



# Article Nonstoichiometric LaO<sub>0.65</sub>F<sub>1.7</sub> Structure and Its Green Luminescence Property Doped with Bi<sup>3+</sup> and Tb<sup>3+</sup> Ions for Applying White UV LEDs

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**Abstract:** Red–green–blue phosphors excited by ultraviolet (UV) radiation for white light LEDs have received much attention to improve the efficiency, color rendering index (CRI), and chromatic stability. The spectral conversion of a rare-earth ion-doped nonstoichiometric LaO<sub>0.65</sub>F<sub>1.7</sub> host was explored with structural analysis in this report. The nonstoichiometric structure of a LaO<sub>0.65</sub>F<sub>1.7</sub> compound, synthesized by a solid-state reaction using La<sub>2</sub>O<sub>3</sub> and excess NH<sub>4</sub>F precursors, was analyzed by synchrotron X-ray powder diffraction. The crystallized LaO<sub>0.65</sub>F<sub>1.7</sub> host, which had a tetragonal space group of *P4/mm*, contained 9- and 10-coordinated La<sup>3+</sup> sites. Optical materials composed of La<sub>1-*p*-*q*</sub>Bi<sub>*p*</sub>Tb<sub>*q*</sub>O<sub>0.65</sub>F<sub>1.7</sub> (*p* = 0 and 0.01; *q* = 0–0.2) were prepared at 1050 °C for 2 h, and the single phase of the obtained phosphors was indexed by X-ray diffraction analysis. The photoluminescence spectra of the energy transfer from Bi<sup>3+</sup> to Tb<sup>3+</sup> were obtained upon excitation at 286 nm in the nonstoichiometric host lattice. The desired Commission Internationale de l'Eclairage (CIE) values of the phosphors were calculated. The intense green La<sub>0.89</sub>Bi<sub>0.01</sub>Tb<sub>0.1</sub>O<sub>0.65</sub>F<sub>1.7</sub> phosphor with blue and red optical materials was fabricated on a 275 nm UV-LED chip, resulting in white light, and the internal quantum efficiency, CRI, correlated color temperature, and CIE of the pc LED were characterized.

Keywords: X-ray diffraction; phosphors; Bi<sup>3+</sup>; Tb<sup>3+</sup> energy transfer; pc LED

## 1. Introduction

Phosphor-converted light-emitting diodes (pc LEDs) have been developed as common light sources for various lighting and display industries [1–5]. Yellow garnet phosphors, such as Ce<sup>3+</sup>-doped Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> compounds, fabricated on blue LED chips are widely used to generate white light sources. LEDs have excellent advantages, such as low cost and easy fabrication; however, they have several weaknesses such as relatively low efficiency, color rendering index (CRI), and chromatic stability [1–5]. Meanwhile, red–green–blue (RGB) pc LEDs excited by ultraviolet (UV) radiation have strengths, such as higher efficiency and a CRI with higher chromatic stability when subjected to different driving currents, compared with blue-excitable pc LEDs [1–5]. Although RGB tri-color phosphors are intricately blended for fabrication on an LED chip, specific mixtures of RGB phosphors can result in tunable color temperatures. When excited by UV radiation in various host lattices, Bi<sup>3+</sup> ions can emit radiation in the blue-to-green wavelength regions associated with  $6s^{1}6p^{1}$  to  $6s^{2}$  transitions [6–10]. The Bi<sup>3+</sup> ion, behaving as a donor, can facilitate energy transfer and improve the emission of light from acceptors in the host structures such as  $Eu^{3+}$  or  $Tb^{3+}$  ions [6–10]. The Bi<sup>3+</sup> and  $Eu^{3+}$  codoped nonstoichiometric LaO<sub>0.65</sub>F<sub>1.7</sub> phosphor was utilized, as a red emitter, under UV excitation in a previous study [6]. The nonstoichiometric LaO<sub>0.65</sub>F<sub>1.7</sub> host has advantageous optical qualities when compared with



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). stoichiometric LaOF compounds [6,11,12]. Rare-earth ion-doped nonstoichiometric hosts show a broad excitation range with stronger Stark splitting. Furthermore, they have better spectral conversion properties owing to their low nonradiative relaxation caused by the low phonon frequency [6,11,12]. The LaO<sub>0.65</sub>F<sub>1.7</sub> lattice, which is stacked by 9-coordinated LaO<sub>2</sub>F<sub>7</sub> and 10-coordinated LaO<sub>3</sub>F<sub>7</sub> layers along the *c*-axis with the tetragonal space group *P4/nmm*, was studied by high-resolution powder neutron diffraction analysis [13]. The single phase of the  $LaO_{0.65}F_{1.7}$  host was synthesized using a high temperature and long reaction period at 1200 °C for 2 d in a nickel-sealed tube [13]. In this study, a LaO<sub>0.65</sub>F<sub>1.7</sub> host was prepared using the flux method at 1050 °C for 2 h in air [6,11]. The nonstoichiometric LaO<sub>0.65</sub>F<sub>1.7</sub> structure was refined using synchrotron powder X-ray diffraction data at room temperature. The luminescence spectra of the  $La_{1-p-q}Bi_pTb_qO_{0.65}F_{1.7}$  (p = 0 and 0.01; q = 0-0.2) phosphors were explored by examining the energy-transfer mechanism from Bi<sup>3+</sup> to  $Tb^{3+}$ . UV-excitable white light was emitted using a green  $La_{0.96}Bi_{0.01}Tb_{0.02}Eu_{0.01}O_{0.65}F_{1.7}$ phosphor with blue and red phosphors on a 275 nm UV-LED chip. The internal quantum efficiency (IQE), CRI, correlated color temperature (CCT), and Commission Internationale de l'Eclairage (CIE) coordinates of the RGB pc LEDs were calculated.

### 2. Experimental Section

Synchrotron powder X-ray diffraction data of the nonstoichiometric  $LaO_{0.65}F_{1.7}$  host were collected at the PLS-II 6D UNIST-PAL beamline of the Pohang Accelerator Laboratory (PAL). The powdered sample was loaded into a quartz capillary (diameter: 200  $\mu$ m) and rotated during the data collection to eliminate the preferred orientation effect. Monochromatic X-rays ( $\lambda = 0.65303$  Å, 18.986 keV) and a charge-coupled device detector (MX225-HS, Rayonix, Evanston, IL, USA) were used in these experiments [14]. The  $LaO_{0.65}F_{1.7}$  structure was refined using the Rietveld refinement program FullProf Suite [15,16]. Phosphors of  $La_{1-p-q}Bi_pTb_qO_{0.65}F_{1.7}$  (p = 0 and 0.01; q = 0–0.2) were prepared by heating the appropriate stoichiometric molar amounts of La<sub>2</sub>O<sub>3</sub> (Alfa 99.9%), Bi<sub>2</sub>O<sub>3</sub> (Alfa 99.99%), and Tb<sub>4</sub>O<sub>7</sub> (Alfa 99.9%) with excess NH<sub>4</sub>F (Alfa 99%) precursor [6,11]. Powdered samples with 1:2 molar ratios of La(Bi,Tb)O<sub>3/2</sub> and NH<sub>4</sub>F were used to prepare the LaO<sub>0.65</sub> $F_{1.7}$ :Bi<sup>3+</sup> and  $Tb^{3+}$  phosphors. The La(Bi,Tb)O<sub>3/2</sub> and NH<sub>4</sub>F precursors were mixed using an agate mortar and pestle and, subsequently, heated at 1050  $^{\circ}$ C for 2 h in air [6,11]. The La<sub>2</sub>O<sub>3</sub> precursor was used after preheating at 700 °C for 3 h to remove hydroxide from the acquired sample. The phase identification of the  $La_{1-p-q}Bi_pTb_qO_{0.65}F_{1.7}$  phosphors was performed using a Shimadzu XRD-6000 powder diffractometer (Cu- $K\alpha$  radiation). The excitation and emission photoluminescent spectra of the phosphors were measured using a spectrofluorometer (Sinco Fluoromate FS-2, Seoul, Korea). The pc LED was fabricated by packing the green  $La_{0.96}Bi_{0.01}Tb_{0.02}Eu_{0.01}O_{0.65}F_{1.7}$ , blue  $Ba_4Ca_5Al_2Si_6O_{24}$ :Ce,Na, and red LaO<sub>0.65</sub>F<sub>1.7</sub>:Bi,Eu phosphors in-between quartz glasses on a 275 nm LED chip (Seoul Semiconductor, Ansan-si, Korea). A spectrometer (USB4000, Ocean Optics, Dunedin, FL, USA) was used to measure the CRI, CCT, CIE coordinates, and IQE of the white-light pc LEDs.

#### 3. Results and Discussion

Rietveld refinement fitting of the synchrotron powder X-ray diffraction data of the nonstoichiometric LaO<sub>0.65</sub>F<sub>1.7</sub> structure at room temperature is shown in Figure 1. Unidentified small impurities at approximately 14° and between 15 and 18°, which are marked, were observed in the experimental XRD data. The refinement and crystal data are presented in Table 1. The nonstoichiometric LaO<sub>0.65</sub>F<sub>1.7</sub> host crystallized in the tetragonal space group *P4/nmm*, which has *a* and *c* cell parameters of *a* = 4.10058 (6) Å and *c* = 5.8468 (1) Å. The refined atomic coordinates, equivalent isotropic displacement parameters with Wyckoff positions, and site occupation factors are listed in Table 2.



Figure 1. Synchrotron XRD pattern of a tetragonal  $LaO_{0.65}F_{1.7}$  sample.

Table 1. Rietveld refinement and crystal data of a  $LaO_{0.65}F_{1.7}$  structure.

Chemical Formula	LaO <sub>0.65</sub> F <sub>1.7</sub>
Radiation type, λ (Å)	Synchrotron (6D-BM), 0.65303
2θ range (deg)	5–35
Crystal system	Tetragonal
Space group	P 4/n m m
Lattice parameter (Å)	a = 4.10058 (6)
	c = 5.8468 (1)
Volume (Å <sup>3</sup> )	V = 98.313(1)
$R_p$	6.11
R <sub>wp</sub>	9.06
R <sub>exp</sub>	4.9
S	1.8
x <sup>2</sup>	3.42

Table 2. Refined atomic coordinates and equivalent isotropic displacement parameters of  $LaO_{0.65}F_{1.7}$ .

Atom	Wyckoff Position	x	у	Z	B <sub>iso</sub>	SOF
La	2c	0.25	0.25	0.2268 (3)	1.02 (6)	1
0	2a	0.75	0.25	0.00	1.1 (5)	0.65
F(1)	2a	0.75	0.25	0.00	1.1 (5)	0.35
F(2)	2b	0.75	0.25	0.50	2.6 (5)	0.86
F(3)	8i	0.25	0.077 (15)	0.652 (10)	4.8 (25)	0.1225

The formula of the LaO<sub>0.65</sub>F<sub>1.7</sub> structure can be expressed as LaO<sub>0.65</sub>F(1)<sub>0.35</sub>F(2)<sub>0.86</sub>F(3)<sub>0.49</sub> based on the calculations of the site occupancies and Wyckoff positions in the unit cell. All possible bonds between the La<sup>3+</sup> cations and O<sup>2-</sup>/F<sup>-</sup> anions in the host lattice from the crystal data contain La-O<sub>4</sub>, La-F(1)<sub>4</sub>, La-F(2)<sub>4</sub>, and La-F(3)<sub>12</sub> as shown in Figure 2 and Table 3.



Figure 2. Polyhedrons of  $LaO_{0.65}F_{1.7}$ , 9-coordinated  $La(O_2F(1)_2)(F(2)_{2.88}V_{1.12})F(3)_{1.96}$ , and 10-coordinated  $La(O_3F(1))(F(2)_4)F(3)_2$  structures.

Table 3. Selected interatomic distances for LaO<sub>0.65</sub>F<sub>1.7</sub>.

Atom	Distance (Å)	
La-O (x4)	2.4418 (3)	
La-F(1) (x4)	2.4418 (3)	
La-F(2) (x4)	2.5990 (4)	
La-F(3) (x4)	2.591 (18)	
La-F(3) (x8)	2.549 (12)	

In La-F(3)<sub>12</sub>, there were four long and eight short La-F(3) bond distances of 2.591 (18) and 2.549 (12) Å, respectively. The polyhedron based on the nonstoichiometric LaO<sub>0.65</sub>F(1)<sub>0.35</sub>F(2)<sub>0.86</sub> F(3)<sub>0.49</sub> structure refinement can be represented as La(O<sub>0.65</sub>F(1)<sub>0.35</sub>)(F(2)<sub>0.86</sub>V<sub>0.14</sub>)(F(3)<sub>0.49</sub>), which contains a vacancy (V) associated with the F(2) anion. In a previous study, the site dependency of 9- and 10-coordinated La<sup>3+</sup> sites in Eu<sup>3+</sup>-doped LaO<sub>0.65</sub>F<sub>1.7</sub> phosphors was reported [6,13]. When Eu<sup>3+</sup> ions were substituted in the LaO<sub>0.65</sub>F<sub>1.7</sub> structure, both 9-coordinated no-inversion and 10-coordinated symmetric inversion sites were observed from the Eu<sup>3+</sup> transitions of the emission spectra, which showed the <sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>2</sub> electric-dipole and <sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>1</sub> magnetic dipole transitions, respectively [6]. The polyhedrons in the LaO<sub>0.65</sub>F<sub>1.7</sub> structure can be distinguished as both 9-coordinated La(O<sub>2</sub>F(1)<sub>2</sub>)(F(2)<sub>2.88</sub>V<sub>1.12</sub>)F(3)<sub>1.96</sub> and 10-coordinated La(O<sub>3</sub>F(1))(F(2)<sub>4</sub>)F(3)<sub>2</sub> as shown in Figure 2 [6,13].

The crystallographic phase of the La<sub>1-*p*-*q*</sub>Bi<sub>*p*</sub>Tb<sub>*q*</sub>O<sub>0.65</sub>F<sub>1.7</sub> (*p* = 0 and 0.01; *q* = 0-0.2) phosphors was identified using powder X-ray diffraction (XRD) patterns. The calculated XRD pattern of the tetragonal LaO<sub>0.65</sub>F<sub>1.7</sub> (ICSD 40371) structure is shown in Figure 3a [13]. Figure 3b–d show the XRD patterns of the nonstoichiometric La<sub>1-*p*-*q*</sub>Bi<sub>*p*</sub>Tb<sub>*q*</sub>O<sub>0.65</sub>F<sub>1.7</sub> phosphors (*q* = 0.01; *q* = 0.1; *p* = 0.01; *q* = 0.1, respectively). The XRD patterns of the obtained phosphors show a single phase, without any visible impurities, indexed to a tetragonal LaO<sub>0.65</sub>F<sub>1.7</sub> structure. The Tb<sup>3+</sup> activator can be located in the 9- and 10-coordinated La<sup>3+</sup> sites of the nonstoichiometric LaO<sub>0.65</sub>F<sub>1.7</sub> structure. When small Tb<sup>3+</sup> ions (*r* = 1.04 Å for an eight coordination number (CN); *r* = 1.095 Å for a nine CN) were substituted for large La<sup>3+</sup> ions (*r* = 1.16 Å for a a 8 CN; *r* = 1.216 Å for a 9 CN; *r* = 1.27 Å for a 10 CN) in the LaO<sub>0.65</sub>F<sub>1.7</sub> host lattice, gradual shifts in the positions of the various Bragg reflections to higher angles were observed as shown in Figure 3b,c. The unit cell contraction of the cell parameters in the La<sub>0.99</sub>Tb<sub>0.01</sub>O<sub>0.65</sub>F<sub>1.7</sub> and La<sub>0.9</sub>Tb<sub>0.1</sub>O<sub>0.65</sub>F<sub>1.7</sub> phosphors occurred from a = 4.0749 (4) and c = 5.8188 (8) Å to a = 4.0689 (3) and c = 5.8057 (7) Å. Meanwhile, when Bi<sup>3+</sup> ions (*r* = 1.17 Å for an eight CN) were substituted for La<sup>3+</sup> ions in the La<sub>0.9</sub>Tb<sub>0.1</sub>O<sub>0.65</sub>F<sub>1.7</sub>

lattice, slight shifts in the positions of the various Bragg reflections to lower angles from the  $La_{0.89}Bi_{0.01}Tb_{0.1}O_{0.65}F_{1.7}$  phosphors (a = 4.0878 (1) and c = 5.8254 (3) Å) were observed as shown in Figure 3c,d, respectively.



**Figure 3.** The calculated XRD patterns of (**a**)  $LaO_{0.65}F_{1.7}$  (ICSD 40371) and the obtained XRD patterns of  $La_{1-p-q}Bi_pTb_qO_{0.65}F_{1.7}$  phosphors (**b**) q = 0.01; (**c**) q = 0.1; (**d**) p = 0.01 and q = 0.1.

Figure 4a shows the excitation and emission spectra of La<sub>0.99</sub>Bi<sub>0.01</sub>O<sub>0.65</sub>F<sub>1.7</sub>, La<sub>0.9</sub>Tb<sub>0.1</sub>O<sub>0.65</sub>F<sub>1.7</sub>, and La<sub>0.89</sub>Bi<sub>0.01</sub>Tb<sub>0.1</sub>O<sub>0.65</sub>F<sub>1.7</sub> phosphors [6]. Previously, the photoluminescence properties of Bi<sup>3+</sup>doped LaO<sub>0.65</sub> $F_{1.7}$  phosphors were explored. The energy levels of the Bi<sup>3+</sup> ions comprise  ${}^{1}S_{0}$ ,  ${}^{3}P_{1}$ (J = 0, 1, or 2), and  ${}^{1}P_{1}$  states. It is known that the  ${}^{1}S_{0} \rightarrow {}^{3}P_{1}$  and  ${}^{1}P_{1}$  transitions arise from spinorbital coupling, but the  ${}^{1}S_{0} \rightarrow {}^{3}P_{0}$  and  ${}^{3}P_{2}$  transitions are forbidden [6–10]. The blue-emitting spectra of the Bi<sup>3+</sup>-doped LaO<sub>0.65</sub>F<sub>1.7</sub> phosphors, attributed to the  ${}^{3}P_{1} \rightarrow {}^{1}S_{0}$  transitions of the Bi<sup>3+</sup> ions, revealed the emission band range from 350 to 650 nm under UV excitation as shown in Figure 4a. The maximum emission intensity was observed in a previous study when the  $Bi^{3+}$ concentration in the host lattice was 1 mol% [6]. The  $La_{0.9}Tb_{0.1}O_{0.65}F_{1.7}$  phosphor was monitored from 400 to 700 nm while under UV excitation. The intense green emission of  ${}^{5}D_{4}$ - ${}^{7}F_{5}$  transition from the Tb<sup>3+</sup> ions was observed near 542 nm as shown in Figure 4a. The individual transitions of Bi<sup>3+</sup> and Tb<sup>3+</sup> ions, with energy transfer from Bi<sup>3+</sup> to Tb<sup>3+</sup> ions in the La<sub>0.99-a</sub>Bi<sub>0.01</sub>Tb<sub>a</sub>O<sub>0.65</sub>F<sub>1.7</sub> (q = 0-0.2) phosphors, occurred under an excitation wavelength of 286 nm as shown in Figure 4b. The energy transfer from Bi<sup>3+</sup> to Tb<sup>3+</sup> operated as a sensitizer and activator, respectively, in the  $La_{0.99-a}Bi_{0.01}Tb_aO_{0.65}F_{1.7}$  (q = 0–0.2) phosphors. The emission of  $Tb^{3+}$  transitions was maximized when the Tb<sup>3+</sup> content in the La<sub>0.99-q</sub>Bi<sub>0.01</sub>Tb<sub>q</sub>O<sub>0.65</sub> $F_{1.7}$  (q = 0–0.2) phosphors was q = 0.1, which was compared with commercially available green LaPO<sub>4</sub>:Ce<sup>3+</sup>/Tb<sup>3+</sup> phosphor in Figure 4a. The green emission of the  $La_{0.89}Bi_{0.01}Tb_{0.1}O_{0.65}F_{1.7}$  phosphor under 286 nm excitation significantly increased by >4 times compared to that of the  $La_{0.9}Tb_{0.1}O_{0.65}F_{1.7}$  phosphor because of the energy transfer from  $Bi^{3+}$  to  $Tb^{3+}$  ions as shown in Figure 4b. The energy-transfer efficiency ( $\eta_T$ ) was estimated using the following formula:

$$\eta_T = 1 - I_S / I_{SC}$$

where I<sub>S</sub> and I<sub>SO</sub> are the luminescence intensities of the Bi<sup>3+</sup> sensitizer in the presence and absence of a Tb<sup>3+</sup> activator, respectively [6–10,17–21]. The energy-transfer mechanism can be represented by linear plots of I<sub>SO</sub>/I<sub>S</sub> versus C<sub>Bi-Tb</sub><sup> $\alpha/3$ </sup>, where C<sub>Bi-Tb</sub> is the concentration of Bi<sup>3+</sup> and Tb<sup>3+</sup> ions, with  $\alpha = 6$ , 8, or 10, corresponding to dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively, in accordance with the Dexter theory [17–22]. In Figure 4c, when  $\alpha = 6$ , 8, and 10, the linear plots showed energy transfers from the Bi<sup>3+</sup> to Tb<sup>3+</sup> ions in the La<sub>0.99–q</sub>Bi<sub>0.01</sub>Tb<sub>q</sub>O<sub>0.65</sub>F<sub>1.7</sub> (q = 0–0.2) phosphors with an R<sup>2</sup> = 0.9954, 0.998, and 0.9906, respectively. When the value of  $\alpha$  was 8, a closer linear plot was determined for the phosphor, and the dipole–quadrupole interaction was involved in the energy-transfer mechanism of the phosphors. The differences on the R-factors between dipole–dipole and dipole–quadrupole mechanisms are quite small when the concentrations

of  $C_{Bi-Tb}$  and  $C_{Tb}$  were selected (Supplementary Materials, Figure S1). Possibly, there are some arguments that determine the energy-transfer process as the dipole–quadrupole interaction mechanism in the phosphors, because the concentration quenching selectively depends on whether it is a donor–donor or donor–acceptor for  $C^{8/3}$  concentration [23]. The efficiency gradually enhanced from 30 to 89% as the Tb<sup>3+</sup> content in the phosphors increased from q = 0.01 to 0.1 as shown in Figure 4d.



**Figure 4.** (a) PL excitation and emission spectra of  $La_{0.99}Bi_{0.01}O_{0.65}F_{1.7}$ ,  $La_{0.9}Tb_{0.1}O_{0.65}F_{1.7}$ ,  $La_{0.9}Bi_{0.01}Tb_{0.1}O_{0.65}F_{1.7}$ , and commercial green  $LaPO_4:Ce^{3+}/Tb^{3+}$  phosphors; (b) the emission spectra of  $La_{0.99-q}Bi_{0.01}Eu_qO_{0.65}F_{1.7}$ , (q = 0-0.2) phosphors under 286 nm excitation; (c) the plot of  $I_{SO}/I_S$  versus  $C_{Bi-Tb} \alpha^{\Lambda/3}$  ( $\alpha = 6, 8$ , and 10); (d) energy-transfer efficiency from  $Bi^{3+}$  to  $Tb^{3+}$  in the phosphors.

As shown in Figure 5, the chromaticity coordinates, *x* and *y*, were in accordance with the desired CIE values from the blue to green wavelength regions for  $La_{0.99-q}Bi_{0.01}Tb_qO_{0.65}F_{1.7}$ (q = 0-0.2) phosphors (EX = 286 nm). When the concentration of Tb<sup>3+</sup> ions in the La<sub>0.99-a</sub>Bi<sub>0.01</sub>Tb<sub>a</sub>  $O_{0.65}F_{1.7}$  (q = 0-0.2) phosphors increased from q = 0 to 0.02 and 0.1, the emission colors exhibited a gradual shift from blue to green emission regions. The CIE values are summarized in the inset of Figure 5, along with the values obtained for the phosphors. The CIE coordinates of the blue and green regions of the phosphor CIE diagram were observed to be x = 0.240 and y = 0.334, x = 0.239 and y = 0.340, x = 0.254 and y = 0.436, and x = 0.267 and y = 0.535 for values of q = 0, 0.01, 0.04, and 0.1, respectively. The emission of the phosphors subject to 312 nm hand-lamp excitation was blue and green. This green-emitting light was adopted for a high color-rendering index to apply to pc UV LEDs. This La<sub>0.89</sub>Bi<sub>0.01</sub>Tb<sub>0.1</sub>O<sub>0.65</sub>F<sub>1.7</sub> phosphor can be prepared as a green-emitting component for fabrication of a 275 nm UV LED chip. The photoluminescence and electroluminescence (EL) spectra resulting from 275 nm UV excitation of the green  $La_{0.89}Bi_{0.01}Tb_{0.1}O_{0.65}F_{1.7}$  phosphor with blue  $Ba_{3.8}Ce_{0.1}Na_{0.1}Ca_5Al_2Si_6O_{24}$  and red  $La_{0.94}Bi_{0.01}Eu_{0.05}O_{0.65}F_{1.7}$  phosphors were monitored as shown in Figure 6, respectively [8,24]. The pc UV LED was prepared at 3.2 V and 20 mA after the phosphors were packaged on a 275 nm LED chip (inset). A CRI ( $R_a$ ) of 94.9 at CCTs of 4373 K with CIE coordinates of x = 0.36and y = 0.37 was determined for the 275 nm chip fabricated with the white-light pc UV LED. The three phosphors could generate white light in the 275 nm UV-executable LED chip. The IQE of the phosphors is expressed as  $\eta_{QE}$  using the following equation [25–28]:

$$\eta_{QE} = \int L_S / (\int E_R - \int E_S)$$

where  $L_S$ ,  $E_S$ , and  $E_R$  are the luminescence integrated emission, excitation spectra of the phosphors, and the integrated excitation spectrum without phosphors in the sphere, respectively. The IQE of the white pc UV LED was approximately 40% under a 275 nm excitation. Color-tunable red, green, and blue phosphors can be diversely fabricated into UV-LED chips, which is an advantage for UV-executable LED applications.



**Figure 5.** The chromaticity coordinates with the desired CIE values of  $La_{0.99-q}Bi_{0.01}Tb_qO_{0.65}F_{1.7}$  (q = 0-0.2) phosphors (EX = 286 nm) and photographs of the green emission light of the phosphors under 286 nm radiation.



**Figure 6.** The emission spectra of RGB phosphors  $(La_{0.94}Bi_{0.01}Eu_{0.05}O_{0.65}F_{1.7}, La_{0.89}Bi_{0.01}Tb_{0.1}O_{0.65}F_{1.7}, and Ba_{3.8}Ce_{0.1}Na_{0.1}Ca_5Al_2Si_6O_{24})$  under 275 nm UV excitation and the electroluminescence spectra and a photograph of the RGB pc LED under 3.2 V and 20 mA.

## 4. Conclusions

The nonstoichiometric LaO<sub>0.65</sub>F<sub>1.7</sub> structure was determined as a tetragonal unit cell (*P4/nmm*) with the cell parameters a = 4.10058 (6) Å and c = 5.8468 (1) Å using synchrotron X-ray powder diffraction. The LaO<sub>0.65</sub>F<sub>1.7</sub> host lattice contained 9- and 10-coordinated La<sup>3+</sup> sites in the 2c Wyckoff position. Optical materials composed of La<sub>1-*p*-*q*</sub>Bi<sub>*p*</sub>Tb<sub>*q*</sub>O<sub>0.65</sub>F<sub>1.7</sub> (p = 0 and 0.01; q = 0-0.2) exhibited photoluminescence spectra characteristic of an energy transfer from Bi<sup>3+</sup> to Tb<sup>3+</sup> upon excitation with 286 nm involving dipole–quadrupole interactions in the phosphors. The desired Commission Internationale de l'Eclairage values of the blue–green phosphors were calculated. The green La<sub>0.96</sub>Bi<sub>0.01</sub>Tb<sub>0.02</sub>Eu<sub>0.01</sub>O<sub>0.65</sub>F<sub>1.7</sub> phosphor was fabricated with blue and red phosphors on a 275 nm UV-LED chip, resulting in white light. The IQE was determined to be approximately 40% under a 275 nm excitation with a CRI (Ra) of 94.9 at CCT of 4373 K and CIE coordinates of x = 0.36 and y = 0.37.

**Supplementary Materials:** The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/ma15124222/s1, Figure S1. The plot of ISO/IS versus CTba/3 (a = 6, 8, 10).

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