

Article

Near-UV-Excitable $\text{Sm}^{3+}/\text{Eu}^{3+}$ -Activated $\text{Na}_3\text{YB}_8\text{O}_{15}$ Red Phosphors with High Thermal Stability for LED Applications

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Abstract

Near-ultraviolet-excitable red phosphors with high thermal stability are desirable for phosphor-converted LED applications, including potential plant-lighting applications. Herein, Sm^{3+} - and Eu^{3+} -activated $\text{Na}_3\text{YB}_8\text{O}_{15}$ phosphors were synthesized by a high-temperature solid-state reaction. Among the investigated compositions, the optimal activator contents were identified as $x = 0.02$ for $\text{Na}_3\text{YB}_8\text{O}_{15}:x\text{Sm}^{3+}$ and $y = 0.70$ for $\text{Na}_3\text{YB}_8\text{O}_{15}:y\text{Eu}^{3+}$, with concentration quenching in both series mainly governed by dipole–dipole interactions. In the $\text{Sm}^{3+}/\text{Eu}^{3+}$ co-doped phosphors, the emission color shifted from orange-red toward red as the Eu^{3+} content increased. At 433 K, the Sm^{3+} -doped, Eu^{3+} -doped, and $\text{Sm}^{3+}/\text{Eu}^{3+}$ co-doped samples retained 119.7%, 93.4%, and 102.3% of their room-temperature integrated emission intensities, respectively. The high thermal stability may be attributed to the structural characteristics of the host, its wide optical band gap, and the temperature-dependent redistribution of Stark and phonon-assisted emission components. A phosphor-converted LED fabricated using $\text{Na}_3\text{YB}_8\text{O}_{15}:0.02\text{Sm}^{3+}, 0.01\text{Eu}^{3+}$ and a commercial 400–405 nm, 5 W near-UV LED chip produced multiband emission that partially overlapped with the absorption bands of both chlorophylls and the P_R and P_{FR} forms of phytochrome. These results suggest that $\text{Sm}^{3+}/\text{Eu}^{3+}$ -activated $\text{Na}_3\text{YB}_8\text{O}_{15}$ is a promising thermally robust, spectrum-adjustable red phosphor for LED applications.

Keywords: thermal stability; $\text{Sm}^{3+}/\text{Eu}^{3+}$; red phosphors; $\text{Na}_3\text{YB}_8\text{O}_{15}$; LED applications

1. Introduction

Rare-earth-doped phosphors have been widely investigated for applications in display technology, plant cultivation lighting, optical temperature sensing, solid-state lighting, and anti-counterfeiting because of their rich electronic energy levels, sharp emission bands, and tunable luminescence properties [1–3]. In controlled-environment agriculture, artificial lighting is increasingly important, as the spectral quality of illumination directly influences plant morphology, photosynthetic efficiency, flowering, and biomass accumulation. Light-emitting diodes (LEDs) are particularly attractive for plant cultivation owing to their high energy efficiency, long operating lifetime, compact dimensions, and excellent spectral controllability [4]. Among the biologically relevant spectral regions, red light is strongly absorbed by chlorophylls and plays an important role in phytochrome-mediated photomorphogenic responses [5,6]. In this regard, phosphor-converted LEDs employing near-ultraviolet (near-UV) chips offer a practical strategy for producing spectrally tunable red emission while avoiding the complex multi-chip configurations associated with



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conventional red–blue or multicolor LED combinations. Sm^{3+} and Eu^{3+} are promising activator ions for this purpose: Sm^{3+} exhibits characteristic orange-red emission bands arising from the $^4\text{G}_{5/2}$ level and can be efficiently excited in the near-UV region around 400 nm, whereas Eu^{3+} produces intense red emission dominated by the hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition [7]. Furthermore, Sm^{3+} to Eu^{3+} energy transfer has been reported in several co-doped hosts and may provide a means of tuning the emission spectrum, making these systems attractive for near-UV-excited plant cultivation lighting and other phosphor-converted LED applications [8–10].

Despite their favorable spectroscopic properties, the practical use of rare-earth-activated phosphors in high-power phosphor-converted LEDs is frequently limited by thermal quenching, because both the LED junction and the phosphor layer can reach elevated temperatures during operation. In particular, many $\text{Sm}^{3+}/\text{Eu}^{3+}$ -activated phosphors exhibit insufficient thermal stability. For example, $\text{Bi}_2\text{O}_3:\text{Sm}^{3+}/\text{Eu}^{3+}$, $\text{Ba}_2\text{SiO}_4:\text{Sm}^{3+}/\text{Eu}^{3+}$, and $\text{BaY}_2\text{ZnO}_5:\text{Sm}^{3+}/\text{Eu}^{3+}$ retain approximately 44% of their initial emission intensity at 423 K, 49% at 423 K, and 55% at 473 K, respectively, relative to their room-temperature intensities [11–13]. Such thermally activated luminescence losses, generally associated with enhanced nonradiative relaxation, can reduce the emission intensity, induce spectral and color instability, and ultimately compromise device reliability. Consequently, phosphors with negligible thermal quenching or thermally stable emission are highly desirable for maintaining stable light output under demanding operating conditions. Borates are particularly promising host materials in this regard because their strong B–O covalent bonds, versatile BO_3/BO_4 structural units, and highly polymerized frameworks can enhance lattice rigidity and help suppress electron–phonon coupling and thermally activated nonradiative relaxation. Several borate phosphors with zero thermal quenching behavior have accordingly been reported, including $\text{LaSc}_3(\text{BO}_3)_4:\text{Eu}^{3+}$, $\text{K}_3\text{Y}(\text{BO}_2)_6:\text{Eu}^{3+}, \text{Na}^+$, $\text{GdAl}_3(\text{BO}_3)_4:\text{Cr}^{3+}$, $\text{NaBaB}_9\text{O}_{15}:\text{Tb}^{3+}$, and $\text{Sr}_3\text{La}(\text{AlO})_3(\text{BO}_3)_4:\text{Dy}^{3+}$ [14–18]. Among rare-earth borates, $\text{Na}_3\text{YB}_8\text{O}_{15}$ (NYB) possesses a distinctive crystal structure in which BO_3 triangles and BO_4 tetrahedra are interconnected to form infinite one-dimensional $[\text{B}_8\text{O}_{15}]^{6-}$ chains [19]. Its rigid polyborate framework, wide optical band gap, and distorted seven-coordinate Y^{3+} sites, which are suitable for substitution by trivalent rare-earth ions, make it a promising host for thermally robust red-emitting phosphors. Nevertheless, the luminescence characteristics, temperature-dependent emission properties, and potential applications of $\text{Sm}^{3+}/\text{Eu}^{3+}$ -doped NYB phosphors in plant cultivation lighting have not yet been systematically investigated.

In this work, a series of Sm^{3+} - and Eu^{3+} -activated NYB phosphors were synthesized through a high-temperature solid-state reaction. A relatively dilute Sm^{3+} concentration range ($x = 0.008\text{--}0.09$) was selected to cover both the initial increase in the number of luminescent centers and the subsequent concentration-quenching region, whereas a broader and higher Eu^{3+} range ($y = 0.3\text{--}1.0$) was investigated because Eu^{3+} emission remained favorable at substantially higher substitution levels. For the co-doped series, the Sm^{3+} fraction was fixed at its independently determined optimum of $x = 0.02$, and a lower Eu^{3+} range ($y = 0.007\text{--}0.04$) was employed to regulate the relative Sm^{3+} and Eu^{3+} emission contributions while retaining the characteristic emissions of both activators. The Sm^{3+} - and Eu^{3+} -activated phosphors showed strong excitation bands at approximately 403 and 394 nm, respectively, and exhibited tunable orange-red to red emission through regulation of the Sm^{3+} and Eu^{3+} contents. Remarkably, at 433 K, NYB:0.02Sm^{3+} , NYB:0.70Eu^{3+} , and $\text{NYB:0.02Sm}^{3+}, 0.01\text{Eu}^{3+}$ exhibited 119.7%, 93.4%, and 102.3%, respectively, of their integrated emission intensities measured at 293 K. Furthermore, a phosphor-converted LED fabricated by combining the selected phosphor with a commercial 400–405 nm, 5 W near-UV LED chip produced multiband emission overlapping the absorption regions of chlorophylls

and phytochrome-related photoreceptors. These results suggest that $\text{Sm}^{3+}/\text{Eu}^{3+}$ -activated NYB is a promising thermally robust red phosphor for spectrum-adjustable phosphor-converted LED applications.

2. Results and Discussion

2.1. Structure and Morphology

Powder X-ray diffraction measurements were performed to investigate the phase composition and structural integrity of the undoped, Sm^{3+} -doped, Eu^{3+} -doped, and $\text{Sm}^{3+}/\text{Eu}^{3+}$ co-doped NYB phosphors. NYB crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ (No. 2), with $Z = 2$. According to the reported single-crystal structural data (CCDC 2206328), the unit-cell parameters are $a = 6.4122(2) \text{ \AA}$, $b = 7.3634(3) \text{ \AA}$, $c = 13.1781(5) \text{ \AA}$, $\alpha = 89.126(2)^\circ$, $\beta = 78.657(2)^\circ$, $\gamma = 66.8170(10)^\circ$, and $V = 559.46(4) \text{ \AA}^3$ [19], as summarized in Table S1. As shown in Figure 1a, the experimental diffraction patterns of the undoped NYB, NYB:0.02 Sm^{3+} , NYB:0.70 Eu^{3+} , and NYB:0.02 Sm^{3+} ,0.01 Eu^{3+} samples are generally consistent with the simulated pattern calculated from the reported single-crystal structure of NYB. No additional diffraction peaks attributable to secondary crystalline phases are detected within the experimental resolution, indicating that the samples are predominantly composed of the NYB phase. The major diffraction peaks are retained after the incorporation of Sm^{3+} and/or Eu^{3+} , although slight deviations in the positions of some reflections can be observed. These small peak shifts may arise from local lattice distortion associated with the substitution of Y^{3+} by Sm^{3+} and Eu^{3+} , because the substituting ions do not have exactly the same ionic radii and local bonding environments as Y^{3+} . Differences in the relative intensities of the experimental and simulated reflections, as well as among the powder samples, may be related to preferred orientation, particle morphology, crystallite size, and differences in the local distribution of the activator ions. The preservation of the characteristic NYB reflections and the absence of impurity peaks suggest that the average host structure remains stable after Sm^{3+} and/or Eu^{3+} doping. Small apparent shifts in several reflections may be associated with local structural perturbations induced by $\text{Sm}^{3+}/\text{Eu}^{3+}$ substitution. However, no Rietveld refinement was performed for the doped samples in the present study. Therefore, changes in the unit-cell parameters cannot be quantitatively determined from the present powder XRD data.

The morphology of the representative NYB:0.02 Sm^{3+} ,0.01 Eu^{3+} phosphor was examined by scanning electron microscopy (SEM). Figure 1b presents the $20,000\times$ SEM image along with the corresponding EDS spectrum, while the $5000\times$ SEM image is shown in Figure S1. Most particles exhibit fractured, plate-like, or block-like morphologies, while smaller grains are attached to the surfaces of larger particles. At higher magnification, the particles show relatively dense surfaces with irregular edges, cleavage steps, and locally layered features. The particles have an average size of $8.98 \mu\text{m}$ and range from 4.63 to $14.14 \mu\text{m}$, as shown in Figure S2 in the Supporting Information. At higher magnification, the particles show relatively dense surfaces with irregular edges, cleavage steps, and locally layered features. The observed aggregation and irregular morphology are typical of phosphor powders prepared by conventional high-temperature solid-state reactions and can be attributed to grain growth, particle collision, surface diffusion, and partial sintering during prolonged calcination. The energy-dispersive X-ray spectroscopy (EDS) spectrum confirms the presence of the constituent Na, Y, B, and O elements, together with the doped Sm and Eu elements, in the selected analysis region. The corresponding semiquantitative EDS results are summarized in Table 1. The measured atomic percentages of Sm and Eu are approximately 0.18% and 0.08%, respectively, demonstrating that both activator ions are detectable in the selected sample. However, because quantitative EDS analysis is less reliable for light elements such as B and O and is influenced by matrix effects, surface

topography, and the selected analysis area, the EDS-derived elemental concentrations and atomic ratios should be regarded as semiquantitative. Combined with the XRD results, the EDS analysis supports the successful incorporation of Sm and Eu into the NYB phosphor.

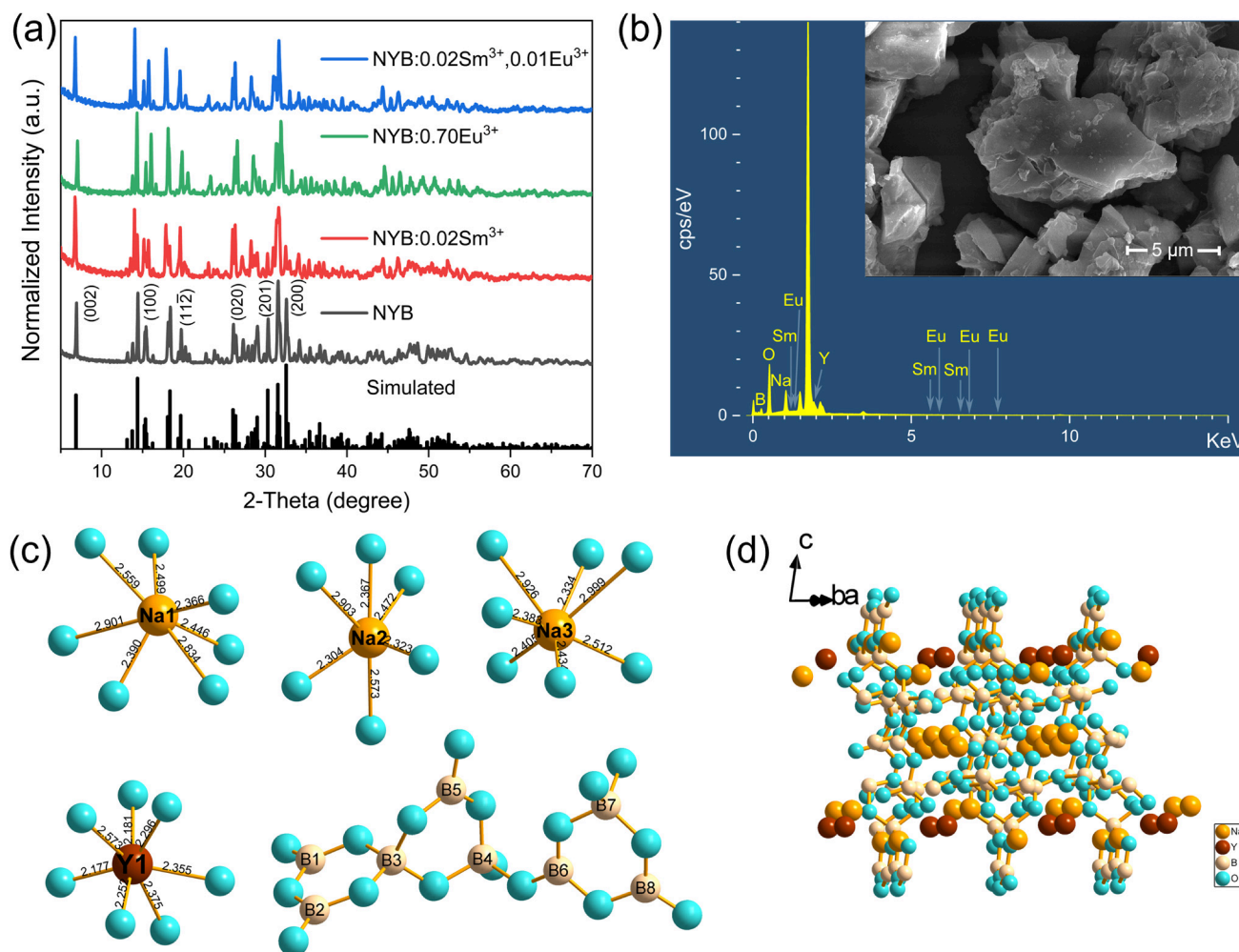


Figure 1. Structural and morphological characterization of NYB-based phosphors: (a) Experimental powder X-ray diffraction patterns of undoped NYB, NYB:0.02Sm³⁺, NYB:0.70Eu³⁺, and NYB:0.02Sm³⁺,0.01Eu³⁺, together with the simulated pattern calculated from the reported single-crystal structural data of NYB (CCDC 2206328) [19]. (b) SEM images and the corresponding EDS spectrum of NYB:0.02Sm³⁺,0.01Eu³⁺. The SEM image was recorded at 20,000× with a 5 μm scale bar. (c) Local oxygen-coordination environments of the crystallographically independent Na and Y sites and the borate fundamental building unit in the triclinic *P*1 NYB structure [19]. (d) Ball-and-stick representation of the NYB crystal structure [19].

Table 1. Semiquantitative EDS elemental composition of the NYB:0.02Sm³⁺,0.01Eu³⁺ phosphor measured in the selected region shown in Figure 1b.

Element	Apparent Concentration	k Ratio	Weight%	Atomic%
B	3.07	0.01233	13.15	24.2
O	21.16	0.06921	42.60	53.73
Na	6.75	0.02851	15.15	14.88
Y	8.2	0.08204	27.29	6.93
Sm	0.33	0.00335	1.18	0.18
Eu	0.18	0.00179	0.63	0.08

The local coordination environments of the cations and the borate building unit shown in Figure 1c were constructed using the previously reported single-crystal crystallographic data of NYB (CCDC 2206328) [19]. Although the NYB crystal is centrosymmetric as a whole, the crystallographically independent Y1 site occupies a general position with local site symmetry C1. The three crystallographically independent Na atoms exhibit different oxygen-coordination geometries. Using the Na–O contacts presented in the structural model, Na1, Na2, and Na3 are coordinated by seven, six, and seven oxygen atoms, respectively, forming distorted NaO₇, Na₂O₆, and Na₃O₇ polyhedra. The Y1 atom is coordinated by seven oxygen atoms to form a strongly distorted YO₇ polyhedron [19]. Because the Y site has no local inversion symmetry, substitution of Sm³⁺ and Eu³⁺ at this site would place the activator ions in distorted seven-coordinate oxygen environments. The borate framework is constructed from eight crystallographically independent B sites. Among them, B1, B2, B5, B6, and B8 are three-coordinate and form five approximately planar BO₃ triangles, whereas B3, B4, and B7 are four-coordinate and form three BO₄ tetrahedra. The longer average B–O distances in the BO₄ tetrahedra are consistent with the increased coordination number of boron. The five BO₃ triangles and three BO₄ tetrahedra are connected by shared oxygen atoms to form a complex [B₈O₁₇]^{10−} fundamental building unit. Neighboring [B₈O₁₇]^{10−} units are further polymerized through corner-sharing oxygen atoms, producing the characteristic one-dimensional infinite [B₈O₁₅]^{6−} chains [19].

As displayed in Figure 1d, the [B₈O₁₅]^{6−} chains are arranged in an approximately parallel manner and are spatially interconnected through the NaO₆/NaO₇ and YO₇ coordination polyhedra, giving rise to the overall three-dimensional crystal framework. The Na⁺ and Y³⁺ ions occupy the spaces between the polyborate chains and contribute to charge balance and structural stabilization [19]. Upon doping, Sm³⁺ and Eu³⁺ are expected to occupy the Y³⁺ sites and therefore become embedded between the rigid borate chains.

2.2. Optical Properties

Figure 2a compares the UV–visible diffuse reflectance spectra of the undoped NYB host and the NYB:0.02Sm³⁺,0.01Eu³⁺ phosphor. The undoped host exhibits a pronounced absorption edge in the ultraviolet region, consistent with the wide-band-gap character of NYB. The optical band gap was estimated using the Kubelka–Munk function [20]:

$$F(R) = \frac{(1 - R)^2}{2R} \quad (1)$$

where R is the measured diffuse reflectance. According to the Tauc relationship,

$$[F(R)h\nu]^n = A(h\nu - E_g) \quad (2)$$

where $h\nu$ is the photon energy, A is a constant, and E_g is the optical band gap. NYB has been reported to behave as a direct-band-gap material [19]; therefore, $n = 2$, and $[F(R)h\nu]^2$ was plotted against $h\nu$. As shown in the inset of Figure 2a, extrapolation of the linear portion of the Tauc plot to $[F(R)h\nu]^2 = 0$ gives an experimental optical band gap of approximately 4.23 eV. The wide band gap helps maintain the localized nature of the Sm³⁺ and Eu³⁺ 4f excited states and may reduce the probability of thermally activated carrier ionization into the host bands, thereby providing a favorable electronic-structure basis for the excellent thermal stability discussed below.

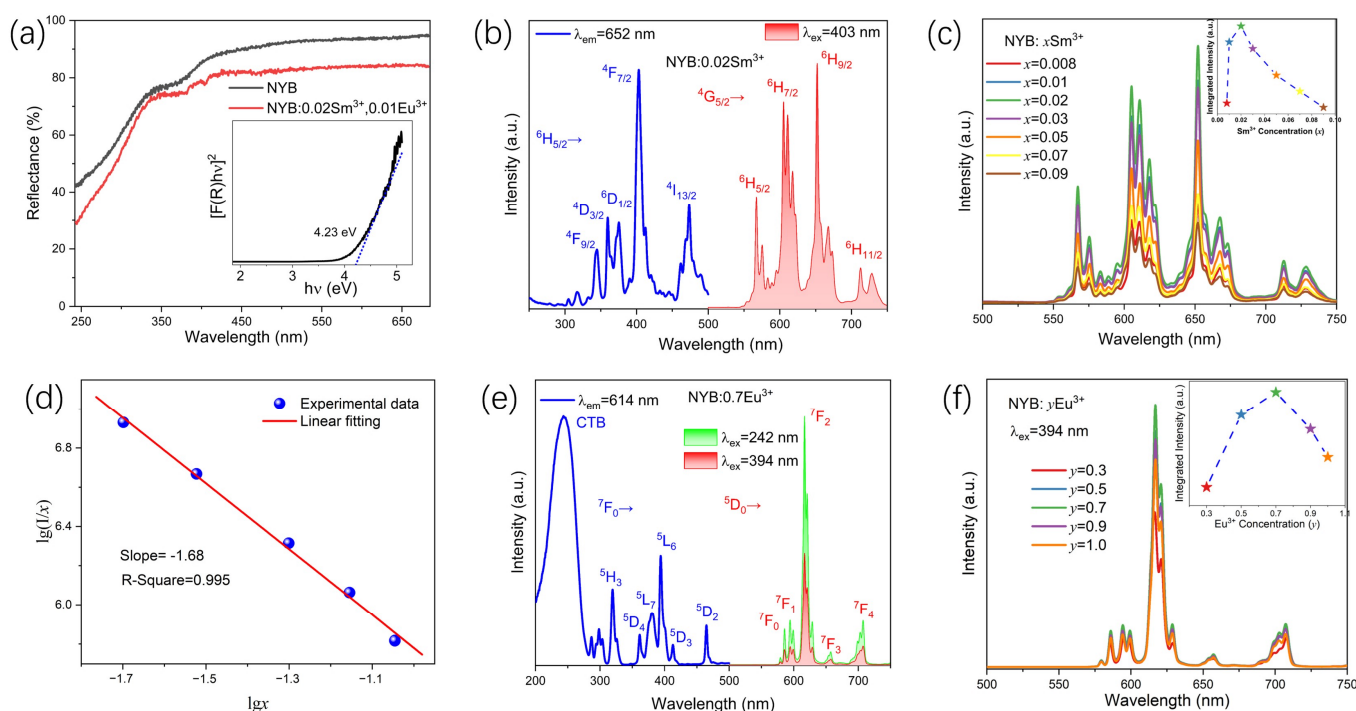


Figure 2. Optical properties of Sm^{3+} - and Eu^{3+} -activated NYB phosphors: (a) UV–visible diffuse reflectance spectra of the undoped NYB host and NYB:0.02 Sm^{3+} ,0.01 Eu^{3+} ; the inset shows the Tauc plot used to estimate the optical band gap of the NYB host. (b) PLE spectrum monitored at 652 nm and PL spectrum excited at 403 nm of NYB:0.02 Sm^{3+} . (c) PL spectra of NYB: $x\text{Sm}^{3+}$ ($x = 0.008$ – 0.09) under 403 nm excitation; the inset shows the dependence of the integrated emission intensity on the Sm^{3+} concentration. (d) Plot of $\lg(I/x)$ versus $\lg(x)$ for NYB: $x\text{Sm}^{3+}$ in the concentration-quenching region. (e) PLE spectrum of NYB:0.70 Eu^{3+} monitored at 614 nm and its PL spectra. (f) PL spectra of NYB: $y\text{Eu}^{3+}$ ($y = 0.3$ – 1.0) under 394 nm excitation; the inset shows the dependence of the integrated emission intensity on the Eu^{3+} concentration.

Figure 2b presents the photoluminescence excitation (PLE) and photoluminescence (PL) spectra of the NYB:0.02 Sm^{3+} phosphor. When the characteristic Sm^{3+} emission at 652 nm was monitored, the PLE spectrum exhibited several narrow excitation bands in the 300–500 nm region, originating from the intra-4f transitions of Sm^{3+} from the ground state $^6\text{H}_{5/2}$ to different excited states. The excitation bands centered at approximately 343, 359, 376, 403, and 473 nm can be assigned to the $^6\text{H}_{5/2} \rightarrow ^4\text{F}_{9/2}$, $^6\text{H}_{5/2} \rightarrow ^4\text{D}_{3/2}$, $^6\text{H}_{5/2} \rightarrow ^6\text{D}_{1/2}$, $^6\text{H}_{5/2} \rightarrow ^4\text{F}_{7/2}$, and $^6\text{H}_{5/2} \rightarrow ^4\text{I}_{13/2}$ transitions, respectively [21,22]. Among them, the excitation band at approximately 403 nm is the most intense, demonstrating that the NYB: Sm^{3+} phosphor can be effectively excited in the near-ultraviolet region and is spectrally compatible with commercially available near-UV LED chips [20]. Under 403 nm excitation, the NYB:0.02 Sm^{3+} phosphor exhibits four principal emission bands centered at approximately 567, 604, 652, and 712 nm. These bands are attributed to the $^4\text{G}_{5/2} \rightarrow ^6\text{H}_J$ transitions of Sm^{3+} , where $J = 5/2, 7/2, 9/2$, and $11/2$, respectively [21,22]. The dominant emission at approximately 652 nm arises from the $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ electric-dipole transition, resulting in the characteristic red emission of Sm^{3+} . The efficient near-UV excitation and multiple red-region emission bands indicate that NYB: Sm^{3+} is a promising red-emitting component for phosphor-converted LED applications.

The concentration-dependent PL spectra of NYB: $x\text{Sm}^{3+}$ ($x = 0.008$ – 0.09) under 403 nm excitation are displayed in Figure 2c. All samples exhibit essentially identical spectral profiles and peak positions, suggesting that the average crystal-field environment of Sm^{3+} does not change markedly over this composition range. As the Sm^{3+} concentration increases, the emission intensity initially increases, reaches a maximum at $x = 0.02$, and subsequently

decreases at higher concentrations. This variation is more clearly shown by the integrated emission intensity plotted in the inset of Figure 2c. At relatively low concentrations, the increased number of Sm^{3+} luminescent centers enhances the overall emission. When the concentration exceeds the critical value of $x_c = 0.02$, the average Sm^{3+} – Sm^{3+} separation decreases, facilitating nonradiative energy migration among neighboring activator ions and ultimately leading to concentration quenching. The critical distance R_c between Sm^{3+} ions can be estimated using Blasse's equation [22]:

$$R_c = 2 \left(\frac{3V}{4\pi x_c N} \right)^{1/3} \quad (3)$$

where V is the unit-cell volume, N is the number of crystallographically available Y^{3+} sites per unit cell, and x_c is the critical Sm^{3+} concentration. The critical distance R_c is calculated to be approximately 29.89 Å. Since this value is substantially larger than 5 Å, direct exchange interaction is unlikely to dominate the concentration-quenching process. Instead, the quenching is primarily attributed to long-range electric multipolar interactions between Sm^{3+} ions.

To identify the specific type of multipolar interaction, the concentration-dependent emission intensity can be analyzed using the Dexter–Van relationship [21]:

$$\frac{I}{x} = k(1 + \beta(x)^{\frac{\theta}{3}})^{-1} \quad (4)$$

where I is the integrated emission intensity, x is the Sm^{3+} concentration, and K and β are constants for a given host under fixed excitation conditions. The parameter θ describes the nature of the multipolar interaction, with $\theta = 6, 8$, and 10 corresponding to dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively. In the concentration-quenching region, Equation (4) can be approximated as follows:

$$\lg\left(\frac{I}{x}\right) = C - \frac{\theta}{3} \lg x \quad (5)$$

As shown in Figure 2d, linear fitting of the $\lg(I/x)$ versus $\lg x$ data yields a slope of -1.68 . Accordingly, the value of θ is calculated to be approximately 5.04, which is closest to the theoretical value of 6, suggesting that dipole–dipole interactions may make the principal contribution to Sm^{3+} concentration quenching.

Figure 2e shows the PLE and PL spectra of the NYB:0.70 Eu^{3+} phosphor. When the dominant Eu^{3+} emission at 614 nm was monitored, the excitation spectrum exhibited a broad band in the 200–280 nm region together with several sharp excitation peaks between approximately 280 and 480 nm. The broad band centered at approximately 242 nm is assigned to the $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$ charge-transfer band, whereas the narrow peaks originate from the characteristic intra-4f transitions of Eu^{3+} . The excitation peaks at approximately 319, 362, 379, 394, 413, and 465 nm are assigned to the ${}^7\text{F}_0 \rightarrow {}^5\text{H}_3$, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_4$, ${}^7\text{F}_0 \rightarrow {}^5\text{L}_7$, ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_3$, and ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ transitions, respectively [23–25]. The intense excitation peak at approximately 394 nm indicates that Eu^{3+} emission in the NYB host can be effectively activated by near-UV excitation. Under excitation at either 242 or 394 nm, the phosphor exhibits characteristic Eu^{3+} emissions centered at approximately 584, 594, 614, 657, and 705 nm. These peaks are assigned to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ transitions with $J = 0, 1, 2, 3$, and 4, respectively [23–25]. The emission spectrum is dominated by the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ electric-dipole transition at approximately 614 nm, whereas the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ magnetic-dipole transition at approximately 594 nm is considerably weaker. The predominance of the electric-dipole transition points to Eu^{3+} ions residing in low-symmetry local environments without inversion symmetry, which is consistent with the crystal structure: although NYB crystallizes

in the centrosymmetric space group $P\bar{1}$, the Y1 site lies at a general position with site symmetry C1 and therefore affords the substituted Eu^{3+} ions a distorted seven-coordinate oxygen environment [19].

The PL spectra of NYB: $y\text{Eu}^{3+}$ ($y = 0.3\text{--}1.0$) recorded under 394 nm excitation are presented in Figure 2f. The characteristic emission peak positions remain nearly unchanged with increasing Eu^{3+} concentration, suggesting that the dominant Eu^{3+} -emitting environment remains similar. In contrast, the emission intensity is strongly concentration-dependent. It initially increases with increasing Eu^{3+} content, reaches its maximum at $y = 0.70$, and then decreases when the Eu^{3+} concentration is further increased. The same tendency is observed in the integrated emission intensities shown in the inset of Figure 2f. The decrease in emission intensity above $y = 0.70$ is attributed to concentration quenching caused by enhanced energy migration among Eu^{3+} ions, followed by nonradiative deactivation at quenching centers. The calculated $\text{Eu}^{3+}\text{--Eu}^{3+}$ critical distance is approximately 9.14 Å, which is larger than 5 Å, suggesting that short-range exchange interaction is unlikely to be the dominant concentration-quenching mechanism. Therefore, the concentration quenching is mainly attributed to long-range electric multipolar interactions. Furthermore, linear fitting of the $\lg(I/y)$ versus $\lg y$ relationship in the concentration-quenching region gives a slope of approximately -1.66 , as shown in Figure S3 in the supporting information. The fitted value of $\theta \approx 4.98$ is nominally closest to 6 and is therefore consistent with a possible dipole–dipole contribution.

The local site symmetry of Sm^{3+} and Eu^{3+} was further assessed via the asymmetry ratio R . For Sm^{3+} , R is the integrated intensity ratio of the electric-dipole $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ transition to the magnetic-dipole $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ transition; Figure S4a shows its variation with Sm^{3+} concentration, yielding an average of 2.10. For Eu^{3+} , R is defined as the integrated intensity ratio of the hypersensitive electric-dipole $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition to the magnetic-dipole $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition; Figure S4b shows the corresponding concentration dependence, giving an average of approximately 5.98. Both ratios greater than 1 are consistent with locally asymmetric and distorted activator environments.

As shown in Figure 3a, the normalized PLE spectra of NYB:0.02 Sm^{3+} , $y\text{Eu}^{3+}$ ($y = 0.007\text{--}0.04$), recorded by monitoring the characteristic Eu^{3+} emission at 614 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$), contain excitation bands attributable to both Eu^{3+} and Sm^{3+} . In addition to the intense $\text{Eu}^{3+} ^7\text{F}_0 \rightarrow ^5\text{L}_6$ transition at approximately 394 nm, a distinct excitation band appears at approximately 403 nm and is assigned to the $\text{Sm}^{3+} ^6\text{H}_{5/2} \rightarrow ^4\text{F}_{7/2}$ transition. The PL spectra obtained under selective excitation further clarify the luminescence behavior of the $\text{Sm}^{3+}/\text{Eu}^{3+}$ system. Under 403 nm excitation, Sm^{3+} is efficiently excited, and Figure 3b displays emissions from both Sm^{3+} and Eu^{3+} . The Sm^{3+} emissions arise from the $^4\text{G}_{5/2} \rightarrow ^6\text{H}_j$ transitions, including the bands near 567, 604, 652, and 712 nm, whereas the Eu^{3+} emissions originate from the $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions, particularly the intense $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission at 614 nm. With increasing Eu^{3+} concentration, the contribution of Eu^{3+} emission becomes progressively more prominent, while the Sm^{3+} emission near 567, 604, and 652 nm is generally weakened, suggesting possible excitation-energy transfer from Sm^{3+} to Eu^{3+} . Under direct Eu^{3+} excitation at 394 nm (Figure 3c), the spectra are dominated by the Eu^{3+} emissions near 594, 614, 657, and 705 nm. It should be emphasized that several Sm^{3+} and Eu^{3+} emission bands overlap substantially: the Sm^{3+} emission near 604 nm overlaps with the Eu^{3+} bands at 594 and 614 nm, while the Sm^{3+} band near 652 nm overlaps with the $\text{Eu}^{3+} ^5\text{D}_0 \rightarrow ^7\text{F}_3$ emission near 657 nm; their long-wavelength emissions around 705–712 nm also partially coincide.

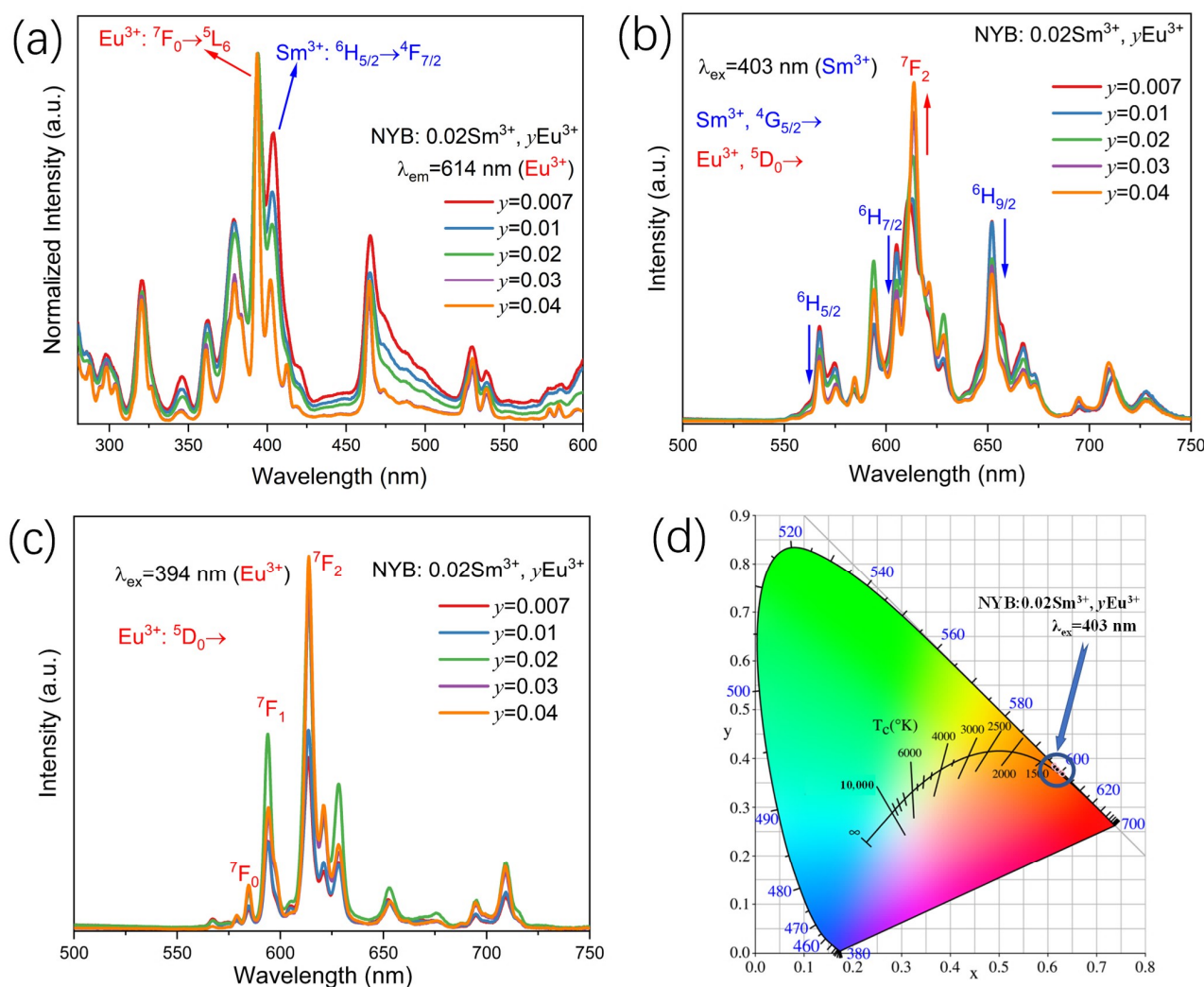


Figure 3. PLE, PL, and color-tuning properties of Sm³⁺/Eu³⁺ co-doped NYB phosphors: (a) Normalized PLE spectra of NYB:0.02Sm³⁺, yEu³⁺ (y = 0.007, 0.01, 0.02, 0.03, and 0.04), monitored at the Eu³⁺ ⁵D₀ → ⁷F₂ emission at 614 nm. (b) PL spectra of NYB:0.02Sm³⁺, yEu³⁺ under 403 nm excitation, corresponding to the Sm³⁺ ⁶H_{5/2} → ⁴F_{7/2} transition. (c) PL emission spectra of NYB:0.02Sm³⁺, yEu³⁺ under 394 nm excitation, corresponding to the Eu³⁺ ⁷F₀ → ⁵L₆ transition. (d) CIE chromaticity diagram of NYB:0.02Sm³⁺, yEu³⁺ under 403 nm excitation.

The redistribution of the Sm³⁺ and Eu³⁺ emission components is accompanied by a systematic variation in the output color, as illustrated by the CIE chromaticity coordinates in Figure 3d. The corresponding chromaticity coordinates are summarized in Table S2 of the Supporting Information. Under 403 nm excitation, the Eu³⁺-free NYB:0.02Sm³⁺ sample exhibits coordinates of (0.6137, 0.3849), corresponding to orange-red emission. With increasing Eu³⁺ concentration, the chromaticity coordinates generally shift toward larger x and smaller y values, changing to (0.6301, 0.3685) at y = 0.04. This movement toward the red edge of the CIE diagram reflects the increasing contribution of the intense Eu³⁺ ⁵D₀ → ⁷F₂ emission and demonstrates that the emission color can be tuned from orange-red to red by adjusting the Eu³⁺ content. Together with its effective excitation in the near-ultraviolet region and its red-emission components relevant to plant photoreceptors, this tunability makes Sm³⁺/Eu³⁺ co-doped NYB a potential red-emitting phosphor for spectrum-adjustable phosphor-converted LED applications, including possible future use in plant-lighting systems.

2.3. Thermal Stability

For clarity, three representative phosphors were selected for the temperature-dependent study: NYB:0.02Sm³⁺ as the optimized Sm³⁺-activated sample, NYB:0.70Eu³⁺ as the optimized Eu³⁺-activated sample, and NYB:0.02Sm³⁺, 0.01Eu³⁺ as the selected Sm³⁺/Eu³⁺ co-doped sample used for LED fabrication. As shown in Figure 4a, under excitation at 403 nm, NYB:0.02Sm³⁺ retains the characteristic Sm³⁺ emission profile over the temperature range of 293–433 K, and the principal emission maxima remain close to their original transition positions. Notably, the spectral components on both sides of the principal emission peaks become progressively stronger and broader with increasing temperature. For example, the intensities near approximately 644 and 661 nm, located on the two sides of the dominant 652 nm emission, increase noticeably. Similar temperature-induced enhancement and broadening are also observed at the shoulders of the other Sm³⁺ emission bands. The corresponding integrated PL intensities over 500–780 nm are summarized in Figure 4b. Rather than undergoing conventional thermal quenching, the integrated emission intensity of NYB:0.02Sm³⁺ increases gradually with temperature. At 433 K, the integrated intensity reaches 119.7% of its value at 293 K, demonstrating pronounced zero thermal quenching behavior over 293–433 K.

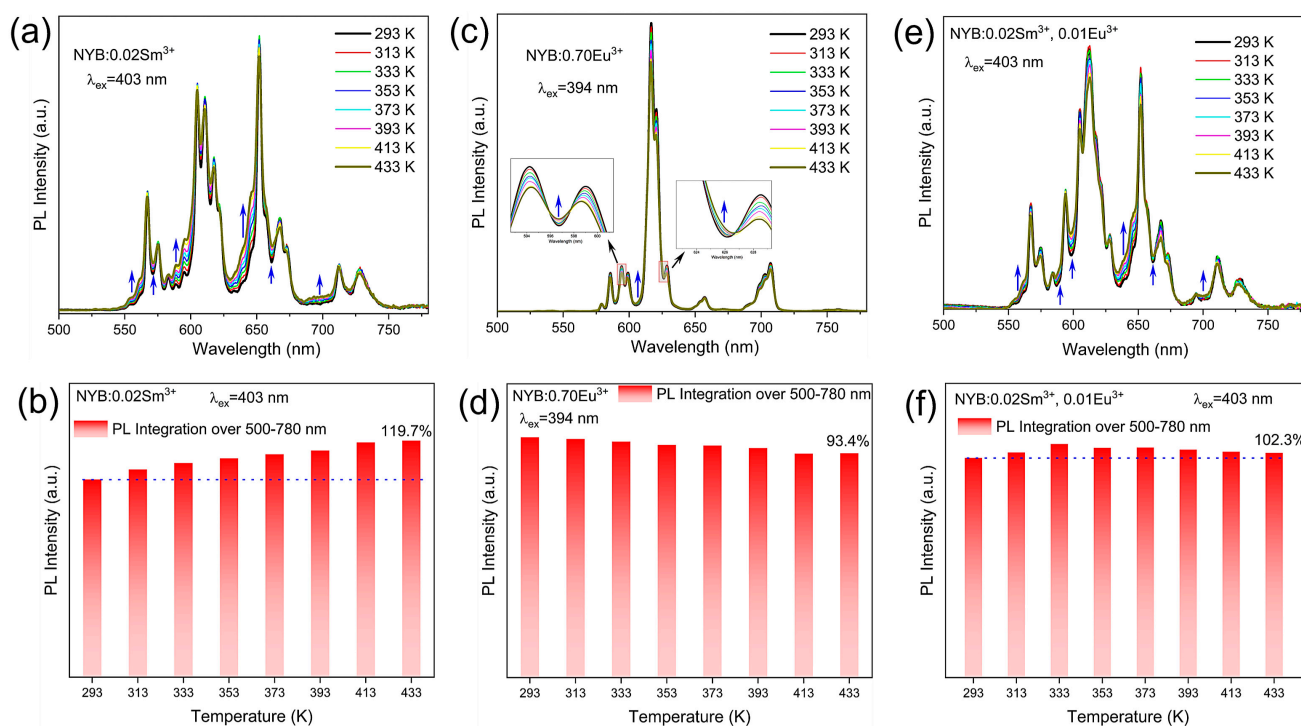


Figure 4. Temperature-dependent luminescence properties of NYB:0.02Sm³⁺, NYB:0.70Eu³⁺, and NYB:0.02Sm³⁺, 0.01Eu³⁺ phosphors over 293–433 K: (a) PL emission spectra and (b) temperature-dependent integrated PL intensity of NYB:0.02Sm³⁺ under 403 nm excitation. (c) PL emission spectra and (d) temperature-dependent integrated PL intensity of NYB:0.70Eu³⁺ under 394 nm excitation. (e) PL emission spectra and (f) temperature-dependent integrated PL intensity of NYB:0.02Sm³⁺, 0.01Eu³⁺ under 403 nm excitation.

A related but weaker temperature-dependent spectral variation is observed for NYB:0.70Eu³⁺ under 394 nm excitation, as shown in Figure 4c. The positions of the characteristic Eu³⁺ emissions remain essentially unchanged from 293 to 433 K, confirming the stability of the Eu³⁺-emitting environment. The enlarged regions around the ⁵D₀ → ⁷F₁ and ⁵D₀ → ⁷F₂ emission bands reveal a modest redistribution of intensity and slight broadening on the sides of the emission components as the temperature increases. In contrast to the

Sm³⁺-doped sample, however, the dominant Eu³⁺ emission peaks exhibit a moderate reduction in intensity. As shown in Figure 4d, the integrated PL intensity decreases only slightly over the investigated temperature interval and retains 93.4% of its room-temperature value at 433 K. Thus, although weak thermal quenching occurs in the Eu³⁺-only sample, its emission remains highly stable at elevated temperatures.

Figure 4e shows the temperature-dependent PL spectra of the Sm³⁺/Eu³⁺ co-doped NYB:0.02Sm³⁺,0.01Eu³⁺ phosphor under 403 nm excitation. The spectra contain the characteristic emissions of both Sm³⁺ and Eu³⁺, and no appreciable displacement of the principal emission maxima is detected upon heating. Similar to the Sm³⁺-only sample, the low-intensity components and shoulders on both sides of several emission bands become enhanced and broadened with increasing temperature. At the same time, the relative changes in the overlapping Sm³⁺ and Eu³⁺ emission components indicate a temperature-dependent redistribution of excitation energy within the co-doped system. As shown in Figure 4f, the integrated PL intensity initially increases slightly and remains at 102.3% of its room temperature value at 433 K. The co-doped phosphor therefore exhibits apparent zero thermal quenching over 293–433 K. For comparison, under the same 403 nm excitation, NYB:0.02Sm³⁺,0.02Eu³⁺ and NYB:0.02Sm³⁺,0.04Eu³⁺ retain 100.0% and 104.6%, respectively, of their room-temperature integrated PL intensities at 433 K (Figure S5).

The high thermal stability of the Sm³⁺/Eu³⁺-doped NYB phosphor may be associated with the structural characteristics of the host, its wide optical band gap, and the temperature-dependent redistribution of Stark and phonon-assisted emission components. First, NYB features a three-dimensional framework composed of infinite [B₈O₁₅]^{6−} chains interconnected by Na–O and Y–O coordination polyhedra. The strong covalent B–O bonds and the corner-sharing polyborate network provide a relatively rigid local environment for Sm³⁺ and Eu³⁺ ions occupying the distorted Y³⁺ sites. Such structural rigidity can restrict thermally induced changes in the activator coordination environment, reduce the amplitudes of relevant lattice vibrations, and thereby suppress electron–phonon-mediated nonradiative relaxation. Similar relationships between rigid borate frameworks and high luminescence thermal stability have been reported for LaSc₃(BO₃)₄:Eu³⁺, K₃Y(BO₂)₆:Eu³⁺, Na⁺, GdAl₃(BO₃)₄:Cr³⁺, NaBaB₉O₁₅:Tb³⁺, Sr₃La(AlO)₃(BO₃)₄:Dy³⁺, and Li₄Ca₂B₈O₁₆:Eu³⁺ phosphors [14–18,26]. Second, the optical band gap of NYB is approximately 4.23 eV, confirming its wide-band-gap character. A wide band gap may keep the excited 4f states of Sm³⁺ and Eu³⁺ well separated from the conduction band, thereby suppressing thermal ionization and subsequent nonradiative trapping. This interpretation is consistent with observations in other highly thermally stable borates. For example, the wide-band-gap phosphors GdGa₃(BO₃)₄:Cr³⁺, K₇SrY₂B₁₅O₃₀:Eu³⁺, and Li₄Ca₂B₈O₁₆:Eu³⁺ retain approximately 94%, 97.3%, and 90.9% of their room-temperature emission intensities at 423, 413, and 423 K, respectively [26–28]. Third, the temperature-dependent changes in the spectral profiles suggest that thermal redistribution among Stark components and enhancement of phonon-assisted transitions also contribute to the apparent high thermal stability behavior. In the crystal field of NYB, the Sm³⁺ ⁴G_{5/2}-emitting multiplet and the ⁶H_J terminal multiplets are split into several Stark sublevels. As the temperature increases, the higher Stark sublevels of the ⁴G_{5/2} multiplet can become thermally populated according to the Boltzmann distribution, opening additional radiative channels to the Stark components of the ⁶H_J multiplets. Meanwhile, stronger electron–phonon coupling at elevated temperatures causes thermal broadening and increases the contribution of phonon-assisted sidebands. These processes can account for the progressive enhancement of the weak components and shoulders on both sides of the principal Sm³⁺ emission bands, including the features near 644 and 661 nm adjacent to the dominant 652 nm emission. For Eu³⁺, the nondegenerate ⁵D₀-emitting state does not undergo Stark splitting, whereas the ⁷F_J terminal multiplets are Stark-split in the

low-symmetry NYB crystal field; enhanced electron–phonon coupling at elevated temperatures therefore causes modest spectral broadening and intensity redistribution around the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ bands.

To place the thermal performance of the $\text{Sm}^{3+}/\text{Eu}^{3+}$ -doped NYB phosphor, Table 2 compares their normalized emission-intensity retention with that of representative thermally stable phosphors reported in the literature. The co-doped composition NYB:0.02 Sm^{3+} , 0.01 Eu^{3+} performs on par with several zero thermal quenching borates [14–17]. Notably, the 119.7% intensity retention of NYB:0.02 Sm^{3+} signifies pronounced zero thermal quenching behavior, surpassing the values reported for many other thermally robust phosphors measured at comparable temperatures [25–29]. It also compares favorably with representative non-borate Sm^{3+} -activated phosphors, which retain only 56.9–88.2% of their initial intensities at 423–498 K [21,30,31]. Taken together, these comparisons suggest that the $\text{Sm}^{3+}/\text{Eu}^{3+}$ -doped NYB phosphor possesses favorable luminescence thermal stability and has promising potential for application in LED devices, particularly considering the elevated temperatures generated during LED operation.

Table 2. Thermal stability of some reported luminescent phosphors.

Host Lattice	Dopant(s)	Thermal Behavior	Temperature (K)	Ref.
$\text{Na}_3\text{YB}_8\text{O}_{15}$	$\text{Sm}^{3+}, \text{Eu}^{3+}$	102.3%	433 K	This work
$\text{Na}_3\text{YB}_8\text{O}_{15}$	Sm^{3+}	119.7%	433 K	This work
$\text{Na}_3\text{YB}_8\text{O}_{15}$	Eu^{3+}	93.4%	433 K	This work
$\text{LaSc}_3(\text{BO}_3)_4$	Eu^{3+}	102.3%	548 K	[14]
$\text{K}_3\text{Y}(\text{BO}_2)_6$	Eu^{3+}	107%	550 K	[15]
$\text{GdAl}_3(\text{BO}_3)_4$	Cr^{3+}	100.2%	423 K	[16]
$\text{NaBaB}_9\text{O}_{15}$	Tb^{3+}	100%	523 K	[17]
$\text{Sr}_3\text{La}(\text{AlO})_3(\text{BO}_3)_4$	Dy^{3+}	138%	573 K	[18]
$\text{LuY}_3(\text{BO}_3)_4$	Eu^{3+}	93%	423 K	[25]
$\text{Li}_4\text{Ca}_2\text{B}_8\text{O}_{16}$	Eu^{3+}	90.9%	423 K	[26]
$\text{K}_7\text{SrY}_2\text{B}_{15}\text{O}_{30}$	Eu^{3+}	97.3%	413 K	[27]
$\text{GdGa}_3(\text{BO}_3)_4$	Cr^{3+}	94%	423 K	[28]
$\text{Y}_2(\text{MoO}_4)_3$	Eu^{3+}	57.9%	423 K	[29]
BaZnB_4O_8	$\text{Tb}^{3+}, \text{Eu}^{3+}$	90.2%	423 K	[32]
$\text{Ca}_2\text{ScSbO}_6$	Sm^{3+}	77.5%	498 K	[31]
$\text{Sr}_3\text{CaNb}_2\text{O}_9$	Sm^{3+}	56.9%	473 K	[30]
$\text{Ca}_2\text{GaTaO}_6$	Sm^{3+}	88.2%	423 K	[21]

2.4. LED Device Performance

Figure 5 presents the optical and thermal characteristics of the phosphor-converted LED fabricated by combining the NYB:0.02 Sm^{3+} , 0.01 Eu^{3+} phosphor with a commercial 400–405 nm, 5 W near-UV LED chip. When a forward current was applied, carrier recombination in the semiconductor chip generated near-UV electroluminescence. Part of this radiation was absorbed by the $\text{Sm}^{3+}/\text{Eu}^{3+}$ -activated phosphor and converted into orange-red and red photoluminescence. Figure 5a compares the EL spectrum of the device with the absorption spectra of chlorophyll A, chlorophyll B, and the red- and far-red-absorbing forms of phytochrome, denoted as P_R and P_{FR} , respectively. To enable a direct comparison of their spectral distributions, all spectra were normalized by their respective integrated spectral areas. Chlorophyll A is the principal photosynthetic pigment involved in light harvesting and photochemical energy conversion, whereas chlorophyll B serves as an accessory pigment that broadens the usable absorption range and transfers the absorbed excitation energy to chlorophyll A. Phytochromes perceive red and far-red light through the photo interconversion between the P_R and P_{FR} states and thereby regulate various light-dependent processes associated with plant growth and development. The device spectrum contains the residual emission of the near-UV chip together with the character-

istic orange-red and red emissions originating from Sm^{3+} and Eu^{3+} . In the visible region, these Sm^{3+} and Eu^{3+} emission bands partially overlap the absorption bands of chlorophyll A and chlorophyll B as well as the absorption regions associated with P_R and P_{FR} . To quantitatively evaluate the spectral matching, the spectral overlap degree was calculated using the equations proposed by Jou et al. [33]:

$$\phi = \frac{\int P(\lambda) d\lambda}{\int P_{phy}(\lambda) d\lambda} \quad (6)$$

$$P(\lambda) = \begin{cases} P_l(\lambda) & \text{if } P_{phy}(\lambda) > P_l(\lambda) \\ P_{phy}(\lambda) & \text{if } P_{phy}(\lambda) \leq P_l(\lambda) \end{cases} \quad (7)$$

where λ is the wavelength, and P_l and P_{phy} represent the area-normalized emission spectrum of the LED device and the area-normalized absorption spectra of chlorophyll A, chlorophyll B, and the photoreceptor-related P_R and P_{FR} forms, respectively. The calculated overlap degrees of the LED emission with P_R , P_{FR} , chlorophyll A, and chlorophyll B are 58.3%, 43.1%, 37.1%, and 40.2%, respectively. The simultaneous spectral overlap with the two chlorophylls and both phytochrome forms suggests that the device can provide photons over several biologically relevant wavelength regions. These results support its potential as a red-emitting component for plant cultivation lighting.

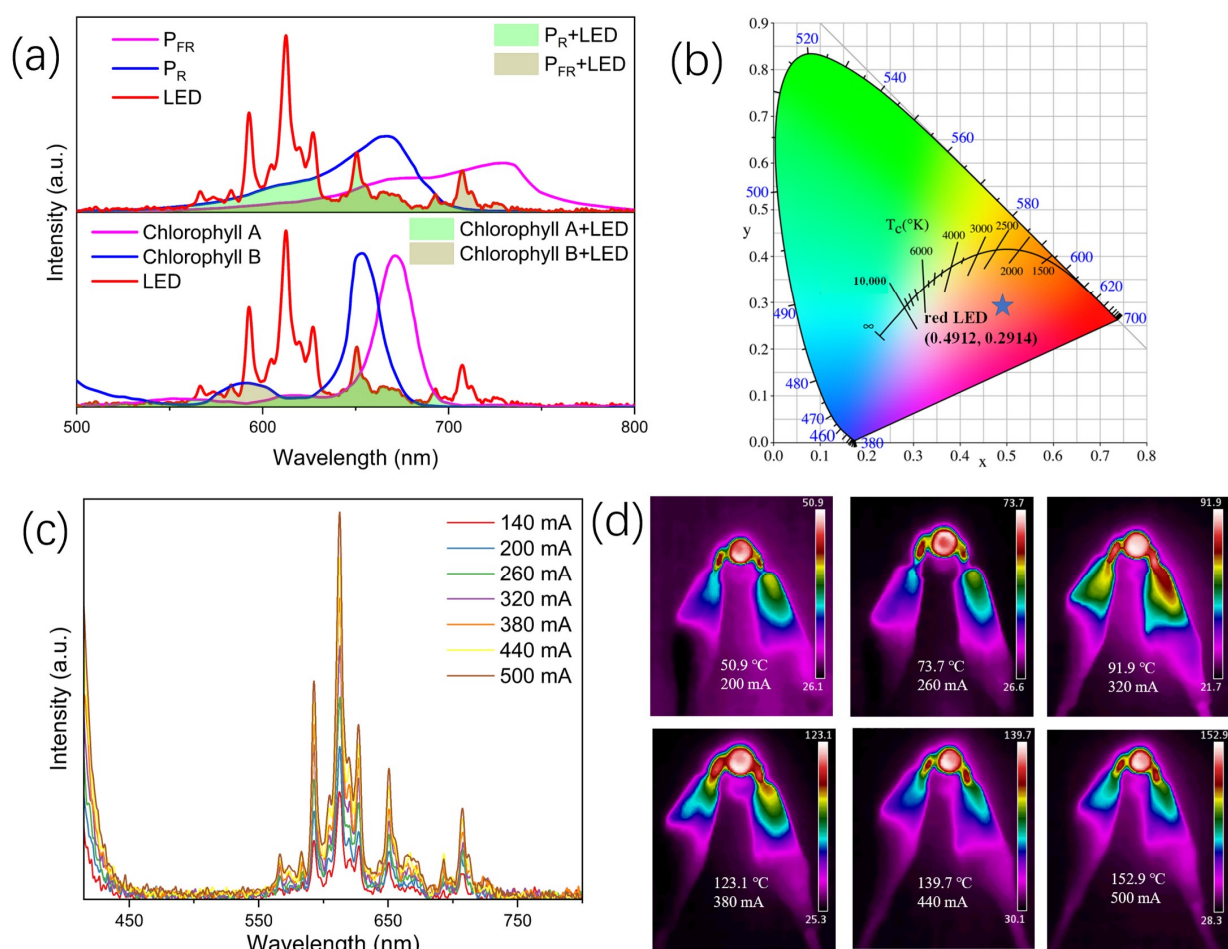


Figure 5. Optical and thermal characteristics of the phosphor-converted LED fabricated using $\text{NYB:0.02Sm}^{3+}, 0.01\text{Eu}^{3+}$ and a commercial 400–405 nm, 5 W near-UV LED chip: (a) Area-normalized EL spectrum of the LED device compared with the absorption spectra of chlorophyll A, chlorophyll B, and the P_R and P_{FR} forms of phytochrome. (b) CIE 1931 chromaticity coordinates of the LED device. (c) Current-dependent EL spectra of the device. (d) Thermal infrared images of the phosphor layer.

As shown in Figure 5b, the CIE 1931 chromaticity coordinates of the device are determined to be (0.4912, 0.2914), placing its emission in the reddish region of the chromaticity diagram. Figure 5c presents the EL spectra recorded at driving currents ranging from 140 to 500 mA. As the current increases, the emission intensity increases progressively, whereas the characteristic peak positions and overall spectral profiles remain nearly unchanged. These results demonstrate good spectral and color stability of the fabricated device over the investigated current range. The thermal infrared images in Figure 5d show that the maximum surface temperature of the phosphor layer increases markedly with increasing driving current. The measured maximum temperature of 152.9 °C (≈ 426 K) at 500 mA falls within the range of the temperature-dependent PL measurements (293–433 K), where the NYB:0.02Sm³⁺, 0.01Eu³⁺ phosphor retains 102.3% of its room-temperature integrated emission intensity at 433 K. Therefore, the high thermal stability observed in the powder is directly relevant to maintaining the converted spectral output of the device under high-current operation. Together with the simultaneous overlap of the device emission with chlorophyll and phytochrome absorption regions, these results indicate the potential of this phosphor for further development in phosphor-converted LED devices.

3. Materials and Methods

3.1. Sample Preparation

Sm³⁺ and Eu³⁺-activated NYB phosphors were synthesized via a conventional high-temperature solid-state reaction. The nominal compositions of the Sm³⁺ doped, Eu³⁺ doped, and Sm³⁺/Eu³⁺ co-doped samples are expressed as Na₃Y_{1-x}Sm_xB₈O₁₅ (NYB: xSm³⁺), Na₃Y_{1-y}Eu_yB₈O₁₅ (NYB: yEu³⁺), and Na₃Y_{1-x-y}Sm_xEu_yB₈O₁₅ (NYB: xSm³⁺, yEu³⁺), respectively, where x and y denote the fractions of Y³⁺ sites nominally substituted by Sm³⁺ and Eu³⁺. The selection of the heat-treatment temperatures was guided by the previously reported synthesis of Na₃YB₈O₁₅ by Huang et al. [19]. Although their crystal-growth procedure employed a flux-assisted route, the reported thermal treatment provided a useful reference for the formation temperature and thermal stability range of the Na₃YB₈O₁₅ phase. Stoichiometric amounts of Na₂CO₃ (99.8%), Y₂O₃ (99.99%), Sm₂O₃ (99.99%), Eu₂O₃ (99.99%), and H₃BO₃ (99.8%) were thoroughly mixed and ground in an agate mortar. All starting materials were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China, and used without further purification. The resulting mixtures were preheated in air at 450 °C for 10 h. After cooling to room temperature, the preheated products were reground to improve compositional homogeneity and subsequently calcined in air at 780 °C for 40 h under the same atmosphere. The calcination temperature was chosen to lie below the reported decomposition temperature of Na₃YB₈O₁₅, approximately 831 °C, while remaining sufficiently high to promote precursor conversion, solid-state diffusion, and crystallization of the polyborate framework [19]. The nominal compositions, sample designations, and heat-treatment conditions of the synthesized NYB-based phosphors are summarized in Table S3 in the supporting information. Finally, the as-prepared products were ground into fine powders for subsequent characterization. A phosphor-converted LED was fabricated using the NYB:0.02Sm³⁺, 0.01Eu³⁺ phosphor and a commercial 400–405 nm, 5 W near-ultraviolet LED chip. The phosphor powder was homogeneously mixed with silicone and coated directly onto a commercial 400–405 nm, 5 W near-UV LED chip. The coated chip was subsequently packaged as an LED device.

3.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku MiniFlex 600 diffractometer (Rigaku, Tokyo, Japan) with Cu K α radiation ($\lambda = 0.15406$ nm). The morphology and elemental distribution of the samples were examined using a Sigma

300 field-emission scanning electron microscope (FE-SEM; Zeiss, Oberkochen, Germany) equipped with an EDS system. Diffuse reflectance spectra were recorded using a UV–visible spectrophotometer (UV-3600 Plus, Shimadzu, Kyoto, Japan). PLE and PL spectra were measured using an F-4600 fluorescence spectrophotometer (Hitachi, Tokyo, Japan) equipped with a 150 W xenon lamp. The surface temperature of the phosphor-converted LED was monitored using an infrared thermal imaging camera (UTi120S, Unit, Dongguan, China) under different forward currents. Thermal images were recorded after the device reached a stable operating temperature under each current condition. The spectral and colorimetric characteristics of the packaged LED were measured using an HAAS-2000 spectroradiometer system (EVERFINE, Hangzhou, China). Electroluminescence spectra were recorded under different forward currents from 140 to 500 mA.

4. Conclusions

In summary, Sm^{3+} - and Eu^{3+} -activated $\text{Na}_3\text{YB}_8\text{O}_{15}$ phosphors were prepared by a high-temperature solid-state reaction and evaluated from powder-level luminescence to packaged phosphor-converted LED performance. The XRD patterns of the undoped and doped samples were consistent with the $\text{Na}_3\text{YB}_8\text{O}_{15}$ phase. Under near-UV excitation, Sm^{3+} produced characteristic emissions at approximately 567, 604, 652, and 712 nm, whereas Eu^{3+} emission was dominated by the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition near 614 nm. Increasing the Eu^{3+} content shifted the emission color from orange-red toward red. Importantly, NYB:0.02Sm^{3+} , NYB:0.70Eu^{3+} , and $\text{NYB:0.02Sm}^{3+}, 0.01\text{Eu}^{3+}$ retained 119.7%, 93.4%, and 102.3%, respectively, of their room-temperature integrated emission intensities at 433 K. This favorable thermal performance is likely associated with the host structure and wide optical band gap, together with thermally induced redistribution among the Stark-split and phonon-assisted emission components. A phosphor-converted LED was fabricated by incorporating $\text{NYB:0.02Sm}^{3+}, 0.01\text{Eu}^{3+}$ into a silicone conversion layer coated on a 400–405 nm near-UV chip. The packaged device exhibited residual near-UV chip emission together with the characteristic Sm^{3+} and Eu^{3+} emissions, and its spectral profile remained nearly unchanged as the forward current increased from 140 to 500 mA. The device emission showed overlap degrees of 58.3%, 43.1%, 37.1%, and 40.2% with the absorption spectra of P_R , P_{FR} , chlorophyll A, and chlorophyll B, respectively. Moreover, the phosphor-layer temperature reached approximately 426 K at 500 mA, while the co-doped phosphor retained 102.3% of its room-temperature emission intensity at 433 K. These results indicate that $\text{Sm}^{3+}/\text{Eu}^{3+}$ -activated $\text{Na}_3\text{YB}_8\text{O}_{15}$ is a thermally stable and color-tunable phosphor candidate for phosphor-converted LED applications.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/inorganics14090235/s1>, Table S1: Crystallographic data of $\text{Na}_3\text{YB}_8\text{O}_{15}$ obtained from the reported single-crystal structure; Table S2: Chromaticity coordinates of $\text{NYB:0.02Sm}^{3+}, y\text{Eu}^{3+}$ phosphors under 403 nm excitation; Table S3: Nominal compositions and synthesis conditions of the NYB-based phosphors; Figure S1: SEM image of the $\text{NYB:0.02Sm}^{3+}, 0.01\text{Eu}^{3+}$ phosphor recorded at a magnification of 5000 $\times$. The scale bar corresponds to 30 μm ; Figure S2: The particle size distribution histogram of $\text{NYB:0.02Sm}^{3+}, 0.01\text{Eu}^{3+}$; Figure S3: Plot of $\lg(I/y)$ vs. $\lg y$ for $\text{NYB: } y\text{Eu}^{3+}$; Figure S4: Variation in asymmetry ratio (R) as a function of (a) Sm^{3+} and (b) Eu^{3+} concentrations; Figure S5: Temperature-dependent luminescence properties of $\text{NYB:0.02Sm}^{3+}, 0.02\text{Eu}^{3+}$, and $\text{NYB:0.02Sm}^{3+}, 0.04\text{Eu}^{3+}$ phosphors over 293–433 K. (a) PL emission spectra and (b) temperature-dependent integrated PL intensity of $\text{NYB:0.02Sm}^{3+}, 0.02\text{Eu}^{3+}$ under 403 nm excitation. (c) PL emission spectra and (d) temperature-dependent integrated PL intensity of $\text{NYB:0.02Sm}^{3+}, 0.04\text{Eu}^{3+}$ under 403 nm excitation.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

LED	light-emitting diode
UV	ultraviolet
NYB	Na ₃ YB ₈ O ₁₅
EL	electroluminescence
XRD	X-ray diffraction
SEM	scanning electron microscope
EDS	energy-dispersive X-ray spectroscopy
PLE	photoluminescence excitation
PL	photoluminescence

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