

Preparation and near infrared emission research of $\text{YBO}_3:\text{Ce}^{3+},\text{Yb}^{3+}$ nanosheets

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ABSTRACT

Two kinds of special morphology of $\text{Y}_{0.97}\text{Ce}_{0.01}\text{Yb}_{0.02}\text{BO}_3$, nanosheets and micro-flowers composed of nanosheets, were synthesized by solvothermal method at pH 8.0 before treatment. All kinds of phosphors can transform the light in near ultraviolet range of 320~380 nm to the light in near infrared region of 900~1100 nm, where Ce^{3+} ion was the sensitizing agent and Yb^{3+} ion was the activating agent. photoluminescence of the sample prepared by aging at 200°C for 12h under the condition of pH 8.0, and 0.250M aqueous solution of $\text{RE}(\text{NO}_3)_3$ is the strongest.

Keywords: solar cells; near infrared quantum cutting; solvothermal; nanosheets; micro-flower structure.

1 INTRODUCTION

Silicon cells have lower sensitivity at violet wavelength region with a wavelength response range located at 400-1100nm determined by the band-gap (2.4eV), and are good at absorbing 900-1100nm. Sunlight of less than 400nm accounting for 9.28% of the solar energy on the ground can not only be absorbed a bit by silicon solar cells, but also reduce the conversion efficiency and make the solar cells performance decline^[1]. In recent years, in order to increase the conversion efficiency of silicon cells, a lot of professional researches how to transform UV light to near infrared light.

At present, near infrared quantum cutting come true by cooperative energy transfer from a sensitizing ion to two activating ions, which were doped into many different kinds of host materials. The activating agent is only Yb^{3+} , but the

sensitizing agent is a lot, such as, Ce^{3+} , Pr^{3+} , Nd^{3+} , Eu^{2+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Tm^{3+} and so on^[2-4].

This paper research the $\text{YBO}_3:\text{Ce}^{3+},\text{Yb}^{3+}$ phosphor, due to the following advantages: the material of YBO_3 is good transparency in UVU; Ce^{3+} ion is great absorption cross-section and wide excitation band; there is not energy reverse transfer between Ce^{3+} ions and Yb^{3+} ions.

2 EXPERIMENTAL

2.1 solvothermal synthesis of samples

Yttrium nitrate hexahydrate (Kanto 99.99%), cerium(III) nitrate hexahydrate (Kanto,99.99%) and ytterbium nitrate hexahydrate (Kanto 99.99%) were dissolved in 10.0ml of ultrapure water to respectively prepare 0.125M or 0.250M aqueous solution of $\text{RE}(\text{NO}_3)_3$ ($\text{RE}=\text{Y,Ce}$). 2.5, 5 or 10 mmol of tributyl borate was dissolved in 20.0 ml of ethanol. Then $\text{RE}(\text{NO}_3)_3$ solution was added into the ethanol solution, followed by adding a small quantity of ammonia water to adjust the pH value. Resulting white suspension was stirring at room temperature for 2 h and transferred into a Teflon-lined stainless steel autoclave. Then this autoclave was sealed and heated at 200°C for 12 h. After cooling to room temperature, the suspension was washed with ultrapure water by centrifugation at 9,000 rpm for 10 min four times to obtain the precipitate. This precipitate was dried at 70°C for 24 h to obtain the powdered sample^[5,6]. Finally the samples were heated at 850°C for 2 h^[7].

To investigate the influences of preparation conditions on structural and luminescent properties, samples were prepared under the following experimental conditions: (i) the pH value ranging from 6 to 10 for the precursor

suspension before solvothermal treatment; (ii) nominal molar ratio of rare-earth nitrates to tributyl borate, RE/B, 1/1, 1/2, 1/4; (iii) aqueous solution ratio of $\text{RE}(\text{NO}_3)_3$, 0.125M, 0.250M.

2.2 Characterization

The powder X-ray diffraction (XRD) profiles were measured using an X-ray diffractometer (Rigaku, Rint 2000) with a $\text{Cu K}\alpha$ radiation source. Scanning electron microscopy (SEM) images were recorded by a JEOL JSM-6390 system. The PL spectra and NIR spectra were measured using a Hitachi F-7000 spectrophotometer equipped with a 150W Xe lamp as an excitation source. All the measurements were performed at room temperature.

3 RESULTS AND DISCUSSION

3.1 Influences of pH value

To investigate the influences of the pH value before solvothermal treatment on the structural properties of the products and to find out the crystallization condition for vaterite-type YBO_3 , samples were prepared by aging at 200°C for 12 h under the condition of RE/B=1/1, Ce^{3+} 1 at%, Yb^{3+} 2 at%, 0.125M aqueous solution of $\text{RE}(\text{NO}_3)_3$, and various pH value, such as, pH=3, 4, 5, 6, 7, 8, 9, 10.

Figure 1(a) shows the SEM image of the sample prepared at pH 8, and the powder disperses the most uniformly in all products with different pH value. The phosphor powder consists of a large amount of nanosheets, whose thickness is from 30nm to 45nm.

3.2 Influences of nominal molar ratio of RE/B

To investigate the influences of nominal molar ratio of RE/B on the structural properties of the products, samples were prepared by aging at 200°C for 12h under the condition of pH 8.0, Ce^{3+} 1 at%, Yb^{3+} 2 at%, 0.125M aqueous solution of $\text{RE}(\text{NO}_3)_3$, and RE/B=1/2, or 1/4.

Figure 1(b) shows the SEM image of the sample prepared under the condition of RE/B=1/2, and we finds that

the phosphor powder also consists of a lot of nanosheets, whose average thickness is 40nm. Comparing figure 1(a) with figure 1(b), nanosheets structure synthesized under the condition of RE/B=1/2 is more obvious than under the condition of RE/B=1/1, and there is on stack. So, other things being equal, nanosheets disperse more uniformly with the increase of tributyl borate dosage.

Figure 1(c) shows the SEM image of the sample synthesized under the condition of RE/B=1/4, and there are mass flowers whose average size is $5\mu\text{m}$. The micro-flower was assembled by a few piece of nanosheets which average thickness is also 40nm. Consequently, Nanosheets are combined to produce a new type of structure, when nominal molar ratio of RE/B reaches 1/4.

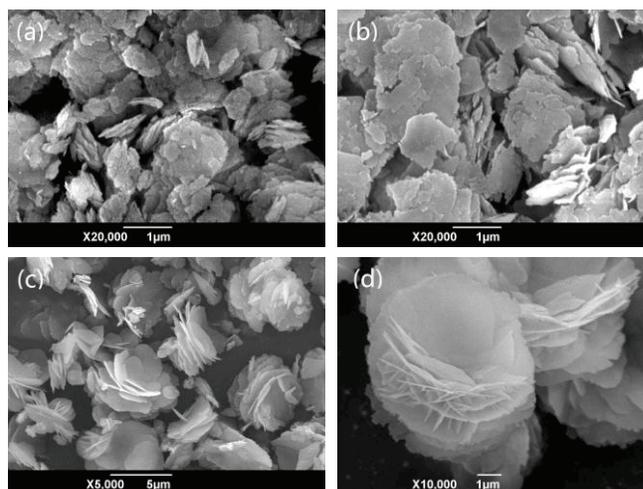


Figure 1: SEM images of all samples
The image (a) of RE/B=1/1, 0.125M;
The image (b) of RE/B=1/2, 0.125M;
The image (c) of RE/B=1/4, 0.125M;
The image (d) of RE/B=1/4, 0.250M.

3.3 Influences of aqueous solution ratio of $\text{RE}(\text{NO}_3)_3$

To investigate influences of aqueous solution ratio of $\text{RE}(\text{NO}_3)_3$ on the structural properties of the products, samples were prepared by aging at 200°C for 12h under the condition of pH 8.0, RE/B=1/4, Ce^{3+} 1 at%, Yb^{3+} 2 at%, and 0.250M aqueous solution of $\text{RE}(\text{NO}_3)_3$.

Figure 1(d) shows the SEM image of the powder prepared

under the condition of 0.250M aqueous solution of $\text{RE}(\text{NO}_3)_3$, pH=8, and RE/B=1/4. In contrast to figure 1(c), the micro-flower are composed of plenty of nanosheets which thickness is from 18nm to 45nm, and the structure of micro-flowers is more distinct.

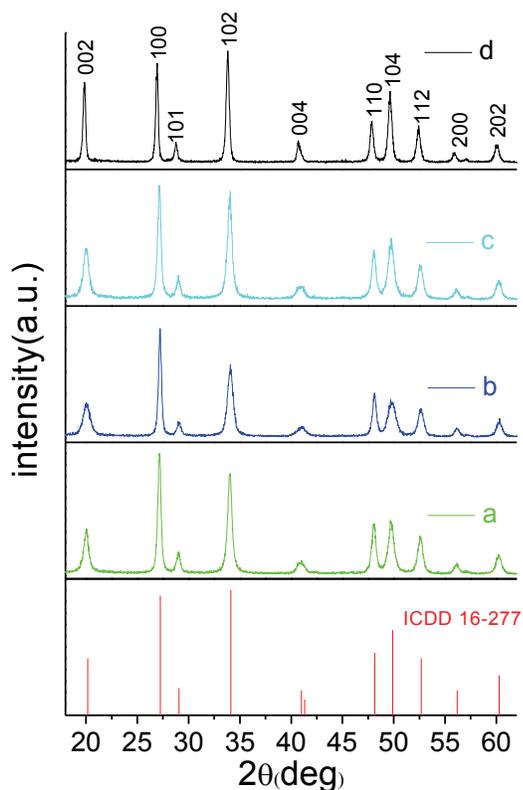


Figure 2: XRD profiles of ICDD and all samples
 The profile (a) of RE/B=1/1, 0.125M;
 The profile (b) of RE/B=1/2, 0.125M;
 The profile (c) of RE/B=1/4, 0.125M;
 The profile (d) of RE/B=1/4, 0.250M.

Figure 2 shows XRD profiles of the ICDD card data of vaterite-type YBO_3 and the samples prepared at different nominal molar ratio of RE/B and aqueous solution ratio of $\text{RE}(\text{NO}_3)_3$. Four kinds of samples all have the same diffraction peaks located at different degree of 2θ and the same hexagonal structure corresponding to the the ICDD card data of vaterite-type YBO_3 . Therefore, the phase-pure YBO_3 crystallizes and Ce^{3+} or Yb^{3+} ions doped is into crystal lattice.

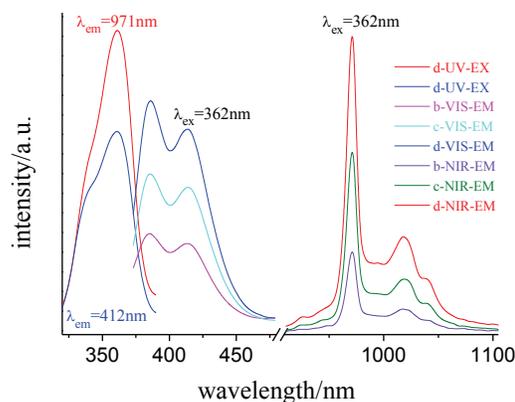


Figure 3: Right portion is photoluminescence excitation spectra of the sample (d) detected by $\lambda_{em}=412\text{nm}$ ($\text{Ce}^{3+}: 5d \rightarrow 4f$ transition) and $\lambda_{em}=971\text{nm}$ ($\text{Yb}^{3+}: {}^2F_{5/2} \rightarrow {}^2F_{7/2}$), respectively; Middle and left portions are respectively visible photoluminescence spectra of the samples (b) (c) (d) and NIR photoluminescence spectra of the samples (b) (c) (d) excited by $\lambda_{ex}=362\text{nm}$.

Figure 3 shows photoluminescence excitation spectra of the sample (d), visible emission spectra of the samples (b) (c) (d), and NIR emission spectra of the samples (b) (c) (d). In emission spectra, there are three peaks located at 385nm, 412nm and 971nm respectively, under 362nm excitation of all the phosphors. In excitation spectra, the excitation profiles of 412nm and 971nm have the same 362nm excitation peak and the same wave form. Consequently, an intense near infrared spectrum (NIR) emission 960~1020 nm of $\text{Yb}^{3+}: {}^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition was obtained, because of the cooperative energy transfer (CET) from one Ce^{3+} ion to two Yb^{3+} ions. $\text{YBO}_3: \text{Ce}^{3+}, \text{Yb}^{3+}$ phosphors can transform the light in near ultraviolet range of 320~380 nm to the light in near infrared region of 900~1100 nm, where Ce^{3+} ion was the sensitizing agent and Yb^{3+} ion was the activating agent. Similar result has been reported by several works in terms of solid state and hydrothermal syntheses^[8-10].

At the same time, we find that the relative intensity of the visible and NIR emission of the sample (d) is the strongest in all phosphors. This result suggest that the photoluminescence of phosphor with micro-flower structure is stronger than with nanosheet structure, and the more petal of micro-flower is, the stronger the photoluminescence is.

4 CONCLUSIONS

$Y_{0.97}Ce_{0.01}Yb_{0.02}BO_3$ nanosheets were prepared at pH=8.0 before treatment, and dispersed more uniformly with the increase of tributyl borate dosage. Nanosheets are combined to produce a new type of structure, when nominal molar ratio of RE/B reaches 1/4. In addition, photoluminescence of the sample prepared by aging at 200 °C for 12h under the condition of pH 8.0, and 0.250M aqueous solution of $RE(NO_3)_3$ is the strongest. All kinds of phosphors can transform the light in near ultraviolet range of 320~380 nm to the light in near infrared region of 900~1100 nm, where Ce^{3+} ion was the sensitizing agent and Yb^{3+} ion was the activating agent.

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