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Synthesis of $CaTiO_3$:Pr,Al phosphors by a peroxide-based route and their photoluminescence properties

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Abstract A enhanced photoluminescence red phosphor of $CaTiO_3$:Pr,Al has been synthesized by a peroxide-based route (PBR) and high temperature sintering method. The synthesizing conditions have been optimized in this work. The effect of sintering temperature and boron on the preparation, structure, and photoluminescence were studied by X-ray powder diffraction (XRD), emission, and excitation spectra at room temperature. The red emission is attributed to $^1D_2 \rightarrow {}^3H_4$ transition of Pr^{3+}, and the excited energy comes from the UV absorption of host and transfers to 4*f*–5*d* band of Pr^{3+}. Also, the studies include analysis of charge compensation and Pr^{3+} concentration effects. Compared with conventional solid-state reaction methods, the PBR significantly lowered temperatures of synthesis, shortened reaction time, and enhanced the photoluminescence intensity.

Introduction

Perovskite-type praseodymium-doped $CaTiO_3$:Pr is one kind of the promising red phosphors due to the red emission ($^1D_2 \rightarrow {}^3H_4$ transition of Pr^{3+}) with CIE coordinates at $x = 0.680$ and $y = 0.311$, very close to the coordinates at the "ideal red" [1]. $CaTiO_3$:Pr phosphor has been the object of many investigations for optical imaging or laser purposes [2, 3]. In order to enhance its luminescent properties, much attention has been paid during the past decade to the preparation method and on the material composition. Several chemical synthesis techniques, such as solid state reactions [4, 5] and polymeric precursor methods [6], have been applied to prepare $CaTiO_3$:Pr phosphors. The addition of Al^{3+} into $CaTiO_3$:Pr has been reported to greatly enhance the emission intensity [2, 7]. Pr^{3+} substitutes for the Ca^{2+} site in the $CaTiO_3$ lattices and a positive charge defect is formed. Such charge defect hampers the process of energy transfer from the host to Pr^{3+}, but it can be compensated by the negative charge defect when Ti^{4+} ion is substituted by Al^{3+} ion, consequently leading to the reinforcement of the optical performances.

A peroxide-based route (PBR) has been applied to synthesis of metatitanates, for instance, $Bi_2Ti_2O_7$ [8], $PbTiO_3$ [9], and $CdTiO_3$ [10]. This method from technological point of view exhibits some important advantages compared to the conventional method for obtaining titanates: significantly lower temperatures of synthesis, shorter reaction time, avoiding the milling and homogenizing of the raw materials and of the final product. As a result the obtained metatitanates are of higher purity, with fine crystalline structure and homogeneous grain-size composition.

In this study, red emitting $CaTiO_3$: Pr, Al phosphor was synthesized using the PBR method and the luminescent properties were investigated. In addition, the effect of Pr^{3+} concentration, the concentrations of Al^{3+} codoped, the addition of boric acid as a flux agent, as well as the sintering temperature, were investigated and discussed.

Experimental

The flowchart in Fig. 1 summarizes the synthesis of $CaTiO_3$:Pr,Al. $TiO(OH)_2$ was obtained by the hydrolysis of

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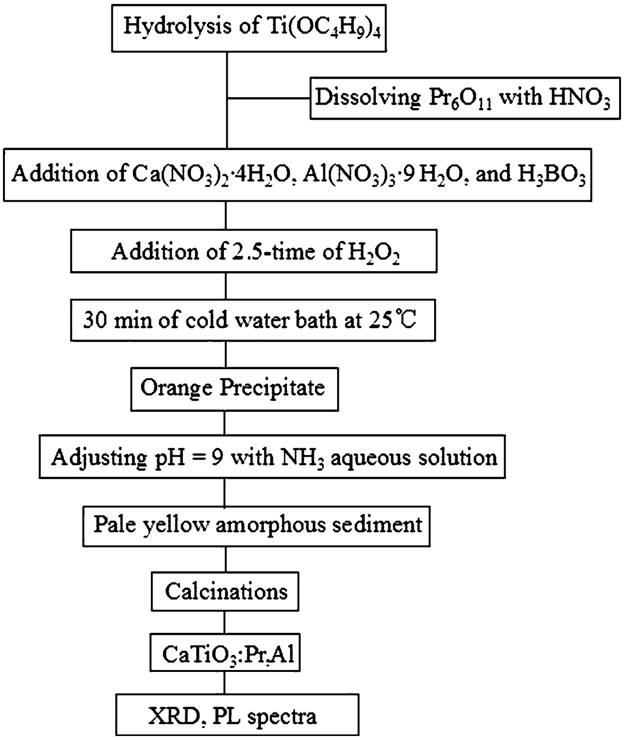

Fig. 1 Flowchart for preparing CaTiO$_3$:Pr,Al by a PBR method

tetra-*n*-butyl titanate (Ti(OC$_4$H$_9$)$_4$, TTIP, and AR grade) as follows:

$$Ti(OC_4H_9)_4 + 3H_2O \rightarrow TiO(OH)_2 + 4C_4H_9OH$$

Pr$_6$O$_{11}$ (3N grade) was dissolved with HNO$_3$ to convert into Pr(NO$_3$)$_3$ completely. Ca(NO$_3$)$_2$·4H$_2$O (AR grade), Al(NO$_3$)$_3$·9H$_2$O (AR grade), H$_3$BO$_3$ (AR grade), and Pr(NO$_3$)$_3$ solution were added. H$_2$O$_2$ (30%, AR grade) with a molar ratio concentration of 2.5 (H$_2$O$_2$/TTIP), was used to facilitate dissolving TiO(OH)$_2$ in water. The mixture was put into a cold-water bath and an orange precipitate was formed. Ammonia aqueous solution (29%, AR grade) was added until obtaining pH = 9. Pale yellow amorphous sediment was obtained. After heated at 900 °C for 1 h in air, CaTiO$_3$: Pr,Al phosphor was obtained.

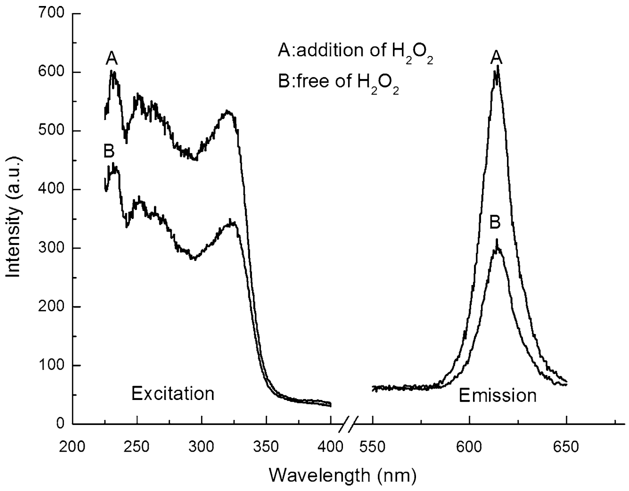

Fig. 2 Typical excitation–emission profiles of CaTiO$_3$:Pr,Al prepared by the PBR method

The sintered powder was characterized by X-ray diffraction in a 2θ range from 10° to 80°, using a Burker D8 (Burker Co., German) with Cu K_α radiation. Photoluminescence (PL) spectra at room temperature were recorded using a Perkin-Elmer LS-55 (Perkin-Elmer Co., USA) luminescence spectrometer with a xenon discharge lamp.

Results and discussions

Figure 2 shows the excitation and emission spectra at room temperature of CaTiO$_3$:0.1%Pr, 0.5%Al,0.3B phosphor prepared at 900 °C with H$_2$O$_2$ addition (Sample A) and without H$_2$O$_2$ addition (Sample B), respectively. The dominant peak of the emission spectra is near 613 nm (under 252 nm excitation), which is assigned to the transition $^1D_2 \rightarrow {}^3H_4$ of Pr^{3+}, and no other obvious emission peaks can be seen in visible range. The broad excitation peaks of 250–350 nm correspond to 4*f*–5*d* transition of Pr^{3+} (under 613 nm emission) [2]. The 4*f*–4*f* transition peaks are weak comparing with the 4*f*–5*d* transitions and are not present in Fig. 2. A considerable enhancement of UV excitation in the required UV spectral range was obtained in CaTiO$_3$:0.1%Pr,0.5%Al,0.3B phosphor with H$_2$O$_2$ addition. The absorption at 252 nm increases to 50%. It is observed that the red emission at 613 nm is nearly double for samples with H$_2$O$_2$ addition compared to that without H$_2$O$_2$ addition.

The intensity of the red luminescence of Pr^{3+} in CaTiO$_3$ depends severely on the preparation method and on the material composition. It is known that TiO(OH)$_2$ and hydrogen peroxide gives a yellow peroxo complexes gel in neutral solution. If a solution of Ca(NO$_3$)$_2$ is added at pH = 9, an amorphous precipitate containing calcium and titanium is formed. In opposition to the dry method, the PBR processes were conducted in liquid phases so that each component can be accurately controlled and uniformly mixed, even at lower temperatures than in the solid state. As a consequence, PBR-processed powders are characterized a better crystallinity and a denser microstructure than powders prepared in the solid state. These two characteristics account for the observation of high luminescence intensities, as confirmed in the present work.

Figure 3 presents the XRD pattern of CaTiO$_3$:0.1%Pr, 0.5%Al,0.3B phosphors sintered at different temperatures for 1 h under air, from 700 to 1,000°C. The crystallization of orthorhombic $CaTiO_3$ (JCPDS 22-0153, ▼) appears clearly after thermal treatment at 700 °C. As the sintering temperature is increase up to 800 °C peaks related to orthorhombic $CaTiO_3$ increase, together with new peaks detected. The new peaks are related to rutile (JCPDS 21-1276, ◇) and $Ca(BO_2)_2$ (JCPDS 22-0522, ◆) which could be formed by interaction at high temperature with the boric acid flux. This process will be further discussed below.

Figure 4 reveals the effect of the sintering temperature on the PL intensity of $CaTiO_3$:0.1%Pr, 0.5%Al,0.3B phosphor prepared by the PBR method. The low intensity PL emission (centered at 613 nm) was observed from the particles prepared at 700 °C. The red emission intensity is enhanced as the temperature of the preparation is raised up to 900 °C, followed by a weak decrease of this intensity for samples sintered at temperatures above 900 °C. The orthorhombic $CaTiO_3$ structure of the phosphor is maintained after thermal treatments at high temperature and the degree of crystallization increases progressively as the sintering temperature is raised. The improved crystallinity leads to increased energy-transfer efficiency from $CaTiO_3$ to Pr^{3+} centers, resulting in the PL enhancement. Therefore, a progressive increase of PL intensity along with the increase of the treating temperature is observed. On the other hand, non-luminescent TiO_2 and $Ca(BO_2)_2$ will form at high treating temperatures. In this case, the resulting mixed sample exhibits a weakened photoluminescence.

The minor amount of H_3BO_3 was introduced as flux in the experiment since it was proved to be effective in stimulating the host lattice formation and grain growth [11, 12]. The molar ratio of B/Ti varied from 0 to 0.5. The effect of H_3BO_3 on the crystal structure of phosphor particles prepared by the PBR method sintered at 900 °C is shown in Fig. 5. It is evident that the addition of boric acid results in the phase impurity of the particles. With increasing the amount of boric acid, the diffraction of rutile became stronger and stronger. Finally, for molar ratio of B/Ti above 0.3, the characteristic peaks of $Ca(BO_2)_2$ appears and their intensity increase at the expensive of orthorhombic $CaTiO_3$ peaks. Thus at higher molar ratio of B/Ti, H_3BO_3 strongly participated in the reactions with CaO as well as TiO_2 wherefore $Ca(BO_2)_2$ and TiO_2 was obtained along with $CaTiO_3$ phase.

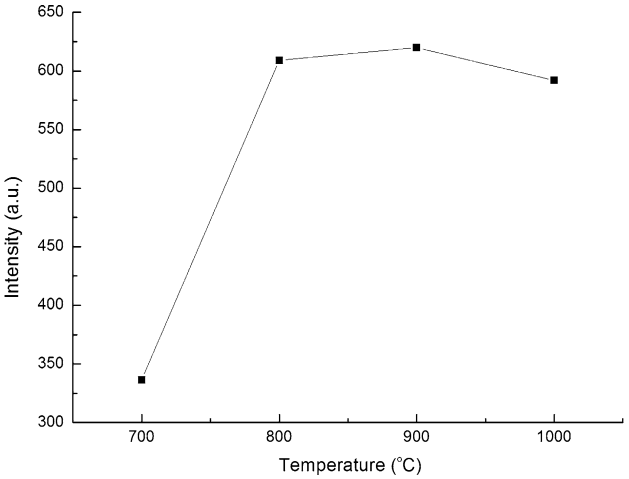

Fig. 4 Relationship between PL intensity of $CaTiO_3$: 0.1%Pr, 0.5%Al, 0.3B phosphors and sintering temperature

The effect of H_3BO_3 flux on the PL properties of phosphors is shown in Fig. 6. At low flux concentrations (below 0.3), the PL intensity was improved by increasing the flux concentration. In contrast, at high flux concentrations (above 0.3), the PL intensity decreased with increasing H_3BO_3 concentration. The intensity of PL at concentration of 0.3 is almost treble that of samples

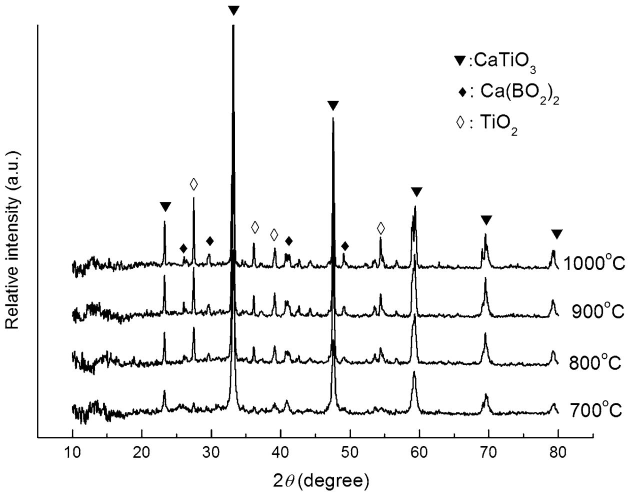

Fig. 3 XRD pattern of $CaTiO_3$:Pr,Al,0.3B sintered at different temperatures

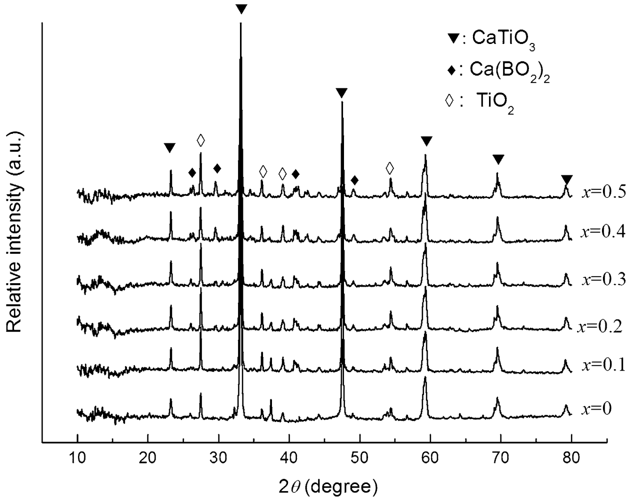

Fig. 5 XRD pattern of $CaTiO_3$: 0.1%Pr, 0.5%Al, *x*B sintered at 900 °C

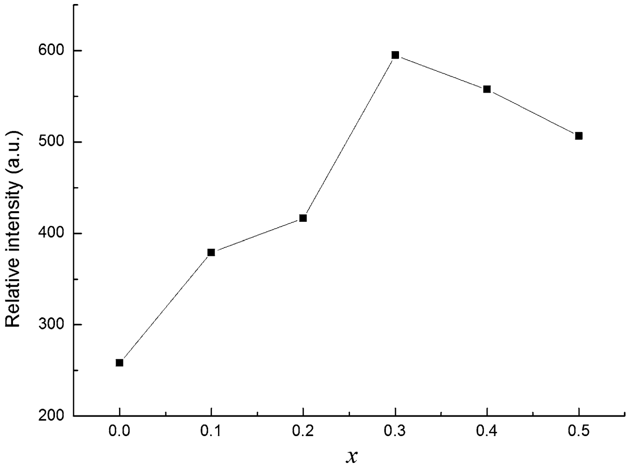

Fig. 6 PL intensity of $CaTiO_3$: 0.1%Pr, 0.5%Al, *x*B sintered at 900 °C

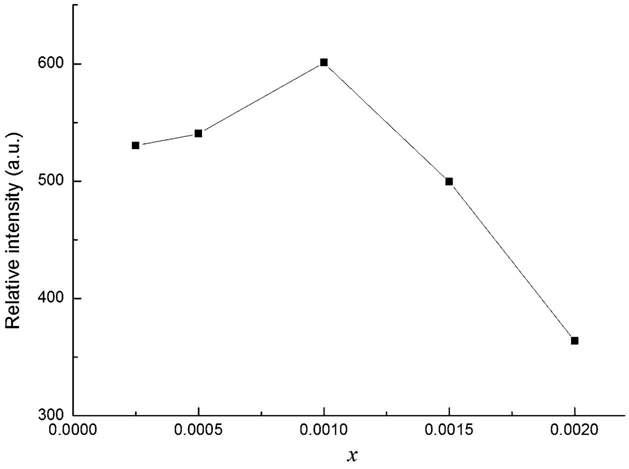

Fig. 7 PL intensity of $CaTiO_3$: *x*Pr, 0.5%Al, 0.3B sintered at 900 °C

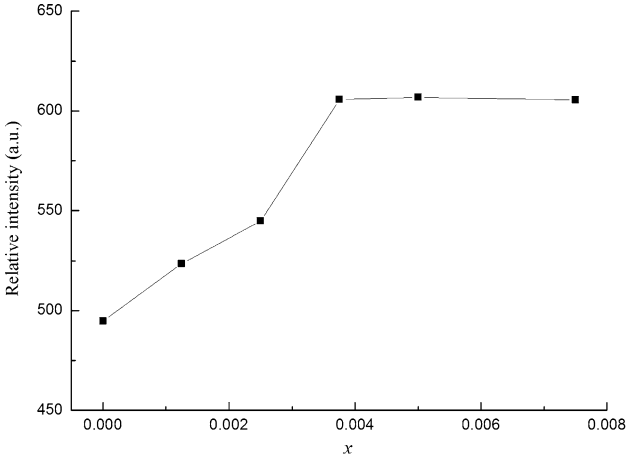

Fig. 8 PL intensity of $CaTiO_3$: 0.1%Pr, *x* Al, 0.3B sintered at 900 °C

prepared without H_3BO_3 flux. In the sintering process, H_3BO_3 stimulates the formation of $CaTiO_3$ phosphors and help to produce dense ceramics at 900 °C. This is responsible for the improvement of PL. It was also observed that H_3BO_3 induces the formation of non-luminescent TiO_2 and $Ca(BO_2)_2$. Thus, a large content of boron does not increase but decrease the PL intensity.

The dependence of the PL intensity on the Pr^{3+} concentration for $CaTiO_3$:*x*Pr,0.5%Al,0.3B (*x* varies from 0.025 to 0.2%) is shown in Fig. 7. The emission intensity depends also strongly on the Pr^{3+} concentration. With an increase in the Pr^{3+} concentration, the emission intensity of $CaTiO_3$:Pr,Al phosphor increases gradually. The PL is systematically maximum for Pr^{3+} molar percentage of 0.1. Above this value, a quenching rapidly occurs, probably due to an energy transfer through Pr-Pr interaction [1].

Figure 8 shows the relationship between the PL intensity of the red $CaTiO_3$:0.1%Pr,*x*Al,0.3B (*x* varies from 0 to 0.75%) phosphor and the concentration of Al^{3+}. In Fig. 8, the PL intensity increases with increasing concentration of Al^{3+}. The PL intensities become saturated as the Al^{3+} concentration beyond 0.4%. Therefore, the optimal concentration of Al^{3+} is about 0.5%. Due to the ionic radius of Pr^{3+} (101.3 pm) similar to Ca^{2+} (99 pm), Pr^{3+} substitutes for Ca^{2+} site, and a positive charge defect is formed [7]. According to the theory of charge compensation, the charge defect can be compensated effectively when a Ti^{4+} ion is substituted by an Al^{3+} ion. Consequently, the optical performance is reinforced.

Conclusions

Red-emitting phosphors $CaTiO_3$:Pr,Al has been prepared using the PBR. The synthesizing conditions have been optimized in our work and the PL intensity of the phosphor has been enhanced using the PBR method and using boric acid flux. The Al addition contributes to charge compensation that eliminates more charge defects and leads to an increase of red PL intensity.

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