

Rare-Earth-activated NaCaPO₄ Orthophosphate Phosphors: A Comprehensive Review

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Abstract—Generally, sodium calcium phosphate (NaCaPO₄) appeared as promising a host lattice for doping rare-earth elements to obtain new luminescent materials usable on solid-state lighting. This comprehensive review synthesizes recent research on Ce³⁺, Eu³⁺, Eu²⁺, Dy³⁺, and Tb³⁺ activated NaCaPO₄ phosphors, examining their synthesis methodologies, structural properties, photoluminescence characteristics, energy transfer mechanisms, and potential applications in white light-emitting diodes (WLEDs) and radiation dosimetry. The orthorhombic structure of NaCaPO₄, with its rigid three-dimensional network of tetrahedral phosphate groups, provides an excellent matrix for activator ion incorporation while maintaining exceptional thermal and chemical stability. Combustion synthesis, sol-gel methods and solid-state reactions have recently produced highly-efficient phosphors with adaptable emission colors as well as increased quantum yields and superior thermal stability compared to conventional commercial phosphors such as YAG: Ce³⁺.

Index Terms—sodium calcium phosphate (NaCaPO₄), rare-earth, Orthophosphate

I. INTRODUCTION AND BACKGROUND

1.1 Evolution of White-Light LED Phosphors

The phosphor-converted white light-emitting diode (pc-WLED) technology has become a game changer for solid-state lighting [1] to produce significant advantages compared to conventional incandescent and fluorescent lamps such as higher energy efficiency, longer operational lifetime, lower environmental pollution and high power consumption.[2] [3][4] Ever since the first commercial implementation of white LEDs based on a blue InGaN chip with YAG:Ce³⁺ yellow phosphor, [4] much effort

has been devoted to realize better alternative phosphor systems due to the inherent limitations associated with blue plus yellow approaches including thermal quenching and low color rendering index (CRI), halos from color separation as well as some limits in flexible tuning of chromaticity due to lack of red emission.[2][5]

1.2 Significance of NaCaPO₄ Host Lattice

Among orthophosphate host materials with the general formula ABPO₄ (where A represents monovalent alkali cations and B represents divalent alkaline-earth cations), sodium calcium phosphate (NaCaPO₄) has gained substantial attention as an emerging host lattice for rare-earth luminescent materials.[6][7]. This orthorhombic phosphate exhibits several distinctive characteristics that make it particularly suitable for LED applications: strong absorption in the ultraviolet region due to PO₄³⁻ groups, moderate phonon energy enabling efficient energy transfer, exceptional thermal and chemical stability,[8] high optical damage threshold, and remarkable capacity for structural accommodation of various rare-earth dopant ions through multi-site occupancy mechanisms.[9] The rigid three-dimensional network of tetrahedral PO₄ groups in the NaCaPO₄ structure[10] can effectively surround and isolate divalent self-ions produced during synthesis, facilitating reduction processes such as Eu³⁺→Eu²⁺ conversion in controlled atmospheres.[11]

1.3 Motivation for Rare-Earth Activation Studies

The systematic investigation of Ce³⁺, Eu³⁺, Eu²⁺, Dy³⁺, and Tb³⁺ activation in NaCaPO₄ is driven by multiple objectives: (1) achieving tunable visible emission

spanning blue, green, yellow, orange, and red regions through judicious choice and concentration optimization of rare-earth dopants; [12][13] (2) understanding multi-site occupancy phenomena and their consequences for optical properties; (3) developing single-phase phosphors capable of generating white light without requiring complex phosphor blending; (4) investigating energy transfer pathways between co-doped rare-earth ions to enable color tunability and efficient light conversion; (5) optimizing synthesis techniques to enhance luminescence efficiency and particle morphology; and (6) exploring emerging applications including radiation dosimetry and persistent luminescence. [14], [14], [15], [16], [17], [18]

II. STRUCTURAL PROPERTIES AND CHARACTERIZATION

2.1 Crystal Structure of NaCaPO₄

NaCaPO₄ crystallizes in the orthorhombic system (Buchtwaldite structure, space group Pn21a [4]) with lattice parameters: $a = 0.6797$ nm, $b = 0.9165$ nm, and $c = 0.5406$ nm. The structure comprises four distinct crystallographic sites: three crystallographically different calcium positions (Ca1, Ca2, Ca3) and one sodium position (Na), all coordinated by tetrahedral phosphate groups (PO₄³⁻). X-ray diffraction patterns of NaCaPO₄ match JCPDS No. 29-1193, confirming the single-phase orthorhombic structure. [6] The presence of multiple calcium coordination environments is particularly significant for rare-earth doping, as it enables multi-site occupancy of dopant ions and influences the local crystal field experienced by the activator ions. [19]

2.2 Ionic Radii Considerations and Dopant Incorporation

Doping of rare-earth ions preferably depends upon crystallographic sites based on ionic radii matching with host cations. For example, Eu³⁺ (ionic radius 1.066 Å) preferentially substitutes Ca²⁺ ions (ionic radius 1.12 Å) over Na⁺ (1.24 Å) or P⁵⁺ (0.17 Å) due to closer radii similarity. Similarly, Eu²⁺ (1.25 Å) shows strong preference for Ca²⁺ sites due to both ionic radii matching and equal valence. This selective site occupancy fundamentally influences the local symmetry experienced by dopant ions and

consequently determines their spectroscopic properties and luminescence efficiency. [19]

2.3 Defect Chemistry and Charge Compensation

When trivalent rare-earth ions such as Ce³⁺, Eu³⁺, Dy³⁺, or Tb³⁺ substitute for divalent Ca²⁺ ions in the NaCaPO₄ lattice, charge compensation mechanisms become essential to maintain electrical neutrality. Computational and experimental studies reveal that the most energetically favorable charge compensation strategy involves creation of Na⁺ antisite defects (Na'_a), where Na⁺ ions substitute for Ca²⁺ positions. [9] For example, incorporation of two Eu³⁺ ions requires two compensating Na'_a defects, creating the charge balance: $2\text{Eu}^{3+}_a + 2\text{Na}'_a \leftrightarrow 3\text{Eu}^{2+}_a + \text{one oxygen vacancy}$. Atomistic modeling calculations indicate that the Ca2 site is the most probable location for Eu dopant incorporation, with solution energies of 2.15 eV for Eu³⁺ and 0.81 eV for Eu²⁺, significantly lower than substitution at other sites. [19]

III. SYNTHESIS METHODOLOGIES

3.1 High-Temperature Solid-State Reaction (SSR)

The conventional high-temperature solid-state reaction method involves mixing stoichiometric amounts of precursor materials (Na₂CO₃, CaCO₃, NH₄H₂PO₄, and rare-earth oxides or nitrates) followed by calcination at elevated temperatures (typically 900-950°C) for extended durations (3-6 hours) under controlled atmospheres. [14] The SSR method offers advantages including industrial scalability, relatively simple equipment requirements, and effective crystallite formation. However, the high firing temperatures and prolonged sintering times can lead to particle agglomeration and limitations in controlling final morphology. [20][21] For Eu²⁺-containing phosphors, SSR requires subsequent reduction firing in N₂/H₂ atmospheres to optimize the divalent europium concentration and achieve maximum luminescence efficiency. The critical transfer distance (R_c) for energy transfer among dopant ions calculated using Blasse's theory is approximately 15 Å for Eu²⁺ in NaCaPO₄. [18]

3.2 Combustion Synthesis Method

Combustion synthesis is a quick alternative synthesis method as it uses the exothermic oxidation of organic fuels that are present in an aqueous precursor solution

to produce enough heat to achieve temperatures suitable for obtaining phases.[22] In this method, metal nitrates ($\text{Ca}(\text{NO}_3)_2$, NaNO_3 , rare-earth nitrates) and $\text{NH}_4\text{H}_2\text{PO}_4$ are dissolved in deionized water along with citric acid (chelating agent) and combustible organic compounds such as urea or glycine. Upon heating to approximately 200-250°C, the mixture undergoes spontaneous, self-sustaining combustion producing a voluminous precursor powder. Subsequent calcination at 600°C for 6 hours yields highly crystalline phosphor powder. The combustion is particularly advantageous: very short synthesis time (minutes to hours vs. several hours for SSR), reduced agglomeration and very fine particles synthesize, controllable morphology by parameter optimization with respect to the final compound, and superior optical properties over conventional SSR.[23] [24]

3.3 Sol-Gel Combustion (SGC) Method

Sol-gel combustion technique combines advantages of both sol-gel chemistry and combustion synthesis, involving formation of a chelated metal-citrate complex gel followed by controlled combustion and calcination.[17] In this approach, metal nitrates and phosphoric acid are dissolved in deionized water, citric acid (chelating agent, 1:5 molar ratio of metals: citric acid) is added, and polyethylene glycol-400 (PEG-400) serves as a network former. The solution is evaporated at 120°C to form a viscous gel, followed by controlled heating to 450°C initiating combustion. The resulting black fluffy porous precursor is ground and sintered at 800°C for 3 hours. Comparative studies demonstrate that SGC-synthesized Eu^{3+} : NaCaPO_4 phosphors exhibit significantly enhanced emission intensity compared to SSR and molten salt synthesis methods, indicating superior incorporation efficiency and reduced defect concentration. The SGC method produces particles in the nano- to deep-micrometer size range with controlled morphology and high compositional homogeneity.[25]

IV. PHOTOLUMINESCENCE PROPERTIES OF RARE-EARTH ACTIVATED NaCaPO_4

4.1 Ce^{3+} -Activated NaCaPO_4 Phosphors

4.1.1 Spectroscopic Characteristics

Ce^{3+} -doped NaCaPO_4 phosphors exhibit characteristic luminescence properties dominated by parity-allowed $4f \rightarrow 5d$ transitions. Under vacuum ultraviolet (VUV)

to ultraviolet (UV) excitation, excitation spectra reveal seven distinct excitation bands at approximately 331, 296, 275, 261, 243, 213, and 198 nm, attributed to transitions from the $4f^1$ ground state ($^2F_{5/2}$ and $^2F_{7/2}$) to various 5d energy levels. These multiple excitation peaks result from multi-site occupancy of Ce^{3+} ions across the three distinct calcium crystallographic positions in the NaCaPO_4 structure, each experiencing different crystal field environments. However, emission spectra typically display only two main bands at approximately 371 and 399 nm, suggesting either very similar emission wavelengths from different Ce^{3+} sites or efficient energy transfer from higher-energy sites to the lowest-energy site. The broad excitation extending from 250-450 nm with principal peak around 370-380 nm matches well with UV-LED emission spectra (350-410 nm), making Ce^{3+} : NaCaPO_4 particularly suitable for UV-excited phosphor-converted LEDs.[26][6]

4.1.2 Excitation and Emission Mechanisms

The luminescence mechanism involves initial photon absorption exciting Ce^{3+} electrons from the $4f^1$ ground state to higher 5d orbital states. Due to the extended radial wavefunctions of 5d orbitals, the 5d energy is strongly dependent on the crystal field environment, resulting in large Stokes shifts characteristic of Ce^{3+} luminescence.[27] The subsequent radiative $5d \rightarrow 4f$ transition produces UV emission centered around 370-380 nm.[28] The luminescence decay time is characteristically short (30-36 nanoseconds), consistent with parity-allowed transitions, making Ce^{3+} : NaCaPO_4 potentially suitable as scintillation material for detecting ionizing radiation and thermal neutrons.[26][6]

4.1.3 Doping Concentration Effects and Quenching

Investigation of Ce^{3+} concentration effects in NaCaPO_4 reveals nonlinear relationships between dopant concentration and luminescence intensity. At low concentrations ($x < 0.05$ in $\text{Na}_{1-x}\text{Ca}_{1-2x}\text{Ce}_x\text{PO}_4$), emission intensity increases proportionally with Ce^{3+} concentration. However, X-ray excited luminescence measurements indicate absolute light yields of approximately 6500 photons/MeV for $x = 0.005$, substantially lower than commercial scintillators such as $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ (~26,000 ph/MeV) and $\text{Gd}_2\text{SiO}_5:\text{Ce}^{3+}$ (~9000 ph/MeV), suggesting opportunities for further optimization.[26]

4.2 Eu^{3+} -Activated NaCaPO_4 Phosphors

4.2.1 Red Emission Properties

Eu^{3+} -doped NaCaPO_4 phosphors exhibit characteristic red luminescence dominated by $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($j = 1, 2, 3, 4$) transitions, with the prominent $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition at approximately 594-619 nm. Under near-UV excitation ($\lambda_{\text{ex}} = 392\text{-}393$ nm), the emission spectrum typically displays a dominant peak at 594-595 nm (orange-red, $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition) with secondary peaks at 614 nm and 621 nm (red, $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition). The broad excitation band spanning 250-450 nm with maximum around 390-395 nm provides excellent spectral overlap with near-UV LED emission characteristics. The electric dipole $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is hypersensitive to the local crystal field environment, offering a sensitive probe of europium site symmetry and local distortions.[29]

4.2.2 Concentration Quenching Mechanisms

Studies of Eu^{3+} -doped NaCaPO_4 synthesized by various methods reveal that the critical quenching concentration is approximately 0.05 mol% when synthesized by SSR. Above this concentration, non-radiative energy transfer between Eu^{3+} ions become dominant, progressively reducing the quantum yield. The energy transfer occurs primarily through multipole-multipole interactions following Dexter's theory, with electric quadrupole-quadrupole interactions identified as the primary mechanism at high dopant concentrations. The calculated critical transfer distance $R_c \approx 15$ Å represents the distance at which energy transfer efficiency becomes significant. Sintering atmosphere significantly influences luminescence: phosphors prepared by $\text{Ar-N}_2\text{H}_2$ sequential sintering show dramatically enhanced green emission (for Eu^{2+}) or more efficient red emission (for Eu^{3+}) compared to single-atmosphere synthesis.[30]

4.3 Eu^{2+} -Activated NaCaPO_4 Phosphors (Green Phosphor)

4.3.1 Green Emission Characteristics

Eu^{2+} -doped NaCaPO_4 represents a novel green-emitting phosphor with exceptional potential for near-UV LED applications. Under near-UV excitation ($\lambda_{\text{ex}} = 373\text{-}400$ nm), the phosphor exhibits intense bluish-green emission centered at 505 nm, corresponding to the allowed $4\text{f}^65\text{d}^1 \rightarrow 4\text{f}^7$ dipole transition. The excitation spectrum displays a broad band extending from 250-450 nm, with principal peak at 373 nm

showing excellent spectral overlap with near-UV LED characteristics. [11]

4.3.2 Reduction and Stabilization of Eu^{2+} States

The $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ reduction in NaCaPO_4 requires specific synthesis conditions. High-temperature solid-state reaction under reducing atmosphere (typically $\text{N}_2/\text{H}_2 = 95:5$ at 850°C) preferentially produces the divalent state. The tetrahedral coordination by oxygen in the phosphate network effectively isolates and stabilizes the Eu^{2+} ion against reoxidation. Four conditions essential for Eu^{3+} reduction to Eu^{2+} in the NaCaPO_4 matrix are: (1) absence of powerful oxidizing ions in the host lattice; (2) sufficient positive charges on dopant ions exceeding valence requirements; (3) capability of charge compensation by defects; and (4) appropriate host structure based on tetrahedral anion groups. The NaCaPO_4 lattice satisfies all four conditions, enabling intrinsic reduction processes.[18]

4.3.3 Concentration Optimization

Studies of Eu^{2+} concentration effects reveal that emission intensity increases monotonically with doping concentration up to approximately 0.05 mol%, beyond which concentration quenching becomes dominant. The critical transfer distance for Eu^{2+} - Eu^{2+} energy transfer is calculated as $R_c \approx 15$ Å, comparable to Eu^{3+} systems. The mechanism of energy transfer at high concentrations involves non-radiative processes mediated by electric multipole interactions, with exchange interaction having characteristic distances around 5 Å.[18]

4.4 Dy^{3+} -Activated NaCaPO_4 Phosphors

4.4.1 Multi-Color Emission Capability

Dy^{3+} -doped NaCaPO_4 phosphors exhibit characteristic multi-color emission when excited by near-UV radiation ($\lambda_{\text{ex}} \approx 349$ nm), producing three distinct emission bands: blue emission at 482 nm ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ transition), yellow emission at 576 nm ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ transition), and weaker red emission components. The emission color appears white or warm-white to the human eye due to the balanced intensity of blue and yellow components, offering significant advantages for warm white lighting applications compared to conventional cool-white YAG: Ce^{3+} systems that are deficient in red spectral content.[31]

4.4.2 Potential for Integrated White-Light Phosphors

The simultaneous availability of blue and yellow emission from a single Dy^{3+} -doped phosphor

represents a promising approach to single-phase white-light generation. By optimizing Dy^{3+} doping concentration, the relative intensities of blue and yellow can be adjusted to achieve desired color temperature and chromaticity coordinates. [6], [31]

4.4.3 Thermoluminescence and Dosimetry Applications

Beyond photoluminescence applications for LEDs, NaCaPO_4 : Dy^{3+} phosphors demonstrate remarkable thermoluminescence (TL) properties suitable for radiation dosimetry. When irradiated with gamma rays (Co^{60} , Cs^{137}) or high-energy carbon ion beams (75 MeV C^{6+}), the phosphor produces characteristic TL glow curves with distinct peaks reflecting trapping levels created during irradiation. The TL intensity exhibits linear dose response in the low-dose region and gradually saturates at higher doses. Trapping parameters determined by glow curve deconvolution analysis reveal multiple trap centers with varying thermal stabilities, reflecting complex point defect chemistry in the phosphate lattice. [31], [32]

4.5 Tb^{3+} -Activated and $\text{Tb}^{3+}/\text{Eu}^{3+}$ Co-Doped NaCaPO_4

4.5.1 Green Emission from Tb^{3+}

Terbium-activated NaCaPO_4 produces characteristic green emission under UV excitation, dominated by $^5\text{D}_4 \rightarrow ^7\text{F}_j$ transitions ($j = 6, 5, 4, 3$). The green emission from Tb^{3+} is highly efficient due to the allowed electric dipole nature of transitions and limited competing non-radiative decay pathways. The principal emission occurs around 545-550 nm, overlapping the photopic luminosity function maximum and providing high visual brightness perception.[15][14]

4.5.2 Energy Transfer from Tb^{3+} to Eu^{3+}

When Tb^{3+} and Eu^{3+} are co-doped in NaCaPO_4 , efficient resonant energy transfer occurs from the excited $^5\text{D}_4$ level of Tb^{3+} to the $^5\text{D}_0$ level of Eu^{3+} , enabling tunable yellow-emitting phosphors. Energy transfer efficiency systematically increases with Eu^{3+} concentration, reaching approximately 92.5% at 0.10 mol% Eu^{3+} when 0.04 mol% Tb^{3+} is maintained. The energy transfer mechanism analysis demonstrates quadrupole-quadrupole interactions as the dominant process, consistent with Dexter's theory predictions. Emission color can be tuned from pure green ($x = 0$, no Eu^{3+}) through intermediate yellow-green ($x = 0.02$ -0.06) to deep yellow ($x = 0.10$) by controlling Eu^{3+} concentration, producing CIE chromaticity

coordinates ranging from (0.315, 0.671) to (0.482, 0.501).[15]

4.5.3 Color Tuning and LED Applications

The systematic color tuning capability in $\text{Tb}^{3+}/\text{Eu}^{3+}$: NaCaPO_4 systems positions these phosphors as promising candidates for warm-white and yellow-emitting near-UV LEDs. A single phosphor composition can generate any desired emission color within the green-to-yellow spectral region simply by controlling dopant concentrations. This eliminates the need for phosphor blending in RGB systems while providing superior color rendering compared to dual-phosphor systems.

4.6 $\text{Tb}^{3+}/\text{Mn}^{2+}$ Co-Doped NaCaPO_4

4.6.1 Red Emission Enhancement

Manganese doping in Tb^{3+} -containing NaCaPO_4 provides an alternative approach to generating red emission and tuning overall white light properties. Under UV excitation, $\text{Tb}^{3+}/\text{Mn}^{2+}$ co-doped phosphors exhibit the characteristic green emission of Tb^{3+} along with red emission bands attributed to Mn^{2+} at octahedral oxygen coordination sites. [4]

4.6.2 Energy Transfer Mechanism from Tb^{3+} to Mn^{2+}

Detailed photoluminescence studies confirm efficient energy transfer from Tb^{3+} (sensitizer) to Mn^{2+} (activator) through both direct resonant transfer and Förster-type mechanisms. By systematically varying Mn^{2+} concentration from 0 to 0.30 mol% while maintaining 0.30 mol% Tb^{3+} , the luminescence color can be continuously tuned from pure green to deep red, with CIE coordinates spanning the full visible spectrum. The maximum emission intensity typically occurs at intermediate Mn^{2+} concentrations (0.07-0.10 mol%), reflecting optimization between increased activation centers and concentration quenching effects.[4]

4.6.3 Near-UV LED Applications

The $\text{Tb}^{3+}/\text{Mn}^{2+}$ co-doped NaCaPO_4 system demonstrates excellent potential for near-UV LED applications, offering complete spectral tunability between green and red emission colors. By adjusting dopant concentrations, a single phosphor formulation can generate white light with any desired correlated color temperature and color rendering index, significantly simplifying LED packaging and color control compared to multi-phosphor approaches.[4]

V. COMPARATIVE PERFORMANCE OF SYNTHESIS METHODS

Systematic comparative studies of SSR, MSS, and SGC methods for Eu^{3+} : NaCaPO_4 synthesis reveal significant differences in product characteristics:

Property	SSR	MSS	SGC
Synthesis Time	6-8 hours	4-5 hours	2-3 hours
Sintering Temperature	950°C	800°C	800°C
Emission Intensity	Baseline	$\sim 1.2 \times$ baseline	$\sim 1.5 \times$ baseline
Crystallite Size	0.5-2 μm	0.2-1 μm	50-500 nm
Particle Agglomeration	Significant	Moderate	Minimal
Phase Purity	Excellent	Excellent	Excellent

The better performance of SGC synthesis with respect to the photoluminescence intensity can then be ascribed to a few several factors, such as enhanced crystallinity due to rapid heating, lower particles agglomeration allowing full occupancy of dopant sites, limited thermal degradation of precursor complex structures and formation with altered morphology which results in high specific surface area.[29]

Doped NaCaPO_4	Emission colour	CIE coordinates	Cite
$\text{NaCaPO}_4:0.3\text{Tb}^{3+}$	Green	0.315, 0.671	[14]
$\text{NaCaPO}_4:0.3\text{Tb}^{3+}, 0.1\text{Eu}^{3+}$	Yellow	0.482, 0.501	[15]
$\text{NaCaPO}_4:0.3\text{Tb}^{3+}, 0.3\text{Mn}^{2+}$	Deep Red	0.687, 0.311	[33]
$\text{NaCaPO}_4:0.05\text{Eu}^{2+}$	Bluish-Green	$\sim 0.35, \sim 0.55$	[29]

These coordinates span substantial portions of the visible color space, enabling systematic color tuning through dopant concentration variation.

While complete CRI analysis requires multi-wavelength reference standards and complex calculations, preliminary estimates for NaCaPO_4 -based phosphors can be obtained from spectral characteristics. Systems exhibiting continuous spectral distributions from 400-700 nm without sharp spectral gaps generally show CRI values exceeding 80, substantially superior to conventional YAG:Ce^{3+} (typically 70-75 CRI). The enhanced color rendering derives from better representation of spectral regions critical for human color perception, particularly the red region where YAG:Ce^{3+} is markedly deficient.[34]

VII. RADIATION DOSIMETRY APPLICATIONS

7.1 Thermoluminescence Properties for Dosimetry
Beyond solid-state lighting applications, $\text{NaCaPO}_4:\text{Dy}^{3+}$ phosphors exhibit promising

6. CIE Chromaticity Characterization and Color Rendering Index

The emission colors of the phosphors and their corresponding lighting applications can also be quantitatively assessed from photoluminescence measurements combined with CIE (Commission Internationale de l'Eclairage) chromaticity analysis. Published CIE coordinates for various NaCaPO_4 -based phosphors include:

thermoluminescence (TL) characteristics suitable for radiation dosimetry. TL is the delayed luminescence occurring upon heating of a material after exposure to ionizing radiation, resulting from carriers released from radiation-induced trap centers. TL glow curves for Co^{60} -irradiated $\text{NaCaPO}_4:\text{Dy}^{3+}$ reveal multiple peaks in the 50-300°C temperature range, indicating trap states with varying thermal activation energies.[32]

7.2 Dose-Response Characteristics

Systematic irradiation of $\text{NaCaPO}_4:\text{Dy}^{3+}$ with doses ranging from 10-500 Gy reveals approximately linear dose response in the 10-100 Gy range, with slight sub linearity at higher doses. The linearity is expressed as: $I_{\text{TL}} \propto D^n$ where $n \approx 1$ for low-to-moderate doses and approaches 0.9-0.95 at high doses due to trap saturation. The linear dose response indicates potential suitability for routine dosimetry applications requiring wide dynamic range.

7.3 High-Energy Ion Beam Response

Notably, NaCaPO₄: Dy³⁺ exhibits robust TL response to high-energy carbon ion beams (75 MeV C⁶⁺), producing characteristic glow curves without saturation at ion fluences exceeding 10¹² ions/cm², a feature rare among commercial phosphors. This capability positions NaCaPO₄: Dy³⁺ as a candidate material for dosimetry in advanced cancer radiotherapy protocols employing carbon ion beams. The TL dose response for C⁶⁺ irradiation is comparable to gamma-ray response at equivalent absorbed doses, indicating that energy deposition mechanism (continuous slowing down of densely ionizing heavy ions vs. sparse ionization from Compton scattering) does not fundamentally alter trap center formation and release dynamics.[32]

friendly lighting with adjustable color temperature.[35]

- Display Backlighting: Single-phase phosphors reduce color gamut variation with viewing angle compared to multi-phosphor systems[4]

8.2 Integration with Advanced LED Chip Technologies

Emerging high-power near-UV LEDs (wavelength 360-400 nm) based on AlGaIn semiconductors show improved reliability and efficiency compared to traditional InGaIn blue chips. NaCaPO₄-based phosphor systems are optimally matched to these near-UV emissions, enabling more efficient energy conversion and superior color rendering in next-generation pc-WLEDs.[20], [31], [36]

VIII. EMERGING APPLICATIONS

8.1 Advanced Lighting Applications

Beyond conventional RGB white-light LED systems, NaCaPO₄-based phosphors are finding applications in specialized lighting contexts:

- Human-Centric Lighting: Tunable Dy³⁺ and Tb³⁺/Eu³⁺ systems enable circadian-rhythm-

IX. COMPARISON WITH YAG: Ce³⁺ SYSTEMS

While YAG: Ce³⁺ dominates commercial white-LED markets due to its maturity and proven reliability, NaCaPO₄-based phosphors offer several advantages and complementary properties:

Characteristic	YAG: Ce ³⁺	NaCaPO ₄ : Dy ³⁺	NaCaPO ₄ : Eu ³⁺	NaCaPO ₄ : Tb ³⁺ /Eu ³⁺
Excitation Peak	460 nm	349 nm	393 nm	369 nm
Emission Color	Yellow (530 nm)	White/Warm	Red (595 nm)	Yellow (542 nm)
Color Rendering Index	70-75	80-85	N/A	80-85
Thermal Stability	Moderate	Good	Excellent	Good
Single-Phase White	No	Yes	No	No
Tunable Color	Limited	Excellent	No	Excellent
Cost	Low	Moderate	Moderate	Moderate
	[37]	[31]	[30]	[15]

X. CONCLUSION

Rare-earth doped NaCaPO₄ orthophosphate phosphors are an important innovation for solid-state lighting technology, enabling ultrafine color tuning, high color rendering index and improved thermal stability than traditional phosphor systems. The orthorhombic crystalline structure with various calcium coordination can induce complicated energy transfer channels and multi-wavelength photoluminescence in single phase. The activation mechanisms of Ce³⁺, Eu³⁺, Eu²⁺, Dy³⁺

and Tb³⁺ have been systematically characterized depending on the transition metal ions and in terms of their luminescence properties ranging from ultraviolet to red bands. The synthesis techniques at advanced level, especially sol-gel combustion route, are tailored for the preparation of high-efficiency phosphors with controlled morphology and improved quantum yields. The energy transfer mechanisms between co-doped rare-earth ions highlighted in this work allow unprecedented color-tuning properties, enabling continuous adjustment of chromaticity coordinates via

concentration changes. Color rendering indices in the range of 80–85 markedly outperform commercial YAG: Ce³⁺ systems (70–75) especially for red spectral regions that are important for natural-like color perception. Graft NaCaPO₄ based thermally stable phosphors offer higher luminescence intensity at high temperature compared with traditional phosphors, which suitable for high-power LED applications.

Apart from conventional lighting applications, the NaCaPO₄ host matrix has also been shown to have utility in radiation dosimetry via thermoluminescence (TL) properties in upper energy bands. Single phosphor formulations integrating multiple functionalities (lighting, thermal and persistent luminescence) pave the way for highly advanced smart lighting systems.

Though significant strides have been made, there are still technological hurdles to cross with regards to scaling the laboratory synthesis methods to industrial production, long-term field demonstration of efficacy, and phosphor-in-glass/ceramic integration approaches.

This combination of evolving near-UV LED chip technologies with novel NaCaPO₄ phosphor science will enable the solid-state lighting systems of tomorrow to be more energy efficient, exhibit outstanding color quality and unparalleled tunability than any systems available today. NaCaPO₄-based phosphors will be uniquely positioned to complement and, in some cases potentially replace conventional phosphor systems applicable for demanding lighting applications focused on color rendering quality and tunability as research progresses and manufacturing methods mature.

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