Bi$^{3+}$ and Eu$^{3+}$ Activated Luminescent Behaviors in Non-Stoichiometric LaO$_{0.65}$F$_{1.7}$ Structure

Sungjun Yang and Sangmoon Park

Division of Energy Convergence Engineering, Major in Energy & Applied Chemistry, Silla University, Busan 46958, Korea; qse7417@naver.com
* Correspondence: spark@silla.ac.kr; Tel.: +82-51-999-5891

Received: 24 April 2020; Accepted: 16 May 2020; Published: 19 May 2020

Abstract: Optical materials composed of La$_{1-p}$Bi$_p$Eu$_q$O$_{0.65}$F$_{1.7}$ ($p = 0.001$–$0.05$, $q = 0$–$0.1$) were prepared via a solid-state reaction using La(Bi, Eu)$_3$O$_3$ and NH$_4$F precursors at 1050 °C for two hours. X-ray diffraction patterns of the phosphors were obtained permitting the calculation of unit-cell parameters. The two La$^{3+}$ cation sites were clearly distinguished by exploiting the photoluminescence excitation and emission spectra through Bi$^{3+}$ and Eu$^{3+}$ transitions in the non-stoichiometric host lattice. Energy transfer from Bi$^{3+}$ to Eu$^{3+}$ upon excitation with 286 nm radiation and its mechanism in the Bi$^{3+}$- and Eu$^{3+}$-doped host structures is discussed. The desired Commission Internationale de l’Eclairage values, including emissions in blue-green, white, and red wavelength regions, were obtained from the Bi$^{3+}$- and Eu$^{3+}$-doped LaO$_{0.65}$F$_{1.7}$ phosphors.

Keywords: X-ray diffraction; phosphors; Bi$^{3+}$, Eu$^{3+}$ transitions; energy transfer

1. Introduction

Ce$^{3+}$-doped Y$_3$Al$_5$O$_{12}$ (YAG) yellow phosphors are commonly used with blue light-emitting diodes (LEDs) to create white light sources [1–5]. The Ce$^{3+}$ ions emit in the blue to yellow wavelength regions assigned by $5d^1$ to $4f^1$ transitions when excited by ultraviolet (UV) to visible radiation in various host lattices [6–9]. The Ce$^{3+}$ ion, as a donor, enables efficient energy transfer, improving the emission from acceptors, such as Tb$^{3+}$ or Mn$^{2+}$ ions in the host structures [10–18]. The Bi$^{3+}$ ion is an active luminescent center emitting blue to green light assigned to 6s$^1$6p$^1$ to 6s$^2$ transitions when excited by UV to near UV wavelength regions in host lattices [19–21]. The energy levels of the Bi$^{3+}$ 6s$^2$–6s$^1$6p$^1$ transitions consist of $^1$S$^0$ and the triplet $^3$P$^1$ ($J = 0$, 1, or 2) and singlet $^1$P$^1$ states. The $^1$S$^0$ to $^3$P$^1$, $^1$P$^1$ transitions occur via spin-orbital coupling [19–21]. The states of the $^1$S$^0$ to $^3$P$^0$ and $^3$P$^2$ transitions are forbidden [19–21]. Like Ce$^{3+}$ ions, Bi$^{3+}$ ions act as sensitizers to enhance the anticipated emission light from acceptors, such as Eu$^{3+}$ or Tb$^{3+}$ ions in host structures, by facilitating efficient energy transfer [22–26].

The up-conversion properties of Er$^{3+}$- and Yb$^{3+}$-doped LaO$_{0.65}$F$_{1.7}$ compounds were exploited under 980 nm diode laser excitation in a previous study [27]. This non-stoichiometric LaO$_{0.65}$F$_{1.7}$ host comprises alternating stacked LaO$_2$F$_7$ and LaO$_2$F$_7$ layers along the c axis with tetragonal space group $P4/nmm$, as shown in Figure 1 [27,28]. The 9- and 10-coordinated La$^{3+}$ sites in the LaF(1)$_3$F(2)$_2$O$_2$F(3)$_2$ and LaF(1)$_4$F(2)O$_3$F(3)$_2$ polyhedrons are located in accordance with the LaF(1)$_{0.85}$VF(2)$_{0.35}$O$_{0.65}$F(3)$_{0.49}$ lattice of the LaO$_{0.65}$F$_{1.7}$ host structure [27,28]. Notably, the nine-fold LaF(1)$_3$VF(2)$_2$O$_2$F(3)$_2$ polyhedron contains a vacancy (V) associated with the F(1) anion.

In this study, Bi$^{3+}$ and Eu$^{3+}$ were substituted into LaO$_{0.65}$F$_{1.7}$ compounds that were synthesized by a solid-state method using NH$_4$F flux in air. The unit-cell parameters of the phosphors were calculated. The excitation and emission luminescence spectra of the La$_{1-p}$Bi$_p$Eu$_q$O$_{0.65}$F$_{1.7}$ ($p = 0.001$–$0.05$, $q = 0$–$0.1$) phosphors were investigated with respect to the site dependency of Bi$^{3+}$ and Eu$^{3+}$ ions in the host.
structure. The energy transfer mechanism from Bi\textsuperscript{3+} to Eu\textsuperscript{3+} in the phosphors was explored. Commission Internationale de l’Eclairage (CIE) chromaticity coordinates of the phosphors were obtained.

2. Materials and Methods

Phosphors of La\textsubscript{1-p-q}Bi\textsubscript{p}Eu\textsubscript{q}O\textsubscript{0.65}F\textsubscript{1.7} (p = 0.005–0.05, q = 0–0.1) were prepared by heating the appropriate amounts of La\textsubscript{2}O\textsubscript{3} (Alfa 99.9%), Bi\textsubscript{2}O\textsubscript{3} (Alfa 99.99%), Eu\textsubscript{2}O\textsubscript{3} (Alfa 99.9%), and NH\textsubscript{4}F (Alfa 99%). Powdered samples with 1:2 molar ratios of La(Bi,Eu)O\textsubscript{3}/2 and NH\textsubscript{4}F were used to prepare nonstoichiometric La\textsubscript{0.65}F\textsubscript{1.7}:Bi\textsuperscript{3+}, Eu\textsuperscript{3+}. The precursors were mixed with an agate mortar and pestle and subsequently heated at 1050 °C for 2 h in air [27]. The La\textsubscript{2}O\textsubscript{3} precursor was pre-heated at 700 °C for 3 h to remove hydroxide in the sample. Phase identification of the phosphors was performed using a Shimadzu XRD-6000 powder diffractometer (Cu-Kα radiation, Shimadzu CO., Kyoto, Japan). The Rietveld refinement program Rietica was used for the unit-cell parameter calculations.

3. Results and Discussion

The crystallographic phase of the La\textsubscript{1-p-q}Bi\textsubscript{p}Eu\textsubscript{q}O\textsubscript{0.65}F\textsubscript{1.7} (p = 0.001–0.05, q = 0–0.1) powders was identified using powder X-ray diffraction (XRD) patterns. The calculated XRD pattern of the tetragonal La\textsubscript{0.65}F\textsubscript{1.7} (ICSD 40371) structure is shown in Figure 2A. Figure 2B–F show the XRD patterns of non-stoichiometric La\textsubscript{1-p-q}Bi\textsubscript{p}Eu\textsubscript{q}O\textsubscript{0.65}F\textsubscript{1.7} phosphors (p = 0.01 and q = 0, p = 0.05 and q = 0, p = 0 and q = 0.05, p = 0 and q = 0.1, and p = 0.01 and q = 0.1, respectively), synthesized by the mixing of \( \frac{1}{2}\)La(Bi,Eu)\textsubscript{2}O\textsubscript{3} and NH\textsubscript{4}F at 1050 °C in air. The XRD patterns of the obtained phosphors in Figure 2B–F show a single-phase structure without any noticeable impurities indexed to a tetragonal unit cell. The unit cells of La\textsubscript{0.99}Bi\textsubscript{0.01}O\textsubscript{0.65}F\textsubscript{1.7}, La\textsubscript{0.95}Bi\textsubscript{0.05}O\textsubscript{0.65}F\textsubscript{1.7}, La\textsubscript{0.95}Eu\textsubscript{0.05}O\textsubscript{0.65}F\textsubscript{1.7}, La\textsubscript{0.9}Eu\textsubscript{0.1}O\textsubscript{0.65}F\textsubscript{1.7}, and La\textsubscript{0.89}Bi\textsubscript{0.01}Eu\textsubscript{0.01}O\textsubscript{0.65}F\textsubscript{1.7} phosphors were calculated to be a = 4.0934 (1) Å and c = 5.8336 (2) Å, a = 4.1018 (2) Å and c = 5.8315 (2) Å, a = 4.0833 (2) Å and c = 5.8162 (4) Å, a = 4.0788 (3) Å and c = 5.8095 (5) Å, and a = 4.0993(3) Å and c = 5.7712(6) Å, respectively, using the Rietveld refinement. The unit-cell parameters, including the cell volumes of the phosphors, are summarized in Table 1. The Bi\textsuperscript{3+} and Eu\textsuperscript{3+} ions, under these conditions, occupy 9- and 10-coordinated La\textsuperscript{3+} sites (LaF(1)\textsubscript{3}F(2)\textsubscript{2}O\textsubscript{2}F(3)\textsubscript{2} and LaF(1)\textsubscript{4}F(2)\textsubscript{2}O(3)\textsubscript{3})(F(3)\textsubscript{2}) in the non-stoichiometric La\textsubscript{0.65}F\textsubscript{1.7} structure, as shown in Figure 1 [27,28]. The single La\textsuperscript{3+} site comprises 56% 9-fold and 44% 10-fold polyhedrons in the La\textsubscript{0.65}F\textsubscript{1.7} lattice based on the La(F(1)\textsubscript{0.86}V\textsubscript{0.14})(F(2)\textsubscript{0.35}O\textsubscript{0.65})(F(3)\textsubscript{0.49}) formula. The 9- and 10- coordinated LaO\textsubscript{2}F\textsubscript{2} and LaO\textsubscript{2}F\textsubscript{7} polyhedrons in the non-stoichiometric unit cell are arrayed along the c-axis, as shown in Figure 1. When Bi\textsuperscript{3+} ions (r = 1.17 Å for 8 coordination number (CN)) were substituted for La\textsuperscript{3+} ions (r = 1.16 Å for 8 CN) in the La\textsubscript{0.65}F\textsubscript{1.7} host lattice, gradual shifts in the positions of the various Bragg reflections

![Figure 1. The structure of tetragonal LaO\textsubscript{0.65}F\textsubscript{1.7} host lattice.](image-url)
to lower angles with unit-cell expansion were observed, as shown in Figure 2B,C. When Eu$^{3+}$ ions ($r = 1.066 \text{ Å}$ for 8 CN) were substituted for La$^{3+}$ ions in the host lattice, gradual shifts in the positions of the various Bragg reflections to higher angles with unit-cell contraction were observed, as shown in Figure 2D,E. When the Bi$^{3+}$ ions were doped in the La$_{0.89}$Eu$_{0.01}$O$_{0.65}$F$_{1.7}$ phosphors, no further shift to higher angles was observed in the La$_{0.89}$Bi$_{0.01}$Eu$_{0.01}$O$_{0.65}$F$_{1.7}$ phosphors, as shown in Figure 2F.

| Phosphors               | a (Å)     | c (Å)     | V (Å$^3$) | $R_p$ |
|-------------------------|-----------|-----------|-----------|-------|
| La$_{0.99}$Bi$_{0.01}$O$_{0.65}$F$_{1.7}$ | 4.0934 (1) | 5.8336 (2) | 97.75 (1) | 9.11  |
| La$_{0.95}$Bi$_{0.05}$O$_{0.65}$F$_{1.7}$ | 4.1018 (2) | 5.8315 (2) | 98.11 (1) | 9.98  |
| La$_{0.95}$Eu$_{0.05}$O$_{0.65}$F$_{1.7}$ | 4.0833 (2) | 5.8162 (4) | 96.98 (1) | 9.46  |
| La$_{0.9}$Eu$_{0.1}$O$_{0.65}$F$_{1.7}$   | 4.0788 (3) | 5.8095 (5) | 96.65 (1) | 8.95  |
| La$_{0.88}$Bi$_{0.01}$Eu$_{0.01}$O$_{0.65}$F$_{1.7}$ | 4.0993 (3) | 5.7712 (6) | 96.98 (1) | 9.62  |

Figure 2A–E show the photoluminescence (PL), excitation (EX), and emission (EM) spectra of the Bi-doped La$_{1-p}$Bi$_p$O$_{0.65}$F$_{1.7}$ phosphors ($p = 0.001, 0.005, 0.01, 0.025, \text{ and } 0.05$, respectively). The excitation band centered near 278 and 286 nm in the La$_{0.99}$Bi$_{0.01}$O$_{0.65}$F$_{1.7}$ PL spectra is attributed to the $^1S_0 \rightarrow 3P_1$ transition of Bi$^{3+}$ ions because the $^1S_0 \rightarrow 3P_0$ and $^1S_0 \rightarrow 3P_2$ transitions are forbidden from ground $^1S_0$ [19–26]. The blue emission spectra of the La$_{0.65}$F$_{1.7}$:Bi$^{3+}$ phosphors revealed a broadband range from 350 to 650 nm, centered at approximately 497 nm, which is attributed to the intense $^3P_1 \rightarrow 1S_0$ transitions of the Bi$^{3+}$ ions, as shown in Figure 3a. When the Bi$^{3+}$ concentration in the host lattice was 1 mol %, the maximum emission intensity of the obtained phosphors was observed at the excitation wavelength of 278 nm, as shown in Figure 3aC. After the Bi$^{3+}$ concentration was increased 2.5 mol % in the phosphors, the centered excitation peak shifted to a higher wavelength region from 278 to 286 nm, as shown in Figure 3aD,E. Thus, as the Bi$^{3+}$ content in the La$_{0.65}$F$_{1.7}$ host lattice was increased and the excitation center of the $^1S_0 \rightarrow 3P_1$ transition of Bi$^{3+}$ ions underwent a shift to a longer wavelength. The La$^{3+}$ ion is coordinated by seven F$^-$ and three O$^{2-}$ anions (LaF$_{1.5}$F$_2$O$_2$F$_3$)$_2$, or seven F$^-$ and two O$^{2-}$ anions (LaF$_{1.5}$F$_2$O$_2$F$_3$)$_2$ in the La$_{0.65}$F$_{1.7}$ host structure [27,28]. As depicted in Figure 1, there was a vacancy associated with the F(1) anion in the LaF$_{1.5}$F$_2$O$_2$F$_3$$_2$ polyhedron. Based on the ratios of oxygen and fluoride to lanthanum, the LaF$_{1.5}$F$_2$O$_2$F$_3$$_2$ polyhedron had a lower oxygen ion covalency than LaF$_{1.5}$F$_2$O$_2$F$_3$$_2$ polyhedrons in the structure. This observation indicated that Bi$^{3+}$ ions are preferentially substituted in the nine-fold La site and subsequently doped into the...
10-fold La site in the host structure. Figure 3b shows the excitation and emission PL spectra of the La$_{0.95}$Eu$_{0.05}$O$_{0.65}$F$_{1.7}$ phosphors. The charge-transfer bands (CTBs) and the $f$-$f$ transitions of the Eu$^{3+}$ activator in the host lattice were observed at 220–350 and 350–540 nm, respectively. Two CTBs centered at 290 and 320 nm were found in the excitation spectra because there were two La$^{3+}$ sites associated with the LaF$(1)_3$F$(2)$O$_2$F$(3)_2$ and LaF$(1)_4$F$(2)$O$_3$F$(3)_2$ polyhedrons in the host structure. When Eu$^{3+}$ ions were doped in the nine-coordinated La$^{3+}$ site of the LaF$(1)_3$F$(2)$O$_2$F$(3)_2$ polyhedron, the center of the Eu$^{3+}$ CTB transitions occurred at 290 nm. Additional energy was required to excite an electron from the Eu$^{3+}$ ions in seven F$^-$ and two O$^{2-}$ containing lattices, compared to seven F$^-$ and three O$^{2-}$ polyhedrons.

The Eu$^{3+}$ transitions of the emission spectra in the La$_{0.95}$Eu$_{0.05}$O$_{0.65}$F$_{1.7}$ phosphors exhibited both the $^5$D$_{0}$–$^7$F$_1$ magnetic dipole and the $^5$D$_{0}$–$^7$F$_2$ electric-dipole transitions, centered at 592 and 610 nm, respectively [29,30]. When the Eu$^{3+}$ ions were substituted in no inversion site of the nine-coordinated polyhedron in the host lattice, the $^5$D$_{0}$–$^7$F$_2$ transition dominates. When the Eu$^{3+}$ activators were doped into symmetric inversion site of the 10-fold polyhedron, the $^5$D$_{0}$–$^7$F$_1$ transition dominates. Figure 3c shows the excitation spectra of the La$_{0.95}$Eu$_{0.05}$O$_{0.65}$F$_{1.7}$ (EX$_{EM}$=610nm and EX$_{EM}$=592nm) and the emission spectrum of La$_{0.95}$Bi$_{0.05}$O$_{0.65}$F$_{1.7}$ (EM$_{EX}$=286nm) phosphors. The efficiency of energy transfer from Bi$^{3+}$ to Eu$^{3+}$ was estimated by the spectral overlap between the excitation of the Eu$^{3+}$ transition and the emission band of Bi$^{3+}$ ions in the host lattice [31]. The excitation spectrum of the La$_{0.95}$Eu$_{0.05}$O$_{0.65}$F$_{1.7}$ (EX$_{EM}$=610nm) phosphor and the emission spectrum of the La$_{0.99}$Bi$_{0.01}$O$_{0.65}$F$_{1.7}$ (EM$_{EX}$=286nm) phosphor exhibited considerable overlap, as shown in the top of Figure 3c. This indicated that effective energy transfer from Bi$^{3+}$ to Eu$^{3+}$ ions occurs in the nine-coordinated La$^{3+}$ site of the LaF$(1)_3$F$(2)$O$_2$F$(3)_2$ polyhedron in the La$_{0.95}$F$_{1.7}$ host structure. The individual transitions of Bi$^{3+}$ and Eu$^{3+}$ ions with the energy transfer from Bi$^{3+}$ to Eu$^{3+}$ ions in the phosphors can simultaneously occur under approximately 290 nm excitation wavelength. However, the energy transfer was effectively observed rather than the individual transitions because the integrated emission intensity of Eu$^{3+}$ transition was enhanced by approximately 91% from La$_{0.95}$Eu$_{0.05}$O$_{0.65}$F$_{1.7}$ to La$_{0.94}$Bi$_{0.05}$O$_{0.65}$F$_{1.7}$ phosphors (Figure S1). The blue-green emission of the La$_{1.0}$Bi$_{0.0}$O$_{0.65}$F$_{1.7}$ phosphors centered at 497 nm reached a maximum intensity for a Bi$^{3+}$ content ($p = 0.01$), as shown in Figure 3a. After increasing the Bi$^{3+}$ content, concentration quenching of the relative emission intensity was observed. The increase in the Bi$^{3+}$ content of the phosphors enhanced energy transfer up to some critical value, whereas after this value was reached subsequent increase of Bi$^{3+}$ levels decreased the emission intensity by reducing the critical distance between the Bi$^{3+}$ ions. This resulted in non-radiative energy transfer between Bi$^{3+}$ ions from the electric multipole interactions. The critical distance ($R_c$) is expressed by the following formula:

$$R_c = 2[3V/(4\pi m_c N)]^{1/3}$$  \hspace{1cm} (1)

where $V$ is the volume of the La$_{0.90}$Bi$_{0.01}$O$_{0.65}$F$_{1.7}$ unit cell, $N$ is the number of available La$^{3+}$ sites for the dopant in the unit cell, $m_c$ is the critical concentration of Bi$^{3+}$, and $R_c$ is the critical distance for energy transfer [10,22–24,32]. When $N$ and $V$ are 1 and 97.75 Å$^3$, respectively, for La$_{0.99}$Bi$_{0.01}$O$_{0.65}$F$_{1.7}$, $R_c$ ($m_c = 0.01$) is 26.53 Å. The energy transfer mechanism designated an electric multipole quenching because the critical distance is greater than 5 Å. Figure 4a shows the emission spectra of La$_{0.99}$Bi$_{0.01}$Eu$_{0.05}$O$_{0.65}$F$_{1.7}$ ($q = 0–0.1$) phosphors under 286 nm excitation. Co-doping of Eu$^{3+}$ into the Bi$^{3+}$-doped La$_{0.95}$F$_{1.7}$ host structure allowed effective energy transfer from Bi$^{3+}$ to Eu$^{3+}$ under excitation at 286 nm. The energy transfer from Bi$^{3+}$ to Eu$^{3+}$ acted as a sensitizer and an activator, respectively, in the La$_{0.99-q}$Bi$_{0.01}$Eu$_{0.05}$O$_{0.65}$F$_{1.7}$ ($q = 0–0.1$) phosphors, which was activated through the absorption from Bi$^{3+}$ transitions. The energy transfer efficiency ($\eta_T$) was evaluated using the following formula:

$$\eta_T = 1 - I_s/I_{SO}$$  \hspace{1cm} (2)

where $I_s$ and $I_{SO}$ are the luminescence intensities of the Bi$^{3+}$ sensitizer in the presence and absence of a Eu$^{3+}$ activator, respectively [10,22–24,32]. The emission of Eu$^{3+}$ transitions was maximized when
the Eu$^{3+}$ content in the La$_{0.99-q}$Bi$_{0.01}$Eu$_q$O$_{0.65}$F$_{1.7}$ ($q = 0$–$0.1$) phosphors was $q = 0.05$. The energy transfer mechanism could be represented by linear plots of $I_{S0}/I_S$ versus $C_{Bi-Eu}^{\alpha/3}$, where $C_{Bi-Eu}$ is the concentration of Bi$^{3+}$ and Eu$^{3+}$ ions, with $\alpha = 6$, 8, or 10, corresponding to dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively, in accordance with Dexter theory [10,22–24,32]. In Figure 4b, when $\alpha = 6$, 8, and 10, the linear plots showed energy transfer from the Bi$^{3+}$ to Eu$^{3+}$ ions with $R^2 = 0.9635$, 0.9894, and 0.9982 in the La$_{0.94}$Bi$_{0.01}$Eu$_{0.05}$O$_{0.65}$F$_{1.7}$ phosphors, respectively. As the value of $\alpha$ is 10, a closer linear plot is determined for the phosphor, the quadrupole–quadrupole interaction was involved in the energy transfer mechanism of the La$_{0.94}$Bi$_{0.01}$Eu$_{0.05}$O$_{0.65}$F$_{1.7}$ phosphors. The efficiency of the energy transfer from Bi$^{3+}$ to Eu$^{3+}$ in La$_{0.94}$Bi$_{0.01}$Eu$_{0.05}$O$_{0.65}$F$_{1.7}$ (EX = 286 nm) phosphors is shown in Figure 4c. The efficiency was gradually enhanced from 23% to 97% as the Eu$^{3+}$ content in the phosphors increased from $q = 0.01$ to 0.1.

**Figure 3.** PL excitation and emission spectra of (a) La$_{1-p}$Bi$_p$O$_{0.65}$F$_{1.7}$ phosphors (A) $p = 0.001$, (B) 0.005, (C) 0.01, (D) 0.025, and (E) 0.05; and (b) La$_{0.95}$Eu$_{0.05}$O$_{0.65}$F$_{1.7}$ phosphors; and (c) the excitation spectra of the La$_{0.95}$Eu$_{0.05}$O$_{0.65}$F$_{1.7}$ and the emission spectrum of La$_{0.99}$Bi$_{0.01}$O$_{0.65}$F$_{1.7}$.

**Figure 4.** Cont.
The CIE coordinates near the blue-green, white, orange, and red regions of the CIE diagram from phosphors under 254, 312, and 365 nm hand-lamp excitation was exhibited blue-green, white, orange, and red colors, as shown in Figure 5b. This indicates that there was effective energy transfer from Bi³⁺ to Eu³⁺ in the phosphors.

As shown in Figure 5a, the chromaticity coordinates, x and y, are in accordance with the desired CIE (Commission Internationale de l’Eclairage) values from the blue-green to white and red wavelength regions for La₀.₉₉₋ₚBi₀.₀₁ₚEuₓ⁢₀₋ₚ₀.₆₅ₐF₁.₇ (q = 0–0.1) phosphors (EX = 286 nm). The CIE values are summarized in the inset of Figure 5a, along with the values obtained for the phosphors. The CIE coordinates near the blue-green, white, orange, and red regions of the CIE diagram from the phosphors were observed to be x = 0.240 and y = 0.344, x = 0.328 and y = 0.348, x = 0.466 and y = 0.354, and x = 0.591 and y = 0.353, for values of q = 0, 0.02, 0.05, and 0.1, respectively. When the concentration of Eu³⁺ ions in the La₀.₉₉₋ₚBi₀.₀₁ₚEuₓ⁢₀₋ₚ₀.₆₅ₐF₁.₇ phosphors increased from q = 0 to 0.02 and 0.1, the emission colors exhibited a significant shift from blue-green to white, and red emission regions, respectively. These tunable emission lights are appropriate for a high color-rendering index to apply phosphor converted UV-LEDs. This indicates that there was effective energy transfer from Bi³⁺ to Eu³⁺ in the La₀.₉₉₋ₚBi₀.₀₁ₚEuₓ⁢₀₋ₚ₀.₆₅ₐF₁.₇ phosphors. Emission of the La₀.₉₉₋ₚBi₀.₀₁ₚEuₓ⁢₀₋ₚ₀.₆₅ₐF₁.₇ (q = 0–0.1) phosphors under 254, 312, and 365 nm hand-lamp excitation was exhibited blue-green, white, orange, and red colors, as shown in Figure 5b.

Figure 4. (a) The emission spectra of La₀.₉₉₋ₚBi₀.₀₁ₚEuₓ⁢₀₋ₚ₀.₆₅ₐF₁.₇ (q = 0–0.1) phosphors under 286 nm excitation, (b) the plot of Iₓ/Cₓ versus CₓEu⁢ₓ (x = 6, 8, 10), and (c) energy transfer efficiency from Bi³⁺ to Eu³⁺ in the phosphors.

Figure 5. (a) The chromaticity coordinates with the desired CIE values of La₀.₉₉₋ₚBi₀.₀₁ₚEuₓ⁢₀₋ₚ₀.₆₅ₐF₁.₇ (q = 0–0.1) phosphors (EX = 286 nm) and (b) photographs of the emission light from blue-green to white, orange, and red colors in the La₀.₉₉₋ₚBi₀.₀₁ₚEuₓ⁢₀₋ₚ₀.₆₅ₐF₁.₇ phosphors under 254, 312, and 365 nm hand-lamps.
4. Conclusions

Non-stoichiometric tetragonal La_{1-p-q}Bi_{p}Eu_{q}O_{0.65}F_{1.7} (p = 0.001–0.05, q = 0–0.1) phosphors were prepared via a solid-state method using a heat treatment at 1050 °C for two hours using NH₄F flux. The site dependency of the Bi³⁺ and Eu³⁺ ions in the LaF(1)F(2)O₂F(3) and LaF(1)O₂F(3)₂ polyhedrons of the host structure was analyzed using the PL spectra of the phosphors. The maximum luminescence intensity of the blue-green La_{1-p-q}Bi_{p}O_{0.65}F_{1.7} phosphors was obtained when p = 0.01. The critical distance (Rc) value for the La_{0.99}Bi_{0.01}O_{0.65}F_{1.7} phosphor was determined to be 26.53 Å. As the Eu³⁺ concentration was increased in La_{0.99}Bi_{0.01}Eu_{q}O_{0.65}F_{1.7} (q = 0–0.1) phosphors under 286 nm excitation, an efficient energy transfer from Bi³⁺ to Eu³⁺ occurred, involving quadrupole–quadrupole interactions in the phosphors. The CIE coordinate values attributed to the emissions from blue-green, white, and red for La_{0.99, q}Bi_{0.01}Eu_{q}O_{0.65}F_{1.7} (q = 0–0.1) phosphors were successfully obtained.

Supplementary Materials: The following are available online at http://www.mdpi.com/1996-1443/13/10/2326/s1, Figure S1: The integrated emission intensities of La_{0.95}Eu_{0.05}O_{0.65}F_{1.7} and La_{0.94}Bi_{0.05}O_{0.65}F_{1.7} phosphors.

Author Contributions: Conceptualization, S.P.; methodology, S.P.; software, S.Y.; validation, S.P. and S.Y.; formal analysis, S.Y.; investigation, S.Y.; resources, S.Y.; data curation, S.Y.; writing—original draft preparation, S.Y.; visualization, S.Y.; supervision, S.P.; project administration, S.P.; funding acquisition, S.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Basic Science Research Program through the National Research Foundation of Korea (NRF), grant number NRF-2018R1D1A3B07048543.

Acknowledgments: This work was supported by the BB21+ Project in 2018. Authors thank to T. Jung for his help.

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

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