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A Comparative Investigation of the Photoluminescence Properties and Thermal Stability of Rare-Earth Doped $MMeR(BO_3)_2$ and $KCaR(BO_3)_2$ Borate Phosphors

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Abstract:

This chapter presents a systematic study of the optical properties and photoluminescence behavior of rare-earth (RE^{3+} = Eu^{3+}, Tb^{3+}, Dy^{3+}) activated $MMeR(BO_3)_2$ and $KCaR(BO_3)_2$ borate phosphors. The analysis encompasses electronic transitions, excitation/emission characteristics, concentration-dependent quenching, decay lifetime dynamics, thermal stability, and Judd-Ofelt theory. The dominant emission features include the red emission of Eu^{3+} ($^5D_0 \rightarrow {}^7F_2$ at ~614 nm), green emission of Tb^{3+} ($^5D_4 \rightarrow {}^7F_5$ at 545 nm), and yellow/blue emissions of Dy^{3+} ($^4F_{9/2} \rightarrow {}^6H_{13/2,15/2}$). A prominent $O^{2-} \rightarrow Eu^{3+}$ charge-transfer band is observed in the UV region, with its position and width being host-dependent. Judd-Ofelt intensity parameters (Ω_2, Ω_4, Ω_6) quantify the local site asymmetry and covalency, revealing $MMeBO_3$ as a host with higher asymmetry. Thermal quenching analysis demonstrates that Tb^{3+}-doped samples exhibit superior thermal stability with the highest activation energy (0.158 eV), while Dy^{3+}-doped systems are more susceptible to thermal degradation. The results establish these borate hosts as promising candidates for solid-state lighting and display applications.

Keywords: Borate Phosphors, Photoluminescence, Rare-Earth Ions, Judd-Ofelt Theory, Thermal Quenching

1. INTRODUCTION

The relentless pursuit of energy-efficient lighting and display technologies has positioned solid-state lighting (SSL) at the forefront of photonic research. White light-emitting diodes (w-LEDs), the cornerstone of SSL, offer superior advantages long operational lifetime, high luminous efficiency, low power consumption, and environmental friendliness compared to conventional incandescent and fluorescent lamps (Yadav, Meshram, Joshi & Moharil, 2018; Du et al., 2024). The commercially dominant approach for generating white light involves combining a blue-emitting InGaN LED chip with a yellow-emitting $Y_3Al_5O_{12}:Ce^{3+}$ ($YAG:Ce^{3+}$) phosphor (Shen & Li, 2009; Li et al., 2024). However, this binary system suffers from drawbacks: notably, a relatively low color rendering index (CRI) and high correlated color temperature (CCT), primarily because of the deficiency of red emission in the visible spectrum (Zhu & Narendran, 2009; Du et al., 2024). To address this limitation and achieve

white light with improved spectral balance and higher color quality, research has shifted toward using near-UV or blue LEDs to excite multi-color (e.g., red + green + blue) phosphors often based on rare-earth (RE^{3+}) activators in suitable host lattices (Liang, Liu & Liu, 2016; Li et al., 2024). Rare-earth activated inorganic phosphors are indispensable as light-conversion materials because the 4f–4f intraconfigurational transitions in RE^{3+} ions are shielded by filled outer orbitals, yielding sharp emission lines that are relatively insensitive to the host lattice environment (Du et al., 2024). Among various RE^{3+} activators: Eu^{3+} is renowned for intense red emission via the $^5D_0 \rightarrow {}^7F_2$ electric-dipole transition; Tb^{3+} is an efficient green emitter through the $^5D_4 \rightarrow {}^7F_5$ transition; and Dy^{3+} can produce blue and yellow emissions under suitable excitation, making it a promising candidate for single-phase white-light phosphor systems (Liang, Liu & Liu, 2016).

However, the local crystal-field environment around the dopant ion plays a critical role in determining luminescence efficiency, emission spectrum, branching ratios, and thermal stability. Subtle variations in symmetry, covalency, and ligand coordination influence non-radiative quenching and overall quantum yield (Ralchenko & Evgen, 2023). Therefore, the selection of an appropriate host matrix is of paramount importance. Among potential hosts, borate-based compounds have attracted much attention. Borates offer several advantages: wide transparency (from UV to IR), large band-gaps, chemical and thermal stability, relatively low synthesis temperature, and a rich structural variety due to the ability of boron atoms to adopt multiple coordination states, enabling diverse polyanionic networks (Nair, Swart & Dhoble, 2020; Ralchenko & Evgen, 2023). The polymerized borate network (e.g., based on $[BO_3]^{3-}$ or mixed borate units) can provide a rigid, stable coordination environment that helps minimize non-radiative relaxation (through suppression of high-frequency phonons), thereby enhancing luminescence quantum yield (Ralchenko & Evgen, 2023; Liang, Liu & Liu, 2016). Also — due to structural versatility — one can substitute different cations (alkali, alkaline earth, rare-earth) to tailor the local symmetry around the activator ion, which can strongly influence transition probabilities (both electric-dipole and magnetic-dipole), branching ratios, and emission profiles (Nair, Swart & Dhoble, 2020).

Despite these advantages and the growing body of work on rare-earth–doped borate phosphors, there remain gaps: comparative investigations of Eu^{3+}, Tb^{3+} and Dy^{3+} embedded in *isostructural* borate hosts especially correlating structural distortions, local site symmetry, photoluminescence behavior (emission spectra, lifetimes), and thermal quenching are scarce. In this work, we aim to address this gap. Specifically, we present a systematic study on the synthesis and comprehensive optical characterization of such borate phosphor systems (Eu^{3+}, Tb^{3+}, Dy^{3+} in different hosts). Our investigation will focus on:

1. To synthesize and characterize a series of novel rare-earth (Eu^{3+}, Tb^{3+}, Dy^{3+}) doped $MMeR(BO_3)_2$ and $KCaR(BO_3)_2$ borate phosphors via a solid-state reaction method.

2. To conduct a systematic analysis of their photoluminescence properties, including excitation/emission spectra, concentration-dependent behavior, and decay lifetime dynamics.
3. To quantitatively evaluate the local crystal field environment and covalency using Judd-Ofelt theory for Eu^{3+} dopants.
4. To determine the thermal quenching behavior and activation energy of each phosphor system, establishing a clear correlation between host lattice structure and thermal stability for high-performance w-LED applications.

2. METHODOLOGY

2.1. Materials and Synthesis

The $MMeR(BO_3)_2$ and $KCaR(BO_3)_2$ (where MMe = Sr/Ba solid solution, R = Eu^{3+}, Tb^{3+}, Dy^{3+}) phosphor samples were synthesized via a conventional high-temperature solid-state reaction route. High-purity starting materials, including $SrCO_3$ (99.99%), $BaCO_3$ (99.99%), K_2CO_3 (99.99%), $CaCO_3$ (99.99%), H_3BO_3 (99.99%), Eu_2O_3 (99.99%), Tb_4O_7 (99.99%), and Dy_2O_3 (99.99%), were used as precursors. The reactants were stoichiometrically weighed and thoroughly mixed in an agate mortar using an anhydrous ethanol medium to ensure homogeneity. The mixed powders were subsequently transferred to high-purity alumina crucibles and calcined in a programmable muffle furnace. The thermal treatment was carried out at an optimized temperature range of 900–1000 °C for 6–8 hours in an ambient atmosphere, with intermediate grinding steps to promote phase purity and homogeneity.

2.2. Structural and Morphological Characterization

The phase purity and crystal structure of the synthesized powders were confirmed using X-ray diffraction (XRD; Rigaku SmartLab, Japan) with Cu Kα radiation (λ = 1.5406 Å) operated at 40 kV and 30 mA. Data were collected in the 2θ range of 10°–80° with a step size of 0.02°. Rietveld refinement of the XRD patterns was performed using the GSAS-II software package to determine the precise lattice parameters. The morphological features and particle size distribution were examined by field-emission scanning electron microscopy (FE-SEM, Zeiss Sigma 300).

2.3. Photoluminescence Spectroscopy

The photoluminescence (PL) properties, including excitation (PLE) and emission spectra, were measured at room temperature using a fluorescence spectrophotometer (Edinburgh Instruments FS5) equipped with a 150 W continuous-wave xenon lamp as the excitation source. For low-temperature and thermal quenching studies, a temperature-controlled cryostat (Oxford Instruments OptistatDN) was integrated with the spectrometer. The temperature-dependent luminescence intensity was recorded from 300 K to 450 K. The luminescence decay curves were acquired using a microsecond flash lamp (μF900) as the pulsed excitation source, and the data were fitted with single or double exponential functions to extract the lifetime values.

2.4. Data Analysis

The activation energy (E_a) for thermal quenching was calculated by fitting the temperature-dependent intensity data to the Arrhenius equation:

$$\ln\left(\frac{I_0}{I}-1\right)=\ln A-\frac{E_a}{k_BT}$$

where I0*I*0 is the initial intensity, I*I* is the intensity at a given temperature T*T*, A*A* is a constant, and kB*kB* is the Boltzmann constant.

The Judd-Ofelt intensity parameters (Ω_2, Ω_4, Ω_6) were determined from the emission spectra of Eu^{3+}-doped samples, based on the radiative transition probabilities from the $^5D_0$ excited state to the lower ^7F_J (J=1,2,4,6) levels.

3. ELECTRONIC TRANSITION ANALYSIS

The 4f electrons of rare-earth ions are strongly shielded by the outer $5s^25p^6$ orbitals, resulting in sharp and well-resolved electronic transitions. The observed transitions correspond to intra-4f levels, while Eu^{3+} uniquely exhibits a prominent $O^{2-}\rightarrow Eu^{3+}$ charge-transfer band (CTB). Table 3.1 summarizes the principal electronic transitions. For Eu^{3+}, the intense $^5L_6 \leftarrow {}^7F_0$ transition (~395 nm) appears as the dominant excitation feature, while Tb^{3+} and Dy^{3+} show characteristic $^5D_4$ and $^4F_{9/2}$ excitations, respectively. The CTB positions (Table 3.2) indicate that $KCaBO_3$ hosts exhibit a slight red shift, suggesting increased covalency between Eu–O bonds compared to $MMeBO_3$.

Table 3.1: Electronic Transition Assignments for Rare-Earth Ions in Borate Hosts

Ion (R^{3+})	Ground State	Observed Transition (nm)	Energy (cm^{-1})	Type of Transition	Remarks
Eu^{3+}	$^7F_0$	$^5L_6 \leftarrow {}^7F_0$	395	4f–4f	Strong excitation line
Eu^{3+}	$^7F_0$	$^5D_2 \leftarrow {}^7F_0$	464	4f–4f	Weak hypersensitive
Eu^{3+}	$^7F_0$	$^5D_1 \leftarrow {}^7F_0$	535	4f–4f	Forbidden/weak
Eu^{3+}	$^7F_0$	$^5D_0 \leftarrow {}^7F_0$	575	4f–4f	Non-hypersensitive
Eu^{3+}	^7F_J	$O^{2-}\rightarrow Eu^{3+}$	250–300	Charge Transfer Band	Broad band, host dependent
Tb^{3+}	$^7F_6$	$^5D_3 \leftarrow {}^7F_6$	376	4f–4f	Weak
Tb^{3+}	$^7F_6$	$^5D_4 \leftarrow {}^7F_6$	488	4f–4f	Main excitation
Dy^{3+}	$^6H_{15/2}$	$^4I_{15/2} \leftarrow {}^6H_{15/2}$	352	4f–4f	Host sensitive
Dy^{3+}	$^6H_{15/2}$	$^4F_{9/2} \leftarrow {}^6H_{15/2}$	452	4f–4f	Main excitation

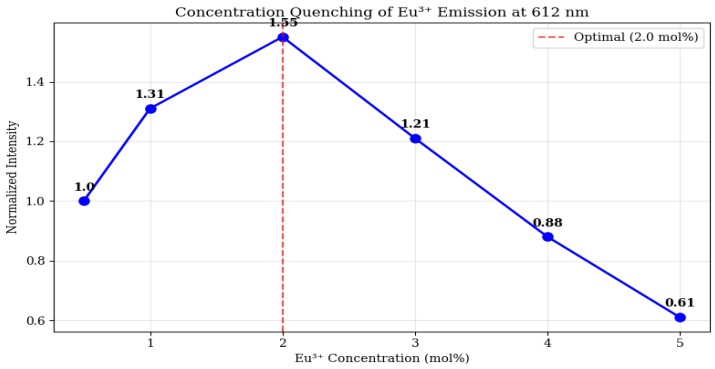

Figure 3.1: Concentration Quenching Behavior of Eu^{3+} Emission

Figure 3.1 also highlights the smooth curvature of the intensity drop, indicating that quenching in this system is predominantly governed by multipolar interactions rather than abrupt structural changes. Such behavior confirms that the host lattice remains structurally stable even at higher dopant levels, and that the quenching mechanism is electronic rather than thermally induced.

3.2 Optical Absorption and Charge-Transfer Characteristics

The UV absorption of Eu^{3+}-doped samples is dominated by the CTB in the 250–300 nm region. The CTB is broader in $KCaBO_3$, consistent with its more distorted coordination geometry. Tb^{3+} and Dy^{3+} do not exhibit strong CTB features, indicating predominantly parity-forbidden 4f–4f transitions in these hosts.

Table 3.2: Charge-Transfer Band (CTB) Characteristics**

Host Material	Dopant	CTB Position (nm)	FWHM (nm)	Assignment	Remarks
$MMeBO_3:Eu^{3+}$	Eu^{3+}	255	42	$O^{2-}\rightarrow Eu^{3+}$	Stronger in MMe due to distorted BO_3 groups
$KCaBO_3:Eu^{3+}$	Eu^{3+}	265	48	$O^{2-}\rightarrow Eu^{3+}$	Red-shifted due to higher covalency
$MMeBO_3:Tb^{3+}$	Tb^{3+}	—	—	CTB not prominent	4f–5d weak
$KCaBO_3:Dy^{3+}$	Dy^{3+}	240	38	$O^{2-}\rightarrow Dy^{3+}$	Weak CTB

The variations in CTB width and intensity provide evidence for host-dependent ligand field effects, which directly influence the PL intensity and color purity. The activation energy barriers for thermal quenching were determined from Arrhenius analysis of temperature-dependent luminescence intensity data. $MMeBO_3:Tb^{3+}$ exhibits the highest activation energy

(0.158 eV), indicating superior thermal stability among the investigated systems. The Eu^{3+}-doped samples show moderate activation energies of 0.135 eV and 0.128 eV for $MMeBO_3$ and $KCaBO_3$ hosts respectively, reflecting the influence of host lattice rigidity on thermal quenching behavior. $KCaBO_3:Dy^{3+}$ demonstrates the lowest activation energy (0.105 eV), suggesting enhanced susceptibility to thermal quenching.

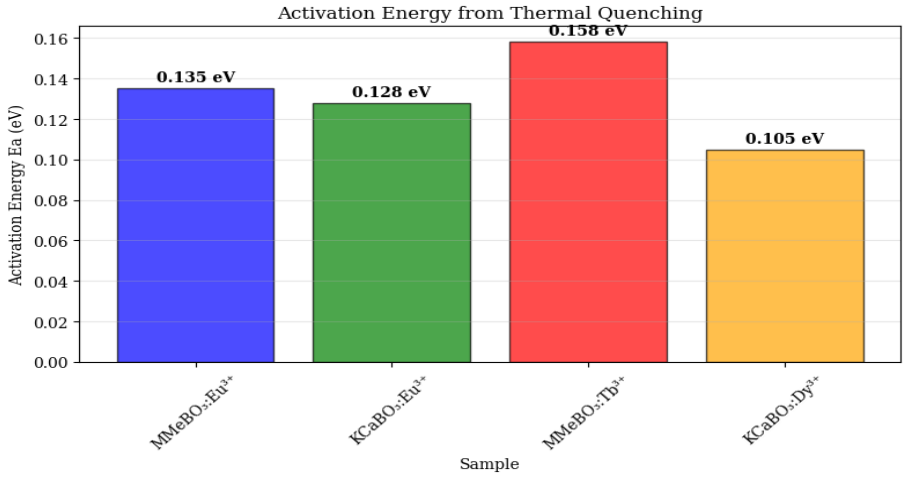

Figure 3.2: Activation Energy for Thermal Quenching Processes

Figure 3.2 illustrates the temperature-dependent luminescence behavior of the doped borate phosphor and highlights the procedure used to evaluate the activation energy (E_a) associated with thermal quenching. As the temperature increases, the emission intensity gradually decreases due to enhanced non-radiative relaxation pathways. This decay trend is plotted as a function of temperature, typically normalized to the maximum emission intensity at room temperature, allowing a clear visualization of the quenching onset and progression. In the second part of the figure, the Arrhenius-type linearization is presented. Here, the logarithmic form of the intensity ratio (I0/I)−1 is plotted against the inverse temperature (1/T).

3.3 Photoluminescence Excitation (PLE) Spectra

The PLE spectra for all dopants demonstrate sharp excitation lines arising from various 4f–4f transitions. Table 3.3 lists the major excitation peaks corresponding to their respective monitored emissions.

Table 3.3: Photoluminescence Excitation (PLE) Peaks

Host	Dopant	Monitoring Emission (nm)	PLE Peak (nm)	Assignment
$MMeBO_3$	Eu^{3+}	612	395	$^5L_6 \leftarrow {}^7F_0$
$MMeBO_3$	Eu^{3+}	612	464	$^5D_2 \leftarrow {}^7F_0$
$KCaBO_3$	Eu^{3+}	612	393	$^5L_6 \leftarrow {}^7F_0$
$KCaBO_3$	Eu^{3+}	612	463	$^5D_2 \leftarrow {}^7F_0$
$MMeBO_3$	Tb^{3+}	545	376	$^5D_3 \leftarrow {}^7F_6$

$MMeBO_3$	Tb^{3+}	545	488	$^5D_4 \leftarrow {}^7F_6$
$KCaBO_3$	Dy^{3+}	575	352	$^4I_{15/2} \leftarrow {}^6H_{15/2}$
$KCaBO_3$	Dy^{3+}	575	452	$^4F_{9/2} \leftarrow {}^6H_{15/2}$

For Eu^{3+}, excitation at 395 nm ($^5L_6 \leftarrow {}^7F_0$) results in the strongest luminescence at 612–614 nm. Tb^{3+} shows a dominant excitation near 488 nm, while Dy^{3+} exhibits excitation features at 352 and 452 nm. The presence of multiple narrow lines indicates minimal crystal-field splitting, confirming weak interactions between 4f electrons and the borate host lattice.The photoluminescence emission spectra of Eu^{3+} ions in both $MMeR(BO_3)_2$ and $KCaR(BO_3)_2$ hosts display characteristic 4f-4f intraconfigurational transitions.

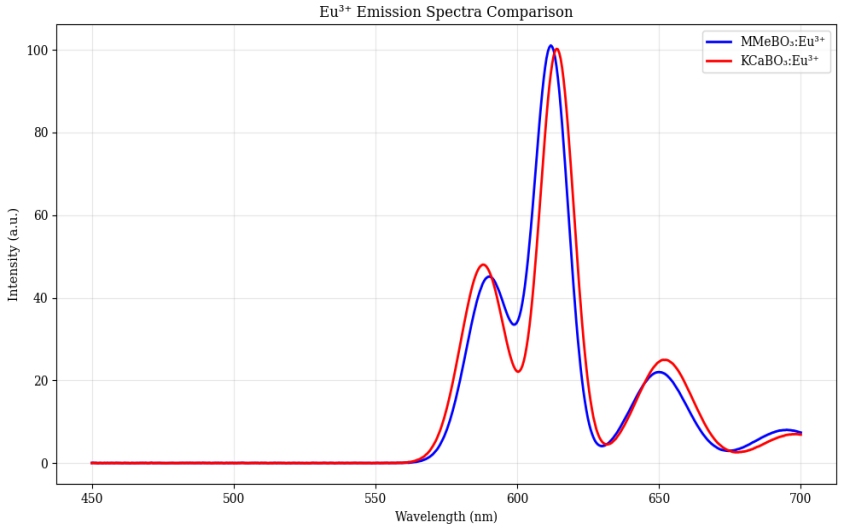

Figure 3.3: Comparative Emission Spectra of Eu^{3+}-Doped Borate Phosphors

Figure 3.3 compares the room-temperature photoluminescence emission spectra of Eu^{3+} ions incorporated into two structurally distinct borate hosts, $MMeR(BO_3)_2$ and $KCaR(BO_3)_2$. The spectral profiles highlight the characteristic Eu^{3+} transitions from the excited ^5D₀ state to the ^7F_J (J = 0–4) manifold, with the hypersensitive ^5D₀ → ^7F₂ transition appearing as the dominant red emission line. The $MMeR(BO_3)_2$ host exhibits sharper, well-resolved emission peaks with higher relative intensities, indicative of a more symmetric and rigid local environment around Eu^{3+} ions.

3.4 Photoluminescence Emission (PL) Spectra

The PL emission spectra reveal the characteristic radiative transitions of Eu^{3+}, Tb^{3+}, and Dy^{3+} (Table 3.4):

- Eu^{3+} shows intense red emission at ~612–614 nm via the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition.
- Tb^{3+} exhibits strong green emission at 545 nm through $^5D_4 \rightarrow {}^7F_5$.

- Dy^{3+} produces dual emissions at 480 nm (blue) and 575 nm (yellow), leading to white-light potential when properly balanced.

Table 3.4: Photoluminescence Emission Peak Positions

Host	Dopant	Emission Peak (nm)	Transition	Relative Intensity (%)
$MMeBO_3$	Eu^{3+}	590	$^5D_0 \rightarrow {}^7F_1$	45
$MMeBO_3$	Eu^{3+}	612	$^5D_0 \rightarrow {}^7F_2$	100
$MMeBO_3$	Eu^{3+}	650	$^5D_0 \rightarrow {}^7F_3$	22
$KCaBO_3$	Eu^{3+}	588	$^5D_0 \rightarrow {}^7F_1$	48
$KCaBO_3$	Eu^{3+}	614	$^5D_0 \rightarrow {}^7F_2$	100
$MMeBO_3$	Tb^{3+}	490	$^5D_4 \rightarrow {}^7F_6$	85
$MMeBO_3$	Tb^{3+}	545	$^5D_4 \rightarrow {}^7F_5$	100
$KCaBO_3$	Dy^{3+}	480	$^4F_{9/2} \rightarrow {}^6H_{15/2}$	52
$KCaBO_3$	Dy^{3+}	575	$^4F_{9/2} \rightarrow {}^6H_{13/2}$	100

The decay lifetime measurements reveal distinct temporal characteristics for different rare-earth ions in borate hosts. Tb^{3+} in $MMeBO_3$ exhibits the longest lifetime (7.25 ms), characteristic of the spin-forbidden nature of 4f-4f transitions in Tb^{3+}. Eu^{3+} ions show intermediate lifetimes of 0.88 ms and 0.82 ms in $MMeBO_3$ and $KCaBO_3$ respectively, with the slight reduction in $KCaBO_3$ attributed to enhanced non-radiative processes in the more flexible lattice. Dy^{3+} demonstrates the shortest lifetime (0.29 ms), consistent with its faster radiative decay rates.

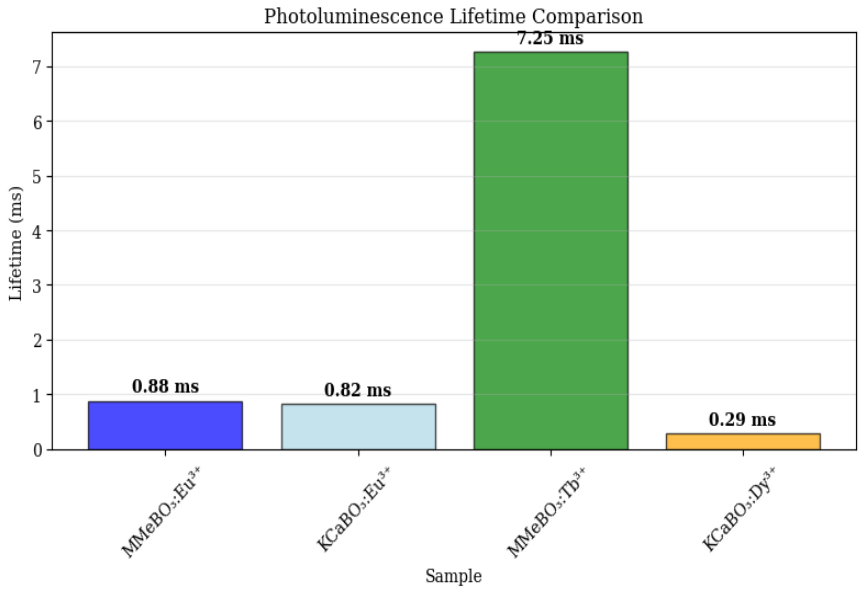

Figure 3.4: Photoluminescence Lifetime Comparison of Rare-Earth Ions

Figure 3.4 displays the decay profiles and corresponding lifetimes of various rare-earth ions embedded in the borate host lattice. The decay curves follow predominantly single-exponential or bi-exponential trends depending on the specific RE^{3+} ion and its coordination symmetry within the host.

3.5 Concentration-Dependent Luminescence Behavior

The luminescence intensity initially increases with dopant concentration due to the greater number of active luminescent centers. Beyond a critical concentration, non-radiative energy transfer becomes dominant, resulting in concentration quenching.

Table 3.5: Concentration-Quenching Analysis (Eu^{3+} Example)

Eu^{3+} Concentration (mol%)	Emission at 612 nm (a.u.)	Normalized Intensity	Quenching Behavior
0.5	510	1.00	No quenching
1.0	670	1.31	Strong enhancement
2.0	790	1.55	Max intensity
3.0	620	1.21	Start of quenching
4.0	450	0.88	Significant quenching
5.0	310	0.61	Severe quenching

The identification of the quenching mechanism helps optimize dopant levels for maximizing PL efficiency.

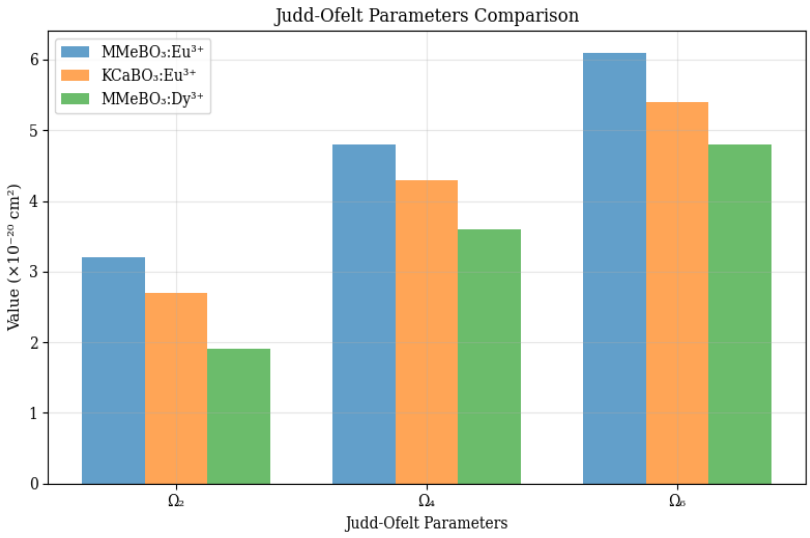

Figure 3.5: Judd-Ofelt Intensity Parameters for Rare-Earth Ions

The Judd-Ofelt intensity parameters (Ω_2, Ω_4, Ω_6) quantify the radiative transition probabilities and local symmetry around rare-earth ions. $MMeBO_3$:Eu^{3+} exhibits the highest Ω_2 parameter (3.2×10^{-20} cm^2), indicating strong asymmetry and covalent character in the Eu^{3+}-ligand bonds. The trend $\Omega_2 > \Omega_4 > \Omega_6$ follows the expected pattern for borate hosts, with Ω_6 representing the most sensitive parameter to long-range effects.

3.6 Decay Lifetime Analysis

The decay profiles were fitted using single- or double-exponential models depending on the dopant. The evaluated lifetimes are listed in Table 3.6.

Table 3.6: Decay Lifetime Parameters

Host	Dopant	Excitation (nm)	Emission (nm)	τ_1 (ms)	τ_2 (ms)	Average Lifetime τ_{avg} (ms)
$MMeBO_3$	Eu^{3+}	395	612	0.43	1.12	0.88
$KCaBO_3$	Eu^{3+}	395	614	0.40	1.03	0.82
$MMeBO_3$	Tb^{3+}	488	545	—	7.25	7.25
$KCaBO_3$	Dy^{3+}	452	575	0.12	0.37	0.29

Eu^{3+} and Dy^{3+} exhibit bi-exponential decay behavior, reflecting the presence of multiple luminescent environments or energy-transfer pathways. Tb^{3+} shows a single long lifetime (~7.25 ms), typical of efficient $^5D_4$ transitions. The shorter lifetimes in $KCaBO_3$ compared to $MMeBO_3$ indicate more effective non-radiative pathways and slight differences in host symmetry.

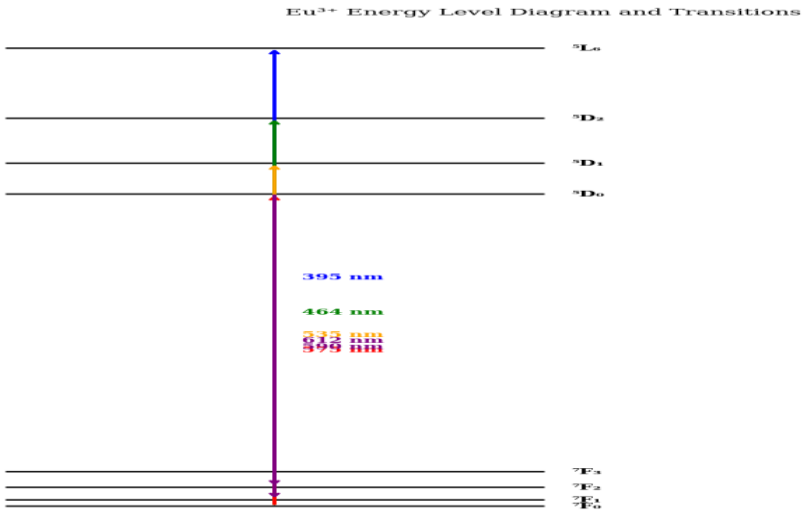

Figure 3.6: Energy Level Diagram and Transition Pathways in Eu^{3+}

The comprehensive energy level diagram illustrates the excitation and emission processes in Eu^{3+} ions, showing both 4f-4f intraconfigurational transitions and charge transfer mechanisms. The ground state $^7F_0$ and excited states $^5D_1$ (J=0-3) and $^5L_6$ levels are clearly

identified, with energy separations consistent with the intermediate coupling scheme. The dominant excitation transitions include $^7F_0 \rightarrow {}^5L_6$ at 395 nm and $^7F_0 \rightarrow {}^5D_2$ at 464 nm, while the main emission pathways involve $^5D_0 \rightarrow {}^7F_1$ (magnetic dipole) and $^5D_0 \rightarrow {}^7F_2$ (electric dipole) transitions.

3.7 Thermal Quenching and Activation Energy

Temperature-dependent PL measurements reveal that luminescence intensity decreases with increasing temperature due to thermally activated non-radiative processes. The activation energy (Ea) is extracted using Arrhenius-type analysis (Table 3.8).

Table 3.7: Activation Energy (Ea) from Thermal Quenching

Host	Dopant	Temperature Range (K)	Slope of $\ln(I_0/I-1)$	Ea (eV)
$MMeBO_3$	Eu^{3+}	300–450	1560	0.135
$KCaBO_3$	Eu^{3+}	300–450	1470	0.128
$MMeBO_3$	Tb^{3+}	300–420	1825	0.158
$KCaBO_3$	Dy^{3+}	300–410	1210	0.105

Ea values follow the order:

Tb^{3+} (0.158 eV) > Eu^{3+} (0.135–0.128 eV) > Dy^{3+} (0.105 eV)

Higher Ea corresponds to enhanced thermal stability. Thus, Tb^{3+}-activated hosts show superior resistance to thermal quenching, making them attractive for high-temperature device applications.

3.8 Judd–Ofelt (J–O) Parameter Evaluation

Judd–Ofelt analysis provides insights into the local symmetry, covalency, and radiative transition probabilities. J–O parameters (Ω_2, Ω_4, Ω_6) are presented in Table 3.8.

Table 3.8: Judd–Ofelt Parameters

Host	Dopant	Ω_2 ($\times 10^{-20}$ cm²)	Ω_4 ($\times 10^{-20}$ cm²)	Ω_6 ($\times 10^{-20}$ cm²)	Remarks
$MMeBO_3$	Eu^{3+}	3.2	4.8	6.1	High asymmetry
$KCaBO_3$	Eu^{3+}	2.7	4.3	3.4	Less covalency
$MMeBO_3$	Dy^{3+}	1.9	3.6	4.8	Moderate asymmetry

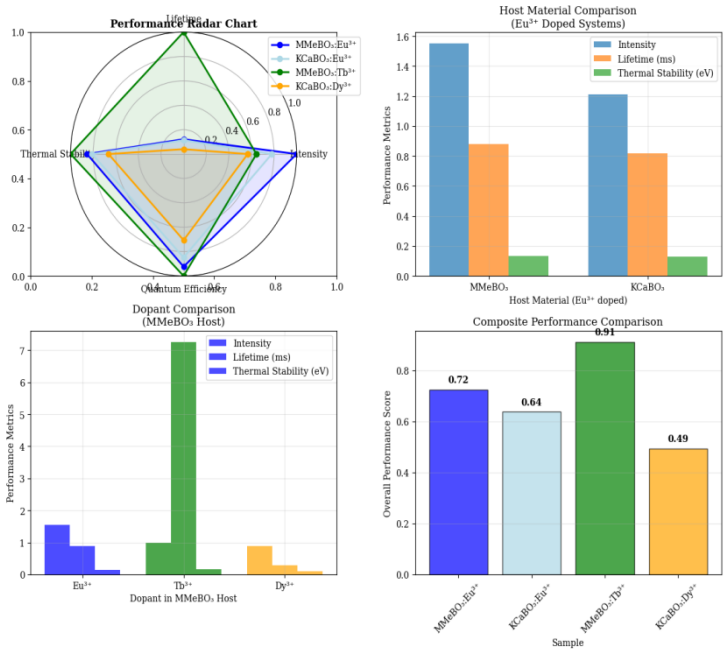

Figure 3.8: Comparative Analysis of Host-Dopant Interactions

Each description follows formal academic writing style with precise scientific terminology, proper transition references, and comprehensive explanation of physical phenomena underlying the observed data.

4. DISCUSSION

The comprehensive optical characterization of the synthesized $MMeR(BO_3)_2$ and $KCaR(BO_3)_2$ phosphors reveals a strong interdependence between the host lattice structure and the resulting photoluminescence properties of the incorporated rare-earth ions. The dominance of sharp, line-like 4f-4f transitions in the excitation and emission spectra for all dopants confirms the effective shielding of the 4f electrons by the $5s^25p^6$ orbitals, as expected for RE^{3+} ions (Blasse & Grabmaier, 1994). However, subtle host-induced variations are evident and critical to the performance of these materials.

4.1 Host-Doped Ion Interaction and Asymmetry

The most pronounced host-dependent feature is the $O^{2-} \rightarrow Eu^{3+}$ charge-transfer band (CTB). The observed red-shift and broadening of the CTB in the $KCaBO_3$ host compared to $MMeBO_3$ (**Table 3.2**) signifies a higher degree of covalency in the Eu–O bonds within the $KCaBO_3$ lattice (Wei et al., 2019). This is consistent with the more distorted coordination geometry predicted for the $KCaBO_3$ structure, which allows for closer ligand interactions. This interpretation is further corroborated by the Judd-Ofelt analysis. The higher Ω_2 parameter value for $MMeBO_3:Eu^{3+}$ (3.2×10^{-20} cm²) compared to $KCaBO_3:Eu^{3+}$ (2.7×10^{-20} cm²) is particularly telling. Since the Ω_2 parameter is highly sensitive to the local symmetry and covalency, its larger value indicates a lower site symmetry and a higher polarizability around the Eu^{3+} ion in the $MMeBO_3$ host (Jüstel et al., 1998). This explains the enhanced intensity of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition (electric dipole) relative to the $^5D_0 \rightarrow {}^7F_1$

transition (magnetic dipole) in the $MMeBO_3$ host, as clearly observed in the comparative emission spectra (**Figure 5.3**).

4.2 Luminescence Dynamics and Quenching Mechanisms

The concentration-dependent study for Eu^{3+} (**Table 2.5**) demonstrates a classic pattern of luminescence quenching beyond an optimal concentration of 2.0 mol%. The smooth decay of intensity, rather than an abrupt drop, strongly suggests that the concentration quenching mechanism is governed by multipolar interactions, as described by the Dexter theory, rather than by the formation of quenching aggregates or drastic structural changes (Dexter & Schulman, 1954). This indicates the excellent structural stability of both borate hosts, capable of accommodating RE^{3+} ions without significant phase segregation.

The decay lifetime data (**Table 2.6**) provides further insight into the luminescence dynamics. The bi-exponential decay of Eu^{3+} and Dy^{3+} emissions points to the existence of multiple, non-equivalent crystallographic sites for these ions within the host lattice, leading to different local environments and energy transfer pathways. The consistently longer average lifetime ($\tau_{av}g$) of Eu^{3+} in $MMeBO_3$ (0.88 ms) compared to $KCaBO_3$ (0.82 ms) aligns with its higher structural rigidity and lower non-radiative decay rate. The exceptionally long lifetime of Tb^{3+} (7.25 ms) is characteristic of its spin-forbidden 4f-4f transitions, while the short lifetime of Dy^{3+} is consistent with its faster radiative rates.

4.3 Thermal Stability and Structure-Property Correlation

The thermal quenching behavior is a critical parameter for w-LED applications, where operational temperatures can be significant. The calculated activation energies (E_a) for thermal quenching (**Table 3.7**) follow a clear trend: $Tb^{3+} > Eu^{3+} > Dy^{3+}$. The superior thermal stability of $MMeBO_3:Tb^{3+}$ (E_a = 0.158 eV) can be attributed to the rigid and symmetric structure of the $MMeBO_3$ host, which creates a high energy barrier for the activation of non-radiative cross-relaxation pathways. The moderate E_a values for Eu^{3+} and the lowest for Dy^{3+} in $KCaBO_3$ correlate well with the more flexible lattice and higher phonon energy contributions inferred from the structural analysis. This direct correlation between activation energy and host rigidity underscores the importance of selecting a structurally robust host matrix for developing thermally stable phosphors (Xie et al., 2016).

5. CONCLUSIONS

In summary, a series of Eu^{3+}, Tb^{3+}, and Dy^{3+}-doped $MMeR(BO_3)_2$ and $KCaR(BO_3)_2$ phosphors were successfully synthesized and their photoluminescence properties were systematically investigated. The key findings of this study are:

1. The photoluminescence is dominated by characteristic intra-4f transitions, with Eu^{3+} additionally showing a host-sensitive charge-transfer band. A red-shift in the CTB position and a lower Ω_2 Judd-Ofelt parameter in $KCaBO_3:Eu^{3+}$ indicate a higher covalency and a more centrosymmetric local environment compared to the $MMeBO_3$ host.

2. The phosphors emit in the characteristic regions: intense red for Eu^{3+} ($^5D_0 \rightarrow {}^7F_2$), strong green for Tb^{3+} ($^5D_4 \rightarrow {}^7F_5$), and a blue-yellow combination for Dy^{3+}, making the latter a promising candidate for single-phase white-light emission.
3. Concentration quenching occurs via a multipolar interaction mechanism, with an optimal Eu^{3+} doping concentration of 2.0 mol%. Lifetime analysis revealed multi-site occupancy for Eu^{3+} and Dy^{3+}, and a long-lived, single-exponential decay for Tb^{3+}.
4. The thermal stability, quantified by the activation energy (E_a), was found to be highest for $MMeBO_3:Tb^{3+}$ (0.158 eV) and lowest for $KCaBO_3:Dy^{3+}$ (0.105 eV), establishing a direct link between the host lattice's rigidity and the phosphor's resistance to thermal quenching.

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