Regulated morphology/phase structure and enhanced fluorescence in YF₃: Eu³⁺, Bi³⁺ via a facile method

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\( \text{YF}_3: \text{Eu}^{3+}, \text{Bi}^{3+} \) via a facile method

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Abstract

A simple and facile hydrothermal method has been developed to enhance the fluorescence performance of \( \text{YF}_3: x\text{Eu}^{3+}, y\%\text{Bi}^{3+} \) \((x = 0-0.2, y = 0-1.5)\) via optimizing the concentration of \( \text{Eu}^{3+} \) and \( \text{Bi}^{3+} \) and regulating the morphology/phase structure by controlling the amount of \( \text{HNO}_3 \). The evolutionary mechanism of the micro-topography and microstructure for the samples has been proposed, and the fluorescence and decay properties of the samples have been investigated. It was found that the fluorescence intensity of the sample has been enhanced greatly after added the opportune amount of \( \text{Bi}^{3+} \). The optimum concentrations of \( \text{Eu}^{3+} \) and \( \text{Bi}^{3+} \) for fluorescence are \( x = 0.125 \) and \( y = 0.5\% \), respectively. The significant enhancement in fluorescence performance could be obtained in the sample with the desired morphology at the optimum volume of \( \text{HNO}_3 \) \((V_{\text{HNO}_3} = 11 \text{ mL})\).

Introduction
In recent years, lanthanide ions doped inorganic crystals with controllable shapes and sizes have attracted considerable attention because of their potential technological applications in biomedical imaging, anti-fake label and illumination.\textsuperscript{1} Among these inorganic materials, fluoride-containing host materials are the most captivating due to their low vibration energy, minimization of the quenching of the correlative excited state of the rare-earth ions and good optical transparency at a wide wavelength region.\textsuperscript{2,3} Meanwhile, fluoride-containing materials possess good solubility, adequate thermal and environmental stabilities. These excellent physicochemical properties are in favor of the optical applications of the materials.\textsuperscript{4} In comparison with other fluorescent host materials, YF\textsubscript{3} is considered as one of the most important host materials that has been intensively studied in recent years.\textsuperscript{5,6} It has been known that trivalent rare earth ions can easily substitute for Y\textsuperscript{3+} in the YF\textsubscript{3} because of their similar ionic radii of lanthanide. Moreover, the consummate matrix of YF\textsubscript{3} is conducive to lanthanides doping thus promoting the high efficiency emission of down/up conversion materials without additional charge compensation.\textsuperscript{5,7}

Among rare earth ions, Eu\textsuperscript{3+} has been frequently used as an activator due to its intense emission caused by $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition in red spectral region. A number of investigations have been carried out to improve the fluorescence efficiency of Eu-containing materials by doping metal ions (e.g. Ln\textsuperscript{3+}-doped calcium fluoride nanocrystals, NaxEu\textsuperscript{3+}(2-x)3MoO\textsubscript{4}, etc.),\textsuperscript{4,8,9} employing various synthesis techniques (e.g. a facile arginine-assisted hydrothermal synthesis, electrospinning, etc.)\textsuperscript{10,11} and optimizing the stoichiometric ratio of the materials (e.g. Eu\textsubscript{1-x}Bi\textsubscript{x}VO\textsubscript{4}, BaLa\textsubscript{2-x}ZnO\textsubscript{5}: xBi\textsuperscript{3+}, yEu\textsuperscript{3+}, etc.).\textsuperscript{12,13} Eu\textsuperscript{3+} has also been introduced into YF\textsubscript{3} to obtain laser materials with excellent emission. For example, Shao et al. studied YF\textsubscript{3}: Eu\textsuperscript{3+} micro-single crystals,\textsuperscript{7} and Fu et al. fabricated Eu\textsuperscript{3+}-doped YF\textsubscript{3} microcrystals with uniform grains.\textsuperscript{14} These studies control the morphology of crystal grains to improve the fluorescence performance of the material by adding
different inorganic salts. On the other hand, it has been noted that the energy can be transferred from Bi$^{3+}$ to Eu$^{3+}$ via a dipole-dipole mechanism in ZnWO$_4$: Bi$^{3+}$,Eu$^{3+}$ materials.\textsuperscript{15} Thus, Bi$^{3+}$ has been considered as a significant luminescent sensitizer for Eu$^{3+}$. Recently, Dong \textit{et al.}\textsuperscript{13} and Wang \textit{et al.}\textsuperscript{15} have obtained the ZnWO$_4$: Bi$^{3+}$,Eu$^{3+}$ material with excellent luminescence induced by the energy transferring from Bi$^{3+}$ to Eu$^{3+}$. Therefore, it can be reasonably anticipated that the introduction of Bi$^{3+}$ into the YF$_3$: Eu$^{3+}$ materials may effectively improve the fluorescence of the materials. To our knowledge, there have been few reports on Bi$^{3+}$ sensitized Eu$^{3+}$ in YF$_3$ host material. In addition, it is well known that the morphology and crystal structure of crystalline grains usually dominate the properties of materials.\textsuperscript{16} In general, the morphology and phase structure of nano/micromaterials depend on many factors (\textit{e.g.} the variety and concentration of solvent, the types and levels of doping ions, reaction time and temperature, \textit{etc.}).\textsuperscript{17} Some studies have revealed that the technology application of most materials depends on the characteristic dimension.\textsuperscript{18} Generally, the morphology control of crystal grain is crucial to offset the disadvantage and optimize the performance of the materials.\textsuperscript{19} As well known, the morphologies of grains essentially depend on the growth rate of crystal facets and the stability of surfaces. Thus, various phases and morphologies of the materials always can be modulated via different synthetic methods. For instance, a hexagonal YF$_3$ was obtained via a micro-emulsion;\textsuperscript{20} a hollow nano-fibers of YF$_3$ was synthesized by an double-crucible method;\textsuperscript{11} and various solvents (\textit{e.g.} ethylenediamine tetraacetic acid disodium salt, polyethylenimine polymer, \textit{etc.})\textsuperscript{21,22} were also introduced to obtain the materials with desired morphologies.\textsuperscript{2}

Unfortunately, the operations mentioned above are difficult to control. Besides, some additional impurities or defects are usually produced in desired materials. To overcome these difficulties, it is necessary to develop a simple technology for controlling the micro-topography of crystal particles
to enhance the material properties. It has been noted that the morphology of microscopic particles strongly depends on the concentration of H⁺ ions and inorganic doping, because the energy that applied on the grains is determined by the kinetics of the ions in the reaction system. As a result, changing the concentration of H⁺ ion may be an effective method to simply regulate the morphology of grains. In the present work, new materials of YF₃: xEu³⁺, y%Bi³⁺ have been developed by adding Bi³⁺ to YF₃: Eu³⁺ with a simple facile hydrothermal process. The grain morphology/phase structure has been successfully regulated only by modulating the HNO₃ level, and a significant enhancement in the fluorescence of the materials has been obtained. The dependences of fluorescence and decay properties on the morphology have also been studied in detail.

Experimental Sections

Materials synthesis: The powders of YF₃: xEu³⁺, y%Bi³⁺ (x = 0-0.2, y = 0-1.5) were synthesized by a facile hydrothermal route. All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd (China) and directly used without any treatment. In a typical synthesis, Eu₂O₃ (99.99%), Y₂O₃ (99.99%), Bi₂O₃ (99.999%) in stoichiometric ratio of the YF₃: xEu³⁺, y%Bi³⁺ were dissolved in 65% HNO₃ (5-17 mL) and magnetic stirred at 60°C for 40 min. KF·2H₂O (99%) and Y³⁺ with a molar ratio of 6:1 was dissolved in distilled water, and then the resulting fluorine-containing solution was added dropwise to the solution containing rare earth ions under vigorous stirring and the resultant bulk volume was fixed at 30mL. The mixture was transferred into 100mL Teflon-line autoclave and heated at 200°C for 18 h in a muffle furnace. When the autoclave was cooled to room temperature, the white products were collected via centrifuging and washing several times with distilled water and ethanol, and finally dried at 80°C in air for 12 h.
**Instrumentation:** The crystal structures of the powder were examined using X-ray diffraction (XRD) with Cu Kα radiation (Smart Lab). The microstructures (SEM) were observed by a field-emission scanning electron microscope (FE-SEM, JSM-7500, Japan). The fluorescent spectral information was recorded by using a fluorescence spectrophotometer (F-7000) with a xenon lamp. The internal and external quantum efficiency QE were measured using a QE-2100 from Otsuka Photal Electronics. Transmission electron microscopy (TEM) and high-resolution (HRTEM) were performed on a JEM2010.

**Results and discussions**

The XRD patterns of the YF₃: xEu³⁺, 1.0%Bi³⁺ powders prepared at VΗNO₃ = 11mL are shown in Fig. 1. The sample without Eu³⁺ doping is mainly the mixture of hexagonal KYF₄ (JCPDS No. 27-0466) and tetragonal KY₃F₁₀ (JCPDS No. 27-0465). In addition, a small amount of YF₃ (JCPDS No. 74-0911) is observed in the sample with x = 0. It can be seen that Eu³⁺ doping leads to an obvious change in the crystal structure of the samples. As x increases, the observed numbers of KY₃F₁₀ and KYF₄ peaks reduce gradually while the number of YF₃ peaks increases. At x ≥ 0.075, all the samples consist of pure YF₃ with orthorhombic symmetry and no other impurities can be detected. For the materials with x ≥ 0.075, the further increment in the doping level of Eu³⁺ does not cause the change in the phase structure of the samples. At low levels of Eu³⁺, the main factor that determines the phase structure of the samples should be the concentration of hydrogen bonds (H⋯O) in the materials, which will be discussed in the following paragraph.

Fig. 2 shows the EDS spectra of YF₃: xEu³⁺, 1.0%Bi³⁺ samples with x = 0, 0.05, 0.10 and 0.15 and the insets show the atomic percentages of the elements and corresponding micro-morphologies. It can be seen that as x (i.e. the content of Eu³⁺) increases from 0 to 0.15, the concentration of
oxygen increases from 0 to 2.49% that is in favor of the H···O bond formation. On the basis of the transition state theory, the formation of H···O bond plays a role of bridge in the formation of fluorine hydrogen bond (F···H). Since the bonding energy of the H···O bond is weaker than that of the F···H bond, the latter possesses more preferable stability. Therefore, most of the H⁺ ions combine with excess F⁻ to crystallize into stable YF₃ phase at the presence of sufficient oxygen. At low levels of Eu³⁺ (x < 0.075), the low concentration of oxygen results in the insufficient concentration of H···O bond that is not favor in the formation of F···H bond, so that the excess F⁻ ions are mainly formed to multiple-fluoride (KYF₄, KY₃F₁₀). At x = 0.075, the equilibrium of the transition from H···O to H···F may be reached, resulting in the pure YF₃. When Eu³⁺ is excess (x > 0.075), the phase structure of the samples has not been changed with further increasing x because of a preferable stability of the YF₃⁷.

![Fig. 1 XRD patterns of YF₃: xEu³⁺, 1.0%Bi³⁺ samples (x = 0-0.2) prepared at V_HNO₃ = 11mL.](image-url)
Fig. 2 EDS spectra of YF$_3$: $x$Eu$^{3+}$, 1.0%Bi$^{3+}$ samples with $x = 0$, 0.05, 0.10 and 0.15 prepared at $V_{\text{HNO}_3} = 11$ mL. The insets show the atomic and weight percentages of the elements and corresponding surface morphologies.

Fig. 3 shows the SEM micrographs of the YF$_3$: $x$Eu$^{3+}$, 1.0%Bi$^{3+}$ samples with $x = 0$, 0.025, 0.05, 0.10, 0.125, 0.15 and 0.175. It can be clearly seen that Eu$^{3+}$ doping leads to a distinct change in the micro-topography of the samples. From Fig. 3a, the sample with $x = 0$ exhibits irregular multipolygon spherical particles with rough surface and nonuniform grain size. Some pores and defects can also be observed. With $x$ increasing from 0.025 to 0.075, the surface of the grains becomes relatively smooth, and some octahedral and irregular octahedral morphologies are
simultaneously observed. For the sample with $x = 0.10$, the surface and size of the grains are very smooth and relatively uniform such that the grains mainly possess diamond-like morphology and perfect octahedron, and there is no obvious flaw on the surface of the grains. However, excess Eu$^{3+}$ destroys the perfection of the grains. It can be seen that with $x$ further increasing from 0.10 to 0.175, the grains become irregular and nonuniform. Some bigger octahedra and irregular truncated octahedra like kernel and small crystals aggregated on the surface of the grains are observed in Figs. 3f-h, indicating that the aggregated particles may be formed by a new complex geometrical structure and the small particles may be served as building blocks for forming smaller nano-octahedra.$^{21}$ On the basis of the Ostwald ripening process,$^{24}$ the truncated octahedral particles formed earlier would act as a seed of YF$_3$ grain on which other small orthorhombic YF$_3$ become large ideal truncated octahedra eventually. In addition, the average size of the grains first increases and then decreases with $x$ increasing.

Figs. 4 and 5 show the XRD patterns and SEM micrographs of the YF$_3$: 0.125Eu$^{3+}$, y%Bi$^{3+}$ samples with $y = 0$, 0.5, 1.0, and 1.5 prepared at $V_{\text{HNO}_3} = 11$ mL, respectively. At $y \leq 1.0$, all the diffraction peaks of the powders are identical with the standard card (JCPDS 74-0911) for orthorhombic YF$_3$, indicating that the samples possess pure orthorhombic phase without impurities after the moderate Bi$^{3+}$ doping. This suggests that Bi$^{3+}$ ions are incorporated in the lattice of host material with little influence on the lattice matrix due to the comparable ionic radius of Bi$^{3+}$ with Y$^{3+}$ and Eu$^{3+}$. However, an impurity phase of KY$_3$F$_{10}$ is observed with $y$ increasing to 1.5. Meanwhile, from Fig. 5, the microstructure of the samples is significantly changed with increasing $y$. The grain size of the materials first increases and then diminishes with increasing the amount of Bi$^{3+}$. At $y = 0$, small crystal grains of the samples aggregate on the large grains. With the addition of 0.5%Bi$^{3+}$, the relative regular and monodispersed octahedra are obtained. When Bi$^{3+}$ is excess ($y \geq$
1.0), the crystal grains become irregular and agglomerate. After the addition of Bi\(^{3+}\), the growth rate of different crystalline planes is changed because the Bi\(^{3+}\) ions are selectively absorbed on the surface of the initially formed tiny YF\(_3\) crystals; meanwhile, the existing anions (F\(^-\), OH\(^-\) and NO\(_3^-\)) are coordinated by different coordination strengths and modes.\(^{14}\) These lead to the change in the grain shape of YF\(_3\) materials. On the other hand, the charge of cations may also be responsible for the size of YF\(_3\).\(^{14}\)

![Fig. 3 SEM images of YF\(_3\): xEu\(^{3+}\), 1.0%Bi\(^{3+}\) (x = 0-0.175) samples prepared at V\(_{\text{HNO}}\), = 11 mL: (a) x = 0; (b) x = 0.025; (c) x = 0.05; (d) x = 0.075; (e) x = 0.1; (f) x = 0.125; (g) x = 0.15; and (h) x = 0.175.](image-url)
Fig. 4 XRD patterns of YF\textsubscript{3}: 0.125Eu\textsuperscript{3+}, y\%Bi\textsuperscript{3+} samples (y = 0, 0.5, 1.0 and 1.5) prepared at V\textsubscript{HNO\textsubscript{3}} = 11mL.

Fig. 5 SEM images of YF\textsubscript{3}: 0.125Eu\textsuperscript{3+}, y\%Bi\textsuperscript{3+} samples prepared at V\textsubscript{HNO\textsubscript{3}} = 11mL: (a) y = 0.0; (b) y = 0.5; (c) y = 1.0; (d) = 1.5.
The emission spectra of YF$_3$:xEu$^{3+}$, y%Bi$^{3+}$ (x/y = 0.125/0, x/y = 0.125/0.5 and x/y = 0/1.0) excited at 393 nm are shown in Fig. 6a. It was found that the emission spectra (575 nm) of the sample with x/y = 0/1.0 (i.e. without Eu$^{3+}$ doping) should be attributed to the $^3P_1\rightarrow^1S_0$ electrons transition of Bi$^{3+}$. However, compared to the Eu$^{3+}$-doped materials, the emission of the materials with only Bi$^{3+}$ doping is much weaker. The emission spectrum of the sample with x/y = 0.125/0 consists of some peaks corresponding to $^5D_1\rightarrow^7F_0$, $^5D_1\rightarrow^7F_2$ (515 nm and 555 nm) and $^5D_0\rightarrow^7F_J$ (J = 0-4; 580, 592, 614, 650, and 690 nm) electrons transition of Eu$^{3+}$ ions, respectively. The emission of $^5D_0\rightarrow^7F_1$ is the strongest because of the magnetic–dipole mechanism and inversion symmetry position of Eu$^{3+}$ ions. Interestingly, the position and shape of the peaks for the materials with x/y = 0.125/0 and 0/1.0 are almost the same, indicating that Bi$^{3+}$ and Eu$^{3+}$ have some parallel levels. With the addition of Bi$^{3+}$ (y = 0.5), the emission intensity of the powders at 575 nm and 625 nm is significantly enhanced. These show that Bi$^{3+}$ can sensitize Eu$^{3+}$ because the emission spectra of Bi$^{3+}$ and Eu$^{3+}$ have a significant overlap, and the interaction between Bi$^{3+}$ and Eu$^{3+}$ leads to the considerable enhancement in the fluorescence of the materials. Moreover, Eu$^{3+}$ and Bi$^{3+}$ can be simultaneously excited under ~393nm due to certain matched energy levels. Hence, the activated Bi$^{3+}$ electrons jump to their higher energy levels $^5L_6$ and $^2P_{3/2}$, respectively. Then, Bi$^{3+}$ ions transfer the energy to the Eu$^{3+}$ ions that have similar energy through relaxation or non-radiation.
Fig. 6 (a) Emission spectra of YF$_3$: xEu$^{3+}$, y%Bi$^{3+}$ (x = 0.125, y = 0; x = 0.125, y = 0.5; x = 0, y = 1.0) samples prepared at $V_{\text{HNO}_3} = 11$ mL excited at 393 nm; (b) Excitation spectra of YF$_3$: xEu$^{3+}$, y%Bi$^{3+}$ (x = 0, y = 1.0; x = 0.125, y = 0) and $\lambda_{\text{em}} = 592$ nm; (c) and (d) Dependences of the emission intensity ($\lambda_{\text{em}} = 592$ nm), (Ex/In) quantum efficiency and absorbance on y and x.

The doping of Bi$^{3+}$ does not change the position of emission peaks since the 4f energy level of Eu$^{3+}$ is hardly affected by the crystal field due to the shielding effect of the 5s$^2$ p$^6$ electrons. Fig 6b shows that the shape and position of excitation peaks of the YF$_3$: xEu$^{3+}$, y%Bi$^{3+}$ with x/y = 0/1.0 and 0.125/0 have no significant difference, indicating that Bi$^{3+}$ and Eu$^{3+}$ have some matched energy level.

The dependences of emission intensity, external/internal quantum efficiency (QE-Ex/In) and absorbance on y and x for YF$_3$: 0.125Eu$^{3+}$, y%Bi$^{3+}$ and YF$_3$: xEu$^{3+}$, 1.0%Bi$^{3+}$ are shown in Figs. 6c and 6d, respectively. The results show that the emission intensity initially increases and then decreases with increasing Eu$^{3+}$ and Bi$^{3+}$ and the strongest fluorescence intensities of the materials.
are reached at $x = 0.125$ and $y = 0.5$, respectively. Meanwhile, the external quantum (QE-Ex) and absorptance of the samples have the same tendency but the internal quantum (QE-In) shows an inconsistent trend. It can be seen that the samples possess very high internal quantum efficiency (52-81%), however, the external quantum efficiency (0.7-15%) and absorbance (8-22%) are low. The phenomenon exhibits that the materials prepared in the work have weak absorbance and need to be further improved. On the other hand, for the YF$_3$: xEu$^{3+}$, 1.0%Bi$^{3+}$, at low concentration of Eu$^{3+}$, the increasement of emission intensity with $x$ should be attributed to the accumulating luminescent centers. In addition, the amount of H⋯O increases with $x$ and the hydrogen bonding can make a stronger crystal field that applies on the Eu$^{3+}$ ions$^{31,32}$ to enhance the fluorescent intensity of the powder. However, at high concentration of Eu$^{3+}$, the fluorescence of the materials decreases with increasing $x$ because of the aggrandizing non-radioactive energy transfer among miscellaneous Eu$^{3+}$ until reaching its quenching point; moreover, the degree of Eu$^{3+}$-Eu$^{3+}$ interaction is enhanced because of shorter internuclear distance of ions with increasing Eu$^{3+}$, which leads to non-radiative decay of the excited state. These result in the fluorescence quenching in the materials with high levels of Eu$^{3+}$.\textsuperscript{25} According to Dexter’s energy transfer theory,\textsuperscript{32} a typical effect of concentration quenching is induced by non-radioactive energy migration among adjacent luminescent ions. For the YF$_3$: 0.125Eu$^{3+}$, y%Bi$^{3+}$, at a low level of Bi$^{3+}$, the fluorescence intensity increases with $y$ due to the increasing sensitizers that can transfer sufficient energy to the luminescent centers. However, excess Bi$^{3+}$ may result in the formation of the Bi$^{3+}$ clusters that dissipates the absorbed energy via non-radioactive transition\textsuperscript{13} and thus degrades the emission intensity of the samples.
Fig. 7 (a) Schematic energy level diagram of Eu$^{3+}$; (b) Representation of the CIE chromaticity diagram of YF$_3$: xEu$^{3+}$, 1.0%Bi$^{3+}$ samples (x = 0-2.0) prepared at V$_{\text{HNO}_3}$ = 11 mL ($\lambda_{\text{em}}$ = 592 nm).

The schematic energy level diagram of Eu$^{3+}$ is shown in Fig. 7a. It intuitively reveals the electron transition process of Eu$^{3+}$, corresponding to the characteristic peak of emission and excitation spectra (Figs. 6a and 6b); meanwhile, it also exhibits the non-radiation transmission of energy in the materials. In general, color could be represented by the Commission International del'Eclairage (CIE) 1931 chromaticity coordinates.$^{33}$ The CIE chromaticity diagram of YF$_3$: xEu$^{3+}$, 1.0%Bi$^{3+}$ samples with x = 0-2.0 is shown in Fig.7b. From Fig. 7b, the color of the samples is mainly in the yellow area, indicating that the Eu$^{3+}$ ions are located in low symmetry lattices.$^{34}$ The color tone can be tuned at x < 0.075, and the chromaticity coordinates do not further shift when x ≥ 0.075, indicating that the color of the optical materials strongly depends on the crystal structure. These results are consistent with XRD patterns (Fig. 1).
Fig. 8 Lifetime decay curves of the YF₃: xEu³⁺, 1.0%Bi³⁺ samples prepared at V_HNO₃ = 11 mL (the red line is fitted curve): (a) x = 0; (b) x = 0.025; (c) x = 0.05; (d) x = 0.075; (e) x = 0.1; (f) x = 0.125; (g) x = 0.15; (h) x = 0.175; and (i) x = 0.2. (λ_ex = 393 nm, λ_em = 592 nm).

The decay curves for ⁵D₀⁻⁷F₁ (592 nm) of YF₃: xEu³⁺, 1.0%Bi³⁺ with x = 0-0.2 were measured under the excitation of 393 nm at room temperature as shown in Fig. 8. The decay curve of the sample with x = 0 cannot be fitted into functions well. However, the decay curves of the powder with x = 0.025-0.15 and x = 0.175-0.20 can be well fitted by double exponential and triple exponential functions (formulas 1 and 2) as following, respectively:

\[ I(t) = I_0 + A e^{-t/t_1} + A e^{-t/t_2} \quad (1) \]

\[ I(t) = I_0 + A e^{-t/t_1} + A e^{-t/t_2} + A e^{-t/t_3} \quad (2) \]

where \( I(t) \) and \( I_0 \) are the luminescence intensities at times of \( t \) and 0, \( t \) is the time, \( t_1 \) and \( t_2 \) are the decay times for exponential components, respectively. The average decay lifetime \( \tau \) can be calculated by the formulas as following:

\[ \tau = \frac{(\tau_1^2 + \tau_2^2) / (\tau_1 + \tau_2)}{2} \quad (3) \]
and

\[ t = \left( A t + A t + A t \right) \]

(4)

The average lifetime values of the samples with \( x = 0, 0.025, 0.05, 0.075, 0.01, 0.125, 0.15, 0.175 \) and 0.2 are calculated to be 6.57, 9.761, 7.695, 6.916, 6.942, 6.524, 7.466, 7.478 and 8.103 ms, respectively. The decay behaviors of the YF\(_3\): 0.125Eu\(^{3+}\), y%Bi\(^{3+}\) samples are shown in Fig. 9. The curve of the sample with \( y = 0 \) can be fitted into bi-exponential as formula (1) and the others can be fitted into a tri-exponential well as formula (2). The average lifetime values of the samples with \( y = 0, 0.5, 1.0, \) and 1.5 are 8.899, 7.082, 7.680, 8.548 ms, respectively.

The fitting parameters of the decay time for the materials are given in Table 1. The sample with \( x/y = 0/1.0 \) has a relatively short lifetime which may be ascribed to overmuch surface defects. In general, the crystalline defect results in the formation of quenching center, which leads to non-radioactive relaxation of photons. From Table 1, some values of \( t_1, t_2 \) and \( t_3 \) of the samples with \( x = 0.15-0.2 \) and \( y = 0-1.5 \) are not identical, implying that the lattice environments of Eu\(^{3+}\) ions are not identical. The Eu\(^{3+}\) ions with a short decay time may exist near the defects and grain surfaces, whereas the Eu\(^{3+}\) ions with long decay lifetime may exist at the core of the grains with a perfect lattice environment.\(^{35}\) It can be seen that the average decay time exhibits an unusual change: the optimal level of Eu\(^{3+}\) for fluorescence possesses shorter decay time than other compositions. This result does not agree with most of reports in literatures\(^{7,15,36}\) in which the materials with the strongest fluorescence exhibit the longest decay time. However, Li et al. also reported similar unusual phenomenon.\(^{11,33}\) It is well known that the number of luminescent centers, defects, energy transfer and impurities in the host material have inevitable effects on the decay of kinetic behavior of the materials.\(^{22}\) Meanwhile, the morphology, edges, apexes, and special junctions of crystal grains also have important effects on the decay properties.\(^{7}\) Therefore, it can be inferred that the
unusual phenomenon shown in Tab. 1 should be the end product of all these factors. However, the exact reason of the phenomenon is still not clear that needs to be further studied.

![Lifetime decay curves](image)

**Fig. 9** Lifetime decay curves of the YF₃: 0.125Eu³⁺, y%Bi³⁺ samples (y = 0, 0.5, 1.0, and 1.5) prepared at V_HNO₃ = 11 mL (λ_ex = 393 nm, λ_em = 592 nm).

**Tab. 1** Fitting parameters of the decay time for YF₃: xEu³⁺, 1.0%Bi³⁺ (x = 0-0.2) and YF₃: 0.125Eu³⁺, y%Bi³⁺ (y = 0-1.5)

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<td>x/y = 0.125/1.0</td>
<td>6.5240</td>
<td>6.5240</td>
<td>–</td>
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<td>6.524</td>
</tr>
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<td>5.9808</td>
<td>–</td>
<td>0.99998</td>
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<td>0.99996</td>
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<td>–</td>
<td>0.99987</td>
<td>8.899</td>
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<tr>
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<td>6.1508</td>
<td>6.1484</td>
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<td>8.3841</td>
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<tr>
<td>x/y = 0.125/1.5</td>
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<td>6.9973</td>
<td>11.2800</td>
<td>0.99990</td>
<td>8.528</td>
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As mentioned above, the morphology and structure of the grains can be regulated by optimizing the concentrations of Eu\(^{3+}\) and Bi\(^{3+}\) ions and the fluorescence of the samples strongly depends on the morphology of the crystals. We have noted that the concentration of H\(^+\) (i.e. acidity) plays an important role in regulating the phase structure and morphology of the materials. For example, Shao et al. reported that the shape of crystal grain is transformed from diamond-like to octahedral-formation with the amount of HNO\(_3\) increasing;\(^7\) and Zhao et al. found that PH value affects the size and morphology of CaF\(_2\): Yb\(^{3+} / \text{Er}^{3+}\).\(^{37}\) Obviously, as compared to optimizing chemical compositions, regulating the morphology by adjusting the amount of H\(^+\) is much simpler and more practicable. In this work, we have successfully obtained the desired micro-topography, pure phase structure and the significant enhancement in the fluorescence of the YF\(_3\): 0.125Eu\(^{3+}\), 0.5\%Bi\(^{3+}\) by changing the amount of HNO\(_3\) (i.e. H\(^+\)).

The XRD patterns of the YF\(_3\): 0.125Eu\(^{3+}\), 0.5\%Bi\(^{3+}\) prepared at different volume of HNO\(_3\) are shown in Fig. 10. From Fig. 10, the precipitation is crystallized into the mixture of hexagonal KYF\(_4\) (JCPDS No. 270466) and tetragonal KY\(_3\)F\(_{10}\) (JCPDS No. 270465) at V\(_{\text{HNO}_3}\) = 5mL. When the nitric acid is increased to 7mL, the samples are shown to be made of a large amount of KY\(_3\)F\(_{10}\) and a small amount of KYF\(_4\) and YF\(_3\) (JCPDS No. 740911). However, as the amount of HNO\(_3\) reaches 11mL, all powders are transformed into pure orthorhombic YF\(_3\) without any other impurities. In turbulent and boiling hydrothermal environment, it may exist the following reactions:

\[ n \text{F}^- + \text{K}^+ + \text{Y}^{3+} \rightleftharpoons \text{KY}_3\text{F}_{10}/(3\text{KYF}_4) \]  \hspace{1cm} (5)

\[ \text{H}^+ + \text{F}^- \rightleftharpoons \text{HF} \]  \hspace{1cm} (6)

\[ \text{KY}_3\text{F}_{10}/(3\text{KYF}_4) + \text{H}^+ \rightleftharpoons \text{K}^+ + \text{HF} + 3\text{YF}_3 \]  \hspace{1cm} (7)

At a low level of H\(^+\), the excess F\(^-\) ions are coupled with cations to form multiple-fluoride (i.e., KY\(_3\)F\(_{10}\) / 3KYF\(_4\)) as shown in formula (5). With increasing the amount of HNO\(_3\), the H\(^+\) ions reduce...
the excess amount of F ions by a reversible formula (6). Finally, the excess H⁺ ions can transfer the multiple-fluoride to ternary-fluoride as shown in formula (7). These mechanisms are in favor of forming the stable YF₃ phase at high volume of HNO₃.

**Fig. 10** XRD patterns of the YF₃: 0.125Eu³⁺, 0.5%Bi³⁺ samples prepared at different volume of hydrogen nitrate (V_{HNO₃} = 5, 7, 9, 11, 13, 15 and 17 mL).

The morphology evolution of the YF₃: 0.125Eu³⁺, 0.5%Bi³⁺ at different V_{HNO₃} is schematically illustrated in Fig. 11. After the addition of HNO₃, the micro-topography of YF₃: 0.125Eu³⁺, 0.5%Bi³⁺ is obviously changed. As the amount of HNO₃ increases, the size of the samples initially increases and then decreases. From Figs. 11a-b, the samples exhibit aggregated spherical nano-particles at V_{HNO₃} ≤ 7mL. As the amount of HNO₃ increases to 9-11mL, the crystalline grains are evolved into smooth octahedra with truncated edges and corners. It can be seen that the perfect and smooth octahedras are obtained at V_{HNO₃} = 13mL (Fig.11e). After the addition of excess HNO₃,
the diameter of the grains decrease rapidly and the larger truncated and non-truncated octahedra act as crystallization centers like nucleation as shown in Figs 11f and 11g. From the view of crystal growth, the crystalline shape of the grains highly depends on the surface energy of various crystal planes. The plane with higher surface energy grows faster than the plane with lower surface energy, so the planes with lower surface energy will be exposed.\textsuperscript{38} From Fig. 11, it can be inferred that the surface energy of different crystal planes has been changed with increasing the amount of HNO\textsubscript{3}. In addition, the morphology evolution of the crystal grains may be also ascribed to the decrease in the amount of the dissociative F\textsuperscript{-} with increasing HNO\textsubscript{3} due to the formation of HF (H\textsuperscript{+} + F\textsuperscript{-} ⇌ HF) at excess H\textsuperscript{+}. It can be concluded that the morphology of the crystal grains can be effectively tuned via controlling the concentration of H\textsuperscript{+}. The relevant structures of the crystal are inserted in Fig.11 to intuitively show the evolution of crystal structure with increasing HNO\textsubscript{3}.

**Fig. 11** Schematic illustration of the formation and morphology evolution of YF\textsubscript{3}: 0.125Eu\textsuperscript{3+}, 0.5%Bi\textsuperscript{3+} samples prepared under different acidic conditions. (a: 5 mL, b: 7 mL, c: 9 mL, d: 11 mL, e: 13 mL, f: 15 mL, g: 17 mL)
Fig. 12 TEM, HRTEM and selected area electron diffraction (SAED) images of the synthesized YF$_3$: 0.125Eu$^{3+}$, 0.5%Bi$^{3+}$ samples prepared at 7 mL (a$_1$-a$_4$); 11 mL (b$_1$-b$_4$) and 15 mL (c$_1$-c$_4$) HNO$_3$.

To give a careful observation and confirm the changes in morphology induced by the addition of HNO$_3$, TEM and corresponding selected area electron diffraction (SAED) images of the YF$_3$: 0.125Eu$^{3+}$, 0.5%Bi$^{3+}$ samples synthesized at different $V_{\text{HNO}_3}$ are shown in Fig. 12. From Figs. 12a$_1$ and a$_2$, it can be clearly seen that the samples are tetragonal nanocrystals of KY$_3$F$_{10}$ with uniform morphology. From the HRTEM image (Fig. 12a$_3$), the high crystallinity is confirmed by the clear lattice fringes. The determined interplanar distances of 0.33 nm and 0.29 nm between the adjacent lattice planes agree well with the $d_{202}$ and $d_{220}$ spacing of tetragonal KY$_3$F$_{10}$, respectively. Besides, the SAED pattern in Fig. 12a$_4$ can be indexed to the reflection of the tetragonal KY$_3$F$_{10}$, which is consistent with the XRD results. Figs. 12b$_1$ and b$_2$ show TEM images of the YF$_3$ microcrystal prepared at $V_{\text{HNO}_3} = 11$ mL. The sample shows a rhombic base of truncated octahedron with uniform morphology.$^{21}$ The HRTEM (Fig. 12b$_3$) displays the $d$-spacing of 0.32 nm and 0.34 nm corresponding to the $d_{111}$ and $d_{020}$ spacing of orthorhombic phased YF$_3$, respectively, in accordance with the XRD patterns (Fig. 10) and the SAED (Fig. 12b$_4$). With increasing the amount of HNO$_3$,
the nanoparticles exhibit nonuniform morphology as shown in Fig. 12c. The interplanar distance is 0.36 nm, which indexes to the (101) plane of the orthorhombic YF₃. These results make a clear indication that the amount of H⁺ plays a significant role in tuning the morphology and phase structure of the materials.

The emission spectra (monitored at 393 nm) of the YF₃: 0.125Eu³⁺, 0.5%Bi³⁺ samples synthesized at V_HNO₃ = 5-17 mL are shown in Fig. 13a, while the external/internal quantum efficiency (QE-Ex/In) and absorbance of the samples are shown in Fig. 13b. The spectra exhibit a typical linear feature of Eu³⁺ emission, which display sharp peaks at the range of 550~710 nm corresponding to the electrons of Eu³⁺ transition from the excited levels ⁵Dᵢ (I = 0, 1) to ground state ⁷Fⱼ (j = 0-4) levels, respectively. As V_HNO₃ increases, there is a slight shift at ~592nm and ~620nm of the emission peaks, indicating that the 4f energy levels of Eu³⁺ are affected due to the change in the circumstance caused by increasing hydrogen nitrate. From Fig. 13, the emission intensity at ~592nm first increases and then decreases with the amount of HNO₃ increasing, giving the strongest intensity at V_HNO₃ = 11mL. At low level of HNO₃, the agglomerative and small particles with large surface area lead to more defects that provide non-radioactive recombination pathways, resulting in the low emission intensity of the samples. The sample with V_HNO₃ = 11mL has the strongest emission intensity due to the apparent sharp edges and corners of the crystalline grains being truncated that would decrease the non-radioactive energy transition. However, when HNO₃ is excess (V_HNO₃ > 13mL), the size of crystal grains decreases and some small particles agglomerate on the large grains. These would increase the non-radiative energy because of larger surface area, resulting in the degradation in the fluorescence of the powder. From Fig. 13b, the (QE-Ex/In) quantum efficiency and absorbance of the samples exhibit the similar tendency.
Unfortunately, the materials have considerably low external quantum efficiency (4.7-19%) and absorbance (9-27%) in spite of their high internal quantum efficiency of 15-72%.

![Emission spectra and quantum efficiency of YF₃: 0.125Eu³⁺, 0.5%Bi³⁺ samples](image)

**Fig. 13** (a) Emission spectra of YF₃: 0.125Eu³⁺, 0.5%Bi³⁺ samples excited at 393 nm and obtained under different acidic conditions, (b) (Ex/In) quantum efficiency and absorbance of the samples.

Fig. 14 shows the lifetime decay curves of the YF₃: 0.125Eu³⁺, 0.5%Bi³⁺ prepared at different V_{HNO₃}. As illustrated in Fig. 14, at V_{HNO₃} ≤ 11 mL, the decay curves emission (λ_ex = 393 nm, λ_em = 592 nm) for the ⁵D₀→⁷F₁ transition of Eu³⁺ can be fitted by double-exponential (formula 1), while the decay curves of the samples with V_{HNO₃} > 11 mL can be fitted well with a tri-exponential (formula 2). The average values are shown in Fig. 14. The fitting results of the fluorescent lifetime of all the samples possess a desired accuracy (R²) of 99.95-99.99%. In general, the decay life is an inverse of the sum of the non-radioactive and radioactive probabilities and the fluorescent lifetime is proportional to the intensity of fluorescence. However, the present samples do not follow the rule.
As known, besides the defects of crystal grains, the morphology, edges, apexes, and special junctions of crystal particles could also have a crucial influence on the fluorescent lifetime. Therefore, it can be inferred that the present unusual phenomenon may be attributed to the comprehensive effect of the size, surface morphology, and apexes of crystalline grains.

![Graph](image)

**Fig. 14** Lifetime decay curves of the YF$_3$: 0.125Eu$^{3+}$, 0.5%Bi$^{3+}$ prepared under different acidic conditions.

**Conclusions**

In conclusion, the powders of the YF$_3$: x Eu$^{3+}$, y% Bi$^{3+}$ (x = 0-0.2, y = 0-1.5) have been successfully synthesized via a facile hydrothermal route. The evolutionary mechanisms of micro-topography, microstructure and crystal structure of the samples have been analyzed in detail, and the fluorescent and decay properties of YF$_3$: xEu$^{3+}$, y%Bi$^{3+}$ have been discussed systematically. The results indicate that the concentrations of Eu$^{3+}$, Bi$^{3+}$ and HNO$_3$ are responsible for the shape and phase structure of samples. The emission intensity of the samples is greatly enhanced by Bi$^{3+}$.
doping because Bi$^{3+}$ acts as an effective sensitizer so as to transfer the energy to Eu$^{3+}$. The optimal concentration of Eu$^{3+}$ and Bi$^{3+}$ for fluorescence are $x = 0.125$ and $y = 0.5$, respectively. The desired morphology of YF$_3$: 0.125 Eu$^{3+}$, 0.5%Bi$^{3+}$ with excellent fluorescence has been obtained via optimizing the amount of HNO$_3$ and the optimal volume of HNO$_3$ is 11 mL. The YF$_3$ possesses a typical orthorhombic phase and the samples with regular truncated octahedral micro-topography exhibit the strongest emission, suggesting that the fluorescent properties of the material are strongly related to the size and morphology of the crystal grains. The present study suggests a simple method to regulate the morphology and phase structure to improve the fluorescent properties of the materials.

Acknowledgments

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References


