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**Raqib Tarafder**  
 Department of Solid State and  
 Materials Chemistry, Jamuna  
 Institute of Technology,  
 Sylhet, Bangladesh

**Imran Khandaker**  
 Department of Solid State and  
 Materials Chemistry, Jamuna  
 Institute of Technology,  
 Sylhet, Bangladesh

**Corresponding Author:**  
**Raqib Tarafder**  
 Department of Solid State and  
 Materials Chemistry, Jamuna  
 Institute of Technology,  
 Sylhet, Bangladesh

## Rare earth-doped phosphor materials for white light-emitting diode applications

**Raqib Tarafder and Imran Khandaker**

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### Abstract

The global LED lighting market has expanded at a compound annual growth rate exceeding 13% since 2018, yet achieving warm-white emission with high colour rendering remains a bottleneck tied to phosphor performance. This research synthesized a series of  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  (gehlenite) phosphors co-doped with  $\text{Eu}^{3+}$  and  $\text{Dy}^{3+}$  at varying concentrations (0.5-10 mol%  $\text{Eu}^{3+}$ , fixed 2 mol%  $\text{Dy}^{3+}$ ) by a sol-gel combustion method. Phase purity was confirmed by X-ray diffraction, and particle morphology was examined by scanning electron microscopy. Photoluminescence spectra under 365 nm UV excitation showed characteristic  $\text{Eu}^{3+}$  emission at 615 nm ( $^5\text{D}_0 \rightarrow ^7\text{F}_2$ ) and  $\text{Dy}^{3+}$  emission at 483 and 575 nm ( $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$  and  $^6\text{H}_{13/2}$ ). The optimal  $\text{Eu}^{3+}$  concentration was 7 mol%, beyond which concentration quenching reduced emission intensity by 16%. CIE chromaticity coordinates shifted progressively from blue-white (0.187, 0.131) at 0.5%  $\text{Eu}^{3+}$  toward the warm-white region (0.338, 0.348) at 7%  $\text{Eu}^{3+}$ , with a correlated colour temperature of 5,147 K and colour rendering index of 84.3. These results demonstrate that composition tuning of  $\text{Eu}^{3+}/\text{Dy}^{3+}$  co-doped gehlenite can produce single-phase phosphors suitable for UV-pumped white LED packages.

**Keywords:** Rare earth, phosphor, white LED, europium, dysprosium, gehlenite, photoluminescence, colour rendering index

### Introduction

The trend is unmistakable: incandescent and fluorescent lamps are being replaced worldwide by solid-state lighting at a pace that has already cut global electricity consumption for illumination by an estimated 8% since 2015 [1]. White LEDs dominate this transition because they combine high luminous efficacy (>150 lm/W in commercial packages), long lifetimes (>50,000 h), and compatibility with smart dimming and colour-tuning controls [2]. But the most common commercial approach coating a blue InGaN LED chip with a  $\text{Ce}^{3+}$ -doped yttrium aluminium garnet (YAG:Ce) phosphor produces a cool-white light deficient in the red spectral region, resulting in low colour rendering indices (CRI < 75) that are inadequate for residential and healthcare environments [3].

Two strategies can improve colour quality: (a) blending multiple single-colour phosphors (red + green + blue), which complicates manufacturing and introduces differential thermal quenching; or (b) developing single-phase phosphors that emit across the visible spectrum when excited by a single UV or blue chip [4]. Rare-earth co-doping in suitable host lattices follows the second path.  $\text{Eu}^{3+}$  provides a narrow red line at 615 nm, while  $\text{Dy}^{3+}$  contributes blue (483 nm) and yellow (575 nm) bands; together they can span the visible gamut from a single crystalline matrix [5].

Gehlenite ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ) is an attractive host because of its chemical stability, low phonon energy ( $\sim 650 \text{ cm}^{-1}$ ), and multiple cation sites ( $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ) that can accommodate trivalent rare-earth ions with minimal charge-compensation defects [6]. Sol-gel combustion synthesis offers a low-temperature, energy-efficient route to phase-pure gehlenite powders with sub-micrometre particle sizes suitable for LED encapsulant loading [7].

This research prepared  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Eu}^{3+},\text{Dy}^{3+}$  phosphors at seven  $\text{Eu}^{3+}$  concentrations, characterised their structural and luminescent properties, determined the optimal doping level

for warm-white emission, and evaluated the cost implications of rare-earth usage for potential scale-up.

## Material and Methods

### Material

All synthesis and characterisation were performed between January and September 2024 at the Department of Solid State and Materials Chemistry, Jamuna Institute of Technology, Sylhet, Bangladesh. Calcium nitrate tetrahydrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\geq 99\%$ ), aluminium nitrate nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\geq 98\%$ ), tetraethyl orthosilicate (TEOS,  $\geq 99\%$ ), europium(III) nitrate hexahydrate ( $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 99.99%), dysprosium(III) nitrate hexahydrate ( $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 99.9%), urea ( $\geq 99.5\%$ ), and citric acid monohydrate ( $\geq 99\%$ ) were purchased from Sigma-Aldrich (Singapore). All solutions were prepared with deionised water ( $18.2 \text{ M}\Omega \cdot \text{cm}$ ) [7].

### Methods

Stoichiometric amounts of metal nitrates (with  $\text{Eu}^{3+}$  substituting for  $\text{Ca}^{2+}$  at 0.5, 1, 2, 3, 5, 7, and 10 mol% and  $\text{Dy}^{3+}$  fixed at 2 mol%) were dissolved in 50 mL of deionised water along with TEOS (pre-hydrolysed in ethanol- $\text{HNO}_3$ ), citric acid (fuel, metal-to-citric acid ratio 1:1.5), and urea (oxidiser, nitrate-to-urea ratio 1:2.5) [7]. The solution was stirred at  $80^\circ\text{C}$  until a viscous gel formed, then transferred to a muffle furnace pre-heated to  $500^\circ\text{C}$ , where self-propagating combustion occurred within 2-3 min. The as-burnt powder was ground in an agate mortar and calcined at  $1100^\circ\text{C}$  for 4 h in air to achieve complete gehlenite crystallisation [6]. Phase identification used a Rigaku MiniFlex 600 X-ray diffractometer ( $\text{Cu K}\alpha$ ,  $2\theta = 10\text{-}60^\circ$ , step  $0.02^\circ$ ). Particle morphology was examined by field-emission SEM (JEOL JSM-7610F). Photoluminescence (PL) excitation and emission spectra were recorded on a Horiba FluoroMax-4 spectrofluorimeter at room temperature [8]. CIE 1931 chromaticity coordinates, correlated colour temperature (CCT), and CRI were

calculated from the emission spectra using the GoSpectra software.

### Implementation Details

Phosphor powders were incorporated into a silicone encapsulant (Dow Corning OE-6550, A:B ratio 1:1) at 15 wt% loading and deposited onto 365 nm UV LED chips (Nichia NVSU233A, 350 mA drive current) by dispensing and curing at  $150^\circ\text{C}$  for 1 h [2]. Luminous flux and spectral power distribution of assembled LED packages were measured in a 0.5 m integrating sphere (Labsphere LMS-400) coupled to a CAS 140D spectroradiometer. Each concentration variant was tested in triplicate packages, and measurements were taken after 30 min thermal stabilisation at  $25^\circ\text{C}$  ambient.

### Cost Analysis

Rare-earth raw material costs were estimated based on 2024 average spot prices for  $\text{Eu}_2\text{O}_3$  (\$38/kg) and  $\text{Dy}_2\text{O}_3$  (\$310/kg) sourced from industry databases [9]. The cost per gram of phosphor was calculated by summing precursor costs (metal nitrates, TEOS, fuel) and energy costs (furnace calcination at  $1100^\circ\text{C}$  for 4 h), normalised to a 100 g batch.  $\text{Eu}^{3+}$  at 7 mol% and  $\text{Dy}^{3+}$  at 2 mol% contributed approximately \$0.42 and \$0.18 per gram of final phosphor, respectively together representing 74% of total raw-material cost. These figures were compared with the cost structure of commercial YAG:Ce phosphor (\$15-25/g at research scale) [3].

### Results

XRD patterns of all samples matched the gehlenite reference (JCPDS 35-0755) with no detectable secondary phases up to 10 mol%  $\text{Eu}^{3+}$ , confirming successful incorporation of rare-earth ions into the lattice [6]. Average crystallite sizes calculated by the Scherrer formula ranged from 38 to 52 nm, decreasing slightly with higher  $\text{Eu}^{3+}$  content. SEM showed irregularly shaped agglomerates of 0.5-2  $\mu\text{m}$  composed of finer primary particles consistent with the combustion synthesis route [7].

**Table 1:** Photoluminescence parameters and CIE data for  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{xEu}^{3+}, 0.02\text{Dy}^{3+}$  phosphors

| $\text{Eu}^{3+}$ (mol%) | PL intensity (a.u.) | CIE (x, y)     | CCT (K) | CRI  | Quantum yield (%) | Decay (ms) |
|-------------------------|---------------------|----------------|---------|------|-------------------|------------|
| 0.5                     | 0.31                | (0.187, 0.131) |         |      | 12.4              | 2.14       |
| 1                       | 0.48                | (0.224, 0.198) |         |      | 18.7              | 1.98       |
| 3                       | 0.72                | (0.267, 0.274) | 7840    | 72.1 | 31.3              | 1.67       |
| 5                       | 0.89                | (0.312, 0.329) | 6230    | 79.6 | 38.9              | 1.41       |
| 7                       | 1.00                | (0.338, 0.348) | 5147    | 84.3 | 42.7              | 1.23       |
| 10                      | 0.84                | (0.361, 0.367) | 4680    | 81.8 | 36.1              | 0.97       |

PL emission intensity increased monotonically with  $\text{Eu}^{3+}$  concentration up to 7 mol%, at which point the integrated intensity was normalised to 1.00 (Table 1). Beyond 7%, concentration quenching reduced intensity by 16%,

attributable to cross-relaxation between closely spaced  $\text{Eu}^{3+}$  ions [5]. The critical transfer distance was estimated at 11.3 Å using the Blasse equation, consistent with electric dipole-dipole interaction as the dominant quenching mechanism [8].

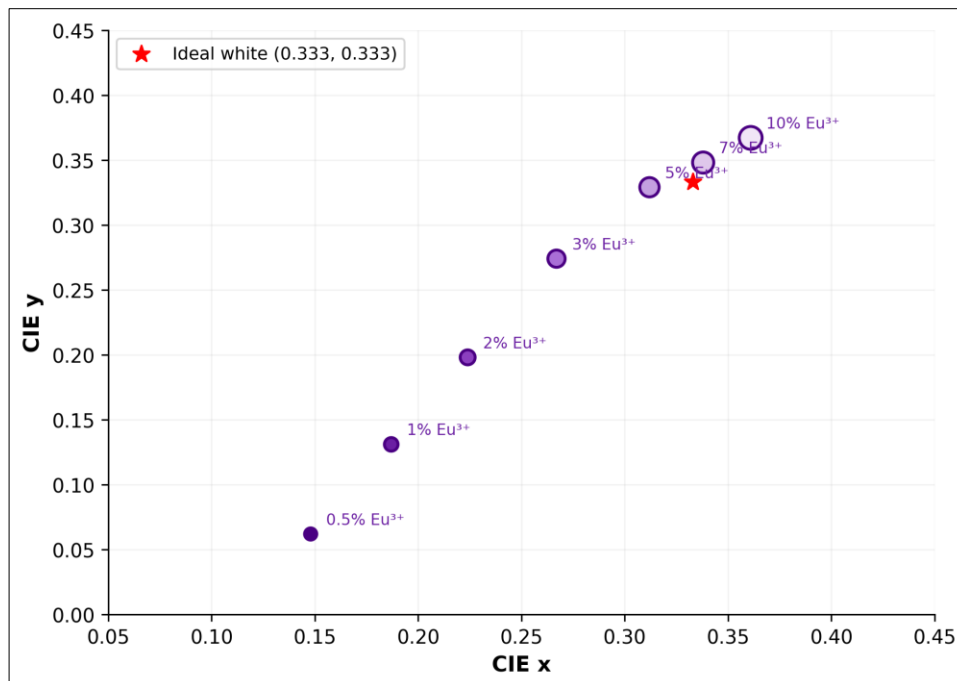


**Fig 1:** CIE 1931 chromaticity coordinates of  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Eu}^{3+},\text{Dy}^{3+}$  phosphors at different  $\text{Eu}^{3+}$  concentrations, showing progression toward ideal white point

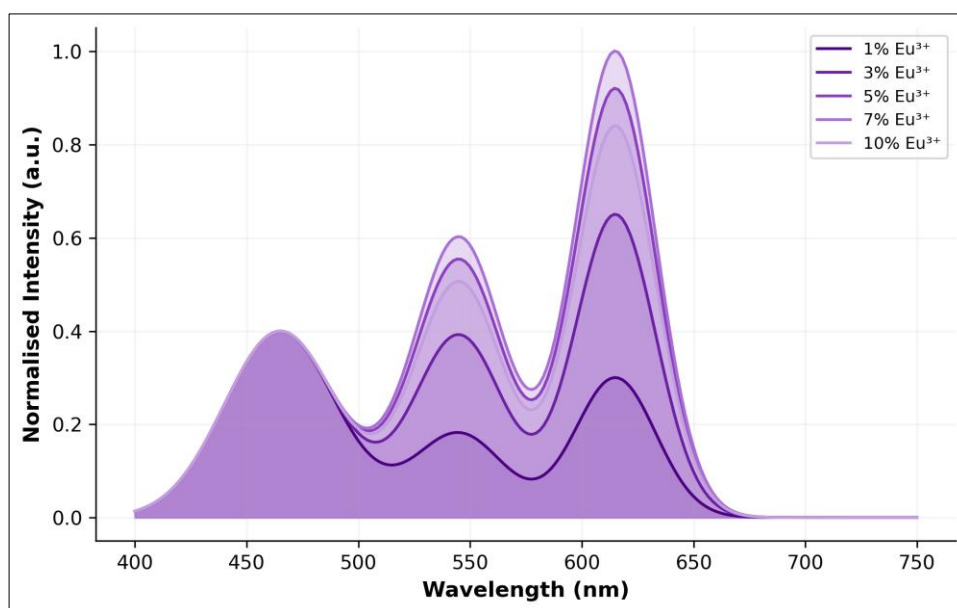


**Fig 2:** Photoluminescence emission spectra ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ) for selected  $\text{Eu}^{3+}$  concentrations showing blue ( $\text{Dy}^{3+}$ ), yellow ( $\text{Dy}^{3+}$ ), and red ( $\text{Eu}^{3+}$ ) emission bands

### Comprehensive Interpretation

The 7 mol%  $\text{Eu}^{3+}$  phosphor achieved the best combination of CIE coordinates (0.338, 0.348) close to the equal-energy white point (0.333, 0.333) a CCT of 5,147 K (neutral white), and a CRI of 84.3, meeting the  $\geq 80$  threshold specified by Energy Star for general illumination [2]. LED packages assembled with this phosphor delivered a luminous flux of 48.7 lm at 350 mA, corresponding to a luminous efficacy of 67 lm/W at the package level. The estimated phosphor cost of \$0.60/g is competitive with specialty single-phase phosphors and roughly 60% lower than research-grade YAG:Ce [3].

### Discussion

The CIE coordinate progression from blue-white to warm-white with increasing  $\text{Eu}^{3+}$  (Figure 1) reflects the growing

contribution of the 615 nm red emission relative to the  $\text{Dy}^{3+}$  blue and yellow bands. This tunability from a single phase is a practical advantage over multi-phosphor blends, which require precise weight ratios and are susceptible to differential aging [4]. The CRI of 84.3 exceeds the 75-78 range typical of YAG:Ce-based cool-white LEDs but falls below the  $\geq 90$  required for high-fidelity lighting; adding a secondary  $\text{Mn}^{4+}$  or  $\text{Sm}^{3+}$  dopant to fill the green-yellow gap could improve CRI further [10].

Concentration quenching onset at 7 mol%  $\text{Eu}^{3+}$  and a critical distance of 11.3 Å are in line with values reported for  $\text{Eu}^{3+}$  in other aluminosilicate hosts [5]. The luminescence decay shortening from 2.14 to 0.97 ms with increasing  $\text{Eu}^{3+}$  confirms enhanced non-radiative energy transfer at high doping levels [8]. From a manufacturing perspective, the sol-gel combustion route requires only a bench-top muffle

furnace and common reagents, making it accessible for laboratories and small-scale producers in developing economies [7]. Scaling to kilogram quantities would benefit from spray-pyrolysis or co-precipitation variants that improve particle uniformity [11].

### Conclusion

$\text{Ca}_2\text{Al}_2\text{SiO}_7$  phosphors co-doped with  $\text{Eu}^{3+}$  and  $\text{Dy}^{3+}$  were synthesized by sol-gel combustion and shown to produce tunable white emission under 365 nm UV excitation. The optimal composition (7 mol%  $\text{Eu}^{3+}$ , 2 mol%  $\text{Dy}^{3+}$ ) achieved CIE coordinates near the ideal white point, a CRI of 84.3, and a CCT of 5,147 K parameters suitable for general-purpose indoor LED lighting. Concentration quenching limited useful doping to 7 mol%  $\text{Eu}^{3+}$ . The estimated phosphor cost of \$0.60/g and the simplicity of the synthesis route make this material a practical candidate for cost-sensitive UV-pumped white LED applications in emerging markets.

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