Hybrid precursors synthesis and optical properties of LnNbO$_4$:Bi$^{3+}$ blue phosphors and Bi$^{3+}$ sensitizing of on Dy$^{3+}$'s luminescence in YNbO$_4$ matrix

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Abstract

In this paper, Bi$^{3+}$ doped with LnNbO$_4$:Bi$^{3+}$ (Ln = La, Gd and Y) and YNbO$_4$:Bi$^{3+}$, Dy$^{3+}$ phosphors have been synthesized by a modified chemical co-precipitation process with hybrid precursors. Their micromorphology and particle sizes were characterized by X-ray diffraction (XRD) and scanning electronic microscopy (SEM). The photoluminescence data for LnNbO$_4$:Bi$^{3+}$ indicated that the emission peak positions for Bi$^{3+}$ showed red-shifts comparing to that of NbO$_4^{3-}$ for undoped LnNbO$_4$ hosts. Besides this, it was found that Bi ion can enhance the emission intensity of Dy$^{3+}$ in YNbO$_4$ host lattice when the Bi ion concentration is lower than 3 mol%. Moreover, the influence of Bi$^{3+}$ concentration on the luminescent properties of YNbO$_4$ was examined, which shows that the optimum concentration was 1 mol% and concentration quenching occurred.

Keywords: Phosphors; Chemical synthesis

1. Introduction

Green, red and blue phosphors play crucial roles in our daily life due to their wide applications [1]. Among them, blue phosphors are hard to achieve and become the key problem to be desiderated. In the past decade, the main work focused on phosphor zinc sulfide silver (ZnS:Ag), because it is one of the most efficient blue phosphors which were broadly used in the low-voltage application, such as field emission displays [2]. Besides this, Sr$_2$CeO$_4$ is also a promising blue phosphor which was firstly introduced by Danielson et al. [3,4]. However, it was found that the sulfide phosphors like ZnS:Ag have disadvantages for FED application due to degradation for low-voltage cathodoluminescence [5–7], which motivate many scientists to search new nonsulfide blue phosphors. Recently, Bi$^{3+}$ doped with LaInO$_3$ and YNbO$_4$ have been shown to be potential and efficient blue phosphors for FED [8,9]. It was well-known that the Bi$^{3+}$ can be used as not only an activator but also a sensitizer of luminescence. Considerable theoretical and experimental works have been done on the luminescent properties of Bi$^{3+}$ ions and energy transfer from Bi$^{3+}$ ion to Bi$^{3+}$ ion or to another activator in different host lattices [10–13]. Usually, the emission spectra of Bi$^{3+}$ ions presents a structureless broad band and the peak position of the band varies from the UV region into the red region with differ host lattice, which depend on these factors, such as covalency, coordination number, site symmetry and network rigidity [14–17]. Rare earth niobates are efficient hosts for Bi$^{3+}$ known as self-activated luminescent materials and YNbO$_4$:Bi$^{3+}$ phosphor particles have been synthesized by Lee et al., whose luminescent nature has been investigated using the calculated partial density of states in the framework of density functional theory [18–20].

The aim of this article is to introduce a novel synthesis technology employed in preparing LnNbO$_4$:Bi$^{3+}$, YNb$_x$P$_{1-x}$O$_4$:Bi$^{3+}$ and YNbO$_4$:Bi$^{3+}$, Dy$^{3+}$ with varying Bi$^{3+}$ concentration phosphors and discuss the luminescent properties of those phosphors in details. We use rare earth coordination polymers with ortho-hydroxybenzoic acid as the precursors of rare earth oxides components for they readily form infinite chain-like polymeric structure similar to organic polymer template [21,22]. Polyethylene glycols (PEG), Nb$_2$O$_5$ and Bi(NO$_3$)$_3$·5H$_2$O were composed to assemble inorganic/organic
hybrid precursor by a modified in situ chemical co-precipitation process. Urea was used to modify the decomposition behavior and ammonia for the pH value. Through an in situ wet chemical co-precipitation process, multi-component hybrid polymeric precursors were constructed to afford those phosphors.

2. Experimental

2.1. Synthesis of LnNbO4:x mol% Bi3+ and YNb1−xP1+3 mol% Bi3+

All samples were prepared by in situ co-precipitation method. The initiative materials Gd2O3, Y2O3, La2O3 and Dy2O3 were firstly dissolved into concentrated nitric acids. Then the preparation of the precursors was described in details in the following: superfluous salicylic acid (HSal) (6.0 mmol) was dissolved into 95% ethanol and its pH value was then adjusted to 7.0–8.0 with ammonia solution. Then the rare earth nitrates solutions Gd(NO3)3 was added. After being stirred for an hour, the urea and PEG were added into the above solutions with appropriate ratio to RE3+. After an hour, the solutions were heated to 70 ºC and the pH value was adjusted to about 7.5. At the same time, the Nb2O5 and proper Bi(NO3)3·5H2O powder were added into the solutions. After this, the solutions were stirred at 70 ºC for 30 min so that they became homogenous systems. At last, precursors were achieved after being stirred for 2 h and were heat-treated at the temperature 1100 ºC for about 5 h to obtain GdNbO4:Bi3+. Using the same method, other phosphors have also been synthesized. The scheme for the synthesis can be shown as below:

Gd(NO3)3 + HSal + NH3·H2O → [RE(Sal)3]n coordination polymer

+ Nb2O5 + PEG + NH2·CO·NH2 + Bi(NO3)3·5H2O + NH3·H2O
→ GdNbO4:Bi3+ + CO2↑ + H2O↑ + NH3↑ + NO2↑

2.2. Synthesis of YNbO4:x mol% Bi3+ and 5 mol% Dy3+

The synthesis procedure was adopted as the above mentioned except for Dy(NO3) was introduced.

2.3. Physical measurements

The particle size was characterized by means of X-ray diffraction (XRD; Bruke, D8-Advance, 40 kV and 20 mA, Cu Kα). The morphology and microstructure were characterized with scanning electronic microscope (SEM; Philips XL-30). Excitation and emission spectra at room temperature were determined with Perkin-Elmer LS-55 model fluorophotometer (excitation slit width = 10 nm and emission width = 5 nm).

3. Results and discussion

Fig. 1A (a–c) gave the XRD patterns of LnNbO4:Bi3+. It can be seen that the structures of LaNbO4:Bi3+ (a) and GdNbO4:Bi3+ (c) phosphors were similar to that of YNbO4:Bi3+ (b). The polycrystalline powders were indexed to crystallize in monoclinic system and X-rays diffraction data of the monoclinic LnNbO4:Bi3+ was used to identify the crystalline M-fergusonite phase. Fig. 1B shows the XRD pattern for YNb0.2P0.8O4:Bi3+ (a) and YNb0.3P0.7O4:Bi3+ (b) which were found to belong to the same structure except for the peaks’ intensities. As we know, YPO4 belong to the usual zircon-type tetrahedral xenotime structure and YNbO4 show the tetrahedral fergusonite structure. So the XRD pattern for YNbxP1−xO4:Bi3+ (a and YNb0.3P0.7O4:Bi3+ (b) crystalline powders.

The mean particle size can be roughly determined from the broadening of the peaks by using the Scherrer formula [24,25].

\[ D_{hkl} = \frac{k\lambda}{\beta(2\theta) \cos \theta} \]  

where \( \beta(2\theta) \) is the width of the pure diffraction profile in radians, \( k \) is 0.9, \( \lambda \) the wavelength of the X-rays (0.154056 nm), \( \theta \) the diffraction angle and \( D_{hkl} \) is the average diameter of the crystallite. By fitting various peaks to this formula and taking into account the instrumental broadening, we obtained values in the range of 0.5–1.0 μm sizes.

Using the scanning electron microscope we obtain some interesting morphologies of samples. Fig. 2 shows the representative morphologies of LnNbO4:Bi3+ and YNb0.9P0.1O4:Bi3+. The typical crystalline grain of all products is estimated to be around 0.5–1.0 μm in dimension. Also, SEM exhibits some interesting morphologies, which exists some conglomeration.
among the crystalline grain because of the high temperature 1100 °C of thermal decomposition. To explain this phenomenon, we suggest that the rare earth coordination polymers and the organic polymer were used to form the interpenetrating polymeric network for they show the similar infinite polymeric structure [26]. So from the co-precipitation composition, the hybrid precursors with microporous fragment structure, which can control the morphology of the final phosphors’ particle, can be assembled with rare earth coordination polymers, PEG (organic polymer) and other functional components (Nb2O5, etc.). After the thermal decomposition, organic components lose and the particles of phosphors present such microstructure. Therefore, this preparation technology connecting the assembly of hybrid material with synthesis of micrometer material can be expected to be a candidate for the synthesis of other luminescent materials based on rare earth oxides.

As shown in Fig. 3, all the excitation spectra of LaNbO4:Bi3+ (A), YNbO4:Bi3+ (B), GdNbO4:Bi3+ (C) and undoped YNbO4 (D) have the similar features. They consist of two bands in the region of 220–280 nm ascribing to the transition from [NbO4]3+: 1A1–1T2, 1A1–1T1 [27], which shows the energy transfer between [NbO4]3+ and Bi3+. It can be seen that although those band shape and the peak position are well-matched in the excitation spectra of LnNbO4:Bi3+ and YNbO4, there also exists some difference. LnNbO4:Bi3+ has a strong band at 300 nm. Obviously this is a Bi effect that influences the optical properties of the niobate group. It was reported that the HOMO has more O 2p character than Bi 6s character in LnNbO4 and the introduction of Bi ion in the LnNbO4 will distort the structure stronger [20,27]. So the charge transfer from O 2p to Bi 6p can occur easily in LnNbO4:Bi3+, which was responsible for the band at 300 nm in LnNbO4:Bi3+. Also, it was found that the excitation intensity can be ordered as follows: La<Y<Gd, indicating that the Gd3+ took part in the energy transfer process. The energy transfer process in GdNbO4:Bi3+ may be described as follows: the energy from the excitation source excited NbO43+ firstly, and then the energy was trapped by Gd3+ and migrated along them until it is trapped by Bi3+. At the same time, the NbO43+...
can transfer the energy to activator directly. Therefore, the luminescent intensity of Bi\(^{3+}\) in GdNbO\(_4\) is stronger than that of Y and La analogs.

Besides this, the emission spectra under the excitation of 223, 243 and 300 nm, respectively, have been shown in Fig. 3. The peak position of emission spectra excited with the shorter wavelength is 420 nm, whereas the emission spectra excited with the longer wavelength shows the main band around 440 nm. Obviously the longer excitation wavelength is favorable for the luminescence of Bi\(^{3+}\). Also, Fig. 4 shows the emission spectra of YNbO\(_4\) and LnNbO\(_4\):Bi\(^{3+}\) excited with 300 nm, which presents the maximum band around 417 and 440 nm, respectively. When the incorporation of Bi\(^{3+}\) into the LnNbO\(_4\), it is obviously that the emission peak position was shift to the longer wavelength region, which indicates that the luminescence of NbO\(_4^{3-}\) mainly affected by the Bi\(^{3+}\). It was well-known that the emission band of pure LnNbO\(_4\) was ascribed to the charge transfer transition from the O to the empty orbit 4d of Nb and the Bi 6p is lower energy than that of Nb 4d. Therefore, as for self-activated host, NbO\(_4^{3-}\) firstly excited by the excitation source, and then the charge was transferred to the activator Bi\(^{3+}\). This is the reason why the peak position of emission band was shift to the long wavelength and the emission intensity of LnNbO\(_4\):Bi\(^{3+}\) is obviously weaker than that of pure LnNbO\(_4\). Besides this, under UV excitation, the GdNbO\(_4\):Bi\(^{3+}\) presents brighter blue-emitting than Y and La analogs. The result can be explained as in the above paragraph and is coincident with the work done by David et al. [28]. In order to study the luminescent nature of Bi\(^{3+}\) in LnNbO\(_4\), PO\(_4^{3-}\) was used to replace NbO\(_4^{3-}\). The result is shown in Fig. 5. From the Fig. 5, it can be seen that with the added content of PO\(_4^{3-}\) increasing, the luminescent intensity of YNbO\(_4\):Bi\(^{3+}\) proportionally decreases, indicating that the luminescence of Bi\(^{3+}\) is mainly affected by NbO\(_4^{3-}\).

Besides this, the influence of Bi\(^{3+}\) concentration on the luminescent properties of YNbO\(_4\):Bi\(^{3+}\) phosphors have been investigated. As given in Fig. 6, it was seen that the optimum concentration of Bi ion was 1 mol% and the corresponding emission intensity decreases dramatically with the increases of concentration at the range of 1–5 mol%. This is a typical property named concentration quenching affected by many factors. As we know, the interaction between ions is one of important factors. When the concentration is higher, the interaction between Bi ions becomes active due to the distance between Bi ions, which will dissipate the absorption energy nonradiately.

Except for the activator, Bi ion also can be used as an efficient sensitizer for the luminescence of other activators, such as Eu\(^{3+}\) and Dy\(^{3+}\). Fig. 7 shows the excitation spectra of YNbO\(_4\):Eu\(^{3+}\) (A) and YNbO\(_4\):3 mol% Bi\(^{3+}\), 5 mol% Dy\(^{3+}\) (B). The band peak at 300 nm is observed in the excitation spectra of YNbO\(_4\):3 mol% Bi\(^{3+}\), 5 mol% Dy\(^{3+}\) and other bands in both spectra are well-matched in the region of 200–280 and 350–460 nm. The presence of the strong absorption band of PO\(_4^{3-}\) overcomes the emission from Eu\(^{3+}\) and Dy\(^{3+}\).
Fig. 7. Excitation spectra of YNbO₄:Dy³⁺ (A) and YNbO₄:Bi³⁺, Dy³⁺ (B) and powder particles.

Bi³⁺ at 300 nm for the Dy³⁺ emission at 570 nm indicates the Bi³⁺ → Dy³⁺ energy transfer. As seen in Fig. 8, the characteristic lines resulting from the f-f transition of Dy³⁺ are identified in both emission spectra of YNbO₄:Dy³⁺ and YNbO₄:3 mol% Bi³⁺, 5 mol% Dy³⁺, corresponding to ⁴F₀/²→⁶H₁₅/₂ (480 nm) and ⁴F₀/²→⁶H₁₃/₂ (570 nm). Besides this, it can be found the relationship of emission intensity of Dy³⁺ and the concentration of Bi³⁺ in YNbO₄:ₓ mol% Bi³⁺, 5 mol% Dy³⁺. When the content of Bi³⁺ is increasing from 1 to 3 mol%, the intensity of ⁴F₀/²→⁶H₁₅/₂ (480 nm) and ⁴F₀/²→⁶H₁₃/₂ (570 nm) transitions are increasing too, which proves that the efficient energy transfer process between Bi³⁺ and Dy³⁺ exists. Therefore, it is clear that Bi functions as a sensitizer for Dy³⁺. However, when the concentration of Bi reaches 5 mol%, the strengthening of emission intensity was very limited. That is to say, the sensitized effectiveness of Bi on the Dy emission intensity was reduced. The reason was when Bi concentration was more than 3 mol%, the distance between Bi and Bi would be near enough to cause efficient Bi–Bi energy transfer process, which reduced the probability of energy transfer from Bi to Dy [29].

4. Conclusion

In summary, we have achieved Bi doped with fergusonite orthoniobates blue phosphors from the hybrid precursors. SEM shows that products present interesting micromorphology with particle sized of micrometer dimension. Because Gd plays an important role in the process of energy transfer, the blue emission intensity of GdNbO₄:Bi³⁺ is stronger than that of Y and La analog. Besides this, YNbO₄:Bi³⁺ appears concentration quenching phenomenon at the range of 0.5–5 mol%. Moreover, in Bi³⁺ and Dy³⁺ co-doped YNbO₄ phosphors, we found that when the content of Bi³⁺ is low to 3 mol%, the Bi can strengthen the Dy³⁺ emission, but at high concentration of Bi, the sensitized effectiveness decreases.

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References


Fig. 8. Emission spectra of Bi³⁺ and Dy³⁺ co-doped YNbO₄ powder particles under excitation of 272 nm.