

Article

Quantum Cutting in Ultraviolet B-Excited $\text{KY}(\text{CO}_3)_2\text{Tb}^{3+}$ Phosphors

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Abstract: Highly efficient quantum cutting $\text{KY}(\text{CO}_3)_2\text{Tb}^{3+}$ phosphors excited by ultraviolet B (UVB) and ultraviolet C (UVC) were investigated. The structural and spectroscopic properties were characterized by XRD analysis and fluorescence spectrophotometry, respectively. The results showed that the monoclinic crystal structure of $\text{KY}(\text{CO}_3)_2\text{Tb}^{3+}$ remained in the Tb^{3+} doping range of 0–100%. In the excitation spectrum, two intense excitation peaks were observed in the ultraviolet range. Under the excitation of 283 nm, the maximum quantum efficiency of $\text{KY}(\text{CO}_3)_2\text{Tb}^{3+}$ could reach 119%. However, the most efficient quantum cutting occurred at the $^5\text{K}_8$ excited state in the cross-relaxation of $^5\text{K}_8 + ^7\text{F}_6^5\text{D}_4 + ^5\text{D}_4$. The Tb^{3+} content could be selected arbitrarily in the $\text{KY}(\text{CO}_3)_2$ host without any concentration quenching. Optimal quantum cutting concentrations of Tb^{3+} in $\text{KY}(\text{CO}_3)_2$ were 0.7 and 0.3 for the excitation of UVB and UVC, respectively. UVB-excited phosphors are more popular with high transparency in products such as glass or resin. A quick response code was fabricated by resin to show the hidden information clearly. Therefore, the highly efficient phosphor could be a candidate material for the application in information identification technology.

Keywords: quantum cutting; Tb^{3+} ; ultraviolet B; phosphors



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1. Introduction

Quantum cutting is the process of converting a single photon into two or more photons [1–4]. The quantum cutting efficiency is often larger than 100%. Vacuum ultraviolet and short-wave ultraviolet are often used as excitation sources for quantum cutting [5]. High-energy photons could excite ground-state electrons to higher excited-state energy levels, and the energy level of the intermediate excited state could be used as a bridge for the energy transfer to achieve multi-photon emission. As one of the rare-earth ions in visible light emission, Tb^{3+} has a large energy gap between the $^5\text{D}_4$ excited state and the ground state for less influence on the multi-phonon relaxation [6]. The large proportion of green-light emissions from the $^5\text{D}_4$ to $^7\text{F}_5$ transition makes the $^5\text{D}_4$ level of Tb^{3+} meet the requirement of efficient quantum cutting [1,7]. In efficient quantum cutting of Tb^{3+} , the appropriate host environment and intermediate excited state are used to achieve energy level matching between two different or identical ions for energy transfer. In the research of single-ion quantum cutting of Tb^{3+} , the quantum efficiencies of $\text{K}_2\text{YF}_5\text{Tb}^{3+}$ [1], $\text{Ca}_9\text{Y}(\text{PO}_4)_7\text{Tb}^{3+}$ [8], and $\text{Ba}_9\text{Lu}_2\text{Si}_6\text{O}_{24}\text{Tb}^{3+}$ [9] excited at 245, 222, and 251 nm were 121.3%, 157.2%, and 144%, respectively. In the level matching, the $^5\text{D}_4$ energy level of Tb^{3+} was directly used as an intermediate excited state to transfer the excited-state electrons [8]. If both $^5\text{D}_3$ and $^5\text{D}_4$ excited states of Tb^{3+} participate in the $^7\text{F}_j$ ($j = 6, 5, 4, 3$) luminescence emission at the same time, there is an emission competition between the two excited levels [7], and the emission efficiency of $^5\text{D}_4$ level in the visible region is reduced. On the other hand, energy transfer can also be realized with the aid of other ions for a suitable level matching. In the $\text{CeO}_2\text{Tb}^{3+}/\text{Yb}^{3+}$ [10], $\text{BaGdF}_5\text{Tb}^{3+}$ [11], and $\text{NaGdF}_4\text{Ho}^{3+}/\text{Yb}^{3+}$ [2]

materials, Yb^{3+} and Gd^{3+} could be used as an energy transfer bridge to achieve quantum cutting efficiency of 164, 177, and 179.8%, respectively. To sum up, the direct energy transfer processes, an appropriate host, and energy level matching are necessary key conditions to achieve high efficiency of quantum cutting in luminescence materials.

In Stokes emission, most excitation wavelengths of quantum cutting are located in the short-wave or vacuum ultraviolet regions for visible light emission, such as 142 nm [12], 222 nm [13], and 251 nm [9]. However, there are few reports on quantum cutting excited by middle-wave ultraviolet light due to the limitation of exciting photon energy and the lack of matching energy levels. Middle-wave ultraviolet light has relatively good penetrability in air, resin, or glass. If the quantum cutting phosphor excited by ultraviolet B is developed, the application of phosphor in lamps, decoration, and anti-counterfeiting could be greatly improved and expanded [1]. We studied the luminescent spectra of Tb^{3+} in $\text{KTb}(\text{CO}_3)_2$ system in detail [14]. The larger excitation intensities exist in the ultraviolet B-excited spectrum, which has a potential application in quantum cutting for efficient luminescence. Compared with Tb, the rare-earth Y has a relatively cheaper price, which has a similar ionic radius and the zero electron of 4f configuration [15,16]. It is possible for Y^{3+} to completely substitute Tb^{3+} in $\text{KTb}(\text{CO}_3)_2$ as a luminescent host. In the luminescent emission of Tb^{3+} -doped $\text{KY}(\text{CO}_3)_2$, the energy of the exciting photons could be further reduced by the emission transitions of the excited electrons to the lower $^5\text{D}_4$ excited state. In this contribution, quantum cutting, spectral characterizations, and decay time of Tb^{3+} -doped $\text{KY}(\text{CO}_3)_2$ were investigated in short- and middle-wave ultraviolet ranges.

2. Materials and Methods

$\text{KY}_{1-x}(\text{CO}_3)_2:x\text{Tb}^{3+}$ ($\text{KYC}:x\text{Tb}^{3+}$) phosphors were synthesized by the hydrothermal method [14]. The raw materials of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%) and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%) were bought from the Shanghai xianding Biotechnology Co., Ltd. (Shanghai, China). First, $(1-x)$ mmol $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and x mmol $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved into 3 mL of deionized water for the mixture solution. Then, the mixture was added dropwise to the 25 mL K_2CO_3 solution (0.55 mol/L) under vigorous stirring. The pH value of the mixed solution was adjusted to 9.5 by the dilute nitric acid. The final solution was transferred to the 50 mL Teflon autoclave, which was reacted at 200 °C for 8 h with a heating rate of 5 °C/min. Deionized water and ethanol were used to wash the precipitate. The phosphor was prepared after drying at 60 °C for 40 min in the air.

A quick response code (QR code) was prepared by the epoxy resin and phosphor. First, the phosphor could be dispersed well in epoxy resin by stirring. After the two substances were fully mixed, the mold was used to fabricate the desired object under heating at 100 °C for 60 min in the air.

The crystal structures were analyzed by the X-ray powder diffraction in the range of 10–70° (PANalytical, Almelo, The Netherlands). The morphologies and energy dispersive spectrum (EDS) were imaged with a cold field emission scanning electron microscopy (Regulus 8220, Hitachi High-Tech Co., Tokyo, Japan). The excitation spectra and emission spectra were measured by a FLS920 fluorescence spectrophotometer (Edinburgh Instruments, Livingston, UK) with the excitation of 450 W Xe-lamp. Using BaSO_4 as a reference, the absolute quantum efficiency (QE) was measured by the integrating sphere within the FLS920 sample chamber in a direct and indirect method. The decay curves were tested with the use of the 60 W microsecond flashlamp (Edinburgh Instruments, Livingston, UK).

3. Results and Discussion

3.1. Crystal Structures

Figure 1 shows the X-ray diffraction patterns of $\text{KYC}:x\text{Tb}^{3+}$ samples. When x increased from 0 to 1, the diffraction peaks of $\text{KYC}:x\text{Tb}^{3+}$ were consistent with that of monoclinic $\text{KDy}(\text{CO}_3)_2$ (JCPDS:1-88-1423) [17]. There were no foreign diffraction peaks, and it indicated that Tb^{3+} -doped KYC is a pure monoclinic phase. In the KYC lattice, Tb^{3+} and Y^{3+} with similar ion radii could be substituted for each other in any proportion. On the right side

of Figure 1, when $x = 0$, the value of KYC diffraction angle at (002) was larger than that of $\text{KDY}(\text{CO}_3)_2$ because the radius of Y^{3+} (1.019 Å) was smaller than Dy^{3+} (1.027 Å) [16]. As x increased, the diffraction peak corresponding to the (002) crystal plane was shifted toward a small angle. Therefore, the variation of cell parameters indicated that the environment of Tb^{3+} is modified slightly in the KYC lattice.

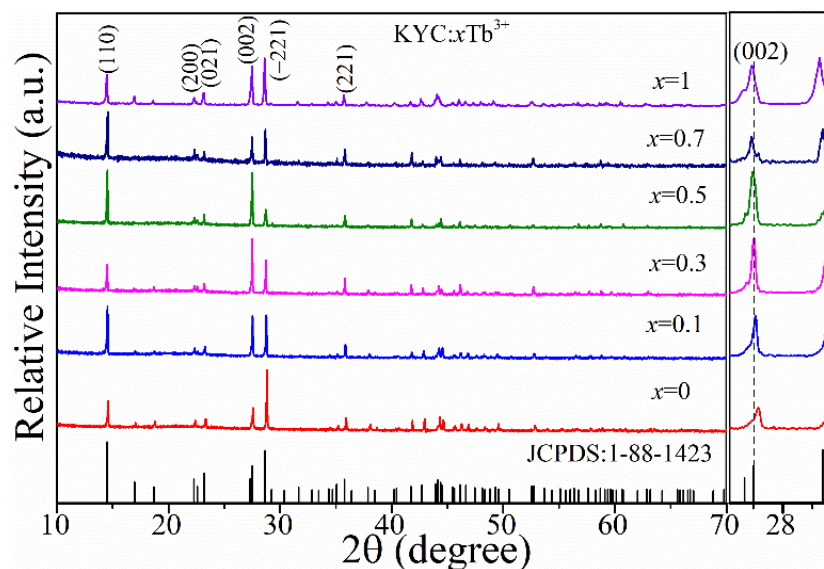


Figure 1. X-ray diffraction spectra of $\text{KYC}:\text{xTb}^{3+}$ ($x = 0, 0.1, 0.3, 0.5, 0.7, 1$).

3.2. Morphologies and Element Analysis

The morphologies of $\text{KYC}:\text{xTb}^{3+}$ at different x values are shown in Figure 2. When x value was 0.01, the phosphor exhibited as a single monoclinic particle with a size of 40–60 μm in Figure 2a. With the increase in Tb^{3+} ion concentration, the growth rate of the nucleus was obviously accelerated. Small monoclinic crystal particles aggregated with each other to form a large particle (Figure 2b–d). When the x further increased to 0.7 and 1, individual grains grew larger and easily fractured into small pieces (Figure 2e–f). A small area was selected from Figure 2d, and energy dispersive spectroscopy of Figure 2g was taken to demonstrate the existence of K, Y, Tb, and O elements in Figure 2h–l. From the element distribution maps, K, Y, and Tb ions were well-dispersed in $\text{KYC}:\text{0.5Tb}^{3+}$. The relative elemental composition was close to the original stoichiometric ratio.

3.3. Luminescence Spectra

Figure 3 shows the luminescence spectra of $\text{KYC}:\text{xTb}^{3+}$. From the excitation spectra presented in Figure 3a, the whole excitation spectrum of Tb^{3+} was mainly composed of $4f^8-4f^75d^1$ transition in the range of 200–300 nm and $4f^8-4f^8$ transition in the range of 300–390 nm [3,18,19]. In the f–d transition, there were mainly two strong excitation peaks at 245 and 283 nm, corresponding to the transition from the 7F_6 ground state to 7D_J and 9D_J levels [9], respectively. When the Tb^{3+} ion doping concentration is low, the excitation intensity corresponding to 7D_J is much greater than 9D_J because 7D_J transition is spin-allowed and 9D_J transition is spin-prohibited [9]. As the doped concentration of Tb^{3+} increases, the relative exciting intensity of $^7D_J/{}^9D_J$ is decreased due to the sensitive f–d transition in the variation of $\text{KYC}:\text{Tb}^{3+}$ crystal field [20]. When the concentration of Tb^{3+} ion was greater than 10%, the 9D_J forbidden transition of Tb^{3+} was gradually abolished. The intensity of the excitation peak at 283 nm increased significantly in $\text{KYC}:\text{Tb}^{3+}$, and it indicated that ultraviolet B could be used for efficient excitation. Compared with ultraviolet C and vacuum ultraviolet, ultraviolet B has higher transmittance in glass, resin, and polymer materials. The longer-wavelength UV light is more suitable for the excitation of luminescence emission of $\text{KYC}:\text{Tb}^{3+}$ in the luminescent products.

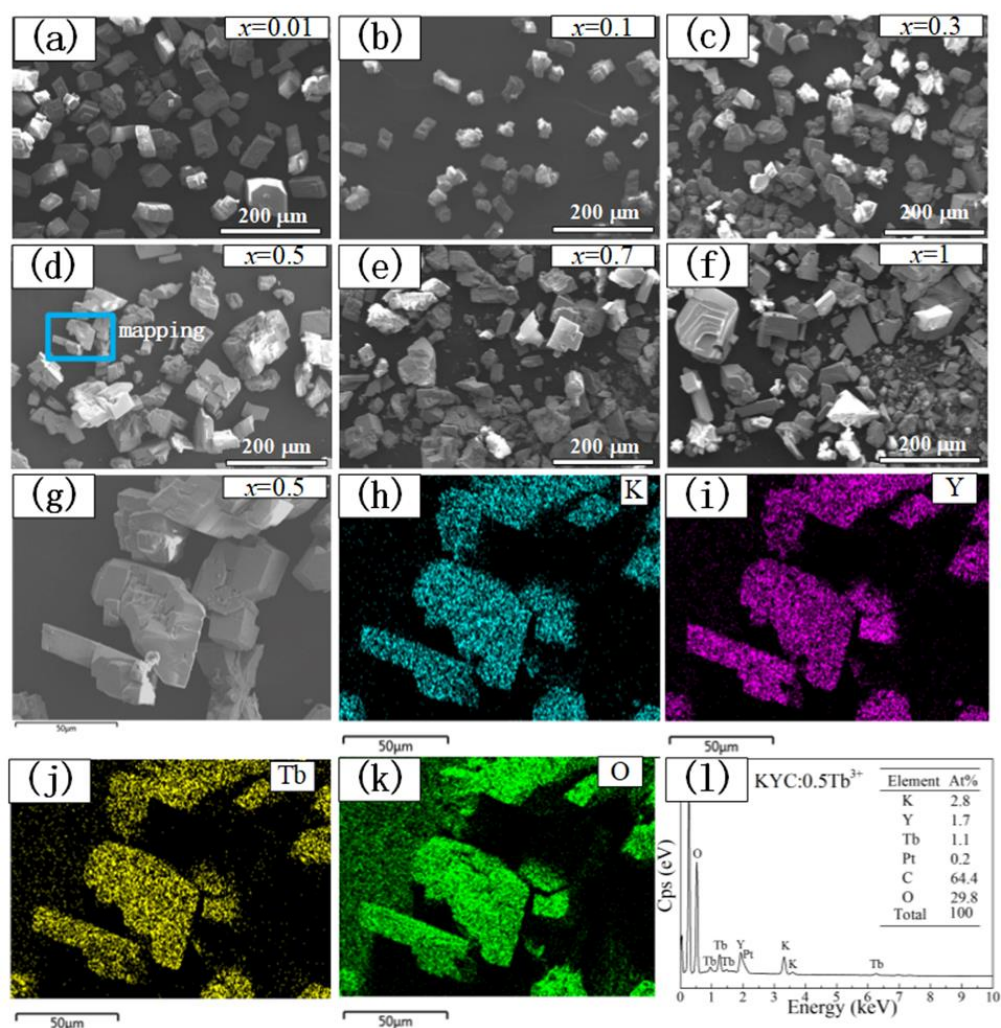


Figure 2. (a–f) Morphologies of $\text{KYC}:\text{xTb}^{3+}$ ($x = 0.01, 0.1, 0.3, 0.5, 0.7, 1$); (g) Selected area of $\text{KYC}:\text{0.5Tb}^{3+}$; (h–k) Element mapping of K, Y, Tb, and O; (l) Energy dispersive spectroscopy analysis.

Low doping concentration is convenient to characterize the transition process of a single excited-state electron between different levels. Figure 3b shows the emission spectra of Tb^{3+} -doped KYC at $x = 0.001$. From the spectra, the intense emission peaks were mainly located in the range of 480–640 nm over the whole spectrum for the exciting wavelength of 245 and 283 nm, corresponding to the transition of $^5\text{D}_4 \rightarrow ^7\text{F}_j$, respectively [21]. In the literature, it can be often found that there is a competitive emission between $^5\text{D}_3$ and $^5\text{D}_4$ of Tb^{3+} at low concentrations during the de-population process of the excited electron state [11]. A larger emission region reduces the proportion of green-light emission intensity [22]. When 283 nm was adopted as the excitation wavelength, only two emission bands were located at 376 and 543 nm. Two different emissions indicate that the electrons in the highest excited state are decayed to the ground state through at least two intermediate excited states. When 351 nm was used as the excitation wavelength, these two kinds of emission bands could also be observed. As it is shown in Figures S1 and S2, the broadband emission peak intensity at 376 nm gradually decreased with the increase in Tb^{3+} doping concentration. When 376 nm was directly used as the excitation wavelength, the excited-state electron could relax to $^5\text{D}_4$ level to achieve luminescence emission. A suitable crystal lattice environment is also a key factor for the intense emission [23]. Therefore, in the KYC host, especially for excitation at 245 nm of Tb^{3+} , there is no competitive emission between $^5\text{D}_3$ and $^5\text{D}_4$ levels, and the high efficiency of Tb^{3+} in the KYC host has more advantage in green-light emission than that of other hosts, owing to the single and direct energy transfer level of $^5\text{D}_4$.

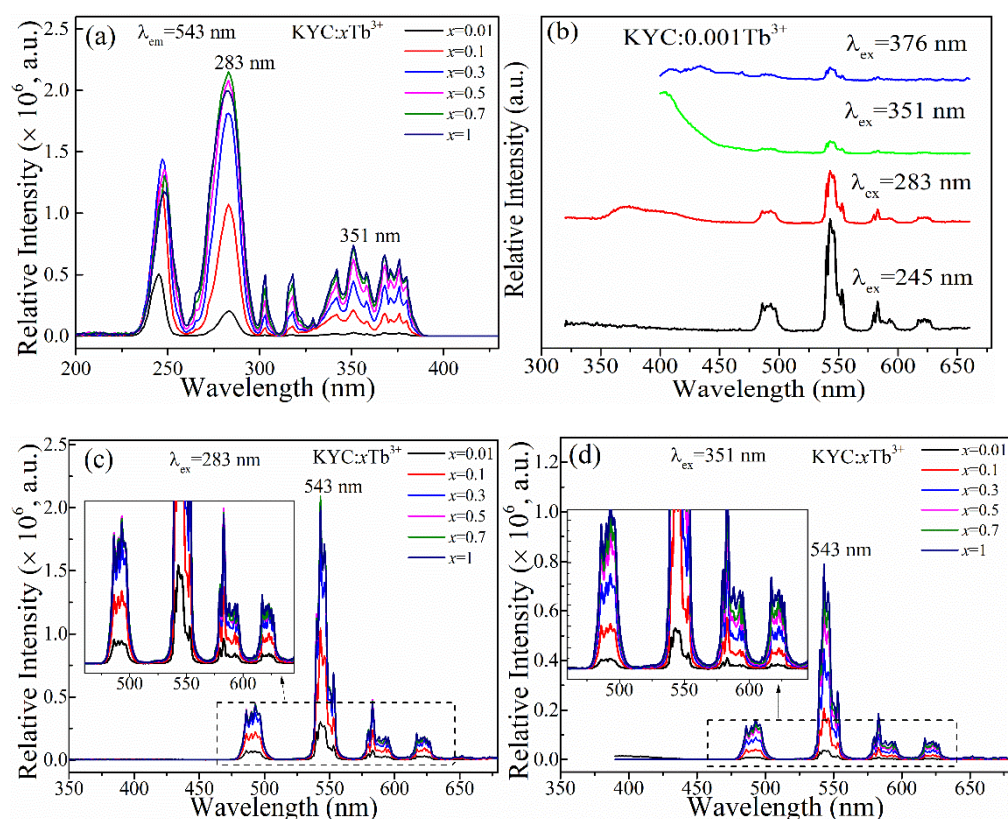


Figure 3. Luminescence spectra of $\text{KYC}:x\text{Tb}^{3+}$: (a) excitation spectra; (b) emission spectra of $\text{KYC}:0.001\text{Tb}^{3+}$; (c) emission spectra excited at 283 nm; (d) emission spectra excited at 351 nm.

As is shown in Figure 3c, the emission intensity of the green light at 543 nm was increased rapidly with the increase in Tb^{3+} -doped concentration in KYC. When x was larger than 0.3, the increase rate of 543 nm emission intensity was slowed down. When we used 351 nm as the excitation wavelength, the luminescence was similar to that of 283 nm excitation, but the emission intensity was slightly lower, which was about 50% of that of 283 nm under the same conditions in Figure 3d. The emission intensity was more intense under the 283 nm excitation than under 351 nm due to the larger excitation intensity in Figure 3a excitation spectra. Meanwhile, we also found that $\text{KYC}:1\text{Tb}$, where Tb^{3+} was completely substituted for Y^{3+} , could emit strong green light without any concentration quenching [14].

3.4. Energy Level Diagram

Figure 4 gives a schematic diagram of the electron transition on the excited-state energy level of Tb^{3+} . As can be seen from the diagram, electrons at the $^7\text{F}_6$ level were excited to the $^5\text{K}_8$ level by the 245 nm excitation light. The energy levels $^5\text{K}_8$, $^5\text{F}_4$, $^5\text{D}_4$, $^7\text{F}_0$, and $^7\text{F}_6$ of Tb^{3+} were at 40,749, 35,380, 20,545, 5703, and 74 cm^{-1} , respectively [24]. The $^5\text{K}_8 \rightarrow ^5\text{D}_4$ energy gap of 20204 cm^{-1} was similar to that of $^7\text{F}_6 \rightarrow ^5\text{D}_4$ (20471 cm^{-1}). The excited-state electrons could transfer energy directly to the $^5\text{D}_4$ level by the cross-relation: $^5\text{K}_8 + ^7\text{F}_6 \rightarrow ^5\text{D}_4 + ^5\text{D}_4$ (process 1), and then, the two excited-state electrons transferred back to the $^7\text{F}_j$ ($j=6, 5, 4, 3$) for the quantum cutting emission at 493, 543, 583, and 623 nm, respectively. Under the excitation at 283 nm, the ground-state electrons of $^7\text{F}_6$ were excited to the $^5\text{F}_4$ level [1]. Then, the excited-state electrons returned to the two lower excited states $^5\text{G}_6$ and $^5\text{D}_4$. A proportion of excited-state electrons could transfer in a way of $^5\text{F}_4$ and $^5\text{G}_6$ to $^7\text{F}_j$ with a broad emission (360–420 nm), which is clearly shown in Figure 3b. It is worthwhile to note that the energy gaps were almost the same between $^5\text{F}_4 \rightarrow ^5\text{D}_4$ (14835 cm^{-1}) and $^7\text{F}_0 \rightarrow ^5\text{D}_4$ (14842 cm^{-1}). The other proportions of excited-state electrons could more easily return to $^5\text{D}_4$ with the cross-relation: $^5\text{F}_4 + ^7\text{F}_0 \rightarrow ^5\text{D}_4 + ^5\text{D}_4$ (process 2). Finally, two excited-state electrons of $^5\text{D}_4$ transferred to $^7\text{F}_j$ in a quantum cutting emission.

Under the excitation of 351 nm, the excited electrons at the 5L_9 level could return to the 5G_6 level through vibration relaxation and then transfer to 7F_J with the board emission, which is shown in Figure 3b. The other electrons returned to 5D_4 with the cross-relation between $^5G_6 \rightarrow ^5D_4$ and $^7F_6 \rightarrow ^7F_0$, and the visible light could be emitted for the transition from 5D_4 to 7F_J , which was the same as the excitation process of 376 nm.

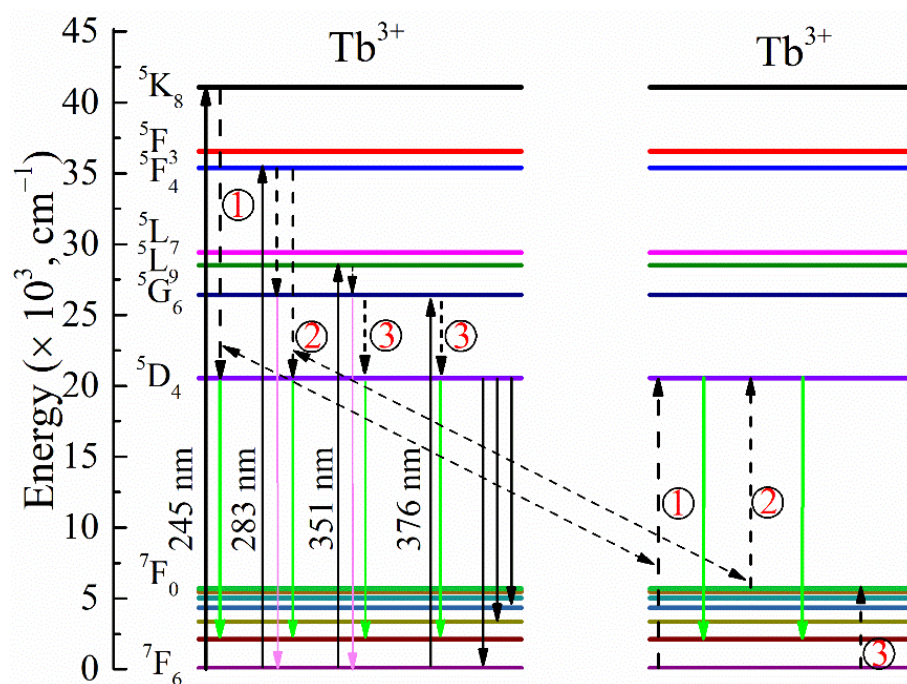


Figure 4. Energy level diagram of KYC:Tb³⁺.

Table 1 shows the quantum efficiency (QE) of KYC:*x*Tb³⁺ excited at 245, 284, and 351 nm. Since the Xenon lamp has low emission intensity below 250 nm [8], the QE values were measured under the fixed excitation at 245 nm for the Tb³⁺ spin-allowed transition. From the tendency of value variation, the QEs increased rapidly with the increase in Tb³⁺ doping concentration. The higher QE was due to simple and direct transition processes between 5G_6 and 5D_4 , which were the most efficient energy transfer processes. When 283 nm was used as an exciting wavelength, the quantum efficiency reached 109% at *x* = 0.3. As the doping concentration continued to increase, the increasing rate of quantum efficiency became slower. The maximum value was 119% for KYC:0.7Tb³⁺. Under the excitation of 351 nm, the QE value could increase with the increase in the Tb³⁺ concentration. From the analysis of QE value, it was concluded that KYC, in comparison with phosphate [8], silicate [9], and fluoride [11], could emit green light with high efficiency by Tb³⁺ doping. In addition, we will further adopt different preparation methods to control the morphology of samples for better luminescence performance in the future [25,26].

Table 1. Quantum efficiency of KYC:*x*Tb³⁺ excited at different wavelengths.

Materials	QE245nm	QE283nm	QE351nm	References
<i>x</i> = 0.01	138%	23%	5%	This work
<i>x</i> = 0.1	172%	70%	22%	This work
<i>x</i> = 0.3	177%	109%	43%	This work
<i>x</i> = 0.5	171%	115%	64%	This work
<i>x</i> = 0.7	160%	119%	67%	This work
<i>x</i> = 1	148%	113%	72%	This work
Ca ₉ Y(PO ₄) ₇ :Tb ³⁺	157% (250 nm)			[8]
Ba ₉ Lu ₂ Si ₆ O ₂₄ :Tb ³⁺	144% (251 nm)			[9]
K ₂ GdF ₅ :Tb ³⁺	177% (240 nm)			[11]

3.5. Decay Curves

Figure 5a shows the luminescence decay curves at different Tb^{3+} concentrations in $\text{KYC}:x\text{Tb}^{3+}$. As can be seen from the figure, the decay curves for different concentrations of $\text{KYC}:x\text{Tb}^{3+}$ could be single exponential for the emission process. It was indicated that the excitation electrons of $^5\text{D}_4$ state have a longer lifetime than those of the $^5\text{K}_8$ level. As the doping level increased, the cross-relaxation between the two Tb^{3+} became more intense, and the excited-state electrons decayed faster. The variation in lifetime as a function of x is shown in Figure 5b. It is seen that the lifetime of 543 nm green light decreased with the increase in Tb^{3+} content. The variation in lifetime was small when x was less than 0.1. When x was increased, the green emission lifetime at 543 nm decreased rapidly, which indicated that there is a faster energy migration process between the two Tb^{3+} ions in the crystal lattice of KYC. The fast migration process of excited-state electrons enables $\text{KYC}:\text{Tb}^{3+}$ to be an efficient green-light-emitting phosphor.

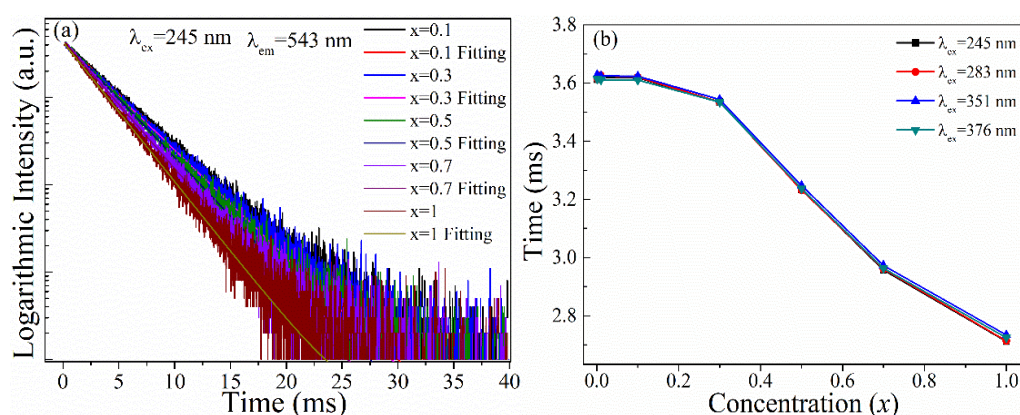


Figure 5. Decay curves (a) and energy level lifetimes (b) of $\text{KYC}:x\text{Tb}^{3+}$.

4. Quick Response Code

Quick response (QR) code is widely used in our life for information identification, health codes, trademark and product introduction, and so on. A highly efficient phosphor could enhance the QR code recognition in poor lighting conditions. Figure 6 shows the application of information identification for the luminescent QR code of $\text{KYC}:\text{Tb}^{3+}$ under the 365 nm LED irradiation. The chromaticity coordinate is (0.3387, 0.5916) in Figure 6a. The point position of $\text{KYC}:\text{Tb}^{3+}$ phosphor is in green field. Compared to a common QR code (Figure 6b), the luminescent QR code could be more easily identified in the darkness. Moreover, we can use QR codes to store some information or product introduction, especially in places where the space is small but where a lot of information needs to be expressed. The extended information can be easily obtained by scanning a QR code with a mobile phone in Figure 6c, such as “Huaibei Normal University”. In addition, the information can be kept secret by hiding the QR code under the transparent surface of a product. When information needs to be viewed, the QR code is displayed by ultraviolet excitation.

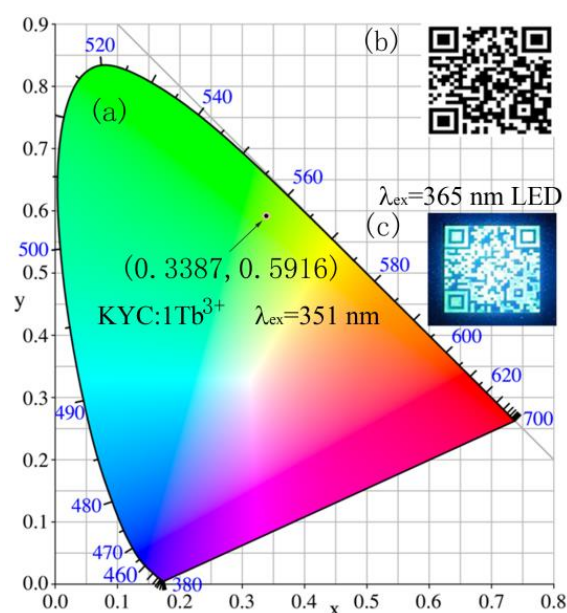


Figure 6. (a) Chromaticity point of phosphor; (b) Quick response code; (c) Quick response code excited by 365 nm LED.

5. Conclusions

The KYC: $x\text{Tb}^{3+}$ ($x = 0\sim 1$) phosphors were prepared by the hydrothermal method. The excited spectra, emission spectra, quantum cutting, and decay curves were measured and discussed. The ultraviolet wavelengths of 245, 283, and 351 nm were used to excite the phosphors. The exciting intensity of 245 and 283 nm (f–d transition) was larger than that of 351 nm (f–f transition). All the emissions were mainly attributed to the transition from $^5\text{D}_4$ to $^7\text{F}_j$ ($j = 6, 5, 4, 3, 2$). Visible quantum cutting of KYC: $x\text{Tb}^{3+}$ was observed at two excitation wavelengths of 245 nm and 283 nm. The optimal quantum cutting efficiency was ascribed to the simple and direct cross-relaxation transition under the 245 nm excitation: $^5\text{K}_8 + ^7\text{F}_6 \rightarrow ^5\text{D}_4 + ^5\text{D}_4$. The longest excitation wavelength of quantum cutting was 283 nm, which had the maximum QE value of 119% in KYC:0.7Tb $^{3+}$. The high-efficiency KYC:Tb $^{3+}$ phosphors could be potentially used in applications related to information identification.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ma15176160/s1>, Figure S1: Emission spectra of KYC: $x\text{Tb}^{3+}$ ($x = 0.001, 0.01, 0.1$) excited at 283 nm; Figure S2: Emission spectra of KYC: $x\text{Tb}^{3+}$ ($x = 0.001, 0.01, 0.1$) excited at 351 nm.

Author Contributions: Conceptualization, D.L. and G.Z.; methodology, D.L.; validation, D.L. and G.Z.; formal analysis, D.L. and G.Z.; investigation, D.L.; resources, D.L.; data curation, D.L.; writing—original draft preparation, D.L.; writing—review and editing, D.L.; visualization, D.L.; supervision, D.L.; project administration, D.L.; funding acquisition, D.L. All authors have read and agreed to the published version of the manuscript.

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

References

1. Tuyen, V.P.; Quang, V.X.; Khaidukov, N.M.; Thanh, L.D.; Ca, N.X.; Van Hao, N.; Van Nghia, N.; Van Do, P. $K_2YF_5:Tb^{3+}$ single crystal: An in-depth study of spectroscopic properties, energy transfer and quantum cutting. *Opt. Mater.* **2020**, *106*, 109939. [CrossRef]
2. Yu, X.; Li, H.; Li, X.; Jiang, Y.; Zheng, R.; Wu, H.; Song, Z.; Jiang, Z.; Zhao, P. Up-conversion luminescence and near-infrared quantum cutting of Ho^{3+}/Yb^{3+} co-doped hexagonal $NaGdF_4$ phosphors. *J. Mater. Sci. Mater. Electron.* **2021**, *32*, 21032–21043. [CrossRef]
3. Hien, N.; Ca, N.; Kien, N.; Luyen, N.; Do, P.; Thanh, L.; Van, H.; Bharti, S.; Wang, Y.; Thuy, N. Structural, optical properties, energy transfer mechanism and quantum cutting of Tb^{3+} doped ZnS quantum dots. *J. Phys. Chem. Solids* **2020**, *147*, 109638. [CrossRef]
4. Katayama, Y.; Tanabe, S. Spectroscopy and $1\mu m$ Luminescence by Visible Quantum Cutting in Pr^{3+} - Yb^{3+} Codoped Glass. *Materials* **2010**, *3*, 2405–2411. [CrossRef]
5. Zhang, F.; Wang, Y.; Tao, Y. Photoluminescence Properties of $Li_6Gd(BO_3)_3:Tb^{3+}$ Under VUV/UV Excitation. *Phys. Procedia* **2012**, *29*, 55–61. [CrossRef]
6. Loiko, P.; Volokitin, A.; Mateos, X.; Dunina, E.; Kornienko, A.; Vileshnikova, E.; Aguiló, M.; Díaz, F. Spectroscopy of Tb^{3+} ions in monoclinic $KLu(WO_4)_2$ crystal application of an intermediate configuration interaction theory. *Opt. Mater.* **2018**, *78*, 495–501. [CrossRef]
7. Zhang, Q.Y.; Huang, X.Y. Recent progress in quantum cutting phosphors. *Prog. Mater. Sci.* **2010**, *55*, 353–427. [CrossRef]
8. Zhang, F.; Xie, J.; Li, G.; Zhang, W.; Wang, Y.; Huang, Y.; Tao, Y. Cation composition sensitive visible quantum cutting behavior of high efficiency green phosphors $Ca_9Ln(PO_4)_7:Tb^{3+}$ ($Ln = Y, La, Gd$). *J. Mater. Chem. C* **2017**, *5*, 872–881. [CrossRef]
9. Liu, Y.; Zhang, J.; Zhang, C.; Jiang, J.; Jiang, H. High Efficiency Green Phosphor $Ba_9Lu_2Si_6O_{24}:Tb^{3+}$: Visible Quantum Cutting via Cross-Relaxation Energy Transfers. *J. Phys. Chem. C* **2016**, *120*, 2362–2370. [CrossRef]
10. Lu, C.-H.; Yeh, C.-H.; Som, S. Synthesis of Tb^{3+} - Yb^{3+} coactivated CeO_2 phosphors for two-photon assisted quantum cutting applications. *Chem. Phys. Lett.* **2020**, *748*, 137383. [CrossRef]
11. Jaiswal, S.R.; Sawala, N.S.; Nagpure, P.A.; Bhatkar, V.B.; Omanwar, S.K. Visible quantum cutting in Tb^{3+} doped $BaGdF_5$ phosphor for plasma display panel. *J. Mater. Sci. Mater. Electron.* **2017**, *28*, 2407–2414. [CrossRef]
12. Jaiswal, S.R.; Sawala, N.S.; Nagpure, P.A.; Barde, W.S.; Omanwar, S. The Highly Efficient Inorganic $SrF_2:Gd^{3+}, Eu^{3+}$ Phosphor for Mercury Free Fluorescence Lamps. *Adv. Mat. Res.* **2022**, *1171*, 17–24.
13. Mou, R.; Jiang, P.; Cong, R.; Yang, T. Structure and composition-dependent photoluminescence for $Ca_8MgGd_{1-x}Tb_x(PO_4)_7$ ($0 \leq x \leq 1$). *J. Solid State Chem.* **2021**, *298*, 122116. [CrossRef]
14. Li, D.; Zhu, G.; Zhao, X. High efficiently color-tunable emission in $KTb(CO_3)_2:Eu^{3+}$ phosphors. *Opt. Mater.* **2021**, *119*, 111310. [CrossRef]
15. Palilla, F.C.; Levine, A.K.; Rinkevics, M. Rare Earth Activated Phosphors Based on Yttrium Orthovanadate and Related Compounds. *J. Electrochem. Soc.* **1965**, *112*, 776–779. [CrossRef]
16. Shannon, R. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr. A* **1976**, *32*, 751–767. [CrossRef]
17. Kutlu, I.; Kalz, H.-J.; Wartchow, R.; Ehrhardt, H.; Seidel, H.; Meyer, G. Kalium-Lanthanoid-Carbonate, $KM(CO_3)_2$ ($M = Nd, Gd, Dy, Ho, Yb$). *Z. Anorg. Allg. Chem.* **1997**, *623*, 1753–1758. [CrossRef]
18. Lin, D.; Du, P. Room temperature synthesis of Tb^{3+} -activated BiF_3 green-emitting nanoparticles with high thermal stability for near-ultraviolet white light-emitting diodes. *Appl. Phys. A* **2021**, *127*, 65. [CrossRef]
19. Lu, Y.; Wang, J.; He, L.; Hao, C.; Wang, F.; Zhang, J. Preparation and fluorescence properties of $MgAl_2O_4:Tb^{3+}$ nanorod-like phosphors. *Mater. Res. Express* **2022**, *9*, 065009. [CrossRef]
20. He, D.; Yu, C.; Cheng, J.; Li, S.; Hu, L. Effect of Tb^{3+} concentration and sensitization of Ce^{3+} on luminescence properties of terbium doped phosphate scintillating glass. *J. Alloys Compd.* **2011**, *509*, 1906–1909. [CrossRef]
21. Jiang, P.; Li, Z.; Lu, W.; Ma, Y.; Tian, W. The pH Value Control of Morphology and Luminescence Properties of $Gd_2O_3:Sr^{2+}$ Phosphors. *Materials* **2022**, *15*, 646. [CrossRef] [PubMed]
22. Xie, M.; Tao, Y.; Huang, Y.; Liang, H.; Su, Q. The Quantum Cutting of Tb^{3+} in $Ca_6Ln_2Na_2(PO_4)_6F_2$ ($Ln=Gd, La$) under VUV–UV Excitation: With and without Gd^{3+} . *Inorg. Chem.* **2010**, *49*, 11317–11324. [CrossRef] [PubMed]
23. Atuchin, V.V.; Aleksandrovsky, A.S.; Chimitova, O.D.; Krylov, A.S.; Molokeev, M.S.; Bazarov, B.G.; Bazarova, J.G.; Xia, Z. Synthesis and spectroscopic properties of multiferroic β' - $Tb_2(MoO_4)_3$. *Opt. Mater.* **2014**, *36*, 1631–1635. [CrossRef]
24. Carnall, W.T.; Fields, P.R.; Rajnak, K. Electronic Energy Levels of the Trivalent Lanthanide Aquo Ions. III. Tb^{3+} . *J. Chem. Phys.* **1968**, *49*, 4447–4449. [CrossRef]
25. Zhumanova, K.; Akhmetzhanov, N.; Kang, M.S.; Molkenova, A.; Raja, I.S.; Kim, K.S.; Han, D.-W.; Atabaev, T.S. Terbium and barium codoped mesoporous silica nanoparticles with enhanced optical properties. *Mater. Lett.* **2022**, *323*, 132500. [CrossRef]
26. Khan, S.; Choi, Y.; Ahn, H.-Y.; Han, J.H.; Ju, B.-K.; Chung, J.; Cho, S.-H. Control of Particle Size in Flame Spray Pyrolysis of Tb -doped Y_2O_3 for Bio-Imaging. *Materials* **2020**, *13*, 2987. [CrossRef] [PubMed]