ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/26aug1420

Recent Advances in Red-Emitting Phosphors: A Comparative Review of Eu^{3+}, Eu^{2+} and Mn^{4+} Activated Materials

J. Shivakumara[1]; H. M. Dayananda[2]; G. Chandrashekaraiah[3*]

[1] Department of Physics, Government First Grade College, Kunigal-572130, India
[2] Department of Physics, Government First Grade College, Kadur, Chikmagalur - 577548, India
[3*] Department of Physics, Government First Grade College, Gubbi - 572216, India

Presenting Author: J. Shivakumara
Corresponding Author: G. Chandrashekaraiah*

Publication Date: 2026/09/08

Abstract: Red-emitting phosphors are essential components of modern solid-state lighting, wide-gamut displays, laser lighting, optical sensors and emerging photonic technologies. The development of efficient red phosphors has received considerable attention because conventional red emitters often suffer from insufficient absorption in the blue spectral region, thermal quenching, broad emission or poor chemical stability. This review summarizes recent progress in inorganic red-emitting phosphors activated mainly by Eu^{3+}, Eu^{2+} and Mn^{4+} ions, with emphasis on photoluminescence characteristics and suitability for blue-light-excited white light-emitting diodes (WLEDs) and display applications. Eu^{3+} phosphors generally provide sharp and highly colour-pure red emission near 610–620 nm, whereas Eu^{2+} offers broad and compositionally tunable emission extending into the deep-red region. Mn^{4+}-activated fluoride phosphors exhibit narrow-band red emission and are particularly attractive for wide-colour-gamut displays. Representative materials are compared in terms of excitation wavelength, emission maximum, quantum efficiency, decay lifetime and thermal stability. Direct comparison is complicated by differences between internal quantum efficiency, external quantum efficiency and quantum yield. Recent results demonstrate quantum efficiencies exceeding 90% for selected systems, although the measurement conditions must always be specified. Remaining challenges include thermal quenching, moisture sensitivity, synthesis complexity, spectral reabsorption and cost. Future development is expected to focus on host-lattice engineering, defect control, surface protection, large-crystal growth and computationally assisted phosphor discovery.

Keywords: *Eu^{2+} Phosphor; Eu^{3+} Phosphor; Mn^{4+} Phosphor; Red Emission; Solid-State Lighting; Thermal Stability; Quantum Efficiency; Wleds.*

How to Cite: J. Shivakumara; H. M. Dayananda; G. Chandrashekaraiah (2026) Recent Advances in Red-Emitting Phosphors: A Comparative Review of Eu^{3}+, Eu^{2}+ and Mn^{4}+ Activated Materials. *International Journal of Innovative Science and Research Technology*,11(8), 3122-3126. https://doi.org/10.38124/ijisrt/26aug1420

I. INTRODUCTION

Phosphor-converted white light-emitting diodes (pc-WLEDs) have become an important solid-state lighting technology because of their high efficiency, long operating lifetime and compactness. A typical WLED combines a blue or near-ultraviolet LED chip with photoluminescent converters. The red component is important because it improves colour rendering and permits warmer correlated colour temperatures [1], [2].

An efficient red phosphor should ideally absorb strongly in the 400–480 nm region, emit between approximately 600 and 660 nm, exhibit high quantum efficiency, low thermal quenching, suitable decay kinetics and good chemical stability. For display applications, narrow emission bandwidth is

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/26aug1420

additionally desirable because it enables a wider colour gamut [3].

Eu^{3+}, Eu^{2+} and Mn^{4+} represent three complementary activator strategies. Eu^{3+} produces characteristic line emission around 610–620 nm; Eu^{2+} provides host-dependent 5d–4f emission that can be tuned from orange to deep red; and Mn^{4+} produces narrow red emission in suitable fluoride and oxide hosts [4]–[6].

II. LUMINESCENCE MECHANISMS

- *Eu^{3+}-Activated Phosphors*

Eu^{3+} has a $4f^6$ configuration. Shielding of the 4f electrons by the outer 5s and 5p orbitals makes its emission wavelengths comparatively insensitive to the host. The dominant red emission is commonly the $^5D_0 \rightarrow {}^7F_2$ transition near 610–620 nm. The sharp lines provide excellent colour purity, but the 4f–4f transitions are parity forbidden, making direct blue excitation comparatively weak. Charge-transfer excitation and host-to-Eu^{3+} energy transfer are therefore important [2], [8].

- *Eu^{2+}-Activated Phosphors*

Eu^{2+} has a $4f^7$ ground state and broad 5d→4f emission. The 5d level is strongly affected by crystal-field splitting and covalency, making the emission highly host dependent. Nitride and oxynitride hosts are particularly effective for red emission because strong Eu–N interactions lower the excited 5d state [3], [7]. $CaAlSiN_3:Eu^{2+}$ is a representative red nitride phosphor, while $Sr[LiAl_3N_4]:Eu^{2+}$ and $Sr[Li_2Al_2O_2N_2]:Eu^{2+}$ demonstrate high-performance narrow or relatively narrow red emission [11]–[15].

- *Mn^{4+}-Activated Phosphors*

Mn^{4+} has a $3d^3$ configuration and can produce characteristic narrow red emission when incorporated into suitable octahedral sites. Fluoride hosts such as K_2TiF_6 and K_2SiF_6 are particularly important for display and lighting applications [5], [6]. Their main limitations have historically included relatively weak absorption, long decay times and moisture sensitivity, but crystal engineering and surface protection have improved practical performance [16], [19], [20].

III. COMPARATIVE PHOTOLUMINESCENCE PERFORMANCE

Table 1 summarizes representative Eu^{3+}-activated materials. Values are reproduced as reported in the cited studies; NR denotes not reported.

Table 1 : Representative Eu^{3+} activated red phosphors.

Host: Activator	Excitation	Emission	Quantum efficiency	Lifetime	Thermal parameter
$Y_2O_3:Eu^{3+}$	UV	612 nm	80.88%	1.570 ms	NR
$Li_2Al_2Si_3O_{10}:Eu^{3+}$	394 nm	615 nm	31.5%	0.388 ms	$E_a = 1803\ cm^{-1}$
$NaCa(PO_3)_3:Eu^{3+}$	NUV	~612 nm	86% IQY	NR	~90.17% at 150 °C
$CaWO_4:Eu^{3+},Al^{3+}$	NUV	~615 nm	Improved	NR	Improved thermal stability
$CaLa_2ZnTi_2O_9:Eu^{3+}$	395/465 nm	615 nm	84.36% IQY	NR	$E_a = 0.230$ eV

Table 2 : Representative Eu^{2+} activated red phosphors.

Host:Activator	Excitation	Emission	Quantum efficiency	Lifetime	Thermal performance
$CaAlSiN_3:Eu^{2+}$	460 nm	Broad red	71% IQE	NR	Good
$CaAlSiN_3:Eu^{2+}$ ceramic	Blue	~650 nm	~60% EQE	NR	Improved
$CaAlSiN_3:Eu^{2+}$ phosphor-in-glass	Blue	Red	53% EQE	NR	Good
$Sr[LiAl_3N_4]:Eu^{2+}$	Blue	~650 nm	High	NR	>95% relative efficiency at 200 °C
$Sr[Li_2Al_2O_2N_2]:Eu^{2+}$	Blue	614 nm	≥80%	790 ns	Excellent
$CaAlSiN_3:C,Eu^{2+}$	Blue	656.8→650.2 nm	NR	775.3→721.7 ns	Improved quenching behaviour

The $CaAlSiN_3:Eu^{2+}$ value of 71% is specifically internal quantum efficiency under 460 nm excitation and should not be confused with EQE [11]. Likewise, IQE, EQE and QY are not interchangeable metrics. The reported $K_2TiF_6:Mn^{4+}$ values of 93.06% IQE and 69.09% EQE illustrate the distinction [18].

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/26aug1420

Table 3 : Representative Mn^{4+} Activated Red Phosphors.

Host:Activator	**Excitation**	**Emission**	**Quantum efficiency**	**Lifetime**	**Thermal/moisture performance**
$K_2TiF_6:Mn^{4+}$	Blue	632.7 nm	93.06% IQE; 69.09% EQE	NR	97.5% intensity at 150 °C
$Na_2SiF_6:Mn^{4+},Li^{+}$	Blue	~630 nm	99.83% QY	NR	Good
$Cs_2NbOF_5:Mn^{4+}$	Blue	~630 nm	~82% IQE	NR	High moisture resistance
$K_2SiF_6:Mn^{4+}$	Blue	~630 nm	78.5% EQE	NR	$T_{1/2}$ > 500 K
$K_2SiF_6:Mn^{4+}$ large crystal	Blue	~630 nm	97% IQE; 82% EQE	NR	82% intensity at 500 K
$K_2SiF_6:Mn^{4+}$ large crystal	Blue	~630 nm	97% IQE; 82% EQE	NR	80.7% after 5 h water immersion

Comparison of Eu^{3+}, Eu^{2+} and Mn^{4+}

Table 4 : Overall Comparison of Major Red-Phosphor Activators.

Parameter	**Eu^{3+}**	**Eu^{2+}**	**Mn^{4+}**
Principal transition	4f–4f	5d–4f	3d–3d
Typical red emission	610–620 nm	610–680 nm	610–660 nm
Emission bandwidth	Very narrow	Broad to narrow	Narrow
Blue excitation	Moderate	Excellent in suitable hosts	Moderate
Colour purity	Excellent	Host dependent	Excellent
Spectral tunability	Limited	Excellent	Moderate
Typical lifetime	ms	µs range	ms range
Thermal stability	Host dependent	Excellent in many nitrides	Improving; host dependent
Moisture stability	Generally good	Generally good	Often challenging in fluorides
Main application	Lighting, displays, sensing	WLEDs, LDs	Displays/WLEDs

Eu^{3+} is preferred where spectral precision and colour purity dominate. Eu^{2+} provides strong excitation and broad spectral engineering, particularly in nitride/oxynitride hosts. Mn^{4+} provides narrow red emission well suited to wide-gamut displays, although environmental stability remains a key consideration [3], [5], [7].

IV. THERMAL STABILITY AND QUANTUM EFFICIENCY

Thermal quenching occurs when increasing temperature enhances non-radiative relaxation. An Arrhenius-type expression is commonly used to describe the temperature dependence of emission intensity:

$$I(T) = I_0 / [1 + A\ exp(-E_a / k_B T)]$$

Where $I(T)$ is the emission intensity at temperature T, I_0 is the low-temperature intensity, A is a constant, E_a is the activation energy for thermal quenching and k_B is Boltzmann's constant. The temperature $T_{1/2}$, at which emission falls to half of its reference value, is another practical stability indicator.

Recent measurements show that thermal stability is strongly host dependent. Eu^{2+} nitrides benefit from rigid host frameworks and strong covalent bonding, whereas Mn^{4+} fluoride phosphors increasingly rely on compositional optimization, surface protection and crystal-growth control [3], [19], [20].

V. DESIGN STRATEGIES AND APPLICATIONS

Current red-phosphor development increasingly relies on rational host-lattice engineering. For Eu^{3+}, modification of the local coordination environment, charge compensation and controlled substitution can improve radiative emission and reduce concentration quenching [2], [8].

For Eu^{2+}, crystal-field splitting, covalency and local coordination determine the 5d energy level and hence the emission wavelength. Nitride and oxynitride hosts are especially promising for long-wavelength emission [3], [7]. For Mn^{4+}, control of the octahedral environment, Li^{+} incorporation, surface modification and crystal-growth engineering can enhance efficiency and stability [16], [19], [20].

Important applications include pc-WLEDs, wide-gamut displays, laser lighting, plant-growth lighting and optical sensing. For high-power lighting and laser applications, thermal conductivity and long-term stability are as important as room-temperature photoluminescence efficiency.

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/26aug1420

VI. CHALLENGES AND FUTURE PERSPECTIVES

No single activator system currently satisfies all requirements of a practical red phosphor. Eu^{3+} offers excellent colour purity but comparatively weak direct blue excitation. Eu^{2+} offers strong excitation and tunability, but high-performance nitride synthesis can be complex. Mn^{4+} offers narrow-band emission but fluoride hosts may exhibit moisture sensitivity and thermal degradation.

Future research should emphasize host-lattice engineering, defect control, protective surface coatings, thermal management, large-crystal growth and computationally assisted materials discovery. Reporting should also be standardized: excitation wavelength, emission maximum, FWHM, IQE, EQE, lifetime, $T_{1/2}$ and environmental stability should be stated with measurement conditions so that literature values can be compared reliably.

VII. CONCLUSION

Eu^{3+}, Eu^{2+} and Mn^{4+} activated phosphors provide complementary routes to efficient red emission. Eu^{3+} systems are characterized by sharp and colour-pure emission, Eu^{2+} systems provide strong excitation and broad spectral tunability, and Mn^{4+} systems offer narrow-band red emission suitable for wide-gamut displays. Recent developments have substantially improved quantum efficiency, thermal stability and environmental durability. Nitride/oxynitride Eu^{2+} phosphors and Mn^{4+} fluoride crystals are particularly promising for next-generation WLED and display technologies. Continued progress will depend on balancing spectral performance with thermal stability, chemical durability, synthesis cost and compatibility with commercial LED and laser architectures.

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