Synthesis and characterization of erbium doped lead-free halide perovskites.

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1. INTRODUCTION

Halide perovskites have garnered significant attention in recent years due to their exceptional optoelectronic properties. The structural versatility of these materials, represented by the general formula ABX_3, has enabled applications in photovoltaics, light-emitting diodes (LEDs), and photodetectors. However, the widespread adoption of lead-based perovskites is hindered by two major challenges: the inherent toxicity of lead and the poor stability of these materials under ambient conditions. These drawbacks have catalyzed a vigorous search for lead-free alternatives that retain the desirable properties of their lead-based counterparts while offering enhanced stability and environmental friendliness.

Among the most promising lead-free candidates are double perovskites with the formula $A_2B'B''X_6$. The double perovskite $Cs_2AgInCl_6$ (CAIC) has emerged as a notable material due to its wide bandgap, stability, and potential for doping with various ions to induce novel optical properties. Another intriguing lead-free system is $Cs_4MnBi_2Cl_{12}$ (CMBC), a heterometallic perovskite with a two-dimensional structure.

Trivalent rare-earth (RE) ions, particularly Er^{3+}, are of immense interest for photonic applications due to their well-defined 4f-4f electronic transitions. These transitions give rise to sharp, defining emission lines. Doping RE ions into lead-free perovskite hosts offers a promising strategy to combine the stability and favorable properties of these materials with the narrow-band luminescence of RE dopants.

This work investigates the synthesis and optical properties of Er^{3+} doped CAIC and CMBC lead-free perovskites. The primary objectives are to synthesize these materials via a hydrothermal method, perform emission and excitation spectroscopy to identify the characteristic transitions of the RE dopants, and to examine the influence of the host lattice on their spectroscopic behavior. Comparative studies to the erbium doped, lead-based compound KPb_2Cl_5 are also included to provide a benchmark for understanding host-dependent optical properties.

2. METHODS

2.1 Material Synthesis

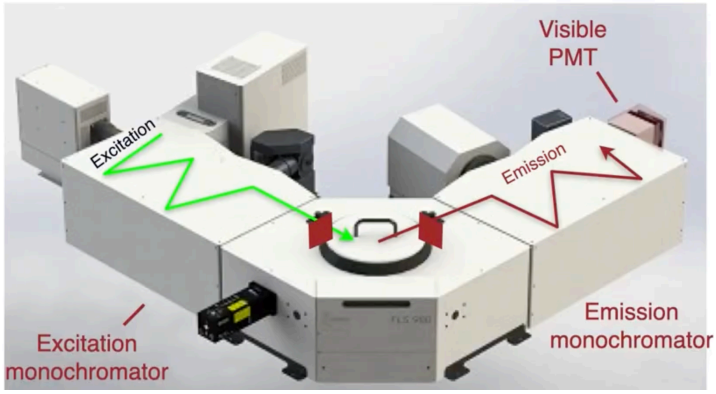
The Er^{3+} doped CAIC and CMBC materials were synthesized using a hydrothermal method which provided a high pressure and high temperature environment for material synthesis. The synthesis approach involved weighing the stoichiometric proportions of the required binary compounds; for CAIC: 2xCsCl, AgCl, $InCl_3$ and for CMBC: 4xCsCl, 1x $MnCl_2$, 2x$BiCl_3$, respectively. The weighed materials were placed in a tightly sealed teflon vessel with 10 mL of HCl before being heated in a furnace at 180°C for 48 hours. After heating, the material is allowed to cool to room temperature before being retrieved, washed with ethanol, and dried.

Figure 1. Teflon Vessel and Stainless Steel Jacket

2.2 Optical Characterization

Optical characterization was performed using emission and excitation spectroscopy. Emission spectra were acquired by exciting the samples with specific wavelengths, such as UV light or blue laser excitation at 405 nm and 450 nm. Excitation spectra were obtained by monitoring the emission intensity at a fixed wavelength while scanning the excitation wavelength. Excitation spectra are useful for identifying the energy levels involved in the excitation process and are analogous to absorption spectra, allowing the identification of host absorption bands and RE ion transitions that lead to luminescence.

Figure 2. Spectrofluorometer Setup



Screenshot of the FLS980 spectrometer (taken from [4] at 23:17)

All observed features were analyzed by calculating the transition energies obtained from the Dieke diagram and assigning them to the known electronic energy levels of Er^{3+} ions. The relationship between wavelength and energy is given by:

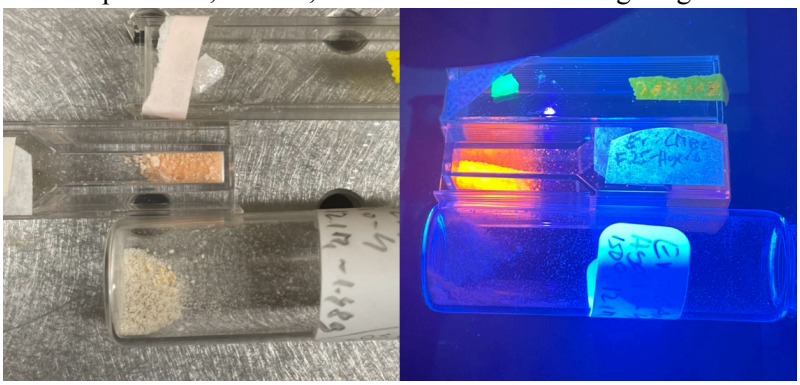
$\lambda = 10^7 \div \Delta E$

where ΔE is the transition energy in cm^{-1} and λ is the wavelength in nm. For example, the observed emission peak at approximately 660 nm in CMBC corresponds to:

$\lambda = 10^7 \div 15200\ cm^{-1} = 657.9\ nm$

This energy matches the expected energy difference between the $^4F_{9/2}$ and $^4I_{15/2}$ manifolds of Er^{3+}, confirming the assignment of this emission to the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition. Similar calculations were performed for all observed absorption and emission peaks to verify their assignments to specific Er^{3+} electronic transitions.

Figure 3. Er-doped KPC, CMBC, and CAIC in Ambient Lighting vs UV Lighting

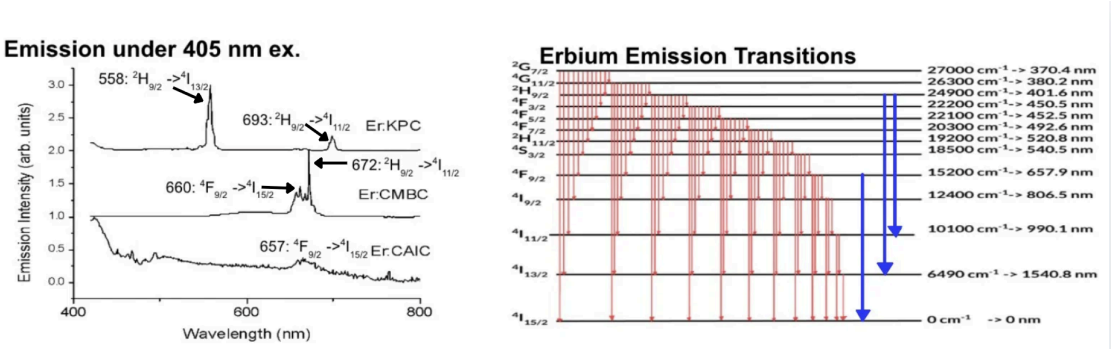


3. FINDINGS

3.1 Emission Spectroscopy of Er^{3+}-Doped Perovskites

Out of the three Er^{3+}-doped materials, KPC and CMBC exhibited identifiable transitions in both emission and excitation spectroscopy that were consistent with the known energy levels of Er^{3+}. Under UV light, CAIC exhibited no fluorescence while CMBC fluoresced orange and KPC fluoresced green. This stark variation in emission color and intensity suggests that the host material's crystal field symmetry and phonon energy play a critical role in the 4f-4f transitions of Er^{3+}. The absence of fluorescence in CAIC, despite its identical dopant concentration, points to non-radiative relaxation pathways which are likely due to high-energy vibrational modes in the CAIC lattice that quench the excited state of Er^{3+} before photon emission can occur.

Figure 4. Emission Scans and Calculated Erbium Transitions

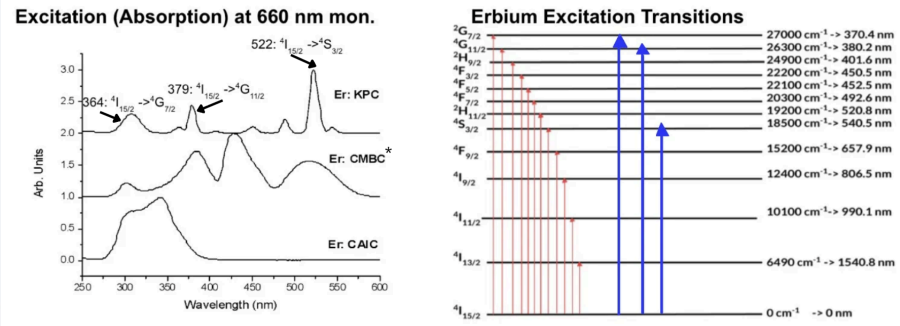


Black arrows identify highlighted peaks. Blue arrows mark electronic transitions assigned to each peak.

3.2 Excitation Spectroscopy of Er^{3+}-Doped Perovskites

Er: KPC displayed multiple well-defined excitation peaks that correspond to characteristic Er^{3+} electronic transitions. Er: CMBC, in contrast, exhibited broad excitation bands that more closely align with transitions associated with manganese (Mn^{2+}) rather than Er^{3+}, indicating a stronger influence of the host lattice on the observed optical behavior. This is a critical finding: it implies that in CMBC, the Er^{3+} ions are either being efficiently sensitized by Mn^{2+} via energy transfer, or the excitation energy is preferentially absorbed by the host matrix itself and then transferred to the Er^{3+} dopant. The broad Mn^{2+} bands dominate the spectrum because the Mn^{2+} concentration or its oscillator strength is significantly higher than that of the parity-forbidden Er^{3+} transitions. Despite not having any emission, Er: CAIC shows excitation in the 300 nm range similar to the Er: KPC and Er: CAIC, indicating that the ground-state absorption of Er^{3+} is intact, but the subsequent excited-state dynamics are entirely governed by the CAIC lattice. Specifically, its defect density or bandgap alignment, which funnel energy into heat rather than light.

Figure 5. Excitation Scans and Calculated Erbium Transitions



Black arrows identify highlighted peaks. Blue arrows mark electronic transitions assigned to each peak.
**No distinct Er^{3+} transitions are resolved; the broad features are attributed to Mn^{2+}-related absorption bands.*

4. CONCLUSIONS

Hydrothermal synthesis is an effective route for producing optically active Er^{3+}-doped lead-free halide perovskites, yielding materials with strong visible fluorescence and host-dependent emission properties. This is likely due to the enhanced crystallinity and reduced defect densities promoted by the high-temperature, high-pressure growth environment.

The host matrix exerts decisive control over Er^{3+} luminescence, with Er:CMBC and Er:KPC exhibiting strong visible fluorescence under UV excitation, while Er:CAIC remains completely dark. This confirms that the CAIC lattice possesses high-energy phonon modes or intrinsic defect states that create efficient quenching channels, effectively short-circuiting the radiative decay pathway.

The excitation mechanism is fundamentally host-dependent: Er:KPC displays sharp, well-defined excitation peaks that map directly to characteristic Er^{3+} 4f-4f transitions, indicating that the KPC lattice allows for direct excitation of the Er^{3+} dopant. In contrast, Er:CMBC exhibits broad excitation bands dominated by Mn^{2+}-related interactions, suggesting that excitation energy is preferentially absorbed by the host matrix or sensitizer and subsequently transferred to Er^{3+}; a sensitization pathway that could be strategically exploited for broadband light harvesting. Notably, despite these differences in excitation behavior, both Er:KPC and Er:CMBC produce sharp emission features characteristic of Er^{3+}, confirming that the energy ultimately populates the same emissive levels regardless of the initial absorption pathway.

Collectively, these findings establish Er^{3+}-doped lead-free perovskites as a highly tunable platform for photonic applications. The ability to modulate emission color, efficiency, and excitation pathways simply by altering the host composition positions these materials as promising candidates for photonics, optical sensing, and bioimaging technologies, while circumventing the toxicity issues associated with lead-based perovskites. Overall, this work establishes a foundation for the continued development of RE-doped lead-free perovskites as less toxic alternatives to lead-based optical materials.

REFERENCES

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