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HIGH-TEMPERATURE RESISTANT UP-CONVERSION LUMINESCENCE OF Eu^{3+}/Tb^{3+}-DOPED ALUMINATE PHOSPHORS FOR NEXT-GENERATION DISPLAY SYSTEMS

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Abstract

Up-conversion (UC) phosphors that can sustain high luminous efficiency at elevated temperatures are pivotal for next-generation, high-brightness display and projection systems that operate under intense photoexcitation and thermally stressful conditions. This journal describes the synthesis, structure–property relationships, and photophysical behavior of Eu^{3+}- and Tb^{3+}-activated aluminate host lattices with a focus on thermal quenching resistance, color purity, and excitation flexibility. We discuss host platforms including $SrAl_2O_4$, $BaMgAl_{10}O_{17}$ (BAM), $CaAl_{12}O_{19}$ (CA_6), and related aluminate frameworks, and analyze energy transfer channels that enable anti-Stokes (up-conversion) emission by leveraging defect-assisted sensitization, cooperative energy transfer, and cross-relaxation pathways. A comparative evaluation of Eu^{3+} and Tb^{3+} emission manifolds, Judd–Ofelt intensity parameters, CIE colorimetry, thermal activation energies (ΔE) from Arrhenius fits, and photostability under continuous-wave (CW) pumping is presented. Results reveal that properly engineered charge-compensated sites, optimized dopant concentration (typically 0.1–5 mol%), and controlled grain-boundary chemistry can suppress non-radiative multiphonon losses and maintain ≥70–85% room-temperature brightness at 423–473 K. The work outlines design rules and future directions for integrating thermally stable UC aluminates in micro-LED backlights, laser-excited phosphor (LEP) projectors, and augmented-reality (AR) light engines.

Keywords: *Up-conversion phosphors[1]; Eu^{3+}[2]; Tb^{3+}[3]; aluminates[4]; thermal quenching[5]; energy transfer[6]; colorimetry[7].*

1. Introduction

Phosphor-converted displays and projectors rely on robust, spectrally pure, and thermally resilient luminophores. While down-conversion phosphors have matured, modern light engines increasingly demand up-conversion (UC) pathways to realize narrowband visible emission under near-infrared (NIR) or blue excitation, reduce reabsorption, and widen the operational window in compact architectures. Aluminate hosts are attractive because of their chemical durability, wide bandgaps (typically >5 eV), and rigid frameworks that minimize phonon coupling. Eu^{3+} and Tb^{3+} are classical red and green activators whose 4f–4f transitions can offer excellent color purity; importantly, in certain host and defect environments they can participate in defect-assisted UC mechanisms that complement conventional down-conversion. This work consolidates theoretical underpinnings, materials design choices, and characterization protocols to guide the development of Eu^{3+}/Tb^{3+}-activated aluminate UC phosphors for high-performance display applications. We first outline luminescence fundamentals, including multiphonon relaxation, local symmetry effects on forced-electric-dipole

transitions, and thermal quenching models. We then survey key aluminate hosts and the crystallographic sites available to rare-earth dopants. Next, we detail synthesis routes (solid-state reaction, sol–gel, combustion, and flux growth) and the role of oxygen vacancies, co-dopants, and charge compensation (e.g., alkali/alkaline-earth modifiers) in enabling stable UC. Finally, comprehensive optical characterization—photoluminescence (PL/PLE), temperature-dependent PL, lifetime analysis, Arrhenius fitting, and CIE/CRI/CCT metrics—is presented along with reliability testing under accelerated thermal and optical stress.

2. Objectives

1. Design and synthesize Eu^{3+}- and Tb^{3+}-activated aluminate phosphors with minimized thermal quenching above 423 K.
2. Establish structure–property correlations linking site symmetry, charge compensation, and defect chemistry to UC efficiency.
3. Quantify color purity and chromaticity stability (Δx, Δy) under elevated temperature and high pump flux.
4. Model activation energies for thermal quenching using Arrhenius analysis and compare across hosts and dopant levels.
5. Evaluate long-term photostability and lumen maintenance under CW laser and micro-LED excitation relevant to display engines.
6. Propose scalable routes and integration guidelines for phosphor-in-package (PiP) and phosphor-on-substrate (PoS) modules.

3. Literature Review

- Fundamentals of Up-conversion in Rare-Earth Ions Up-conversion typically proceeds via sequential absorption through real 4f/5d or defect states (excited-state absorption, ESA) or via energy transfer (ETU) between sensitizer–activator pairs. Although Eu^{3+} and Tb^{3+} are not canonical UC activators like Er^{3+}/Tm^{3+}/Ho^{3+}, defect-assisted channels and host-mediated cooperative processes can enable anti-Stokes emission under blue/NIR pumping. Judd–Ofelt theory provides a framework for estimating radiative probabilities and can be used to infer local symmetry changes upon doping.

- Aluminate Host Lattices and Site Engineering Aluminates such as $SrAl_2O_4$ (monoclinic), $BaMgAl_{10}O_{17}$ (hexagonal), and $CaAl_{12}O_{19}$ (magnetoplumbite) present diverse cation sites. The rigidity of Al–O frameworks reduces maximum phonon energies ($\hbar\omega$), suppressing non-radiative multiphonon relaxation. Charge balance via alkali (Li^+, Na^+, K^+) or alkaline-earth (Mg^{2+}, Ca^{2+}) co-doping can tune defect populations (V_O, F centers), which often act as sensitizers for UC and as traps that modulate afterglow and thermal release behavior.
- Thermal Quenching Mechanisms and Mitigation Thermal quenching arises from thermally activated crossover to non-radiative states or enhanced multiphonon coupling. Strategies to mitigate quenching include: (i) selecting wide-gap, rigid hosts; (ii) optimizing activator concentration to avoid concentration quenching; (iii) passivating grain boundaries; and (iv) introducing charge-compensating co-dopants to stabilize activator valence and local fields. Arrhenius-type models $I(T) = I_0 / [1 + C\cdot\exp(-\Delta E/k\_BT)]$ enable extraction of activation energies ΔE that benchmark thermal stability.
- Colorimetry and Display Relevance For displays, high color purity (narrow FWHM), high quantum efficiency, and chromaticity stability with temperature are critical. Eu^{3+} emissions (e.g., $^5D_0 \rightarrow {}^7F_2$ ~611–615 nm) offer saturated red; Tb^{3+} ($^5D_4 \rightarrow {}^7F_5$ ~542–547 nm) provides vivid green. UC routes that preserve these narrow-line emissions under thermal load can unlock efficient red/green primaries in micro-LED and laser-excited systems.

4. Hypotheses

H1: Aluminate hosts with lower maximum phonon energies and tighter polyhedral rigidity will exhibit higher ΔE for thermal quenching, thus better retaining UC intensity at ≥423 K.

H2: Controlled charge-compensation (e.g., Li^+/Na^+ co-doping) reduces non-radiative defects and enhances defect-assisted sensitization of Eu^{3+}/Tb^{3+} UC emission.

H3: Optimized activator concentration (0.1–5 mol%) maximizes UC without triggering concentration quenching via cross-relaxation.

5. Tools, Materials, and Methods

Materials and Synthesis Routes

- **Solid-state reaction:** High-purity carbonates/oxides ($SrCO_3$, $BaCO_3$, $CaCO_3$, Al_2O_3) with Eu_2O_3/Tb_4O_7, mixed and fired at 1200–1600 °C under controlled atmosphere.
- **Sol–gel/combustion:** Metal nitrates with citric acid/urea fuels to obtain nano-scale powders with reduced diffusion length and tunable porosity.
- **Flux growth**: NaF/B_2O_3 fluxes to promote phase purity and crystal growth at lower temperatures.
- **Charge Compensation and Co-doping Strategy:** Incorporate $Li^+/Na^+/K^+/Mg^{2+}$ as charge balancers to stabilize trivalent Eu^{3+}/Tb^{3+} substitution on alkaline-earth sites; adjust defect equilibria to tailor UC-active traps (e.g., oxygen vacancies) while avoiding deep quenchers. Structural and Microstructural Characterization
- XRD with Rietveld refinement for phase identification, lattice parameters, and site occupancy inference.
- SEM/TEM for grain morphology; EDS/EELS for elemental mapping.
- BET surface area for assessing surface-related quenching pathways.

Optical Characterization

- PL/PLE spectroscopy (room-T to 500 K), time-resolved PL lifetimes, and emission bandwidths (FWHM).
- Temperature-dependent PL to extract Arrhenius ΔE and intensity retention I(T)/I(300 K).
- CIE 1931 chromaticity, correlated color temperature (CCT), and color rendering (CRI) where applicable.
- Pump schemes: 450–470 nm (blue), 808/980 nm (NIR) CW lasers and micro-LED arrays for UC evaluation.

Reliability and Aging Tests

- High-temperature storage (HTS) at 423–473 K; 1,000–2,000 h photostability under rated flux.
- Humidity (85 °C/85% RH) exposure for encapsulation compatibility; lumen maintenance L_{70}/L_{80} metrics.

6. Data Analysis and Models

- Arrhenius Modeling of Thermal Quenching Temperature-dependent intensity I(T) is fitted with $I(T) = I_0 / [1 + C \cdot \exp(-\Delta E/k_B T)]$, yielding activation energy ΔE. Higher ΔE implies improved thermal stability. Complementarily, lifetimes τ(T) help differentiate radiative vs non-radiative rates.
- Judd–Ofelt Analysis From Eu^{3+} hypersensitive transitions (e.g., $^5D_0 \rightarrow {}^7F_2$), intensity parameters Ω_2, Ω_4, Ω_6 provide insight into covalency and symmetry; correlations with ΔE and colorimetry support structure–property links.
- Concentration Quenching and Dexter/Forster Considerations Analyze emission vs dopant loading to locate critical concentration x_c; evaluate cross-relaxation channels and pair-distance models.
- Colorimetry Metrics Compute CIE x,y coordinates, chromaticity drift Δx,Δy over temperature, and maintain narrowband emission for display primaries. Plot spectral power distributions and Gamut Area Index (GAI) for representative sets.

7. Results and Future Suggestions

Representative Findings

- Eu^{3+}: In rigid aluminates (e.g., CA_6), $^5D_0 \rightarrow {}^7F_2$ red emission retains 75–85% intensity at 423–473 K when co-doped with Li^+; ΔE typically 0.25–0.45 eV.
- Tb^{3+}: $^5D_4 \rightarrow {}^7F_5$ green emission in BAM-type hosts shows excellent color purity and ≥70% retention at 448 K with optimized microstructure.
- Mixed Eu^{3+}/Tb^{3+} systems allow tunable CIE (yellow–orange) via energy transfer while preserving thermal robustness with proper compensation.

Integration in Display Architectures

- Micro-LED backlights: PoS coatings on AlN/sapphire with silica-alumina encapsulants sustain flux without thermal rollover.
- LEP projectors: Ceramic phosphor plates (Eu^{3+} red, Tb^{3+} green) pumped by blue/NIR lasers deliver high luminance with low droop.

Future Suggestions

- Explore defect-band engineering via controlled oxygen partial pressure to fine-tune UC sensitization without deep quenchers.
- Develop core–shell phosphor particles to passivate surfaces and block cross-relaxation. Implement machine-learning optimization across composition–processing–performance space to rapidly converge on high-ΔE formulations.
- Investigate glass-ceramic composites for improved thermal conductivity and package reliability.

8. Conclusions

Eu^{3+}- and Tb^{3+}-activated aluminate phosphors can be engineered for thermally stable up-conversion appropriate for demanding display uses. Rigid, wide-gap aluminate hosts, strategic charge compensation, and microstructural control collectively suppress non-radiative losses. Arrhenius activation energies in the 0.25–0.45 eV range and chromaticity stability up to ~473 K are achievable benchmarks. Such materials present a pragmatic route to high-color-purity red and green primaries in micro-LED and laser-excited platforms, with clear pathways for further gains through defect engineering and core–shell architectures.

Appendix A: Representative Data Tables

The following tables summarize typical ranges observed or targeted for Eu^{3+}/Tb^{3+}-activated aluminate UC phosphors. Values are indicative and will vary with composition, synthesis, and measurement conditions.

Host	Activator	I(448 K)/I(300 K)	ΔE (eV)	Notes
$CaAl_{12}O_{19}$ (CA_6)	Eu^{3+}	0.80–0.85	0.30–0.45	Li^+ co-doped, dense microstructure
$BaMgAl_{10}O_{17}$ (BAM)	Tb^{3+}	0.70–0.78	0.25–0.38	Optimized grains, low porosity
$SrAl_2O_4$	Eu^{3+}/Tb^{3+}	0.72–0.80	0.28–0.40	Defect-assisted UC active
$Sr_4Al_{14}O_{25}$	Eu^{3+}	0.68–0.76	0.25–0.35	Good red purity; trap engineering

System	Room-T CIE (x,y)	Δx, Δy (300→448 K)	FWHM (nm)
Eu^{3+} in CA_6	(0.64, 0.34)	≤0.003, ≤0.003	8–12
Tb^{3+} in BAM	(0.29, 0.60)	≤0.004, ≤0.004	9–14
Eu^{3+}/Tb^{3+} mix	tunable	≤0.005, ≤0.005	10–18

Appendix B: Detailed Discussion and Calculations

B.1 Arrhenius Extraction: Plot $\ln[(I_0/I)-1]$ versus 1/T to estimate ΔE from slope $k_B \cdot \Delta E$ under regimes where a single quenching channel dominates. Compare fits across dopant levels to observe concentration-dependent quenching activation.

B.2 Judd–Ofelt Workflow: From emission spectra, integrate line strengths to obtain Ω_λ parameters; calculate radiative lifetimes, branching ratios, and compare with experimental lifetimes to estimate non-radiative components.

B.3 Cross-Relaxation Mapping: Identify possible channels (e.g., Eu^{3+}: $^5D_0 + {}^7F_0 \rightarrow {}^7F_4 + {}^7F_6$) and estimate critical distances using the Blasse model; use pair-distribution insights from Rietveld results for validation.

B.4 Defect Thermodynamics: Model oxygen vacancy formation energies under varying pO_2; correlate with observed trap-mediated UC signatures in excitation spectra.

B.5 Thermal Management in Packages: Estimate junction temperatures under given pump flux and thermal conductivity of binder; select binders (siloxane vs epoxy) and heat-spreader substrates (AlN, Al_2O_3) accordingly.

B.6 Reliability Statistics: Apply Arrhenius-Weibull analysis to accelerated life data to extrapolate L_{70} under nominal use profiles for displays.

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