Preface

Inorganic halide perovskite $CsPbX_3$ (X=Cl, Br, or I) refers to a class of perovskite materials that have garnered significant attention for their optical applications. These materials exhibit remarkable optoelectronic properties, making them suitable for a variety of applications, including solar cells, light-emitting diodes (LEDs), photodetectors, and lasers. $CsPbX_3$ perovskites exhibit high photoluminescence quantum yield (PLQY), which is essential for efficient light emission in LEDs and other photonic devices. This high PLQY results from their direct bandgap and efficient radiative recombination. By varying the halide composition (Cl, Br, I), the bandgap of $CsPbX_3$ can be tuned across a wide spectral range from the ultraviolet (UV) to the near-infrared (NIR). This tunability allows for the customization of perovskites for specific optical applications, such as multi-color LEDs and tunable lasers.

In the progress of halide perovskite, Tsutomu Miyasaka and colleagues at University of Yokohama published a groundbreaking paper in 2009 demonstrating the use of methyl ammonium lead iodide ($CH_3NH_3PbI_3$) as a light-absorbing layer in dye-sensitized solar cells, achieving modest efficiency [1]. This work spurred significant interest in perovskites for photovoltaic applications. Between 2009 and 2012, efficiencies of perovskite solar cells rapidly improved from around 3% to over 10%. In 2013, The efficiency of perovskite solar cells surpassed 15%, making them competitive with other thin-film technologies. This milestone was achieved through advancements in material synthesis, device engineering, and interface optimization. Researchers and scientific groups working in this area then began exploring halide perovskites for LEDs applications. It was found that the perovskite nanocrystals (quantum dots) exhibits high PLQYs, leading to the development of efficient perovskite LEDs. The $CsPbX_3$ nanocrystals and quantum dots offer additional advantages, such as enhanced quantum confinement effects, leading to superior optical properties. These nanostructures are being explored for applications in displays, bioimaging, and quantum computing. Efforts to improve the stability and scalability of perovskite materials intensified since about 2017. Within a year, $CsPbX_3$ perovskites have been successfully integrated into various optoelectronic devices, demonstrating high performance. For instance, perovskite solar cells have achieved power conversion efficiencies exceeding 25%, while perovskite LEDs have demonstrated high brightness and efficiency.

Despite all these promising properties of $CsPbBr_3$ and progress in various optoelectronic applications, stability issue particularly under moisture and UV exposure is the important concern. Recent research has focused on enhancing the stability of $CsPbX_3$ perovskites under operational conditions. Techniques such as surface passivation, incorporation of protective layers, compositional engineering, doping metal ions, casing it into different molecular structures and development of more robust material formulations have led to improved stability, making these materials more viable for commercial applications. Secondly, the presence of lead in $CsPbX_3$ perovskites raises concerns about toxicity and environmental impact. Research into lead-free alternatives and effective recycling methods is essential for sustainable development. Scaling up the production of high-quality $CsPbX_3$ materials and devices while maintaining performance and uniformity is a significant challenge. Advances in fabrication techniques and material processing are needed to facilitate large-scale applications.

There are many techniques to synthesize the $CsPbX_3$, in powder-based techniques includes solid state reaction, cold sintering, etc.[2], and solution-based techniques include hot-injection, anti-solvent assisted low temperature, convection, solvothermal, ultra-sonication, and microwave [3]. The hot-injection method is of the best solution based synthesis techniques of $CsPbBr_3$ for the uniform particles size distribution in the nano-scale (NCs, QDs). We have synthesized $CsPbBr_3$ and Eu-doped $CsPbBr_3$ NCs size below 20 nm using hot-injection method. Detailed synthesis procedures are discussed in Chapter 3. Exploring the synthesis techniques for the scalability, we have synthesized $CsPbBr_3$ attached Lanthanide metal organic framework (Ln-MOF) and $CsPbCl_{1.5}Br_{1.5}$ attached Ln-MOF using hydrothermal method followed by anti-solvent assisted technique. Detailed synthesis steps are explained in Chapter 4 and Chapter 5.

Main objective of this thesis is to study the investigation of the optical properties of $CsPbX_3$ as well as the properties enhancement in the presence of different Ln^{3+}-ions. The thesis is divided into seven Chapters. The brief explanation of each Chapter is given below:

Chapter 1 summarizes the various types of inorganic halide perovskite, structure, and optoelectronic properties of $CsPbX_3$ (X=Cl, Br, I), obtained after literature survey. The optoelectronic properties enhancement after the Ln^{3+}-ion doping and its emerging applications are summarized in this Chapter. The spectroscopy of the Ln^{3+}-ions (specially Eu^{3+}, Er^{3+}, Yb^{3+}, Tb^{3+}) are discussed in detail. The Ln-MOF which is porous material provide room to $CsPbX_3$, to intercalate into the framework is discussed. Also, the properties of the thermally stable scandate materials ($LnScO_3$) very suitable for the upconversion (UC)-based optical-thermometry is summarized in this Chapter.

Chapter 2 lists all the precursors used for the synthesis of the sample in this thesis work. Synthesis techniques, such as hot-injection method, solution-processed hydrothermal method, and gel-combustion method are discussed in detail. Sample characterization techniques such as X-ray diffraction (XRD), high-resolution transmission electron microscope (HR-TEM) and scanning electron microscope (SEM), ultra-violete (UV)-visible-near infrared (NIR) absorption, Fourier transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS), photoluminescence (PL) spectroscopy working principle are discussed in brief. Along with this software used for the data analysis named FullProf, ImageJ, color calculator CIE 1931, and OriginPro 9.0, etc., are briefed.

In **Chapter 3** structural and optical behaviors of $CsPbBr_3$ and Eu^{2+}: $CsPbBr_3$ halide perovskite NCs synthesized by using the hot-injection method are studied. The PL emission of synthesized $CsPbBr_3$ and Eu^{2+}: $CsPbBr_3$ NCs under different excitation wavelengths is recorded and behaviors of the blue and green emissions peaks are monitored. We have also studied the effect of multi-wavelength stimuli response on the PL spectra of Eu-doped $CsPbBr_3$ NCs. Detailed decay dynamics was also performed and analyzed to see the effect of Eu^{2+}-ion in $CsPbBr_3$ NCs.

In **Chapter 4,** pristine Eu-MOF and Eu-MOF interfaced with $CsPbBr_3$ ($CsPbBr_3$@Eu-MOF) is synthesized using a hydrothermal method. The Eu-MOF and $CsPbBr_3$@MOF characterized for its structural, morphological, and optical properties. Color-tunable emission of $CsPbBr_3$@Eu-MOF under different excitation wavelengths, which makes it highly suitable for encryption and decryption of security codes in anti-counterfeiting applications is investigated. Also, the energy transfer mechanism among the metal-centered (Eu^{3+}), charge transfer band (CTB), and guest-centered ($CsPbBr_3$) emission in $CsPbBr_3$@Eu-MOF is studied.

Chapter 5 strategize to explore the single-phase $CsPbCl_{1.5}Br_{1.5}$@Tb/Eu-MOF for WLEDs application. The Tb/Eu-MOF is synthesized via a hydrothermal method and then post-treated to form $CsPbCl_{1.5}Br_{1.5}$@Tb/Eu-MOF. The energy transfers mechanisms among the organic linker, Tb^{3+}, Eu^{3+} ions, and the halide perovskite $CsPbCl_{1.5}Br_{1.5}$ are thoroughly studied. In the $CsPbCl_{1.5}Br_{1.5}$@Tb/Eu-MOF for WLEDs, the red component of the RGB spectrum is achieved by the Eu^{3+} ion, the green by the Tb^{3+} ion, and the blue by the characteristic broad emission of $CsPbCl_{1.5}Br_{1.5}$. The CIE color coordinates of the $CsPbCl_{1.5}Br_{1.5}$@Tb/Eu-MOF photoluminescence emission are calculated to be very close to the standard white light coordinates (0.333, 0.333). In addition to this, “W” pattern is developed on different substrate for optical encryption and decryption purpose. The encrypted patterns show color change under different wavelengths light illumination and thus can be used for strategic anti-counterfeiting application.

In **Chapter 6** to overcome one of the research gaps in the field of optical properties of Ln-doped $GdScO_3$ and photon upconversion (UC) emission, $GdScO_3$ and Yb^{3+}, Er^{3+} co-doped $GdScO_3$ nanocrystals were synthesized at low temperature utilizing self-propagated gel-combustion synthesis technique. The synthesized materials structural and optical properties were characterized and studied using various spectroscopic measurement techniques. For the first time, the photon UC properties of Yb^{3+}, Er^{3+}-ions in $GdScO_3$ nanocrystals were investigated. The synthesized sample show high thermal stability. These properties were applied in non-contact, luminescence-based optical thermometry, functioning effectively within the temperature range of 299 – 473 K.

Chapter 7 concludes all the experimental works and literature survey done for the thesis and briefs its future scope for the researchers working in this area of interest.