Fabrication and luminescence of BiPO₄:Tb³⁺/Ce³⁺ nanofibers by electrospinning

Yuguo Yang, Bing Liu, Yuanyuan Zhang, Xianshun Lv, Lei Wei, Xuping Wang*

New Materials Research Institute, Shandong Academy of Sciences, Jinan 250014, China

Abstract: BiPO₄:Tb³⁺/Ce³⁺ nanofibers are synthesized by a simple electrospinning process and followed by a calcination treatment. The nanofibers are characterized by TG-DSC, XRD, FT-IR, SEM, TEM, and spectrophotometer. The calcined BiPO₄:Tb³⁺/Ce³⁺ nanofibers have a monoclinic phase and the diameters are in the range of 80-200 nm. The SEM and TEM images show that the nanofibers are mesoporous and composed of lots of linked nanoparticles. Under an excitation at 369 nm, BiPO₄:Tb³⁺ and BiPO₄:Tb³⁺/Ce³⁺ nanofibers show characteristic emission bands originating from the ⁵D₄ → ⁷F_j (j=6, 5, 4, and 3) transitions of Tb³⁺ ions. The luminescent properties of BiPO₄:Tb³⁺ indicate that the quenching concentration for Tb³⁺ ions in BiPO₄ host is about 15mol%. The co-doped Ce³⁺ ions can improve the emission intensity through the energy transfer from Ce³⁺ to Tb³⁺ ions.

Keywords: BiPO₄:Tb³⁺/Ce³⁺; Nanofibers; Electrospinning; Luminescence.

1. Introduction

Bismuth phosphate (BiPO₄) is one of important inorganic phosphates and has three different modifications including hexagonal phase, low-temperature monoclinic phase, and high-temperature monoclinic phase [1], which has applications in fields of catalysts [2], ion sensing [3], and separating radioactive elements [4]. Also, it is

* wangxp@sdas.org (Corresponding author: Xuping Wang)

reported as a better luminescent host for rare earth ions [5]. Such rare earth ions doped BiPO₄ powders are potential candidates for photonic and luminescent applications. As a result, rare earth ions doped BiPO₄ nano/micro crystals with different phases and morphologies are synthesized by different methods [6-15]. Generally speaking, rare earth ions occupy the sites of Bi³⁺ ions because of the comparable ionic radius of Bi³⁺ ions with those of rare earth ions. And the main difference between hexagonal and monoclinic phase of BiPO₄ is the number of near neighbor oxygen atoms around Bi³⁺ ions. In the case of hexagonal and monoclinic BiPO₄, Bi³⁺ ions are surrounded by eight and nine near neighbor oxygen atoms, respectively [1]. Since luminescent properties of nano/micro crystals have close relation with their phase, morphology, and particle size [16], rare earth ions doped BiPO₄ nano/micro crystals often show different luminescent properties.

In recent years, much attention has been paid to the synthesis of one-dimensional (1D) nanos/micro crystals, which exhibit novel physical and chemical properties due to their unique and fascinating characteristics for huge ratio of diameter to length and superior mechanical toughness. These fibers have potential applications in textiles, optical detectors, filtration, and vivo imaging. For example, some scientists as well as artists have developed much simple color-changing system that can apply to textiles using various nanofibers [17]. Also, fibrous materials used for filter provide advantages of high filtration efficiency and low air resistance, because of the very high surface area to volume ratio and resulting high surface cohesion, as well as the possibility of recycle usage of electrospun membrane [18]. It has been reported that

Eu³⁺ ions show higher quantum efficiency values in 1D Y₂O₃ fibers than those of bulk powders [19]. The mesoporous structure of fibers will influence the electro-hole pairs' recombination rates, which further influences the luminescent properties of samples [20, 21]. Therefore, inorganic rare earth ions doped luminescent fibers are drawn great attention because of their geometry advantage and excellent luminescent efficiency. For the synthesis of nano/micro fibers, electrospinning is an effective route. Some inorganic fibers have been synthesized by this method [22-28]. Herein, we report on the synthesis of BiPO₄:Tb³⁺/Ce³⁺ fibers by electrospinning. As we all know, the particle size plays a key role in the dynamics of electron-hole recombination process [29]. The synthesis and luminescence of hexagonal BiPO₄:Tb³⁺/Ce³⁺ nanoparticles have been reported [30, 31]. In this work, we synthesize monoclinic BiPO₄:Tb³⁺/Ce³⁺ nanofibers comprising of lots of small nanoparticles by electrospinning process. The phase, morphology, and luminescence of synthesized fibers are studied carefully. To the best of our knowledge, it is the first time to report the fabrication of BiPO₄:Tb³⁺/Ce³⁺ nanofibers by electrospinning process and relating luminescent properties.

2. Materials and methods

The synthesis of BiPO₄:Tb³⁺/Ce³⁺ fibers by electrospinning can be divided into two steps, namely the preparation of spinnable precursor sols and the electrospinning of BiPO₄:Tb³⁺/Ce³⁺ fibers. In the preparation of sols, Bi(NO₃)₃·5H₂O, (NH₄)₃PO₄·3H₂O, Tb(NO₃)₃·6H₂O, Ce(NO₃)₃·6H₂O and citrate acid were used as raw materials. Deionized water was used as solvent. Polyvinyl Pyrrolidone (PVP, M_w =

1300000) was used as surfactant. In a typical synthesis of sols, 0.3 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 0.06 mmol of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 0.04 mmol of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 2.5 mmol of citrate acid were added into 10 mL of deionized water under continuous magnetic stirring to form a suspension, and 0.4 mmol of $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ was also added into 10 mL of deionized water under continuous magnetic stirring to form a solution. Then, the above suspension and solution were mixed under continuous magnetic stirring with the appropriate addition of nitric acid for obtaining the pH value of 1, and it was mixed with 10 mL of PVP solution (0.12 g/mL). Finally, the obtained mixture was dissolved into anhydrous ethanol to form spinnable precursor sols. In the process of electrospinning, the precursor sol was drawn into the needle tube, and the inner diameter of the needle is 0.5 mm. The distance between the spinneret and collector was fixed at 10 cm and the high voltage supply was maintained at 15 kV. The spinning rate was controlled at 1 mL/h. The composite fibers were annealed at 600 °C for 3 h in air with a heating rate of 2 °C /min.

Thermogravimetry and differential scanning calorimeter (TG-DSC) were implemented on Labsys evo STA Simultaneous thermal analyzer (France) in air with a heating rate of 10 °C/min. The X-ray powder diffraction (XRD) measurements were carried out on a Rigaku-Dmax 2500 diffractometer using Cu K α radiation ($\lambda=0.15405\text{nm}$). The successful doping of rare earth ions was confirmed by an Oxford ISIS-300 Energy dispersive spectrometer (EDS). FT-IR spectra were measured with a Perkin-Elmer 580B infrared spectrophotometer with the KBr pellet technique. The morphology and structure of the samples were inspected by an

FESEM-4800 field emission scanning electron microscope (SEM, Hitachi) and an FEI Tecnai G2 S-Twin transmission electron microscope (TEM). Brunauer–Emmett–Teller (BET) specific surface area of the powders was analyzed by nitrogen adsorption in a Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA). The luminescence was performed on a HitachiF-7000 spectrophotometer equipped with a 150W xenon lamp as the excitation source. The decay curves were obtained from a Lecroy Wave Runner 6100 digital oscilloscope (1GHz) using a tunable laser (pulse width=4 ns, gate=50 ns) as excitation source (Continuum Suncite OPO).

3. Results and discussion

The thermal behaviors of the as-prepared gel fibers were investigated by a TG-DSC measurement. Fig.1 shows the TG-DSC curves of the $\text{BiPO}_4:0.15\text{Tb}^{3+}/0.10\text{Ce}^{3+}$ gel fibers after heat-treatment in air with a heating rate of 10 °C/min. As shown in the TG curves, there are four main stages of weight loss. The weight loss of the first stage (50-260 °C) comes from evaporation of water and alcohol. The second loss stage in the range of 260-355 °C can be ascribed to the removal of nitrate and citric acid [32, 33]. The next two stages in the range of 355-450 °C and 450-530 °C should result from the decomposition of the side and main chains of PVP [34]. When the temperature reaches above 530 °C, there is no change in weight loss, indicating the formation of stable inorganic phase. In the corresponding DSC curve, the exothermic peaks at 336, 428, and 513 °C originate from the decomposition of citric acid and nitrate, side and main chains of PVP, respectively.

Based on the TG-DSC results, the gel fibers are calcined at 600 °C for 3 h. Fig.2 gives the XRD patterns of $\text{BiPO}_4\text{:}0.15\text{Tb}^{3+}$, $\text{BiPO}_4\text{:}0.10\text{Ce}^{3+}$ and $\text{BiPO}_4\text{:}0.15\text{Tb}^{3+}/0.10\text{Ce}^{3+}$ calcined fibers. After the heat-treatment at 600 °C for 3 h, well-defined diffraction peaks can be observed in XRD patterns of $\text{BiPO}_4\text{:}0.15\text{Tb}^{3+}$, $\text{BiPO}_4\text{:}0.10\text{Ce}^{3+}$ and $\text{BiPO}_4\text{:}0.15\text{Tb}^{3+}/0.10\text{Ce}^{3+}$ nanofibers. All diffraction peaks are well according with the JCPDS No. 80-0209, which indicates the formation of monoclinic BiPO_4 phase. This manifests that the precursor samples have crystallized into BiPO_4 at this temperature. No peaks from second phase can be observed, indicating that the rare earth ions have been built into BiPO_4 host lattice effectively. The monoclinic BiPO_4 belongs to the $\text{P}21/\text{n}$ space group. The cations locate at two different kinds of sites in the crystal structure: Bi^{3+} ions locate at the eight coordinated sites and P^{5+} ions locate at the four coordinated sites.

The EDS spectra of $\text{BiPO}_4\text{:}0.15\text{Tb}^{3+}$, $\text{BiPO}_4\text{:}0.10\text{Ce}^{3+}$, and $\text{BiPO}_4\text{:}0.15\text{Tb}^{3+}/0.10\text{Ce}^{3+}$ nanofibers further indicate the occupation of Tb^{3+} and Ce^{3+} ions to Bi^{3+} ions in BiPO_4 host. The main elements in these nanofibers are O, P, Bi, Tb, and Ce, as shown in Fig.3. On the basis of EDS results, the atom ratios are calculated. The atom ratios of $\text{BiPO}_4\text{:}0.15\text{Tb}^{3+}$, $\text{BiPO}_4\text{:}0.10\text{Ce}^{3+}$ and $\text{BiPO}_4\text{:}0.15\text{Tb}^{3+}/0.10\text{Ce}^{3+}$ nanofibers are calculated to be 0.852:1:4:0.148, 0.902:1:4:0.098 and 0.755:1:4:0.147:0.098, respectively. The calculated values are close to the initially stoichiometric raw materials. The ionic radius of Bi^{3+} in the eightfold coordination is 1.11 Å, while the ionic radii of Ce^{3+} and Tb^{3+} are 1.143 and 1.04 Å, respectively. Such quite close values and similar electronic structures provide very favorable conditions

for Bi^{3+} replacement by Ce^{3+} or Tb^{3+} ions. The EDS results illustrate these substitutions.

To further verify the phase of $\text{BiPO}_4\text{:Tb}^{3+}/\text{Ce}^{3+}$ gel and nanofibers, the FT-IR spectra are given. Fig.4 gives the FT-IR spectra of $\text{BiPO}_4\text{:0.15Tb}^{3+}/\text{0.10Ce}^{3+}$ gel and nanofibers. There are two absorption bands peaking at 1655 and 3445 cm^{-1} in the FT-IR spectra of $\text{BiPO}_4\text{:0.15Tb}^{3+}/\text{0.10Ce}^{3+}$ gel fibers and nanofibers, which can be ascribed to the bending and symmetric stretching vibrations of $-\text{OH}$ group coming from the adsorbed water. The other absorption peaks in the range of 1100-3000 cm^{-1} for the FT-IR spectrum of gel fibers are characteristic vibrations of PVP [35]. The absorption bands in the range of 400-1100 cm^{-1} for the FT-IR spectra of $\text{BiPO}_4\text{:0.15Tb}^{3+}/\text{0.10Ce}^{3+}$ gel fibers and nanofibers originate from the characteristic vibrations of PO_4^{3-} . For the $\text{BiPO}_4\text{:0.15Tb}^{3+}/\text{0.10Ce}^{3+}$ nanofibers, the absorption bands at 1002 and 1068 cm^{-1} can be assigned to the ν_3 asymmetric stretching vibration of P-O bonds and the band at 925 cm^{-1} is attributed to the ν_1 symmetric vibration, as well as the bending vibrations of O-P-O linkages appear around 519, 550, and 614 cm^{-1} [8]. These results further demonstrate the formation of monoclinic phase.

To show the morphology and size of the samples, the SEM and TEM images are obtained. Fig.5 shows the SEM and TEM images of $\text{BiPO}_4\text{:0.15Tb}^{3+}/\text{0.10Ce}^{3+}$ gel and nanofibers. As shown in Fig.5A, the gel fibers with diameters in the range of 150-350 nm have the smooth surface, and the length is up to the scale of centimeter. The fibrous structure is retained on the whole except that a small amount of fibers are broken after the calcination process at 600 $^{\circ}\text{C}$ for 3 h, as shown in Fig.5B. Also, it can

be seen that the as-formed nanofibers are shrinkage and the diameter of fibers has drastically decreased to be in the range of 80-200 nm after the calcination, resulting from the decomposition of PVP and $(\text{NH}_4)_3\text{PO}_4$ [36]. And the fibers surface becomes rough because of the decomposition of PVP and the formation of crystallites. The TEM image of nanofibers further indicates the typical fibrous morphology and the nanofibers are comprised of small nanoparticles with sizes in the range of 10-20 nm, as shown in Fig.5C. It can be seen that the fibers are mesoporous after the calcinations. The BET specific surface areas of the $\text{BiPO}_4:0.15\text{Tb}^{3+}$, $\text{BiPO}_4:0.10\text{Ce}^{3+}$ and $\text{BiPO}_4:0.15\text{Tb}^{3+}/0.10\text{Ce}^{3+}$ have also been investigated by using nitrogen adsorption-desorption measurement. The BET specific surface areas of $\text{BiPO}_4:0.15\text{Tb}^{3+}$, $\text{BiPO}_4:0.10\text{Ce}^{3+}$ and $\text{BiPO}_4:0.15\text{Tb}^{3+}/0.10\text{Ce}^{3+}$ are calculated to be 48.6, 48.1 and 47.2 g/m^2 , respectively.

It has been reported that BiPO_4 is an excellent host lattice for the luminescence of various optically active rare earth ions due to its favorable physical properties [5]. In the present study, the luminescence of Ce^{3+} , Tb^{3+} , and $\text{Ce}^{3+}/\text{Tb}^{3+}$ ions doped BiPO_4 nanofibers are studied carefully. Fig.6 shows the excitation (left) and emission (right) spectra of $\text{BiPO}_4:x\text{Tb}^{3+}$ nanofibers. In the excitation spectrum of $\text{BiPO}_4:0.15\text{Tb}^{3+}$ nanofibers monitored at 545 nm, excitation peaks associated with $4f \rightarrow 5d$ transitions (in the range of 250-300 nm) and $4f \rightarrow 4f$ transitions (in the range of 300-400 nm) can be observed. The former is assigned to the transitions from the lower energy level of the $4f^8$ configuration to the energy levels of $4f^75d^1$ of Tb^{3+} , resulting in a direct excitation into Tb^{3+} , but for the latter, the well-shielded 4f shell by 5s and 5p shells

results in little effect of crystal field on the energy levels [37]. The lower intensity of $4f \rightarrow 5d$ transitions than that of $4f \rightarrow 4f$ transitions has been observed in some Tb^{3+} ions doped phosphates [38, 39], which should relate with the feature of the crystal-field splitting of the excited 5d-state of the Tb^{3+} ions [40]. According to the analysis of the excitation spectra, the strongest excitation wavelength is identified at 369 nm originating from the $^7F_6 \rightarrow ^5G_6$ transition of Tb^{3+} ion. Under the excitation at 369 nm, $\text{BiPO}_4:\text{xTb}^{3+}$ (x=0.05, 0.10, 0.15, and 0.20) nanofibers show characteristic emission bands coming from the $^5D_4 \rightarrow ^7F_j$ (j=6, 5, 4, and 3) transitions of Tb^{3+} ions. The spectra clearly show strong 5D_4 emissions and no significant 5D_3 emissions are observed due to efficient cross-relaxation processes [41]. Clearly, the relative intensities of Tb^{3+} emissions are affected highly by the concentration in the host and the concentration has no influence on the positions of the emission transitions. The emission intensity increases with the increasing Tb^{3+} concentration up to 15mol% and then decrease, which indicates the quenching concentration for Tb^{3+} ions in BiPO_4 host may be 15mol%.

For phosphors with sensitizer and activator, the effective energy transfer occurs when the emission spectrum of sensitizer overlaps with the excitation spectrum of activator [42]. To confirm the overlap of the emission spectrum of Ce^{3+} with the excitation spectrum of Tb^{3+} , Ce^{3+} single doped BiPO_4 sample is also synthesized. Fig.7 shows the excitation and emission spectra of $\text{BiPO}_4:0.10\text{Ce}^{3+}$ samples. As shown in Fig.7A, the excitation spectrum monitored at 415 nm exhibits the band peaking at 363 nm, which can be ascribed to the 4f-5d transitions of Ce^{3+} ions. Under

the excitation at 363 nm, BiPO₄: Ce³⁺ shows the broad emission band peaking at 415 nm, as shown in Fig.7B. And this broad emission band can be distinguished into two well-separate Gaussian components with maxima at 396 nm and 427 nm, as shown in Fig.7C and Fig.7D. The typical doublet band is due to the transition of the Ce³⁺ ions from the 5d excited state to the ²F_{5/2} and ²F_{7/2} ground states. From Fig.6 and Fig.7, we can see the overlap between the emission band of Ce³⁺ and the f-f absorptions of Tb³⁺, which indicates the possible resonance type energy transfer from Ce³⁺ to Tb³⁺ in BiPO₄ host.

Conventionally, Ce³⁺ and Tb³⁺ co-doped phosphor materials are developed with a view to generate efficient green light due to energy transfer from Ce³⁺ to Tb³⁺ ions, and efficient green light emission along with blue and red light emission from the same material is essential for developing materials for white light displays [43]. Fig.8 shows the excitation spectrum (left) of BiPO₄:0.15Tb³⁺/0.10Ce³⁺ nanofibers and emission spectra (right) of BiPO₄:0.15Tb³⁺/yCe³⁺ (y=0, 0.05, 0.10, and 0.15) nanofibers. In the excitation spectrum monitored at 545 nm, there are weak absorption bands in the range of 250-300 nm and a strong band peaking at 366 nm. The weak bands originate from the 4f⁸ → 4f⁷5d¹ transition of Tb³⁺. According to the excitation spectra of Ce³⁺ or Tb³⁺ single doped samples, the band at 366 nm should be induced by the overlap of 4f → 5d transitions from Ce³⁺ and Tb³⁺. Under the excitation at 369 nm, BiPO₄:0.15Tb³⁺/yCe³⁺ (y=0, 0.05, 0.10, and 0.15) nanofibers show characteristic emission bands of Tb³⁺ ions. The shape and positions of emission bands are similar to those of Tb³⁺ single doped samples. However, the co-doped Ce³⁺ ion can improve the

intensities of Tb^{3+} emission. The emission intensities of Tb^{3+} ions increase firstly with the increasing Ce^{3+} concentration and reach a maximum at the concentration of 10mol%. But the emission intensities of Tb^{3+} ions decrease if we further increase the Ce^{3+} concentration. The decrease of emission intensity at the higher Ce^{3+} concentration is caused by the energy migration among the dopants at high concentrations [44]. Also, it must be noted that there is an emission band of Ce^{3+} , which suggests the partly energy transfer from Ce^{3+} to Tb^{3+} in the BiPO_4 host. Yan [40] and Lakshminarayana [41] have reported the synthesis and luminescence of $\text{BiPO}_4:\text{Ce}^{3+}/\text{Tb}^{3+}$ nanoparticles with hexagonal phase by the precipitation method. According to Luwang's report, the significant decrease of luminescence intensity will be observed after the phase transformation from tetragonal to hexagonal for $\text{YPO}_4:\text{Eu}^{3+}/\text{Bi}^{3+}$ phosphors, which is related to the association of the water molecules in the hexagonal phase of YPO_4 [45]. This also will happen for the hexagonal phase $\text{BiPO}_4:\text{Ce}^{3+}/\text{Tb}^{3+}$ phosphors. Herein, $\text{BiPO}_4:\text{Ce}^{3+}/\text{Tb}^{3+}$ phosphors with monoclinic phase higher stability than that of hexagonal phase $\text{BiPO}_4:\text{Ce}^{3+}/\text{Tb}^{3+}$.

In order to well understand the energy-transfer process, the decay curves of $\text{BiPO}_4:0.15\text{Tb}^{3+}/y\text{Ce}^{3+}$ nanofibers were measured by monitoring the emission at 545 nm, as shown in Fig.9. All the decay curves fit well with the formula of $I = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2) + I_0$, where I_0 and I is the emission intensity, A_1 and A_2 are constants, τ_1 and τ_2 are the short and long lifetimes for the exponential components, respectively. The decay lifetimes (τ) can be calculated as $\tau = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$ [46]. The decay lifetimes for $\text{BiPO}_4:0.15\text{Tb}^{3+}/y\text{Ce}^{3+}$ ($y=0, 0.05, 0.10, \text{ and } 0.15$)

nanofibers are 3.20, 1.91, 1.73, and 2.06 ms, respectively. The energy efficiency can be expressed using the equation of $\eta = 1 - \tau_s/\tau_{s0}$, where τ_{s0} and τ_s are the lifetimes of the emission band at 545 nm in the absence and presence of Ce^{3+} ions, respectively [47]. The detailed values for $\text{BiPO}_4:0.15\text{Tb}^{3+}/y\text{Ce}^{3+}$ samples are shown in Table 1. From Table 1, we can see that the codoping Ce^{3+} ions of 5mol% and 10mol% will decrease the values of τ but further increasing Ce^{3+} concentration (15mol%) induces the increase the decay time, which is according with the results of emission spectra. All of these results indicate the energy transfer from Ce^{3+} to Tb^{3+} in BiPO_4 host [48].

According to the energy transfer theories of Dexter and Schulman, two luminescence center within a certain distance may be in resonance and may transfer the excitation energy from a donor to an acceptor, and concentration quenching is due to the energy transfer from one activator to another in many cases until an energy sink in the lattice is reached [49]. There are two competing and opposite effects of Ce^{3+} concentration on luminescent properties of $\text{BiPO}_4:\text{Tb}^{3+}/\text{Ce}^{3+}$ samples, namely an increase in Ce^{3+} - Ce^{3+} interaction and an increase in the extent of energy transfer between Ce^{3+} and Tb^{3+} . As Ce^{3+} concentration increases in the lattice, the extent of Ce^{3+} - Ce^{3+} interaction increases due to the reduced Ce^{3+} - Ce^{3+} internuclear distances and this leads to an energy transfer among different Ce^{3+} ions followed by a non-radiative decay of the excited state. On the other hand, with an increase in Ce^{3+} concentration, the extent of energy transfer between Ce^{3+} and Tb^{3+} increases as there is a number of Ce^{3+} has potential possibility to transfer energy to Tb^{3+} . The appropriate co-doped concentration of Ce^{3+} benefits to the energy transfer between

Ce^{3+} and Tb^{3+} ions in BiPO_4 host and accelerates the non-radiative recombination rate, which results in the increase of emission intensity and the decrease of decay lifetime.

4. Conclusion

$\text{BiPO}_4:\text{Tb}^{3+}/\text{Ce}^{3+}$ nanofibers are synthesized by a simple electrospinning process and followed by a heat-treatment at 600 °C. The TG-DSC shows that a stable inorganic phase can be formed after 530 °C. The XRD and FT-IR results show that the calcined $\text{BiPO}_4:\text{Tb}^{3+}/\text{Ce}^{3+}$ nanofibers have a monoclinic phase. The SEM and TEM images show that the gel fibers have smooth surface, but the calcined nanofibers are mesoporous and composed of the linked nanoparticles. Under an excitation at 369 nm, $\text{BiPO}_4:\text{Tb}^{3+}$ and $\text{BiPO}_4:\text{Tb}^{3+}/\text{Ce}^{3+}$ nanofibers show characteristic emission bands originating from the $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($j=6, 5, 4$, and 3) transitions of Tb^{3+} ions. The emission intensity of $\text{BiPO}_4:\text{Tb}^{3+}$ increases with the increasing Tb^{3+} concentration up to 15mol% and then decreases. The emission intensity of $\text{BiPO}_4:\text{Tb}^{3+}/\text{Ce}^{3+}$ also increase with the increasing Ce^{3+} concentration up to 10mol% and then decreases. The appropriate co-doped concentration of Tb^{3+} benefits to the energy transfer between Ce^{3+} and Tb^{3+} ions in BiPO_4 host and accelerates the non-radiative recombination rate, which results in an increase of emission intensity and a decrease of decay lifetime.

Acknowledgements

This work is supported financially by the National Science Foundation of China (Grant Nos. 51102158, 51202135 and 51302158), the Science and Technology Develop Project in Shandong Province (Grant No. 2013GGX10203), Natural Science Foundation of Shandong Province (Grant No. ZR2014EMQ004), and Youth

Foundation of Shandong Academy of Sciences (Grant Nos. 2013QN011, 2014QN027 and 2014QN028).

References

1. Y. Ni, J.M. Hughes, A.N. Mariano, Crystal chemistry of the monazite and xenotime structures, *American Mineralogist* 80 (1995) 21-26.
2. T-S. Chang, L. Guijia, C-H. Shin, Y.K. Lee, S-S. Yun, Catalytic behavior of BiPO_4 in the multicomponent bismuth phosphate system on the propylene ammoxidation, *Catalysis Letters* 68 (2000) 229-234.
3. K. Iitaka, Y. Tani, Y. Umezawa, Orthophosphate ion-sensors based on a quartz-crystal microbalance coated with insoluble orthophosphate salts, *Analytica Chimica Acta* 338 (1997) 77-87.
4. M. Charyulu, K. Venugopal Chetty, D. Phal, V. Sagar, S. Sagar, S. Pawar, R. Swarup, V. Ramakrishna, V. Venugopal, Recovery of americium from nitric acid solutions containing calcium by different co-precipitation methods, *Journal of Radioanalytical and Nuclear Chemistry* 251 (2002) 153-154.
5. B.S. Naidu, B. vishwanadh, V. Sudarsan, R.K. Vatsa, BiPO_4 : A better host for doping lanthanide ions, *Dalton Transactions* 41 (2012) 3194-3203.
6. M. Guan, J. Sun, F. Tao, Z. Xu, A host crystal for the rare-earth ion dopants: synthesis of pure and Ln-doped urchinlike BiPO_4 structure and its photoluminescence, *Crystal Growth and Design* 8 (2008) 2694-2697.
7. M. Roming, C. Feldmann, Synthesis and characterization of nanoscaled BiPO_4 and $\text{BiPO}_4\text{:Tb}$, *Journal of Materials Science* 44 (2009) 1412-1415.

8. M. Zhao, G. Li, L. Li, L. Yang, J. Zheng, Structures and polymorph-sensitive luminescence properties of BiPO₄/Eu grown in hydrothermal conditions, *Crystal Growth and Design* 12 (2012) 3983-3991.
9. P. Arunkumar, C. Jayajothi, D. Jeyakumar, N. Lakshminarasimhan, Structure-property relations in hexagonal and monoclinic BiPO₄:Eu³⁺ nanoparticles synthesized by polyol-mediated method, *RSC Advances* 2 (2012) 1477-1485.
10. C. Fu, G. Li, M. Zhao, L. Yang, J. Zheng, L. Li, Solvent-driven room-temperatures synthesis of nanoparticles BiPO₄:Eu³⁺, *Inorganic Chemistry* 51 (2012) 5869-5880.
11. S. Liu, W. Zhang, Z. Hu, Z. Feng, X. Sheng, Y. Liang, Synthesis and luminescent properties of Eu³⁺ and Dy³⁺ doped BiPO₄ phosphors for near UV-based white LEDs, *Journal of Materials Science: Materials in Electronics* 24 (2013) 4253-4257.
12. X.Y. Sun, X.D. Sun, J. He, X.G. Li, J.F. Lv, Synthesis and luminescence of BiPO₄:xEu³⁺ powders by solid state reaction method, *Ceramics International* 40 (2014) 7647-7650.
13. S.Q. Yan, Synthesis and luminescence of BiPO₄:Tb³⁺ nanowires by a hydrothermal process, *Materials and Manufacturing Processes* 30 (2015) 591-594.
14. X. Shi, Y. Liu, J. Zhang, K. Zhang, J. Li, H. Zuo, P. Li, Enhanced luminescence properties of BiPO₄:Eu³⁺ phosphors prepared by hydrothermal method, *Ceramics International* 41 (2015) 6683-6686.
15. X. Shi, Y. Liu, J. Zhang, K. Zhang, P. Li, H. Zuo, J. Li, Effects of pH and Sm³⁺

- doping on the structure, morphology and luminescence properties of $\text{BiPO}_4\text{:Sm}^{3+}$ phosphors prepared by hydrothermal method, *Ceramics International* 41 (2015) 3162-3168.
16. Y. Yang, Synthesis and luminescent properties of $\text{LaPO}_4\text{:Eu}^{3+}$ microspheres, *Materials Science and Engineering B* 178 (2013) 807-810.
 17. A. Laforgue, Electrically controlled colour-changing textiles using the resistive heating properties of PEDOT nanofibers, *Journal of Materials Chemistry* 20 (2010) 8233-8235
 18. J. Wu, N. Wang, Y. Zhao, L. Jiang, Electrospinning of multilevel structured functional micro-/nanofibers and their applications, *Journal of Materials Chemistry A* 1 (2013) 7290-7305
 19. H. Yu, H. Song, G. Pan, S. Li, Z. Liu, X. Bu, T. Wang, S. Lu, H. Zhao, Preparation and luminescent properties of europium-doped yttria fibers by electrospinning, *Journal of Luminescence* 124 (2007) 39-44.
 20. J. Hou, Z. Wang, S. Jiao, H. Zhu, 3D $\text{Bi}_{12}\text{TiO}_{20}/\text{TiO}_2$ hierarchical heterostructure: Synthesis and enhanced visible-light photocatalytic activities, *Journal of Hazardous Materials* 192 (2011) 1772-1779.
 21. H. Tang, K. Prasad, R. Sanjines, P.E. Schmid, F.J. Levy, Electrical and optical-properties of TiO_2 anatase thin-films, *Journal of Applied Physics* 75 (1994) 2042-2047.
 22. X. Li, M. Yu, Z. Hou, G. Li, P. Ma, W. Wang, Z. Cheng, J. Lin, One-dimensional $\text{GdVO}_4\text{:Ln}^{3+}$ (Ln=Eu, Dy, Sm) nanofibers: Electrospinning preparation and

- luminescence properties, *Journal of Solid State Chemistry* 184 (2011) 141-148.
23. F. Ye, S. Dong, Z. Tian, S. Yao, Z. Zhou, S. Wang, Fabrication of the PLA/Sr₂MgSi₂O₇:Eu²⁺, Dy³⁺ long-persistent luminescence composite fibers by electrospinning, *Optical Materials* 36 (2013) 463-466.
 24. P. Du, L. Song, J. Xiong, H. Gao, Z. Xi, S. Guo, N. Wang, J. Chen, Electrospinning fabrication and luminescent properties of SrMoO₄:Sm³⁺ nanofibers, *Journal of Alloys and Compounds* 540 (2012) 179-183.
 25. W. Ma, W. Yu, X. Dong, J. Wang, G. Liu, Electrospinning preparation and up-conversion luminescence properties of LaOBr:Er³⁺ nanofibers and nanoribbons, *Chemical Engineering Journal* 244 (2014) 531-539.
 26. B. Li, H. Zhang, A. Lan, H. Tang, Ca_(3-x)Sr_x(PO₄)₂:Eu²⁺ nanofibers: Electrospinning fabrication and tunable luminescence, *Superlattices and Microstructures* 86 (2015) 425-429.
 27. H. Bian, S. Ma, A. Sun, X. Xu, G. Yang, J. Gao, Z. Zhang, H. Zhu, Characterization and acetone gas sensing properties of electrospun TiO₂ nanorods, *Superlattices and Microstructures* 81 (2015) 107-113.
 28. M. Nasr, A.A. Chaaya, N. Abboud, M. Bechelany, R. Viter, C. Eid, A. Khoury, P. Miele, Photoluminescence: A very sensitive tool to detect the presence of anatase in rutile phase electrospun TiO₂ nanofibers, *Superlattices and Microstructures* 77 (2015) 18-24.
 29. X. Chen, S. Shen, L. Guo, S.S. Mao, S. S. Semiconductor-based photocatalytic hydrogen generation. *Chemical Reviews* 110 (2010) 6503-6570.

30. S. Yan, Synthesis and luminescence of $\text{BiPO}_4\text{:Ln}^{3+}$ ($\text{Ln} = \text{Ce}^{3+}, \text{Tb}^{3+}$) phosphors, *Journal of Materials Science: Materials in Electronics* 25 (2014) 2803-2807.
31. G. Lakshminarayana, T.D. Dao, K. Chen, Manoj Sharma, T. Takeda, M.G. Brik, I.V. Kityk, Sarabjot Singh, T. Nagao, Effect of different surfactants on structural and optical properties of Ce^{3+} and Tb^{3+} co-doped BiPO_4 nanostructures, *Optical Materials* 39 (2015) 110-117.
32. F. Zhou, X. Zhao, H. Xu, C. Yuan, CeO_2 spherical crystallites: synthesis, formation mechanism, size control, and electrochemical property study, *The Journal of Physical Chemistry C* 111 (2007) 1651-1657.
33. K.X. Yao, H.C. Zeng, ZnO/PVP nanocomposite spheres with two hemispheres, *The Journal of Physical Chemistry C* 111 (2007) 13301-13308.
34. Y.K. Du, P. Yang, Z.G. Mou, N.P. Hua, L. Jiang, Thermal decomposition behaviors of PVP coated on platinum nanoparticles, *Journal of Applied Polymer Science* 99 (2006) 23-26.
35. S.P. Hyun, E.K. Kyoung, Y. Heechang, P. Eunsu, S.H. Gyeong, J.B. Allen, Factors in the metal doping of BiVO_4 for improved photoelectrocatalytic activity as studied by scanning electrochemical microscopy and first-principles density-functional calculation, *The Journal of Physical Chemistry C* 115 (2011) 17870-17879.
36. D. Hou, W. Luo, Y. Huang, J.C. Yu, X. Hu, Synthesis of porous $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ nanofibers by electrospinning and their enhanced visible-light-driven photocatalytic properties, *Nanoscale* 5 (2013) 2028-2035.

37. H. Lai, A. Bao, Y. Yang, Y. Tao, H. Yang, Y. Zhang, L. Han, UV luminescence property of $\text{YPO}_4\text{:RE}$ ($\text{RE} = \text{Ce}^{3+}, \text{Tb}^{3+}$), *The Journal of Physical Chemistry C* 112 (2008) 282-286.
38. B.V. Ratnam, M. Jayasimhadri, G.B. Kumar, K. Jang, S.S. Kim, Y.I. Lee, J.M. Lim, D.S. Shin, T.K. Song, Synthesis and luminescent features of $\text{NaCaPO}_4\text{:Tb}^{3+}$ green phosphor for near UV-based LEDs, *Journal of Alloys and Compounds* 564 (2013) 100-104.
39. F. Yang, H.G. Ma, Y.F. Liu, Q.B. Liu, Z.P. Yang, Y. Han, A new green luminescent material $\text{Ba}_3\text{Bi}(\text{PO}_4)_3\text{:Tb}^{3+}$, *Ceramics International* 39 (2013) 2127-2130.
40. E. Nakazawa, The lowest 4f-to-5d and charge-transfer transitions of rare earth ions in YPO_4 hosts, *Journal of Luminescence* 100 (2002) 89-96.
41. M. Bettinelli, A. Speghini, F. Piccinelli, J. Ueda, S. Tanabe, Energy transfer processes in $\text{Sr}_3\text{Tb}_{0.90}\text{Eu}_{0.10}(\text{PO}_4)_3$, *Optical Materials* 33 (2010) 119-122.
42. C. Jin, H.X. Ma, Y.F. Liu, Q.B. Liu, G.Y. Dong, Q.M. Yu, Tunable luminescence properties and energy transfer in $\text{Ba}_3\text{Lu}(\text{PO}_4)_3\text{:Ce}^{3+}, \text{Tb}^{3+}$ phosphors, *Journal of Alloys and Compounds* 613 (2014) 275-279.
43. S. Nigam, V. Sudarsan, R.K. Vatsa, J. Ghattak, P.V. Satyam, Improved energy transfer between Ce^{3+} and Tb^{3+} ions at the interface between $\text{Y}_2\text{Sn}_2\text{O}_7\text{:Ce}^{3+}, \text{Tb}^{3+}$ nanoparticles and silica, *The Journal of Physical Chemistry C* 113 (2009) 8750-8755.
44. Y. Chen, D. Luo, L. Luo, X. Wang, T. Tang, W. Luo, Luminescence of $\text{Ce}^{3+}/\text{Tb}^{3+}$ ions in lithium-magnesium aluminosilicate glasses, *Journal of Non-Crystalline*

- Solids 386 (2014) 124-128.
45. M.N. Luwang, R.S. Ningthoujam, S.K. Srivastava, R.K. Vatsa, Disappearance and recovery of luminescence in Bi^{3+} , Eu^{3+} codoped YPO_4 nanoparticles due to the presence of water molecules up to 800 °C, Journal of the American Chemical Society 133 (2011) 2998-3004.
46. Y.X. Liu, A.Y. Lan, Y. Jin, G.Q. Chen, X. Zhang, $\text{Sr}_3\text{Bi}(\text{PO}_4)_3:\text{Eu}^{2+}$, Mn^{2+} : Single-phase and color-tunable phosphors for white-light LEDs, Optical Materials 40 (2015) 122-126.
47. X.W. Zhang, Z. Zhao, X. Zhang, A. Marathe, D.B. Cordes, B. Week, J. Chaudhuri, Tunable photoluminescence and energy transfer of $\text{YBO}_3:\text{Tb}^{3+}$, Eu^{3+} for white light emitting diodes, Journal of Materials Chemistry C 1 (2013) 7202-7207.
48. Z.Y. Hou, R.T. Chai, M.L. Zhang, C.M. Zhang, P. Chong, Z.H. Xu, G.G. Li, J. Lin, Fabrication and luminescence properties of one-dimensional $\text{CaMoO}_4:\text{Ln}^{3+}$ ($\text{Ln} = \text{Eu}, \text{Tb}, \text{Dy}$) nanofibers via electrospinning process, Langmuir 25 (2009) 12340-12348.
49. D.L. Dexter, J.H. Schulman, Theory of concentration quenching in inorganic phosphors, The Journal of Chemical Physics 22 (1954) 1063-1070.

Figure Captions

Figure 1 TG-DSC curves of $\text{BiPO}_4:0.15\text{Tb}^{3+}/0.10\text{Ce}^{3+}$ gel fibers

Figure 2 XRD patterns of $\text{BiPO}_4:0.15\text{Tb}^{3+}$, $\text{BiPO}_4:0.10\text{Ce}^{3+}$ and $\text{BiPO}_4:0.15\text{Tb}^{3+}/0.10\text{Ce}^{3+}$ nanofibers

Figure 3 EDS spectra of $\text{BiPO}_4:0.15\text{Tb}^{3+}$, $\text{BiPO}_4:0.10\text{Ce}^{3+}$, and $\text{BiPO}_4:0.15\text{Tb}^{3+}/0.10\text{Ce}^{3+}$

Figure 4 FT-IR spectra of $\text{BiPO}_4:0.15\text{Tb}^{3+}/0.10\text{Ce}^{3+}$ gel and nanofibers

Figure 5 SEM images of $\text{BiPO}_4:0.15\text{Tb}^{3+}/0.10\text{Ce}^{3+}$ gel (A) and nanofibers (B), and TEM image of a nanofiber (C)

Figure 6 Excitation spectrum (left) $\text{BiPO}_4:0.15\text{Tb}^{3+}$ nanofibers and emission (right) spectra of $\text{BiPO}_4:x\text{Tb}^{3+}$ ($x=0.05, 0.10, 0.15$, and 0.20) nanofibers

Figure 7 Excitation and emission spectra of $\text{BiPO}_4:0.10\text{Ce}^{3+}$ sample

Figure 8 Excitation spectrum of $\text{BiPO}_4:0.15\text{Tb}^{3+}/0.10\text{Ce}^{3+}$ and emission spectra of $\text{BiPO}_4:0.15\text{Tb}^{3+}/y\text{Ce}^{3+}$ ($y=0.05, 0.10$, and 0.15) nanofibers

Figure 9 Luminescence decay curves of $\text{BiPO}_4:0.15\text{Tb}^{3+}/y\text{Ce}^{3+}$ ($y=0.05, 0.10$, and 0.15) nanofibers

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Table 1

Table 1 Decay times and energy transfer efficiency of BiPO₄:0.15Tb³⁺/yCe³⁺ (y=0, 0.05, 0.10, and 0.15) nanofibers

Samples	τ_1	A ₁	τ_2	A ₂	τ (ns)	η (%)
y = 0	0.02	887	3.26	298	3.20	/
y = 0.05	0.25	2841	3.15	303	1.91	40.3
y = 0.10	0.17	3832	2.83	325	1.73	45.9
y = 0.15	0.19	3067	2.94	423	2.06	35.6