Lanthanide Interfaced Inorganic Halide/Oxide Perovskites for Optical Applications

Thesis submitted in fulfilment
for the Award of

Doctor of Philosophy
in
Physics
by

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Year of Submission
2024

Chapter 7: Conclusions and Future Perspective

7.1 Conclusion of the Present Investigation

In this thesis work, different compositions of inorganic halide perovskite ($CsPbX_3$; X=Cl, Br) have been synthesized using various synthesis methods, such as hot-injection, and ligand-assisted reprecipitation methods. A detailed discussion of the synthesis methods is given in Chapter 2. Lanthanide ions (Ln^{3+}) have their unique optical properties, including ladder-like energy levels, sharp emission, and long luminescence lifetimes, which make them suitable for various applications. The Ln^{3+}-ions have been used as a dopant to increase the optoelectronic properties of $CsPbX_3$. Ln-doping can passivate defects within the perovskite structure, thereby impacting charge carrier dynamics and overall material stability, as discussed in Chapter 3. Ln^{3+}-ions doping into $CsPbX_3$ enhance their photoluminescence (PL) properties. Energy transfer occurs from the perovskite matrix to the lanthanide ions and vice-versa, resulting in characteristic Ln^{3+}-emissions along with $CsPbX_3$ emission. Interfacing $CsPbX_3$ with different host matrix such as lanthanide metal organic framework (Ln-MOF), increases the stability of $CsPbX_3$. The Ln-MOFs have beautiful morphology, as bi-flower like morphology of Eu-MOF and bi-directional needle like morphology of Tb/Eu-MOF are shown in Chapter 4 and 5, respectively. These Ln-MOFs have a porous structure, that helps in incapsulating the $CsPbX_3$. The $CsPbBr_3$@Eu-MOF is explored for the ant-counterfeiting application, while $CsPbCl_{1.5}Br_{1.5}$@ Tb/Eu-MOF shows anti-counterfeiting and white light emission applications. Also, Yb^{3+}, Er^{3+}: $GdScO_3$ oxide perovskite NCs is synthesised via the gel-combustion method for the optical thermometry application. The complete work is based on the lanthanides doped $CsPbX_3$ and $GdScO_3$ materials, and inorganic halide perovskites interfaced lanthanide metal organic frame works. The materials have beensynthesized using different synthesis techniques for various optical studies and future applications, the overall conclusion of the thesis work can be summarized as follows:

The first work investigates the structural and optical properties of pristine and Europium (Eu)-doped $CsPbBr_3$ halide perovskite nanocrystals (NCs) synthesized via the hot-injection method. Eu-doping enhances the crystallinity of $CsPbBr_3$ NCs and significantly reduces the average particle size from 19 nm to approximately 7 nm. The bandgap (E_g) of the undoped $CsPbBr_3$ NCs is determined to be 2.31 eV, and it increases slightly to 2.35 eV upon Eu^{2+}-ion doping. The undoped $CsPbBr_3$ NCs exhibit a sharp emission peak at 515 nm in the green spectral region with a full width at half maximum (FWHM) of about 24 nm. In contrast, Eu-doped $CsPbBr_3$ NCs show two distinct emission peaks at 498 nm (FWHM ~20 nm) and 442 nm (FWHM ~13 nm). The additional emission peak at 442 nm is attributed to the $4f^6(^7F_J)5d^1 \rightarrow 4f^7$ transition of Eu^{2+}-ion. The shift in green emission for the doped NCs is linked to the reduced particle size from 19 nm to 7 nm. Detailed decay dynamics reveal that the average decay time for $CsPbBr_3$ monitored at 515 nm is 7.27 ns, while for Eu-doped $CsPbBr_3$, the decay times are 5.80 ns and 8.89 ns for the 498 nm and 442 nm emission peaks, respectively. The Commission Internationale de l'Eclairage (CIE 1931) chromaticity coordinates of Eu-doped $CsPbBr_3$ emission spectra were analyzed under different excitation wavelengths, showing minimal variation. The luminous efficacy of radiation (LER) for undoped $CsPbBr_3$ NCs is calculated to be 447 lm/W, while for Eu-doped $CsPbBr_3$ NCs, it ranges between 138-179 lm/W. Notably, the color purity of the emission spectra exceeds 85% under various excitations. These optical characteristics suggest that $CsPbBr_3$ and Eu-doped $CsPbBr_3$ NCs have potential applications in blue LEDs, color displays, and anti-counterfeiting technologies.

As discussed, the stability issue of the $CsPbX_3$ is a major concern. Doping metal-ion, surface capping, growing stable cell on the $CsPbX_3$ core, etc., may increase the stability of $CsPbX_3$. Metal organic frameworks (MOFs) are porous materials, which provide room to the nanomaterials to intercalated into it. The Eu-MOF is synthesized by the hydrothermal method and further a hybrid of this is formed with $CsPbBr_3$ i.e. $CsPbBr_3$@ Eu-MOF. It has a tetragonal structure with space group $P4_322$. Synthesized Eu-MOF has bi-flower morphology whose mid portion and conical part length both are below 10 μm. The conical part of the bi-flower consists of many squared rods of square size ~200 nm. In UV-visible-NIR absorption spectrum, characteristic absorption edge of $CsPbBr_3$ is present. The PL emission spectrum as well as elemental analysis using SEM-EDX, confirms successful formation of the $CsPbBr_3$@Eu-MOF. Excitation wavelength-dependent PL emission of $CsPbBr_3$@Eu-MOF shows variation in the emission peak intensity. The (x, y) coordinate covers the whole green to red region in the CIE 1931 diagram. The maximum LER value achieved is 359 lm/W, and the maximum color purity is 94.4% which is significant for optical applications. The CIE 1931 (x, y) coordinates for the different excitation wavelength show the suitability of the materials for the optical anti-counterfeiting application. The pattern “LMDD” is encrypted on four different substrates (white paper, butter paper, green plastic, and aluminum foil) and the color change of the patterns under different excitation wavelengths has been thoroughly studied. The overall visualization and the chemical stability of the encrypted patterns on green plastic [“LMDD”-G] is the best among all the four substrates studied. This clearly suggest the suitability of developed material for anti-counterfeiting application.

Further, in a luminescent guest center encapsulated Ln-MOFs, luminescence emission can occur from the guest molecules, Ln^{3+}-ions, and organic linker. To understand the energy-transfer among these luminescent centers, Tb/Eu-MOF and $CsPbCl_{1.5}Br_{1.5}$ (CPCB) encapsulated CPCB@ Tb/Eu-MOFs hybrid have been synthesized using hydrothermal method. The Tb/Eu-MOF form bi-directional needle-like morphology. The single tetragonal phase of Tb/Eu-MOFs and CPCB@ Tb/Eu-MOFs are verified by the LeBail fitting of the XRD data. Successful incorporation of the inorganic halide perovskite CPCB into Tb/Eu-MOF is evidenced by the characteristic absorption band observed in the UV-visible spectrum and the peak in the PL emission. The Tb^{3+}/Eu^{3+}-ion and O^{2-} form the CTB. This band acts as an antenna for sensitizing the Tb^{3+} and Eu^{3+}-ions. The energy transfer scheme among Tb^{3+} and Eu^{3+}-ions, as well as CPCB, is also studied in detail. The CTB effectively excites the Tb^{3+} and Eu^{3+}-ions, but not the CPCB. At the same time, the energy transfers from Tb^{3+} to Eu^{3+}-ions also takes place but the reverse is not observed. In the PL emission spectrum of CPCB@ Tb/Eu-MOFs for the RGB color mixing, the red part is observed from Eu^{3+}-ion, the green part is observed from Tb^{3+}-ion, and the CPCB contributes the blue part. CIE 1931 (x, y) color coordinate of the c-CPCB@ Tb/Eu-MOF emission is calculated, that is very close to the white light coordinate (0.333, 0.333) suitable candidate for white light applications. To the best of our knowledge, this is the first report on CPCB luminescent guest-centered Tb/Eu-MOF for WLED application. Excitation wavelength-dependent PL emission of CPCB@ Tb/Eu-MOFs is also recorded, and the CIE (x, y) color coordinate is calculated. It gives different color sensations to the human eyes. Integrating this idea, pattern "W" was developed on various surfaces (borosilicate glass, aluminum foil, transparent plastic) for optical anti-counterfeiting application. The stability of the "W-BG" pattern is checked in ambient conditions and encounters with water and propanol solution. Results show that CPCB@ Tb/Eu-MOFs is very suitable for white light emission and for optical anti-counterfeiting applications.

The Ln^{3+}-ions pairs such as Er^{3+}-Yb^{3+}, Ho^{3+}-Yb^{3+}, Tm^{3+}-Yb^{3+} exhibit non-linear photon upconversion (UC) phenomena in certain host materials. The UC emission is somehow difficult to achieve in $CsPbX_3$ because of week crystal field effect. The oxide perovskite $GdScO_3$, known for its wide bandgap (~5 eV) and thermal stability, has been investigated as a host for Yb^{3+} and Er^{3+} ions. Nanocrystalline powders of $GdScO_3$ and Yb^{3+}, Er^{3+}: $GdScO_3$ were synthesized using the gel-combustion method. Optimization of the doping concentrations of Er^{3+} and Yb^{3+} ions in this host was performed to maximize luminescence intensity. Remarkably, this material exhibits strong near-infrared (NIR) to visible UC emission under 980 nm continuous-wave (CW) laser excitation, as well as down-shifting emission under UV-blue excitation. To the best of our knowledge, this study was the first to report on the UC properties of Yb^{3+}, Er^{3+} co-doped $GdScO_3$. Additionally, Yb^{3+}, Er^{3+}: $GdScO_3$ demonstrates excellent temperature sensitivity, making it suitable for sensing applications. The maximum absolute sensitivity achieved is $10.49 \times 10^{-3}\ K^{-1}$ at 423 K, and the maximum relative sensitivity is $11.79 \times 10^{-3}\ K^{-1}$ at 299 K, with a thermal resolution of 0.4 K, which surpasses that of many other oxide perovskite materials. This material holds significant potential for use as a non-contact, luminescence-based optical temperature sensor, particularly in environments such as coal mines and high-temperature metal industries. It may also be applicable in the optoelectronic industry for monitoring heat-related damage in electronic circuits.

Overall, it can be concluded that the stability and optical properties of the $CsPbX_3$ can be enhanced by interfacing with the Ln^{3+}-ions and metal organic frameworks for the different optoelectronic applications such as color and white LEDs, optical encryption and decryption, optical thermometry, etc. At the same time Ln^{3+}-ions doped high bandgap material $GdScO_3$ is suitable for the non-invasive optical thermometry.

7.2 Outlook for Future Work

For the future perspective the following works are proposed for a deep understanding of the various interaction within the inorganic halide perovskites molecules for the various optoelectronic applications.

- Surface engineering to enhance the stability as well as properties of $CsPbX_3$.
- Doping Ln^{3+}-ions pairs such as Er^{3+}-Yb^{3+}, Ho^{3+}-Yb^{3+}, Tm^{3+}-Yb^{3+}, etc., into $CsPbX_3$ for the UC emission.
- Optoelectronic behaviors study in $CsPbX_3$ encapsulated transition metals-MOFs.
- Exploring these materials for the evergreen applications such as solar cell, energy storage, sensing, etc.