Implanting bismuth in color-tunable emitting microspheres of (Y, Tb, Eu)BO$_3$ to generate excitation-dependent and greatly enhanced luminescence for anti-counterfeiting applications

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**ABSTRACT**

To prevent counterfeiting, a lot of advanced security technologies have been developed, including luminescent printing. Therefore, the pigments with advanced security features are urgently pursued for luminescence printing-based anti-counterfeiting technology. Here, micron-sized spheres of hexagonal-structured and color-tunable emitting (Y, Tb, Eu, Bi)BO$_3$ have been rapidly synthesized by microwave processing, followed by a proper annealing. Incorporation of Bi$^{3+}$ greatly enhances the emission intensity of Eu$^{3+}$ and of Tb$^{3+}$. Under the excitation at 260 nm, the spheres exhibit UV emission at 330 nm $(^5P_1\rightarrow^7S_0 \text{ transition of Bi}^{3+})$, green emission at 546 nm $(^D_{4\pi}\rightarrow^F_3 \text{ transition of Eu}^{3+})$ and orange-red emission at 592 nm $(^D_{4\pi}\rightarrow^F_1 \text{ transition of Eu}^{3+})$, mainly due to the three energy transfer processes of Bi$^{3+}$→Tb$^{3+}$, Bi$^{3+}$→Eu$^{3+}$, and Tb$^{3+}$→Eu$^{3+}$. However, under the excitation at 230 nm, the Tb$^{3+}$→Eu$^{3+}$ energy transfer contributes to the orange-red emission of Eu$^{3+}$ and the green emission of Tb$^{3+}$, in the absence of Bi$^{3+}$ emission. The maximum energy transfer efficiency of Bi$^{3+}$→Eu$^{3+}$ and Tb$^{3+}$, and Tb$^{3+}$→Eu$^{3+}$ is 63% and 50% for (Y$_{0.883}$Tb$_{0.02}$Eu$_{0.007}$Bi$_{0.007}$)BO$_3$. The (Y$_{0.963}$Tb$_{0.02}$Eu$_{0.007}$)BO$_3$ spheres exhibit a distinct excitation-dependent luminescence behavior. Facile switching the excitation wavelength from 260 nm to 230 nm yields emission color changing from orange to green yellow, which possesses the advanced security feature.

**1. Introduction**

Recently, counterfeiting has grown to be a serious global threat, which includes the duplication of currencies, electronic products, merchandise, passports, official documents, pharmaceuticals, and so on [1]. Counterfeiting has caused enormous loss to the economy and a constant risk to the health and safety of consumers [1,2]. To prevent counterfeiting, a lot of advanced security technologies have been developed, including radio frequency identification, hologram attachment, isotope tracking and luminescent printing [3]. Among above anti-counterfeiting technologies, luminescence printing attracted much attention, because of its low production costs, being eco-friendly and hard to counterfeit [4,5]. Therefore, developing the pigments with advanced security features, such as a single excitable dual emissive luminescence [3] or excitation dependent color tunable luminescence [6,7], is the general trend in luminescence printing-based anti-counterfeiting technologies. Recently, fluorescent patterns based on up-conversion materials have been developed for anti-counterfeiting, because of their high-level security [8–11]. Yttrium orthoborate of YBO$_3$, possessing a hexagonal vaterite-type structure, exhibits low toxicity, high chemical stability, and vacuum ultraviolet transparency [12–15]. More importantly, the Y site in this structure can be facile substituted with various RE$^{3+}$ ions (RE = rare earth). Therefore, YBO$_3$ is a good host lattice for luminescence studies. Eu$^{3+}$, Tb$^{3+}$, and Eu$^{3+}$/Tb$^{3+}$ activated YBO$_3$ phosphors are the important red, green, and color-tunable emitting phosphors finding wide applications in areas such as fluorescent lamps, white light-emitting diodes, plasma display panels, flat panel displays, and field emission displays [12–16]. It is widely accepted that activator Eu$^{3+}$ occupies the Y$^{3+}$ site in hexagonal YBO$_3$:Eu$^{3+}$ with the point symmetry of $S_6$, thus the $^5D_{0}\rightarrow^7F_1$ transition of Eu$^{3+}$ takes the dominate role [17]. Therefore, the solid-solution phosphor always exhibits orange-red emission at ~590 nm. While under exposure to UV light, YBO$_3$:Tb$^{3+}$ displays the typical green emission at ~546 nm ($^D_{4\pi}\rightarrow^F_5$ transition of Tb$^{3+}$), and color-tunable photoluminescence can be found in solid solution phosphor of Y/Tb/Eu ternary system through an
efficient energy transfer from Tb$^{3+}$ to Eu$^{3+}$ ions [18–20]. Recently, it was reported that doping Bi$^{3+}$ in rare-earth borates could effectively manipulate the synthetic/thermal stable temperature [21]. In addition, further doping Bi$^{3+}$ in Y/Tb/Eu ternary system is a good idea to take advantage of the sensitization effect of Bi$^{3+}$ to obtain a single-phase phosphor with color-tunable and greatly improved emission by manipulating the doped concentrations of Bi$^{3+}$, Eu$^{3+}$, and Tb$^{3+}$ in YBO$_3$ [22].

Usually, rare-earth borates, such as REBO$_3$, RE$_2$O$_3$, and RE$_3$BO$_6$, were synthesized through typical solid-state reactions at high temperatures or sol-gel technology followed by calcinations [12–16]. Because the final products are always featured large size, irregular shape and significant aggregation, they are limited in application of high-definition displays. However, phosphor particles of spherical shape and uniform size are desirable in high-definition displays to improve the resolution and the overall luminescent performance. The spherical engineering of rare-earth borates is of great importance, but remains a considerable challenge in particle science. Very recently, precursor route is reported as an effective way to synthesize well-dispersed and uniform spheres of rare-earth borates. Colloidal moydite spheres of RE(B(OH)$_3$)$_3$CO$_3$ in micron size have been facilely synthesized by a modified homogeneous precipitation (HP), which were used as precursors for synthesizing REBO$_3$ (RE = Y, Gd, Eu) phosphor spheres [14,15]. Subsequently, submicron spheres of RE$_2$O$_3$ (RE = Eu-Yb, Y) have been converted from their colloidal precursor spheres (amorphous phase form) synthesized via homogeneous precipitation [16]. In this work, micron-sized moydite spheres of M(B(OH)$_3$)$_3$CO$_3$ (M = Y, Tb, Eu, Bi) quaternary system have been rapid synthesized by microwave processing, and the precursor converted into (Y, Tb, Eu, Bi)BO$_3$ color-tunable emitting phosphor by a proper annealing. The effects of Bi$^{3+}$ incorporation on crystal structure and luminescent behavior were investigated by detailed characterizations of XRD, FE-SEM, HR-TEM, STEM, PLE/PL spectroscopy, and fluorescence decay analysis. The (Y, Tb, Eu, Bi)BO$_3$ spheres exhibit an excitation-dependent luminescence, with emission color changing from green-yellow to orange by switching the excitation wavelength. The prepared spheres are the potential luminescent pigment to prevent counterfeiting by generating advanced security feature safety levels.

2. Experimental section

2.1. Synthesis

The starting rare-earth sources are Y$_2$O$_3$, Tb$_3$O$_7$, and Eu$_2$O$_3$ all 99.99% pure products purchased from Huizhou Ruier Rare-Chem. Hi-Tech. Co. Ltd (Huizhou, China). Bi(NO$_3$)$_3$·5H$_2$O and other reagents are of analytical grade and were purchased from China pharmaceutical group chemical reagent Co. LTD (Shanghai, China). The nitrate solution of RE$^{3+}$ was prepared by dissolving the corresponding oxide with a slightly excessive amount of nitric acid, followed by evaporation at ~90°C to dryness to remove the superfluous acid. In a typical synthesis, 0.225 mol of H$_2$BO$_3$, 0.5 mol of urea (CO(NH$_2$)$_2$), and 120 mL of ethylene glycol (EG) were dissolved in the mixed nitrate solution to make a total volume of 1000 mL, which was then homogenized under magnetic stirring at 25°C for 30 min. In all the cases, the total concentration of RE$^{3+}$ and Bi$^{3+}$ was kept constant at 0.015 mol/L. The mixed transparent solution was heated to ~95°C within 10 min in a microwave, and then cooled to ~70°C after reacting at ~95°C for another 120 min. The resultant colloidal particles were collected via centrifugation, washed with distilled water for three times to remove byproducts, rinsed with absolute ethanol, and then dried in air at 50°C for 24 h. (Y, Tb, Eu, Bi)BO$_3$ was obtained by calcining the precipitation products under flowing O$_2$ gas (200 mL/min) at 800°C for 2 h with a heating rate of 10°C/min at the ramp stage.

2.2. Characterization techniques

Phase identification was performed by X-ray diffractionmetry (XRD, Model Smart Lab, Rigaku, Tokyo, Japan) operating at 40 kV/40 mA using nickel filtered Cu Kα radiation and a scanning speed of 6.0° 2θ/min. Morphologies of the products were observed via field emission scanning electron microscopy (FE-SEM, Model JSM-7001 F, JEOL, Tokyo) and transmission electron microscopy (TEM, Model JEM-2000FX, JEOL, Tokyo). Elemental mapping was performed using scanning transmission electron microscopy (STEM, Model JEM-2000FX, JEOL, Tokyo). X-ray photoelectron spectroscopy (XPS) data were measured using an X-ray photoelectron spectrometer (Model Axis Supra, Kratos Analytical Ltd., Manchester, UK) with monochromatized Al Kα X-ray radiation. The measurements were performed using an ultrahigh vacuum chamber with a base pressure below 3 × 10$^{-9}$ Torr at room temperature. The binding energies were calibrated by using C 1 s (284.8 eV) of carbon impurities as reference. Photoluminescence and fluorescence decay of the phosphors were analyzed with an FP-8600 fluorospectrophotometer (Jasco, Tokyo). Fluorescence decay kinetics of Bi$^{3+}$ emission was measured at room temperature on a HORIBA scientific modular fluorescence lifetime system (Model DeltaFlex, HORIBA Jobin Yvon IBH Ltd., Scotland).

3. Results and discussion

3.1. Morphology and phase structure

Colloidal moydite microspheres of M(B(OH)$_3$)$_3$CO$_3$ (M = Y, Tb, Eu, Bi) were facilely and rapidly
synthesized by a microwave-assisted homogenous precipitation. Figure 1(a–c) shows FE-SEM morphologies of three typical samples, that are \(Y_{0.945}Eu_{0.05}Bi_{0.005}(B(OH)_4)CO_3\), \((Y_{0.973}Tb_{0.02}Bi_{0.007})(B(OH)_4)CO_3\), \((Y_{0.923}Tb_{0.02}Eu_{0.05}Bi_{0.007})(B(OH)_4)CO_3\). The results show that the microspheres with a diameter of \(\approx 1-2\ \mu m\) were synthesized in all cases. The XRD patterns in Figure 2(a) indicate that the obtained spheres are identified along with the orthorhombic-structured moydite \(Y(B(OH)_4)CO_3\) (JCPDS No. 78–2062), and no impurity peaks were observed. Because the ionic sizes of \(Tb^{3+}\), \(Eu^{3+}\) and \(Bi^{3+}\) (for eightfold coordination) are \(r_{Tb^{3+}} = 0.1066\ nm, r_{Eu^{3+}} = 0.1040\ nm, r_{Bi^{3+}} = 0.1170\ nm\), which are larger than that of \(Y^{2+}\) (for eightfold coordination, \(r_{Y^{2+}} = 0.1019\ nm\)) [23], incorporation of \(Tb^{3+}, Eu^{3+}\) and \(Bi^{3+}\) in \(Y(B(OH)_4)CO_3\) results in larger cell constants than that of \(Y(B(OH)_4)CO_3\). Thus, the diffraction peaks slightly shift to the small angle side with incorporation of \(Tb^{3+}, Eu^{3+}\) and \(Bi^{3+}\).

Figure 1(c–f) shows high-resolution XPS spectra of \(Tb\) 3d subshell, and the f-f transitions within the 4f configuration of the \(Eu^{3+}\) ions [14–16]. However, another strong excitation band at 260 nm appeared in the presence of \(Bi^{3+}\) \((x = 0.001–0.01)\), which is assigned to the \(1^5S_0^--1^3P_1\) transition of \(Bi^{3+}\) [24,25]. Because the \(1^5S_0^--1^3P_1\) transition of \(Bi^{3+}\) (260 nm) is more intense than the CTB (230 nm), the 260 nm is the most efficient excitation wavelength for \((Y_{0.95-x}Eu_{0.05})Bi_{0.005}BO_3\) systems.

**3.2. Luminescence behavior of (Y, Eu, Bi)BO_3 and (Y, Tb, Bi)BO_3 spheres**

Figure 4(a) shows the excitation spectra of \((Y_{0.95-x}Eu_{0.05}Bi_{0.005})BO_3\) spheres. For \(x = 0\) sample, the spectrum consists of a wide absorption band ranging from 200 nm to 250 nm (centered at 230 nm) and several weak peaks at around \(\approx 320, \approx 395\) and \(\approx 466\ nm\), which are ascribed to the charge-transfer band (CTB) between the \(O^2-\) and \(Eu^{3+}\) ions and the \(f-f\) transitions within the 4f configuration of the \(Eu^{3+}\) ions [14–16]. However, another strong excitation band at 260 nm appeared in the presence of \(Bi^{3+}\) \((x = 0.001–0.01)\), which is assigned to the \(1^5S_0^--1^3P_1\) transition of \(Bi^{3+}\) [24,25]. Because the \(1^5S_0^--1^3P_1\) transition of \(Bi^{3+}\) (260 nm) is more intense than the CTB (230 nm), the 260 nm is the most efficient excitation wavelength for \((Y_{0.95-x}Eu_{0.05})Bi_{0.005}BO_3\) systems.
Bi$_x$BO$_3$ spheres. Under excitation at 260 nm, the emission spectra show emission peaks at ~592 nm, ~610 and ~627 nm, ~650 and ~673 nm, and ~694 and ~708 nm, which are assigned to the typical $^5D_0 \rightarrow ^7F_J$ transition of Eu$^{3+}$ ions respectively [26] (Figure 4(b)). Because activator Eu$^{3+}$ occupies the Y$^{3+}$ site in hexagonal structure with the point symmetry of $S_6$, the magnetic dipole $^5D_0 \rightarrow ^7F_1$ transition of Eu$^{3+}$ at 592 nm takes the dominate role, rather than the forced electric dipole $^5D_0 \rightarrow ^7F_2$ transition of Eu$^{3+}$ ions at ~610 and ~627 nm [12–16]. However, a broad emission band ranging from 275 nm to 375 nm with the maximum at 330 nm appeared with increasing $x$ from 0 to 0.001, and the emission became more intense at a higher $x$ value (Bi$^{3+}$ content). Because of the incorporation of Bi$^{3+}$, stronger emission intensity of Eu$^{3+}$ was observed, and the emission intensity at 592 nm increased by 710% with increasing $x$ from 0 to 0.005 (Figure 4(b)), indicating an efficient energy transfer from Bi$^{3+}$.
to Eu\(^{3+}\). However, further increasing the x value above 0.005 yielded a weakened emission, suggesting the optimized concentration for Bi\(^{3+}\) ions is 0.005. Under excitation at 230 nm (CTB for Eu\(^{3+}\)), the emission spectra show emission of Eu\(^{3+}\), in the absence of Bi\(^{3+}\) emission (Figure 4(d)), indicating that the energy transfer from CTB to Bi\(^{3+}\) does not exist. Figure 4(c) shows UV-vis absorption spectra of (Y\(_{0.95}\)Eu\(_{0.05}\))BO\(_3\) and (Y\(_{0.945}\)Eu\(_{0.05}\)Bi\(_{0.005}\))BO\(_3\), and an intense transition band \(\text{S}_0\rightarrow\text{P}_1\) of Bi\(^{3+}\) ions at 260 nm appeared for Bi\(^{3+}\)-containing sample, giving the direct evidence of Bi\(^{3+}\rightarrow\text{Eu}\^{3+}\) energy transfer.

Figure 4(e) shows PLE spectra of (Y\(_{0.986}\)Tb\(_{0.02}\)Bi\(_{0.003}\))BO\(_3\). The PLE spectrum recorded by monitoring the green emission at 546 nm (\(\text{S}_2\rightarrow\text{F}_3\) transition of Tb\(^{3+}\)), exhibits a broad transition band ranging from 220 to 300 nm, with two strong bands centered at \(\sim\)234 nm and \(\sim\)260 nm, which are corresponding to the well-documented \(4f^8\rightarrow4f^75d^1\) transition of Tb\(^{3+}\) [18,27] and \(1\text{S}_0\rightarrow1\text{P}_1\) transition of Bi\(^{3+}\) [24,25]. Upon UV excitation at \(\sim\)260 nm, the spheres displayed the typical emissions of Tb\(^{3+}\) at \(\sim\)491 nm, \(\sim\)546 nm, \(\sim\)586 nm, and \(\sim\)622 nm, which are assigned to the \(3\text{D}_2\rightarrow3\text{F}_j\) (\(J = 6\)–3) transitions of Tb\(^{3+}\) [18,27], respectively (Figure 4(f)). Obviously, the green emission at \(\sim\)546 nm (\(3\text{D}_2\rightarrow3\text{F}_5\) transition of Tb\(^{3+}\)) takes the dominated role. Similarly, incorporation of Bi\(^{3+}\) also enhances the emission intensity of Tb\(^{3+}\). The emission intensity at 546 nm increased by 1150% with increasing x from 0 to 0.007 (Figure 4(f)), indicating an efficient energy transfer from Bi\(^{3+}\) to Tb\(^{3+}\). However, further increasing the x value above 0.007 yielded a weakened emission, which is similar to that observed for (Y\(_{0.95-x}\)Eu\(_{0.05}\)Bi\(_{x}\))BO\(_3\) spheres. Incorporation of Bi\(^{3+}\) in borate host enhances the absorption of the optical excitation, which can effectively promote the energy transfer from Bi\(^{3+}\) ions to the activated Eu\(^{3+}\) and Tb\(^{3+}\) ions and thus enhancing the emission intensity. However, a higher Bi\(^{3+}\) concentration would lead to the internal consumption between Bi\(^{3+}\) ions through energy transfer and nonradiative transition, which makes the energy transfer of Bi\(^{3+}\rightarrow\text{Eu}\^{3+}\) and Bi\(^{3+}\rightarrow\text{Tb}\^{3+}\) become weak. Therefore, the most intense orange-red emission and green emission were found for (Y\(_{0.945}\)Eu\(_{0.05}\)Bi\(_{0.005}\))BO\(_3\) and (Y\(_{0.973}\)Tb\(_{0.02}\)Bi\(_{0.007}\))BO\(_3\). Similarly, under excitation at 234 nm (\(4f^8\rightarrow4f^75d^1\) transition of Tb\(^{3+}\)), the emission spectra only show emission of Tb\(^{3+}\), in the absence of Bi\(^{3+}\) emission (Figure 4(d)), indicating that the energy transfer from Tb\(^{3+}\) to Bi\(^{3+}\) does not exist.

3.3. Luminescence behavior of (Y, Tb, Eu, Bi)BO\(_3\) spheres

Usually, Tb\(^{3+}\) and Eu\(^{3+}\) need different excitation wavelengths for their respective emissions, and thus mixing two phosphors cannot efficiently tune the mission color (though can). The Tb\(^{3+}/\text{Eu}\^{3+}\) co-doped borates may have the advantage of emitting tunable colors under one single excitation wavelength, through the energy transfer from Tb\(^{3+}\) to Eu\(^{3+}\). Therefore, (Y\(_{0.973}\)Tb\(_{0.02}\)Eu\(_{0.05}\)Bi\(_{0.007}\))BO\(_3\) spheres were investigated here. The PLE spectra recorded by monitoring the orange-red emission at 592 nm (\(\text{C}_0\rightarrow\text{F}_5\)) of (Y, Tb, Eu, Bi)BO\(_3\) spheres, as shown in Figure 4(e), clearly showed the typical emissions of Tb\(^{3+}\), Eu\(^{3+}\), and Bi\(^{3+}\).
transition of Eu$^{3+}$) and the green emission at 546 nm (5D$_{4}$→7F$_{5}$ transition of Tb$^{3+}$) exhibit different excitation bands in Figure 5(a, b). Obviously, the 1S$_{0}$→3P$_{1}$ transition of Bi$^{3+}$ at 260 nm is stronger than the CTB at 230 nm (Figure 5(a)), but weaker than 4f$^{8}$→4f$^{7}$5d$^{1}$ transition of Tb$^{3+}$ at 234 nm (Figure 5(b)), indicating that the energy transfer of Bi$^{3+}$→Eu$^{3+}$ is more efficient than that of Bi$^{3+}$→Tb$^{3+}$. Under the excitation of 230 nm and 260 nm, the characteristic emissions of both Tb$^{3+}$ and Eu$^{3+}$ simultaneously appeared on the PL spectra, with the green Tb$^{3+}$ emission at 546 nm (5D$_{4}$→7F$_{5}$ transition of Tb$^{3+}$) monotonically decreasing with increasing $y$ (Figure 5(c, d)), which is conforming to the tendency observed from the PLE spectra. Accordingly, successively stronger Eu$^{3+}$ emission at 592 nm (5D$_{0}$→7F$_{1}$ transition of Eu$^{3+}$) was seen for the $y = 0$–0.09 samples. The reduced Eu$^{3+}$ emission at $y = 0.11$ is suggestive of concentration quenching. The above results suggest efficient energy migration in transitioning from Tb$^{3+}$ to Eu$^{3+}$. It is interesting to find that the PL spectra exhibit characteristic emissions of 3P$_{1}$→1S$_{0}$ transition of Bi$^{3+}$ at 330 nm except for the typical emissions of Tb$^{3+}$ and Eu$^{3+}$ ions under the excitation at
260 nm (Figure 5(d)). The UV emission at 330 nm ($^1\text{P}_1 \rightarrow ^3\text{S}_0$ transition of $\text{Bi}^{3+}$) and the green emission at 546 nm ($^6\text{D}_4 \rightarrow ^7\text{F}_5$ transition of $\text{Tb}^{3+}$) monotonically decrease with increasing $y$ from 0 to 0.11 (Figure 5(d)). But the $\text{Eu}^{3+}$ emission at 592 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition of $\text{Eu}^{3+}$) became stronger at a higher $y$ value until it above 0.09 (Figure 5(d)). It is interesting found that the intensity of $\text{Eu}^{3+}$ emission under excitation at 260 nm increased faster than that under excitation at 230 nm. The $I(^5\text{D}_0 \rightarrow ^7\text{F}_1)/I(^6\text{D}_4 \rightarrow ^7\text{F}_5)$ intensity ratio (monitoring $I_{592}/I_{546}$) under excitation at 260 nm increased from 0.98 at $y = 0.01$ to $\sim 53.5$ at $y = 0.11$, which is much larger than that under excitation at 230 nm (Figure 5(e)). Thus, the emission color of (Y$_{0.973-y}$Tb$_{0.02}$Eu$_y$B$_{0.007}$)BO$_3$ spheres moved faster from green to red region by $\text{Eu}^{3+}$ doping under excitation at 260 nm which are in good agreement with the results for CIE chromaticity diagram (Figure 6). The above results also indicate that varying the Eu content from 0 to 0.11 yielded color tunable emission from green to red (Figure 6). From above results, a probable energy transfer

![Figure 5](image)

**Figure 5.** (a,b) PLE and (c,d) PL spectra of (Y$_{0.973-y}$Tb$_{0.02}$Eu$_y$B$_{0.007}$)BO$_3$ spheres. (e) is the $I(^5\text{D}_0 \rightarrow ^7\text{F}_1)/I(^6\text{D}_4 \rightarrow ^7\text{F}_5)$ intensity ratio under excitation at 260 nm and 230 nm, as a function of $y$ value (Eu content).
process among Bi$^{3+}$, Tb$^{3+}$, and Eu$^{3+}$ ions are demonstrated in Figure 7(a). Under ultraviolet-light (260 nm) excitation, the ground-state electrons of Bi$^{3+}$ ions at $1S_0$ level are promoted to the $3P_1$ level. Then, the $3P_1 \rightarrow 1S_0$ transition of Bi$^{3+}$ contributes to the 330-nm emission, along with the three possible energy transfer processes of Bi$^{3+} \rightarrow$ Tb$^{3+}$, Bi$^{3+} \rightarrow$ Eu$^{3+}$, and Tb$^{3+} \rightarrow$ Eu$^{3+}$, which finally contributes to the green emission of Tb$^{3+}$ and orange-red emission of Eu$^{3+}$. However, under the excitation at 234 nm (4f$^8$ → 4f$^7$5d$^1$ transition of Tb$^{3+}$), the Tb$^{3+} \rightarrow$ Eu$^{3+}$ energy transfer contributes to the orange-red emission of Eu$^{3+}$, along with the green emission of Tb$^{3+}$ from the $5D_4 \rightarrow 7F_j$ transition.

In order to investigate the energy transfer efficiency, lifetimes of the 330-nm Bi$^{3+}$ emission and 546-nm Tb$^{3+}$ emission were analyzed against the Eu$^{3+}$ content ($0 \leq y \leq 0.11$) (Figure 7(b,c)). In the absence of Tb$^{3+}$ and Eu$^{3+}$, the lifetime of Bi$^{3+}$ is 210 ns (Figure S2), and it decreases to 194 ns in the presence of 2% Tb$^{3+}$ (Figure S2), indicating the energy transfer from Bi$^{3+}$ to Tb$^{3+}$. The lifetime of Bi$^{3+}$ decreased from 194 ns for $y = 0$ to 11 ns for $y = 0.11$. The shortened lifetime of Bi$^{3+}$ emission at higher Eu content (Figure 7(b) and Figure S2) confirms the energy transfer process from Bi$^{3+}$ to Tb$^{3+}$ and Eu$^{3+}$. In the absence of concentration quenching, the efficiency ($\eta_{ET}$) of the Bi$^{3+} \rightarrow$ Eu$^{3+}$ and Tb$^{3+}$ energy transfer can be calculated from the fluorescence lifetime with $\eta_{ET} = 1 - \tau/\tau_0$, where $\tau$ and $\tau_0$ are the fluorescence lifetime of the Bi$^{3+}$ emission in the presence and absence of the acceptor [18,26].

3.4. Excitation dependent emission and prospect of application

The (Y, Tb, Eu, Bi)BO$_3$ spheres exhibited an excitation-dependent luminescence behavior. Taking (Y$_{0.973}$-yTb$_{0.02}$Eu$_y$Bi$_{0.007}$)BO$_3$ as an example, the phosphor exhibited two kinds of PL spectra under the excitation at various wavelengths (Figure 8(A)). Under the excitation at 260 nm, the sample emits UV emission at 330 nm ($3P_1 \rightarrow 1S_0$ transition of Bi$^{3+}$), green emission at 546 nm and orange red emission at 592 nm, with the intensity of green emission close to that of orange red emission. Therefore, the sample
emits orange color with the CIE coordinates of (0.45, 0.45) (Figure 8(B)). The external and internal quantum efficiencies are ~34% and 65%, respectively. The distinct emission color from orange to green yellow can be achieved by facile switching the excitation wavelength from 260 nm to 230 nm (Figure 8(C)), which indicate that the phosphor is the potential anti-counterfeiting pigment. Recently, some research groups have made efforts to developing dual emissive pigments based on different excitation wavelengths [3,28,29]. Here, the excitation-dependent emitting (Y, Tb, Eu, Bi)BO₃ spheres with advanced security feature would be a member of the luminescent-pigment family to prevent counterfeiting by generating advanced security feature safety levels.

4. Conclusion

In this work, micron-sized moydite spheres of M(B(OH)₄)₂CO₃ (M = Y, Tb, Eu, Bi) ternary and quaternary systems have been rapid synthesized by microwave processing, and the precursor converted into hexagonal-structured and color-tunable emitting phosphor of MBO₃ rare earth borates by a proper annealing. Incorporation of Bi³⁺ does not significantly affect the crystal structure of the phosphors, but it greatly enhances the emission intensity of Eu³⁺ and of Tb³⁺. Under the excitation at 260 nm (¹S₀→³P₁ transition of Bi³⁺), the (Y, Tb, Eu, Bi)BO₃ spheres exhibit UV emission at 330 nm (³P₁→¹S₀ transition of Bi³⁺), green emission at 546 nm (³D₄→⁷F₅ transition of Tb³⁺) and orange-red emission at 592 nm (³D₀→⁷F₁ transition of Eu³⁺), mainly due to the three possible energy transfer processes of Bi³⁺→Tb³⁺, Bi³⁺→Eu³⁺, and Tb³⁺→Eu³⁺. However, under the excitation at 234 nm (⁴f₈→⁴f₇⁵d¹ transition of Tb³⁺), the Tb³⁺→Eu³⁺ energy transfer contributes to the orange-red emission of Eu³⁺ and the green emission of Tb³⁺ from the ⁵D₄→⁷F₅ transition, in the absence of Bi³⁺ emission. The maximum energy transfer efficiency of Bi³⁺→Eu³⁺ and Tb³⁺→Eu³⁺ of 63% and 50% for (Y₀.883Tb₀.02Eu₀.09Bi₀.007)BO₃ sample. The (Y₀.963Tb₀.02Eu₀.01Bi₀.007)BO₃ spheres exhibited a distinct excitation-dependent luminescence behavior, with emission color from orange to green yellow being achieved by facile switching the excitation wavelength from 260 nm to 230 nm. The excitation-dependent emitting (Y, Tb, Eu, Bi)BO₃ spheres with advanced security feature would be a member of the luminescent-pigment family to prevent counterfeiting by generating advanced security feature safety levels.
Disclosure statement

No potential conflict of interest was reported by the authors.

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References

[1] Kanika KP, Singh S, Gupta BK. A novel approach to synthesise a dual-mode luminescent composite pigment for uncloneable high-security codes to combat counterfeiting. Chem – Eur J. 2017;23(67):17144–17151.

[2] Deisingh AK. Pharmaceutical counterfeiting. Analyst. 2005;130(3):271–279.

[3] Gangwar AM, Kanika KG, Papanai GS, et al. Single excitable dual emissive novel luminescent pigment to generate advanced security features for anti-counterfeiting applications. J Mater Chem C. 2019;7(44):13867–13877.

[4] You M, Zhong J, Hong Y, et al. Inkjet printing of upconversion nanoparticles for anti-counterfeit applications. Nanoscale. 2015;7(10):4423–4431.

[5] Zhao J, Jin D, Schartner EP, et al. Single-nanocrystal sensitivity achieved by enhanced upconversion luminescence. Nat Nanotechnol. 2013;8(10):729–734.

[6] Shi C, Shen X, Zhu Y, et al. Excitation wavelength-dependent dual-mode luminescence emission for dynamic multicolor anticounterfeiting. ACS Appl Mater Interfaces. 2019;11(20):18548–18554.

[7] Li M, Yao W, Liu J, et al. Facile synthesis and screen printing of dual-mode luminescent NaYF4:Er,Yb(Tm)/carbon dots for anti-counterfeiting applications. J Mater Chem C. 2017;5(26):6512–6520.

[8] Yao WJ, Tian QY, Wu W. Tunable emission of upconversion fluorescence for security applications. Adv Optical Mater. 2019;7:1801171.

[9] Chen X, Yao WJ, Wang Q, et al. Designing multicolor dual-mode lanthanide-doped NaLuF4:Y2O3 composites for advanced anticounterfeiting. Adv Optical Mater. 2020;8:1901209.

Figure 8. (A) Excitation dependent emission spectra of (Y0.963Tb0.02Eu0.01Bi0.007)BO3 spheres. (B) is CIE chromaticity diagram of (Y0.963Tb0.02Eu0.01Bi0.007)BO3 under excitation at 230 nm (point a) and 260 nm (point b). (C) is schematic illustration for excitation dependent emission and anti-fake application.
Yao WJ, Tian QY, Liu J, et al. Preparation and RGB upconversion optic properties of transparent anti-counterfeiting. Nanoscale. 2017;9:15982–15989.

Yao WJ, Tian QY, Tian B, et al. Dual upconversion nanophotonswitch for security encoding. Sci China Mater. 2019;62(3):368–378.

Newnham RE, Redman MJ, Santoro RP. Crystal structure of yttrium and other rare-earth borates. J Am Ceram Soc. 1963;46(6):253–256.

Mishra KC, DeBoer BG, Schmidt PC, et al. Electronic structures and nature of host excitation in borates. Ber Bunsenges Phys Chem. 1998;102(12):1772–1782.

Zhu Q, Wang S, Li JG, et al. Spherical engineering and space-group dependent luminescence behavior of YBO$_3$: Eu$^{3+}$ red phosphors. J Alloy Compd. 2018;731:1069–1079.

Zhu Q, Wang S, Li X, et al. Well-dispersed (Y$_{0.95-x}$Gd$_x$Eu$_{0.05}$)(B(OH)$_4$)$_3$CO$_3$ colloidal spheres as a novel precursor for orthoborate red phosphor and the effects of Gd$^{3+}$ doping on structure and luminescence. CrystEngComm. 2018;20(32):4546–4555.

Zhu Q, Fan Z, Wang S, et al. Uniform colloidal spheres for RE$_2$BO$_6$ (RE = Eu-Yb, Y) and excitation-dependent luminescence of Y$_2$BO$_3$: Eu$^{3+}$ red phosphor. J Am Ceram Soc. 2019;102(12):7448–7461.

Li L, Zhou S, Zhang S. Crystal structure and charge transfer energy of the vaterite-type orthoborate YBO$_3$: Eu. Solid State Sci. 2008;10(9):1173–1178.

Zhu Q, Li S, Wang Q, et al. Grafting of terbium (III) complexes onto layered rare-earth hydroxide nanosheets to fabricate novel optical fiber temperature sensors. Nanoscale. 2019;11(6):2795–2804.

Zhu Q, Xu Z, Li X, et al. Tetragonal (Y,Ln)PO$_4$·nH$_2$O (Ln=Tb/Eu) colloidal spheres for color tunable photoluminescence and the effects of hydration. Opt Mater. 2019;92:71–80.

Zhu Q, Li S, Jin J, et al. Luminescent thermometry by a Y/Eu Binary Layered rare-earth hydroxide (LRH) via in situ intercalation with neutral terbium (III) complexes. Chem Asian J. 2018;13(24):3664–3669.

Sun X, Jiang P, Gao W, et al. Ambient-pressure stabilization of β-Gd$_3$O$_5$ by doping with Bi$^{3+}$ and color-tunable emissions by co-doping with Tb$^{3+}$ and Eu$^{3+}$: the first photoluminescence study of a high-pressure polymorph. Chem Asian J. 2017;12(12):1353–1363.

Wang Z, Li JG, Zhu Q, et al. Tartrate promoted hydrothermal growth of highly [001] oriented (La$_{0.95}$Bi$_x$Eu$_{0.05}$)PO$_4$ (x=0-0.01) nanowires with enhanced photoluminescence. Mater Des. 2017;126:115–122.

Shannon RD. Revised effective ionic radii and systematic study of inter atomic distances in halides and chalcogenides. Acta Cryst. 1976;32(SEP1):751–767.

Chen L, Jiang Y, Yang Y, et al. The energy transfer of Bi$^{3+}$ →Eu$^{3+}$ and Bi$^{3+}$ →Tb$^{3+}$ in YBO$_3$ host to produce light. J Phys D Appl Phys. 2009;42(21):215104.

Liang Z, Mo F, Zhang X, et al. Luminescence of the LiMgBO$_3$: Eu$^{3+}$,Bi$^{3+}$ phosphor. J Lumin. 2014;151:47–51.

Tao L, Yang L, Lou Y, et al. Bright white-light upconversion from core-shell nanocrystals through interfacial energy transfer. Dyes Pigm. 2018;154:87–91.

Li J, Li W, Xia D, et al. Dynamic coordination of natural amino acids-lanthanides to control reversible luminescent switching of hybrid hydrogels and anti-counterfeiting. Dyes Pigm. 2019;166:375–380.

Li P, Peng P, Li Y. Dual-mode luminescent colloidal spheres from monodisperse rare-earth fluoride nanocrystals. Adv Mater. 2009;21(19):1945–1948.

Gangwar AK, Gupta A, Kedawat G, et al. Highly luminescent dual mode polymeric nanofiber-based flexible mat for white security paper and encrypted nanotaggant applications. Chem - Eur J. 2018;24(38):9477–9484.