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Sythessis and charazterizations of a new optoelectronic material

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Green phosphor of Y(BO_3, PO_4): Ce, Tb was synthesized by means of the sol-gel and conventional solid state methods. The thermal formation process was characterized by the thermogravimetric analysis (TG) and (DTA). The effects of synthesis conditions on the crystal and morphological structures were investigated using the X-ray diffraction (XRD) and Scanning Electronic Mcirosocpy (SEM). The results revealed that Y(BO_3, PO_4): Ce, Tb phosphors with the monocline structure and high purity were successfully prepared by the sol-gel method. Furthermore, the products synthesized by the sol-gel method showed a well developed crystal structure, small particle size, narrow size distribution and high luminescent performances. The product synthesized at 1050 for 2h had better emission intensity.

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Keywords: Synthesis, Sol-gel method, Optical properties

1. Introduction

Rare-earth doped multi-component oxides have been widely studied, among which phosphors excited by vacuum ultraviolet (VUV) show great potential application in plasma display panels (PDP). Borophosphates, M_2BPO_5 (M=Na, K) were synthesized for the first time in 1911[1]. Subsequently Palkina et al. [2] synthesized $Ln_7O_8(BO_3)(PO_4)_2$(Ln=La, Pr, Nd, Cd, Dy) in solid-stated method in 1984. In 1997, Jing et al. [3] prepared $MBPO_5$:Yb^{2+} and $MBPO_5$:Eu^{2+} in air, and have measured the peaks in their excitation and emission fluorescence spectra as well as half-widths of emission. Recently, the synthesis of CaBPO5: RE(RE=Eu, Tb) by the hydrothermal synthesis reaction, and the photoluminescent characteristics of Ce^{3+} were investigated and compared with that of products prepared by solid state reaction at a high temperature [4].

Sol-gel method has attracted great interest as an excellent approach in preparing inorganic-organic hybrid materials and been employed to prepare fluorescent powder thanks to its many advantages such as better purity, good homogeneity of products and lower synthesis temperature [5-8]. Borophosphates are usually synthesized via precipitation. The difficulty to obtain sol-gel borophosphates stems chiefly from the need to balance the chemical reactivities of the metal organic precursors for boron and phosphorus. Several parameters such as pH, electronegativity and monomer functionality have been studied [9,10].

In this paper we prepared a ternary system Y_2O_3:B_2O_3:P_2O_5 lanthanum borophosphate [11-14] by the sol-gel method and investigated its fluorescence.

2. Experimental

2.1. Synthesis

Y(BO_3, PO_4): Ce^{3+}, Tb^{3+} powders were synthesized via the sol-gel method. All of the chemical reagents used in this experiment were of analytical grade and without further treatment. Stoichiometric amount of Tb_4O_7, Y_2O_3, $Ce(NO_3)_3\cdot 6H_2O$ and $(NH_4)_2HPO_4$ was dissolved in nitric acid to get the nitrate solution. The nitrate solution was under vigorous stirring on an electromagnetic stirrer. If the solution became transparent, it was cooled down to the room temperature. Meanwhile, a certain ratio of citric acid was dissolved in ethanol absolute. Such solution was mixed with the nitrate solution under ultrasonic oscillation. Subsequently, a certain ratio of tributyl borate was added into the mixed solution slowly under stirring on an electromagnetic stirrer and the white deposition appeared. Ethanol absolute was added drop wise to make the solution transparent again. At last, the mixture was treated in water bath at 80℃. A highly transparent gel of polyester was gained after several hours and dry gel powders were obtained after drying.

The dried powders were placed in a small crucible, which was then placed in a large crucible. The space between the small crucible and the large one was filled with activated charcoal to form reducing atmosphere. The set of crucibles was put into the oven and sintering at 350 ^{o}C for 2 hours and then calcined at 1050℃for 2h to form Y(BO_3, PO_4): Ce, Tb.

2.2. Characterizations

Powder samples as prepared were characterized with X-ray diffraction (Y-2000, China) with Cu Kα radiation at

0.154178 nm, scanning electron microscopy (SEM, Philips, Sirion200), spectrophotometer (Shimadzu, Japan, RF-5301PC) and Diamond thermogravimetric analysis and differential thermal analysis analyzer (TG/DTA, America, N5350030) in a nitrogen atmosphere in a range of 0~1000 ^{o}C with a heating rate of 10℃·min^{-1}.

3. Results and discussion

3.1 Thermoanalysis of Dried Gel

Fig.1 shows the TG and DTA curves of the dry gel powders. As shown in Fig. 1, an obvious weight loss about 33% can be found between 130~255 ^{o}C mainly due to the loss of water. In accordance with the weight loss, an exothermal peak presents at 234 ^{o}C in the DTA curve. Then a small exothermal peak at 310 ^{o}C is found, according to partial decomposition of organic compounds, and there is about 5% weight loss between 255~350 ^{o}C. Subsequently, another obvious exothermal peak emerges at 406 ^{o}C and about 15% weight loss happens between 350~458 ^{o}C thanks to the decomposition of nitrate and boron. The weight loss amounts to about 55% till 500 ^{o}C. The TG curve tends to level off after 900 ^{o}C owing to the formation and crystallization of products. Thus, the dry gel powders are designed to be pre-sintered at 350 ^{o}C to remove the organic compounds and then at higher temperature than 900 ^{o}C to obtained the products.

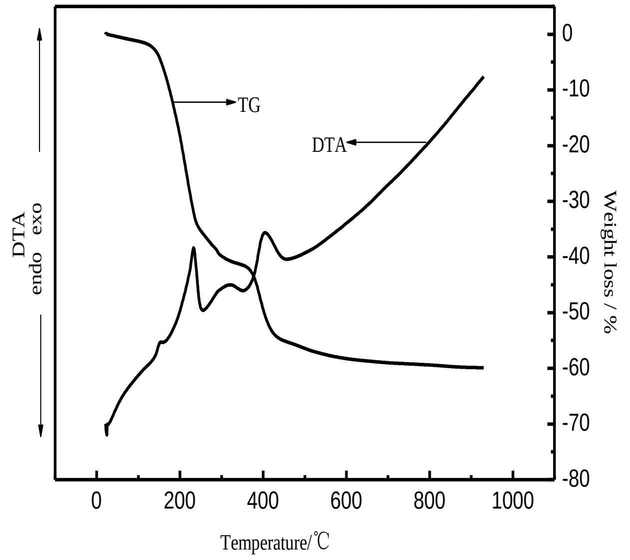

Fig. 1. TG and DTA curves of the dry gel powders.

3.2. Crystal structure

Fig. 2 shows the XRD patterns of the samples heat-treated at different temperatures and. The peaks of YAG are not found at 700^{o}C, which indicates that the sample is amorphous and agrees with the thermal analysis. At 900^{o}C, the YAG peaks are found. This indicates the formation of the YAG phase. However, $YAlO_3$ (YIG) and Al_2O_3 interphases are also found in the XRD pattern. At 1050^{o}C, the fully-crystallized phase is identified as the pure YAG structure. Traditionally, the synthesis temperature of solid-state sintering methods is higher than 1800^{o}C. Apparent structural changes can be found after Gd was doped because of the larger d value, and a small shift can be observed toward lower 2θ values with respect to the standard pattern. This can be explained in terms of an expansion in the crystallographic unit cell owing to the gadolinium dopant with a larger radius.

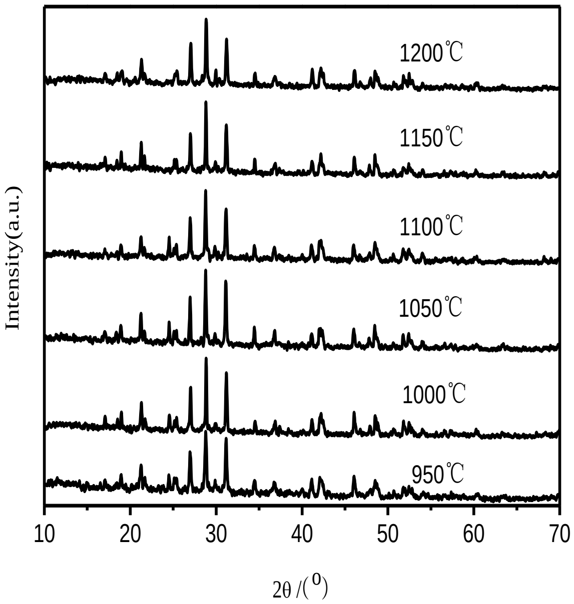

Fig. 2. XRD patterns of products calcined at different times.

3.3. Morphology structure

Typical Scanning Electron Microscope (SEM) images of $Y(BO_3, PO_4)$: Ce, Tb precursor and its final nano-phosphor are shown in Fig. 3. Both products were finally treated at 1050 ^{o}C for 2h.The precursor is the net structure of citric acid, and the powders are very large. The final product at 1050^{o}C is about 30~50nm, which is far smaller than the products prepared by solid state reactions. It can be observed that the phosphors exhibit in general uniform grain size. This is required for good brightness during their processing. Meanwhile, the morphology is similar and nearly spherical. It is known that the use of spherical phosphors should increase the screen brightness and improve the resolution because of lower scattering and higher packing densities.

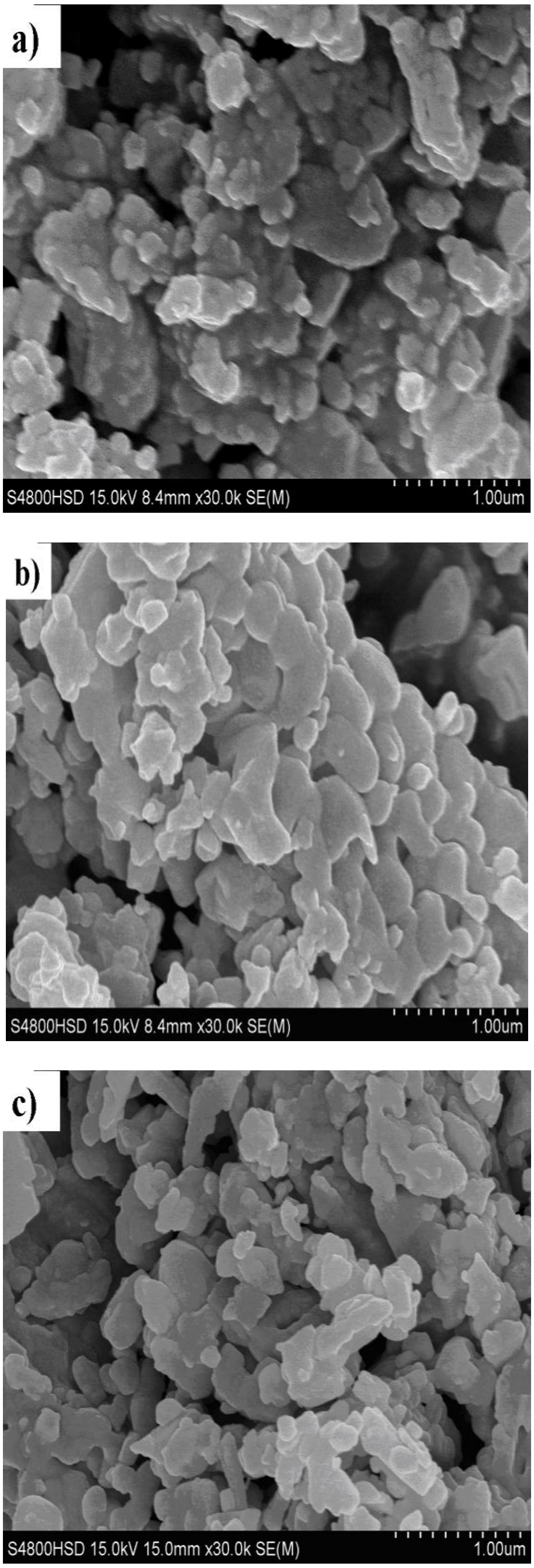

Fig. 3. SEM micrographs of Y(BO_3, PO_4): Ce, Tb particlesa)950 °C ;b)1050 °C ;c)1150 °C.

3.4. Luminescent properties

The lowest absorption electron transition of Tb^{3+} is $4f^8 \rightarrow 4f^7 5d$. Ultraviolet light cannot afford the excitation energy because the transition needs high energy. Furthermore, 4f-4f electron transition is forbidden because of the selection rule. So Tb^{3+} cannot be excited effectively by ultraviolet light. Ce^{3+} functions as sensitizer for its $4f \rightarrow 4f^0 5d$ electron transition which needs lower excitation energy than Tb^{3+}.

Fig. 4 shows the relationship of photoluminescence intensity with the ration of x in $(Y_{1-x}Tb_x)_2O_3 \cdot 0.8P_2O_5 \cdot 0.3B_2O_3$. The PL increase with the increasing of concentration of Tb^{3+} from 0.08 to 0.2, and reaches a maximum at x=0.02, then the decrease observed at higher Tb^{3+} concentrations is due to concentration quenching. Fig. 5 shows relationship between fluorescence intensity and the concentration of Tb in $(Y_{1-x-y}Ce_yTb_x)_2O_3 \cdot 0.8P_2O_5 \cdot 0.3B_2O_3$with Ce^{3+} and without Ce^{3+}.

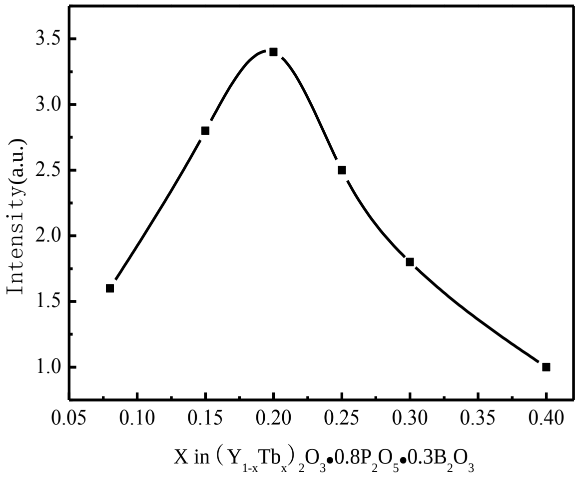

Fig. 4. The relationship between fluorescence intensity and the concentration of Tb in $(Y_{1-x}Tb_x)_2O_3 \cdot 0.8P_2O_5 \cdot 0.3B_2O_3$.

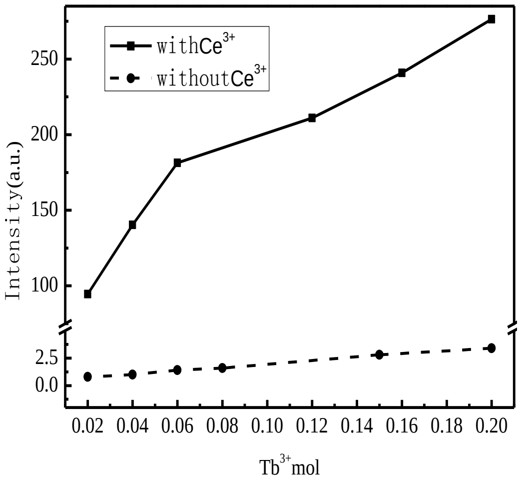

Fig. 5. The relationship between fluorescence intensity and the concentration of Tb in $(Y_{1-x-y}Ce_yTb_x)_2O_3 \cdot 0.8P_2O_5 \cdot 0.3B_2O_3$.

The emission intensity at 543 nm under excitation of 259 nm for the products at different sintering temperatures is shown in Fig. 5. It can be found that the PL intensities increase with increasing sintering temperatures and level off after 1100℃. Also, the products by sol-gel method have higher brightness than that by solid-stated method. But when the temperature preponderates over 1050℃, the intensity will get down. It may due to the volatilization of B or the temperature quenching effect. The lower annealed temperature is not good for the formation of crystallized state, the particles are easier to sinter but hard to disperse, and the Ce^{3+} and Tb^{3+} ions are easy to be oxidized to Ce^{4+} and Tb^{4+}, all this lead to decrease the luminous efficiency. The well-developed crystal structure of the product at 1050℃, as confirmed by XRD and SEM, contributes to the highest PL intensity.

4. Conclusions

$Y(BO_3, PO_4)$: Ce, Tb phosphors were prepared by a sol-gel method of 1050°C, which was lower than the temperature for the traditional method. The particle size was about 30-50nm and the morphology was nearly spherical. The excited spectrum was at about 270 nm, and the main emission spectrum was at 543 nm. The luminescent intensity of green emission increased with Tb content initially, and then decreased. If the content of Tb was 0.02, the green luminescence was optimal owing to the co-excited effect of Ce ions and Tb ions.

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