Blue-green tunable color of Ce$^{3+}$/Tb$^{3+}$ coactivated NaBa$_3$La$_3$Si$_6$O$_{20}$ phosphor via energy transfer

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A series of color tunable phosphors NaBa$_3$La$_3$Si$_6$O$_{20}$:Ce$^{3+}$, Tb$^{3+}$ were synthesized via the high-temperature solid-state method. NaBa$_3$La$_3$Si$_6$O$_{20}$ crystallizes in noncentrosymmetric space group Ama2 with the cell parameters of $a = 14.9226(4)$ Å, $b = 24.5215(5)$ Å and $c = 5.6241(2)$ Å by the Rietveld refinement method. The Ce$^{3+}$ ions doped NaBa$_3$La$_3$Si$_6$O$_{20}$ phosphors have a strong absorption band from 260 to 360 nm and show near ultraviolet emission light centered at 378 nm. The Ce$^{3+}$ and Tb$^{3+}$ ions coactivated phosphors exhibit color tunable emission light from deep blue to green by adjusting the concentration of the Tb$^{3+}$ ions. An energy transfer of Ce$^{3+} \rightarrow$ Tb$^{3+}$ investigated by the photoluminescence properties and lifetime decay, is demonstrated to be dipole–quadrupole interaction. These results indicate the NaBa$_3$La$_3$Si$_6$O$_{20}$:Ce$^{3+}$, Tb$^{3+}$ phosphors can be considered as potential candidates for blue-green components for white light emitting diodes.

By virtue of the special merits of high brightness, energy-efficient, life-durable, and environmentally friendly, the white light emitting diodes (w-LEDs) made from blue or near-ultraviolet (n-UV) emitting LEDs chips coated with phosphors have the potential to overtake incandescent and fluorescent lighting types$^{4,5}$. In 1996, the w-LEDs fabricated from the blue-emitting InGaN LED chips combined with the yellow-emitting phosphors (YAG:Ce$^{3+}$) were commercialized$^6$. Unfortunately, this technology has the following problems: low color rendering index due to two-color mixing, and low color reproducibility due to the strong dependence of white color purity on the quality of phosphors$^{6–11}$. To solve these problems, the w-LEDs had been fabricated employing blue, green and red emitting phosphors excited by a blue or n-UV chip$^{12–14}$. However, the strong reabsorption of blue light by red and green phosphors reduces the luminescence efficiency in this system$^{15,16}$. To overcome these disadvantages, vigorous attentions were received to exploit the emission-tunable phosphors with strong absorption in n-UV region$^{17,18}$. Simultaneously, an energy transfer can obviously improve the luminescent efficiency and color reproducibility as well as widen the emission spectra of phosphors.

After years of efforts, a series of promising phosphors had been developed, such as fluorides$^{19}$, silicates$^{20,21}$, phosphates$^{22}$, orthovanadates$^{22,23}$, borates$^{24,25}$, tungstates/molybdates$^{26,27}$, nitrides$^{28,29}$, aluminates$^{30–32}$, etc. Among them, the silicate compounds as luminescent hosts were intensively studied because of their remarkable stability of physical and chemical properties, flexible crystal structures and relatively easy preparation process. Among rare earth ions, the Tb$^{3+}$ ion is the best candidate for green component due to its predominant $^5D_4$–$^7F_5$ transitions$^{33}$. However, the electric dipole transitions within the $4f$ configurations of the Tb$^{3+}$ ion is spin forbidden, resulting in the weak intensity of its absorption in the n-UV region and the narrow width. Thus, a suitable sensitizer is always necessary for the phosphors activated by the Tb$^{3+}$ ion. It is well known that the Ce$^{3+}$ ion is an excellent sensitizer transferring a part of its energy to an activator such as the Tb$^{3+}$ ion depending on its lowest 5d state and broad absorption and emission bands from the allowed 4f–5d transitions$^{34}$. In this work, we reported a novel silicate host phosphor, NaBa$_3$La$_3$Si$_6$O$_{20}$:Ce$^{3+}$, Tb$^{3+}$ for the excitation by a n-UV LED chip, and the crystal structure, luminescent properties and energy transfer mechanism between the Ce$^{3+}$ ion and the Tb$^{3+}$ ion had been thoroughly investigated.

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Results and Discussion

Crystal structure and phase formation. Figure 1(a) demonstrates the observed and calculated XRD patterns as well as their difference for the Rietveld refinement of NaBa₃La₃Si₆O₂₀. In the refinement, an initial structure model and atomic positions of NaBa₃Eu₃Si₆O₂₀ were adopted for the structure refinement 35,36. NaBa₃La₃Si₆O₂₀ crystallizes in the noncentrosymmetric space group Ama2 and unit cell parameters are obtained as a = 14.9226(4) Å, b = 24.5215(5) Å and c = 5.6241(2) Å, which are slightly larger than those of NaBa₃Eu₃Si₆O₂₀ due to large ionic radius of La³⁺ ion 37. As shown in Fig. 1(c), the basic structural units are distorted (SiO₄)⁴⁻ tetrahedra which are further linked by the Ba, La, and Na atoms to build a complex three-dimensional framework. The Na atoms which are surrounded by six oxygen adopt distorted pentagonal-pyramidal geometry, the Ba₁ and Ba₂ atoms coordinated to seven and eight oxygen are in distorted trigonal prism and cube configuration. In the structure of NaBa₃La₃Si₆O₂₀, there are two kinds of La sites, implying that there are two possible types of Ce³⁺ ions in the NaBa₃La₃Si₆O₂₀:Ce³⁺ samples. The La₁ atoms are coordinated to seven oxygen atoms to form pentagonal bipyramid while the La₂ surrounded by eight oxygen atoms are in square anti-prism environment (Fig. 1(d)).

Figure 1(b) shows the selected XRD patterns of the as-synthesized representative samples of NaBa₃La₃Si₆O₂₀ and NaBa₃La₃Si₆O₂₀:0.007Ce³⁺, yTb³⁺ (0 ≤ y ≤ 0.30) and the quantitative analysis of all the samples illustrate that the doping of Ce³⁺ or/and Tb³⁺ are successful (Supplementary Table S1). Also, it can be seen that all the diffraction peaks of the selected phosphors match well with the NaBa₃La₃Si₆O₂₀ phase. Even at high doping concentration of the Tb³⁺ ion (30%), the XRD patterns of phosphors are almost same with that of undoped phase, which illustrates the excellent stability and accommodation capacity for doped ions of crystal structure of the NaBa₃La₃Si₆O₂₀ host. The XRD profiles for the Rietveld refinement of the single element doped and co-doped samples and the coordination, occupancy and isotropic displacement parameter for all samples are listed (Supplementary Figs S1–S7, Tables S2–S9).

Photoluminescence properties and energy transfer. As shown in Fig. 2(a), the PLE spectra of the NaBa₃La₃Si₆O₂₀:0.007Ce³⁺ sample consist of three absorption bands centered at around 254, 282 and 331 nm, which arise from the electronic transitions between the ground state (2F⁵/₂ and 2F⁷/₂) and the levels of ⁵d excited split by crystal field of the Ce³⁺ ion 38. Under the excitation wavelength of 331 nm, the Ce³⁺ ion doped NaBa₃La₃Si₆O₂₀ sample shows an asymmetric emission band extending from 340 to 500 nm with the maximum at 378 nm, indicating a possible spectral overlap originating from different luminescence centers. It is obvious that one type of Ce³⁺ ions gives rise to two emission band due to the transitions from the lowest ⁵d excited states to two ground states (⁵F₂/₂ and ⁵F⁷/₂) respectively 39. However, the emission band of the NaBa₃La₃Si₆O₂₀:0.007Ce³⁺ sample can be decomposed into four Gaussian components A–D peaking at 364, 380, 394 and 410 nm with the energy gaps between A and C is 2092 cm⁻¹, that of B and D is 1926 cm⁻¹, which are close to the theoretical value of 2000 cm⁻¹ 40,41. These results imply that there should be two kinds of Ce³⁺ ions, which is consistent with the previous investigation on the crystal structure that there are two kinds of different chemical environment of La³⁺ ions in the NaBa₃La₃Si₆O₂₀ host.

As given in Fig. 2(b), the PL intensity of the NaBa₃La₃Si₆O₂₀:xCe³⁺ samples increases gradually with the increase of the doping concentration of the Ce³⁺ ions and reaches the maximum when the x value is 0.007,
and then begins to decrease due to concentration quenching. It is also indicated that the Ce³⁺ ion is a sensitizer for the Tb³⁺ ion and an energy transfer of Ce³⁺ → Tb³⁺ is crucial to enhance green emission of the Tb³⁺ ion and achieve color tunable emission light. Therefore, the optimal concentration of the Ce³⁺ ion in the NaBa₃La₃Si₆O₂₀:xCe³⁺ samples is confirmed to be 0.007.

Generally, the critical distance $R_c$ between the Ce³⁺ ions can be calculated with the following equation given by Blasse:

$$R_c = \frac{3V}{4\pi xN^{3/5}}$$

where $V$ is the volume of unit cell, $x$ is the critical concentration of doped ions, where the emission intensity of phosphors reaches the maximum, $N$ is the number of host cations per unit cell. For the NaBa₃La₃Si₆O₂₀:0.007Ce³⁺ sample, $N = 12$, $V = 2057.989 \, \text{Å}^3$, $R_c$ is calculated to be about 25.00 Å. Dexter noted a non-radiative energy transfer usually was attributed to exchange or multipole – multipole interaction in oxide phosphors and the exchange interaction was valid only when the $R_c$ was shorter than 5 Å. In consequence, the concentration quenching mechanism of the Ce³⁺ ions in the NaBa₃La₃Si₆O₂₀:xCe³⁺ samples is dominated by the multipole – multipole interaction.

Figure 3(a) depicts the PLE and PL spectra of the NaBa₃La₃Si₆O₂₀:xCe³⁺,yTb³⁺ phosphors (a), and the NaBa₃La₃Si₆O₂₀:0.007Ce³⁺, 0.20Tb³⁺ phosphor (b).

Figure 2. (a) The PLE (dark solid line) and PL spectra (red solid line) of the NaBa₃La₃Si₆O₂₀:0.007Ce³⁺ sample and the Gaussian peaks fitting (the green dashed lines of the Ce³⁺ (1) and the blue dashed lines of the Ce³⁺ (2)). (b) The PL spectra of the NaBa₃La₃Si₆O₂₀:xCe³⁺ samples with varying concentration of the Ce³⁺ ions.

Figure 3. The PLE and PL spectra of the NaBa₃La₃Si₆O₂₀:xCe³⁺,yTb³⁺ phosphors (a), and the NaBa₃La₃Si₆O₂₀:0.007Ce³⁺, 0.20Tb³⁺ phosphor (b).
the Tb³⁺ ions. The emission intensity of the NaBa₃La₃Si₆O₂₀:Tb³⁺ samples under excitation wavelength of 268 nm is larger than that under 378 nm, because the intensity of the absorption peak centered at 268 nm is more intense than that at 378 nm. However, the emission light intensity monitored at 268 nm is less than that at 374 nm in the NaBa₃La₃Si₆O₂₀:Ce³⁺, Tb³⁺ phosphors. These results verify that it is the overlap between f-f transition (peaking at 374 nm) but not f-d transition (peaking at 268 nm) of the Tb³⁺ ions and the emission band of the Ce³⁺ ions induce the energy transfer. Figure 3(b) also shows the excitation spectrum of the NaBa₃La₃Si₆O₂₀:0.007Ce³⁺, 0.20Tb³⁺ phosphor monitored at 378 nm (the Ce³⁺ ions emission) is similar to that of at 542 nm (the Tb³⁺ ions emission) except the difference of luminous intensity, which provides another evidence for energy transfer of Ce³⁺→Tb³⁺.

To further investigate the sensitized luminescence of the Tb³⁺ ions by the Ce³⁺ ions, the emission spectra of the NaBa₃La₃Si₆O₂₀:0.007Ce³⁺, yTb³⁺ phosphors were measured (Fig. 4). Although the amount of the Ce³⁺ ions is fixed, their emission intensity gradually decreases along with the increase of the concentration of the Tb³⁺ ions. The result indicates that a lot of Tb³⁺ ions as acceptors accelerate energy diffusion of donors, which speeds up the average transfer rate of Ce³⁺→Tb³⁺.

Figure 5 and Table 1 show the variation of Commission International deL’Eclairage (CIE) chromaticity coordinates of the NaBa₃La₃Si₆O₂₀:0.007Ce³⁺, yTb³⁺ phosphors (0 ≤ y ≤ 0.3) excited under 331 nm and the pictures of the NaBa₃La₃Si₆O₂₀:0.007Ce³⁺, yTb³⁺ phosphors (0 ≤ y ≤ 0.3) in a 365 nm UV box.

Energy transfer mechanism. In general, the energy transfer from a sensitizer to an activator in oxide may take place via exchange interaction or electric multipolar interaction. The separation distance $R_{Ce,Tb}$ can be also estimated from equation (1). Here, $x$ is the total concentration of the Ce³⁺ and Tb³⁺ ions, where the
The luminescence intensity of sensitizer is half of that in samples lack of activator. For the NaBa₃La₃Si₆O₂₀:0.007Ce³⁺, yTb³⁺ phosphors, the value of $x_{\text{Ce}³⁺}$ and $x_{\text{Tb}³⁺}$ is about 0.021 and 0.75 respectively, thus $R_{\text{Ce}-\text{Tb}}$ is calculated to be about 7.5 Å. Since exchange interaction was restricted to distances of about 4 Å, the energy transfer mechanism of $\text{Ce}³⁺ \rightarrow \text{Tb}³⁺$ should mainly be electric multipolar interaction. According to Dexter’s energy transfer expressions of multipolar interaction and Reisfeld’s approximation, the following relation can be given as:

$$\eta_0 / \eta \propto C_{\text{Ce}³⁺+\text{Tb}³⁺}^{n/3}$$

(2)

where $\eta_0$ and $\eta$ are the luminescence quantum efficiency of the Ce³⁺ ions in absence and presence of the Tb³⁺ ions, $n = 6, 8$ and 10 are corresponding to dipole–dipole, dipole–quadrupole and quadrupole–quadrupole interactions, respectively. The value $\eta_0 / \eta$ is approximately estimated by the ratio of related luminescence intensity $I_0/I$, $I_0$ is the intrinsic luminescence intensity of the Ce³⁺ ions, and $I$ is the luminescence intensity of the Ce³⁺ ions in presence of the Tb³⁺ ions. Figure 6(a–d) illustrates the relationships between $I_0/I$ and $C_{\text{Ce}³⁺+\text{Tb}³⁺}^{n/3}$ as well as $I_0/I$ and $C_{\text{Ce}³⁺+\text{Tb}³⁺}^{n/3}$. The $R^2$ value is reasonable in Fig. 6(b,c), implying the energy transfer of Ce³⁺ → Tb³⁺ may occur via dipole–dipole or dipole–quadrupole interaction. However, Sommerdijk stated the probability of energy transfer of Ce³⁺ → Tb³⁺ via electric dipole–dipole interaction was less likely, therefore, dipole – quadrupole interaction should mainly contribute to energy transfer of Ce³⁺ → Tb³⁺.

### Table 1. The comparison of the CIE chromaticity coordinates of the NaBa₃La₃Si₆O₂₀:0.007Ce³⁺, yTb³⁺ phosphors ($\lambda_{\text{ex}} = 331$ nm).

| No. of points in CIE diagram | Sample compositions                | CIE coordinates (x, y) |
|------------------------------|-----------------------------------|------------------------|
| a                            | $y = 0.00$                         | (0.163, 0.019)         |
| b                            | $y = 0.05$                         | (0.181, 0.131)         |
| c                            | $y = 0.10$                         | (0.195, 0.222)         |
| d                            | $y = 0.15$                         | (0.208, 0.303)         |
| e                            | $y = 0.20$                         | (0.216, 0.348)         |
| f                            | $y = 0.25$                         | (0.223, 0.389)         |
| g                            | $y = 0.30$                         | (0.235, 0.472)         |

Figure 6. The dependence of $I_0/I$ of the Ce³⁺ ions on (a) $C_{\text{Ce}³⁺+\text{Tb}³⁺}^6$, (b) $C_{\text{Ce}³⁺+\text{Tb}³⁺}^{6/3}$, (c) $C_{\text{Ce}³⁺+\text{Tb}³⁺}^{8/3}$, (d) $C_{\text{Ce}³⁺+\text{Tb}³⁺}^{10/3}$. 

- **R²** value is reasonable in Fig. 6(b,c), implying the energy transfer of Ce³⁺ → Tb³⁺ may occur via dipole–dipole or dipole–quadrupole interaction. However, Sommerdijk stated the probability of energy transfer of Ce³⁺ → Tb³⁺ via electric dipole–dipole interaction was less likely, therefore, dipole – quadrupole interaction should mainly contribute to energy transfer of Ce³⁺ → Tb³⁺.
In order to further validate the energy transfer process, the room temperature decay curves for the $4f$-$5d$ (centered at 378 nm) transition of the Ce$^{3+}$ ions in the NaBa$_3$La$_3$Si$_6$O$_{20}$:0.007Ce$^{3+}$, $y$Tb$^{3+}$ (y = 0.05, 0.10, 0.15, 0.20, 0.25 and 0.30) excited at 330 nm are shown in Fig. 7. For existing two types of Ce$^{3+}$ ions in topic phosphors, the decay curves should be well fitted with a typical two exponential function:

$$\tau = \tau_1 + \tau_2$$

where $I(t)$ and $I_0$ are the luminescence intensity at time t, $A_1$ and $A_2$ are the fitting constants, $\tau_1$ and $\tau_2$ represent the decay time for the exponential components. Then the average lifetime ($\tau^*$) can be calculated to be 24.5, 22.6, 21.7, 20.5, 20.0, 19.2 and 17.3 by the following formula:

$$\tau^* = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$$

The decay time of the Ce$^{3+}$ ions decreases as increase of the concentration of the Tb$^{3+}$ ions, which strongly demonstrates the energy transfer of Ce$^{3+}$ $\rightarrow$ Tb$^{3+}$.

Subsequently the energy levels model for the energy transfer processes of Ce$^{3+}$ $\rightarrow$ Tb$^{3+}$ was investigated. As given in Fig. 8(a), the Ce$^{3+}$ ion absorbs light firstly, then it jumps from the ground states ($^2$F$_{7/2}$) to the excited states (5d energy levels), subsequently the excited state Ce$^{3+}$ ion returns to the lowest level of 5d levels by giving off excess energy to its surroundings, eventually goes back to the $^2$F$_{7/2}$ or $^2$F$_{5/2}$ ground states by a radiative process. The energy transfer efficiency of Ce$^{3+}$ $\rightarrow$ Tb$^{3+}$ should increase as the increase of the concentration of the Tb$^{3+}$ ions due to more neighboring Tb$^{3+}$ ions around the Ce$^{3+}$ ions. Finally the energy level transitions of $^5$D$_{j}$ to $^7$F$_{J}$ ($J$ = 3, 4, 5 and 6) produce the characteristic emission of the Tb$^{3+}$ ions.

The energy transfer efficiency $\eta_T$ from the Ce$^{3+}$ ions to the Tb$^{3+}$ ions can be calculated according to the following equation:

$$\eta_T = 1 - \frac{I_f}{I_0}$$
where $I_0$ and $I_y$ are the emission light intensity of the sensitizer with and without an activator, respectively. In the NaBa$_3$La$_2$Si$_6$O$_{20}$:0.007Ce$^{3+}$, yTb$^{3+}$ samples, the Ce$^{3+}$ ion is a sensitizer and the Tb$^{3+}$ ion is an activator. The $\eta$ values can be calculated as 7.06%, 16.71%, 28.95%, 37.04%, 48.95%, 78.31%, as a function of y ($y=0.15, 0.30, 0.45, 0.60, 0.75, 0.90$), respectively (Fig. 8(b)). The energy transfer of Ce$^{3+} \rightarrow$ Tb$^{3+}$ is consistent with the conclusion that the energy transfer efficiency increases as the increase of the concentration of the Tb$^{3+}$ ions due to more neighboring Tb$^{3+}$ ions around the Ce$^{3+}$ ions and is equivalent to that of the reported K$_2$MgSi$_2$O$_6$:Ce$^{3+}$, Tb$^{3+}$ silicate phosphor.

**Conclusion**

A series of novel NaBa$_3$La$_2$Si$_6$O$_{20}$:Ce$^{3+}$, Tb$^{3+}$ phosphors were prepared by solid state method. The energy transfer process of Ce$^{3+} \rightarrow$ Tb$^{3+}$ has been demonstrated to be dipole – quadrupole interaction. The tunable colors from deep blue to green can be realized by varying the doping concentration of the Tb$^{3+}$ ions.

**Experimental Section. Compounds synthesis.** The NaBa$_3$La$_2$Si$_6$O$_{20}$:Ce$^{3+}$, Tb$^{3+}$ phosphors were synthesized by high temperature solid state method. Na$_2$CO$_3$ (A.R.), BaCO$_3$ (A.R.), SiO$_2$ (A.R.), La$_2$O$_3$ (99.99%), CeO$_2$ (99.99%), and Tb$_2$O$_3$ (99.99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All of the initial chemicals were used without further purification. Stoichiometric amounts of the above-mentioned chemicals were ground thoroughly by an agate mortar, packed tightly in an alumina crucible. The temperature of the fur-

**Material characterization.** The powder XRD measurements were taken on a Bruker D8 X-ray diffractometer with a Cu Kα source ($\lambda=1.5418\ァ$) in the angular range from 5° to 80° with a scanning step of 0.15. The structure refinement was carried out with the General Structure Analysis (GSAS) and EXPGUI software. XRD Rietveld profile refinements of the structural models were performed using the General Structure Analysis (GSAS) software. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were obtained by an FLS-980 fluorescence spectrophotometer equipped with a 450 W Xe light source. The photoluminescence lifetime curves were measured on an FLS-920 fluorescence spectrophotometer equipped with a laser as light source. All measurements were performed at room temperature. The element analyses of samples were performed by the (X-ray economic perspective.

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Acknowledgements
We acknowledge the financial support from the National Natural Science Foundation of China (Grant No. 51502307) and Key Laboratory of Coordination Chemistry and Functional Materials in Universities of Shandong, Dezhou University.

Author Contributions
M.X. developed the idea and supervised the project, Z.J. and M.X. conducted the experiments and wrote the paper. All authors discussed the results.

Additional Information
Supplementary information accompanies this paper at http://www.nature.com/srep
Competing financial interests: The authors declare no competing financial interests.
How to cite this article: Jia, Z. and Xia, M. Blue-green tunable color of Ce³⁺/Tb³⁺ coactivated NaBa₃La₃Si₆O₂₀ phosphor via energy transfer. Sci. Rep. 6, 33283; doi: 10.1038/srep33283 (2016).

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