Combination of white phosphors is needed to obtain white light. However, the production of yellow light by mixing NUV/UV diode chips with blue phosphor is challenging. One approach is to use a red phosphor to create a practical white LED with a Ra of up to 90 from commercially available blue phosphor and optimized libraries. The production of white light with high color rendering is demonstrated by preparing yellow phosphor that contains a red emission component with Bi⁢⁺⁺, Eu⁢⁺⁺, Y⁢³⁺ and Gd⁢³⁺ concentrations. Some good candidates for green and blue phosphors have been developed for NUV/UV tricolor WLEDs, but promising red phosphors have not yet been found. Therefore, the production of yellow light by mixing green emission from Bi⁢⁺⁺ with red emission from Eu⁢⁺⁺ in YVO₄:Eu⁺⁺ host is promising. The role of Gd³⁺ as an intermediate in energy transfer from Bi³⁺ to Eu⁺⁺/Tb³⁺ activators has been observed; and the energy transfer paths of VO₄³⁻ → Eu⁺⁺, Gd³⁺ → Eu⁺⁺, and Gd³⁺ → VO₄³⁻ → Eu⁺⁺ were also demonstrated. In addition, the production of two photons with one photon incidence, which is called quantum cutting, was reported in GdVO₄:Eu⁺⁺ under high-energy vacuum ultraviolet excitation. In view of the higher atomic weight of Gd than Y, the thermal stability of Eu⁺⁺ or Bi³⁺ luminescence in GdVO₄ host may be better than that in YVO₄ host. These phenomena beg the question regarding which host, among pure GdVO₄, GdVO₄ co-doped with Y³⁺ (denoted as (Gd,Y)VO₄), and YVO₄ co-doped with Gd³⁺ (denoted as (Y,Gd)VO₄), is the best for Bi³⁺ and Eu⁺⁺ activators to produce ideal yellow light for WLEDs. Furthermore, the light balance between the green emission from Bi³⁺ and the red emission from Eu⁺⁺ is critical to obtaining white light, especially when Bi³⁺ is used as the activator for yellow phosphor.

1. Introduction

Solid-state light-emitting diodes (LEDs) have attracted considerable interest in recent years for their superior properties such as long lifetime, high efficiency, low-voltage driving, great reliability, non-mercury and environmental friendliness. Although great advances have been made in LEDs, the obstacles to further development remain substantial. Presently, most commercially available white light-emitting diodes (WLED) are produced by combining blue luminescence from LED chips with yellow luminescence from Y₃Al₅O₁₂:Ce³⁺ (YAG:Ce³⁺) phosphor. The major drawbacks of YAG-based WLEDs are their poor color rendering (Ra) and thermal quenching at high temperature. As a novel alternative, the combination of near-ultraviolet/ultraviolet (NUV/UV) GaInN diode chip with red, green and blue phosphors to generate white light was highly favored. Some good candidates for green and blue phosphors have been developed for NUV/UV tricolor WLEDs, but promising red phosphors have not yet been found. Therefore, the production of yellow light by mixing green emission from Bi³⁺ with red emission from Eu³⁺ in YVO₄:Eu³⁺ host is promising. The role of Gd³⁺ as an intermediate in energy transfer from Bi³⁺ to Eu³⁺/Tb³⁺ activators has been observed; and the energy transfer paths of VO₄³⁻ → Eu³⁺, Gd³⁺ → Eu³⁺, and Gd³⁺ → VO₄³⁻ → Eu³⁺ were also demonstrated. In addition, the production of two photons with one photon incidence, which is called quantum cutting, was reported in GdVO₄:Eu³⁺ under high-energy vacuum ultraviolet excitation. In view of the higher atomic weight of Gd than Y, the thermal stability of Eu³⁺ or Bi³⁺ luminescence in GdVO₄ host may be better than that in YVO₄ host. These phenomena beg the question regarding which host, among pure GdVO₄, GdVO₄ co-doped with Y³⁺ (denoted as (Gd,Y)VO₄), and YVO₄ co-doped with Gd³⁺ (denoted as (Y,Gd)VO₄), is the best for Bi³⁺ and Eu³⁺ activators to produce ideal yellow light for WLEDs. Furthermore, the light balance between the green emission from Bi³⁺ and the red emission from Eu³⁺ is critical to obtaining white light.
which depends on the blue component in a tri-color system. Therefore, the ratio of Bi\(^{3+}\) to Eu\(^{3+}\) content must be optimized, as must that of Gd\(^{3+}\) to Y\(^{3+}\). Optimizing the quaternary elements with a number of variable concentrations by synthesizing and characterizing samples one-at-a-time using conventional methods is time-consuming and costly. Furthermore, it is very difficult to provide a dynamic prospect between luminescence properties and multi-composition variation by using conventional methods, but a combinatorial chemistry approach, which utilizes parallel synthesis and high-throughput screening strategies, is facile enough to accomplish full factorial experiments.

Based on these analyses, a combinatorial approach was adopted to optimize Y\(^{3+}\), Gd\(^{3+}\), Bi\(^{3+}\) and Eu\(^{3+}\) contents in vanadates. A special single-mass yellow phosphor that emits red and green dual colors has been successfully screened out from a (Gd-Y-Bi-Eu)VO\(_4\) quaternary system and the production of warm white light was demonstrated by preparing a practical LED from the optimized yellow phosphor and commercially available blue phosphor.

2. Experimental

Combinatorial libraries were synthesized by ink-jetting precursor solutions into micro-reactors using a home-made ink-jet delivery system as in our earlier investigation,\(^{18}\) in the order V → Y/Gd → Bi → Eu → V → Y/Gd → Bi → Eu. The precursor solutions were prepared by dissolving appropriate amounts of Gd(NO\(_3\))\(_3\)·6(H\(_2\)O) (99.99%), Y(NO\(_3\))\(_3\)·6(H\(_2\)O) (99.9%), NH\(_4\)VO\(_3\) (98%), Eu(NO\(_3\))\(_3\)·5H\(_2\)O (99.99%), and Bi (99.5%) in de-ionized water. NH\(_4\)VO\(_3\) solution was prepared by adding a suitable amount of NH\(_4\)OH to de-ionized water and heating to 70–80 °C to accelerate dissolution. The Bi\(^{3+}\) solution was prepared by adding a suitable amount of nitric acid to de-ionized water before the Bi was added, and heating to 70–80 °C. After drying at 60–70 °C, the micro-reactors that contained the precursors were pre-sintered at 600 °C for 3 h, and then sintered at 1100 °C for 3 h to yield the final combinatorial library.

The overall luminescence of the combinatorial library of samples was characterized with a photographic method using a digital camera. The emission spectrum of each sample in the library was obtained using a combinatorial scanning fluorescence characterization system.\(^{19}\) It comprised mainly of a Hg lamp, a portable optical fiber spectrometer (Ocean Optics, Inc., model SD2000), and an x-y stage. The materials library was fixed on the x-y stage. The materials library was fixed on the bottom of the reactor. A light shield was used to prevent interference from other samples.

3. Results and discussion

3.1 Combinatorial experimental results

Fig. 1 presents the composition map of the (Gd\(_{1-s-t}\)Bi\(_s\)Eu\(_t\))VO\(_4\) (a), (Gd\(_{1-s-t}\)Y\(_s\)Bi\(_t\)Eu\(_t\))VO\(_4\) (b) and (Y\(_{1-s-t}\)Gd\(_s\)Bi\(_t\)Eu\(_t\))VO\(_4\) (c) (r = 0–0.750, s = 0–0.050, t = 0–0.060) combinatorial libraries and luminescence photographs of every sample in the library under 365 nm excitation. When no Bi\(^{3+}\) was co-doped (s = 0) into samples, only faint red emission from Eu\(^{3+}\) was observed in the three combinatorial libraries and the luminescence of Eu\(^{3+}\) increased with Eu\(^{3+}\) concentration from t = 0 to 0.045. However, bright luminescence is observed with Bi\(^{3+}\) co-doped into samples (s = 0.005–0.050). When the Eu\(^{3+}\) concentration was t = 0 to 0.060, the brightness increased with Bi\(^{3+}\) content from s = 0.005 to 0.040 and then decreased slightly from s = 0.040 to 0.050. On the other side, strong green emission of Bi\(^{3+}\) is observed when no Eu\(^{3+}\) is co-doped into samples (t = 0), and the intensity of this green emission increases with Bi\(^{3+}\) concentration from s = 0 to s = 0.040. When the concentration of Bi\(^{3+}\) is kept at s = 0.005 to 0.050, the emission color changes gradually from green to orange as the Eu\(^{3+}\) concentration increases from t = 0 to 0.060. Therefore, the energy of Eu\(^{3+}\) emission under 365 nm originates from Bi\(^{3+}\) absorption; and Eu\(^{3+}\) can not emit efficiently under 365 nm excitation without Bi\(^{3+}\) providing energy. More importantly, the tuning of emission color with various Bi\(^{3+}\) and Eu\(^{3+}\) content ratios is demonstrated vividly here.

The overall luminescence in Fig. 1 (a) declines from the top to bottom as the Eu\(^{3+}\) concentration increases from t = 0 to 0.060. When the concentrations of Eu\(^{3+}\) and Bi\(^{3+}\) were kept the same, the relative luminescence of the equivalent samples in Fig. 1 (b) is brighter than that in Fig. 1 (a) as the Y\(^{3+}\) concentration increases from r = 0.150 to 0.750; and comparatively, the overall luminescence of samples in Fig. 1 (b) exceeds that of those in Fig. 1 (a), indicating that co-doping with the proper amount of Y\(^{3+}\) improves the luminescence efficiency of GdVO\(_2\)Bi\(^{3+}\),Eu\(^{3+}\). As further verified by combing with Fig. 1 (c), the overall luminescence declines rapidly from the top to bottom as the Gd\(^{3+}\) concentration increases from r = 0.150 to 0.750. These phenomena suggest that the luminescence of Y\(^{3+}\) dominant samples under 365 nm excitation is much better than that of Gd\(^{3+}\) dominant samples as far as the same Bi\(^{3+}\) and Eu\(^{3+}\) contents are concerned.

Fig. 2 (a), (b) and (c) present the luminescence of the (Gd\(_{1-s-t}\)Bi\(_s\)Eu\(_t\))VO\(_4\) (a), (Gd\(_{1-s-t}\)Y\(_s\)Bi\(_t\)Eu\(_t\))VO\(_4\) (b) and (Y\(_{1-s-t}\)Gd\(_s\)Bi\(_t\)Eu\(_t\))VO\(_4\) (c) combinatorial libraries, respectively, under 254 nm excitation. The figures differ considerably from Fig. 1 (a), (b) and (c) in both color and brightness. When the Bi\(^{3+}\) content is zero (s = 0 but t = 0.005–0.060), strong red emission from Eu\(^{3+}\) is observed and the luminescence increases with the Eu\(^{3+}\) content.
concentration from $t = 0.005$ to $t = 0.045$. With respect to the other samples ($s = 0.005–0.050$, and $t = 0–0.060$), although green emission from Bi$^{3+}$ is observed under 254 nm excitation, red emission from Eu$^{3+}$ dominates when the Eu$^{3+}$ concentration is at least that of Bi$^{3+}$. The bottom left-hand area below the diagonal dividing line from the top left to the bottom right is clearly brighter than the top right-hand area, because the VO$_4^{3-}$ ligand can efficiently absorb 254 nm excitation energy and transfer it to the Eu$^{3+}$ activators; however, this process is inefficient under 365 nm excitation. The higher luminance under 365 nm excitation after co-doping with Bi$^{3+}$ demonstrates that co-doping Bi$^{3+}$ into (Gd,Y)VO$_4$:Eu$^{3+}$ makes it more suitable for use in NUV WLEDs because of the red-shift of the absorption edge. All equivalent samples in combinatorial library, which contain the same Bi$^{3+}$ and Eu$^{3+}$ contents in Fig. 2 (a), (b) and (c), have similar emission color but with significant differences in brightness. These differences must originate from the variation in Y$^{3+}$ and Gd$^{3+}$ contents. Luminance in pictures is affected by visual function of eyes when judged with naked eye. To analyze quantitatively emission color and luminous efficiency, the following spectra are obtained.

Fig. 3 displays the emission spectra of samples with $s = 0–0.050$, $t = 0.005$, or $r = 0/0.150$ in the (Gd$_{1-s-t}$Bi$_s$Eu$_t$)VO$_4$ (a), (Gd$_{1-r-s}$Y$_r$Bi$_s$Eu$_t$)VO$_4$ (b) and (Y$_{1-r-s}$Gd$_r$Bi$_s$Eu$_t$)VO$_4$ (c) combinatorial libraries under 365 nm excitation, as corresponding to samples in the second row in the combinatorial libraries. One broad emission band and several emission lines are observed. Without Bi$^{3+}$ co-doping ($s = 0$), only several emission lines are observed. Therefore, the broad emission band is associated with Bi$^{3+}$ and the emission lines originate from Eu$^{3+}$. The lines at 592, 618, 650, and 702 nm are attributed to the $^4D_0 \rightarrow ^4F_J$ ($J = 1, 2, 3, 4$) transitions of Eu$^{3+}$, because the $4F - 4f$ transition of Eu$^{3+}$ with the $4f^55s^2$ electronic configuration is forbidden by parity. The broad emission band with a peak at 540 nm is attributed to the $^4P_1 \rightarrow ^4S_0$ transition of Bi$^{3+}$ because of the broad band configuration, which is allowed by both parity and spin selection by mixing of the singlet state with the triplet state.

As Fig. 3 (a), (b) and (c) shown, the luminescence intensity of Bi$^{3+}$ increases with Bi$^{3+}$ concentration from $s = 0$ to 0.050 when Eu$^{3+}$ concentration is constant; that of Eu$^{3+}$ also increases when the concentration of Eu$^{3+}$ does not change. This is because the distance between Bi$^{3+}$ and Eu$^{3+}$ becomes shorter as the Bi$^{3+}$ concentration increases, increasing the probability of the transfer of the energy absorbed by Bi$^{3+}$ to Eu$^{3+}$. This result suggests that Bi$^{3+}$ transfers its absorption energy to Eu$^{3+}$ to emit light. Given that the Bi$^{3+}$ concentration remains unchanged, the emission intensity of Eu$^{3+}$ will also increase with its concentration, except for concentration quenching. The insets in Fig. 3 plot the variations in the relative height of the Bi$^{3+}$ emission peak at 540 nm and the Eu$^{3+}$ emission peak at 618 nm with Bi$^{3+}$ concentration. Here, the height of the (Gd$_{0.955}$Bi$_{0.050}$Eu$_{0.005}$)VO$_4$ emission peak at 540 nm is set to 100%, and the same as in the following. The growth curves in the insets of Fig. 3 (a), (b) and (c) differ from each other, revealing that Y$^{3+}$ and Gd$^{3+}$ have different effects on luminescence.

Fig. 4 presents the emission spectra of samples with $s = 0.040$, $t = 0–0.060$, or $r = 0–0.750$ in the (Gd$_{1-s-t}$Bi$_s$Eu$_t$)VO$_4$ (a), (Gd$_{1-r-s}$Y$_r$Bi$_s$Eu$_t$)VO$_4$ (b) and (Y$_{1-r-s}$Gd$_r$Bi$_s$Eu$_t$)VO$_4$ (c) combinatorial libraries under 365 nm excitation, corresponding to samples in the fifth column in the combinatorial libraries.
Even though the Bi\(^{3+}\) concentration remains constant, the intensities of Eu\(^{3+}\) emissions increase with \(t\) from 0 to 0.060, while the intensities of all emissions from Bi\(^{3+}\) decrease as Eu\(^{3+}\) concentration increases from \(t = 0\) to \(t = 0.060\), because too much of the absorption energy of Bi\(^{3+}\) is transferred to Eu\(^{3+}\) with the shortening of the distance between Bi\(^{3+}\) and Eu\(^{3+}\). As expected, these results further demonstrate that the transfer of energy from Bi\(^{3+}\) to Eu\(^{3+}\) provides energy for Eu\(^{3+}\) to emit light under NUV excitation. The insets in Fig. 4 (a), (b) and (c) show that the intensity of Bi\(^{3+}\) emission at 540 nm declines continuously and the intensity of Eu\(^{3+}\) emission at 618 nm increases neither linearly nor parabolically, as Eu\(^{3+}\) content increases. Moreover, the variation among the relative height of Eu\(^{3+}\) emission, as shown in the insets in Fig. 4 (a), (b) and (c), also suggests that the Y\(^{3+}\) and Gd\(^{3+}\) contents have differently affected the transfer of energy from Bi\(^{3+}\) to Eu\(^{3+}\). For samples with a given Eu\(^{3+}\) concentration, the relative emission intensities from Bi\(^{3+}\) in Fig. 4(a), (b) and (c), as far as the equivalent concentration is concerned, are all similar; however, the emission intensity of Eu\(^{3+}\) is greatly improved by co-doping with a little Y\(^{3+}\) or by adding Y\(^{3+}\) until it dominates, indicating that energy is more favorably transferred from Bi\(^{3+}\) to Eu\(^{3+}\) in a YVO\(_4\) host than that in GdVO\(_4\).

The emission spectra of other samples are omitted here, but Fig. 5 (a), (b) and (c) plot the relative photoluminescence intensities of every sample in the combinatorial libraries of (Gd\(_{1-s-t}\)Bi\(_{s}\)Eu\(_{t}\))VO\(_4\) (a), (Gd\(_{1-r-s-t}\)Y\(_{r}\)Bi\(_{s}\)Eu\(_{t}\))VO\(_4\) (b) and (Y\(_{1-r-s-t}\)Gd\(_{r}\)Bi\(_{s}\)Eu\(_{t}\))VO\(_4\) (c) under 365 nm excitation, as corresponding to the fifth column in Fig. 1.

Even though the Bi\(^{3+}\) concentration remains constant, the intensities of Eu\(^{3+}\) emissions increase with \(t\) from 0 to 0.060, while the intensities of all emissions from Bi\(^{3+}\) decrease as Eu\(^{3+}\) concentration increases from \(t = 0\) to \(t = 0.060\), because too much of the absorption energy of Bi\(^{3+}\) is transferred to Eu\(^{3+}\) with the shortening of the distance between Bi\(^{3+}\) and Eu\(^{3+}\). As expected, these results further demonstrate that the transfer of energy from Bi\(^{3+}\) to Eu\(^{3+}\) provides energy for Eu\(^{3+}\) to emit light under NUV excitation. The insets in Fig. 4 (a), (b) and (c) show that the intensity of Bi\(^{3+}\) emission at 540 nm declines continuously and the intensity of Eu\(^{3+}\) emission at 618 nm increases neither linearly nor parabolically, as Eu\(^{3+}\) content increases. Moreover, the variation among the relative height of Eu\(^{3+}\) emission, as shown in the insets in Fig. 4 (a), (b) and (c), also suggests that the Y\(^{3+}\) and Gd\(^{3+}\) contents have differently affected the transfer of energy from Bi\(^{3+}\) to Eu\(^{3+}\). For samples with a given Eu\(^{3+}\) concentration, the relative emission intensities from Bi\(^{3+}\) in Fig. 4(a), (b) and (c), as far as the equivalent concentration is concerned, are all similar; however, the emission intensity of Eu\(^{3+}\) is greatly improved by co-doping with a little Y\(^{3+}\) or by adding Y\(^{3+}\) until it dominates, indicating that energy is more favorably transferred from Bi\(^{3+}\) to Eu\(^{3+}\) in a YVO\(_4\) host than that in GdVO\(_4\).

The emission spectra of other samples are omitted here, but Fig. 5 (a), (b) and (c) plot the relative photoluminescence intensities of every sample in the combinatorial libraries of (Gd\(_{1-s-t}\)Bi\(_{s}\)Eu\(_{t}\))VO\(_4\) (a), (Gd\(_{1-r-s-t}\)Y\(_{r}\)Bi\(_{s}\)Eu\(_{t}\))VO\(_4\) (b) and (Y\(_{1-r-s-t}\)Gd\(_{r}\)Bi\(_{s}\)Eu\(_{t}\))VO\(_4\) (c) under 365 nm excitation, as corresponding to the fifth column in Fig. 1.

Even though the Bi\(^{3+}\) concentration remains constant, the intensities of Eu\(^{3+}\) emissions increase with \(t\) from 0 to 0.060, while the intensities of all emissions from Bi\(^{3+}\) decrease as Eu\(^{3+}\) concentration increases from \(t = 0\) to \(t = 0.060\), because too much of the absorption energy of Bi\(^{3+}\) is transferred to Eu\(^{3+}\) with the shortening of the distance between Bi\(^{3+}\) and Eu\(^{3+}\). As expected, these results further demonstrate that the transfer of energy from Bi\(^{3+}\) to Eu\(^{3+}\) provides energy for Eu\(^{3+}\) to emit light under NUV excitation. The insets in Fig. 4 (a), (b) and (c) show that the intensity of Bi\(^{3+}\) emission at 540 nm declines continuously and the intensity of Eu\(^{3+}\) emission at 618 nm increases neither linearly nor parabolically, as Eu\(^{3+}\) content increases. Moreover, the variation among the relative height of Eu\(^{3+}\) emission, as shown in the insets in Fig. 4 (a), (b) and (c), also suggests that the Y\(^{3+}\) and Gd\(^{3+}\) contents have differently affected the transfer of energy from Bi\(^{3+}\) to Eu\(^{3+}\). For samples with a given Eu\(^{3+}\) concentration, the relative emission intensities from Bi\(^{3+}\) in Fig. 4(a), (b) and (c), as far as the equivalent concentration is concerned, are all similar; however, the emission intensity of Eu\(^{3+}\) is greatly improved by co-doping with a little Y\(^{3+}\) or by adding Y\(^{3+}\) until it dominates, indicating that energy is more favorably transferred from Bi\(^{3+}\) to Eu\(^{3+}\) in a YVO\(_4\) host than that in GdVO\(_4\).
Eu3+, reducing the non-radiative transfer of energy between Bi3+ ions, and promoting total emission from Bi3+ and Eu3+. Therefore, the luminescence is highest at s = 0.050 and t = 0.005 for Bi3+ and Eu3+ concentrations, respectively. As the Eu3+ concentration increases to s = 0.015, the luminescence intensity declines substantially. One reasonable explanation is that too much energy is captured by Eu3+, strongly affecting the Bi3+ luminescence. Accordingly, when Bi3+ and Eu3+ concentrations are less than 0.050 and 0.005, respectively, improving emission from both Bi3+ and Eu3+ by co-doping Eu3+ into (Gd,Y)VO4:Bi3+ is beneficial. This result suggests that the critical concentration for the transfer of energy among Bi3+ ions is s = 0.040–0.050 in the (Gd,Y)VO4 host.

A factor other than efficiency that determines whether phosphors can be used in LEDs is color quality. Fig. 6 (a) and (b) present the color coordinates (CIE(x,y)) and color rendering index (Ra) of emission spectra of (Gd0.960-r-tYrBi0.040Eut)VO4 (a) and(Y0.960-r-tGdrBi0.040Eut)VO4 (b) under 365 nm excitation. The CIE coordinates of the commercially available blue phosphor of Sr3MgSi2O8:Eu2+ (3128) is also included.

Fig. 6  The correlated color temperature (Tc), color rendering index (Ra) and color coordination (CIE(x,y)) of emission spectra of (Gd0.960-r-t YrBi0.040Eut)VO4 (a) and(Y0.960-r-tGdrBi0.040Eut)VO4 (b) under 365 nm excitation. The CIE coordinates of the commercially available blue phosphor of Sr3MgSi2O8:Eu2+ (3128) is also included.

Eu3+, reducing the non-radiative transfer of energy between Bi3+ ions, and promoting total emission from Bi3+ and Eu3+. Therefore, the luminescence is highest at s = 0.050 and t = 0.005 for Bi3+ and Eu3+ concentrations, respectively. As the Eu3+ concentration increases to s = 0.015, the luminescence intensity declines substantially. One reasonable explanation is that too much energy is captured by Eu3+, strongly affecting the Bi3+ luminescence. Accordingly, when Bi3+ and Eu3+ concentrations are less than 0.050 and 0.005, respectively, improving emission from both Bi3+ and Eu3+ by co-doping Eu3+ into (Gd,Y)VO4:Bi3+ is beneficial. This result suggests that the critical concentration for the transfer of energy among Bi3+ ions is s = 0.040–0.050 in the (Gd,Y)VO4 host.

A factor other than efficiency that determines whether phosphors can be used in LEDs is color quality. For both (Gd0.960-r-t YrBi0.040Eut)VO4 and (Y0.960-r-tGdrBi0.040Eut)VO4, the correlated color temperature declines as Eu3+ concentration increases from t = 0 to t = 0.030, indicating that co-doping with Eu3+ promotes the production of warm light. The color rendering index increases with Eu3+ concentration from t = 0 to t = 0.015 and then decreases as Eu3+ concentration increases further to t = 0.030, suggesting that co-doping with a little Eu3+ improves the color rendering index of (Gd,Y)VO4:Bi3+ while too much Eu3+ detrimentally affects it. In addition, the x value of CIE coordinates of (Y1-r-s Gd0.960-r-tBi0.040Eut)VO4 emission spectra is slightly larger than that of (Gd1-r-s YrBi0.040Eut)VO4 when the value of r is no higher than 0.3 for Gd3+ and Y3+ co-dopant contents, respectively, suggesting that energy is more efficiently transferred to Eu3+ and emitted in the Y3+ dominated system. The (Gd0.645Y0.355Bi0.040Eut)VO4 (35) and (Y0.645Gd0.355Bi0.040Eut)VO4 (35) samples had the highest Ra values, 87.66 and 87.78, respectively. These values were higher than that of YAG-based LED around 75–80, but lower than the value of 90–100 for the classified 1A grade of Ra. Here, the emission spectra have no blue component, as shown in Fig. 4. If it did, the Ra value would be higher.

The CIE coordinates of commercially available blue phosphor for NUV WLEDs, such as (0.1576, 0.0836) for Sr3MgSi2O8:Eu2+ (3128), is also presented in Fig. 6. Since white light can be produced by mixing polychromatic light, an ideal WLED with high Ra can be tuned by coating blue phosphor and the optimized yellow phosphor onto a NUV diode chip with a CIE range of 0.3850 ≤ x ≤ 0.5296 and 0.4177 ≤ y ≤ 0.5220, as indicated by the triangle in Fig. 6.

3.2 Conventional experimental results

To refine the above results obtained with combinatorial approach and study the thermal stability and mechanism of luminescence, some bulk samples were synthesized by the conventional solid state reaction method from sources Gd2O3.

Fig. 7  XRD patterns of samples of (Gd1-r-s-rGd0.955Bi0.040Eut)VO4 (r = 0, ..., 1.0) and standard GdVO4 and YVO4.
Y2O3 (99.9%), NH4VO3 (98%), Eu(NO3)3 $\cdot$ 5H2O (99.99%), and Bi2O3 (99.5%). The same sintering technique as was used to synthesize the combinatorial library was employed, except that the raw materials in a stoichiometric ratio were thoroughly ground before sintering. The photoluminescence (PL) of the bulk samples was measured using a FluoroMax-3 spectrometer. Thermal quenching luminescence was obtained using a heating apparatus (THMS-600) in combination with the spectrometer. The crystal structure of the bulk samples was identified by X-ray diffraction (XRD) analysis using an X’Pert PRO advanced automatic diffractometer with Cu Kα radiation, operated at 45 kV and 40 mA.

Fig. 7 presents the XRD patterns of experimentally synthesized (Gd1–rYr)0.955Bi0.040Eu0.005VO4 (r = 0, 0.1, 0.25, 0.40, 0.55, 0.70, 0.85 and 1.0), which can be indexed to standard GdVO4 (JCPDS: 86–0996) and YVO4 (JCPDS: 17–0341). As shown in Fig. 7, the value of 2θ increases with Y3+ concentration from zero, through 10%, 30%, 50%, 70%, and 85%, to 100% that of Gd3+, indicating that the parameters of crystal lattice decrease as the concentration of Y3+ increases from r = 0 to r = 1.0 in (Gd1–rYr)0.955Bi0.040Eu0.005VO4 system. This is because the radius of Gd3+ is larger than that of Y3+ (Gd3+: 0.94 Å; Y3+: 0.89 Å). The crystal parameters, varying with Gd3+/Y3+ ratios, were obtained by calculations according to the Bragg formulation of X-ray diffraction

$$2d\sin\theta = n\lambda$$

and are nearly linear as shown in Fig. 8. This result is consistent with Vegard’s law. Therefore, the complete solid solutions are obtained in the quaternary (Gd,Y,Bi,Eu)VO4 system.

Fig. 9 reveals the emission spectra of bulk samples of (Gd1–rYr)0.955Bi0.040Eu0.005VO4 under 365 nm excitation. As consistent with above, every sample had one broad emission band with several lines. The emission lines are
attributed to \(^5D_0 \rightarrow ^7F_j\) (\(j = 0, 1, 2, 3, 4\)), as described above, and the broad emission is attributed to the \(^3P_1 \rightarrow ^1S_0\) transition of Bi\(^{3+}\). The inset in Fig. 9 plots the relative emission intensity, determined by integrating emission spectra in the region 400–700 nm, which are 29%, 33%, 54%, 64%, 83%, 92%, 102%, and 100% for \(r = 0, 0.1, 0.25, 0.40, 0.55, 0.70, 0.85, \) and 1, respectively, in \((\text{Gd}_{1-r}\text{Y}_r)_{0.955}\text{Bi}_{0.040}\text{Eu}_{0.005}\text{VO}_4\) system. This figure clearly shows that the integrated intensity of emission almost increases with \(Y^{3+}\) concentration from \(r = 0\) to \(r = 1.0\) but is maximum at \(r = 0.85\).

The gradual change in the Gd\(^{3+}/Y^{3+}\) contents result in large variations in the Eu\(^{3+}\) environment, as demonstrated from the relative intensity of the \(^5D_0 \rightarrow ^7F_2\) and \(^5D_0 \rightarrow ^7F_1\) emission at 618 and 594 nm shown in Fig. 10. The increase in the Y\(^{3+}\) content results in a decrease of the ratio of Eu\(^{3+}\) emission intensity at 618 nm to 594 nm. This decrease is related to a higher symmetry of the Eu\(^{3+}\) environment in the Y\(^{3+}\) host than in the Gd\(^{3+}\) one (the ionic radius of Y\(^{3+}\) is 0.89 and Gd\(^{3+}\) is 0.94), because the purely magnetic dipole \(^5D_0 \rightarrow ^7F_1\) transition being considered of constant dipole strength while the electronic dipole \(^5D_0 \rightarrow ^7F_2\) transition of Eu\(^{3+}\) is sensitive to the symmetry of the crystal lattice.\(^{25}\)

The temperature of the substrate of LED lamps usually increases to 100–150 °C and even higher for street lamps, because heat is produced continuously during LED operation. The thermal stability of LED luminescence depends strongly on phosphors. Here, the thermal stability of luminescence of \((\text{Gd}_{1-r}\text{Y}_r)_{0.955}\text{Bi}_{0.040}\text{Eu}_{0.005}\text{VO}_4\) under 365 nm excitation was measured at 25, 50, 100, 150, 200, 250, and 300 °C, from which we can observe that the intensity of Eu\(^{3+}\) emission still increases while the intensity of Bi\(^{3+}\) emission decreases with temperature increasing. The peak of Bi\(^{3+}\) emission bands blue-shift with the increase of temperature. The 365 nm excited emission spectra of \((\text{Gd}_{1-r}\text{Y}_r)_{0.955}\text{Bi}_{0.040}\text{Eu}_{0.005}\text{VO}_4\) and \((\text{Gd}_{0.30}\text{Y}_{0.70})_{0.955}\text{Bi}_{0.040}\text{Eu}_{0.005}\text{VO}_4\) have the same configuration with that of \((\text{Gd}_{0.15}\text{Y}_{0.85})_{0.955}\text{Bi}_{0.040}\text{Eu}_{0.005}\text{VO}_4\) except intensity. The relative luminescence intensity, determined by integrating emission spectra from 400 to 700 nm, and the relative emission intensity at 25 °C was normalized to 100%, as a function of temperature is displayed in Fig. 12. The integrated intensity, including both the contribution from Bi\(^{3+}\) emission and the contribution further increases from 100 to 300 °C. The relative intensities of \((\text{Gd}_{1-r}\text{Y}_r)_{0.955}\text{Bi}_{0.040}\text{Eu}_{0.005}\text{VO}_4\), \((\text{Gd}_{0.15}\text{Y}_{0.85})_{0.955}\text{Bi}_{0.040}\text{Eu}_{0.005}\text{VO}_4\), and \((\text{Gd}_{0.30}\text{Y}_{0.70})_{0.955}\text{Bi}_{0.040}\text{Eu}_{0.005}\text{VO}_4\) emissions at 150 °C are 95%, 95% and 99%, respectively, of that at 25 °C. These values are far higher than that of most phosphors, such as Y\(_3\)Al\(_5\)O\(_{12}\):Ce\(^{3+}\) and (Sr,Ba)Si\(_2\)O\(_4\):Eu\(^{2+}\) for yellow, (Ba,Sr)SiO\(_4\):Eu\(^{3+}\) and Lu\(_3\)Al\(_5\)O\(_{12}\):Ce\(^{3+}\) for green, and (Sr,Ca)\(_2\)Si\(_5\)N\(_8\):Eu\(^{2+}\) and (Sr,Ca)\(_2\)SiAl\(_3\)N\(_3\):Eu\(^{2+}\) for red, that are commonly used in LEDs.\(^{23}\)

The positive effect of Gd\(^{3+}\) in improving the thermal stability of YVO\(_4\):Bi\(^{3+}\), Eu\(^{3+}\) luminescence is clearly exhibited. Combining the above results, we can conclude that the best composition range that maximizes the efficiency of luminescence, presents good color rendering of emission, and has good thermal stability of luminescence is 0.7 < \(r < 1.0\), 0.04 < \(s < 0.05\) and \(t < 0.015\) for \((\text{Gd}_{1-r}\text{Y}_r)_{0.955}\text{Bi}_{0.040}\text{Eu}_{0.005}\text{VO}_4\).
that Y3+. Therefore, the activation energy of YVO4:Bi3+,Eu3+ is that of YVO4, because the atomic weight of Gd3+ is higher than Eu3+.

The presence of Bi3+ absorption in the excitation by monitoring Eu3+ emission at 618 nm indicates there is energy transfer from Bi3+ to Eu3+. The same is the energy transfer from VO43- to Eu3+ as demonstrated by the presence of VO43- absorption in the excitation of Bi3+. From the above combinatorial libraries, we have concluded that the transfer of energy from Bi3+ to Eu3+ is a typical resonance. The match of energy levels is necessary for the resonance of energy transfer according to the formula of Dexter.16

\[
P_{SA} = \frac{2\pi}{\hbar} \int |\langle S' | H_{SA} | S \rangle|^2 \delta(E_E - E_S) dE_E
\]

where the matrix represents the interaction (and HSA is the interaction Hamiltonian) between the initial state |SSA⟩ and the final state |S'⟩; S and A represent the emitter and the absorber; gS(E) and gA(E) are normalized optical line shape functions, and the integral represents the spectral overlap, respectively. Moreover, energy may transfer from polyanions of VO43- to Eu3+ through charge transfer.24 Thus, the transfer of energy in the (Gd-Y-Bi-Eu)VO4 system can be depicted schematically as Fig. 14.

Conclusions

Instead of developing a red phosphor individually, a special yellow phosphor that emits red and green simultaneously is desired for combining with a blue phosphor and NUV diode chip to produce white light with high color rendering. This special yellow phosphor has been screened out from a (Gd-Y-Bi-Eu)VO4 quaternary system by using a combinatorial approach. When the emission color, luminous efficiency and thermal stability of luminescence are all considered, the best composition range that is most desirable for producing white light is optimized as (Gd1-r-s-t-YrBisEut)VO4 with 0.7 < r < 1.0, 0.040 < s = 0.050 and 0 < t < 0.015, depending on the blue phosphor (CIE coordinates) and diode chip (excitation wavelength) used. When excited with NUV, (Gd,Y)VO4:Eu3+ cannot emit efficiently for the deficiency of energy transfer from host to activator. Doping with Bi3+ makes (Gd,Y)VO4:Eu3+ more suitable for use as a NUV LED phosphor, for promoting the red-shift of the excitation band. A little Gd3+ co-doped into YVO4:Bi3+,Eu3+ is helpful for improving the thermal stability of luminescence, but too much detrimentally affects its luminescence efficiency. The mechanisms for these phenomena are exploited.

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