet to the triplet states aided by the spin-orbit coupling that occurs due to the heavy atoms such as Sn, Pb, Br was also made possible in these low dimensional perovskites.

It has clearly been established in this thesis that factors such as structural deformations, rigidity of the structure, are very important criteria in terms of creating self-trapped excitons and broadband emission. Furthermore, the thesis has also highlighted that low dimensional perovskites represent a great potential with its vast parametric space that is opportune for implementation of rational design methodology to identify the right material combinations that could be considered as attractive alternatives for currently used phosphors.

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Chapter 1

Introduction

This chapter briefly contextualizes the research area and the motivation for the thesis. It presents an overview of the history of light sources, broadband emission, various solid-state lighting devices such as blue LEDs and white LEDs. A brief description of various phosphor materials for white light LEDs (WLEDs) are also discussed with special emphasis on the use of lower dimensional perovskite materials as phosphors. A gap analysis is also presented to justify the motivation and objectives of the studies presented in the thesis. This chapter concludes with a brief description of the thesis structure.

1.1 History of Light-Emitting Devices

Presently, we are transitioning to greater use of solid-state lighting after three generations of light sources. Initially, fire and torch were used for lighting throughout different periods and are still being used in some parts of the world. The second generation of the light source is the incandescent light bulb after its discovery in 1879 by Thomas Edison. An incandescent bulb consists of a wireframe under vacuum or an inert atmosphere, which glows at high temperatures when an electric current is applied. This results in the emission of visible light along with heat. Initially, a carbon filament was used and later it was replaced with tungsten. The spectral power distribution (SPD) matches with the visible spectrum of sunlight, however, a typical incandescent bulb with a tungsten filament converts only less than 5% of the input power into visible light while the remaining energy is lost as heat. As a result, the luminous efficacy of an incandescent bulb is in the range of 10 – 18 lm/W and it has a low lifetime of 1,000 hours. An incandescent bulb is enough for indoor application whereas commercial buildings need higher efficiency devices. Therefore, fluorescent lamps have been used primarily for this purpose because of its higher luminous efficacy of 50-100 lm/W, which is several times the efficiency of an incandescent bulb. A fluorescent lamp works on the principle of fluorescence, as the name suggests. This lamp is a low-pressure mercury-vapor gas-discharge lamp, which uses fluorescent materials to produce visible light. Gaseous mercury is excited by the applied electric current and it emits high energy ultraviolet light, which in turn excites the fluorescent material coated on the inside surface of the tubes. The disadvantages of using a fluorescent

lamp include the use of hazardous mercury, ultraviolet light emission, and poor color chromaticity due to the poor color mixing as shown in Figure 1.1.

Figure 1.1. Spectral Power Distribution (SPD) Curves of (a) noon sunlight, (b) incandescent bulb, (c) a fluorescent lamp, and (d) difference in white color purity emitted by an incandescent bulb and a fluorescent lamp.

Therefore, the search for light sources with good color quality, without the need for hazardous materials, and with high luminous efficacy has been a priority. In this context, the technologies of solid-state lighting have developed swiftly. As shown in Figure 1.2 the luminous efficiencies of incandescent and fluorescent light sources have remained below 100 lm/W with no improvement in lifetimes. The fourth revolution of lighting known as solid-state lighting started with the invention of the blue-emitting light-emitting diode (LED) by S. Nakamura in 1991¹. They demonstrated the p–n junction GaN LED using the low-temperature GaN buffer and the low-energy electron beam irradiation (LEEBI) treatment. Over the years very significant improvements in luminous efficiencies of LEDs as well as new concepts that led to white-light-emitting diodes (WLEDs) have enabled solid-state lighting to become the most efficient lighting source in the world today.

Figure 1.2. Luminous efficiencies of different lighting technologies².

1.2 Light-Emitting Diodes (LEDs)

The phenomena of broadband emission were observed nearly a century ago in silicon carbide crystals which showed electroluminescence with a broad range of colors including orange, yellow, green and blue when current flowed through it.³ Electroluminescence is defined as the emission of light from the radiative recombination of opposite charge carriers in a material, usually a semiconductor, in response to an applied electric field or current. Upon recombination, energy is released in the form of photons. However, the concept was fully explained only 1920 by Oleg Lossev who studied the electroluminescence phenomenon in p-n junctions.⁴ This laid the foundation of light-emitting diodes (LEDs) with various emission colors such as red, green, amber, etc. for commercial display applications.

Electroluminescence is the phenomena behind the light emission from LEDs. Conventional LEDs are built with doped semiconductor materials: n-type doping with abundant negative charge carriers (electrons) and p-type doping with abundant positive charge carriers (holes), much like a silicon solar cell. When a voltage is applied in the forward bias direction, the depletion region between the two doped layers is decreased until it completely disappears, thereafter charges can be injected across the junction and recombine to give light. The two main recombination events are namely radiative and non-radiative recombination. For radiative recombination, the excess energy is converted into a photon with a wavelength corresponding to the bandgap of the active material. For non-radiative recombination, however, the excess energy is converted to lattice vibrations, also known as phonons. In other words, the electrical energy is converted into heat. The latter recombination case is often undesired as it leads to

lower efficiency of the device and excess heat may reduce the lifespan of the LED. The working mechanism of a typical LED is illustrated in Figure 1.3, showing charge recombination across a p-n junction as well as the radiative and non-radiative recombination events.

Figure 1.3. The general mechanism of light emission from LEDs⁵

1.3 Blue LEDs: Gallium nitride (GaN)

The first commercially available blue Light Emitting Diodes was developed by Nakamura et al. in 1994 using Gallium nitride (GaN) as an active layer.⁶ III-V nitrides have a large and direct bandgap that is suitable for blue light-emitting devices. The band-gap energy of AlGaInN compositions vary between 6.2 and 2.0 eV. However, substrates with perfect lattice-matching for the growth of gallium nitride are unavailable. Sapphire with a mismatch of 13.5% is commonly used. Other options include silicon carbide and magnesium aluminate, which have mismatches of 3% and 9%, respectively. High-brightness blue-emitting, c-plane LEDs grown on foreign substrates like sapphire or silicon carbide have been used in a wide variety of consumer applications and general lighting. By combining the blue light from a GaN-based LED and a well-known yellow-emitting phosphor $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ provided practical highly efficient white light LEDs (WLEDs).⁷ High-quality white light can also be achieved by mixing blue light with other colors as well, including red and green.⁸

1.4 White LEDs (WLEDs)

White LEDs are the recent attraction in lighting applications ranging from indoor to road lighting and so on. Various methods such as wavelength conversion, color mixing, and homo-epitaxial ZnSe are commonly employed to produce WLEDs. Wavelength conversion is a process which involves the complete or partial conversion of an LED's radiation to white light. This can be carried out in many ways. The prominent ones include the combination of a blue LED and yellow phosphor; blue LED and multiple phosphors; ultraviolet LED and blue, green, and red phosphors; and an LED with quantum dots. Among the three, the combination of blue LED with a yellow phosphor (Yttrium Aluminum Garnet) is most cost-effective. This combination results in the emission of yellow and blue light which mixes to convey the appearance of white light. In blue LEDs and several phosphors approach, each of the phosphors emits a different color of light when the blue LED light falls on them. These different colors of light combine with the original blue light to produce white light. This method produces white light with a broader wavelength and better color quality in terms of CRI and correlated color temperature (CCT). Similar phenomena occur when a UV LED is utilised to excite the phosphors. When combining blue LEDs with quantum dots, semiconductor quantum dots (QDs) with crystals size between 2 and 10 nm are coated on top of the blue LED. The blue light emitted by the LED excites the quantum dots. The subsequent emission from the QDs has a wavelength spectrum almost similar to the white light produced by ultraviolet LED along with RGB phosphors. A schematic representation of these methods is depicted in Figure 1.4.⁹⁻¹⁴ Color mixing is another main strategy to produce white light emission. Here LEDs emitting RGB colors are fitted inside a lamp as shown in Figure 1.4, whose intensities are to be varied in order to generate white light. Color mixing is also done using four LEDs where red, blue, green, and yellow are used side by side.

Figure 1.4. Possible device configuration for a white-light-emitting LED. (a) Three red, green, blue-emitting diodes, (b) LED with single phosphors, and (c) LED with three red, green, blue phosphors.

1.5 Phosphors

Phosphors are materials that can emit light upon exposure to ultraviolet radiations (UV) or a beam of electrons. Such luminescent materials are used in a variety of applications such as LEDs, LCDs, displays, X-ray detectors, etc.^{10, 15} Majority of phosphors are wide-bandgap inorganic materials with a host-guest structure. The host could be an oxide, nitride, oxynitride, silicate, sulfide, selenide, halide or oxyhalide moiety and the guest could be a tiny amount of activator ions such as rare-earth or transition metals which acts as the emission centers that can be populated by direct excitation or indirect energy transfers.¹⁶⁻¹⁸ The illustrative emission spectrum of a commercial WLED device is shown in Figure 1.5, which consists of blue emission from gallium nitride-LED and yellow emission from cerium-doped yttrium aluminum garnet (YAG) phosphor.¹⁹

These YAG phosphors require high-temperature solid-state reactions to obtain phase pure materials. The precursors are heated at 1000 to 1600 °C under mixtures of H₂ and N₂ or CO gas, in order to reduce the dopant ions to the desired valence state (e.g., Ce³⁺ instead of Ce⁴⁺ Eu²⁺ instead of Eu³⁺).²⁰ These methods clearly require harsh conditions, such as very high

temperatures and high partial pressures of reactive gases, which will impose limitations on the materials and substrates used. Phosphors are typically coated directly on top of a blue LED and the uniformity of the phosphor coating can drastically affect the light quality. Therefore, oxide phosphors are undesirable since they are not solution-processable into thin uniform coatings, and the high fabrication temperatures can damage the encapsulation materials.

Figure 1.5. PL emission spectrum of a commercial WLED (manufactured by the Nichia Chemical Industries Corporation), consisting of a blue component from a LED, and a yellow/green part from a YAG: Ce phosphor powder-coated above the LED.¹⁹

UV-pumped phosphor-converted devices also suffer energy losses in the light down-conversion process, and thus high performance (e.g. efficiency and spectrum of light emitted) of phosphors are desired. A blue LED with one phosphor may not be enough to cover the entire range of visible light, and multiple phosphors covering a broad range of emission wavelengths are often employed. This approach of multiple phosphors being used is acceptable only if the spectral overlap of different phosphors does not result in self-absorption and losses in emission efficiencies. Consequently, the development of broadband emitting, highly luminescent, and photostable materials which are solution processable with strong absorption in the near-UV region is an attractive objective for practical applications.²¹⁻²³

1.6 Halide perovskite Emitters/Phosphors

Halide perovskites are a class of recently explored optoelectronic materials with a general formula of ABX_3 , where the A site is an organic or inorganic monovalent cation (e.g., $CH_3NH_3^+$ (MA), $CH_3NH_2^+$ (FA), and Cs^+) and the B site represents a divalent cation (e.g.,

Pb^{2+} and Sn^{2+}); the X site is a halogen anion (e.g., Cl^- , Br^- and I^-). The most commonly explored 3D halide perovskites have advantages of solution-processability, tunable bandgap, high optical absorbance coefficient, and balanced charge transport. Perovskite materials have been investigated for photovoltaics since 2009.²⁴ After a decade of development, perovskite materials have proved themselves to be impactful in the field of solar cells, with an incredible and impressive power conversion efficiency over 25%.²⁵ The chemistry of metal halide perovskite can enable bandgap control and color tuning. By controlling the morphology, low dimensional metal halide perovskites, including 2D perovskite nanoplatelets, 1D perovskite nanowires, and 0D perovskite quantum dots, have been developed which display distinct properties from their bulk counterparts, due to quantum size effects (Figure 1.6).²⁶

Figure 1.6. 3D ABX_3 metal halide perovskites and perovskite-related materials with different dimensionalities at both morphological and molecular levels.²⁶

In addition to the most commonly explored ABX_3 perovskites, organic-inorganic metal halide hybrids, containing the same fundamental building block of metal halide octahedra (BX_6), can also form other types of crystallographic structures. Using appropriate organic and inorganic components, low dimensional organic-inorganic metal halide hybrids with 2D, quasi-2D, corrugated-2D, 1D, and 0D structures at the molecular level have been developed and studied.

Apart from their photovoltaic application, perovskite materials display properties relevant to other optoelectronic applications, such as efficient electroluminescence (EL), photoluminescence (PL),²⁷ X-ray response, etc.^{28,29} Perovskite materials are regarded as ideal LED materials because of their tunable bandgap, defect tolerance, both holes and electrons transport capability and solution processability at room temperature using cost-effective raw

materials. The first report on light emission from perovskite materials was by Xing et al. in 2014.³⁰ This study revealed the potential of solution-processed organic-inorganic halide perovskites for optical gain. Ultra-stable amplified spontaneous emission was observed at strikingly low thresholds due to the large absorption coefficients, ultralow bulk defect densities, and slow Auger recombination. Visible spectral tunability (390–790 nm) was also demonstrated which enabled further explorations on light-emitting applications of perovskite materials. There are many metrics used for evaluating device performance of LEDs, such as external quantum efficiency (EQE), internal quantum efficiency (IQE), lifetime, etc. EQE is defined as the ratio of the number of photons emitted from the device to the number of electrons passing through it. Friend et al. first reported perovskite LEDs operating at room temperature with EQE 0.76%.³¹ Subsequently, different ways to achieve device efficiencies were reported.^{32–35} For now, the reported highest EQE of green, red, and infrared perovskite LEDs are 20.3%, 20.7%, and 21.3%, respectively.^{36–38}

The direct bandgap in perovskites has been typically tuned by changing the halide composition which results in narrow emission profiles corresponding to the bandgap. As indicated earlier, changes in the A site cation can result in the formation of perovskites with various dimensionality ranging from 3D to 0D. The light emission from such lower dimensional perovskites can cover the whole visible light region with high photoluminescence quantum efficiency (PLQE).^{39–41} PLQE is a metric relating the efficiency of an emitter. It can be defined as the ratio of the number of emitted photons to the number of absorbed photons. A high PLQE value (near unity) is a necessary criterion to be considered as a candidate emitter to form LEDs with efficient electrical-to-optical conversion. Due to the defect tolerant nature, perovskite materials often produce near-unity PLQE which makes them attractive candidates for white light emission. Moreover, charge transport in lower-dimensional perovskites could be less due to the reduction of dimensionality of the inorganic metal halide layer. Hence, lower-dimensional perovskites with broadband emissions, less charge transport could have potential application as down-conversion phosphor. Recently, several groups have studied the mechanism of white-light emission in layered Pb–X (X = Cl, Br) perovskites and proposed a mechanism based on self-trapping of free excitons.^{42–48} In semiconducting perovskites, the fully occupied valence bands are separated from the fully empty conduction bands by an energy gap E_g , which represents the threshold energy for band-to-band electronic transitions. The extra electron if any present in the conduction band and the hole left behind in the valence band can be visualized as interacting via a Coulomb-like field. This creates bound “electron-hole”

states called excitons with excitation energies lower than the energy gap. These excitons can undergo self-trapping in a lattice deformation obtained through the interaction with lattice. These self-trapped excitons can create transient, light-induced lattice deformations that can be considered as “excited-state” defects and the lattice distortion disappear the following decay to the ground state resulting in luminescence. Since the exciton self-trapping is associated with large-amplitude structural distortions and energetic stabilization, the resulting luminescence is often broad and has a large Stokes shift as observed in 2D Pb-based perovskites upon UV excitation.^{43,44}

1.7 Gap analysis

As introduced earlier, existing white light emitting diodes utilize phosphors for color conversion. Commercial down-conversion phosphors, such as Ce^{3+} : YAG, require high-temperature solid-state reactions to obtain phase pure and high-quality materials.⁴⁹ The harsh conditions, such as very high temperatures and use of reactive gases impose limitations on the materials and substrates used. Most of the phosphors used today are constituted from rare-earth elements, which are of rising demand and decreasing supply due to their other applications. Phosphors free of rare-earth elements, that could be processed easily and make into different physical forms such as powders, thin films, and nanocrystals for UV-LED based white light applications are thus being sought.

Metal halide perovskites have established themselves as extraordinary semiconductors that can be solution-processed and have shown promise in applications broadly in optoelectronics including as phosphors. Despite the great amount of work dedicated to the field of metal halide perovskites, the focus was mainly on 3D perovskites for solar cell and light-emitting applications. At the point of time, this thesis work began, reports exploring the structure-property relationships in 2D perovskites were just being reported. However, very little work has been done on 1D perovskites and 0D hybrid perovskites. For example, by judiciously choosing the organic ammonium cations, it is possible to tune the topology of metal halide octahedra and to produce different dimensional perovskites from higher 3D to moderate 2D, 1D, and to the lower so-called 0D perovskites.

Metal halide perovskite exhibiting broadband emissions have been reported; however, until now, there have been limited reports about white-light-emitting lead halide perovskites with experimental insights into the mechanism of the broadband emission. It has been reported that

fluorescence and phosphorescence could be tuned by varying the constituents of perovskite such as halide, central metal ion, and A-site large ammonium cation. Additionally, the effect of structural modifications such as 3D to 0D formation, nanostructuring, and replacement of lead on emission have not been investigated in detail.

The thesis will thus focus on synthesizing new materials based on compositional substitutions, molecularly induced low dimensionality, nanostructuring, to understand the effect of structure and compositions on the applicability of perovskites as high-performance phosphors. Detailed studies including physical and chemical structural data from X-ray diffraction and nuclear magnetic resonance amongst others, time-resolved, and temperature-dependent photophysical measurements will be carried out. These experimental insights will be combined with density functional theory calculations to extend our understanding of the fundamental questions relating to interactions of the charge carriers with the perovskite lattice, effects of confinement brought about by structuring, as well as the effect of metallic cations on broadband emission from these exceptional perovskite semiconductors.

1.8 Objectives and Scope

As shown in Figure 1.7, the scope of this thesis is to study the unexplored low-dimensional organic-inorganic hybrid metal halide perovskites for broadband emissions and then use the low-dimensional perovskites as down-conversion phosphors in white-light-emitting devices.

Specific objectives include:

The synthesis, material and photophysical characterization of layered, 0D and nanostructured materials including both lead (Pb) based and Pb free perovskites.

To study the effect and compositional changes (structure-property relationship) on the emission properties (broadband) of the above-mentioned perovskites materials.

To understand the mechanism of broadband emission from these newly developed perovskites.

Demonstration of the use of these lower dimensional perovskites as down-conversion phosphors in white LEDs (WLEDs).

Figure 1.7. Schematic representation of the objectives undertaken as part of this thesis.

1.9 Thesis organization

The thesis has been divided into seven chapters. Chapter 1 presents a brief overview of the history of light sources, broadband emission, various solid-state lighting devices such as blue LEDs and white LEDs. A brief description of various phosphor materials for white light LEDs (WLEDs) is also included with special emphasis on the potential of lower dimensional perovskite materials as phosphors. A gap analysis is also presented to justify the motivation and objectives of the studies presented in the thesis.

Chapter 2 presents a detailed literature review of the objectives of the thesis. It starts with a brief introduction to various solid-state lighting devices and materials for phosphor applications. The use of halide perovskites as phosphors to produce white light emission is also discussed with descriptions on lower dimensional perovskites starting from 3D to 0D, their broadband and white light emission, color rendering index (CRI) considerations and the use of these new materials as downshifters for WLEDs.

Chapter 3 documents the experimental details regarding the work presented in chapters 4 to 6. The descriptions regarding the preparation of various ammonium salts in the form of thin films,

powders, single crystals, nanoparticles (NPs), microparticles, their characterization using various analytical techniques such as powder XRD, thermogravimetry (TGA), differential scanning calorimetry (DSC), UV-Vis absorption, steady-state photoluminescence, photoelectron spectroscopy, atomic force microscopy etc are documented in this chapter. Details regarding the fabrication of WLEDs and their photophysical characterizations are also described.

Chapters 4 to 6 presents new investigations on the objectives of the thesis. Chapter 4 documents the investigations on compositional management of lead (Pb) based perovskites for broadband emission. The synthesis, structural and photophysical characterization of the lower dimensional lead halides perovskites and their broadband/white light emission properties are discussed. The effect of i) X-site ion ($X = \text{I/Br/Cl}$) and ii) A-site cations in 2D lead halide perovskites (A_2PbX_4) on the broadband emission are discussed in detail. With the aid of single-crystal X-ray structural data, time-resolved photophysical measurements, and density functional theory calculations, the broadband emission properties of these materials are related to the occurrence of a strong exciton-phonon coupling with the organic lattice, which is independent of surface defects.

Chapter 5 discuss the investigations on the development of lead-free perovskites such as Tin-, and Germanium-based Perovskites. In this chapter, the syntheses and structural characterizations of highly luminescent 0D lead-free perovskites meta-xylylenediammonium tin bromide (m-XDATB), and meta-xylylenediammonium germanium bromide (m-XDAGB) are discussed. The studies on broadband emission using photophysical characterizations are also presented along with the demonstration of m-XDATB, and m-XDAGB as a phosphor in WLEDs.

Chapter 6 describes the applications of the newly developed 0D Perovskites as Luminescent down-shifting Layer (LDSL) for white light-emitting LEDs. Various perovskites such as 1-Butyl-1-methylpyrrolidiniumantimony chloride, 1-Butyl-1-methylpyrrolidiniumantimony chloride (BMPAC), Octylammoniumtin bromide, Octylammoniumtin bromide nanoparticles were synthesized and characterized using solid-state NMR, TEM analysis, etc. The wavelength down conversion properties of these materials was investigated and documented.

Chapter 7 presents the summary of the overall work presented in chapters 4-6, the achievements with respect to each of the objectives listed in chapter 1 and the description of futuristic aspects.

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Chapter 2

Literature Review

Abstract: This chapter presents a detailed literature review of the overall objectives of the thesis. It starts with a brief introduction to various solid-state lighting devices and materials for phosphor applications. The use of halide perovskites as phosphors to produce white light emission is discussed with descriptions on lower dimensional perovskites starting from 3D to 0D, their broadband and white light emission properties. CRI considerations for white light emission and the use of lower dimensional perovskites as materials as downshifters for WLEDs is also introduced.

2.1 Introduction to Light Emitting Devices (LEDs)

Electroluminescence (EL) is the phenomena behind the development of Light Emitting Diodes (LEDs).¹ Electroluminescence is the non-thermal production of light by passing electricity through a semiconducting thin film. It results from recombination of charge carriers (holes and electrons) injected into the semiconductor. If these combine to give a singlet excited-state by excitation of an electron from the HOMO to the LUMO, then symmetry permitted relaxation to the ground-state may occur with the emission of a photon. The color of the emission is determined by the size of the HOMO-LUMO energy gap, which for visible light (380-780 nm) corresponds to 1.5-3.2 eV.

The history of LEDs goes back more than a century. H. J. Round reported light emission from a silicon carbide junction diode in 1907, the first LED ever. In 1927, Losev observed emission from ZnO and SiC diodes.² The first practical visible spectrum LED was developed by Nick Holonyak at General Electric in 1962. Subsequently, laser and LEDs based on III-V semiconductors have dominated the field (Table 2.1). In the decades that followed, LEDs were used extensively in numerical displays and signaling applications. However, only around 1995 high brightness and blue LEDs were developed, which made it possible to use LEDs for general lighting. During 1990s new materials such as InGaP/GaAs, GaInAlN/gallium nitride (GaN), etc. were developed in the search for red and blue lasers.³ These materials were enabled through the organometallic vapor-phase epitaxy (OMVPE) crystal growth techniques.

AlInGaP developed through this technique facilitated the fabrication of high-brightness materials from yellow to red.

Table 2.1. Timeline of the Development of LEDs for Different Colors of Light¹

Color of Light	Wavelength (nm)	Semiconductor Material	Year
IR	850–940	GaAs	The Mid-1970s
Yellow	585–595	GaP	The Mid-1970s
Red	630–660	GaAsP and AlGaAs	The Mid-1980s
Blue	550–570	InGaN	The Mid-1990s
Green	430–505	InGaN	The Mid-1990s
White	450a	InGaN + phosphor (or ed–green–blue–white)	The Mid-1990s

2.1.1 Red LEDs

Red LEDs consists of n doped and p doped GaP layers grown over a n-type gallium phosphide substrate. ¹ On passing an electric current, light is generated at 700 nm due to electron-hole recombination. Under forward bias, minority carriers will diffuse across the neutral region, recombining with the majority carriers of the other side- emitting photons. The LED die is encapsulated in a way that prevents light losses and outcouples light in one direction. For this purpose, the emitting device is mounted inside a hemispherical-shaped shell. The photons of light emitted by the junction are reflected away from the surrounding substrate base and are focused upwards through the domed apex of the LED. The dome serves as a lens concentrating the amount of light.

2.1.2 Blue LEDs: AlInGaN

AlInGaNs have wider bandgaps than AlInGaPs so AlInGaNs emit higher energy light at green, blue, and UV regions .³ Companies like Nichia Chemical, and Lumileds introduced multilumen green LEDs which when combined with red AlInGaP LEDs and blue LEDs enabled large full color signs to form solid-state light sources. Along with of high-brightness blue LEDs, white LEDs (WLEDs) that custom blue AlInGaN LEDs and down-conversion phosphors to convert some of the blue photons into yellow photons were developed. In 1996, the first down-conversion WLED was developed by combining blue LED with a down-converting phosphor layer.⁴ Pioneered by Shuji Nakamura and Gerhard Fasol⁵, this technique still remains the most important means to realize the white light emission. Even today, the

mainstream LEDs are based on AlInGaP for red-to-yellow wavelengths and AlInGaN for blue and near-UV wavelengths.

2.1.3 White LED (WLED)

White light is essential for general lighting purposes because human eyesight is the most comfortable with white light. True WLEDs represents a very challenging goal, and intrinsic white light emitters are very uncommon. However, some possible materials that have been reported include gold containing molecular aggregates and cadmium chalcogenides.⁶ Since “white” does not have a single wavelength but is a mixture of wavelengths, perception of “white” is made possible by assimilation of different wavelengths. As discussed in chapter 1, there are mainly three ways to achieve white light with LEDs.^{1, 6}

The blue light emitted by InGaN LED is down-converted to give yellow light with the help of a phosphor material; the combination of down-converted yellow light and the original blue light results in white color. The second approach utilises an LED producing near UV radiations which is then incident on a single phosphor or multiple phosphors, resulting in visible light. The third approach produces white light by mixing in the correct proportions, the emissions from separate LEDs producing the three complementary colors: red, green, and blue. However this approach is not favoured since it is less cost-effective.

In the first two methods, the different energies of the incoming and outgoing photons from the phosphor is termed the Stokes loss caused by the Stokes shift in their frequencies or wavelengths. This Stokes loss is the principal loss component in the phosphor conversion methods. Among the three methods, wavelength conversion using a phosphor material is more prominent. A schematic representation of various methods for white light generation is presented in Figure 2.1.

Figure 2.1. Schematic representation of various white light emission methods.¹

2.2 Phosphors

2.2.1 Inorganic Phosphors

Phosphors are synthetic materials that can emit light upon exposure to ultraviolet radiations (UV) or a beam of electrons. Such luminescent materials are used in a variety of applications such as LEDs, LCDs, displays, X-ray detectors, etc.^{7,8} To bring about wavelength conversion, the phosphor material absorbs light of one wavelength and emits light of a different wavelength. The wavelength of the emitted photon is typically down-converted (longer wavelength or lower frequency/energy) by the phosphor material. This shift in the excitation and emission wavelengths/frequencies is termed Stokes shift and thus, the light conversion process entails an energy loss. The original emission from the LED in combination with the converted wavelength portion is employed to produce white light. This can be introduced in many ways such as Blue LED with a yellow phosphor, Blue LED with several phosphors, UV LED with phosphors and Blue LED with quantum dots.

Blue LED with yellow phosphor:

This is based on mixing a longer wavelength component of light with a shorter-wavelength component. It involves mixing two colors and is a bicolor system. Generally, a layer of

YAG:Ce³⁺ phosphor (Y_{1-a}Gd_a)₃(Al_{1-b}Ga_bSi₅₋₁₂:Ce³⁺) is applied over a blue InGaN LED integrated into the LED package. Some of the blue light emitted by the LED is absorbed by the phosphor and converted into yellow light.

Blue LED with several phosphors:

The advantage of utilizing many phosphors is the improvement in the color quality of emitted light. The gap between blue and yellow light is filled and thereby the red part of the spectrum is strengthened. Light from such multiband LED has a richer and broader spectrum than obtained by LED with yellow phosphor alone. By appropriate blending of phosphor materials, designers can adjust the tone of the light from cool to warm, enabling both high color rendition and tunable color temperature.

UV LED with phosphors:

This method consists of converting invisible radiation from a UV LED into red, green, and blue lights by using three suitable phosphors in measured amounts and combining the light of three colors together.⁶

Blue LED with quantum dots:

Chalcogenide quantum dots such as CdSe are placed over the blue LED to produce white light with a spectrum like that generated by UV LED with red, green, and blue phosphors. Challenges of this approach are the high cost of nanoparticles, and their nonavailability in uniform size distribution, leading to color mixing difficulties.

2.2.2 Organic Phosphors

Organic phosphorescent emitters have been explored as well. These organic phosphors have significant advantages over fluorescent emitters in optoelectronic materials due to their ability to utilize triplet exciton.^{9, 10} However, organic phosphors with moderate to high emission yields are uncommon. Tang et al. demonstrated crystallization induced high intense phosphorescence in benzophenone derivatives.¹¹ Later, in 2011, Kim and co-workers further demonstrated strategies of utilizing close-pack weak interactions as well as heavy atom effect in order to obtain highly efficient room temperature phosphorescence in doped crystals.¹²

Following these two remarkable reports, a few other reports of purely organic phosphorescent compounds have also appeared.¹³ Selected examples of such white light-emitting small molecules including carbazoles and 1,2,3-triazoles are shown in Figure 2.2.

Figure 2.2. Selected examples of organic small molecules for phosphor applications.¹³

Zhang and co-workers synthesized a purely organic anionic radical compound as its sodium salt which displayed blue phosphorescence in its solution state. However, in solid-state, this compound packs with two different short π - π stacking modes which result in a significant broadening of its emission bands and generates excitation independent white-light emission {CIE coordinates (0.27, 0.32)} with quantum yields of $\sim 5.2\%$.¹⁴ More recently, single pure organic phosphor, namely 4-chlorobenzoyldibenzothiophene as shown in Figure 2.3, emitting white light emission was also reported. Experimental and theoretical studies reveal that the white light emission has emerged from dual phosphorescence, which emission originates from the first and second excited triplet states.¹⁵

Figure 2.3. White light emission from 4-chlorobenzoyldibenzothiophene derivatives under the presence and absence of UV light.¹⁵

Despite these achievements, phosphorescent white-light emissions from organic compounds are not well established. Purely organic materials haven't been able to generate meaningful phosphorescence emissions with appreciable PLQE. In addition to this, the lack of long-term stability at device operating temperatures is also a major concern. Hence researchers are exploring other suitable materials for phosphors; and over the past few years, organic-inorganic hybrid perovskites have emerged as a possible candidate for phosphor applications.

2.3 Organic-Inorganic Hybrid Perovskites – promising phosphor materials

2.3.1 Organic-Inorganic Hybrid Perovskites – Structural Variants

Organic-inorganic hybrid metal halide perovskites represent a very exciting research field. Efficiencies for solar of more than 24%^{16,17} and EQE's of more than 20%¹⁸⁻²⁰ for light emission have been demonstrated in less than 8 years of developments. The advantages of this class of materials include the versatility and tunability of their crystallographic structures and hence their chemical and physical properties.

Figure 2.4. Structures of 3D, 2D, corrugated 2D, 1D, and 0D perovskites.²¹

As shown in Figure 2.4, three-dimensional (3D), two-dimensional (2D), one-dimensional (1D), and zero-dimensional (0D) halide perovskite materials have been realized, as classified by the spatial arrangement of the octahedral metal halide units. Each category of these materials has its unique physical and chemical properties with a variety of potential applications.²¹

3D halide perovskites

3D halide perovskites with the ABX_3 structure, consist of corner-sharing metal halide octahedra that extend in all three dimensions, with small cations fitting into the void spaces between the octahedra. In the ABX_3 structure, A consists of small cations such as methylammonium ($CH_3NH_3^+$) or Cesium cations, B consists of divalent metal cations (e.g., Pb^{2+} , Sn^{2+}), and X consists of halide anions (i.e., Cl^- , Br^- or I^-). The interactions between the inorganic metal halide units result in the formation of electronic bands with potentially large bandwidths. Due to its low exciton binding energy and long-range, balanced carrier diffusion lengths, 3D halide perovskites have emerged as one of the most promising materials for next-generation solar cells.²²⁻²⁵

2D metal halide perovskites/corrugated perovskites

2D and quasi-2D organometal halide perovskites consist of 2D layers of perovskite separated by large organic cations. Such perovskites with single or multiple corner-sharing layers separated by organic cations are regarded as Ruddlesden–Popper-type perovskites with a general chemical formula $A_{n-1}A'_2B_nX_{3n+1}$, where A represents small cations, A' represents

organic cations between different layers, B refers to divalent metal cations, X refers to halides, and n stands for the number of metal halide monolayer sheets between the insulating A' organic layers. The quantum confinement in layered perovskites become becomes stronger with decreasing n and $n = 1$ stands for the condition of monolayer 2D perovskites. Layered (2D) perovskites may be formed with planar metal halide layers sandwiched between organic ligands along the (001) crystallographic plane (Figure 2.4), and alternatively may consist of twisted sheets ripped along the (110) plane of 3D perovskites. Such perovskites are called corrugated perovskites (Figure 2.4).²⁶⁻²⁸ These corrugated perovskites exhibit strong structural distortions and significant quantum confinement effects, resulting in the formation of both free-exciton and self-trapped excited states upon photoexcitation.²⁹⁻³³

1D perovskites

In 1D perovskites, the inorganic metal halide octahedra can be either corner-sharing, edge-sharing, or face-sharing to form the nanowire-like structure with either a linear or zigzag configuration.²¹

0D perovskites

In 0D hybrid perovskites, individual metal halide octahedral anions or metal halide clusters are surrounded and isolated by the organic cations. Their general chemical formula is A_4BX_6 , where A represents monovalent organic cations and BX_6 represents metal halide octahedra.²¹

Perovskite quantum dots are morphological 0D nanostructures or nanoparticles with 3D ABX_3 structures, which are significantly different from molecular 0D perovskites.^{34,35} Molecular 0D perovskite structures are bulk assemblies of individual metal halide octahedral units or clusters. Limited studies are available with or on the organic-inorganic hybrid metal halides with 0D structures. For example, isolated PbI_6^{4-} can be observed together with methylammonium cations and water molecules. However, this crystal phase is unstable and slowly decomposes into PbI_2 . 0D $(CH_3NH_3)_3Bi_2I_9$ was reported recently, with broad emission shifted into the NIR range, while no PLQE was reported.³⁶⁻³⁸

Structural Variations via Lead Substitution: Towards Lead-free Perovskite Optoelectronics

Toxicity of lead element in hybrid perovskite materials is always a safety concern as the lead leakage will result in long-term environmental pollution and could also be harmful to

human's nerve and reproductive system. The perceived toxicity of lead in this class of perovskites is a challenge for the commercialization of related technologies. Therefore, the research community has been seeking the replacement of lead and lead-free perovskites for solar cells and light-emitting devices have been pursued.^{39,40, 41} Although significant attention has been paid to lead-free perovskites and encouraging results have also been achieved, the performance of lead-based perovskites are still superior to their lead-free counterparts.

Figure 2.5. Different lead-free perovskite structures. Sn & Ge share similar electronic structure with Pb, making them highly potential candidates to replace Pb.⁴²

Lately, several elements such as tin, germanium, bismuth, antimony, copper, and manganese have been utilized as a replacement for lead in typical perovskite structures.⁴³⁻

⁴⁹ It induced the formation of different dimensionality in lead-free perovskites as shown in

Figure 2.5. Among these candidates, tin and germanium-based perovskites have received the most attention due to the similarity in properties, which also resulted in the most

promising device performance. The severe stability issue in tin-based perovskite, due to the tin oxidation reaction, is the main factor of causing poor device performance of Sn-based perovskites. Just like their Pb-based counterparts, layered perovskites, 1D perovskites, as well as 0D perovskites have also been prepared, with some of which are of great interest in light emission applications.⁵⁰

2.3.2 Synthesis of Perovskite Materials

Hybrid halide perovskites are typically synthesized through solution-phase mixing of either the metal halide and the organic amine in an acidic solution or the mixing of the ammonium halide and the metal halide in a polar organic solvent. Precursor stoichiometry, solution pH, temperature, and solvent(s) are varied to modulate the crystallinity and the phase distribution. Standard crystallization methods like (i) slow cooling of a hot saturated precursor solution, (ii) the diffusion of a poor solvent (with low perovskite solubility, antisolvent vapor-assisted crystallization (AVAC)), (iii) evaporation followed by concentration of the precursor solution or (iv) layering the precursors to allow for slow interaction at the interfaces, etc. are generally employed for crystallizing halide perovskites.^{51,52} Single crystals are generally obtained by slow cooling of the hot precursor solution. Centimeter-scale single crystals can be obtained by this method for spectroscopic studies⁵³ or device fabrication.^{54, 55} Synthetic strategy to achieve lower-dimensional perovskites depends on the structure of organic ammonium cation. Symmetry, flexibility and number of ammonium group of the organic ammonium cation have role in deciding the dimensionality of perovskites. As the symmetry and flexibility of the organic cations are reduced, the dimensionality of resulting perovskites will be lower. Synthetic method like antisolvent vapor-assisted crystallization (AVAC) was used to make all the perovskites reported in this thesis. The reason for choosing the AVAC is the insolubility of XDA halides in most of the organic solvents, and in aqueous hydrohalic acid as well. *Meta*-xylylenediammonium halides are soluble in DMF at moderate level and *Para*-xylylenediammonium halides are soluble in DMF to some extent, which allowed DMF to be used as solvent for AVAC method. Thin films are generally obtained by spin-coating, slot-die coating, vapor deposition, etc. on substrates. These methods afford uniformly oriented thin films of perovskite materials for both spectroscopic studies and device fabrication.⁵⁶ Spin-coating was adopted to make thin films of perovskites reported in this thesis. solid-state mixing of the precursor powders based on mechanochemical methods and subsequent

annealing is employed for making halide perovskites based on less-soluble metal salts or metal ions such as lanthanides.^{52, 57}

Nanostructured metal halide perovskites such as nanoplatelets, nanosheets, and nanodisks are generally obtained by reducing the thickness of 3D ABX₃ perovskites.⁵⁸⁻⁶⁰ This can be achieved by both solution-phase and vapor-phase methods. For example, Tyagi et al. reported a colloidal synthesis of 2D MAPbBr₃ nanoplatelets with nearly single unit cell thickness and submicron lateral dimensions.⁶¹ Manna et al. reported a room-temperature colloidal synthesis of perovskite nanoplatelets with thickness controlled to 3 to 5 layers.⁶² Chemical vapor deposition (CVD) was also employed to prepare 2D perovskites.⁶³ Single crystalline 1D perovskites can also be obtained by vapor phase, solution phase, hot injection, and templated methods.⁶⁴⁻⁶⁷ Similar methods are also reported for the synthesis of 0D nanocrystals (NCs) or quantum dots (QDs) with all three dimensions in the nanoscale. This includes ligand-assisted reprecipitation (LARP), hot-injection, *in-situ* preparation, and template-assisted methods. LARP was adopted to make nanoparticles reported in this thesis. Finally, the corrugated-2D structure can be achieved by choice of appropriate A-site cations.⁶⁸

2.3.3 Broadband emission from layered perovskite materials

One of the recent development in layered lead halide perovskites is the observance of broadband emission and large Stokes-shift.^{31,69} Studies on white light-emitting perovskites were first reported in 2014 by Karunadasa et al.^{31,70} with the observation of large Stokes shifted (ca. 1 eV and width ca. 0.8 eV) emission (spanning 400–700 nm) from the inorganic layers of 2D perovskites upon UV excitation (Figure 2.6). Optical absorption of white-light-emitting perovskite (*N*-MEDA)PbBr₄ and blue-light-emitting perovskite (*N*-MPDA)PbBr₄ (*N*-MPDA = *N*¹-methylpropane-1,3-diammonium) showed that both materials displayed strong free-excitonic resonances and no below-exciton absorption, suggesting that similar excited states are initially populated in both materials. This report highlighted that white light emission from perovskites would need further studies for unraveling the fundamental mechanisms since these materials were devoid of any chromophores.^{69,71} Based on this study, different groups have explored broadband emission from various perovskite materials with varying structural characteristics. Consequently, many theories and mechanisms were suggested to explain the rationale behind this unique phenomenon. This include, exciton self-trapping, material defects, and dopants albeit with different operative photophysics. The subsequent sections will provide a brief discussion on the mechanistic

aspects of the broadband emission from perovskite materials with respect to material characteristics and photophysics.

Figure 2.6. (A) Absorbance and photoluminescence and (1) crystal structure of (*N*-MPDA)PbBr₄ (inset) UV illumination results in blue emission from (*N*-MPDA)PbBr₄ powder. (B) Absorbance and photoluminescence and (2) crystal structure of (*N*-MEDA)PbBr₄. (inset) UV illumination results in white light emission^{31,72}

Perovskite (*N*-MEDA)PbBr₄ (*N*-MEDA = *N*¹-methylethane-1,2-diammonium) represents a typical (110) perovskite featuring corrugated inorganic layers. It was reported that upon UV excitation, this perovskite emits broadband emission from 400 to 700 nm (Figure 2.6).³¹ The broad emission in (*N*-MEDA)PbBr₄ peaks at ca. 560 nm, with a high-energy shoulder, was attributed to free-excitonic contributions,⁷² although optical absorption spectra are very similar to other (001) perovskites which do not show broadband emission. It was also reported that halide substitutions could broaden the emission spectrum. Increasing the chloride content in (*N*-MEDA)PbBr_{4-x}Cl_x showed a blue-shifting the photoluminescence, increased the phosphor's CRI to 85, and also increased the PLQY from 0.5% in (*N*-MEDA)PbBr₄ to 1.5% in (*N*-MEDA)PbBr_{2.8}Cl_{1.2}. The effect of halide ion substitution was also reported in another (110) perovskite that employed an ethylenedioxy bis-ethylammonium cation; which showed a PLQE of 9% for warm white light with a CRI of 84.⁷⁰ In these (110) perovskites, modification of corrugation lengths and white light emission was also shown using dimethylethane and diammonium ions.

(EDBE)PbBr₄ (EDBE = 2,2'-(ethylenedioxy)bis(ethylammonium)), represents the first example of a white-light-emitting (001) perovskite with flat inorganic layers (Figure 2.7).⁷⁰ The excitonic absorption and bandgap were blue-shifted in this perovskite similar to the effects of halide substitution in (N-MEDA)PbBr_{4-x}Cl_x.⁷⁰ However, the PLQE obtained was lower than (EDBE)PbBr₄. Another example of this category is (001) Pb–Br perovskite (C₆H₁₁NH₃)₂PbBr₄, whose optical characteristics are similar to (EDBE)PbX₄ (X = Cl, Br) perovskites. This perovskite also showed a quenching of the broad emission in (C₆H₁₁NH₃)₂PbBr_{4-x}I_x with an increase in the iodide substitution.⁷³ As described later in Chapter 3, the NTU team (including the author of this thesis) were amongst the research groups to study materials (001) perovskites for white-light-emission with reports as early as 2017 with reports on halide substituted (C₆H₅(CH₂)₂NH₃)₂PbCl₄ and (H₃NCH₂C₆H₁₀CH₂NH₃)PbBr₄ materials.^{74, 75} Variability in layered perovskites (*n* = 3 layers) has also been reported with white light-emitting perovskite (C₂H₅NH₃)₄Pb₃Cl_{10-x}Br_x with the color tunability imparted by controlling the Cl: Br ratio.⁷⁶ These reports suggest that broad-band emission in both (001) and (110) perovskites is influenced by factors including structure, halide substitutions, choice and size of the A-site cation, and the number of layers amongst others.

Figure 2.7. The crystal structures of (A) (EDBE)PbBr₄ (EDBE = 2,2'-(ethylenedioxy)bis(ethylammonium)), (B) (EDBE)PbCl₄, (C) (CyA)₂PbBr₄ (CyA = cyclohexylammonium), and (D) α-(DMEN)PbBr₄ (DMEN = *N*¹,*N*¹-dimethylethane-1,2-diammonium). All showed broadband white light emission.^{28, 52, 54, 60}

2.3.4 Broad-band Emission from perovskites: spectroscopic studies

Broad-band emission has been observed in perovskites in thin films, ball-milled or ground powders, nanostructures, as well as single crystals of diverse perovskites.^{69,70, 72, 75, 77-79} These

observations preclude the possibility that surface defects could be the source of broad or white light emission from perovskites. Studies of PL as a function of excitation intensity displays a linear dependence. If this emission was emanating from defects, a sub-linear behavior would have been observed relating to the defect states becoming saturated.⁸⁰ Furthermore, PL excitation spectra gathered across the wavelength spectrum did not show any changes in PL shapes; and did not display any subgap contributions to the PL spectrum. Temperature dependent PL studies however clearly indicated that with decreasing temperature, the PL spectrum transitions rapidly from broad to narrow emission. At lower temperatures, PLQE of (EDBE)PbBr₄ increases, attaining 85% at 105 K.⁷⁰ This increased emission efficiency and narrowing of the photoluminescence with reduction in temperature is evidence of strong coupling between the electronic transition and lattice vibrations.^{69,70} In (EDBE)PbBr₄, a fit of the temperature-dependent photoluminescence width yields the effective phonon frequency that couples to the electronic transition as 97 cm⁻¹, similar to the energy of the Pb–Br modes obtained from static Raman spectra. This suggests that the inorganic layers play a significant role in the emission process. All the above observations strongly suggest that the broadband emission is not related to defects, materials morphology, or sub gap trap states. Thus, a mechanism based on self-trapping of free excitons is being considered to explain the observed phenomena of broad-band emission in perovskite materials.^{69,70, 72, 75, 77-79}

According to this mechanism, excitons can undergo self-trapping in a lattice deformation obtained through its interaction lattice. These self-trapped excitons can create transient, light-induced lattice deformations that can be considered as “excited-state” defects, in contrast to more permanent lattice defects (vacancies and interstitials).^{70,72} This exciton self-trapping can cause broad Stokes-shifted emission, while the interaction between the self-trapped excitons and permanent defects may lead to heterogeneity in the excited state and lead to emission broadening.^{70, 72} Although the nature of the self-trapped states is yet to be fully understood, a possible analogy between self-trapping in Pb–Br perovskites and in PbBr₂ may be applicable.⁷⁰ It is proposed that self-trapped electrons are localized on Pb²⁺, and combining with another Pb²⁺ may form a Pb₂³⁺ dimer. Similarly, localization of the hole may form Br₂ dimers.

Time-resolved spectroscopic measurements were also used to explore the excited state properties of the white emissive (110) perovskites and that also provided more supportive evidence for the proposed self-trapping mechanisms.⁷² For example, the transient absorbance measurements of blue-emitting (N-MPDA)PbBr₄ (Figure 2.8 B) showed a narrow emission

band, and bleaching below the bandgap, pointing to the existence of sub-band-gap traps which correspond to permanent lattice defects. However, for white light-emitting perovskite (*N*-MEDA)PbBr₄ (Figure 2.8 A), a photo-induced broad sub-band-gap absorption, corresponding to the generation of transient electronic traps was observed, assigned to self-trapped excitons. These self-trapped excitons showed a lifetime of <700ps with a strong wavelength dependence (Figure 2.8 C). The wavelength dependence suggests a distribution of self-trapped sites, and thus it is proposed that excitons could transfer from shallow to deeper traps (Figure 2.8 D) leading to broad-band emission.⁷²

Figure 2.8. Transient absorbance of (A) (*N*-MEDA)PbBr₄ and (B) (*N*-MPDA)PbBr₄ upon excitation at 345 nm. (C) Wavelength-dependent photoluminescence decay times for (*N*-MEDA)PbBr₄. (D) Schematic of exciton self-trapping from the free carrier (FC) or free exciton (FE) state to the distribution of self-trapped states (STEs).⁷²

2.3.5 Broad-band emission from perovskites: Structural considerations

Structural distortion and Broadband emission

As discussed in the previous sections, 3D hybrid halide perovskites are formed by templating the metal lattice with small organic cations, whereas the 2D versions are formed by exfoliating the metal halide sheets by bigger organic cations. The overall structure can be represented as (RNH₃)₂PbX₄ or (NH₃RNH₃)PbX₄. These lower dimensional perovskites are amenable to synthetic variations and to obtain tunable material and photophysical properties, for example, the broadband emissions suitable for phosphor applications discussed in the previous sections. A variety of lower dimensional perovskites based on linear and cyclic organic ammonium cations were reported for white light emission properties (Figure 2.6 and 2.7).^{70, 81} Many of these organic cations are known to effect strong structural distortions of the lead-halide framework to obtain energetically favored in low-dimensional perovskites bearing strong exciton self-trapping properties. A 2D perovskite, (CyBMA)PbBr₄, (Figure 2.9)⁷⁵ was recently reported to display broadband emission ranging from 380–750 nm. In this perovskite,

the cyclic ammonium cation is thought to impart flexibility that allows for a variety of phonon interactions and further induce a strong twist of the PbBr_6 octahedral units and deviation of the Pb Br Pb bond angles from the ideal planar geometry, thus facilitating broadband emission.

Figure 2.9. (a) Crystal structure of (CyBMA)PbBr₄ showing propagation of $[\text{PbBr}_6]^{4-}$ octahedron along the *ac*-plane, (b) packing along the *bc*-plane indicates the twist of the Pb Br chains, (c) (CyBMA)PbBr₄ crystals and films illuminated with UV, (d) Chemical structure of (CyBMA)PbBr₄.⁷⁵

This study marked the first report on the effects of stereoisomerism prevailing in cation for the broadband emission properties, with both *cis* and *trans* diastereomers of the ligand CyBMABr isolated and used for perovskite formation. Due to the steric hindrance, particularly 1,3-diaxial interaction between the methylammonium group and 1,3-axial hydrogens of the *trans* isomer of the ligand hinders the crystallization of the perovskite. However, the *cis* diastereomer successfully formed the 2D HOIP, namely, *cis*-(CyBMA)PbBr₄. It was presumed that the angular tension induced by the *cis* ligand on the inorganic lattice imparted broadband emission in the visible region. Further, Cortecchia et al. compared two perovskites such as (NBT)₂PbI₄ and (EDBE)PbI₄ (NBT = n-butylammonium and EDBE = 2,2-(ethylenedioxy)bis(ethylammonium)) to study the structural distortions of the perovskite lattice on broadband emission (Figure 2.10). The later one showed broad emission. Structural and spectroscopic analysis revealed that this perovskite had larger deformation of the Pb–X bond length and X–Pb–X bond angle and forms the crystallographic defects to facilitate exciton trapping followed by broadband emission.⁷³

Figure 2.10. Structural variation induced steady-state absorption (blue) and photoluminescence (green) of (a) $(\text{NBT})_2\text{PbI}_4$ and (b) $(\text{EDBE})\text{PbI}_4$.⁷³

2.3.6. Broad-band emission from perovskites: theoretical investigations

In addition to structural and spectroscopic studies, theoretical studies are also important to elucidate the origins and mechanistic considerations of broad-band emission.

Figure 2.11. DFT band structures of (a) 3D CsPbI_3 (b) 2D $(\text{NMEDA})\text{PbBr}_4$, A(c) 1D $\text{C}_4\text{N}_2\text{H}_{14}\text{PbBr}_4$.^{82, 83}

The band structure of ideal cubic CsPbI₃ perovskite (Figure 2.11 a) exhibits a direct bandgap at the R point. The conduction band minimum (CBM) consists mainly of the Pb 6p states and the valence band maximum (VBM) is composed of antibonding of Pb 6s and I 5p states⁸².

Figure 2.12. Density of states (DOS) and band structures of $(C_4N_2H_{14}Br)_4SnBr_6$ (a), $(C_4N_2H_{14}I)_4SnI_6$ (b), and (c) Cs_4PbBr_6 . (d) Partial density contours of the hole (i) and the electron (ii) in a relaxed exciton in $(C_4N_2H_{14}Br)_4SnBr_6$ (e) The configuration coordinate diagram of exciton excitation and emission of $(C_4N_2H_{14}Br)_4SnBr_6$. (f) Comparison of the calculated exciton excitation and emission energies of various several 0D and 1D metal halides with the experimental data.⁸⁴

Both CBM and the VBM are isotropic and dispersive (i.e., with large bandwidths), indicating small carrier effective masses along all directions. The dispersive character of the CBM and VBM is partially attributed to the high symmetry of the perovskite structure. Figure 2.11 a-c shows the calculated band structures of the 2D (NMEDA)PbBr₄ and 1D $C_4N_2H_{14}PbBr_4$,

respectively. Flat bands are observed in low-dimensional perovskites due to the broken octahedral connection networks. The bandwidths of the low-dimensional perovskites are smaller than that of 3D perovskites. For the formation of STE, It is necessary for the electronic dimensionality to be reduced in all three directions to localize the carriers and to confine the lattice deformation to a short-rang. The above-mentioned perovskites with broadband emissions have lower electronic dimensionality which facilitates the free charge carriers with heavy effective mass to be confined in the crystal lattice which is vibrating due to thermal excitations, phonons. Polarons with smaller Bohr radius are formed when the carrier-phonon coupling is stronger. The electron and hole polarons can further bind each other Coulombically to form STEs. 0D hybrid perovskites usually show large Stoke shifted emission suitable for phosphor applications. For example, the Bi^{3+} doped 0D perovskite Cs_2SnCl_6 which showed a large Stokes shifted emission with a PLQE $\sim 80\%$. The combination of this material along with a commercial yellow phosphor afforded white LED with high color purity.⁸⁵

Fundamentally, 0D hybrid perovskites are molecular crystals, wherein the size of organic cation defines the electronic coupling between them with metal halide lattice. Figure 2.12 a–c represents the band structures and DOSs for 0D perovskites such as $(\text{C}_4\text{N}_2\text{H}_{14}\text{Br})_4\text{SnBr}_6$, $(\text{C}_4\text{N}_2\text{H}_{14}\text{I})_4\text{SnI}_6$, and Cs_4PbBr_6 . From these figures, the large organic cations in $\text{C}_4\text{N}_2\text{H}_{14}\text{X})_4\text{SnX}_6$ ($\text{X} = \text{Br}, \text{I}$) reduces their electronic coupling with SnX_6 octahedra, leading to flat conduction and valence bands. In the case of Cs_4PbBr_6 , the band dispersion is more prominent due to the smaller size of Cs^+ cations. Finally, in $(\text{C}_9\text{NH}_{20})_2\text{SnBr}_4$, the seesaw shaped SnBr_4^{2-} are exfoliated with large $\text{C}_9\text{NH}_{20}^+$ cations. Consequent to this, a flat metal-halide derived conduction and valence bands are observed here due to the reduced electronic coupling of the organic cations with the metal halide lattices.⁸⁶

Due to the existence of more localized electronic states, 0D perovskites usually show a strong exciton localization and relaxation. The binding energy calculations showed large values for STE binding energies and which indicates that free electrons and holes are nonexistent in these materials at room temperature. Figure 2.12 d shows the structure and the partial charge densities of the electron and holes of the STEs in $(\text{C}_4\text{N}_2\text{H}_{14}\text{Br})_4\text{SnBr}_6$. Here, the exciton localization at the SnBr_6 octahedra imparts the contraction of the Sn-Br bonds and the expansion of the two vertical Sn-Br bonds. However, in the case of $(\text{C}_9\text{NH}_{20})_2\text{SnBr}_4$, the exciton localization at the seesaw structured SnBr_4^{2-} ⁸⁶ transforms its seesaw structure into a nearly planar structure (Figure 2.12 e). Figure 2.12 f shows the calculated as well as the experimental values for the exciton excitation and emission energies for several 0D and 1D

metal halide hybrids. Generally, 0D perovskites with large organic cations and large interstitial space show a high degree of excited-state structural relaxation leading to large Stokes shifted emission. However, inorganic perovskites with smaller cations such as Cs_4PbBr_6 shows small Stokes shift due to their small cation size. Here the reduced cation size imparts a compact crystal structure to these systems, and which limits the extent of the local structural distortion. From this discussion, it is reasonable to assume that strong exciton relaxation has a significant impact on the observed large Stokes shifted emission in 0D perovskites.

2.3.7. Mechanisms for Broadband Emission

Mechanisms for broadband emissions are well explored in three types of materials such as semiconductors, molecular complexes, and luminescent phosphors. In semiconductors, broadband emissions happen due to permanent defect states which form mid-band-gap states, or due to transient defects formed by self-trapped excitons.

Figure 2.13. Schematics of exciton self-trapping.⁷⁷

In molecular complexes, broadband emissions happen due to phosphorescence that involves triplet state of the molecule. In luminescent phosphor, dopants like d-block and f-block metal ions with their respective metal-centered transitions like d-d and f-f transition in the crystal field of host show broadband emissions.

Figure 2.14. Metal-centered s-p transition involving triplet state.

Lower-dimensional perovskites (2D and 1D) have features similar to semiconductors while 0D perovskites are like molecular complexes. Hence all three mechanisms mentioned above (STE, triplet state, and s-p transition) exist in broadband emissions of lower-dimensional perovskites. STE exist typically in semiconductors which have soft lattices, and localized carriers.

Self-trapping may be distinguished between intrinsic, trapping at permanent defect, and extrinsic self-trapping. Intrinsic self-trapping is associated with transient distortions in a lattice and may be visualized by a hard ball (charge carriers) being dropped on deformable sheet (Fig xx). This effect is viewed as reversible and transient; and can be distinguished from a charge carrier being trapped at a permanent defect, viz. indentation in Fig xx. Extrinsic self-trapping may be viewed as the event where the trapping is influenced by a heterogeneity in the lattice (Fig xx). Metal halide perovskites have soft lattices and probably the softness of these lattice is exhibited more easily when the dimensionality of the perovskite is reduced or when the octahedra is tilted out of the inorganic metal halide layer. It is proposed that the mechanism that is seen in perovskites is related to intrinsic self-trapping. Although this has been elucidated in PbBr₂, a complete analysis of the electronic excited states of large and structurally complex systems such as 2D perovskites has been proven to be computationally difficult.

Figure 2.15. Different types of trapping for charge carriers.⁹²

Hybrid perovskites, mainly low-dimensional hybrid perovskites with higher bond angle of bridging halide (metal--halide-metal (indication of out-of-plane tilt of octahedra), have shown existence of STEs and broadband emission. Several detailed studies have been reported to investigate the origins of broad-band emission in (N-MEDA)PbBr_{4-x}Cl_x and (EDBE)PbX₄ systems.^{72, 77} Calorimetric studies concluded that phase transitions were not a factor in the broadband emissions. Time-resolved PL concluded that the emission is related to multiple bands. It was also observed that the PL does not saturate with intensity. If the PL was related to permanent defect concentrations, it would saturate at high excitation power. The absence of such a saturation is argued to be consistent with the hypothesis that self-trapped excitons may be considered to be transient defect states. In these systems, the barrier against self-trapping was estimated to be 10 meV and strong evidence to correlate broadband emission with self-trapped states.

Inorganic perovskites with localized charge carriers and broadband emissions could also be created by making double perovskites using two different B-site metal ions having different electronic configurations. For this case, typically alkali metal ions were used which have different electronic configurations from the typical B-site cations used in metal halide perovskites. These alkali metal ions have less electronic coupling with typical B-site cations, so they reduce the electronic dimensionality of the metal halide network in perovskites. Thus, alkali metal ions help to localize the charge carriers which ultimately leads to short-range

lattice distortions resulting the small polarons. Broad-band emissions have been observed in perovskites prepared as thin films, ball-milled or ground powders, nanostructures, as well as single crystals of diverse perovskites. These observations eliminate the possibility that surface defects source. Excitation power-dependent emission intensity has linear correlation. If defect causes this emission, a sub-linear behavior would have been observed as relating defect states becoming saturated. Furthermore, PL excitation spectra gathered across the wavelength of emission spectrum did not show any changes in PL shapes; and did not display any sub-gap contributions to the PL spectrum. T-dependent PL studies clearly indicated that with decreasing temperature, the PL spectrum transitions rapidly from broad to narrow emission. At lower temperatures, PLQE of (EDBE)PbBr₄ increases, attaining 85% at 105 K.⁷⁰ This increased emission efficiency and narrowing of the photoluminescence with reduction in temperature is evidence of strong coupling between the electronic transition and lattice vibrations. All the above observations strongly suggest that the broadband emission is not related to defects, materials morphology, or sub gap trap states. Thus, a mechanism based on self-trapping of free excitons is being considered to explain the observed phenomena of broad-band emission in perovskite materials

2.4 Perovskites: Considerations for Application as Phosphors

Color quality is typically discussed in the context of specifications set forth by the Commission internationale de l'éclairage (CIE) and encompasses light, illumination, color, and color spaces. In particular, color rendering index (CRI), correlated color temperature (CCT), and chromaticity CIE coordinates are often used to define color quality. The color rendering index (CRI) is a measure of the ability of an emitter to accurately portrays a target object's color (e.g. incandescent light shows a good match with visible light spectrum and can have CRI close to 100).⁸⁷ CCT helps define colors in terms of temperature, with lower color temperatures of ~3000k are termed as 'warm,' while temperatures of 5000k are termed 'cool'. The CIE coordinates define color quality regardless of its brightness; and white light is specified as (1/3, 1/3) on a polar coordinate scale (Figure 2.).⁸⁸

An efficient phosphor should fulfill the following requirements simultaneously.⁶

1. The phosphor should show emission bands spread out over the entire visible range to accurately render all colors referred to as color rendering index (CRI).
2. Its excitation spectrum should overlap with the pumping LED.

3. The emission spectrum and intensity of the phosphor at elevated temperature should resemble with those at room temperature, to allow a stable performance as a function of driving current and ambient temperature.
4. The photoluminescence quantum efficiency (PLQE) should be as high as possible, to maximize the overall electrical-to-optical conversion.
5. The phosphor should be stable.
6. In high power LEDs, the conversion process should not show saturation.

Figure 2.16. Chromaticity diagram of various white-light-emitting perovskites. ⁸⁹

Perovskites phosphors for white light emission

Table 2.2. PLQE, CRI, and CIE values of reported white-light-emitting perovskites ⁹⁰

Perovskite	PLQE (%)	CRI	CIE (x, y)
(N-MEDA)PbBr ₄	0.5	82	(0.36, 0.41)
(EDBE)PbBr ₄	9	84	(0.39, 0.42)
(EDBE)PbCl ₄	2	81	(0.33, 0.39)
α-(DMEN) ₂ PbBr ₄	not reported	73	(0.28, 0.36)
(AEA)PbBr ₄	not reported	87	(0.29, 0.34)
(PEA) ₂ PbCl ₄	<1	84	(0.37, 0.42)

Perovskite	PLQE (%)	CRI	CIE (x, y)
(EA) ₄ Pb ₃ Cl ₁₀	not reported	66	(0.27, 0.39)
(API)PbCl ₄	<1	93	(0.36, 0.37)
(MPenDA)PbBr ₄	3.4	91	(0.24, 0.23)
(CyBMA)PbBr ₄	1.5	not reported	(0.23, 0.29)

Perovskites displaying broad-band emission have potential applications as phosphors in WLEDs. These perovskites afford broad emission (400–700 nm) with high color purity (resolution) and high color rendition. Many of the lead halide perovskites show broadband white light emission with CRI values above 80, a typical threshold value for commercial-quality illumination. Table 2.2 shows the PLQE, CRI, and CIE values for various white-light-emitting perovskite materials.⁹⁰ The highest CRI reported is 93 in (C₃N₂H₄(CH₂)₃NH₃)PbCl₄.⁹⁰ Perovskites are useful for single phosphor LEDs whose emission covers the entire visible spectrum. This is superior to having multiple emitters since they suffer from challenges such as self-absorption due to overlapping absorption and emission spectra of the various components. Additionally, if the different components degrade at different rates, there will be changes to the emission color as well.

(EDBE)PbBr₄ has been reported to be thermally stable to over 200 °C,³⁰ which is above the typical operating temperature for light-emitting diodes.⁷⁹ Additionally, under constant UV illumination, its emission remains unchanged after 3 months under vacuum.³⁰ However, PLQE remains as a challenge. The films of the 2D perovskite (EDBE)PbBr₄⁵³ and microscale crystals of the 1D Pb–Br hybrid (H₃CNH₂(CH₂)₂NH₂CH₃)PbBr₄ showed PLQE values of ca. 9% for warm white light⁹¹ and ca. 12% for cold white light, respectively. These values are significantly lower than those of commercial rare-earth phosphors.⁸⁵ However, unlike inorganic phosphors, these hybrid phosphors are solution-processable and can be easily deposited from solution.⁹²

Perovskite materials as down-conversion phosphors

Figure 2.13. Emission spectra of a UV-pumped white LED using corrugated 2D EDBEPbBr₄ as a single-component white phosphor under different operating voltages. Device image (inset). (B) Emission spectra of a UV-pumped white LED using a blend of (C₄N₂H₁₄Br)₄SnBr₆ and BaMgAl₁₀O₁₇:Eu²⁺ at a 1:1 weight ratio. (C) CIE coordinates for the corrugated 2D (blue star) and the 0D (red square) devices on the CIE1931 chromaticity chart.¹⁶

Lead halide perovskites were also explored for their use as down-conversion phosphors in white LEDs. Corrugated perovskites showed promising potential as down-conversion phosphors. Such corrugated 2D structures can be obtained by cutting 3D perovskites into slices along the (110) crystallographic direction. The strong exciton-lattice coupling present in corrugated perovskite can induce the transient lattice distortion, resulting in the strongly Stokes-shifted broadband emission. A color rendering index (CRI) of 93 has been achieved in N-(3-aminopropyl)-imidazolium tetrachloro-lead perovskite.⁹³ However, obtaining a high PLQEs suitable for practical applications is still challenging. To date, the (EDBE)PbBr₄ showed the highest PLQE of 9% in bulk single crystals and of up to 18% in microscale crystals.⁹⁴ The emission spectra of the white LED based on a microscale (EDBE)PbBr₄ were measured at different voltages, of which the emission structure exhibits little-to-no voltage dependence, as shown in Figure 2.13 a-c. For microscale (EDBE)PbBr₄, a CIE color coordinate (0.30, 0.42) was achieved from the emission at 3.0 V as shown in Figure 2.13 c with a CCT of 6519 K, corresponding to a “cold” white light. However, the PLQEs of reported for corrugated 2D perovskites still do not satisfy the requirement of down-conversion LEDs.

Figure 2.14. (a) Electroluminescence under varying forward bias current; (b) electroluminescence of devices after aging at 85 °C for 0 to 96 h; (c) emission spectrum of the prototype device; (d) voltage versus brightness and luminous efficiency of prototype device.⁹⁵

Recently Ma et al. have reported a series of UV-pumped WLEDs, in which BAM:Eu²⁺ is used as a blue phosphor, and a series of 0D organic metal halide hybrids, (Ph₄P)₂MnBr₄, (C₄N₂H₁₄Br)₄SnBr₆, and (Ph₄P)₂SbCl₅, as green, yellow, and red phosphors, respectively (Figure 2.14). These WLEDs can produce full-spectrum white light with extremely high CRIs of up to 99, excellent deep-red color rendering, R₉s of up to 99, and superior color quality scale (CQS) values. By carefully controlling the phosphor blend ratios, white emissions with CCTs ranging from 3000 to 6000 K, have been demonstrated, which perfectly emulates sunlight at different times of day.⁹⁵

2.5 Summary and outlook

Halide perovskites materials offer a versatile platform for exploiting light for energy and lighting applications. Progress has been made in improving the stability and scalability of these materials for solar cell fabrications. Exploration has been expanded to light emission

properties of these materials to develop energy-efficient solid-state lighting devices with wide color gamut. Most layered perovskites absorb in the ultraviolet (UV) or near-UV region and can emit light in the blue to the infrared region of the electromagnetic spectrum. By capitalizing the mastery in synthesis and optimization techniques, significant progress has been achieved in reducing the dimensionality of perovskite material from 3D to 0D. Such lower dimensional perovskites showed extremely broad emission spanning the entire visible spectrum with high color rendition index (CRI). High CRI value is a prerequisite for qualifying a light source to be used in solid-state light emission devices. The origin of the broadband emission in perovskite materials has been related to electron-hole pairs, permanent lattice defects, transient light-induced defects, ligand-field transitions in the inorganic layers and molecular chromophores in the organic layers. At the application level, the broadband white light emission of these molecularly and morphologically engineered perovskite materials has been demonstrated as phosphors for white LEDs.

Although much progress has been achieved in tuning the chemistry and photophysics of lower dimensional perovskites for white light emission devices, there is still a large space for material development by effecting systematic changes in the composition, structure, morphology, dimensionality, etc. and that sets the stage for the study presented in the subsequent chapters of this thesis.

2.8 References

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Chapter 3

Experimental Methodology

This chapter summarizes the experimental and characterization techniques used to address the objectives and hypotheses of this thesis. It begins with the rationale for synthesis of materials, followed by characterization. Lastly, discussed about the principles of characterization techniques utilized during the course of study.

3.1 Materials Synthesis

3.1.1 Preparation of Ammonium Salts

Ammonium salts were prepared by acid-base reaction of amine (base) and hydrohalic acid at low temperature under vigorous stirring. Respective ammonium salts were prepared by the slow addition of respective hydrohalic acids to the respective amine in methanol at 0 °C under vigorous stirring. The amount of hydrohalic acid depends on the number of amine group present in the amine compound. In the case of phenethylammonium, one mole equivalent of acid was used whereas 2 mole equivalents were used in the case of xylylenediammonium. After stirring the solution for an hour, methanol and water were removed using a rotary evaporator under reduced pressure at 60 °C. If necessary, methanol was added to form an azeotropic mixture with water to remove the latter completely. Ammonium salt thus produced was washed with diethyl ether to remove the unreacted amine. Ammonium salt was dissolved in methanol and reprecipitated by adding diethylether. This process was repeated for a few times to get the pure ammonium salts. Finally, the ammonium salts were dried under vacuum at 50 °C for 12 hr.

3.1.2 Preparation of perovskite thin films and powders

Preparation of perovskite samples were done by making perovskite solution in a typical way of dissolving the respective ammonium salts and metal halides in polar organic solvents followed by processing it into either thin films or powders. A solution of organic ammonium metal halide perovskites with chemical formula $A_mM_nX_o$ were prepared by dissolving m mmol of organic monoammonium halide and n mmol of metal halide in DMSO or DMF at 100 °C. Solutions with excess of $PbBr_2$ were prepared by dissolving excess $PbBr_2$ in 1.0 M perovskite solutions. Final concentrations of the solutions were fixed at 1.0 molar. Thus produced

perovskite solutions were spin-coated on ITO substrates at 4000 rpm for 30 seconds then annealed at 100 °C for 30 mins. These as-prepared thin films were used for XRD, FESEM, UV-Vis, and photoluminescence studies. The powder sample of $\text{PEA}_2\text{PbCl}_4$ and *m*-XDALB were prepared by drop-casting a sol-gel solution on a glass substrate and dried at 100 °C for a few hours. The powdery material was finely grinded and used for XRD measurements. The *m*-XDALB powder was prepared by precipitation method in which the antisolvent diethylether was added to perovskite solution slowly added under vigorous stirring. This resulted in the precipitation of *m*-XDALB which was collected by filtration and washed with diethylether and finally dried at 50 °C under vacuum.

3.1.3 Growing the Single crystals

Figure 3.1. Schematic representation of the set-up used to grow the single crystals using antisolvent vapor-assisted crystallization method.

Single-crystals of perovskites were grown by a typical antisolvent vapour-assisted crystallization (AVAC) method where perovskite solutions were made in polar solvents and non-polar or less polar solvents were used as antisolvent. Schematic representation of the set-up used to grow the single crystals using AVAC is shown in Figure 3.1. The solubility of ammonium salts and metal halides are good in DMSO, but DMSO has the ability to form coordination bonds with metal ions. Hence, it is not desirable to grow a single-crystals from DMSO solutions. Hence, *N,N*-dimethylformamide (DMF) is used to make perovskites solutions. Different antisolvents like diethylether, methanol, nitromethane were used for different perovskites. These crystals were used for single-crystal X-ray diffraction (XRD) measurements and also for ultrafast optical spectroscopic studies. Single-crystal data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3.1.4 Preparation of Nano- and micro-particles

PEPC nanoparticles were prepared by ligand-assisted reprecipitation (LARP) method where perovskite precursors and ligands (typically longer alkylamine) were dissolved in polar solvents. These perovskite solutions were added swiftly into non-polar antisolvent, which resulted in the formation of perovskite nanoparticles. PbCl_2 (0.100 mmol, 27.8 mg) along with phenethylamine (0.24 mmol, 29.0 mg) and octylamine ligand (0.16 mmol, 26.4 μl) were dissolved in 500 μl of DMF followed by the addition of hydrochloric acid (50 μl). The reaction mixture was sonicated for a few minutes to form a clear solution. Around 200 μl of this solution was slowly added into a 2 ml hexane solvent under vigorous stirring at room temperature. This mixture was further stirred for five minutes. Quick addition of acetone to this mixture led to nanoparticles of $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbCl}_4$. Microparticles of butylammonium tin bromide were prepared by ultrasonication method in which mixer of toluene and single crystals of BTB were used. Ultrasonication was done for 30 mins at 90 % power.

3.2 Materials Characterizations Techniques

3.2.1 Powder X-ray diffraction

Powder X-ray diffraction was used to check phase purity of perovskites of various form like powder, thin film, microparticle and nanoparticle. Constructive interference of monochromatic X-rays and crystalline materials is the fundamental for X-ray diffraction. X-rays are produced by a cathode ray tube (CRT), then filtered to get monochromatic radiation, followed by collimated to concentrate, and finally directed toward the sample. The interaction of the incident X-rays with the material produces constructive interference when conditions satisfy Bragg's Law ($n\lambda = 2d \sin \Theta$) (Figure 3.2). The wavelength of electromagnetic radiation is related to the lattice spacing and the diffraction angle in the Bragg's Law. Finally, the diffracted X-rays are detected, processed and counted. By collecting the diffracted signals through a range of 2Θ angles, all possible diffraction directions of the lattice should be obtained due to the random orientation of the powdered material. Diffraction peaks are converted into d-spacings which allows to identify the material due to specific set of d-spacings.

Figure 3.2. Schematic representation of Bragg's equation.

The phase purity was analyzed by powder X-ray diffraction (PXRD) pattern collected with a Bruker D8 Advance diffractometer (Bragg-Brentano geometry) equipped with a Cu K α X-ray tube operated at 40 kV and 40 mA, scanned using a step size of 0.02° and time per step of 1 s. The XRD measurements were carried out using perovskite single crystals, thin films and powder samples to analysis their structural properties as well crystallinity.

3.2.2 Solid-state nuclear magnetic resonance (ssNMR)

Multinuclear NMR was used to check the purity of all the 0D perovskites prepared in this thesis work. All NMR experiments in this study were completed on a Bruker Avance III HD 600 MHz spectrometer with a Bruker 4 mm HXY MAS probe. Spectral simulation of the NMR spectra was achieved via *dmfit*.^[1]

The ^1H solid-state NMR experiments were completed at 14.1 T ($\nu_0(^1\text{H}) = 600.18$ MHz) with MAS frequencies of 12 KHz. A ^1H one-pulse sequence was employed and resulting data was referenced with respect to adamantane ($\text{C}_{10}\text{H}_{16(\text{s})}$; $\delta_{\text{iso}} = 1.82$ ppm). The ^{13}C solid-state NMR experiments were completed at 14.1 T ($\nu_0(^{13}\text{C}) = 150.92$ MHz) with an MAS frequency of 12 KHz. A ^{13}C CPMAS pulse sequence was employed and resulting data was referenced with respect to adamantane ($\text{C}_{10}\text{H}_{16(\text{s})}$; $\delta_{\text{iso}} = 38.48, 40.49$ ppm). A ^1H $\pi/2$ pulse length of 2.5 μs , determined on adamantane, and a recycle delay of 8.5 s were used in all experiments. The ^{13}C and ^{119}Sn CPMAS experiments employed a contact pulse length of 4000 μs , and utilised high-power proton decoupling. The ^{207}Pb solid-state NMR experiments were completed at 14.1 T ($\nu_0(^{207}\text{Pb}) = 125.55$ MHz) under static conditions. A ^{207}Pb Hahn echo pulse sequence was employed and resulting data was referenced with respect to 1.1M $\text{Pb}(\text{NO}_3)_{2(\text{aq})}$ ($\delta_{\text{iso}} = 2965.7$ ppm).^[2] The ^{207}Pb Hahn echo experiments utilised $\pi/2$ and π pulses of 5 and 10 μs , determined

on $\text{Pb}(\text{NO}_3)_{2(\text{aq})}$, with a recycle delay of 5 s and an echo delay of 76 μs . The ^{119}Sn solid-state NMR experiments were completed at 14.1 T ($\nu(^{119}\text{Sn}) = 223.81 \text{ MHz}$) with an MAS frequency of 12 KHz. A ^{119}Sn CPMAS pulse sequence was employed and resulting data was referenced with respect to $\text{SnO}_{2(\text{s})}$ ($\delta_{\text{iso}} = 604.3 \text{ ppm}$). The synthesised various perovskite crystals and powder samples characterised using NMR to understand the phase purity.

3.2.3 Thermogravimetric analysis (TGA)

Thermogravimetry measures the mass change in a sample that happens in any of the following processes i.e. evaporation, oxidation, and decomposition. The mass difference is sent as TG signal (Figure 3.3). Thermogravimetric analyses were done on a TGA Q500 V6.7 (TA Instruments) over a temperature range from 25 °C to 900° C at a ramp of 10 °C/min under nitrogen flux of 60 mL/min. Various synthesized perovskites materials (phenethylammonium lead halide perovskites PEPC, PEPB, meta-xylylenediammonium lead bromide (m-XDALB) and meta-xylylenediammonium tin chloride (m-XDALC), meta-xylylenediammonium tin bromide (m-XDATB), and meta-xylylenediammonium germanium bromide (m-XDAGB), etc) to understand their thermal stability

Figure 3.3. Schematic diagram of a thermogravimetry apparatus.

Figure 3.1 Figure 3.3 represents the schematic diagram of a calorimetry apparatus.

3.2.4 Differential scanning calorimetry (DSC)

DSC measure the heat change in a sample that happens in any of the following processes i.e. phase change and melting. DSC thermograms of various perovskite powder samples were collected on a Q10 V9.9 build calorimeter (TA Instruments) in order to understand their phase stability. All measurements were at carried out at a rate of 10 °C/min under nitrogen flow rate of 60 ml/min. The minimum temperature was -50 °C and the maximum temperature was 20 °C below the degradation temperature of the compound.

Figure 3.4. Schematic diagram of a calorimetry apparatus.

3.2.4 UV-Vis absorption spectroscopy

UV-Vis-NIR spectrophotometer is an instrument to measure the electronic transitions that occur in various materials. These electronic transitions could absorb light in any region from deep UV to IR. Hence, UV-Vis absorption spectra were collected in the range of 300–800 nm using a UV-Vis-NIR spectrophotometer (Shimadzu UV3600). The instrument operates by sending a beam of light with particular intensity through a sample and measuring the intensity of the light reaching a detector. The wavelength and intensity change of the light gives information about the chemical structure and photophysical process occurs within the sample. Spectrum can be revealed in terms of transmittance, absorbance or reflectance of energy in the

wavelength range between from deep UV to NIR (Figure 3.5). Electromagnetic radiation contains photons with different energy corresponding to different wavelength. Different samples absorb different electromagnetic radiation depending on their band gaps. This process is the basis for absorption spectroscopy and Beer-Lambert law describes this process.

In a double-beam instrument, the light from the source is split into two beams before it reaches the sample. One beam is traveled through the blank sample and the other beam passes through the sample to the light is splitter into a beam of light from a suitable light source is passed through a grating monochromator. Then the light passes through the sample before reaching the detector.

Thin film of perovskites on quartz substrates were used directly in absorption mode. Powder samples of perovskites were blended with barium sulfate (BaSO_4) to analysis the optical band gap of the perovskites powder. For all powder samples BaSO_4 used as a reference material.

Figure 3.5. Schematic diagram of the typical components of spectrometer.

3.2.5 Steady-state, and time-resolved photoluminescence spectroscopy

Photoluminescence spectrophotometer is an instrument to measure the relaxation of the excited state that occur in various materials. Steady-state photoluminescence spectrum was collected using Shimadzu RF-5301pc spectrofluorophotometer. For all measurements, the 340 nm excitation beam is passed through a short pass filter to remove residual 800 nm photons in the beam. To prevent a second order diffracted laser peak (due to the grating) from appearing the

PL spectrum at 680 nm, a long pass filter is also used to remove any scattered laser radiation in the emission. In addition, spectral corrections using monochromator and charge-coupled device (CCD) response functions were also carried out to obtain the final PL spectra.

The laser wavelengths (310 and 340 nm) used for PL measurements are obtained using a Coherent OPerA-Solo optical parametric amplifier from a 800 nm input pulse laser. The 800 nm pulse laser originates from a Coherent Libra regenerative amplifier (1 KHz, 50 fs, 800 nm), which is seeded by a Coherent Vitesse oscillator (50 fs, 80 MHz). For all measurements, the excitation laser beam is passed through a short pass optical filter to remove residual 800 nm photons in the beam. For steady-PL measurements, the emissions are collected using a backscattered PL configuration and dispersed using a 300 g/mm spectrometer (Acton, Spectra Pro 2500i). A long pass filter is also used to remove any scattered laser radiation in the emission, which is important in preventing a second order diffracted laser peak (due to the grating) from appearing in the PL spectrum at the visible wavelengths. In addition, spectral corrections using monochromator and charge-coupled device (CCD) response functions were also carried out to obtain the final PL spectra. For time-resolved PL measurements, the back-scattered emissions were temporally resolved using an Optronis OptoscopeTM streak camera system with an ultimate ~10 ps resolution at the fastest scan speed.

3.2.7 Photoelectron Spectroscopy in Air

Photoelectron spectroscopy in air (PESA) measurements were done to measure the work function of the semiconductors. PESA was conducted with a Riken Keiki AC-2 spectrometer with a power setting of 800 nW and a power number of 0.5. A thin film of perovskite on ITO was used for the PESA analysis.

3.2.8 Atomic Force Microscopy

AFM measurements were conducted using a Bruker Icon microscope to check the topology of the nanomaterials. All measurements were performed in the standard tapping mode with OTESPA-R3 tips from Bruker.

3.2.9 Field Emission Scanning Electron Microscopy (FESEM)

FESEM was used to check the morphology of the films, powder, and single-crystals. Electron emission source is cold cathode field emitter which does not produce heat. The electron

emission is attained by keeping the filament in a high electrical potential gradient. Then electrons are focused and deflected by electronic lenses to attain a narrow scan beam which will interact with object. As a sequence, secondary electrons are released from the each bombard of electron beam with sample surface in the raster process. A detector catches the secondary electrons and produces an electronic signal which is transformed and amplified to a video scan-image. Electron beam interaction with object produces an X-rays also which is processed with different detector to a different image which helps to identify the element that constitute the sample. Surface morphology images were recorded using field emission scanning electron microscope (JEOL, JSM-7600F).

Figure 3.6. Schematic diagram of Field Emission Scanning Electron Microscopy (FESEM)

3.3 Device Fabrications and Characterizations

3.3.1 Fabrication of a White-Light Emitting Device.

Phosphors (30 mg) at different weight ratios were mixed with 1.0 g of polydimethylsiloxane (PDMS) elastomer and 0.3 g of curing agent. These viscous solutions were put in a waffle pack to control the shape and thickness of the mould. Thin film moulds were removed after ageing overnight. In case of m-XDAGB, presence of phosphorous acid kills the curing agent, so curing did not occur. In this case, the viscous PDMS elastomer mixed with phosphors spincoated on quartz plate and thus prepared thin films were used for measuring the figures of merit of white lights produced.

3.3.2 Photoluminescence Quantum Yield (PLQY):

PLQY was calculated using the following equation: $\eta_{QE} = I_S / (E_R - E_S)$, where the I_S is the intensity of the incident light

3.3.3 Commission internationale de l'éclairage (CIE 1931):

Quality of the light emitted from the phosphor is need to be evaluated in order to find their suitability in their applications. For illustration, the incandescent and fluorescent lamp emit white color but the hues are different. Therefore, in order to avoid the inaccuracy in characterizing the light, *Commission Inernationale de l' Eclairage* (CIE, International Commission of Illumination) established a mathematically defined color space (Figure 3.7) and a set of parameters, which define any emission in terms of two chromaticity coordinates, x and y . As shown in Figure 1, the vertexes of the triangle are the CIE coordinates of three primary red, green, and blue colors. In the middle area, the white light equal-energy point is (0.33, 0.33). In fact, as long as the CIE coordinates of OLEDs are located near (0.33, 0.33), the colors are considered to be white (e.g., (0.26, 0.27), (0.47, 0.43), (0.54, 0.39), (0.49, 0.41), (0.36, 0.50) and (0.39, 0.53)).

Eye sensitivity to color is dependent on angle of view, hence the CIE 1931 X, Y and Z tristimulus values are defined using a 2° field of view. The tristimulus values are calculated using the following integrals:

$$X = \frac{1}{2\pi} \int_{380}^{780} I(\lambda) x(\lambda) d\lambda \quad (\text{equation 1})$$

$$Y = \frac{1}{2\pi} \int_{380}^{780} I(\lambda) y(\lambda) d\lambda \quad (\text{equation 2})$$

$$Z = \frac{1}{2\pi} \int_{380}^{780} I(\lambda) z(\lambda) d\lambda \quad (\text{equation 3})$$

Where λ is the wavelength in nanometers, I is the SPD of a specific light source at particular wavelength and x , y , and z are the color matching functions at the wavelength.

Figure 3.7. Diagram of the Commission International de L'Eclairage (CIE) chromaticity.¹

Finally, the respective CIE 1931 chromaticity values (x , y , and z) are calculated by normalizing the tristimulus values.

$$x = \frac{X}{X + Y + Z}$$

$$y = \frac{Y}{X + Y + Z}$$

$$z = \frac{Z}{X + Y + Z}$$

with $z = 1 - x - y$

it is sufficient to represent color using two of the chromaticity values. Conventionally, color are quantified using chromaticiy coordinates instead of tristimulus values. Only chromoaticiy coordinates x and y are used CIE 1931 color spot.

<http://www.lrc.rpi.edu/programs/nlpip/lightinganswers/lightsources/appendixb1.asp>

3.3.4 Color Rendering Index (CRI).

It is a measure of the ability of the light source in reproducing the true color of the object with comparison to a familiar light source like daylight and incandescent light.

3.3.5 Correlated Color Temperature (CCT).

CRI”- correlated color temperature, indicates the ability of the light source to reveal the color of the objects faithfully in comparison with an ideal or natural light source.

3.3.6 Spectrophotometer (LED)

A basic measuring equipment essential to detect sample concentration and color information by using LED and color sensor. Purity and wavelength information can be detected by CIE diagram, and the concentration can be estimated with purity information.

3.4 References

1. Zhang, L.-R.; Li, X.-L.; Luo, D.; Xiao, P.; Wenping, X.; Song, Y.; Ang, Q.; Liu, B., *Materials* **2017**, *10*, 1378.

Chapter 4

Composition management of lead (Pb) based perovskites for broadband emission

4.1 Introduction

The LED device performance of 3D halide perovskites was restricted $< 1\%$ because of their large grain size and poor surface coverage as well as from a low PLQE due to self-quenching effects and lattice defects which often led to non-radiative recombination.¹²⁻¹⁴ Therefore, formation of small grain size or formation of the lower dimensional structures (formed using addition of long chain organic cation) are more preferred to spatially limit carrier diffusion thus enhancing the radiative recombination and hence high PLQY.¹⁵

In addition, 3D, quasi -2D or 2D perovskites exhibit a narrowband emission with small Stokes shift mainly because of radiative recombination of free excitons (excited electron hole pairs). Basically, these structures are the ‘morphologically’ controlled lower dimensional perovskites and by controlling the size or shape (nanowires, nanorods, nanosheets and quantum dots) quantum confinement can be achieved to tune their physical properties. In addition, these structures are intrinsically formed by corner-sharing metal halide octahedra and the structures as well as properties are derived from their 3D counterpart. The ‘molecular level’ low-dimensional materials are another class of lower dimensional materials formed by isolated metal halide octahedra separated by organic cations. Their properties are invariant with their crystal size, and their bulk crystals also display the intrinsic properties of a single unit structure also known as ‘corrugated structures’. Broadband emission can be achieved with such corrugated lower dimensional structures (2D, 1D, and 0D perovskites) as a result of efficient exciton self-trapping or excited state structural deformation.¹⁶⁻¹⁸ In other terms, strongly exciton lattice coupling (exciton-phonon) creates transient elastic lattice distortions i.e. “excited-state defects”, such deformations stabilize the exciton to emit a broadband with a large Stokes shift. Thus in order to obtain a broadband emission, the formation of ‘corrugated’ lower dimensional layered structures or formation of bulk assembly of ‘metal halide clusters’ are the better choices.

2D perovskite structures for LED

Generally, lower-dimensional organic-inorganic hybrid metal halide perovskites synthesized using simple long alkyl chain ammonium cations generally form a templated well-ordered layered structure due to their weak Van der Waals interactions between the long hydrocarbon chains. On the other hand, lower dimensional perovskites synthesized using aromatic/aryl ammonium cations form distorted layered structures due to their strong π - π interaction between rigid aryl groups in ammonium cations. The strong π - π interaction between aryl ammonium cations restrict the structural freedom of Pb-octahedra, which create tilt in octahedra and results in the formation of distorted layered structures. The formation of distorted structures usually creates a defect states, which are responsible for formation of self-trap excitons, which could emit as a broadband. The nature of the cation as well as of halide ions present in the perovskite structure (3D, 2D or quasi 2D) plays an important role on a broadband emission.¹⁹

Figure 4.1. X-ray structures of 2,2'-(ethylenedioxy)bis(ethylammonium) lead halide (EDBE)[PbX₄], where (a), (b) and (c) denoted for Cl, Br and I. Here H atoms are not shown in figure to avoid the confusion and the respective color sphere represents the atoms Pb-Turquoise, I -purple, Br, -brown, Cl,-orange, O- red, N-blue, and C -gray. The insets of the figure exhibit lead-halide coordination. Reprinted with permission from ref.¹⁹.

The effect of halide ion on the broadband emission was studied previously by Karunadasa et.al. and co-workers.¹⁹ They have observed the broad emission over entire visible range from 2D (EDBE)PbCl₄ perovskite as compared to 2D (EDBE)PbBr₄ and (EDBE)PbI₄ [(EDBE)-(ethylenedioxy)bis(ethylammonium)]. This is attributed to the more pronounced structural distortion for the Cl containing 2D perovskite (EDBE)[PbCl₄] as compared to 2D (EDBE)[PbBr₄/I₄] perovskite.¹⁹ The X-ray structures of 2D (EDBE)[PbCl₄/Br₄/I₄] perovskites are shown in Figure 4.1. Figure 4.1 represents the coordination environment for the metal ion

[Pb(II)] (i.e. interaction between halide and the Pb(II) ion] in inorganic octahedra (PbX_6). The broadband emission observed for (EDBE)PbCl₄ was attributed to strong electron phonon coupling due to lattice deformation as well as presence of intrinsic trap states. The origin of the white-light emission was attributed to electron-phonon coupling and self-trapped excitons.¹⁹⁻²⁰ In addition, Yanguai *et al.* conducted in-depth experimental investigations on the white-light emission behavior in thin films of cyclohexylammonium lead bromide $(\text{C}_6\text{H}_{11}\text{NH}_3)_2\text{PbBr}_4$.²¹ The authors proposed that the luminescence arises from self-trapped states with energy barriers of approximately 10 meV. These self-trapped excitons were mostly attributed to excitons localized in the inorganic lattice.

There are enormous possibilities to build a library of novel lower dimensional perovskites materials/ structures by varying either organic cations or halide anions and thus formed structures can be utilized for various optoelectronic applications including a white light-emitting diodes (LEDs). But, so far there are very few reports available about white light emission using lower dimensional perovskites, which can provide experimental insights on mechanism of a broadband emission.

In this chapter, the synthesis, structural and photophysical characterization of the corrugated or ‘molecular level’ low-dimensional lead halides perovskites were carried out to realize a broadband/white light emission. The effect of X-site halide anions and A-site cations on the lower dimensional perovskite structures was studied to attain a broadband emission. Accordingly, lower dimensional perovskites structures were prepared by varying X- site anion as well as A-site cations to realize a broadband emission as well as to understand the mechanism for the same. The results were discussed in detail with the support of morphological, photophysical and theoretical characterization.

4.2 Effect of X-site halide ions (PEPC, PEPB and PEPI)

Phenethylammonium halide ion ($\text{C}_6\text{H}_5\text{C}_2\text{H}_5\text{NH}_3\text{X}$, as shown below) was chosen particularly to prepare a lower dimensional 2D perovskites (A_2MX_4) in order to achieve broadband emission. The strong π - π interactions among the phenyl groups bring rigidity in perovskites structure and presence of ethyl group further may further extent it to enhance the structural distortion in perovskite structures to achieve a broadband emission. Refer to Figure 4.2.

Figure 4.2. Chemical structure of Phenethylammonium halide ion ($\text{C}_6\text{H}_5\text{C}_2\text{H}_5\text{NH}_3\text{X}$), where $\text{X} = \text{Cl}^-$, Br^- or I^-

Additionally, structural origin for white light emission was more or less accounted for the out-of-plane distortion of metal-(-halide)-metal bond. Therefore, it may be possible that by changing halide ions could also be change the structural deformation or create molecular corrugation to achieve broadband emission. Hence, 2D phenethylammonium lead halide perovskites were prepared by changing the halide ions i.e. $((\text{C}_6\text{H}_5\text{C}_2\text{H}_5\text{NH}_3)_2\text{PbCl}_4/\text{Br}_4/\text{I}_4)$, hereafter referred as PEPC/B/I to achieve a broadband emission (Table 4.1).

Table 4.1. Name of the 2D perovskites structures preliminary screening to achieve broadband emission along with their band gap (E_g in eV) and photoluminance (PL in nm) peak position. 2D phenethylammonium lead chloride/bromide/iodide (PEPC/PEPB/PEPI) perovskites. Thin Film-TF, Single crystal-SC, Nanoparticles -NPs

Perovskites	Band gap (E_g) (eV)	PL peak position (nm)	Possibility of Broadband emission
PEPI (TF)	2.30	421	No
PEPB (TF)	2.95	526	No
PEPC (TF)	3.48	400-900	Yes
PEPC (SC)		400-900	Yes
PEPC (Powder)		400-900	Yes
PEPC (NPs)		400-900	Yes

The UV and PL spectra of the thin films of 2D PEPC, 2D PEPBr and 2D PEPI perovskites are depicted in Figure 4.3. . Broad photoluminescence (PL) peak spanning from ~ 400 nm to ~ 900 nm was observed for the PEPC clearly reveals the signature of broadband emission (**Figure**

4.9b). While a narrow emission peak ($\sim 10\text{nm}$ to 20nm) for 2D PEPBr and 2D PEPI was noted at 418 nm and 540 nm respectively.²² The 2D PEPC was observed to be potential candidate to emit broadband at room temperature over a visible range as compared to 2D PEPB and 2D PEPI. Subsequently, 2D perovskites were further characterized to understand their properties and the mechanism of emission.

Figure 4.3. Superimposed (a) UV-Visible and (b) Photoluminance spectra of 2D Phenyl ammonium lead iodide/ bromide/chloride (PEPI/PEPB/PEPC) perovskites. The PEPC exhibit the broad band emission over 400-900 nm (kindly refer Figure 4.9b), while PEPI and PEPB exhibit narrow band emission.

Synthesis 2D PEPC

The phenethylammonium lead chloride ((PEA)₂PbCl₄, i.e. PEPC was synthesized in all four different forms i.e. as a single crystal, powder, thin film as well as nanoparticles to confirm that white light emission is an intrinsic property of PEPC and emission is not because of presence of defect states created during material formation. Further the photo physical measurements were carried out to probe the origin of white-light emission.

Single crystals of PEPC was prepared using anti-solvent vapor assisted crystallization. In brief, PEPC was dissolved in DMF and nitromethane was used as an anti-solvent to accelerate the crystal growth. In this growth process, the diffusion of nitromethane vapor was controlled slowly (over a week) into the perovskite solution in order to form good quality single crystals. Thin film of PEPC was prepared by spin coating 0.20 M perovskite solution in DMSO followed by annealing at 100 °C. The PEPC power was collected from, drop casting the perovskite

precursor on glass substrate, annealed it at 100°C, finely grinded and collected. Thus prepared thin film and powder of PEPC were used for the further characterization.

Nanoparticles of PEPC were prepared using ligand assisted reprecipitation method (LARP) with octylamine and oleic acid as ligand and capping agent respectively.²³ In order to optimize the capping ligand concentration, the nanoparticles formations were also carried out at different octyl ammonium concentration (namely 0.07, 0.16, 0.12 and 0.08mmole).

4.2.1 Structure identification and characterizations

Figure 4.4 Structure of phenethylammonium lead chloride ((PEA)₂PbCl₄, PEPC). Projection of PEPC viewed along the (a) a- and (b) b-axis, showing the organic ammonium cations intercalating between the 2D lead chloride layers. The Pb atoms are represented in grey, while the iodide atoms are in green. Crystal structure showing the arrangement of the organic ammonium cations intercalated between the 2D inorganic layers in PEPC viewed along the c-axis (c) with and (d) without the phenethylammonium cation shown. The Pb atoms are in grey, while the chloride atoms are in green.

Figure 4.4 shows the unit cell of 2D PEPC, the intercalation of organic ammonium cations between the 2D lead chloride layers, along the a-, b- and c-axis (with and without phenethylammonium cation). PEPC crystallizes in the triclinic space group P-1, consistent with a previous report.²⁴ Interestingly, the unit cell for PEPC is isomorphic with the triclinic PEPB,

but not with the monoclinic PEPI. Ordered layers of corner sharing PbCl_6^{4-} octahedra are sandwiched between the phenethylammonium cation layers, which are stacked contiguously without interleaving. Each layer contains two different type of Pb atoms with different environments (Figure 4.4 c & d). The crystals of PEPC were found to be twinned; the twin law and cell parameters were determined using the program CELL_NOW, and the reflection data were processed and corrections applied using the program TWINABS.²⁵ The twin law is given by $-1\ 0\ 0\ 0\ 1\ 0\ 0\ -0.5\ -1$. The twin law is the set of twin operations mapping two individuals of a twin. It is obtained by coset decomposition of the point group of the twin lattice with respect to the intersection group of the point groups of the individuals in their respective orientations. Some of the Pb and Cl ions were found to be disordered and were refined over two positions with occupancy of ~ 0.83 and ~ 0.17 . One of the amino group was also disordered over two positions with the occupancy of ~ 0.56 and ~ 0.44 . The ethyl groups were, as expected, disordered and appropriate restraints and constraints (SIMU, ISOR and RIGU) were used. One of the reflections (0 0 1) that was affected by beam stop was omitted.

A typical peak position at 2θ at 15.2° confirms the perovskite phase formation. Lower angle 2θ peak (i.e. below $2\theta < 10^\circ$) usually obtained in case of lower dimensional perovskites. X-ray diffraction (XRD) pattern of PEPC powder sample was in almost identical to that of simulated single crystal data as shown in the Figure 4. 5a clearly confirmed the phase purity and crystallinity of the PEPC. Further the superimposed XRD pattern shown in Figure 4. 5b demonstrated the formation of PEPC in thin film as well as in nanoparticles form. The high intensity peak obtained at $2\theta = 5^\circ$, 10° and 15.2° further confirms the phase purity and crystallinity of the 2D PEPC. The typical perovskite peak at 15.2° , noted for the PEPC thin films, corresponds to the 00 l plane indicate highly oriented film formation parallel to the substrate surface (Figure 4. 5b).

Also, the capping layer concentration plays a critical role during nanoparticle formation. For example, addition of excess of capping ligands expected to reduce the ripening of the nuclei and result in more nucleation sites during nanoparticle formation. However, addition of non-optimal concentrations may results in the formation of the octylammonium chloride (C8LC) along with nanoparticles formation. The superimposed xrd patterns of the PEPC nanoparticle synthesized using different capping ligand (i.e. octylamine) concentrations (i.e. 0.07 mmole, 0.16 mmole, 0.12 mmole and 0.08mmole) were depicted in Figure 4. 5c. The peaks at 2θ values

of 8.37° and 12.56° corresponds to the C8LC formation were noted for the nanoparticles synthesized using 0.16 mmole, and 0.12 mmole octyl amine concentration. Hence, the ligand concentration was systematically reduced to 0.070 mmol, which allowed the formation of PEPC nanoparticles alone and avoided any impure phase formation. Further, poor solubility of PEPC in DMF could induce more nucleation sites, which reduces the amount of perovskite nanoparticle in the mother liquid available for the further growth of the nuclei hence small amount of ligand is enough to control the growth of nanoparticles with average size of 10 nm. Probably, swift formation of more nucleation sites lead to the larger polydispersity of PEPC nanoparticles. The XRD spectrum of the PEPC nanoparticles concurs with that of the thin film. The interplanar spacing of PEPC was calculated as 1.67 nm based on the high intensity peak at the 2θ value of 5.27° indicating that these nanoparticles contain six layers of lead (II) chloride.

Figure 4. 5. Superimposed powder X-ray diffraction (XRD) pattern of phenethylammonium lead chloride ((PEA)₂PbCl₄, i.e. PEPC (a) finely ground 2D powder and Single crystal data. (b) Thin film and nanoparticles and (c) nanoparticles synthesized using different octylamine concentration (i.e. 0.07, 0.16, 0.12 and 0.08mmole).

Thermal stability

The thermogravimetric (TGA) analysis of PEPC was performed on powder sample to understand its thermal stability (Figure 4.6a). The negligible weight loss in the temperature range RT to 200 °C was recorded, which confirms the stability of PEPC upto 200 °C in nitrogen atmosphere. After 200 °C, almost ~50 % sudden weight loss was observed (in the range 200 °C -300 °C) may be because of the degradation of organic ligand i.e. phenyl ethyl ammonium chloride. The degradation of the lead chloride (PbCl_2) was recorded after 500 °C. The differential scanning calorimetry (DSC) analysis indicate the phase transition of PEPC at 150 °C, which was beyond the working temperature range of white light LEDs (WLEDs). This clearly reveals that perovskite phase transition would not affect the device performance (Figure 4.6b).

Figure 4.6. (a) Thermogravimetric analysis (TGA) and (b) Differential scanning calorimetry (DSC) measurements of PEPC powder sample. The TGA measurement was carried at 22 °C to 900 °C temperature range with heating rate at 10 °C/min in N_2 atmosphere. DSC was conducted at a rate of 10 °C/min under nitrogen flow rate of 60 ml/min. The minimum temperature was -80 °C and the maximum temperature was 180 °C, well below the degradation temperature of the compound.

Surface morphology

The PEPC forms a microdisk-like morphology with an average lateral size of 3 μm (Figure 4.7a). The topology analysis of the thin film of PEPC was carried out using AFM measurements as shown in Figure 4.7b, which confirms the thicknesses of the disks to be around 60 nm. Figure 4.8a demonstrates transmission electron microscopic (TEM) image of the PEPC nanoparticles. The spherical nanoparticles formation with size ranging from 2 to 20 nm was observed with average, particle size of $\sim 6 \pm 1\text{ nm}$. The high resolution transmission electron microscopy (HRTEM) image as shown in Figure 4.8b displayed lattice fringes of 0.282 nm, which can be indexed to the (006) plane of the triclinic PEPC. The d-spacing in the PEPC nanoparticles was calculated using the reciprocal lattice of the selected area electron diffraction (SAED) pattern as shown in Figure 4.8b, is in good agreement with the values calculated from the powder XRD data.

Figure 4.7. (a) Field emission electron microscopic (FESEM) and (b) Atomic microscopic image of PEPC thin film deposited using a 0.20 M precursor solution. (c) Height profile of the microdisks.

Figure 4.8. (a) Transmission electron microscopic (TEM) image. (b) Selected area diffraction pattern of PEPC nanoparticles.

4.2.2 Photophysical characterizations

Steady state PL measurements

Figure 4.9a shows the absorption spectra of a PEPC thin film and a nanoparticle solution in toluene. The strong excitonic nature of the samples, as a result of dielectric confinement, give rises to a sharp absorption peak at ~ 340 nm which is characteristic of 2D lead halide perovskites.²⁶ Upon resonantly irradiating the excitonic state with 340 nm UV femtosecond pulses, a broad photoluminescence (PL) peaks spanning from ~ 400 nm to ~ 900 nm were noted for PEPC samples prepared in the all various forms i.e. as a single crystal, thin film, powder, and nanoparticles (Figure 4.9b). Photograph of the white light emission excited using 340 nm was shown as an inset of (Figure 4.9b). The PL spectra for PEPC samples prepared in four different forms are almost invariant, and these data suggest an intrinsic origin to the broad emission. However, the photoluminescence quantum efficiency (PLQE) of PEPC prepared using in various forms was measured and found to be less than 1%.

Figure 4.9. (a) Steady-state absorption spectra of PEPC thin film and nanoparticle samples, each showing a strong narrow absorption peak that is characteristic of a strongly confined excitonic system. (b) Steady-state PL spectra of PEPC nanoparticle (NP) solution, powder, thin film, and single-crystal samples, each showing a broad emission that ranges from ~ 400 to ~ 900 nm. The inset shows the photograph of the white light emission excited using 340 nm.

The valence band maximum (VBM) of PEPC was estimated to be -5.6 eV using photoemission spectroscopy in air (PESA) (Figure 4.10) and the conduction band level was calculated as -2.04 eV using the optical band gap of material (3.56 eV). The VBM of this material is almost the same as the VBM of PEPB, which indicates that the halide variation does not influence the VBM.²³

Figure 4.10. Photoemission spectroscopy in air (PESA) analysis of a thin film of PEPC and the inset shows the energy level diagram. Room temperature Raman spectrum in the frequency range of 300 to 1500 cm^{-1} . The labeled Raman frequencies agree with the Raman modes of phenethylammonium chloride ²⁷.

Time-resolved PL (TRPL) measurements

Figure 4.11. (a) Time-resolved PL (TRPL) spectra of the PEPC samples prepared in single crystal, powder, thin film and nanoparticle form measured at ~ 545 nm. The experiments were conducted using 340 nm laser excitation [50 fs, 1 kHz, 7 $\mu\text{J}/\text{cm}^2$ (time-integrated PL) or 15 $\mu\text{J}/\text{cm}^2$ (time-resolved PL)]. (b) TRPL spectra recorded at emission wavelengths of 480, 545, and 610 nm and excited using a 340 nm beam with a laser fluence of 15 $\mu\text{J}/\text{cm}^2$ for a sample containing single crystals. There was no observable change in the average lifetime (~ 3 ns) among the various samples for the measured wavelengths. The inset shows a photograph of the single crystal with dimensions of $\sim 3 \text{ mm} \times 3 \text{ mm}$.

The PL lifetimes measured at the peak position (~ 545 nm) for the thin film, powder, and nanoparticle solution of PEPC were found to be similar to an average lifetime (among these samples) of 4.2 ± 0.9 ns (Figure 4.11a) and also suggested that the surface-to-bulk ratio has

little influence on the decay kinetics. TRPL spectra for a PEPC single crystal measured at three different wavelengths (480, 545, and 610 nm) were also found to be similar to an average lifetime of 3.0 ± 0.4 ns, which suggest emission from the same origin (Figure 4.11b). These results confirm the intrinsic nature of the broad emission.

Figure 4.12. (a) PL Spectrum of PEPC thin film excited with 300 and 340 nm continuous wave source. (b) CIE 1931 coordinates of the samples excited with either 300 nm continuous wave (for thin film sample) or 340 nm pulses (for powder, nanoparticles, single crystal and thin film samples) source.

The PL spectrum excited using a 340 nm continuous wave excitation (generated using a xenon arc lamp) shows a peak blue-shifted with CIE 1931 coordinates in the white region (Figure 4.12a). On the other hand, the CIE 1931 coordinates for the emission excited with femtosecond pulses were found to be in the yellow to orange region on the CIE 1931 color space instead (Figure 4.12b). CW excitation causes significant lattice heating, which introduces higher degrees of interband phonon absorption that blue-shifts the peak.

4.2.3 Density Functional theory calculations

Previously, Ueda *et al.* has reported the disorder in the orientation of phenethylammonium cations in PEPC using ^1H and ^{13}C NMR studies.²⁸⁻²⁹ Different orientations of PEA cations could possibly affect the band structure of PEPC dramatically and could be a source of the white light emission.

Figure 4.13 Crystal structures of PEPC after full relaxation in DFT-GGA calculations (with vdW and SOC), viewed along $\mathbf{a} \times \mathbf{b}$ in panels (a) and (b), and along $\mathbf{b}$ directions in panels (c) and (d). Orientation 1 is in panels (a) and (c), while 2 is in panels (b) and (d).

The density functional theory (DFT) calculations were conducted to examine the effects of the orientation on the band structure. DFT calculations based on the generalized gradient approximation (GGA) predict that PEPC should have a direct band gap at the origin of the Brillouin zone, Γ (Figure 4.14). The calculations based on DFT-GGA underestimate the band gap by about 1.4 eV when spin orbit coupling (SOC) and van der Waals (vdW) corrections were included, compared to the experimental optical band gap value of 3.56 eV. However, the relative predicted band characters should be realistic. Although most frontier electronic bands disperse significantly, some up to about 1 eV along directions in or close to the inorganic layer, those along the stacking direction (Γ -M in Figure 4.14) are much flatter, and in some cases approximately constant throughout the Brillouin zone.

Figure 4.14. Electronic density of states (top row) and band structure (bottom row) of PEPC in orientation 1 (panels (a)-(c)) and 2 (panel (d)). In the panel labels, O1 and O2 denote orientations 1 and 2, no SOC and SOC denote without and with Spin orbit coupling included, while no vdW and vdW denote without and with van der Waals correction added, respectively. Note that in each panel the axis scale for the total/site projected DOS (the left most sub-axis) is different from those for the orbital projected DOS (the three sub-axes to the right) zone.

This feature of nearly dispersionless bands in the direction perpendicular to the layers has been observed and suggested to correspond to poor inter-layer charge transport in many previous studies of related 2D hybrid perovskites.³⁰⁻³⁴ Near the valence band maximum (VBM), the bands are predominantly of Pb 6s character with some hybridization with Cl 3p states, while those near the conduction band minimum (CBM) have predominantly Pb 6p character, again with some hybridization with Cl 3p states.

Table 4. 2Band gap, total energy, atomic volume, and lattice parameters of PEPC

Orientation	vdW	SOC	Band	Total	Atomic	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
			gap ²	energy ³	volume						
			(eV)	(eV/cell)	(Å ³ /cell)						
1	no	no	3.18	12.614	2237.3	11.26	11.37	18.23	99.0	103.8	90.0
1	no	yes	2.39	11.213	2236.2	11.25	11.37	18.23	99.0	103.8	90.0
1	yes	no	3.07	1.419	2047.0	11.00	11.11	17.46	99.2	103.5	90.0

Theory ¹ (DFT-GGA)	1	yes	yes	2.27	0.000	2046.8	11.00	11.11	17.47	99.2	103.5	90.0
	2	no	no	3.12	13.006	2303.7	11.31	11.39	18.68	98.7	104.1	90.0
	2	no	yes	2.39	11.509	2323.2	11.28	11.37	18.84	98.7	103.2	90.0
	2	yes	no	3.01	2.070	2111.2	11.14	11.17	17.62	99.1	102.6	90.0
	2	yes	yes	2.11	0.638	2111.2	11.14	11.17	17.62	99.1	102.6	90.0
Experiment				3.56 ^b		2091.9	11.12	11.20	17.59	99.2	104.5	90.0

¹Values calculated with vdW and SOC are given in shaded cells and bold fonts, respectively.

²Optical and fundamental (electronic) band gap from theory and experiment, respectively.

³All referenced to the value for orientation 1 calculated with vdW and SOC.

As in other Pb containing hybrid perovskites, SOC has a large effect on the electronic structure of PEPC, leading primarily to a lowering of the energies of Pb 6p states and their hybridized Cl 3p states with respect to VBM, hence reducing the band gap by 0.7-0.9 eV for PEPC.

The vdW interactions also affect the electronic structure, presumably due to their substantial effect on the inter-layer spacing. Without vdW corrections, DFT-GGA significantly overestimates the atomic volume and interlayer lattice constant *c* relative to experimental measurements, as shown Table 4. 3, which indicates that vdW interactions play a large role in maintaining the structure of such 2-D layered materials.³⁵ As a result of the significant change in lattice constant, the band gap is also reduced by about 0.1 eV when vdW corrections are included in the calculations.

The bands near the VBM and CBM show negligible contributions from the organic PEA cations (Figure 4.13). However, the different orientations of the PEA cations are found to affect mainly the energy of Pb 6s valence bands, leading to changes of the band gap and also the total energy of PEPC. More specifically, Pb 6s bands are more energetically dispersive when they are in orientation 2 compared to orientation 1 (Figure 4.13), while the conduction bands on the other hand are observed to be less affected. The net effect is that the band gap is decreased by merely 2.27 - 2.11 = 0.16 eV, and the total energy is increased by 0.638 eV/cell in orientation 2, as calculated with DFT-GGA including SOC and vdW corrections. Thus, the band gap fluctuation (587 nm - 546 nm = 40 nm) induced by disordered organic cation is unlikely to be the main cause of the broadband white-light emission, which extends from 400 nm to 900 nm. However, this band gap fluctuation could play a role in broadening the photoluminescence spectrum.

4.2.4 Experimental Evidence of Broadband Emission PL and TRPL measurements

Figure 4.15. Monomolecular recombination (excitonic) in PEPC single crystals. (a) Laser fluence-dependent TRPL spectra of PEPC single crystals in the range of 15–210 $\mu\text{J}/\text{cm}^2$ measured at an emission wavelength of 545 nm. (b) TRPL peak intensities as a function of laser fluence measured at 480, 545, and 610 nm emission wavelengths showing linear behavior. Each experiment was conducted using 340 nm laser excitation (50 fs, 1 kHz).

The decay profiles of PEPC single crystals for the respective laser fluences are shown in Figure 4.15a. with little variation in the kinetics with an increasing laser fluence. The nature of the species contributing to the broad emission can be investigated by monitoring the change in peak TRPL intensity with laser fluence.

Figure 4.16. Self-trapped excitons in PEPC. (a) Temperature-dependent PL spectra of PEPC single crystals. The inset shows the overlaid normalized PL spectrum of PEPC at 20 and 300 K. (b) Integrated PL intensity (black) and fwhm (black) as a function of temperature. The black and blue points are fitted with eqs 1 and 2, respectively. The PL and TRPL measurements were conducted using 340 nm excitation and $3.5 \mu\text{J}/\text{cm}^2$ laser fluence (50 fs, 1 kHz). (c) Pseudocolor TA plot of a PEPC single crystal showing the change in absorption (ΔA) as a function of probe wavelength and probe delay time. (d) TA kinetics of a PEPC single crystal probed at 500, 600, and 700 nm. The inset shows ΔA as a function of probe wavelength at selected delay times. The TA measurements were conducted using 340 nm excitation and $\sim 25 \mu\text{J}/\text{cm}^2$ laser fluence (150 fs, 1 kHz).

A linear dependence between the initial time PL intensity and the laser fluence measured at 480, 545, and 610 nm (Figure 4.15b) can be observed, which suggests monomolecular excitonic recombination taking place. The similar linear trends observed for these three wavelengths also support the assignment of broad emission from identical species. The lack of steady-state PL saturation from the PEPC single crystals also suggests that the emission is not likely to be solely trap-related.

Figure 4.16a shows the temperature-dependent PL spectrum of PEPC single crystals. As the temperature is lowered, the emission intensity increases with a slight narrowing of the full

width at half-maximum wavelength (fwhm) (Figure 4.16, inset). However, such changes do not introduce significant change into the CIE 1931 chromaticity coordinates when the temperature is lowered. Two main processes (with two activation energies) were found to be responsible for the increase in integrated PL intensity with a decrease in temperature (Figure 4.16). The activation energies were obtained using Arrhenius fitting [with a minimum of two exponentials (Figure 4.17 for fitting details) of the form

$$I(T) = \frac{I_0}{1 + Ae^{\frac{E_A}{k_B T}} + Be^{\frac{E_B}{k_B T}}} \quad (1)$$

where I_0 is the integrated PL intensity at 0 K (T), A and B are the pre-exponential amplitudes, k_B is the Boltzmann constant, and E_A and E_B are the average activation energies responsible for the broad emission. The fitting yields an adjusted R2 value of 0.997. The first process, having a small activation (E_A) of 12 ± 1 meV, is likely to be a bound exciton detrapping process. Below 140 K (or equivalently 12 meV), these bound excitons do not have sufficient energy to be converted back to free excitons, giving rise to a higher bound exciton PL intensity. This small activation energy is also comparable to the previously reported value in broad emitting 2D perovskite. On the other hand, the second process possesses a much larger activation energy (E_B) of 120 ± 10 meV. This large energy can be interpreted to be (a) the difference in energy between a free exciton and a bound excitonic state, (b) the difference in energy between a bound excitonic state and the conduction band minimum, or (c) the energy of phonons responsible for nonradiative recombination.

Figure 4.17. (a) Plot of $\ln [(I_0 / I)-1]$ Vs $1 / T$ (K⁻¹) based on data shown in **Figure 4.16b**. The symbols I , I_0 and T have the same meaning as those in equation (1) in the main text. (b)

Temperature-dependent PL kinetics of PEPC single crystals showing significant PL lifetime lengthening at low temperatures. The experiment was conducted using 340 nm excitation with a laser fluence of 3.5 $\mu\text{J}/\text{cm}^2$.

Both hypotheses (a) and (b) can be eliminated because the binding energy in PEPC systems is at least ~ 400 meV.³⁶ The hypothesis c is likely to be responsible for the large activation energy of 120 ± 10 meV (or 968 ± 80 cm^{-1}) as this energy corresponds well to an organic phonon mode²⁷ measured using Raman spectroscopy (Figure 4.17). Therefore, the decrease in PL intensity at higher temperatures is likely due to an increased level of nonradiative recombination (indirect recombination) caused by phonon absorption. The increased level of nonradiative recombination is also reflected in the temperature dependent PL spectrum where significant lifetime shortening is observed at higher temperatures (Figure 4.17) and could also possibly account for the low PLQE of PEPC at room temperature.

In addition, the increased level of nonradiative recombination at higher temperatures could also be due to effects from thermal energy (25 meV) and/or tunnelling processes (probabilistic process with little activation energy required), even though they are not reflected strongly in our experimental findings. The broadening in the fwhm with an increase in temperature can be attributed to a carrier scattering process and can be described using the equation 2.¹⁹

$$\Gamma(T) = \Gamma_0 + \Gamma_{LO}(e^{E_{LO}/k_B T} - 1)^{-1} + \Gamma_{inh}e^{-E_A/k_B T} \quad (2)$$

where Γ_0 is the fwhm at 0 K (T), Γ_{LO} is the exciton LO phonon coupling constant, E_{LO} is the longitudinal-optical phonon energy, and Γ_{inh} is the inhomogeneous broadening coefficient. The second and third terms account for exciton phonon coupling and inhomogeneous broadening (due to the self-trapping) interaction terms, respectively. Herein, we assume that the bound exciton trapping originates from defects responsible for fwhm inhomogeneous broadening. A good fit (with an adjusted R2 value of 0.995) can be obtained using the following parameters: $\Gamma_0 = 581$ meV, $\Gamma_{LO} = 265 \pm 80$ meV, $E_{LO} = 54 \pm 6$ meV, $\Gamma_{inh} = 90$ meV, and $E_A = 12$ meV (Figure 4.16b).

Three conclusions can be obtained from the fitting. (i) The value of Γ_{LO} is approximately twice as large compared to the value obtained from previous broad emitting 2D perovskite (130 ± 7 meV)¹⁹ and comparable to ZnO quantum wells,³⁷ which suggests strong exciton phonon coupling in PEPC. (ii) The LO phonon energy obtained from the fitting coincides well with the

60 meV Raman mode of the organic cation ²⁷ (Figure 4.10b), which is a prerequisite for exciton-phonon coupling to occur. (iii) There exists a self-trapping potential barrier (~ 10 meV) for scattering. Because self-trapped excitons can be treated as bound excitons, the small activation obtained from Arrhenius equation fitting can therefore be assigned to the self-trapping barrier energy. Unlike the conclusion of Hu et al. who found self-trapped excitons were attributed to solely the inorganic lattice ³⁸, here the findings indicate that there are major contributions from the organic framework. As such, both the organic and inorganic constituents are important for generating white emission. This was also supported by prior literature, where broad emission is observed by changing either the organic (e.g. (i) (*N*-MPDA)[PbBr₄] to (*N*-MEDA)[PbBr₄]^{20,33} and (ii) PEPB to (C₆H₁₁NH₃)₂PbBr₄²¹) or inorganic components (e.g. (i) PEPB³⁹⁻⁴⁰ to PEPC (this work) and (ii) EDBE(PbI₄) to EDBE(PbCl₄)¹⁹). Further evidence of self-trapped excitons can also be observed using transient absorption spectroscopy. Figure 4.16c shows the pseudocolor TA plot of PEPC single crystals as a function of probe wavelength and probe delay time. A broad featureless photo-induced absorption (PIA) plateau can be observed across the visible probe region (Figure 4.16d inset) and this is consistent with a previous report.³⁸ The kinetics probed at a few visible wavelengths (500, 600, and 700 nm) shows no significant changes in lifetimes (Figure 4.16d) and is consistent with the invariant PL lifetime measured at different wavelengths (Figure 4.11f).

Figure 4. 18. Schematic representation of the main mechanism responsible for broadband emission in the self-trapping process, the excitons scatter off the lattice that results in a shift and broadening of the exciton line.

The broad PIA plateau together with the invariant lifetimes suggest that the probed state cannot be directly excited and populated via transfer from intermediate states. This is also consistent with the self-trapped exciton assignment. In addition, the rise time of these PIA kinetics (limited by the laser pulse width) was fitted to be 100 fs. This value is in the same order of magnitude as the vibrational period of 69 fs (or 60 meV), which is the estimated formation time of the self-trapped excitons.

It is the phonon energy that allows determination of the self trapping location. As such, both the organic and inorganic constituents are important for generating white emission. Schematic representation of the main mechanism responsible for broadband emission in the self-trapping process the excitons scatter off the lattice that results in a shift and broadening of the exciton line depicted in Figure 4. 18. The presence of these excitons results in lattice deformation. The ensuing lattice stabilization gives rise to the self-trapping. As such, the presence of phonon is important for self-trapping, and could be generated via two methods: thermally generated phonon and exciton relaxation.

The thermally generated phonon population (N_{phonon}) can be described by:

$$N_{phonon} = [\exp(\frac{\hbar\Omega_{phonon}}{k_B T}) - 1]^{-1} \quad (3)$$

and is temperature dependent. It reduces at low temperature. On the other hand, phonon emission (Figure S15 - purple arrows), which is independent on phonon occupation number, still plays a role as scatter in the white emission. This means that phonon creation (emission) through phonon creation operator ($a^\dagger$):

$$a^\dagger |n\rangle = (n+1)^{1/2} |n+1\rangle \quad (4)$$

is temperature independent. Consequently, one still observes a broad band emission in Figure 4.16a - (phonon emission is still possible from relaxation of self-trapped excitons to the band minimum – Figure 4. 18- purple arrows) even at low temperatures.

4.2.5 Material stability

Photostability of PEPC

Figure 4.19. Photostability of PEPC and generation of near pure white emission. Room temperature PL peak intensity variation of with continuous 340 nm excitation for ~14 hours for PEPC and ~6 hours for PEPB in N₂ environment using a laser fluence of 2.1 $\mu\text{J}/\text{cm}^2$. Inset shows the normalized PL spectrum of PEPC and PEPB at the time = 0 h.

A broad emitting thin film that demonstrates good photostability and solution processability is ideal for white light-emitting devices applications. PEPC, being a candidate that is solution processable, is attractive for this purpose. However, its photostability has not been reported. Therefore, the photostability of a PEPC thin film was assessed by monitoring the emission peak intensity as a function of time under UV fs laser irradiation in N₂ environment with fluence 2.1 $\mu\text{J}/\text{cm}^2$ at a 1 KHz repetition rate.

After ~14 hours of continuous excitation (or 10^5 laser shots), the thin film showed no significant reduction of peak intensity (Figure 4.19) with a mean and standard deviation value of 0.98 and 0.05 respectively. This measurement demonstrates the photostability of PEPC thin films under UV excitation. This is in contrast to its bromide variant (PEPB) where poor photostability (a reduction in ~80% of PL peak intensity after ~6 hours) is observed with UV excitation (Figure 4.19). The observation of poor photostability in PEPB under UV excitation has also been reported previously by Wei *et al*⁴¹.

Analysis of effect of X-site ion

Room temperature broadband emission over 400nm-900 nm spectral region was observed for 2D PEPC, however narrow band emission was noted for 2D PEPB and PEPI. The broadband

emission noted in PEPC is attributed to strong exciton-phonon coupling with the organic lattice. It is independent of surface defects present.

Therefore, temperature dependent PL analysis of 2D PEPI and PEAB are also discussed in order to understand their excitonic behaviour and hence the resultant emission.

Figure 4. 20. Temperature dependent PL spectrum of PEPI at temperature range 10K to 300 K, shows two distinct emission peaks (peaks 1 and 2). (b) Integrated PL intensity at different temperatures for peak 1 and peak 2.²²

Temperature dependent PL spectra of PEPI exhibited two distinct emission peaks (peaks 1 and 2) (

Figure 4. 20) at ~ 525 nm and ~ 532 nm. The intensity of the peak 2 was observed to be increased by lowering the temperature (

Figure 4. 20a). The origin of peak 1 and peak 2 was attributed to the free excitons, arises from surface bound excitons, and surface bound biexcitons respectively (

Figure 4. 20b).²²

Figure 4. 21 Room temperature steady state PL spectra of the 2D PEPB microplates and thin film. The PL intensity of PEPB microplates was higher than that of the thin film at an identical excitation condition. The fluorescence image of a typical PEPB microplate shown as an inset, $5 \mu\text{m}$. b) Temperature dependent PL spectra of PEPB from 78 to 298 K ranging from 2.7 to 3.5 eV. c) A magnification of temperature dependent PL spectra ranging from 2.7 to 3.5 eV.⁴²

On the other hand, efficient purple-blue emission with narrow linewidth (~ 11 nm) has been reported for PEPB microplates at room temperature, which was due to the band gap transition (Figure 4. 21a). A broad emission peak at low energy region (~ 2 eV) was noted at lower temperature, which was further diminished as the temperature was increased above 238 K (Figure 4. 21b). The presence of the broad emission can be ascribed to trap states in PEPB, resulted from the electron-phonon coupling at the surface. In addition, a slight red shift in the band gap peak position was reported with respect to temperature (Figure 4. 21c). This behaviour is quite common in the most of semiconductors.⁴²

Overall, the excitonic recombination mechanism observed in PEPI, PEPB and PEPC are dissimilar. The changing the X site anion in the perovskite structures affect on their crystallinity, morphology, optical, electronic properties as well as excitonic recombination behaviour.

4.2.6 Summary

Broadband emission from organic-inorganic hybrid perovskites results from the formation of self-trapped exciton and this could be induced by lowering the dimensionality of the hybrid perovskites. Phenethylammonium ion with different halides ions (Cl, Br and I) were utilized to prepared lower dimensional corrugated structures. 2D corrugated perovskite structures prepared using the 2D phenethylammonium lead chloride (PEPC) in four different forms and all exhibit white light emission as compared to that of 2D PEPI and 2DPEPB. It has been realized that nature of halide ions affect the optical properties significantly. DFT calculations and PL measurements showed that the emission arises from the self-trapped exciton and not from the band gap fluctuation that occur due the disordered orientation of the ammonium cations or any surface related trap states. The broadband emission was found to originate from self-trapped excitons predominantly in the organic lattice. These solution-processed materials also possess high color rendering indices, good CIE coordinates, and excellent photo-stability, which are desirable for cool, white light LED applications. Here the importance of judiciously selecting both the organic and inorganic components in 2D perovskites for white light emission was highlighted.

However, it has been observed that the PLQY of the material is less than 1%. Hence it is necessary to explore the different compositions to achieve broadband emission with improved

PLQY. Meanwhile, it has been demonstrated that a lead-free metal halide based 0D perovskites exhibited broadband emission with a near unity PLQE.⁴³⁻⁴⁴ Hence, in the subsequent work, OD lead perovskites was synthesized. Therefore, the phenethylammonium halide cation was replaced with the *meta* and *para*-xylylenediammonium cations to synthesis a ‘Molecular level’ 0D perovskites in form a corrugated structures to achieve white light/broadband emission as well as high PLQY. In addition, the aim was also to study the effect of ‘A’ site cation on the broadband emission.

4.3 Effect of A-site cations (*m*-XDALB, *p*-XDALB and *m*-XDALCl)

The development of hybrid low dimensional perovskite materials for solid-state lighting (SSL) is especially appealing since they typically show broadband emissions which are due to triplet state of metal-centered electronic transition that occurs in molecular zero-dimensional (0D) perovskite and formation of self-trapped excitons in semiconducting 1D and 2D perovskites.^{19, 44-48} However, many reports of semiconducting 1D and 2D lead halide perovskites were reported in the last few years. These perovskites form free excitons (FE) under photoexcitation, due to the dielectric confinement by the organic ammonium layers, and these FEs becomes self-trapped excitons (STEs) when the FEs couple to phonons. This phenomenon is especially significant when the metal halide octahedra are severely distorted from the plane of inorganic layer and the dimensionality of the perovskites is lowered.⁴⁹⁻⁵⁰ Subsequently, the STE will broaden the emission spectrum and also produce a large Stokes-shift.

Zero dimensional (OD) perovskites

The efficient broadband emitting materials using shorter chain alkylidiammonium cations (N1-methylethane-1,2-diammonium (N-MEDA)) and N1-methylpropane-1,3-diammonium (N-MPDA) as templating agents were demonstrated to form corrugated lead halide layers in bulk crystalline materials by Hemamala and co-workers.²⁰ The use of N-MEDA, the short length organic cation, effective in stabilizing the (110) perovskite structure through hydrogen bonding with halides in the adjacent inorganic sheets, while a longer N-MPDA cations can easily separate inorganic sheets in the adjusting layers and stabilize (001) perovskite structures (Figure 4.22). Although, both the perovskites, synthesized using N-MPDA and N-MEDA, exhibited a sharp excitonic absorption at 420 nm and 395 nm respectively. However a broad emission over the whole visible range was noted for the later one, which is attributed to greater electronic confinement of the corrugated sheets.²⁰

Thus the shorter alkyldiammonium cations create the out-of-plane distortion to may direct the assembly of corrugated lead halide layers, while the longer alkyldiammonium cation has more flexibility, hence failed to create the out-of-plane distortion. Thus the A-site cation is also responsible tuning the broadband emission in the lower dimensional perovskites.

Figure 4.22. Representation of X-ray structures a: (001) (N-MPDA)[PbBr₄] and (b) (110) (N-MEDA)[PbBr₄] perovskites (N-MPDA = N1-methylpropane-1,3-diammonium and N-MEDA = N1-methylethane-1,2-diammonium) along with the 3D methyl ammonium bromide perovskite (MAPbBr₃). Reprinted form permission from ²⁰.

In the previous part of the broadband emission study, a white light emission from a 2D perovskite, (C₆H₅C₂H₄)₂PbCl₄ (PEPC), was likely originated from strong coupling of excitons to the organic framework.⁴⁸ The white light emission has also been observed from the 1D perovskite C₄H₁₄N₂PbBr₄ with a PLQE of 20%.⁵¹

In addition, semiconducting 1D and 2D perovskite thin films possibly can be derived by spincoating the 0D perovskite solution with excess of metal halides. Hence, it is possible to study and compare the emissions from triplet state of structurally deformed metal halide molecular complex present in the 0D perovskite and from STE of the semiconducting higher dimensional (1D or 2D) perovskites as shown in Figure 4.23. In the initial set of study, perovskites formation were carried out by utilizing *meta* and *para* xylylenediammonium halide ions to select the potential candidate to achieve broadband emission. Structure of *m*-/ *p*-xylylenediammonium halide ions are shown in Figure 4.24. Accordingly, zero dimensional (0D) perovskites namely *meta* and *para*-xylylenediammonium lead bromide (NH₃CH₂C₆H₄CH₂NH₃)₂PbBr₆, *m*-XDALB/*p*-XDALB) and *meta*-xylylenediammonium lead chloride (NH₃CH₂C₆H₄CH₂NH₃)₂PbCl₆, *m*-XDALC) perovskites were synthesized to understand the effect of A site cation.

Figure 4.23. Representation of the emissions from triplet state of structurally deformed metal halide molecular complex present in the 0D perovskite and from self-trapped exciton (STE) of the semiconducting higher dimensional (1D or 2D) perovskites

Figure 4.24. Structure of *p/m*-xylylenediammonium halide ions

Synthesis of Single crystals of *m*-XDALB, *p*-XDALB and *m*-XDALCl

The single crystals of *m*-XDALB, *p*-XDALB and *m*-XDALCl were prepared using well established anti-solvent vapor assisted crystallization method. In brief, the perovskite precursor solution prepared by mixing one millimole of PbX_2 and two millimole of *m* and *p*-xylylenediammonium bromide/chloride in DMF was ultrasonicated to form a clear solution. Each of the solutions was then incubated in a chamber saturated with the vapor of the anti-solvent, which produced good quality crystals of *m*- and *p*-xylylenediammonium lead halides suitable for single crystal X-ray diffraction. Isopropanol and diethyl ether were used as the anti-solvent for the growth of the chloride and bromide crystals respectively and the crystals were formed after one week. All the compounds grew in the monoclinic crystal system with molecular formulae of $(m\text{-XDA})_2PbBr_6$, $(m\text{-XDA})_2PbCl_6$ and $(p\text{-XDA})_2PbBr_6$.

Table 4.3 Preliminary screening of zero dimensional (OD) perovskites namely *m*- and *p*-xylylenediammonium lead bromide (*m*-XDALB, *p*-XDALB) and *m*-xylylenediammonium lead chloride (*m*-XDALC) to achieve broadband emission.

Perovskites	PL Emission (nm)
<i>m</i> -XDALB	400 - 500
<i>m</i> -XDALB + PbBr ₂	450 - 650
<i>p</i> -XDALB	Limited by the solubility of the precursors
<i>m</i> -XDALC	400 - 500

However poor solubility of *p*-XDALB in common solvents (i.e. dimethylformamide (DMF) and dimethylsulfoxide (DMSO)) limited its further optical characterizations. Therefore, more attention was paid on the *m*-XDALB, and *m*-XDALC perovskites characterization as discussed below.

4.3.1 Structure identification and characterizations

Figure 4. 25 Crystal structure of “0D” perovskites. Projection of meta-xylylenediammonium lead chloride (*m*-XDALC) along (a) a- and (b) b-axis, showing the isolated PbCl_6^{4-} octahedral unit and ammonium cations arranged in alternating layers. (c) and (d) show the unit cells of meta-xylylenediammonium lead bromide (*m*-XDALB) along the a- and b-axis respectively, displaying the organic ammonium cations intercalating between the “0D” lead bromide. The Pb, Cl, Br, and N atoms are represented in black, green, yellow, and blue respectively.

The crystal structures were illustrated along two different axes i.e. a and b in Figure 4. 25. Figure 4. 25a & Figure 4. 25c depicted how the XDA dications intersperse between and stabilize the isolated PbX_6^{4-} octahedral units. On the other hand, Figure 4. 25b & Figure 4. 25d show how the ammonium groups of the XDA cations were spatially trans to each other, and the dications stack parallel to one another. The ammonium groups of the *m*-XDA dications appear to be hydrogen bonded to three halides of three different octahedral PbX_6^{4-} units (Figure 4.26a & Figure 4.26d). Each PbX_6^{4-} unit was crystallographically centrosymmetric with three distinct Pb-X bond lengths, which vary from 2.875 to 2.910 Å for XDALC (Figure 4.26) and from 3.012 to 3.044 Å for the XDALB system Figure 4.26e). In addition, the bond angles for the cis-halides vary from 82.36 to 97.64° in the chloride (Figure 4.26c) and from 81.70 to 98.30° in the bromide system Figure 4.26d), but the trans halide bond angles are all 180° due to the crystallographically imposed symmetry. Daniele et al. have used a quantitative evaluation of the octahedral distortion reported previously and discovered that larger distortions resulted in broadband emission.⁵²⁻⁵³ However, it may has correlation with Stokes' shift and FWHM of the photoluminescence and this will be discussed later. In this case, the variance in octahedral angles σ_{oct}^2 and the octahedral elongation λ_{oct} are calculated to be 33.76° and 1.0092 Å for *m*-XDALC, and 36.38° and 1.0099 Å for *m*-XDALB, which indicate significant distortion from the idealized octahedral geometry.

Figure 4.26. *m*-XDALC and *m*-XDALBr (a & d) -The hydrogen bonding of ammonium protons to three chlorides of three different octahedral PbCl_6^{4-} units. (b & e) and (c & f) show the isolated PbCl_6^{4-} octahedral unit with bond lengths and bond angles respectively.

Nuclear Magnetic Resonance Spectroscopy

The ^{207}Pb NMR spectrum of *m*-XDALB was shown in Figure 4.27b. It contains a single ^{207}Pb component, where $\delta_{\text{iso}} = 595 \pm 1$ ppm, that was split into a multiplet via ^{207}Pb - $^{79/81}\text{Br}$ J-coupling. An agreeable fit of the multiplet was achieved by simulating the spectrum of a single ^{207}Pb component bonded to six identical $^{79/81}\text{Br}$ sites; the details of the fit were given in Table 4.4. The J-coupling in *m*-XDALB was measured as $^1J(^{207}\text{Pb}$ - $^{79/81}\text{Br}) = 2.0 \pm 0.2$ KHz, which was coherent with reported lead halide J-couplings.⁵⁴⁻⁵⁵ The clarity of the observed ^{207}Pb multiplet indicates that the PbBr_6 octahedral unit was highly symmetrical in *m*-XDALB.

Figure 4.27. (a) The ^{207}Pb Hahn echo (static) NMR spectra of *m*-XDALB with the experimental spectrum and the simulated spectrum in blue and red respectively. (b) The ^1H MAS (12 KHz) and (c) the ^{13}C CPMAS (12 KHz) NMR spectra of *m*-XDALB.

Scalar spin coupling to halide nuclei is generally difficult to determine due to the rapid relaxation that characterizes such systems, which effectively decouples the nuclei.⁵⁶ It was therefore hypothesized that the isolated nature of the octahedra, results in a very rigid lattice, giving a slower relaxation of the $^{79/81}\text{Br}$ nuclei, allowing scalar spin coupling to occur.

Table 4.4 The ^{207}Pb NMR parameters of *m*-XDALB, determined via *J*-coupling spectral simulation.

The ^1H and ^{13}C NMR spectra of *m*-XDALB are shown in Figure 4.27b & Figure 4.27c respectively. The ^1H NMR spectrum presents with two broad resonances and three sharp resonances. The broad resonance at ~ 8 ppm contains the phenyl ring and ammonium hydrogen sites while the broad resonance at ~ 3 ppm represents the benzyl CH_2 hydrogens. These resonances were assigned as such in the previous study of *m*-XDATB. Therefore, the sharper resonances in the ^1H NMR spectrum were assigned as organic solvent residue. The sharper ^{13}C NMR spectrum presents with eight sharp resonances: the six resonances at higher frequency (138 - 131 ppm) belong to the phenyl ring whereas the two resonances at lower frequency (45 - 44 ppm) belong to the benzyl CH_2 group. The ^{13}C NMR data confirms the composition

$\delta_{\text{iso}}(^{207}\text{Pb}) / (\text{ppm})$	FWHM / (KHz)	$^1J(^{207}\text{Pb} - ^{79/81}\text{Br}) / (\text{KHz})$	#	<i>I</i>	Multiplet
595 ± 1	1.5 ± 0.2	2.0 ± 0.2	6	3/2	19

of the *m*-XDALB crystal. ^1H and ^{13}C NMR are analogous to that of *m*-XDALB without any visible impurities; ^{207}Pb does not show a multiplet as ^{207}Pb J-coupling to ^{35}Cl is smaller than to ^{81}Br ($1J(^{207}\text{Pb}-^{35}\text{Cl})=300\text{Hz}$)

X-ray diffraction

Simulated and experimental powder XRD patterns of *m*-XDALB and *m*-XDALC were shown Figure 4.28a & Figure 4.26 Figure 4.28b, which confirmed the monoclinic phase formation. The solubility of *m*-XDABr₂ was poor in DMF therefore dimethylsulfoxide DMSO was used to dissolve the ammonium salt and PbBr_2 and the resultant solution was spin coated on a quartz plate and then annealed at 100 °C. The thin film X-ray diffraction (XRD) pattern of the film shows an intense peak at a 2θ value of 8.9° , which is surprisingly inconsistent with the (100) peak of the monoclinic *m*-XDALB (Figure 4.26c).

Figure 4.28. Superimposed simulated and experimental powder XRD pattern of (a) *m*-XDALB and (b) *m*-XDALC. (c) Comparison of thin film XRD patterns of *m*-XDALB with increasing amounts of excess PbBr_2 in DMSO. (d) Thin film XRD data of *m*-XDALB spin-coated from a DMF solution

Thin films were prepared by systematically addition of 0 to 1 molar equivalents of excess PbBr_2 in increments of 0.16 moles, and the XRD patterns of all the films have been summarized in Figure 4.28c. Addition of excess PbBr_2 reduced the intensity of the unknown peak and concurrently increased the intensity of the peaks for the monoclinic *m*-XDALB. Unknown peak at 8.9° was almost disappeared in the film with 0.83 molar equivalents of excess PbBr_2 . However, PbBr_2 was further increased to 1.0 mole and this resulted in the formation of a new and strong peak at 7.9° . This strong peak is due to the formation of semiconducting higher dimensional perovskite with preferred orientation of crystal plane. It has been reported that DMSO form a solvated complex with lead bromide to produce the peak at the 2θ value of 8.9° .⁵⁷⁻⁵⁹ To verify this hypothesis, XRD was recorded by spun coating mXDABr film using

low concentration of DMF due to its poor solubility. However, the unknown peak at 8.9° appeared along with the peaks that corresponds to the formation of *m*-XDALB (Figure 4.28d). This suggests that the diffraction peak at 8.9° likely did not originate from a DMSO-solvated complex. In addition, it has also be confirmed that the unknown phase formation consisted of a different stoichiometry of PbBr_2 and *m*-XDABr₂. Therefore, excess of PbBr_2 added in an attempt to induce formation of the pure *m*-XDALB phase in the thin films. Indeed, addition of excess PbBr_2 to the perovskite solution was found to stimulate formation of the crystallographically characterized phase of *m*-XDALB in the thin films.

As the above prepared films were annealed at 100°C , therefore the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements of *m*-XDALB of thin films were conducted on powder samples to check the thermal stability. For thermal analysis the samples were precipitated from the solution of PbBr_2 and *m*-XDABr₂ in DMF with diethyl ether as an anti-solvent. The TGA thermogram of this material, collected up to 800°C , indicated that it was stable up to at least 250°C (Figure 4.29a). In addition, the DSC thermogram showed no evidence of a phase transition up to 200°C (Figure 4.29b), suggesting that the thin films annealed at 100°C should be stable.

Figure 4.29. (a) Thermogravimetric analysis (TGA) and (b) Differential scanning calorimetry (DSC) of *m*-XDALB. For thermal analysis the samples were precipitated from the solution of PbBr_2 and *m*-XDABr₂ in DMF with diethyl ether as an anti-solvent. The TGA measurement was carried out from 22°C to 800°C with heating rate at $10^\circ\text{C}/\text{min}$ in N_2 atmosphere. (b) Differential scanning calorimetry (DSC) was conducted at a rate of $10^\circ\text{C}/\text{min}$ under nitrogen flow rate of $60\text{ ml}/\text{min}$. The minimum temperature was -80°C and the maximum temperature was 200°C , which is well below the degradation temperature of the compound.

Figure 4.30. (a) Superimposed absorption spectra of *m*-XDALC & *m*-XDALB single crystals and *m*-XDALB thin film prepared using excess of PbBr₂. (b) Photoemission spectroscopy in air (PESA) of *m*-XDALB.

4.3.2 Modeling of Band Levels and Density of States

Powder XRDs of *m*-XDALB *m*-XDALC were confirmed before the crystals were used for photophysical characterizations. As shown in Figure 4.28a & b good match between the experimental data and simulated data was found. The absorption spectra of *m*-XDALC single crystals and *m*-XDALB powders exhibited narrow absorption bands with maxima at 280 and 310 nm for *m*-XDALC and *m*-XDALB respectively (Figure 4.30a).

In order to understand the band levels and band gap of *m*-XDALB, photoelectron spectroscopy in air (PESA) was conducted on powder samples and determined that the valence band maximum (VBM) was -6.06 eV relative to vacuum (Figure 4.30b). By using the band gap obtained from the Tauc plot, we calculated the conduction band maximum (CBM) to be -2.31 eV.

Subsequently performed DFT and TD-DFT calculations on the density of states and the optical absorption spectra to confirm the large band gap of “0D” perovskites. The density of states for the minimum energy configuration was determined using a denser 7x7x7 Gamma k-point mesh, as depicted in Figure 4.31. The calculated band gaps of *m*-XDALC and *m*-XDALB are 3.71 eV (or 334 nm) and 3.41 eV (or 364 nm), respectively. The calculated absorption spectra for *m*-XDALB showed a band maximum at 4.5 eV (276 nm), whereas *m*-XDALC exhibited two blue-shifted overlapping bands at 5.0 eV (248 nm), as illustrated in Figure 4. 32. This blue-

shift of absorption maxima in going from *m*-XDALB to *m*-XDALC was consistent with the trend of increasing band gaps in going up the halide group due to the expected lower density of states.

Figure 4.31. Density of states from DFT calculations for the “0D” perovskites. a) *m*-XDALC and b) *m*-XDALB.

Figure 4. 32. Predicted optical absorption spectra of *m*-XDALB and *m*-XDALC based on TD-DFT calculations.

4.3.3 Photophysical characterization

The PL and TRPL measurement were carried out using *m*-XDALB perovskite in order to understand the as broadband emission as discussed in the proceeding section.

Superimposed absorbance and PL spectra of *m*-XDALB thin film with different amount of PbBr_2 in moles. It clearly indicate that after addition of PbBr_2 in *m*-XDALB thin film observed the broadband emission (Figure 4.33 a and b). The PL spectrum of *m*-XDALB single crystal exhibits a broadband emission that covers from 400 nm to 500 nm with peak maximum at 440 nm, under the photoexcitation of 334 nm (Figure 4.33b). While the PL spectra of *m*-XDABr₂ (*m*-XDALB with excess PbBr_2 , *m*-XDALB + PbBr_2 (1.0mole) thin film exhibited a broadband emission in the visible region from 400 nm to 650 nm. (Figure 4.33c) The observed blue emission for *m*-XDALB single crystal was very weak at room temperature hence measurements were done at low temperatures as shown in (Figure 4.34b). As the temperature was lowered from 280 K to 80 K, the PL of *m*-XDALB single crystal was improved nearly 66 times without change in the PL profile. Similarly, the photoluminescence excitation spectra also showed enhancement of intensity as the temperature was lowered (Figure 4.34c). Generally, organic ionic crystals and metal-organic frameworks provides the rigid environments for the phosphorescent organic moieties, hence enhanced emission can be seen due to suppressed non-radiative decay of triplet excitons, from thermal, moisture, as well as molecular motions. In addition, densely packed crystal structure can protect the phosphorescence from oxygen quenching.⁶⁰⁻⁶¹ Hence, the PL spectra of crystalline *m*-XDABr at 80 K and found it to be emissive.

Figure 4.33. (a) Superimposed absorbance spectra of *m*-XDALB powder with of the 0.05 and 0.83 mole of PbBr₂ (b) Steady state PL spectra of *m*-XDALB with different amount of PbBr₂ (c) Steady-state PL spectra of *m*-XDALB single-crystal measured at 80 K, and *m*-XDALB thin film prepared with excess of 1.0 mole PbBr₂ measured at RT.

Figure 4. 34.(a) Temperature-dependent *m*-XDALB single-crystal PL under excitation wavelength at 334 nm (b) and (c) photoluminescence excitation (PLE) spectra for the emission maximum at 440 nm. PL of (d) *m*-XDALB and (e) *m*-XDABr₂ measured at 80 K.

PLE spectrum of *m*-XDALB measured at 80 K has three peaks at 295 nm, 320 nm and 330 nm and the last two peaks merges together with new peak maximum at 334 nm as the temperature is increased to 230 K (Figure 4.34b). Spectrum measured above this temperature were not clear due weak emission and scattering of light by the powder samples. The weak emission of *m*-XDALB could be due to the overlap of the PLE spectrum of the metal-centered process with absorption spectrum of charge-transfer process. PL and PLE measurements at 230 K shows Stokes's shift of 106 nm and FWHM of PL to be 70 nm, which was relatively small in comparison to other 0D perovskite reported so far. This could be due to the higher distortion

of molecular complex in its ground state indicated by its higher variance in octahedral angles σ^2_{oct} and the higher octahedral elongation so it has less room to exhibit structural distortion under photoexcitation. The narrow absorption bands observed in these samples can be attributed to MLCT/LMCT.

As shown in Figure 4.34c & d, PL spectra of *m*-XDABr₂ (*m*-XDALB with excess PbBr₂) at different excitation wavelengths Figure 4.34d), show emissions in the visible region from 400 nm to 650 nm with vibronic progression but the emissions from *m*-XDALB perovskite do not have vibronic progression (Figure 4.34d). The PL profiles of *m*-XDABr₂ and *m*-XDALB were also different, which undoubtedly indicate that the emission from the *m*-XDALB perovskite was from the metal-centered s-p transitions of Pb-Br octahedra whereas the emission from the organic ammonium bromide crystals could be due to crystallization-induced emission (CIE).

Semiconducting *m*-XDALB₂ thin film (*m*-XDALB + PbBr₂) was investigated to further understand the broadband emission that occurs due to self-trapping of exciton. The excitation wavelength of 360 nm was almost resonant with the excitonic absorption band, which ensures exciton formation and also contributions from the excitonic recombination in the broadband emission (Figure 4.35a). The broadband emission has CIE 1931 coordinates of (0.36, 0.40), which lies in the “white” region (Figure 4.35b). In addition, this emission possesses a good CRI of 82.9 and a CCT of 4805 K, suitable for cool white light applications. The excitonic decay kinetics at ~400nm for this white emitter was also distinctly longer lived compared to samples prepared using 0 and 0.5 equivalents of excess PbBr₂ (Figure 4.35c). Interestingly, the PL kinetics at 500, 550, and 600 nm were found to be invariant (Figure 4.35d) suggesting that a single species was responsible for a broad emission.

Figure 4.35. (a) PL spectrum of *m*-XDALB₂ thin film (*m*-XDALB + PbBr_2) white emitter excited using a 360 nm pulsed laser (50 fs, 1 KHz) with a fluence of 5.7 $\mu\text{J}/\text{cm}^2$. (b) CIE 1931 color plot showing the coordinates of the white emission for *m*-XDALB. (c) TRPL of *m*-XDALB thin films prepared using various amounts of excess PbBr_2 precursor (0, 0.5, and 1 mole). (d) PL decay kinetics of the white emitter measured at various wavelengths (550, 550, and 600 nm). The PL lifetime experiments were conducted using 310 nm pulsed laser excitation (50 fs, 1 KHz) with a fluence of 8.5 $\mu\text{J}/\text{cm}^2$.

4.3.4 Experimental Evidence of Broadband Emission

Time-resolved and variable temperature photoluminescence studies

Figure 4.36. (a) Temperature-dependent PL spectra from 300K to 20K of m -XDALB₂ thin film (m -XDALB + PbBr₂). The inset shows the emission peak intensity of free (400 nm) and bound excitons (600 nm). These bound excitons possess a de-trapping energy of 9.4 ± 0.7 meV. (b) Integrated PL. Color plot depicting the variation of PL intensity with temperature and wavelength for (c) broad emission (~ 600 nm), and (d) free excitonic (~ 400 nm). The experiments were conducted using 310 nm pulsed laser excitation (50 fs, 1 KHz) with a fluence of $4.2 \mu\text{J}/\text{cm}^2$. (e) CIE 1931 coordinates of m -XDALB₂ white emitter at different temperatures (boxed red). (f) Detailed variation of the coordinates as a function of temperature. The coordinates tend towards the white region near room temperature. The experiments were conducted using 310 nm pulsed laser excitation (50 fs, 1 KHz) with a fluence of $4.2 \mu\text{J}/\text{cm}^2$.

Figure 4.36a shows the temperature-dependent PL spectrum of the thin film. The variations in integrated PL intensity and FWHM with temperature are summarized in Figure 4.36b. Upon lowering the temperature, a steady increase in PL peak intensity was observed for the broad emission centered at ~ 600 nm (Figure 4.36a & c). On the contrary, the free excitonic PL intensity centered at ~ 400 nm undergoes non-monotonic behavior with a maximum at $T \sim 120$ K (Figure 4.36a inset & Figure 4.36d). The initial increase could be due to reduced non-radiative recombination of free excitons, while the subsequent decrease could be due to suppressed detrapping of bound excitons into free excitons (see discussion below). These PL spectral changes lead to deviation of the CIE 1931 coordinates from the white region at lower temperatures (Figure 4.36e & d).

The dependence of the broad PL integrated intensity with temperature can be described by a bi-exponential Arrhenius equation 1 (equation 1- *Kindly refer page 22*), E_A and E_B are the average activation energies of two independent processes that are responsible for the broad emission centered at ~ 600 nm. The values of E_A and E_B obtained from the fitting are 9.4 ± 0.7 and 57 ± 3 meV respectively. The fitting yields an adjusted R-squared value of 0.999 (Figure 4.36b). The smaller value of 9.4 ± 0.7 meV likely corresponds to the de-trapping energy of a bound exciton. At low temperatures, bound excitons do not have sufficient energy to overcome the trapping barrier for conversion into free excitons. The presence of this energy is consistent with the behavior of free excitons as shown in the inset of Figure 4.36a. As such, the broad emission may be partly attributed to recombination of bound excitons. The larger value of 57 ± 3 meV cannot be assigned to the bound exciton binding energy, i.e. the energy difference between a bound exciton and the conduction band minimum. Instead, this value likely corresponds to phonons responsible for non-radiative recombination. At low temperatures, the probability of phonon absorption for indirect recombination was reduced. This leads to

increased radiative recombination of the bound excitons, and hence an increase in the PL intensity. This reduction in non-radiative recombination at lower temperatures was also consistent with PL lifetime lengthening at lower temperatures (Figure 4.37a). Importantly, the reduction cannot be attributed to thermal dissipation (25 meV) or tunneling (negligible activation barrier). Additionally, the value of 57 ± 3 meV also coincides with a phonon mode in *m*-xylylenediamine (Figure 4.37b).

Figure 4.37. (a) Temperature-dependent PL decay kinetics of *m*-XDALB thin film with 1 mole equivalents of excess PbBr_2 . A significant PL lifetime lengthening is observed at low temperatures. The experiments were conducted using 310 nm excitation with a laser fluence of $4.2 \mu\text{J}/\text{cm}^2$. (b) Raman spectrum of *m*-xylylenediamine. (c) PL kinetics of *m*-XDALB white with 0.0 (blue), 0.5 (red), and 1.0 (black) moles of excess PbBr_2 . There exists a short lifetime component for the white emitter (1.0 moles of excess PbBr_2 added). Each experiment was conducted using 310 nm excitation with a laser fluence of $8.5 \mu\text{J}/\text{cm}^2$.

The broadening in FWHM with increasing temperatures can be attributed to a carrier scattering process, which can be described by the equation (2) (*Kindly refer page 23*). A good fit (with an adjusted R-squared value of 0.989) can be obtained using the parameters $\Gamma_0 = 504$ meV, $\Gamma_{LO} =$

140 ± 40 meV, $E_{LO} = 17 \pm 2$ meV, $\Gamma_{Inh} = 161$ meV, and $E_A = 9.4$ meV (Figure 4.37b). Three conclusions can be obtained from the fitting. Firstly, the value of Γ_{LO} is comparable to a previously characterized broadband emitting 2D perovskite (130 ± 7 meV),¹⁹ which indicates strong exciton-phonon coupling in *m*-XDALB. This value is also comparable to a exciton-phonon coupled ZnO quantum well system.³⁷ This suggests that self-trapped excitons are responsible for the bound excitons of the broad emission. Secondly, the longitudinal phonon energy obtained from the fitting coincides well with a Pb-Br Stretching frequency,⁶² which indicates self-trapping of excitons to the inorganic framework. Lastly, there exists a scattering potential barrier of 17 ± 2 meV, which is consistent with the small energy obtained from the Arrhenius fitting (Equation (1)).

Figure 4.38. (a) Kinetics of self-trapped excitons in a *m*-XDALB thin film with 1 mole of excess PbBr_2 . (a) Room temperature PL Kinetics measured at 400 nm (free excitons) and 550 nm (self-trapped excitons). (b) Evolution of the kinetics of free excitons (measured at 400 nm) at different temperatures. (c) Pseudocolor TA plot showing the change in absorption (ΔA) as a function of probe wavelength and probe delay time. (d) TA kinetics probed at 450, 500, 550, and 600 nm. Inset shows ΔA as a function of probe wavelength at selected delay times. (e) Short timescale TA kinetics probed at 400, 420, and 440 nm. (f) Proposed schematic summarizing the main processes occurring in this white emitter. The PL experiments were conducted using 310 nm excitation (50 fs, 1 KHz) with a fluence of $8.5 \mu\text{J}/\text{cm}^2$. The TA measurements were conducted using 310 nm excitation (150 fs, 1 KHz) with a fluence of $23.8 \mu\text{J}/\text{cm}^2$.

The formation of self-trapped excitons from free excitons is also reflected in both the PL decay and transient absorption (TA) kinetics. Firstly, there exists short PL lifetime components, which can be assigned to self-trapping (Figure 4.38a). The short lifetime component was found to be

~ 5 ps, which is shorter than the time-resolution of our streak camera (~ 10 ps). In addition, this short component is not evident in samples with 0 and 0.5 moles of excess PbBr_2 , which do not exhibit white emission (Figure 4.38b). Secondly, the population of free excitons is temperature dependent (Figure 4.38b). Despite the highest peak PL intensity at 70K, the population of free excitons after self-trapping is still the lowest. This suggests that the detrapping probability of self-trapped excitons is greatly reduced at low temperatures. Thirdly, there exists a broad photo-induced absorption (PIA) signal ($A > 0$) in the pseudocolor TA plot (Figure 4.38c). This is consistent with indirect formation of self-trapped free excitons and a previously reported TA spectrum.³⁸ The lifetime across this broad and featureless PIA (Figure 4.38d inset) was also unchanged across different probe wavelengths (Figure 4.38d). This behavior was also consistent with invariant PL kinetics measured across the broad emission in Figure 4.35d. These data further confirm that the PIA signal may arise from a single self-trapped excitonic state. Figure 4.38e shows the short time scale kinetics probed at different wavelengths. There exists a short lifetime component in the TA kinetics when the sample was probed away from the featureless PIA region (self-trapped state) towards 400 nm (Figure 4.38e). This concurs with the short timescale PL kinetics in Figure 4.38a. A fit of this short lifetime component gives an ultrafast self-trapping time of 170 ± 150 fs. Based on all our photophysical measurements, it has been proposed that the processes occurring in this white emitter can be summarized in Figure 4.38e and Figure 4.38f. These processes are: (i) laser excitation generates free excitons that recombine with lifetime of (2.77 ± 0.01) ns, (ii) ultrafast self-trapping occurs at (170 ± 150) ps after overcoming a self-trapping barrier of ~ 10 meV, (iii) exciton-phonon scattering broadens the energy linewidth of self-trapped excitonic emission, (iv) self-trapped excitons recombine with lifetime of (2.8 ± 0.1) ns.

4.3.5 Summary

By judiciously selecting the organic cation, it has been able to produce so-called “0D” perovskites with isolated distorted inorganic lead halide octahedra. Particularly, these perovskites serve as platforms for fundamental studies of the structure-property relationship. Moreover, the isolated lead halide octahedra shows broadband emission with peak maximum at 440 nm due to phosphorescence from metal-centered s-p transition that occurs with structural distortion of lead halide octahedra. This work advances the research on 3D, 2D, and 1D organic-inorganic hybrid metal halide perovskites to a “0D” perovskite and illustrates the conversion of 0D to higher dimensional (1D and 2D) perovskites. Remarkably, the self-trapped

excitonic emission from higher dimensional perovskite produced from 0D and excess PbBr_2 have CIE coordinates of (0.36, 0.40), good CRI values of 82.9, and a CCT of 4805 K, which makes the material suitable for cool white light applications.

Overall, it has been observed that the nature of the halide ion (X-ion) as well as cations (A-ion) present in perovskite structures play an important role and can drastically change their optical properties. The 2D PEPC was observed to be a suitable candidate to achieve a broadband emission over the PEPI and PEPBr. Further, the substitution of phenyl ammonium halide cation with xylylenediammonium halide ions change perovskite dimensionality from 2D to 0D and hence their optical and electronic properties.

These solution-processed materials exhibited high color rendering indices, good CIE coordinates, and excellent photo-stability, which are desirable for cool, white light LED applications. However, the low PLQY less than 1% motivated for further experimentation in the direction better performance. Hence the further study was focused in the direction to replace the toxic 'Pb' compounds with 'Sn' and 'Ge' to form 0D perovskites with improved optical properties to achieve a broadband emission.

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Chapter 5

Broadband Emission from Sn and Ge Based Low Dimensional Perovskites

Introduction

To date, light-emitting diodes (LEDs) is widely used in primary lighting application such as electronic displays, medical application and solid-state lighting. Tremendous research efforts have been made in light emitting materials for their wide range of display and lighting applications. Among the light emitters, phosphorescent metal complexes appear to be the important class of light emitters which possess near-unity internal quantum efficiency. In the last few years, hybrid organic-inorganic and all-inorganic halide perovskites have been explored intensively which show remarkable optoelectronic properties, suitable for photovoltaic, LED, photodetectors and transistors. It is also worth to highlight their exceptional photoluminescent properties that allow them to be a promising contender for next generation solid-state lighting.

In light emitting devices, similar to the considerations in solar cells, toxicity as well as long-term stability is a significant concern with lead-based perovskites. These issues would need to be addressed prior to any consideration of industrialization. Different pathways suggested to address the concern surrounding lead include encapsulation at the device level, reducing the amount of lead used at the system level under the toxicity limits, and of course exploring replacements of lead. For the latter, divalent, trivalent, or tetravalent cation-based perovskites may be pursued. With the multitude of structural variations that perovskites offer, this area is rich for structural and compositional approaches to find layered or molecularly lower dimensional Pb-free perovskites.

5.1 Low-dimensional Lead-free Perovskites

Extremely low photoluminescence quantum efficiency in main group metal halides, such as antimony, bismuth, tin, germanium and lead, have previously been reported which is the limiting factor of utilizing them in practical light emitting devices.¹⁻² By using appropriate organic cations, low dimensional organic-inorganic metal halide hybrids with 2D, 1D, and 0D structures can be generated (**Figure 5.1**). Due to its

unique quantum confinement and/or site isolation effects, these low dimensional hybrid perovskites could normally exhibit exceptional properties that are significantly different from typical ABX_3 perovskite counterparts.

Figure 5.1. (a) Images of 0D perovskite under ambient light and UV lamp irradiation and their (b) excitation (dashed lines) and emission (solid lines) spectra of 0D perovskites. (c) Photoimage of the device at off/on states and (d) the emission spectra of the a UV-pumped white LED using $(C_4N_2H_{14}Br)_4SnBr_6$ under different driving currents. (e) TEM image of $(EDBE)PbBr_4$ perovskites and its (f) crystal structure of the halide perovskite with corrugated structure. (g) Image of a UV-pumped white LED (operated at 3.0 V) by using the microscale perovskites as down conversion phosphors

It has been shown that several 0D organic metal halide perovskite crystals exhibit high photoluminescence with near-unity PLQEs. In these perovskite crystals, the $SnBr_6^{4-}$ and $SbCl_5^{2-}$ anionic metal halide species are surrounded by bulky organic cations and thus they are completely isolated from each other. The standalone metal halide species avoids electronic band formation between them, resulted in intrinsic properties of molecular metal halide in the bulk crystals. Thus, significant structural reorganization of excited state would induce the large stokes shifted broadband emission. This could be an effective approach to produce highly emissive materials via trapping luminescent metal halide species within the ionically bonded hybrid perovskites. The key factor of forming such low-dimensional perovskites is the choice of appropriate organic salts that would be able to co-crystallize and yield the isolated metal halide species within the crystal

structure. Hence, the chosen organic cations should be large enough to ensure the complete electronic site isolation of the photoactive metal halide species.

Numerous low-dimensional lead-free perovskites could be synthesized through selection of a range of elements with different oxidation states, ionic sizes and electronic configurations. The formation of low-dimensional perovskites highly depends on the size of A-site cation where the large organic cations would easily separate the metal halide species from each other. On the other hands, B-site cation with higher oxidation states ($>+1$) are generally preferred in low-dimensional perovskites as it could form lesser overall negative charges at metal halide species. This would directly allow the formation of low-dimensional hybrid perovskites which does not require the bridging halides between the metal halide lattices. Hence, metal cations with higher oxidation states are favourable in forming lead-free low-dimensional perovskites. It is believed that the higher-lying valence band levels in lead-free 3D perovskites based on tin and germanium is the root cause of ambient instability. Thus, reducing the metal-halide-metal (M-X-M) bond angle and the dimensionality of perovskites would lower the valence band position, leading to lead-free perovskites with higher stability towards oxygen.

5.1.1 Molecular Level 0D Lead-free Perovskites: Effect of B-site Cations

It would be interesting in exploring the low-dimensional lead-free perovskites for its photoluminescence properties. In the previous chapter, phenethylammonium cation was used to generate 2D perovskite with distorted octahedra which exhibits broadband emission due to the formation of STE in association with lattice distortion. In this chapter, the dimensionality of perovskite was further reduced to molecular level zero-dimensional (0D) perovskites where the anionic metal halide species are completely isolated from each other. To induce the 0D perovskite structure, relatively bulky organic cation, m-xylylenediammonium (m-XDA), was used to form the molecular level zero-dimensional Sn- and Ge-based perovskites.

5.2 Sn-based Perovskites

In this section, the syntheses and structural characterizations of highly luminescent molecular level 0D lead-free perovskites based on meta-xylylenediammonium tin bromide (m-XDATB) and meta-xylylenediammonium germanium bromide (m-XDAGB) are discussed. To understand the effect of B-site cations, the studies on the broadband emission using photophysical characterizations are also presented. Finally, the demonstration of m-XDAGB as a phosphors in white-light-emitting devices are presented together with the evaluation of the figures of merit of WLED.

5.2.1 Structural Identification and Characterizations

Single-crystals of m-XDATB were prepared by an anti-solvent vapor-assisted crystallization method. SnBr_2 and m-XDABr₂ were both dissolved in DMF and the vapor of an anti-solvent, dichloromethane, was allowed to diffuse into the perovskite solution. However, this resulted in the co-crystallization of (m-XDA)₂SnBr₆ and m-XDABr₂ single crystals which are not suitable for single crystal X-ray diffraction analysis. Pure m-XDATB single crystals were eventually obtained by limiting the crystal growth condition with lesser m-XDABr₂ precursor. The resulted m-XDATB 0D perovskite crystal was then collected with the yield of 40% with respect to the amount of SnBr_2 precursor. The crystal structure of m-XDATB is shown in Figure 5.2a, which shows the interspersed divalent XDA cations between the isolated SnBr_6^{4-} octahedral units. Each SnBr_6^{4-} unit is crystallographically centrosymmetric with three distinct Sn-Br bond lengths, which vary from 2.976 to 3.013 Å (Figure 5.2b). On the other hand, Figure 5.2d and Figure 5.2e show that the ammonium groups of the XDA cations are spatially trans to each other, and the dications stack parallel to one another. The ammonium groups of the m-XDA dications appear to be hydrogen bonded to three halides from three different SnBr_6^{4-} octahedra units.

Figure 5.2. (a) Projection of m-XDATB along the c-axis. (b) and (c) show the isolated SnBr_6^{4-} octahedra with bond lengths and bond angles respectively. (a) Projection of m-XDATB along the c-axis and (b) along the b-axis.

The variance in the octahedral elongation of m-XDATB was calculated to be 1.0085 Å, which indicates that there is significant variation in the bond length of the octahedra in comparison to variance in the octahedral elongation of perfect octahedra of methylammonium lead iodide which was 1.0001 Å.⁶ The bond angles for the cis-halides vary from 82.35 to 97.65° (Figure 5.2c), and the trans halide bond angles are all 180° due to the crystallographically imposed symmetry. The variance in octahedral angles σ^2_{oct} found to be 31.39°², which indicate significant distortion of the tin bromide octahedra in comparison to the variance in octahedral angles of perfect octahedral geometry of methylammonium lead iodide which is 0.1584°². Comparing the variances in the bond length and angle, the variance in bond angle is more in this hybrid material.

Multinuclear solid-state nuclear magnetic resonance (NMR) studies were conducted in order to confirm the chemical structure of the Sn-Br octahedra. The ^{119}Sn NMR spectrum of m-XDATB is shown in Figure 5.3a. It contains a single ^{119}Sn component where $\delta_{\text{iso}} = 723.8 \pm 0.8$ ppm that is split into a multiplet via ^{119}Sn - $^{79/81}\text{Br}$ J-coupling. An agreeable fit of the multiplet was achieved (Figure 5.3a) by simulating the spectrum of a single ^{119}Sn component bonded to six identical $^{79/81}\text{Br}$ sites; the details of the fit are given in Figure 5.3. The J-coupling in m-XDATB was measured as $^1J(^{119}\text{Sn}-^{79/81}\text{Br}) = 1.5 \pm 0.1$ KHz which is coherent with $^1J(^{119}\text{Sn}-^{79/81}\text{Br})$ values reported on SnBr_4 (0.92 KHz).⁷ The clarity of the observed ^{119}Sn multiplet indicates that the SnBr_6 octahedral unit is highly symmetrical in m-XDATB.

Figure 5.3. (a). The ^{119}Sn CPMAS (12 KHz) NMR spectra of m-XDATB with the experimental spectrum and the simulated spectrum in blue and red respectively. (b) The ^1H MAS (30 KHz) and (c) ^{13}C CPMAS (12 KHz) NMR spectra of m-XDATB where spinning sidebands have been marked with an asterisk.

Table 5.1 The ^{119}Sn NMR parameters of m-XDATB, determined via J-coupling spectral simulation.

$\delta_{\text{iso}}(^{119}\text{Sn}) / (\text{ppm})$	FWHM /(KHz)	$^1J(^{119}\text{Sn}-^{79/81}\text{Br})$ /(KHz)	#	I	Multiplet
723.8 ± 0.8	0.8 ± 0.1	1.5 ± 0.1	6	3/2	19

The ^1H and ^{13}C NMR spectra of m-XDATB are shown in Figure 5.4b and 5.4c. The ^1H NMR spectrum presents with two broad resonances. The broad resonance at ~ 8 ppm contains the benzyl ring and ammonium hydrogen sites while the broad resonance at ~ 3 ppm represents the benzyl CH_2 hydrogens. The ^{13}C NMR spectrum presents with eight sharp resonances: the six resonances at higher frequency (138 - 131 ppm) belong to the benzyl ring group whereas the two resonances at lower frequency (45 - 43 ppm) belong to the benzyl CH_2 group. The ^{13}C multinuclear NMR data confirms the composition and purity of the m-XDATB crystal.

Material Stability

The oxidative stability of m-XDATB was examined by collecting the XPS survey spectra in the binding energy range from 0 to 800 eV as shown in **Figure 5.4a**. The identified core level peaks for elements in the sample are Sn, Br, C, and N, which confirms all the elements present in m-XDATB. Narrow scan for the binding energies of $d_{3/2}$ and $d_{5/2}$ electron of Sn confirms its existence in one oxidation state (Figure

5.4b). However, the oxidation state of values are reported for these two different Sn is not clear because of the close binding energies of $3d_{5/2}$ for Sn^{4+} and Sn^{2+} and different oxidation states in the literatures. However, single crystal XRD analysis established the molecular formula as $(\text{m-XDA})_2\text{SnBr}_6$ where the oxidation state of Sn is +2 so we confirm that the tin present in this compound is Sn^{2+} .

Figure 5.4. XPS scan of m-XDATB. (a) Survey scan for Sn, Br, C and N, (b) Narrow scan for Sn 3d_{3/2} and 3d_{5/2} orbitals.

In order to realize the reason for the stability of perovskite in air, we conducted photoelectron spectroscopy in air (PESA) on powder samples and determined that the highest occupied molecular orbitals (HOMO) is -5.50 eV relative to vacuum (**Figure 5.5**). Probably, this low-lying HOMO along with good coverage of the organic ammonium cations surrounding the tin ions provide additional air-stability to this bivalent Sn-perovskite.^{2, 8-9}

Figure 5.5. Photoemission spectroscopy in air (PESA) of m-XDATB powder.

The TGA thermogram of this material, collected up to 800 °C, displayed significant weight loss beyond 200 °C (Figure 5.6a). In addition, the cooling curve of the DSC thermogram revealed no evidence of any phase transition between –50 to 175 °C (Figure 5.6b), suggested that this phosphor is stable in the working temperature range of typical LED phosphors.

Figure 5.6. (a) TGA and (b) DSC thermogram of m-XDATB.

5.2.2 Electronic and Photophysical Properties

To understand the nature of the bandgap and orbital characteristics of this ‘0D’ perovskite, ab initio DFT calculations with generalized gradient approximation (GGA) using the PBE functional (detailed in experimental section) were performed. All the octahedra are arranged next to each other and extended along the 100 plane. The shortest distance between two Sn-Br octahedra is 3.934 Å which is close to sum of the van der Waals radii (3.66 Å) of bromine. Hence, charge transfer could occur between the octahedra. In order to confirm this factor, we have carried out DFT calculation to predict the band structure of m-XDATB and it is shown in the Figure 5.7a. The flatness of bands indicates that the intermolecular the electronic coupling between the two octahedra is not apparent hence the octahedra could be considered as molecular compounds for further DFT calculation.

The first principle calculations reveal a direct bandgap of 2.7 eV at Γ . The top of the valence band is separated from the rest of valence band with a forbidden gap of 0.7 eV, similar to other 0D halide perovskites. The atomic projected density states (PDOS) illustrated in Figure 5.7b reveal that the valence bands mostly consists of a mixture of Br p, Sn s, and Sn p orbitals, whereas the conduction band was derived

from the organic molecule. The split-off of the top of the valence band which is contributed by Br p and Sn s orbitals, resulted from strong antibonding coupling between occupied Sn s and Br p orbitals. However, due to long Sn-Sn distance, the band structure along reciprocal space is nearly dispersionless (illustrated in Figure 5.7a). On the other hand, bottom of the conduction band is mainly consists of antibonding states from the XDA molecule. The top of the conduction band derived from hybridization between empty Sn p and Br p orbitals.

Figure 5.7. (a) Band structure, and (b) atomic projected density of states of m-XDATB molecular salt.

The absorption and photoluminescence excitation spectra have been measured using single-crystals of m-XDATB at room temperatures are shown in Figure 5.8a, where the absorption spectrum has a peak at 384 nm and the optical bandgap of the material has been calculated to be 2.85 eV. In addition, the photoexcitation spectrum measured at room temperature for the 509 nm-emission has two peak maxima. The difference between absorption and PLE spectra could be due to charge transfer between metal ion and bromide ligand. Hence, the absorption peak at 385 nm is logically assigned to MLCT/LMCT transition involving either the promotion of 5s² lone pair of the metal to empty d orbital of bromide ion or promotion p electron of bromide to the empty p orbitals of tin ion.¹⁰

Figure 5.8. (a) Absorption and excitation spectra, and (b) Steady-state PL spectrum of m-XDATB.

Subsequently, the emission spectrum was measured under 350 nm excitation, which shows a Gaussian-shaped emission that covers the visible region from 400 to 650 nm as shown in Figure 5.8b. This PL has an emission maximum at 509 nm, a FWHM of 95 nm, and a large Stokes-shift of 160 nm. The PLQY of the m-XDATB was measured using single-crystals to be 60 %, which is one of the highest values reported so far for 0D perovskites.

The absorption spectrum has less absorption in the region where the PLE spectrum overlaps, and this indicate the metal-centered electronic transition is weaker than the other transitions that take place in 0D perovskite. However, in order to further understand the metal-centered electronic transition, we have carried out temperature-dependent steady-state PLE, PL and time-resolved PL measurements. Indeed, PLE spectra measured at room temperature and 80 K showed two peak maxima (340 nm and 305 nm) and five peak maxima (340, 318, 308, 301, and 290 nm) respectively (Figure 5.9).

Figure 5.9. PLE and PL Spectra measured at RT and 80 K. (a) PL excitation spectra for different emission wavelengths at RT (a) and at 80 K (c). (b) Emission spectra for different wavelength excitations at RT (a) and at 80 K (b).

These peaks could be assigned to different bands of Sn^{2+} ion in KBr as reported by Taiju Tsuboi et al.¹¹ Similar emission spectrum under different wavelength excitation, and similar excitation spectrum for different emission peaks (Figure 5.9) indicate that the entire broadband emission arises from the same excited state. Steady-state temperature-dependent PL measurement shows increase in PL intensity and decrease in FWHM with decreasing the temperature. The peak maximum red-shifted until it reached 519 nm as the temperature was reduced to $-150\text{ }^{\circ}\text{C}$, and then blue-shifted to 515 nm with further decrease of the temperature to $-196\text{ }^{\circ}\text{C}$. (Figure 5.10a). The PL decays are well described by a single exponential decays at all the temperatures investigated (Figure 5.10b). This strongly supports that the PL arises from radiative recombination. Moreover, the lifetime is just slightly affected by the temperature decrease. The longer PL lifetime also indicate that the emission is from the spin-forbidden triplet state. The transition from the excited singlet to the triplet state is aided by the spin-orbit coupling that occurs due to the heavy atoms such as tin and bromide. To understand the large Stokes shift

and high PLQY of m-XDATB, DFT calculation was performed in order to determine the energies of singlet and triplet states and observe the structural changes in excited state of Sn-Br octahedra. Generally, nS^2 complexes undergo large structure deformation in their s-p triplets, which will lead to a decrease of the triplet energies.¹²⁻¹³ Probably, bromide is a small and monodentate ligand, which gives more structural freedom for the deformation of the octahedral, thus leading to a large Stokes-shifted PL. The Stokes shift is also dependent on the distortion of the octahedra and also the coordination number.¹

Figure 5.10. (a) Temperature-dependent PL spectra measured from 298K to 77K. (b) PL decay data measured at different temperatures from 298K to 77K.

5.2.3 Demonstration in WLEDs

WLEDs were fabricated by blending the cyan light-emitting m-XDATB perovskite with a red light-emitting sulfoselenide (BUVR03) in order to shift the CIE coordinates of the cyan light emitted by m-XDATB closer to white. The photoluminescence excitation spectrum and photoluminescence spectrum of BUVR03 are shown in Figure 5.11. BUVR03-doped polydimethylsiloxane (PDMS) films were prepared with different ratios of cyan and red emitting phosphors for a remote phosphor LED configuration. A powder sample of m-XDATB in large-scale for device was prepared by drying the perovskite solution on a hotplate, scooping, and grinding the material. The powder XRD peaks confirms the crystal structure of m-XDATB but it is associated with small amount of unreacted m-XDABr₂ (Figure 5.11c).

Figure 5.11. Excitation and PL spectra of powder BUVR03. PL spectra of single-crystals and powder of m-XDATB. Powder XRD pattern of finely ground powder of m-XDATB. Inset figure shows the powder sample under UV light.

The ball-milled m-XDATB sample exhibits similar emissive behavior as that of m-XDATB single-crystal. However, the ball-milled phosphor possesses a slightly blue-shifted emission spectrum (Figure 5.11b), due to the size reduction of the m-XDATB particles. The morphologies of the particles were analyzed by field-emission scanning electron microscopy (FESEM) as shown in Figure 5.12a. Phosphor-based light-emitting devices were fabricated using the phosphor doped PDMS films on top of commercial UV LEDs (340 nm, operated at an applied voltage of 5V) to optically excite the phosphors in the PDMS film. These LEDs exhibited broad PL spectra that cover the visible region from 400 nm to 800 nm as shown in Figure 5.12b. The CIE coordinates for the spectra of pure phosphors and mixed phosphors were obtained and shown in Figure 5.12c.

Figure 5.12. (a) FESEM image of ball-milled powder of m-XDATB. (b) PL spectra of the lights emitted by the devices. (c) CIE 1931 color plot showing coordinates of the lights emitted by the m-XDATB, BUVR03, and mixture of these two phosphors at different ratios.

The values for the mixed phosphors should lie on the line in between the CIE values of the two pure phosphors. However, they may have deviated due to reabsorption of the blue emission band from m-XDATB by BUVR03. Consequently, the emission maximum of m-XDATB is shifted to 518 nm. The colors of the PDMS films under UV excitation are shown in the inset of Figure 5.12c. The color rendering index (CRI), correlated color temperature (CCT), and CIE values of the lights from these devices are summarized in Table 5.2. The mixtures of m-XDATB and BUVR03 at 2:1 and 1:1 ratios showed white-light emissions with the good color qualities (CIE, CRI and CCT).

Table 5.2. Qualities of the broadband light emitted by perovskite phosphors.

	CIE	CRI	CCT
m-XDATB	(0.21, 0.41)	51	8990
2:1	(0.35, 0.43)	86	5144
1:1	(0.40, 0.42)	78	3853
1:2	(0.48, 0.39)	61	2258
BUVR03	(0.69, 0.32)	NA	NA

5.3 Ge-based perovskite

Germanium, similar to tin and lead - a group 14 element, is also potential metal suitable to replace lead in perovskites. In comparison to Pb^{2+} , Ge^{2+} exhibits a higher electronegativity, a more covalent character, and an ionic radius (73 pm) which is smaller than that of Pb^{2+} (119 pm). Beside its nontoxicity, the interest in Ge^{2+} resides in it having a highly stereochemically active 4s² lone pair of electrons, with related strong tendency to be off-center within the octahedral cage. Interestingly, even

though numerous theoretical studies attest to these materials having promising properties for solar cell applications, germanium halide perovskites have only been rarely investigated experimentally. This is most likely due to the instability of the Ge^{2+} ion toward oxidation to Ge^{4+} . The Ge analogues differ from their heavier congeners because they show a pronounced tendency to crystallize in polar space groups.¹⁴ This behavior of germanium iodides has been confirmed by other researchers¹⁵⁻¹⁷ and has been acknowledged with a patent application.

5.3.1 Structural Identification and Characterization

The single-crystals of m-XDAGB were prepared by cooling down a hot solution containing GeO_2 , m-XDABr₂, hydrobromic acid and hypophosphorous acid. Firstly, GeO_2 was dissolved in hydrobromic acid and hypophosphorous acid and a clear solution was obtained at 100 °C with continuous stirring. Subsequently, m-XDABr₂ was added into the solution with constant stirring at 100 °C. Slow cooling of the solution resulted in a growth of high quality single-crystals of m-XDAGB suitable for X-ray diffraction analysis. The resolved unit cell of $(\text{m-XDA})_2\text{GeBr}_6$ is shown in Figure 5.13.¹⁸

Figure 5.13. (a) Crystal structure of the m-XDAGB. Projection of the m-XDAGB along (a) a- and (b) b-, and (c) c-axes showing the isolated GeBr_6 - octahedral units and XDA cations arranged alternately in layers.

The isolated octahedra embedded in the organic matrix are clearly shown. Each Ge-Br octahedron has three different bond lengths which vary significantly from 2.8229 Å to 2.9113 Å (Figure 5.14a). Bond angles between the linear bromides (similar bromides) differ slightly from 179.61 and 179.25 (Figure 5.14b). The bond angle (Br-Ge-Br) between right-angled bromides vary slightly from 87.94° to 92.059° (Figure

5.14c). Quadratic elongation and bond angle variance are measured to be 1.0009 and 1.9125° , which indicate less distorted Ge-Br octahedron.

Figure 5.14. (a) Isolated GeBr_6^{4-} octahedral unit of m-XDAGB. (a) bond lengths, (b) bond angle between linear bromides, and (c) bond angle between right-angled bromides.

Powder XRD pattern of m-XDAGB was depicted in Figure 5.15a, where it matches with the simulated XRD pattern of the same compound. Multinuclear solid-state nuclear magnetic resonance (NMR) studies of m-XDAGB was conducted in order to validate the chemical structure of the Ge-Br octahedron. The ^1H NMR spectra of m-XDAGB is shown in Figure 5.15b. The ^1H NMR spectrum of m-XDAGB presents with two broad resonances. The broad resonance at ~ 8 ppm contains the benzyl ring and ammonium hydrogen sites while the broad resonance at ~ 3 ppm represents the benzyl CH_2 hydrogens. These resonances were assigned as such in the previous studies of m-XDATB and m-XDALB.

Figure 5.15. (a) Powder XRD of m-XDAGB. (b) ^1H MAS (30 KHz) NMR spectrum and (c) ^{13}C CPMAS (12 KHz) NMR spectrum of m-XDAGB (simulated spectrum in blue).

The ^{13}C NMR spectra of m-XDAGB is shown in Figure 5.15c. The ^{13}C NMR spectrum of m-XDAGB presents with 5 sharp resonances where the two resonances at lower frequency (44 - 42 ppm) belong to the benzyl CH_2 group. The 3 resonances at higher frequency (136 - 131 ppm) belong to the phenyl ring, where the central resonance ($\delta_{\text{iso}} = 133.5 \pm 0.2$ ppm) contains 4 overlapping proton components. This is corroborated by the larger intensity of the central resonance. Hence, the ^{13}C NMR data confirms the composition of the m-XDAGB crystal. Purities of m-XDAGB single-crystals was confirmed using XRD and NMR without the presence of GeBr_2 and m-XDABr₂ impurity.

Material Stability

Due to possibility of oxidation reaction of Ge^{2+} under ambient atmosphere, it is essential to elucidate the stability of the resulting 0D Ge-based perovskites. Hence, x-ray photoelectron spectroscopy was conducted, and the results are shown in Figure 5.16. Survey scan for m-XDAGB shows the core level peaks for Ge, Br, C, N and O, which evidenced the presence of all the elements present in the m-XDAGB perovskite (Figure 5.16a). Identified oxygen could be from the phosphorous acid used

in the preparation of perovskite. Narrow scan for the binding energy of $2p_{3/2}$ core level shows single peak at 1218.3 eV which supports the presence of Ge in +2 oxidation state (Figure 5.16b).¹⁸

Figure 5.16. XPS spectra of m-XDAGB. (a) wide scan spectrum for C, N, Ge, and Br orbitals, (b) narrow scan spectrum for Ge $2p_{3/2}$.

In order to use these perovskites as phosphors, thermal stabilities of these perovskites need to be checked. Hence, TGA and DSC thermograms were collected, showing its thermal stability up to 200 °C (Figure 5.17).

Figure 5.17. (a) TGA and (b) DSC thermogram of m-XDAGB.

5.3.2 Photophysical Properties

Photophysical properties of m-XDAGB single-crystals were hence characterized with various optical analysis. Photoluminescence excitation (PLE) and photoluminescence (PL) spectra of m-XDAGB are shown in Figure 5.18. PLE spectrum was collected for the emission maximum at 555 nm which shows a peak

maximum at 330 nm. Hence, m-XDAGB is excited at 330 nm and the photoluminescence spectrum was collected as shown in Figure 5.18b. The emission spectrum covers the visible region from 450 nm to 700 nm with, a FWHM of 110 nm, a peak maximum at 555 nm, and Stokes shift of 225 nm.

Figure 5.18. (a) Absorption and excitation spectra of m-XDAGB. (b) Steady-state PL spectra of m-XDAGB.

The PL and PLE spectra were also recorded at different temperatures which are shown in Figure 5.19. PLE spectra are blue shifted as the temperature is lowered (Figure 5.19c). But PL spectra show narrowing effect without change in the peak position as the temperature is lowered (Figure 5.19d). The room-temperature PL of m-XDAGB is red-shifted to the emissions of its counterparts both m-XDALB and m-XDATB. Similarly, the FWHM of m-XDAGB is larger than the values for its counterparts. Although, all these three different metal ions with nS^2 ground state electronic configuration are in the same organic ammonium matrix, they show different photoluminescence properties. Probably, these differences in PL properties could be correlated with the distortions of different metal halide octahedra that are described using two parameters, quadratic elongation and bond angle variance.⁶ These two values of octahedra decreases from m-XDALB to m-XDATB and then to m-XDAGB.

Probably, the large Stokes shift and FWHM for less distorted metal halide octahedra could be due to the availability of larger room for Jahn-Teller distortion. The reason for different extent of distortions in different metal ion octahedra could be due to inert pair effect.¹³ As shown in the Table 5.3, FWHM and Stokes shift are increasing with decreasing distortion of metal halide octahedron.

Figure 5.19. Spectra measured at RT and 80 K for m-XDAGB. (a) & (c) PL excitation spectra for different emission wavelengths at RT and 80 K respectively. (b) & (d) emission spectra measured at RT and 80 K respectively for excitation at different wavelengths.

Table 5.3. Comparison of octahedral distortions and photophysical properties of different metal halide perovskites.

	m-XDALB	m-XDATB	m-XDAGB
Bond angle variance in deg ²	36.3823	31.3931	1.9125
Quadratic elongation	1.0099	1.0085	1.0009
FWHM (nm)	70*	95	110
Stokes shift (nm)	106*	160	225
PLQY (%)	< 1	60	20

* measured at low temperature

Similarly, comparison of Sn-Br octahedra present in m-XDATB perovskite indicates the larger FWHM and Stokes shift in less distorted metal halide octahedra. In fact, DFT calculations also predicted that m-XDAGB shows higher structural deformation than m-XDATB (bond length variations).¹³ This could also depend on the rigidity of the organic ammonium matrix that can accommodate the structural deformation of the metal bromide octahedra during photoexcitation process. The PLQY was

measured to be 20 % which is higher than the PLQY of m-XDALB and lower than the PLQY of m-XDATB. Here, it is unclear about the factors that influence the PLQYs of these 0D perovskites. However, many factors could be deciding the PLQY like metal-halide bond character, heavy-atom effect, distortion of octahedra and charge transfer between the metal ion and halide ion. PL lifetimes of m-XDAGB was measured as shown in Figure 5.20a and found it to be 3.54 μs . In order to understand further the factors that influences the photophysical properties of these perovskites, density functional theory calculations were carried out.

5.3.3 Demonstration of perovskite phosphors in WLEDs

To incorporate these perovskites in WLEDs, particle sizes of these perovskites were reduced. Microparticles of m-XDAGB were produced by grinding the single-crystals of m-XDAGB in mortar and pestle and sieving through the mesh with pore size of 45 μm . FESEM image of the powder m-XDAGB is shown in Figure 5.20b.

Figure 5.20. (a) PL lifetimes of m-XDAGB. (b) Morphology of the grinded and sieved m-XDAGB powder through mesh with 45 μm pore size.

WLED based on m-XDAGB was fabricated by mixing powder of yellow-emitting m-XDAGB perovskite with the blue-emitting $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ phosphor at 9:1 weigh ratio and then this mixer was mixed with silicone elastomer followed by spin coating on the quartz substrate which was later placed over the pump-UV LED. Emission spectrum was collected as shown in Figure 5.21a and the CIE coordinates was calculated as (0.3205, 0.3870) for the white light which was at (0.3833, 0.4946) earlier for the pure m-XDAGB (Figure 5.21b). CIE coordinates, CRIs, and CCTs are calculated and tabulated for the white light, and yellow lights in Table 5.4. CCT of the

white light indicates that WLED based on m-XDAGB phosphor is suitable for day white application.

Figure 5.21. (a) PL spectra of the white light emitted by the mixture of m-XDAGB, $\text{Ba}_{0.86}\text{Eu}_{0.14}\text{MgAl}_{10}\text{O}_{17}$ at 9:1 ratios. (b) CIE 1931 color plot showing coordinates of the white light.

Table 5.4. Qualities of the broadband light emitted by perovskite phosphors.

	CIE coordinates	CRI	CCT
m-XDAGB	0.3833, 0.4946	48.7	4513
m-XDAGB and blue phosphor at 9:1	0.3205, 0.3870	64	5926

5.4 Summary

Hybrid organic–inorganic perovskites are an important class of semiconducting materials with exceptional structural and property tunability. By choosing appropriate organic and inorganic components, the connectivity of the metal halide polyhedra can be tuned to form 3D, 2D, 1D and molecular level 0D structures surrounded by the organic moieties. Difference in perovskite dimensionality could lead to the unique properties, especially in photoluminescence. For instance, unlike the narrow emissions with small Stokes shifts observed in typical 3D hybrid perovskites, broadband emission with large Stokes shifts has been evidenced in corrugated-2D, 1D and molecular level 0D hybrid perovskites due to the exciton self-trapping or excited state structural deformation. The synthetic versatility of hybrid perovskites allows vast parameter to be explored in novel structures with significant photoluminescence properties.

By judiciously selecting the organic cation, molecular level “0D” perovskites with isolated tin bromide molecular octahedra have been successfully synthesized and characterized. Specifically, the excitons of metal-centered electronic transitions involving triplet states couple with the phonons of the metal halides, gives rise to self-trapping of excitons, which finally causes strongly Stokes shifted broadband emission. This ‘0D’ perovskite serves as a platform for fundamental studies of the structure-property relationships of metal halides complexes, which would otherwise be unstable as a free molecular complex. WLEDs using m-XDATB perovskite along with a red emitting phosphor showed white-light with good figures of merit that makes the material suitable for warm white light applications.

On the other hands, Ge-based perovskite with m-XDA cation showed even larger Stokes shift and FWHM in comparison to its lead and tin counter parts, m-XDALB and m-XDATB respectively. This yellow-emitting *m*-xylylenediammonium germanium bromide exhibits broadband emissions with peak maximums at 555 nm. Emission of *m*-XDAGB covers from 450 to 700 nm with full-width at half-maximum (FWHM) of 110 nm, and PLQY of 20 %. This perovskite were prepared at low temperature by slow cooling processes of hot perovskite solution which can be scaled up easily. White-light emitting devices fabricated using yellow-emitting perovskites and a blue-emitting europium doped barium magnesium aluminate ($\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$) phosphor have shown decent CRI and CCT values.

5.4 References

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Chapter 6

Discussion and Summary

6.1 Material Selection: Structure and Dimensionality

The structural flexibility in hybrid organic-inorganic perovskites offers a massive opportunity for unique and exceptional optoelectronic properties. Therefore, it is essential to seek for multidisciplinary studies to (i) develop the hybrid perovskites with well-confined structures and dimensionalities and (ii) establish a comprehensive understanding on their structure–property relationships, in order to understand the potential of this class of semiconducting materials in the next generation optoelectronic applications.

By selecting appropriate organic and inorganic components, low dimensional organic-inorganic perovskites layered (2D), linear (1D) and isolated (0D) structures at the molecular level can be developed. Owing to its strong effect in quantum confinement and site isolation, generally, these low dimensional perovskites at the molecular level exhibit remarkable and unique optoelectronic properties as compared to the typical perovskites with ABX_3 structure. While tremendous effort has been made in the perovskite research with typical 3D structure, the low dimensional 2D, 1D and 0D perovskites remains relatively underexplored. One of the possible reasons could be the lack of systematic study on the low dimensional perovskites with controlled synthetic protocols. Unlike the plenty of material selection and design rules for conventional 3D systems, rational synthesis criteria and selection of organic components for low dimensional perovskites have not been fully established yet.

In this chapter, a series of number of low dimensional hybrid organic-inorganic perovskites with 2D, 1D and 0D structures are presented (Table 6.1). They will be discussed on their photophysical properties and PL mechanisms in term of their dimensionalities, as well as their potential applications.

Table 6. 1 Summary of structural parameters of the perovskite materials of various dimensionalities including 3D, 2D, 1D and 0D studied during the completion of this study. The data highlighted in brown text is taken from literature.

Perovskite	Dimensionality	Average bond length (Å)	Polyhedral volume (Å ³)	Distortion index (bond length)	Quadratic elongation	Bond angle variance in deg ²	Effective coordination number	M-(μ-X)-M bond angle	Emission
MALI	3D	3.1566	41.9337	0.00598	1.0001	0.1584	5.9776	179.01	NB
CLB		2.9618	34.6397	0.00096	1.0001	0.2416	5.9996	157.42, 165.46	NB
PEPC	2D	Disordered octahedra						151.89, 153.35, ~150	Yes / BB
PEPB		3.0135	36.2372	0.02024	1.0056	16.2443	5.7685	~152.1, ~150.8	NB
PEPI		3.1937	43.1628	0.02036	1.0051	14.6849	5.7851	~148.63, ~150.95	NB
p-XDALB (octahedron 1)	1D	3.0282	36.4713	0.01419	1.0104	36.9592	5.9392	93.58	No
p-XDALB (octahedron 2)		3.0282	36.4237	0.00483	1.0119	44.9134	5.9946		
(DMSO) ₂ PbBr ₂		2.9006	31.0834	0.08226	1.0406	82.9524	3.496		
m-XDALB	0D	3.0222	36.2665	0.00428	1.0099	36.3823	5.9951		No
m-XDALI		Experiments carried out but not successful (PbI ₂ crystallize separately)							-
m-XDATC		2.8494	30.4385	0.00449	1.009	33.05	5.9953		Yes / BB
m-XDATB		2.9958	35.3963	0.00439	1.0085	31.3931	5.9947		Yes / BB
m-XDATI		3.1747	42.1489	0.00477	1.0081	29.4027	5.9946		Yes / BB
BATB		2.9844	35.3764	0.00964	1.0014	4.3024	5.9728		Yes / BB
OATB		SC-XRD data not available							Yes / BB
m-XDAGC		Not prepared							-
m-XDAGB		2.8654	31.336	0.01071	1.0009	1.9125	5.9653		Yes / BB
m-XDAGI		Not prepared							-
m-XDAAC		Square pyramidal structure							No
m-XDAAB		2.8125	29.4817	0.03819	1.0057	14.2421	5.5834		No
(DMSO) ₂ SnBr ₄		2.4098	18.4799	0.07518	1.0129	17.6897	3.7137		Yes / BB
(p-XDA)(DMSO) ₄ PbBr ₄		2.8658	30.8278	0.07141	1.0178	21.9644	3.9797		No
BMPAC		Square pyramidal structure							Yes / BB
TPPAC		2.4786	20.0293	0.07564	1.0156	8.196	3.7324		Yes / BB

NB = narrowband; BB = broadband

MALI = MAPbI₃; CLB = CsPbI₃

6.1.1 Structure-properties relationship

In low dimensional perovskites (2D, 1D and 0D), the isolated metal halide building blocks allow the bulk perovskite materials to exhibit intrinsic optoelectronic properties by confining the photoactive metal halide species with wide-band-gap organic cations, inhibiting the interactions between the metal halide clusters. Unlike typical 3D and 2D perovskites (MALI, CLB, PEPB and PEPC) with narrow emission spectra, corrugated 2D perovskite (PEPC) synthesized in this study shows broad-band emissions due to its highly distorted octahedral metal halide structure. For the corrugated 2D perovskite structure, they could have simultaneous electronic band formation and structural distortions that cause PEPC exhibits photoluminescence from both coexisting direct and self-trapped excited states. Therefore, to obtain a broadband emission in layered 2D perovskites, formation of “corrugated” structure is critical.

“Self-trapped exciton” can be defined as a bound electron–hole pair that is self-trapped as a small polaron in the lattice distortion field in which a strong electron/hole lattice coupling is present. Generally, emission from self-trapped excitons is broadened related to the distortion of the excited-state structure as compared to its ground state. To certain extent, this lattice distortion offers broadening effect to its emission. The phenomenon of exciton self-trapping is commonly observed in metal halide species, where the strong exciton–lattice coupling can be referred as covalent bond formation in its excited state. Briefly, electrons are basically excited to free-exciton excited states upon photoexcitation. It usually undergoes fast decay to its self-trapped states via multiple trapped states with different energies within the materials. This rapid relaxation process through multiple local minima would have resulted in broadband emission. For PEPC, this material possesses large structural distortions as well as its quantum confinement effects (commonly seen in low dimensionality) which eventually result in the formation of both free-exciton and self-trapped excited states upon photoexcitation. Hence, broadband emission has been observed in 2D layered PEPC perovskite with corrugated structure, which is significantly different from conventional 3D and 2D perovskites with narrow emissions.

Furthermore, it can be noticed that the formation of self-trapped excited states is more pronounced in molecular level 0D dimensional perovskites. The formation of self-trapped excitons seem to be more favorable in lower dimensionality. For molecular 0D perovskites (Table 6.1), individual molecular perovskite clusters are completely surrounded and isolated by the bulky organic cations (m-XDA). These molecular 0D hybrid perovskites, mostly tin- and germanium-based, can therefore be considered as a host-guest system with molecular perovskite clusters periodically placed within the wide bandgap matrix. Highly luminescent broadband emissions are observed in these materials with strongly Stokes-shifted PL spectra. Unlike other 3D Sn-based perovskites, these molecular 0D tin and germanium based perovskites also shows remarkable stability in the ambient, with the photoactive perovskite clusters protected by m-XDA organic shells.

Through the structural-property comparison, it can be concluded that the photoluminescence mechanisms of hybrid organic-inorganic perovskites are highly dependent on their dimensionalities: (1) conventional 3D and 2D perovskites with electronic band formation shows emissions direct from their excited states, (2) corrugated 2D perovskites shows emissions from both direct and self-trapped excited states in the presence of electronic band formation and structural distortions and (3) molecular 0D perovskites exhibits emission from the reorganized excited states without electronic band formation. This large structural dependent emission behaviour suggests a significant role in perovskite broadband emission. Nevertheless, these material selection and design rules may lead to rational protocol for white light-emitting hybrid perovskites.

6.1.2 Material Stability

Stability of perovskites is always a critical issue for any optoelectronic devices based on this class of crystalline semiconductor. Stability of typical 3D hybrid perovskites has been intensively investigated as this is the main limiting factor in commercializing perovskite photovoltaics. Lately, low dimensional hybrid organic-inorganic

perovskites have received overwhelming attention due to their higher stability than 3D analogs. The incorporation of bulky organic cations within the three-dimensional inorganic lattices would greatly stabilize the perovskite clusters from ambient environment. Some bulky organic cations can be even utilized to passivate the perovskite surface and protect it from moisture or oxygen induced degradation.

For the corrugated 2D perovskite (PEPC), similar photoluminescent behavior was observed after being stored under ambient condition for several days which indicates the improved stability in the corrugated 2D perovskite structure. On the other hands, molecular level 0D hybrid perovskites have shown their potential as down-conversion light emitters. Thus, stability of this class of materials are mainly focused on their thermal and photo-stability which are crucial for the optically-pumped LED devices. All the molecular level 0D hybrid perovskites with broadband emission (mostly tin- and germanium-based) are exhibit great photo- and thermal-stability which are all thermally stable up to 200 °C. However, the detailed degradation mechanisms for this low dimensional hybrid perovskites have not been fully understood due to the limited material and device study. Based on the current understanding and experimental results, the bulky m-XDA organic moiety serves an important part in stabilizing the perovskites, not only isolating the photoactive perovskite clusters, but also interacting with other components within crystal lattice at both ground states and excited states. Several factors need to be consider in order to achieve low dimensional hybrid perovskites with high thermal and photo-stability including perfect isolation of the quantum nanostructures, chemically robust organic cations, strong ionic, covalent and Van de Waals interaction between organics and inorganic clusters, high formation energy and stabilized excited states.

6.2 Mechanistic Insight in Low Dimensional Perovskites

Table 6.2 tabulates the photophysical properties of representative perovskites with broadband emission in different dimensionalities from 2D, corrugated 2D and 0D. Based on these data, it can be clearly seen that the change in perovskite dimensionality greatly affects the interactions between metal halide species and results in different emission mechanisms and photophysical properties.

Table 6. 2 Photophysical properties of representative perovskites with broadband emission in different dimensionalities from 2D, corrugated 2D and 0D. The data highlighted in brown text is taken from literature.

Perovskite	Dimensionality	Emission	Band gap (eV)	Absorption peak maximum (nm)	PLE peak maximum (nm)	PL peak maximum (nm)	Stokes' shift (nm) PLE	FWHM (nm)	PLQY (%)	PL lifetime (μ s)	CIE	CRI	CCT
PEPC	2D	White / BB	3.56	340	X	~ 560	~ 220	580 (meV)	< 1	4.20 (ns)	0.37, 0.42	84	4426
PEPB		Violet / NB	3.00	405	X	410	5	14	10	0.62 (ns)	X	X	X
PEPI		Green / NB	2.42	516	X	525	9	18	X	X	X	X	X
m-XDATC	0D	Cyan / BB	X	360	330	500	170	100	X	X	X	X	X
m-XDATB		Cyan / BB	2.89	384	350	510	160	95	60	0.58	0.21, 0.41	51	8990
m-XDATI		Brown / BB	2.38	375	385	600	215	not symmetrical	X	X	X	X	X
BATB		Brown / BB	3.54	314	325	615	290	140	X	3.06	0.54, 0.44	72	2034
OATB		Yellow /BB	3.08	X	340	600	260	136	~ 100	3.30	0.49, 0.42	69	2500
m-XDAGB		Yellow /BB	3.22	325	330	555	225	110	20	3.54	0.38, 0.49	48.7	4513
BMPAC		Yellow /BB	X	X	380	590	210	119	~ 100	4.20	X	X	X
TPPAC		Red / BB	X	X	375	648	273	136	~ 100	4.57	X	X	X

Stokes' shift (nm) = PLE maximum - PL maximum (for 0D perovskites)

m-XDATI - Material is not stable so measurements need to be redone but in inert atmosphere

6.2.1 Generality of Broadband Emission and Self-trapping Excitons

Reducing dimensionality of hybrid organic-inorganic perovskites from 3D interconnect polyanionic inorganic networks into lower dimensionality 2D, 1D, or molecular 0D octahedra will result in more localized electronic states and turns into a narrower conduction and valence bands, which facilitate self-trapping of excitons as well as enhanced exciton emission. That is the reason why strong photoluminescence are observed in low-dimensional hybrid perovskites over a wide range of emissive wavelength, especially the highest PLQY in molecular 0D hybrid perovskites. However, the origin of different photophysical properties in hybrid organic-inorganic perovskites with different dimensionality are still poorly understood.

Typical 2D layered hybrid perovskites possess anionic metal halide layers with corner-sharing octahedra separated by layers of bulky organic cations. This kind of structure generally induce narrow photoluminescence at room-temperature due to their radiative recombination of free excitons (excited electron-hole pairs). In Chapter 4, it has been shown that the shape of broadband emission of 2D corrugated PEPC perovskite was basically insensitive in different forms such as polycrystalline thin films, ball-milled powders, large single crystals and nanoparticle solution, possessing almost identical broadband photoluminescence. Similar PL quantum yield of single crystals and powders indicate neither particle edge nor surface sites are involved in its photoluminescence behaviour. Along with its photoluminescence, PEPC also exhibits significantly large Stokes shift. Luminescent materials with large Stokes shifts are particular interesting due to its various applications ranging from bioimaging to luminescent solar concentrators. Several factors determine a large Stokes shift in light-emitting systems such as excited-state intramolecular proton transfer, intramolecular energy transfer, and structure deformation. However, replacing chloride anions with bromide and iodide anions in PEPB and PEPI, unfortunately, induces the formation of planar layered structure and does not give rise to any broadband emission.

On the other hands, substitution on A-site cations from PEA cations with the newly synthesized m-XDA organic cations lead to the formation of molecular 0D perovskites

in which the metal halide clusters are periodically arranged within the wide bandgap m-XDA cationic matrix, forming individual metal halide octahedral anions. It was observed that Stokes shift in these molecular 0D tin or germanium-based perovskites are generally large (> 200 nm), while the largest Stokes shift (290 nm) was observed in BATB tin-based perovskite. With the halide substitution in m-XDA based tin perovskites, the PL peak is gradually shifted from chloride to bromide and iodide analogues. This could be due to the increasing average bond length from 2.85 Å to 3.17 Å. Replacing the m-XDA organic cations with alkylammonium (BA and OA) results in larger Stokes shift and much higher PL quantum yield, where the OATB could reach almost 100 % PLQY. This could attribute to the well-confined or isolated tin bromide clusters in OATB single crystals which offers much higher quantum yield. Meanwhile, m-XDAGB (germanium-based) single crystals relatively large Stoke shift but apparently the PL quantum yield is not as high as the tin analogues. The detailed analysis needs to be done to understand the different of PL quantum yield between tin and germanium based molecular 0D perovskites. However, the broadband emissions observed in this study are primarily stems from exciton self-trapping. The exciton couples strongly to the lattice and generates lattice distortions that can be defined as “excited-state defects”. These structural deformations would able to stabilize the exciton, allowing significant broadband emission with large Stokes shift.

In typical 3D perovskites (MALI), only weak self-trapped emissions are observed at low temperature while emissions from both free-exciton and self-trapped excited states were observed at room temperature. Therefore, molecular 0D structure are expected to promote the formation of self-trapped excited states due to the absence of potential energy barrier between free-exciton and the self-trapped excited states. In molecular 0D perovskites, the photoactive metal halide clusters are embedded in inert organic matrix without any intermolecular interactions or electronic band formation, thus, the photoluminescence from the bulk are dominated by the individual metal halide molecular species.

It is commonly accepted that molecular excited-state structural reorganization is the mechanism accounting for large Stokes shifts in various light-emitting materials, including metal halide complexes in solutions. Upon photoexcitation, metal halide

species are photo-excited to the excited states with high energy that promote ultrafast excited-state structural reorganization to excited states with lower energy and generate large Stokes shifted broadband emission. The microsecond lifetimes that observed in BATB, OATB, m-XDAGB, BMPAC and TPPAC could be the characteristic of phosphorescent emissions from the reorganized excited states of individual metal halide octahedra. Thus, these molecular 0D perovskites allow the transformation of “exciton self-trapping” to the molecular photophysics of “excited-state structural reorganization” as those isolated metal halide clusters can be seen as “molecular species”.

As summary, molecular 0D perovskites (tin and germanium based) with high PL quantum yield and large Stokes shift were realized and their electronic coupling between luminescent metal halide clusters are also crucial for enhancing their photoluminescence quantum efficiency. These high attainable PL quantum yield in broadband emitting molecular 0D metal halides guarantees promising luminescent candidates for next generation efficient solid-state lighting and other optoelectronic applications.

6.3 Electronic Properties: Density functional theory calculation

As the optoelectronic properties of a semiconductor depends on the bandedges, we utilized density functional theory (DFT) to unravel the contribution of molecular orbitals on the band-edge. In conventional 3D perovskites, the A-site cations do not take part in the electronic states near band-edges, however, they indirectly affect bandgap by structural reorganization of the crystal lattice. Similar to conventional 3D perovskites, we also found negligible impact of the organic cations in the band-edge states for PEPC, which is a layered 2D structure. The total DOS and PDOS for 2D PEPC are presented in Figure 1. The valence band maxima are predominantly formed by Cl(*p*) with little contribution from Pb(*s*), while the bottom of the conduction band primarily consists of Pb(*p*) states (DFT figure for PEPC). The electronic bandstructure plot revealed a direct nature of the bandgap at Γ , although severely underestimated from experimental bandgap considering without spin-orbit interaction calculations. As with spin-orbit interaction, the bandgap was further reduced to 2.16 eV which is nearly 1.4

eV smaller than the experimental bandgap of 3.56 eV (Figure 6.1a). Interestingly, no changes in the orbital contributions on the band-edges, except for further separation of Pb 6*p* orbital from the organic contribution in the conduction band. It should be noted here that similar observations were also found in conventional 3D perovskites in which spin-orbit interaction results in decrease in energy levels of Pb 6*p* orbitals. We have also investigated the effect of van der Waals (vdW) interaction which plays a major role in stabilizing the 2D crystal structure. However, the inclusion of vdW interaction does not influence the band-edges. The reduction in bandgap (Figure 6.1a) is due to more accurate estimation of lattice constants, which is overestimated in without vdW correction. Hence, for the rest of the calculation, we did not consider SOC and vdW corrections.

Figure 6.1. Partial density of states (PDOS) of (a) *m*-XTAGB and (b) *m*-XTATB

As the soft lattice is one of the key parameters for self-trapping excitons, the effect should be more pronounced for lower-dimensional crystal structure. The decrease in electronic dimensionality of the perovskites would results in increase in electronic bandgap, exciton binding energies, and dielectric confinement, which should enhance the radiative recombination of the self-trapped excitons. To confirm our hypothesis, we further carried out DFT calculation for 0D *m*-XTATB, *m*-XTALB, and *m*-XTAGB. The first principle calculations reveal a direct bandgap of 2.7 eV for *m*-XTATB, 2.8 eV for *m*-XTAGB, and 3.4 eV for *m*-XTALB. For *m*-XTATB and *m*-XTAGB, the top of

the valence band is separated from the rest of valence band with a forbidden gap, similar to other 0D halide perovskites (Figure 6.1). The atomic projected density states (PDOS) as illustrated in Figure 6.1, reveal that the valence bands mostly consist of a mixture of Br *p* and Sn *s* orbitals, whereas the conduction band is derived from the organic molecule. As we did not consider the effect of spin-orbit coupling, we can fairly assume that deep level bands that originates from hybridizations of Br *p* and Sn *p* would also contribute to the conduction band minima due to spin-orbit coupling. The decrease of metal-halide hybridized state energy levels can also be seen in earlier results with PEPC. However, organic components play a major role in the conduction band, which is strikingly different from conventional 3D perovskites and PEPC, in which the filled counter cation states are far below band-edges. We note here that more detailed calculations are required at this stage for decoupling the role of organic cations. Nevertheless, several organic-inorganic hybrid systems with low-dimensional crystal structure have been reported whose conduction bands are composed of organic cations.¹⁻² Along with the molecular contribution on the band-edges, the dispersion of the bands at the band-edge also changes drastically. To correlate the role of the band dispersion on the photoluminescence properties, we calculated the density of states of m-XTAGB and m-XTALB and illustrated in Figure 6.2. The qualitative features of both Sn- and Ge-based 0D perovskites are found to be very similar, i.e narrow valence band-edges. Hence, the 0D characteristics of the crystal structure can be characterized by the strong dielectric confinement, resulting in narrow valence band maxima and conduction band minima. For the case of PEPC, the confinement is applicable along 001 direction (Γ to M in Brillouin zone), whereas dielectric confinement is present in all three direction for 0D crystal lattice. The less confinement in PEPC can be one of the reasons for low PLQY, apart from having non-radiative recombination. Comparing 0D m-XTATB and m-XTAGB, the dispersion in the valence band is at least 0.1 eV larger for latter, which might be the plausible reason for higher PLQY observed in the former. The narrow band edges promote the creation of bound exciton levels inside the bandgap, while soft lattice reduces the energy cost for local structural distortions. Therefore, STE is more frequently observed in low-dimensional perovskites. The narrow dispersion in both the valence band and the conduction bands of m-XTADB and m-XTALB promote strong

localization of excitons at the metal halide octahedra. The non-emissive nature 0D crystal structure m-XTALB can also be explained by the dispersion in the valence band minima. As illustrated in

Figure 6.2, the dispersion in valence band-edge is quite wider as compared to Sn- and Ge-based analogues, which results in weaker exciton binding energy and eventually zero photoluminescence.

Figure 6.2. Total DOS of (a) m-XTAGB, (b) m-XTATB, and (c) m-XTALB

6.4 References

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Chapter 7

Conclusions and Future Work

7.1 Conclusions and Scientific Contributions

Solid-state lighting and white light emitting devices continue to be a global priority. Commercial white-light sources rely either on multiple light-emitting diodes or on coatings with one or more phosphors, yield an integrated emission that appears white. Due to unequal degradation rates of emitters, efficiency losses, and overlapping absorption and emission energies from different components, these combinations of emitters lead to changes in the color of the emission over time. A single material that emits broadband white light is therefore actively sought. Furthermore, if this single phosphor can be processed at low temperatures and can be solution processed, the industrialization of the same would be of great value. Phosphors based on metal halide perovskites have been recently explored as a potential single component phosphors. It is estimated that, thus far 10-15 perovskite materials for white light emission have been reported; with diverse chemistries for A, B, and X sites, as well as structures ranging from 3D to 0D perovskites. While inorganic phosphors (typically rare earth materials based) rely on defects, dopants, and activators for emission; broad band emission is thought to be an outcome of a combination of design-structure-property of the perovskite. It may even arguably be considered an intrinsic property based on composition-structure of the material. Consequently, many theories and mechanisms have been put forth to explain the rationale behind broad-band emission. These include, exciton self-trapping, material defects, dopants, and the structural nature of the perovskite are all thought to play a role with varying photophysical manifestations. The effect of morphology, molecular dimensionality (e.g. layered or 0D structures), substitutions (replacing A, B, X sites, multi-cation / mixed-halide compositions), chirality, are factors yet to be fully studied in perovskites that have the potential for effective broad band phosphors. Mechanistic studies including excited state dynamics as well as structural origins have been probed experimentally. Several theoretical studies have also been initiated; however it is recognized that capturing all the electronic states of large complex systems like perovskites that have large variability in

both structural as well as electronic dimensionality is computationally challenging. Furthermore, the large compositional space available in low dimensional perovskites includes substituents (for A, B, X sites - both total and partial, multications / multihalides), cationic valence states, volume ratios; leading to possible perovskites combinations that are estimated to be in the range of $10^2 - 10^6$ (ref: ACS Energy Lett. 2017, 2, 837-845). These combinations hold the promise to yield new molecular designs of perovskites that can yield high PLQY and performances that will match the inorganic phosphors widely used today. Overall, although there is consensus that broad band emission is intimately related to self-trapped excitons, rigorous evidence about the same is still lacking. Additionally, there is also agreement that the only way with more in-depth studies into the mechanisms and the structure-property relationships of these materials we can progress from trial and error methods to rational materials discoveries. This thesis very much was motivated by these factors.

7.1.1 Layered perovskites

The starting point of the thesis was to explore lower dimensional 2D, 1D, and 0D materials for broad band emission. Exciton-phonon coupling is known to exist in ionic crystals and also in semiconductors; this effect is also known to affect the charge carrier transport. However, the effects of exciton-phonon coupling on the photophysical properties of materials are relatively less explored. The first reports of broad band emission were from layered perovskites; and in this work, 2D perovskites were synthesized using PEA and halide substitutions (I, Br and Cl). Monoclinic PEPI, triclinic PEPB, and triclinic PEPC with bandgaps of 2.3 eV, 2.95 eV and 3.48 eV respectively were synthesized. Out of the three PEPC showed broad-band emission (400-900 nm), while PEPI and PEPB showed narrow PL emissions (<20 nm FWHM).

PEPC in the form of nanoparticles, single crystals, and films all showed high crystallinity and there was practically no difference in the PL emissions and PL lifetimes (~3-5 ns) confirming that surface-to-bulk ratios did not influence the decay kinetics; and the broad band emission was not emanating from surface defects. Laser

fluence-dependent TRPL spectra of PEPC single crystals demonstrated a monomolecular excitonic recombination in PEPC single crystals. In addition, TRPL measurements carried out at three different wavelength (480, 545, and 610 nm) exhibited a linear behavior due to the monomolecular excitonic recombination also support the assignment of broad emission from identical species. Laser fluence and temperature dependent TRPL spectra of PEPC displayed linear dependence highlighting again that emission is not emanating from defects.

The density functional theory (DFT) calculations was conducted to examine the effects of the orientation on the band structure. Negligible contributions from the organic PEA cation was noted on the VBM and CBM. However, the different orientations of the PEA cations are found to affect mainly the energy of Pb 6s valence bands, leading to changes of the band gap and also the total energy of PEPC. Thus, the band gap fluctuation (587 nm - 546 nm = 40 nm) induced by disordered organic cation is unlikely to be the main cause of the broadband white-light emission, which extends from 400 nm to 900 nm.

Both the organic and inorganic constituents are important for generating white emission. The main mechanism responsible for broadband emission in the self-trapping process the excitons scatter off the lattice that results in a shift and broadening of the exciton line. The presence of these excitons results in lattice deformation. The migration to molecular lower dimensional perovskites, with the softer lattice structures and readily deformable metal halide octahedra, facilitated greater exciton-phonon coupling that led to broadband emission. In the case of the semiconducting 2D PEPC perovskite, deformation of the lattice led to the formation of STEs. Morphology-independent and temperature-dependent broadband emission from the PEPC perovskite demonstrated that the exciton-phonon coupling occurred with the phonon of the organic ammonium cation.

The broad band emitting PEPC thin film were stable till ~200 C, and also demonstrated good photostability and solution processability, which is ideal for white light-emitting devices applications. The PEPC was observed to stable under continuous excitation (or

10^5 laser shots) over ~ 14 hours. However, the PLQE of PEPC prepared using in various forms was measured and found to be less than 1%; and thus, other materials were explored that would be suitable for broad band emission.

7.1.2 0D perovskites based on mXDA, Pb-based

In order to explore the novel lower dimensional perovskite materials for broadband emission as well as to enhance the PLQY, the phenyl ammonium cations were replaced with the xylylenediammonium (xDA) cations. The objective was also to study the effect of 'A' site cation on the broadband emission. The 0D perovskite structures formation was noted using the xDA cation, with these 'molecular level' 0D perovskites in forming a (110) or corrugated structures, that is likely to be more deformable than the layered perovskite; and thus more amenable to STE's and useful to achieve white light/broadband emission as well as high PLQY.

Single crystals of *m*-XDALB, *p*-XDALB and *m*-XDALCl were prepared were prepared using anti-solvent vapor assisted crystallization method, and monoclinic crystals with molecular formulae of $(m\text{-XDA})_2\text{PbBr}_6$, $(m\text{-XDA})_2\text{PbCl}_6$ and $(p\text{-XDA})_2\text{PbBr}_6$ designated as *m*-XDALB, *m*-XDALC and *p*-XDALB respectively were prepared. The broadband emission over 400- 500 nm region was recorded for the *m*-XDALB and *m*-XDALC. However, *p*-XDALB materials were not examined further because of poor solubility in common solvents (e.g. DMF and DMSO). NMR measurements of *m*-XDALB and *m*-XDALC confirmed the composition of perovskites and inferred the pure phase perovskite structure formation without any impurities. Addition of the PbBr_2 in *m*-XDALB led the formation of semiconducting 1D perovskite.

The PL spectrum of *m*-XDALB single crystal exhibits a broadband emission that covers from 400 nm to 500 nm with peak maximum at 440 nm, under the photoexcitation of 334 nm. While the PL spectra of *m*-XDABr₂ + PbBr_2 (referred to as *m*-XDALB₂) exhibited emission in the visible region from 400 nm to 650 nm. Significant improvement in the PL and PL excitation spectral intensity of *m*-XDALB was noted by lowering the temperature from 280 K to 80 K. This enhancement may be attributed to densely packed crystal structures that enhances phosphorescence and diminishes non radiative pathways. The *m*-XDALB₂ thin film show broadband emission (CIE: 0.36,

0.40), which lies in the “white” region, suitable for cool white light applications. The excitonic decay kinetics at ~400nm for *m*-XDALB₂ films showed distinctly longer life times, suggesting that addition of PbBr₂ improved crystallinity and reduced the nonradiative recombination. The decay kinetics at 500, 550, and 600 nm were found to be invariant suggesting that a single species was responsible for a broad emission.

DFT and TD-DFT calculations on the density of states and the optical absorption spectra were conducted to confirm the large band gap of “0D” perovskites. The calculated absorption spectra for *m*-XDALB showed a band maximum at 4.5 eV (276 nm), whereas *m*-XDALC exhibited two blue-shifted overlapping bands at 5.0 eV (248 nm). The blue-shift of absorption maxima in going from *m*-XDALB to *m*-XDALC was consistent with the trend of increasing band gaps in going up the halide group due to the expected lower density of states.

Temperature-dependent (300K to 20K) PL measurements of a *m*-XDALB thin film exhibited the emission peak due to free (at 400 nm) and bound excitons (at 600 nm). Upon lowering the temperature, a steady increase in PL peak intensity was observed for the broad emission centered at ~ 600 nm however, for the free excitonic PL intensity centered at ~400 nm noted non-monotonic behavior with a maximum at T ~ 120 K. The initial increase could be due to reduced non-radiative recombination of free excitons, while the subsequent decrease could be due to suppressed detrapping of bound excitons into free excitons.

At low temperatures, bound excitons do not have sufficient energy to overcome the trapping barrier for conversion into free excitons and the broad emission may be partly attributed to recombination of bound excitons. At low temperatures, the probability of phonon absorption for indirect recombination is reduced. This leads to increased radiative recombination of the bound excitons, and hence an increase in the PL intensity. This reduction in non-radiative recombination at lower temperatures is also consistent with PL lifetime lengthening at lower temperatures. Similar observation were also noted for 2D PEPC.

Based on all our photophysical measurements, it has been proposed that the processes occurring in this white emitter can be summarized as (i) excitation generates free

excitons that recombine with lifetime of (2.77 ± 0.01) ns, (ii) ultrafast self-trapping occurs at (170 ± 150) ps after overcoming a self-trapping barrier of ~ 10 meV, (iii) exciton-phonon scattering broadens the energy linewidth of self-trapped excitonic emission, (iv) self-trapped excitons recombine with lifetime of (2.8 ± 0.1) ns.

This work advances the research on 2D, 1D, and 0D perovskites. The most promising broadband emission observed was from addition of 1 mole excess PbBr_2 , with stability up to 250°C , CIE coordinates of (0.36, 0.40), good CRI values of 82.9, and a CCT of 4805 K, which makes the material suitable for cool white light applications.

7.1.3 Lead-free broad band light emission

In solar cells, the efficiencies of lead-free perovskites have been much inferior to those of the conventional lead-based materials (e.g. $\text{CH}_3\text{NH}_3\text{I}_3$). The motivations of exploring them in light-emission were two-fold: lead replacement, but also exploring the potential changes that could be instituted by Pb substituents towards broad band emission, self exciton trapping, and general to the structure of the 0D perovskites. To understand the effect of B-site cations, Sn and Ge substituents were reacted with the meta-xylylenediammonium (mXDA) materials to form m-XDATB and m-XDATB.

The m-XDATB crystal structure comprised of interspersed divalent XDA cations between the isolated SnBr_6^{4-} octahedral units, with each SnBr_6^{4-} unit being centrosymmetric with three distinct Sn-Br bonds. Characterization by NMR and XRD confirmed the +2 oxidation state for Sn and purity of the single crystals. The variance in the octahedral elongation of m-XDATB was calculated to be $1.0085 \text{ \AA}$, compared with $1.0001 \text{ \AA}$ observed in MALI.

However, due to long Sn-Sn distance, the band structure along reciprocal space was practically dispersionless. While bottom of the conduction band consisted of antibonding states from the XDA molecule, top of the conduction band was derived from hybridization between empty Sn p and Br p orbitals. The emission spectrum covered the visible region from 400 - 650 nm, with a maximum at 509 nm, a FWHM of 95 nm, and a large Stokes-shift of 160 nm. The PLQY of the m-XDATB was measured using single-crystals to be 60 %, which is one of the highest values reported

in the literature. Similar emission spectrum under different wavelength excitation, and similar excitation spectrum for different emission peaks indicated that the entire broadband emission arises from the same excited state. The Stokes shift is also dependent on the distortion of the octahedra, and it is postulated that the structural deformation made possible by the small Br ion, structural changes in the Sn-Br octahedra were some of the factors leading to the large Stokes shift.

WLEDs were fabricated by blending the cyan light-emitting m-XDATB perovskite with a red light-emitting sulfoselenide (BUVR03) in order to shift the CIE coordinates of the cyan light emitted by m-XDATB closer to white. Blends of 2:1 mXDATB:BUVR03 yields CIE (0.35, 0.43) and CRI of 86, and CRT of 5144K. Both ball milled and single crystals of m-XDATB exhibited similar emissive behaviour. TGA thermograms confirmed the stability of the material to at least 200 °C.

Figure 7.1. (a) Summary of the ‘Stokes shift’ observed in the various low dimensional metal halide perovskite materials (including 2D, 1D and 0D) synthesized (studied) during the completion of thesis work to achieve a broadband emission. b) CIE color coordinates of the low dimensional metal halide perovskite materials.

Lead-free 0D perovskites were also formed with Ge^{2+} which has a higher electronegativity and a more covalent character (than Pb). The crystal system of the m-XDAGB was triclinic which is different from the monoclinic crystal systems of the m-XDALB and the m-XDATB. Quadratic elongation was measured to be 1.0009, which indicated less degrees of distortion Ge-Br octahedron; compared with that of the Sn

based materials. Similar to that of mXDATB, the oxidation state of Ge in mXDAGB was also determined to be +2, and the thermal stability was confirmed to be up to 200 °C.

The emission spectrum covers the visible region from 450 nm to 700 nm with, a FWHM of 110 nm, a peak maximum at 555 nm, and Stokes shift of 225 nm. PLE spectra are blue shifted as the temperature is lowered and showed a narrowing effect without change in the peak position at lower temperatures. Similarly, comparison of Sn-Br octahedra present in m-XDATB perovskite indicates the larger FWHM and Stokes shift in less distorted metal halide octahedra. The PLQY measured was 20 %, with the PLQY trend: m-XDATB > m-XDAGB > m-XDATB. The main factors that affect PLQY are still being researched; however, metal-halide bond character, heavy-atom effect, distortion of octahedra, and charge transfer between the metal ion and halide ion are all considered to influence the emission efficiencies. PL lifetimes of m-XDAGB were found to be 3.54 μ s, and the CIE (0.3833, 0.4946) was recorded for the m-XDAGB. White-light emitting were also fabricated using yellow-emitting m-XDAGB and a blue-emitting europium doped barium magnesium aluminate ($\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$) phosphor with good CRI and CCT values. Summary of the ‘Stokes shift’ observed in the various low dimensional metal halide perovskite materials (including 2D, 1D and 0D) synthesized (studied) during the completion of thesis work to achieve a broadband emission along with CIE color are shown in Figure 7.1b.

In summary, this thesis researched the phenomena of broad-band emission emanating from molecularly lower dimensional perovskites. In particular, reducing dimensionality to 2D and 0D increased localization of electronic state, narrower conduction and valence bands, and induced a softer matrix that led to self-trapped excitons. Although mechanistic studies, structural analysis, and theoretical calculations were used to understand the effect of A-site, lead-free elements, and halide substitutions additions, the origin of several photophysical properties are yet to be fully understood. Nevertheless, this thesis has proposed several 2D and 0D materials that have the promise of broad band, white emitting, and or down conversion phosphors. Although the layered perovskites

successfully demonstrated white light emission, the 0D perovskites with isolated tin bromide octahedra also showed remarkable broad band emission properties. Excitons of metal-centered electronic transitions involving triplet states are thought to couple with phonons from metal halides, forming self-trapped excitons that can be correlated with large Stokes shift and broadband emission. It has clearly been established in this thesis that factors such as structural deformations, rigidity of the structure, are very important criteria in terms of creating self-trapped excitons and broad band emission, the perovskites represent a vast parametric space that needs further exploring to find the right material combinations that would be viable replacements for currently used phosphors.

7.2 Future Outlook

This section briefly lists and discusses potential new experiments and directions of research relevant to the phenomena and material systems covered in this thesis.

7.2.1 Tailoring emission from organic fluorophores and metal-halide lattice

The approach followed in this thesis utilised exciton-phonon coupling as the mechanism to induce broadband emission. As indicated, the non-radiative losses associated with phonon modes in the organic ammonium cation is a weakness that needs to be carefully managed. Due to the flexibilities afforded by the choice of A site cation in low dimensional halides, other approaches to induce broadband emission could be pursued. This is in contrast to their 3D counterparts because the size of the templating organics is no longer relevant to the materials formability. However, semiconducting and photophysical features of reported LD hybrids still generally depend on the compositional constituents of their inorganic frameworks. This is because most organic cations employed feature frontier orbitals that are not able to interact with those of halometallate network (i.e. ‘passive’). This eventually leads to the formation of ‘quantum well’ where the organics matrix serving as ‘barriers’ to the inorganic ‘wells’.

If functionalized counteraction molecules (e.g. those with luminescent π -conjugated chromophores) are employed, the cationic molecules will not only serve as templates

and cause indirect perturbations towards luminescent property of the hybrids, but they can also influence the absorption/emission spectra of the materials directly. Thus, it is expected that white-light emission can be generated out of the material when chromophores with suitable emission profiles are employed together with the yellow-light emitting metal-halide lattices. The organic molecular structures can further be tuned (through crystal engineering approach) depending on a) relative position of the organics' molecular energy levels to the excitonic levels or band edges of the semiconducting layer, b) possibility of energy transfer (Forster or Dexter), as well as c) excitonic interaction (Wannier and Frenkel) between both organic and inorganic components (Figure 7.2). Some potential candidates of π -conjugated organic cores that could be employed to achieve the goal include carbazole, tetracene, fluorene, pyrene, and coumarin.

Figure 7.2. Various scenarios of metal halide-organic chromophore electronic structure arrangements.

7.2.2 Transition metal doping of low dimensional halides

Doping impurity ions into chalcogenide nanocrystals such as CdS and ZnS/Se has been established as a proven approach to tuning the properties of the host materials. Electronic and optical properties of 3D perovskite semiconductor nanocrystals can be efficiently modulated by doping different metal ions, such as Mn^{2+} , Sn^{2+} , Cd^{2+} , Zn^{2+} ,

Au^{3+} , and various lanthanide ions. Among these doped metal ions, Mn^{2+} has attracted the most research attention, owing to the intriguing properties of Mn-doped metal halide hybrids due to its highly luminescent red emission. In these nanocrystals, strong sensitized luminescence from d-d transition of Mn^{2+} was observed due to the strong exchange coupling between the charge carriers of the host and dopant d electrons mediating the energy transfer. Thus, one can imagine that in the doped-LD system, the excited state energy would flow from the direct free exciton excited states to both the self-trapped excited states and doping ions simultaneously. As such, efficient dual emission can be obtained from this configuration. Consequently, white-light emission from a single material can be realized if the broadband emissions exhibited by the ‘host’ metal-halide are engineered to occur at blue region of light spectrum. This can be achieved by systematic substitution of either the metal or halide components of the materials’ inorganic framework.

7.2.3 Improving oxidative stability of Sn- and Ge-based LD hybrids.

As shown in this thesis, low dimensional metal halide perovskites have fascinating optoelectronic properties that exceed the benchmarks set for many practical applications. However, the toxicity of Pb-based compounds has been a major problem for its commercialization. Sn- and Ge-based materials are therefore of great interest. However, Sn^{+2} and Ge^{+2} are less stable due to weaker inert pair effect. Herein, we propose some future works to tackle the issue:

Pb-Sn alloy

The most straightforward way to obtain relatively stable materials while reducing their toxicity is by alloying the Pb-based compound with the Sn- and Ge-counterparts. It has been demonstrated in the solar cells case that even with substitution of as much as 50% Pb with Sn, devices with stability being comparable with the pure Pb counterpart can be obtained. Thus, although the structures of the final materials need to be assessed in case if there is phase separations occurring due to the parent compounds being not isostructural, the Pb-Sn alloy is a pathway worth exploring.

a. Formation of thin layer of native-oxides passivation

It was previously reported that the extremely high oxidation activity of Ge^{+2} had enabled the rapid formation of an ultrathin (<5 nm) uniform native- GeO_2 surface passivating layer on top of the corresponding 3D $\text{CsSn}_{0.5}\text{Ge}_{0.5}\text{I}_3$ perovskite. Such extra layer imparts the overall material with superior stability over its pure counterparts CsSnI_3 and CsGeI_3 . Similar approach can thus be applied in our system where Sn^{+2} and Ge^{+2} based LD hybrids are alloyed to form mixed Ge-Sn products. Upon fabrication of the thin films, brief exposure to air will then initiate the formation of the native-oxide layer. Different composition of Sn and Ge will be systematically tuned to investigate the oxide layer formability and techniques, such as incident angles-dependent X-ray photoelectron spectroscopy (XPS) and surface mapping will be carried out to characterize such layer.

b. Reduction of intrinsic defect with sulfur anions

Improving the stability of Sn- and Ge-based materials can also be done by incorporation of small amount of coordinating dianion species such as sulfur (S^{2-}). It was demonstrated previously that when Sn^{+2} was replaced with some Sn^{+4} (due to spontaneous oxidation) during preparation of 3D perovskite, such as MASnI_3 , the resulting final composition was $\text{MA}_{1-2x}\text{S}^{2+}_x\text{Sn}^{+4}_x\text{I}_3$, with the organic cation and tin vacancies. As such, in order to form a defect-free ASnI_3 lattice, it is necessary to balance the additional +2 charge resulted from the oxidation process with additional negative charges to maintain charge neutrality. Dianionic sulfur fulfills this requirement and thus, the presence of sulfur anions during the preparation of S-modified metal-halide hybrid is hypothesized to be capable of reducing intrinsic defects within the materials and as a result, improved inherent stability can be realized.

7.2.4 Enhancing the performance of perovskite solar cells (PSCs) with a LD metal-halide hybrids down-converters.

Due to the lesser number of overlapping metal and halide orbitals in their quantum-confined inorganic lattices, the low dimensional hybrids have absorption in the UV region. Due to the strong exciton-phonon coupling, broadband emissions in the visible light region can be obtained from the materials upon excitation with UV light. Such a large Stoke shift allow the possibility of using these low dimensional hybrids as

candidates for extending the spectral response range of PSCs up to the UV region through extensive absorption of UV light and subsequent visible light re-emission to the perovskite layer. Since 3D perovskite is also known to exhibit low intrinsic chemical instability towards UV-light in a device configuration, the absorption of UV light by the low dimensional hybrids and their conversion into wavelengths that can be utilized by the solar cell is needed.

Preliminary experiments for checking the feasibility of these low dimensional hybrids for luminescent downshifting and increased solar harvesting were carried out. The materials utilised as such luminescent down-shifting layer (LDSL) should have very high photoluminescence quantum yields (PLQYs) approaching unity. However, since the perovskites synthesized within the context of this thesis did not have PLQYs Larger than 60%, they were not suitable. 1-Butyl-1-methyl-pyrollodiniumantimony chloride (BMPAC) was chosen to use as LDSL due to high PLQY (~ 100%) of BMPAC which had been previously reported.¹ Large and transparent single-crystals of BMPAC were prepared from saturated perovskite solution of 1-Butyl-1-methyl-pyrollodinium chloride (2 mole) and antimony chloride (1 mole) in DMF. This solution was left undisturbed for a week which resulted in the growth of larger crystals of BMPAC (Inset of Figure 7.3a). Photoluminescence excitation, and photoluminescence spectra of this material is shown in Figure 7.3a. Excitation spectra of BMPAC has onset in the UV region and covers the deep-UV region. Photoluminescence spectrum shows broadband emission which covers from around 500 nm to 800 nm and has maximum at around 600 nm. UV excitation, yellow emission, and near-unity PLQY impart that this material is suitable to use as luminescent downshifting layer (LDSL) in solar cells.

Hence, we explored its application as LDSL in solar cells. Semi-transparent perovskite solar cells perform poorly in the UV region due to parasitic absorption of doped spiro-OMeTAD under backside illuminations.

Figure 7.3. Schematic representation of figures of merit used to evaluate the BMPAC as LDSL. a) Emission overlap (EO) integral showing the optical absorption, photoluminescence and excitations spectra, b) Emission spectral matching (ESM) integral indicating how the photoluminescence emission of the LDSL overlaps with the optical response of the 3D perovskite solar cell, c) absorption spectral matching (ASM) integral indicating how the solar spectrum could excite the LDSL, and d) EQE spectra of semitransparent PSC with and without LDSL clearly indicating an enhanced response in the UV region.

Hence, semi-transparent perovskite solar cells require LDSL which could convert the high-energy UV-photons to low-energy photons before the light reaches the solar cells. In order to evaluate the suitability to use these perovskite as LDSL, a set of figures of merit like emission overlap integral (EO), emission spectral matching integral (ESM), absorption spectral matching (ASM) integral, and parasitic absorption integral (PA) were calculated and schematic representation of these figures of merit were shown in Figure 7.3c. Figures-of-merit of BMPAC show that BMPAC is suitable to use as LDSL.

Free-standing perovskite single-crystals were placed on top of semi-transparent PSC, and IPCE spectra were collected and shown in Figure 7.3d. The semi-transparent solar

cells were fabricated by replacing the metal electrode with a sputtered transparent conductive oxide layer. IPCE spectra clearly show no IPCE of semi-transparent PSC in the UV-region but LDSL on top of solar cell increased the IPCE from zero to nearly 25%, and this clearly demonstrate the BMPAC as a potential LDSL. However, there was a reduction in the IPCE over the visible region indicating that parasitic optical absorption in the crystal as well as wave-guiding effects in the crystal need to be carefully managed. In addition, the degradation of the BMPAC surface was observed during the measurement due to the interaction of this crystal with moisture. To improve the reliability and practicality of utilising such LDSLs, they need to be processed as thin films instead of the single crystals utilised in the present experiments. Preliminary efforts to synthesize high quality thin films or thin film dispersions of nanoparticles in a polymer matrix of low dimensional luminescent perovskites are detailed in the Appendix.

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APPENDIX

Preparation and preliminary characterization data of linear alkyammonium tin bromides

Butylammonium tin bromide : Single-crystals of the butylammonium tin bromide (BATB) were prepared by a cooling process in which hot perovskite solution of butylammonium bromide (0.92 g, 6.0 mmol) and tin bromide (0.28 g, 1.0 mmol) in acetone (4 ml) at 70 °C was cooled to room temperature slowly. This resulted in the formation of $(\text{C}_4\text{H}_9\text{NH}_3)_6\text{SnBr}_8$ (BATB) which has 0D perovskite structure as shown in Figure A1. This material was further characterized with ssNMR, PL decay, XPS, and XRD (Figure A 1 – Figure A 4). This material undergoes a phase transition upon storage and results in the opaque crystal, so it is not suitable for using as LDSL.

Figure A 1. Crystal structure of the BATB. Projection of the BATB in the different planes showing isolated SnBr_6^{4-} octahedral units and disordered butylammonium ions arranged in layers (c-c bonds are not shown due to disorder of carbon atoms, hydrogens were omitted to make it simple).

Figure A 2. Long photoluminescence decay of BATB single-crystal.

Figure A 3. Powder XRD of BATB microparticles produced by ultrasonication of the single crystals.

Figure A 4. XPS spectra of BATB. a) wide scan, and b) narrow scan.

Octylammonium tin bromide: Similarly, larger, transparent, and thin crystals of octylammonium tin bromide (OATB) were prepared by antisolvent vapor-assisted crystallization where saturated solution of octylammonium bromide (6 mole) and tin bromide (1 mole) were dissolved in DMF and dichloromethane was used as anti-solvent. After 24 hours, crystals were collected and dried for further use. Figure A 5 shows the picture of the crystals under ambient and UV-light. Multinuclear solid-state nuclear magnetic resonance (NMR) studies of BATB and OATB were done in order to confirm the chemical structure of the organic cations and the Sn-Br octahedra. The ^1H NMR spectra of BATB and OATB are shown in Figure A5. The ^1H NMR spectrum of BATB contains multiple sharp resonances over the range of 9 – 0 ppm, which suggests that the sample contains leftover residues of toluene and acetone used in its preparation. Similarly, the OATB spectrum presents with 2 sharp resonances at 3.7 and 1.9 ppm, corresponding to residual THF. The ^{13}C NMR spectra of BATB and OATB are shown in Figure A5b. Both samples contain high-intensity resonances between 42 – 14 ppm (4 for BATB and 8 for OATB) whose chemical shifts correspond to butyl and octyl chain carbons. The additional resonances at higher field in the ^{13}C spectrum of BATB can be assigned as the organic solvent residues (toluene and acetone) predicted from the ^1H NMR data. Analogously, THF appears in the ^{13}C spectrum of BATB with resonances at 68.1 and 26.3 ppm. Hence, the ^{13}C NMR data confirms the composition of the BATB and OATB crystals. Of additional interest are the splittings observed in some of the frequency resonances in the BATB and

OATB ^{13}C NMR spectra. These resonances (15 and 21 ppm for BATB; 14, 28 and 30 ppm for OATB) are all split into two components of unequal intensity. This suggests that two distinct conformations of the n-butylammonium and n-octylammonium chain exist within the crystal structures. The ^{119}Sn NMR spectra of BATB and OATB are shown in Figure A 5c. They both contain single ^{119}Sn components at $\delta_{\text{iso}} = 591 \pm 2$ and -584 ± 1 ppm, respectively. The slight chemical shift difference is a result of the altered chemical environment created by the different cations. An agreeable fit of both resonances was achieved by simulating the spectra using Gaussian/Lorentzian lineshapes. The lineshape of the OATB resonance is roughly 2 times narrower than for BATB. Unlike previous studies on SnBr_6 octahedra compounds, such as *m*-XDATB, no Sn-Br J-coupling was observed. [mXDATB] This is hypothesized to be due to the additional Br atoms adjacent to the SnBr_6 octahedra, which reduce the rigidity of the lattice, inducing faster relaxation of the $^{79/81}\text{Br}$ nuclei in BATB. Due to the faster relaxation, the Br are effectively decoupled from the Sn nuclei.

Figure A 5. NMR of BATB and OATB. a) ^1H NMR, b) ^{13}C NMR, and ^{119}Sn NMR.

Luminescent downshifting layers: Free-standing, transparent, thin, and larger OATB single-crystal was used as LDSL on top of semitransparent PSC, and EQE spectra were collected and shown in Figure A 6. EQE spectra show that there is increase of nearly 20% EQE in the UV region, which clearly demonstrate OATB as LDSL. To improve further the EQE in the UV region two single-crystals were used on top of semitransparent PSC, but this resulted in the drop in the EQE. This indicates that the amount of material available in the single-crystal is enough and the light scattering, and reflection by the crystal and solar cell interfaces are causing the loss in the EQE. Therefore, further improvement could only be achieved by minimizing the scattering, and reflection losses.

Figure A 6. EQE spectra of semitransparent PSCs. a) with and without BMPAC LDSL, and b) with and without OATB LDSL

This could be achieved by making nanoparticles of these perovskites. Hence, nanoparticles of OATB were prepared by simple dissolve and precipitate method where the OATB precursors were dissolved in DMF and this solution was added in the bad solvent toluene swiftly under vigorous stirring. This resulted in the formation of OATB nanoparticles along with OATB microparticles, which was confirmed with TEM characterizations. Figure A 7 shows the TEM images of OATB nanoparticles, and microparticles. Trials of using such particles dispersed in insulating polymeric thin films to be utilized as LDSL are under progress.

Figure A 7. a) TEM image of OATB nanoparticles, b) lattice fringes of OATB nanoparticle, and c) powder XRD of OATB.

List of Publications

First-authored papers

1. **Krishnamoorthy Thirumal**, Wee Kiang Chong, Wei Xie, Rakesh Ganguly, Subas Kumar Muduli, Matthew Sherburne, Mark Asta, Subodh Gautam Mhaisalkar, Tze Chien Sum, Han Sen Soo, Nripan Mathews. Morphology Independent Stable White-Light Emission from 2D Perovskites Driven by Strong Exciton-Phonon Coupling to the Organic Framework, **Chem. Mater.**, **2017**, **29**, 3947–3953. (Impact factor – 10.16. Total number of citations - 51)
2. **Krishnamoorthy Thirumal**, Hong Ding, Chen Yan, Wei Lin Leong, Tom Baikie, Ziyi Zhang, Matthew Sherburne, Shuzhou Li, Mark Asta, Nripan Mathews, Subodh G. Mhaisalkar, Lead-free Germanium Iodide Perovskite Materials for Photovoltaic Application, **J. Mater. Chem A**, **2015**, **3**, 23829–23832 (Impact factor – 10.733. Total number of citations - 250)
3. **Krishnamoorthy Thirumal**, Fu Kunwu, Pablo. P. Boix, HairongLi, Koh Tech Ming, Wei Lin Leong, Satvasheel Powar, Andrew Clive Grimsdale, Michael Gratzel, Nripan Mathews* and Subodh Gautam Mhaisalkar*, Swivel-Cruciform Thiophene Based Hole-Transporting Materials for Efficient Perovskite Solar Cells, **J. Mater. Chem A**, **2014**, **2**, 6305–6309 (**Most accessed article of 2014**, Impact factor – 10.733. Total number of citations - 135)
4. **Krishnamoorthy Thirumal**, Mu Zhi Tang, Akshara Verma, A. Sreekumaran Nair,* Damian Pliszka, Subodh G. Mhaisalkar and Seeram Ramakrishna*, A facile route to vertically aligned electrospun SnO₂ nanowires on a transparent conducting oxide substrate for dye-sensitized solar cells, **J. Mater. Chem**, **2012**, **22**, 2166. (Impact factor–5.9. Total number of citations - 57)
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Co-authored papers

7. Pandihare Cholakkal Harikesh, Bo Wu, Biplab Ghosh, Rohit Abraham John, Stener Lie, **Krishnamoorthy Thirumal**, Lydia Helena Wong, Tze Chien Sum, Subodh Mhaisalkar, Nripan Mathews 'Doping and Switchable Photovoltaic Effect in Lead-Free Perovskites Enabled by Metal Cation Transmutation' *Adv. Mater.* **2018, 30, 1802080**
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