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Color-tunable photoluminescence in $Bi_{3.6}Eu_{0.4}Ti_3O_{12}$/ZnO nanorods composite films

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Abstract

Color-tunable photoluminescence has been realized by constructing $Bi_{3.6}Eu_{0.4}Ti_3O_{12}$/ZnO (BEuT/ZnO) nanorods composite films. The composite films were prepared by a hybrid chemical solution method. Effects of ZnO nanorods on photoluminescence of BEuT were studied. On one hand, the near-band-edge ultraviolet emission of ZnO nanorods can greatly improve the red emission of Eu^{3+} ions in BEuT, and on the other hand, ZnO nanorods can also produce a strong green deep-energy-level luminescence. Our study demonstrates that the color of photoluminescence in the composite films can be tuned from green to yellow to red, through suitable control of ZnO nanorods. The BEuT/ZnO nanorods composite films with the color-tunable photoluminescence may have potential applications for white light emission and other integrated optoelectronic devices.

Keywords: A. Films; B. Nanocomposites; C. Optical properties

1. Introduction

$Bi_4Ti_3O_{12}$ is an attractive lead-free ferroelectric material with layered-perovskite structure. By substituting bismuth ions with lanthanide ions, the ferroelectric properties of $Bi_4Ti_3O_{12}$ can be greatly improved [1–3]. Meanwhile, lanthanide ions have been widely used as luminescence centers in many kinds of fluorescent materials. It has been demonstrated that Eu-doped $Bi_4Ti_3O_{12}$ thin films have good photoluminescence (PL) properties [4,5]. Excited by a UV-light of 350 nm, the Eu-doped $Bi_4Ti_3O_{12}$ thin films can produce two emission bands centered at 594 nm and 617 nm, which are attributed to the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+} ions, respectively. Among the Eu-doped $Bi_4Ti_3O_{12}$ thin films, the composition of $Bi_{3.6}Eu_{0.4}Ti_3O_{12}$ (BEuT) has the strongest emission intensity, and its PL property can be further improved by incorporating ZnO [6,7]. The enhanced PL property was thought to be due to the energy transfer between BEuT and ZnO nanorods, because the near-band-edge emission of ZnO at about 380 nm overlaps the excitation spectra of Eu^{3+} in BEuT. The similar energy transfer between ZnO and Eu^{3+} was also reported in Y_2O_3:Eu^{3+}/ZnO polycrystalline thin films by Chong and co-workers [8,9].

We noted that on one hand, the overlapping between the near-band-edge (NBE) ultraviolet emission at about 380 nm of ZnO nanorods with the excitation spectra of Eu^{3+} in BEuT can greatly improve the red emission of Eu^{3+} ions in BEuT; on the other hand, ZnO nanorods having deep-energy-level defects such as oxygen vacancies can produce a strong green luminescence [10,11]. This provides a possibility of tuning color of photoluminescence by controlling NBE ultraviolet emission and deep-energy-level luminescence of ZnO nanorods in the BEuT/ZnO nanorods composite films. It is known that PL properties including near-band-edge emission and deep-energy-level luminescence of ZnO nanorods are sensitive to the processing parameters [12,13]. Therefore, changing the growth conditions of ZnO nanorods should be an efficient way to realize the tunable color of photoluminescence in the composite films.

In this study, we demonstrate that the luminescence color in BEuT/ZnO nanorods composite films can be

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tuned by constructing composite films composed of BEuT and ZnO nanorods.

2. Experimental procedure

The BEuT/ZnO nanorods composite films were prepared on Si substrates by a hybrid chemical solution method. First, the ZnO nanorods were prepared by a modified seed layer solution growth process described elsewhere [6]. The seed layer was prepared by spin-coating a ZnO solution onto Si substrates followed by annealing at 600 °C for 1 h. Next, the Si substrates with the ZnO seed layers were immersed in a $Zn(NO_3)/NH_4OH$ aqueous solution at 90 °C for different growth times. Afterward, the samples were washed with deionized water and dried in air. Thus, the ZnO nanorods were obtained on Si substrates. The diameters and lengths of the ZnO nanorods can be controlled by changing the growth time and the ammonia concentration in the ZnO precursor solutions. The ZnO nanorods obtained were then coated with BEuT solution by a chemical solution deposition method using a spin-coating technique at a spinning rate of 3000 rpm for 30 s, and were dried on a hotplate at 300 °C for 5 min. The BEuT preparation process, including the solution synthesis, was similar to that in our previous report [4]. The above procedure was repeated 5 times. The samples obtained were annealed at 700 °C for 1 h in air. Thus, the BEuT/ZnO nanorods composite films were obtained.

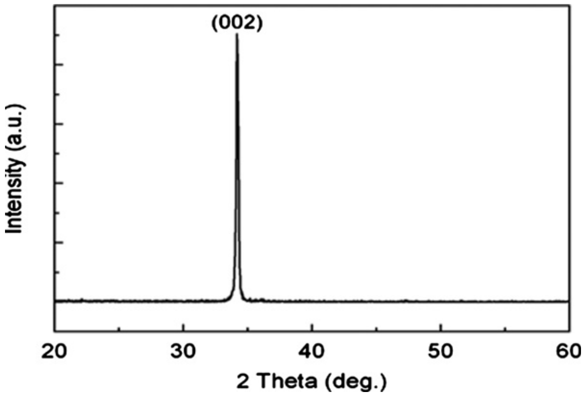

Fig.1. A typical XRD pattern of ZnO nanorods on a Si substrate.

The crystal structure was analyzed by an X-ray diffractometer (XRD, Rigaku, D/MAX 2200 VPC) with working current and voltage of 20 mA and 40 kV, respectively. The surface and cross-sectional morphologies were observed by using a field emission scanning electron microscope (SEM, JEOL LTD, JSM-6330F) and images were taken at 15 kV. Photoluminescence spectra were measured at room temperature using Shimadzu RF-5301PC Spectro-fluorophotometer.

3. Results and discussion

Fig. 1 shows a typical XRD pattern of ZnO nanorods on a Si substrate. A very strong (002) peak is observed, indicating that the ZnO nanorods have a hexagonal wurtzite structure with high c-axis orientation.

Fig. 2 shows the SEM images of ZnO nanorod arrays. The well-aligned ZnO nanorods are confirmed to grow perpendicularly on Si substrates. Each nanorod has a uniform diameter, indicating that the growth anisotropy was well maintained. It can be observed that with increasing growth time, the length of the nanorods increased as well as the diameter.

ZnO nanorods with different growth times exhibit different photoluminescence properties. Fig. 3 shows PL spectra of ZnO nanorods with the growth times of 5 min and 10 min. The excitation wavelength was chosen as 350 nm because the internal band excitation at about 350 nm is more efficient than the intrinsic excitation of

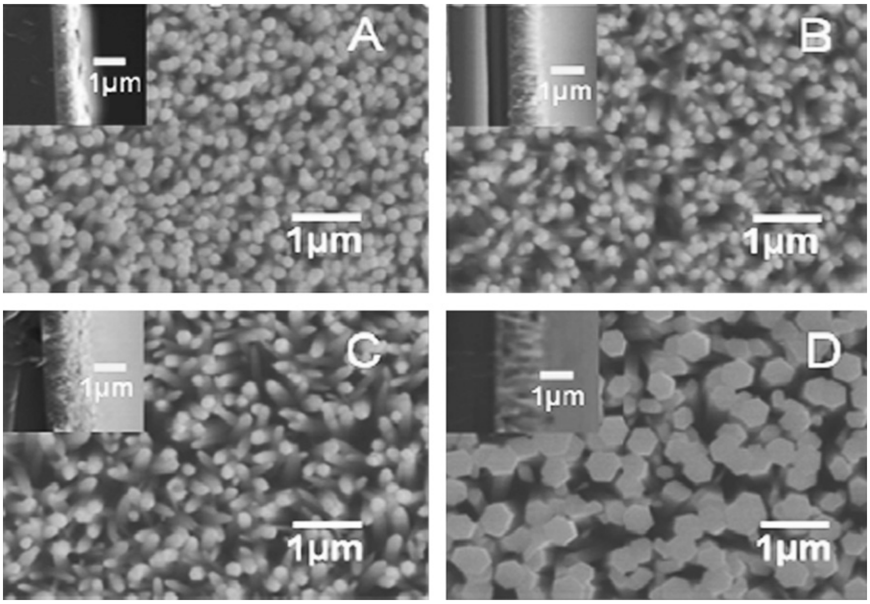

Fig. 2. SEM images of ZnO nanorod arrays on Si substrates with different growth times. The insets are the images of their cross sections. The growth times of ZnO nanorods are (A) 5 min, (B) 10 min, (C) 20 min, and (D) 60 min.

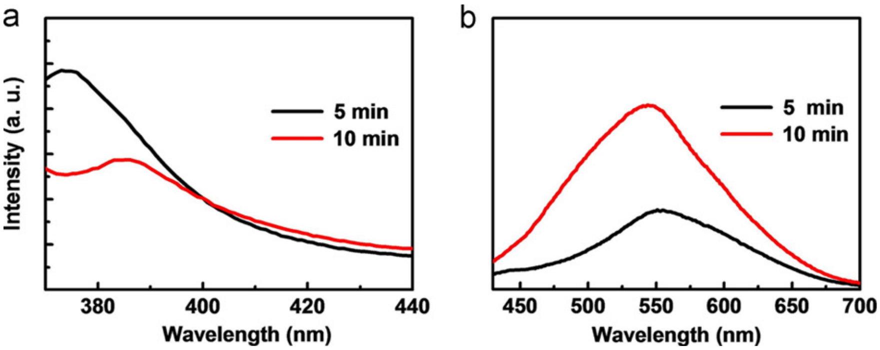

Fig. 3. Emission spectra of ZnO nanorods with the growth times of 5 min and 10 min, under excitation of 350 nm.

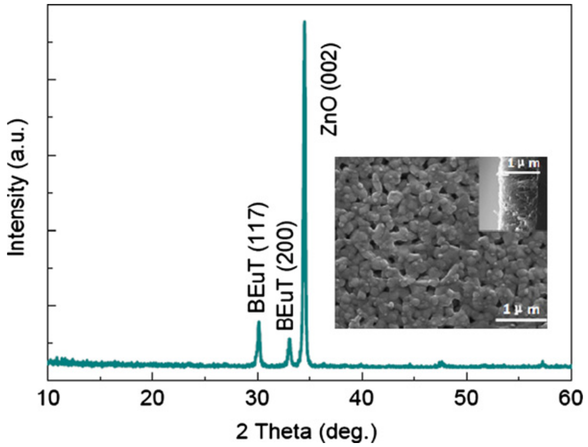

Fig. 4. XRD pattern of BEuT/ZnO nanorods composite films. The ZnO nanorods were grown with the same conditions as those of Fig. 2. The inset is a SEM image of the BEuT/ZnO composite film.

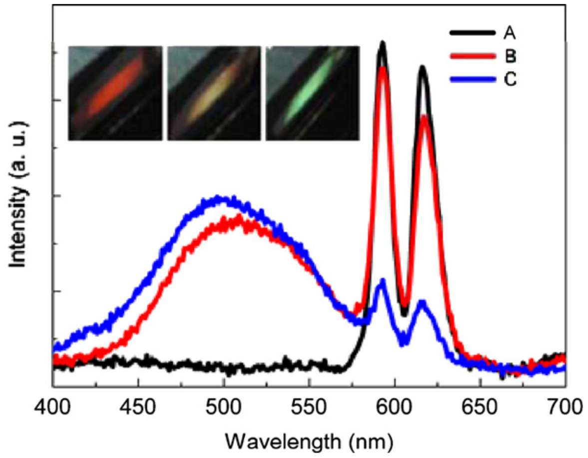

Fig. 5. Photoluminescence spectra of BEuT/ZnO nanorods composite films excitated by 350 nm. The growth times of ZnO nanorods are (A) 5 min, (B) 10 min, and (C) 20 min. The inset shows the photoluminescence photographs taken by a common digital camera, indicating the color changes from red to yellow and to green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

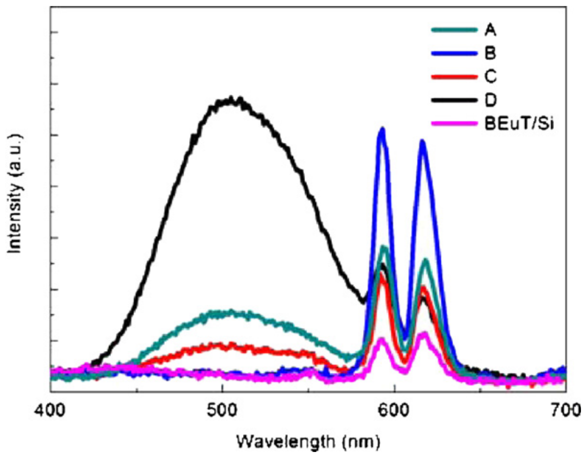

Fig. 6. Photoluminescence spectra of BEuT/ZnO nanorods composite films excitated by 350 nm. The ammonia concentrations are (A) 1.5%, (B) 1.7%, (C) 1.9%, and (D) 2.1%.

Eu^{3+} in BEuT for the ZnO/BEuT composite films [5]. Two major emission bands can be observed in the spectra, i.e. the band at 370 nm–400 nm and the other band at 450 nm–650 nm. The former originates from the NBE emission of ZnO, and the latter is due to the defects such as oxygen vacancies [10]. As the growth time increased, the intensity of NBE emission decreased, whereas the intensity of the green emission increased. This might be due to different defect concentrations in the ZnO nanorods since the ZnO precursor concentration was continuously decreased during the growth process. The defects can trap photo-generated electrons and/or holes, leading to non-radiative recombination of electron–hole pairs.

Fig. 4 shows the XRD pattern of BEuT/ZnO nanorods composite film. The ZnO nanorods were grown with the same conditions as those of Fig. 2. It can be seen that all of the diffraction peaks can be indexed with the Bi-layer perovskite structure of BEuT and hexagonal wurtzite structure of ZnO. The ZnO nanorods still remain high c-axis orientation. No impurity phases were observed. The inset of Fig. 4 shows the corresponding SEM image of the BEuT/ZnO composite films together with its cross-sectional SEM image. Compared with the BEuT thin film on Si (not shown here), the grains of BEuT on ZnO nanorods grew larger. The ZnO nanorods can offer the nucleation sites for the BEuT, promoting the grain growth of BEuT.

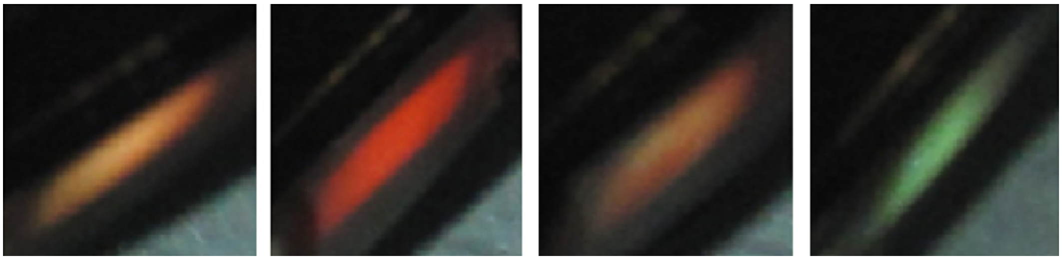

Fig. 7. Photoluminescence photographs of BEuT/ZnO nanorods composite films, indicating the effect of ammonia concentrations on the photoluminescence color of the composite films. Corresponding ammonia concentrations from left to right are 1.5%, 1.7%, 1.9%, and 2.1%.

Fig. 5 shows photoluminescence spectra of BEuT/ZnO nanorods composite films excitated by a UV-light of 350 nm. The spectrum A consisting only of two strong peaks centered at 594 nm and 617 nm attributed to the transitions of $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ of Eu^{3+} ions in Eu-doped $Bi_4Ti_3O_{12}$ corresponds to a red emission [14,15], the spectrum B composed of similar two strong peaks centered at 594 nm and 617 nm and a broad band centered at 500 nm exhibits a yellow emission, and the spectrum C composed of a broad band centered at 500 nm and two weak bands centered at 594 nm and 617 nm shows a green emission. The enhanced red emission in the spectra A and B was thought to be due to radiative energy transfer between BEuT and ZnO nanorods, because the NBE emission of ZnO at about 380 nm, overlaps the excitation spectra of Eu^{3+} in BEuT [6,8]. In comparison, pure BEuT thin films on Si substrates exhibit much lower red emission intensity. The broad band centered at 500 nm was attributed to the luminescence from deep-energy-level defects such as oxygen vacancies in ZnO nanorods [10,11]. The inset of Fig. 5 gives the photoluminescence photos taken by a common digital camera, indicating the color changes from red to yellow and to green.

Similarly, the photoluminescence color of the composite films can be tuned by changing the ammonia concentration in the ZnO precursor solutions for ZnO nanorod growth as shown in Fig. 6. Fig. 7 shows the corresponding color changes for the composite films by changing the ammonia concentration in the ZnO precursor solutions for ZnO nanorod growth.

4. Conclusions

The tunable photoluminescence color in BEuT/ZnO nanorods composite films has been demonstrated by changing the growth conditions of ZnO nanorods such as growth time and ammonia concentration. This can be attributed to the combination of red emission of Eu^{3+} ions in BEuT with the broad green deep-energy-level emission of ZnO nanorods. The near-band-edge emission of ZnO nanorods can greatly improve the red emission of Eu^{3+} ions in BEuT. The BEuT/ZnO nanorods composite films can find applications in white emission and other integrated optoelectronic devices.

Acknowledgments

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