# Highly Efficient Green-Emitting Phosphors $Ba_2Y_5B_5O_{17}$ with Low Thermal Quenching Due to Fast Energy Transfer from $Ce^{3+}$ to $Tb^{3+}$

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**ABSTRACT:** This paper demonstrates a highly thermally stable and efficient green-emitting  $Ba_2Y_5B_5O_{17}:Ce^{3+}$ ,  $Tb^{3+}$  phosphor prepared by high-temperature solid-state reaction. The phosphor exhibits a blue emission band of  $Ce^{3+}$  and green emission lines of  $Tb^{3+}$  upon  $Ce^{3+}$  excitation in the near-UV spectral region. The effect of  $Ce^{3+}$  to  $Tb^{3+}$  energy transfer on blue to green emission color tuning and on luminescence thermal stability is studied in the samples codoped with 1%  $Ce^{3+}$  and various concentrations (0–40%) of  $Tb^{3+}$ . The green emission of  $Tb^{3+}$  upon  $Ce^{3+}$  excitation at 150 °C can keep, on average, 92% of its intensity at room temperature, with the best one showing no intensity decreasing up to 210 °C for 30%  $Tb^{3+}$ . Meanwhile,  $Ce^{3+}$  emission intensity only keeps 42% on average at 150 °C. The high thermal stability of the green emission is attributed to suppression of  $Ce^{3+}$  thermal de-excitation through fast energy transfer to  $Tb^{3+}$ , which in the green-emitting excited states is highly thermally stable such that no lifetime



shortening is observed with raising temperature to 210  $^{\circ}$ C. The predominant green emission is observed for Tb<sup>3+</sup> concentration of at least 10% due to efficient energy transfer with the transfer efficiency approaching 100% for 40% Tb<sup>3+</sup>. The internal and external quantum yield of the sample with Tb<sup>3+</sup> concentration of 20% can be as high as 76% and 55%, respectively. The green phosphor, thus, shows attractive performance for near-UV-based white-light-emitting diodes applications.

## 1. INTRODUCTION

In recent years, white light-emitting diodes (LEDs) have been extensively investigated for application in solid-state lighting.<sup>1-16</sup> In the strategy of phosphor-converted white LEDs, combining blue InGaN LED chips with yellow-emitting phosphors is most common.<sup>17,18</sup> Alternatively, combining near-UV LED chips with red-, green-, and blue-emitting phosphors is also an attractive scheme, because near-UV light can be fully converted to white light with high color rendering index.<sup>19</sup> The latter scheme thus arouses a great research concern.<sup>20–34</sup> Further improving the white LED devices requires not only advances in the near-UV LED chips but also the development of novel phosphors.<sup>35,36</sup>

Efficient phosphors with high thermal stability are desirable for applications. For the purpose of achieving applicable greenemitting phosphors for near-UV LED excitation, rare-earth  $Ce^{3+}$  and  $Tb^{3+}$  codoped materials have been widely studied and made great progress in recent years.<sup>37–42</sup> Wang et al. reported a novel blue-green emitting phosphor NaBaScSi<sub>2</sub>O<sub>7</sub>:Ce<sup>3+</sup>,Tb<sup>3+</sup> with an internal quantum efficiency of 36%. Lin et al. observed highly efficient emission with an internal quantum yield of 45.1% in BaLuSi<sub>3</sub>O<sub>10</sub>:Ce<sup>3+</sup>, Tb<sup>3+</sup>. Additionally, few reports demonstrated a high thermal stability of the green emission. Jin et al. reported that the green emission keeps 80% of its roomtemperature intensity at 150 °C in Gd<sub>4.67</sub>Si<sub>3</sub>O<sub>13</sub>:Ce<sup>3+</sup>, Tb<sup>3+</sup>. Zhang and his co-workers declared that the green emission keeps almost 100% of its room-temperature intensity up to 160  $^{\circ}$ C in an optimized green-emitting LaOBr:Ce<sup>3+</sup>, Tb<sup>3+</sup> phosphor, but the quantum yield was not indicated.

Recently, Hermus et al. reported a novel efficient blueemitting Ba<sub>2</sub>Y<sub>5</sub>B<sub>5</sub>O<sub>17</sub>:Ce<sup>3+</sup> (BYBO:Ce<sup>3+</sup>) phosphor for near-UV excitation.43Accordingly, BYBO could be another attractive host for  $Ce^{3+}$  and  $Tb^{3+}$  codoped green phosphor. The blue emission of Ce<sup>3+</sup> in BYBO, however, shows a quenching temperature of only 130 °C, seemingly unsuitable for achieving thermally stable green emission of Tb<sup>3+</sup> with energy transferred from Ce<sup>3+</sup>. In this paper, we report a thermally stable greenemitting phosphor by adding green-emitting Tb<sup>3+</sup> into BYBO:Ce<sup>3+</sup>. Emission color tuning from blue to green through energy transfer from Ce3+ to Tb3+ was studied by means of photoluminescence (PL) and photoluminescence excitation (PLE) spectra in the samples codoped with 1% Ce<sup>3+</sup> and various concentrations of Tb<sup>3+</sup>.The predominant green emission with the internal and external quantum yield of 76% and 55%, respectively, at room temperature is achieved. Temperature dependence of PL intensity exhibits that the green emission can keep an average of 92% of its room-

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temperature intensity at 150 °C with the best one showing no intensity decreasing up to 210 °C for 30%  $Tb^{3+}$ . The high thermal stability of the green emission was analyzed.

#### 2. EXPERIMENTAL SECTION

**2.1. Materials and Preparation.** The  $Ba_2Y_5B_5O_{17}:Ce^{3+}$ ,  $Tb^{3+}$  samples were synthesized by traditional high-temperature solid-state reaction. The starting materials used for the studied phosphors were  $Ba_2CO_3$  (A.R.),  $H_3BO_3$  (A.R.),  $Y_2O_3$  (4N),  $CeO_2$  (4N),  $Tb_4O_7$  (4N), and they were mixed and ground according to the given stoichiometric ratio. The weighed powder was mixed in an agate mortar and placed in an alumina crucible. This crucible was prefired at 450 °C for 4 h and finally heated at 1200 °C for 8 h in a CO reducing atmosphere. After they cooled to room temperature (RT), the final products were white powders.

2.2. Measurement Characterization. The powder X-ray diffraction (XRD) patterns were collected on a Bruker D8 Focus diffractometer, in the  $2\theta$  range from  $15^{\circ}$  to  $80^{\circ}$  with Cu K $\alpha$  radiation  $(\lambda = 1.54056 \text{ Å})$  operated at 40 kV and 40 mA. The XRD data were collected with step size of 0.02° and count time of 2 s/step. The diffraction pattern was indexed using the TREOR90 program.44 Rietveld analysis was conducted using the GSAS package.<sup>45</sup> The measurements of PL and PLE spectra were performed with a Hitachi F-7000 spectrometer equipped with a 150 W xenon lamp as the excitation source. And the temperature-dependent PL spectra were also performed on F-7000 spectrometer with an external heater. A process controller (OMEGA CN76000) equipped with a thermocouple was used to measure the temperature and control the heating rate. In fluorescence decay measurements, an optical parametric oscillator (OPO) was used as an excitation source, and the signal was detected by a Tektronix digital oscilloscope (TDS 3052). All the measurements were conducted at room temperature unless mentioned specially.

## 3. RESULTS AND DISCUSSION

3.1. Phase Identification and Rietveld Refinements. The phase purities and the crystal structures of the as-prepared powder samples BYBO: 1%  $Ce^{3+}$ , x  $Tb^{3+}(x = 0\%, 2\%, 10\%, 10\%)$ 20%, 30%, 40%) were characterized by XRD at room temperature. All the samples exhibit the almost similar XRD patterns with the diffraction peaks coincident with the Powder Diffraction File No. 00-056-0113 for BYBO. No obvious impurities were detected, indicating that the obtained samples were single phase and that the doped ions were completely dissolved in the BYBO host without significant changes of the crystal structure. To further understand the microstructure of the as-prepared samples, detailed Rietveld refinements were performed. Figure 1a presents the XRD powder patterns of BYBO: 1%  $Ce^{3+}$ , x  $Tb^{3+}$  (x = 2%, 20%, 40%), and Figure 1b shows the Rietveld refinements for BYBO: 1% Ce<sup>3+</sup>, 20% Tb<sup>3+</sup>, as an example. The crystal lattice parameters determined by the Rietveld refinements for the all samples are listed in Table 1.

Figure 2 shows the crystal-structure diagram of BYBO according to the refinement. The compound crystallizes as an orthorhombic crystal system with space group *Pbcn* (No. 60). The lattice parameter (a = 17.44 Å, b = 6.64 Å, c = 13.01 Å) and unit cell volume (V = 1506.989 Å<sup>3</sup>) become larger with increasing Tb<sup>3+</sup> concentration. The cell parameters of BYBO: 1% Ce<sup>3+</sup>, 40% Tb<sup>3+</sup> are a = 17.45 Å, b = 6.67 Å, c = 13.06 Å, and V = 1520.85 Å<sup>3</sup>, respectively. This phenomenon can be ascribed to Ce<sup>3+</sup> (1.14 Å) and Tb<sup>3+</sup> (1.04 Å) substitution for small Y<sup>3+</sup> (1.02 Å). There are two crystallographically independent, fully occupied Y<sup>3+</sup> sites and a third Y<sup>3+</sup> site that is shared with Ba<sup>2+</sup>. These coordination polyhedra form a distorted octahedron around atom Y3, a distorted capped



Figure 1. XRD patterns (a) and Rietveld refinements (b) for BYBO: 1% Ce<sup>3+</sup>, x% Tb<sup>3+</sup>.

trigonal prism around atom Y4, and a distorted pentagonal bipyramid around the mixed Y2/Ba2 site. Ba<sup>2+</sup> mainly occupies one crystallographic position and is mixed with Y<sup>3+</sup> in a 10-coordinate, highly distorted polyhedral. All of the boron atoms are three-coordinated by oxygen forming slightly distorted trigonal planar units.<sup>43</sup> During the refinement of the fully order crystal structure, anomalous isotropic displacement factors were obtained for two of the cation sites, namely, Ba1 and Y2. Statistically mixing Ba and Y on these positions satisfied the refinement allowing the refinement to converge. One of the positions is Ba1/Y1 with a majority Ba, Wyckoff site 8*d*, whereas the second site is Y2/Ba2 with a majority Y, Wyckoff site 4*c*. This phenomenon is not unprecedented and is observed in other borates like Ba<sub>2.55</sub>Y<sub>1.445</sub>B<sub>3</sub>O<sub>9</sub>, where Ba and Y share all crystallographic sites.<sup>46</sup>

3.2. Emission Color Tuning Due to Ce<sup>3+</sup>-Tb<sup>3+</sup> Energy Transfer. Figure 3a shows the PLE and PL spectra of BYBO: 1% Ce<sup>3+</sup>. The PLE spectrum monitored at 445 nm contains three distinctive bands peaked at 265, 308, and 345 nm, which are assigned to the 4f-5d transitions of Ce<sup>3+</sup>. The strong PLE band at 345 nm is well-matched to the near-UV LED chip. Under near UV excitation at 345 nm, the PL spectrum exhibits an asymmetric blue emission band peaked at 443 nm, which is assigned to the transition from the lowest 5d state to the 4f ground state of Ce<sup>3+</sup>.The asymmetric emission band can be well-fitted with two Gaussian bands peaking at 426 nm (23 446  $cm^{-1}$ ) and 464 nm (21 571  $cm^{-1}$ ). Their energy difference is  $\sim$ 1875 cm<sup>-1</sup>, being consistent with the energy separation between the  ${}^{2}F_{7/2}$  and the  ${}^{2}F_{5/2}$  substates of the ground state of Ce<sup>3+,47</sup> The Tb<sup>3+</sup> singly doped BYBO: 2% Tb<sup>3+</sup> presents the well-known green fluorescence with the main emission line at 543 nm, originating from  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  transition, and two weak lines at 585 nm from  ${}^5\mathrm{D}_4{\rightarrow}{}^7\mathrm{F}_4$  and at 625 nm from  ${}^{5}D_{4} \rightarrow {}^{7}F_{3}$  transitions (see Figure 3b). The PLE spectrum of Tb<sup>3+</sup> singly doped sample includes the transitions from the ground-state <sup>7</sup>F<sub>6</sub> to the excited states <sup>5</sup>D<sub>4</sub>, <sup>5</sup>D<sub>3</sub>, and the 4f<sup>7</sup>5d states. Clearly, a big spectral overlap between Ce<sup>3+</sup> PL band and Tb<sup>3+</sup> PLE band corresponding to  ${}^{7}F_{6} \rightarrow {}^{5}D_{4}$  absorption is observed, indicating the possibility of energy transfer from Ce<sup>3+</sup>

x	a (Å)	<i>b</i> (Å)	c (Å)	V (Å <sup>3</sup> )	$R_{\rm WP}$ (%)	$R_{\rm P}$ (%)
0%	17.431 73	6.648 15	13.019 37	1508.799	4.77	3.39
2%	17.432 84	6.649 27	13.020 69	1509.302	4.16	2.95
10%	17.4360	6.649 27	13.0296	1511.608	4.24	3.06
20%	17.445 75	6.659 74	13.04387	1515.490	5.88	3.49
30%	17.449 78	6.665 05	13.05299	1518.110	4.45	2.95
40%	17.4573	6.669 82	13.06156	1520.852	3.98	2.60





Figure 2. Crystal structure schematic diagram of  $Ba_2Y_5B_5O_{17}$  and crystallographically independent cation coordination environments.



Figure 3. PLE and PL spectra of BYBO: 1% Ce<sup>3+</sup> (a), BYBO: 2% Tb<sup>3+</sup> (b), and BYBO: 1% Ce<sup>3+</sup>, 2% Tb<sup>3+</sup> (c).

to Tb<sup>3+</sup> according to Dexter's theory.<sup>48</sup> The energy transfer is confirmed by the luminescent properties of Ce<sup>3+</sup> and Tb<sup>3+</sup> codoped BYBO, as shown in Figure 3c. It is found that the PLE spectrum of BYBO: 1% Ce<sup>3+</sup>, 2% Tb<sup>3+</sup> monitored Tb<sup>3+</sup> emission at 543 nm exhibits only the characteristic PLE bands of Ce<sup>3+</sup> in the near-UV region. Meanwhile, not only Ce<sup>3+</sup>

emission but also strong Tb<sup>3+</sup>emission appear upon Ce<sup>3+</sup> excitation at 345 nm. This phenomenon gives us a confirmation of occurrence of Ce<sup>3+</sup> to Tb<sup>3+</sup> energy transfer, and the excitation of Tb<sup>3+</sup> is governed by energy transfer from Ce<sup>3+</sup> rather than near-UV absorption by Tb<sup>3+</sup> itself.

To understand the effect of energy transfer on luminescent properties of  $Ce^{3+}$  and  $Tb^{3+}$  codoped BYBO, the PL spectra for a fixed 1%  $Ce^{3+}$  but various concentrations of  $Tb^{3+}$  are studied, as shown in Figure 4. It is observed that the intensity of the



**Figure 4.** PL spectra of BYBO: 1%  $Ce^{3+}$ , x%  $Tb^{3+}$  for various  $Tb^{3+}$  concentrations under 345 nm excitation.

Ce<sup>3+</sup> emission decreases rapidly with the increase of Tb<sup>3+</sup> concentration *x*. Meanwhile Tb<sup>3+</sup> emission is enhanced considerably with the increase of *x* up to 20%, reflecting the enhanced energy-transfer efficiency. The Ce<sup>3+</sup> emission becomes very weak, and Tb<sup>3+</sup> emission dominates the PL spectra for  $x \ge 10\%$ , implying the occurrence of highly efficient energy transfer. However, Tb<sup>3+</sup> emission intensity starts to decrease for x > 20%. The decrease is attributed to the Tb<sup>3+</sup>-Tb<sup>3+</sup> internal concentration quenching based on the experimental observation of the fluorescence lifetime shortening of Tb<sup>3+</sup> on increasing *x*, as shown in Figure 5.

On the basis of the data shown in Figures 4 and 5, the Tb<sup>3+</sup> concentration dependence of Ce<sup>3+</sup>, Tb<sup>3+</sup> emission intensities, Tb<sup>3+</sup> fluorescence lifetimes, and energy-transfer efficiencies are obtained and plotted in Figure 5. The efficiencies ( $\eta_{\rm ET}$ ) of energy transfer from sensitizer Ce<sup>3+</sup> to activator Tb<sup>3+</sup> are calculated by<sup>49</sup>

$$\eta_{\rm T} = 1 - \frac{I_{\rm S}}{I_{\rm S0}} \tag{1}$$



**Figure 5.** Fluorescence decay curves of  $Tb^{3+}$  in BYBO: 1%  $Ce^{3+}$ , *x*%  $Tb^{3+}$  after pulse excitation at 345 nm while monitored at 543 nm. The lifetimes correspond to the area under the decay curves.

where  $I_{S0}$  and  $I_S$  denote the luminescence intensity of Ce<sup>3+</sup> in the absence and in the presence of Tb<sup>3+</sup>, respectively. We observe the transfer efficiencies increase monotonously on increasing x and approaching 100% (96%) at 40% Tb<sup>3+</sup>. However, the strongest Tb<sup>3+</sup> emission occurs at 20% Tb<sup>3+</sup>, because the Tb<sup>3+</sup> fluorescence lifetimes, as the indication of Tb<sup>3+</sup> emission efficiencies, decrease with increasing x. We also simulated the Tb<sup>3+</sup> emission intensities using the product of transfer efficiency and Tb<sup>3+</sup> fluorescence lifetime. The simulated intensities coincide well with the directly measured intensities, as shown in Figure 6. The internal and external quantum yield for 20% Tb<sup>3+</sup> is measured to be 76% and 55%, respectively, under 345 nm excitation.

The emission color tuning of  $Ce^{3+}$  and  $Tb^{3+}$  codoped BYBO samples as a function of  $Tb^{3+}$  concentration is illustrated in the Commission International de l'Eclairage (CIE) 1931 chromaticity diagram, as shown in Figure 7. The color can vary from blue (0.1519, 0.1067) to green (0.2820, 0.5028).

**3.3. Thermally Stable Tb<sup>3+</sup> Emission Due to Fast Energy Transfer.** Figure 8 shows the PL spectra of BYBO: 1% Ce<sup>3+</sup>, BYBO: 1% Ce<sup>3+</sup>, 20% Tb<sup>3+</sup>, and BYBO: 1% Ce<sup>3+</sup>, 30% Tb<sup>3+</sup> at different temperatures. It is observed that Tb<sup>3+</sup> emission



**Figure** 7. Emission colors of samples in CIE 1931 chromaticity diagram together with their photograph for BYBO:  $1\% \text{ Ce}^{3+}$ ,  $x\% \text{ Tb}^{3+}$  upon 345 nm excitation. The digital photos of the samples are taken under 365 nm UV lamp irradiation.

declines much slower than  $Ce^{3+}$  emission with increasing temperature. This behavior can be clearly seen in Figure 8 that shows the temperature dependence of the area intensities of  $Ce^{3+}$ ,  $Tb^{3+}$  emissions.

In Figure 9 the Ce<sup>3+</sup> emissions in the codoped BYBO exhibit the similar thermal quenching behavior to Ce<sup>3+</sup> singly doped BYBO and intensity only keeps 42% on average at 423 K (150 °C). The quenching temperature, at which 50% of the roomtemperature intensity is lost, is determined to be ~403 K (130 °C), which is in agreement with the result reported by Hermus et al.<sup>40</sup> More interestingly, the Tb<sup>3+</sup> emissions are thermally stable for all the samples. The green emissions of all the samples at 403 K keep on average 95% of their intensities at room temperature, including the best one, which shows no intensity decreasing from room temperature to 483 K (210 °C)



**Figure 6.** (a)Dependence of  $Ce^{3+}$ ,  $Tb^{3+}$  emission intensities,  $Tb^{3+}$  fluorescence lifetimes, energy-transfer efficiencies on  $Tb^{3+}$  concentration in BYBO:1%  $Ce^{3+}$ , x%  $Tb^{3+}$ . (b) Dependence of  $Tb^{3+}$  emission intensities and simulated  $Tb^{3+}$  emission intensities on  $Tb^{3+}$  concentration in BYBO: 1%  $Ce^{3+}$ , x%  $Tb^{3+}$ . All data are normalized to their individual maximum.



**Figure 8.** PL spectra of BYBO: 1%  $Ce^{3+}$  (a), BYBO: 1%  $Ce^{3+}$ , 20%  $Tb^{3+}$  (b), and BYBO: 1%  $Ce^{3+}$ , 30%  $Tb^{3+}$  (c) at different temperatures under 345 nm excitation.



**Figure 9.** Temperature dependence of  $Ce^{3+}$  emission intensity (a) and  $Tb^{3+}$  emission intensity (b) in BYBO: 1%  $Ce^{3+}$ , *x*%  $Tb^{3+}$  under 345 nm excitation.

for 30% Tb<sup>3+</sup>. At 423 K, the green emission intensities keep an average of 92% at room temperature. To understand the origin of high thermal stability of Tb<sup>3+</sup> emission, we measured the fluorescence lifetimes of Tb<sup>3+</sup> from room temperature to 483 K after Ce<sup>3+</sup> is excited at 345 nm. We found that the lifetimes were not shortened at all on increasing temperature to 483 K, indicating a thermally stable quantum efficiency of the green emission of Tb<sup>3+</sup> in the temperature range of this work. As a result, the thermal behavior of energy-transfer efficiency directly reflects the thermal behavior of Tb<sup>3+</sup> emission. On the basis of thermal activation model, there exists a competition among energy transfer, intrinsic decay, and thermal activation in the 5d state side excitation of Ce<sup>3+</sup> after Ce<sup>3+</sup> is excited. The quantum efficiency of energy transfer as a function of temperature can be written as

$$\eta_{\rm ET} = \frac{W_{\rm ET}}{\gamma_0 + W_{\rm ET} + Ae^{-\Delta E/kT}} \tag{2}$$

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where  $W_{\rm ET}$  is energy transfer rate,  $\gamma_0$  is the intrinsic decay rate of the lowest 5d state of Ce<sup>3+</sup>, and it is independent of temperature, A is a constant,  $\Delta E$  is the activation energy for thermal de-excitation of Ce<sup>3+</sup> 5d states, and k is Boltzmann constant. Equation 2 clearly indicates that a big transfer rate can slow transfer efficiency decreasing as temperature is raised. As shown in Figure 10, the process ① represents fast energy



Figure 10. Energy levels model for the energy-transfer processes of  $Ce^{3+}{\rightarrow}Tb^{3+}.$ 

transfer. If the transfer rate is fast enough to compete with the thermal activation rate, a small thermal quenching of transfer efficiency is expected, and thus a thermally stable  $Tb^{3+}$  emission is observed. One may question why the thermal stability of  $Ce^{3+}$  emission is hardly improved in the presence of energy transfer. The quantum efficiency of sensitizer  $Ce^{3+}$  emission is expressed by

$$\eta_{\rm Ce} = \frac{\gamma_0}{\gamma_0 + W_{\rm ET} + Ae^{-\Delta E/kT}} \tag{3}$$

Similar to eq 2, eq 3 also needs a big transfer rate against thermal de-excitation for slowing the thermal quenching of  $Ce^{3+}$  emission. However, the transfer rates have a wide distribution, because the doped dopants are randomly distributed in space resulting in a distribution of the distance between Ce<sup>3+</sup> and Tb<sup>3+</sup>. Accordingly, the Ce<sup>3+</sup> ions can be classified into two groups in terms of transfer rates shown in Figure 10. One has a slow rate of energy transfer to Tb<sup>3+</sup> marked as  $Tb_{(s)}^{3+}$ , and therefore it makes the main contribution to Ce<sup>3+</sup> emission. The other has a fast transfer rate, and it makes the main contribution to Tb<sup>3+</sup> emission marked as  $Tb_{(f)}^{3+}$ . The process ② stands for relatively slow energy transfer, and we may infer that the  $Ce^{3+}$  with a slow transfer rate cannot compete with the thermal activation process, and then the Ce<sup>3+</sup> emission still shows a pronounced thermal quenching in the codoped BYBO, whereas the Ce3+ with a fast transfer rate (process ①) can compete with the thermal activation process, and thus the Tb<sup>3+</sup> emission shows a high thermal stability.

The fast energy transfer is supported by the behavior of fluorescence decay of  $Ce^{3+}$  in the codoped BYBO as shown in Figure 11. The fluorescence lifetime of  $Ce^{3+}$  is observed to be shortened from 47 ns in the absence of  $Tb^{3+}$  to 22 ns at 40%  $Tb^{3+}$ , decreasing by 53%. Meanwhile, Figure 5 shows that the  $Ce^{3+}$  emission intensity decreases by 96% from 0%  $Tb^{3+}$  to 40%  $Tb^{3+}$ . The small reduction of the lifetimes implies the existence



**Figure 11.** Fluorescence decay curves of  $Ce^{3+}$  in BYBO: 1%  $Ce^{3+}$ , x% Tb<sup>3+</sup> samples after pulse excitation at 345 nm while monitored at 443 nm.

of a fast decay of Ce<sup>3+</sup> emission that is too fast to be detected. The fast decay can result from a fast energy transfer that quenches the Ce<sup>3+</sup> emission rapidly without luminescence detected. The difference between 96% and 53% determines the fast component to be 43% at 40% Tb<sup>3+</sup>. The fast transfer may take place between the nearest Ce<sup>3+</sup>-Tb<sup>3+</sup> pair, as observed in Y<sub>2</sub>O<sub>3</sub>:Er<sup>3+</sup>, Yb<sup>3+</sup> in our previous work.<sup>50</sup>

#### 4. CONCLUSIONS

Green-emitting Ba<sub>2</sub>Y<sub>5</sub>B<sub>5</sub>O<sub>17</sub>:Ce<sup>3+</sup>, Tb<sup>3+</sup> phosphor for near-UV excitation was prepared by high-temperature solid-state reaction. The XRD patterns and Rietveld refinements indicate the purity of the crystal phase for the as-prepared samples. The phosphor shows a blue emission band of Ce<sup>3+</sup> centered at 445 nm and simultaneously a group of green emission lines of Tb<sup>3+</sup> with the main peak at 543 nm through energy transfer from Ce<sup>3+</sup>. Emission color tuning from blue to green was achieved by continuously increasing Tb<sup>3+</sup> concentration to enhance energy transfer. The green emission of  $Tb^{3+}$  dominates the luminescence for  $Tb^{3+}$  concentration of at least 10%. The strongest Tb<sup>3+</sup> emission was observed at 20% Tb<sup>3+</sup> with the external quantum efficiency of 55%. The blue emission of Ce<sup>3+</sup> appears the similar thermal stability to Ce<sup>3+</sup> singly doped sample. The green emissions of all the samples at 423 K keep an average of 92% of their intensities at room temperature, including the best one, which shows no intensity decreasing from room temperature to 483 K for 30% Tb<sup>3+</sup>. The high thermal stability of the green emission upon Ce<sup>3+</sup> excitation is ascribed to suppression of Ce3+ thermal deexcitation by fast energy transfer to thermally stable Tb<sup>3+</sup> emitters. The relatively low thermal stability of Ce<sup>3+</sup> emission in the codoped BYBO is attributed to a slow transfer rate of the emitting Ce<sup>3+</sup> ions that hardly compete with the thermal deexcitation. The greenemitting Ba<sub>2</sub>Y<sub>5</sub>B<sub>5</sub>O<sub>17</sub>:Ce<sup>3+</sup>, Tb<sup>3+</sup> phosphor shows sufficient thermal stability for near-UV-based white LED applications.

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#### Notes

The authors declare no competing financial interest.

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