

# Synthesis of CaTiO<sub>3</sub>: Pr, Al phosphors by sol-gel method and their luminescence properties

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**Abstract** Red long afterglow CaTiO<sub>3</sub>: Pr, Al phosphors have been synthesized by sol-gel method using ethanol as solvent and citric acid as a chelating agent. TG-DTG curves and X-ray diffraction analysis indicate that crystalline calcium titanate has been synthesized at calcining temperature of 700 °C for 5 h. Photoluminescence and decay curves indicate that the luminescence properties of phosphors synthesized by sol-gel method are better than that prepared by solid-state reaction and the sample heated at 900 °C exhibits the optimal luminous property. Using ultrasonic dispersing technique improved the luminescence properties of phosphors.

## Introduction

In recent years, alkaline earth titanates doped with rare earth ions have attracted research interests in the field of photoluminescence since they are suitable hosts with high chemical stability [1–4]. Especially, much work has been concentrated on the phosphors based on Pr<sup>3+</sup> doped perovskite titanate [1, 2, 5–7], which are typically characterized with one strong and sharp emission peak at about 610 nm. In order to enhance the luminous properties, many researchers have studied these phosphors by varying the concentration of activator ion [1, 8], hosts [7, 9–11], different charge compensators [12–14], and

different synthesis methods [15–17]. In addition, the shape of the products has been changed from the single powder to film [18, 19].

The conventional solid-state reaction for preparing long afterglow phosphors requires a high calcining temperature, which induces sintering and aggregation of particles. Furthermore, the milling process to reduce the particle size leads to decreasing of luminescence properties. In order to achieve highly homogeneous ultrafine particles of phosphors and to avoid the milling process, sol-gel has been used extensively. The sol-gel process is an efficient technique for the synthesis of phosphors, due to the good mixing of starting materials and relatively low reaction temperature, resulting in more homogeneous products than those obtained by conventional solid-state reaction synthesis method. Although many researchers have synthesized the phosphors by sol-gel processing, it has been observed that the preparation of the powders by sol-gel procedures leads to significant reinforcement of the red long afterglow intensity and that the starting materials, the stoichiometry, the synthesis routes and the sintering conditions affect strongly the performances of the phosphors [8, 16, 17]. Therefore, it is significant to seek an appropriate route and the condition for synthesizing the red long afterglow Pr<sup>3+</sup>-doped CaTiO<sub>3</sub> phosphor powders by sol-gel method.

In this paper, using ethanol as the solvent, citric acid as chelating agent and Al<sup>3+</sup> as charge composition, red long afterglow CaTiO<sub>3</sub>: Pr, Al phosphors have been synthesized by sol-gel method regardless of the pH value of the solution. In order to enhance the luminescence properties of the phosphors, ultrasonic dispersing technique has been used in the sol-gel process. In addition, the same samples have been synthesized by the solid-state reaction in air.

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## Experimental

### Synthesis

The long afterglow  $\text{CaTiO}_3: 0.1\%\text{Pr}^{3+}, 0.1\%\text{Al}^{3+}$  phosphors were prepared by sol-gel method and conventional solid-state reaction, respectively. The nominal compositions of the samples were  $\text{Ca}_{1-x}\text{Pr}_x\text{Ti}_{1-x}\text{Al}_x\text{O}_3$  ( $x = 0.1\%$ ), in which the charge compensation is provided by the substitution of  $x$  mol%  $\text{Ti}^{4+}$  to  $\text{Al}^{3+}$ .

For sol-gel method,  $\text{Pr}_6\text{O}_{11}$  was dissolved with  $\text{HNO}_3$  to convert into  $\text{Pr}(\text{NO}_3)_3$  completely. Excess  $\text{HNO}_3$  was removed by evaporation in fume cupboard. Appropriate amount of citric acid and tetra-*n*-butyl titanate  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  were dissolved in anhydrous ethanol under a constantly magnetic stirring or an ultrasonic dispersing. After stirring vigorously or dispersing for about 30 min at room temperature, the mixed solution of  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Al}(\text{NO}_3)_3$ , and  $\text{Pr}(\text{NO}_3)_3$  was added drop-wise to the above titanium organic solution slowly to avoid tetra-*n*-butyl titanate hydrolyzing. Increasing the temperature to 80 °C, the solution was evaporated slowly by heating with continuous stirring or dispersing. As ethanol evaporated, the solution became viscous and finally formed a very viscous yellow gel. Xerogel was obtained by drying the gel at 80 °C. After firing at about 400 °C for 2 h, a dark solid mass was obtained from the dried gel. Finally, the dark solid mass was ground to fine powder and sintered at various temperatures from 700 to 1,200 °C in air for 5 h. For solid-state reactions, stoichiometric amounts of  $\text{CaCO}_3$ ,  $\text{TiO}_2$ ,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{H}_3\text{BO}_3$  were mixed together and grounded in agate mortar and then sintered at 1,200 °C for 3 h in air. All chemicals are of the analytical purity, except the  $\text{Pr}_6\text{O}_{11}$  is 99.9%.

### Characterization

The thermal decomposition behavior of the dried gel was examined by thermogravimetric analysis (TGA) using a TGS-2 thermal balance (Perkin-Elmer Co., USA) in static air at a heating rate of 10 °C/min. The crystal structures of the phosphor powders were characterized by X-ray diffraction analysis using a Burker D8 (Bruker Co., Germany) with  $\text{CuK}_\alpha$  radiation. The morphology and dimension of the product were observed by transmission electron microscopy (TEM), which were taken on a Tecnai G20 (FEI Co., Holland) transmission electron microscope. A sample for TEM examination was prepared by depositing an ultrasonically dispersed suspension of powder from a solution of alcohol on a carbon-coated copper grid. Excitation and emission spectra at room temperature were recorded using a Perkin-Elmer LS-55 (Perkin-Elmer Co., USA) luminescence spectrometer with a xenon discharge

lamp. The long afterglow decay curves were measured with the ST-86LA (Pekin Normal University, China) brightness meter after the samples were irradiated with a 9 W conventional tricolor fluorescent lamp for 15 min.

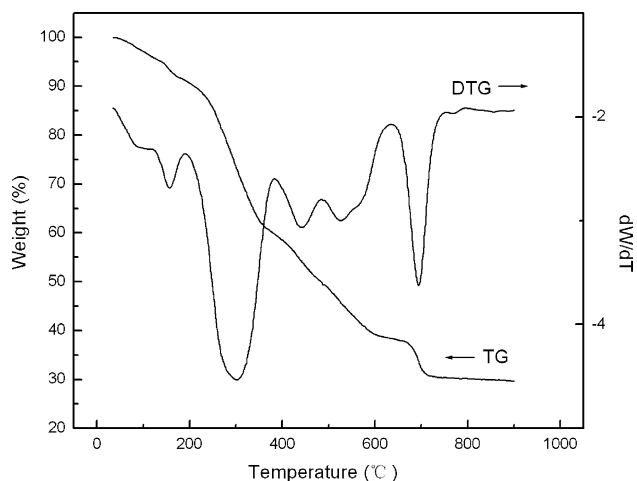
## Results and discussion

### Characterization of polymeric precursor

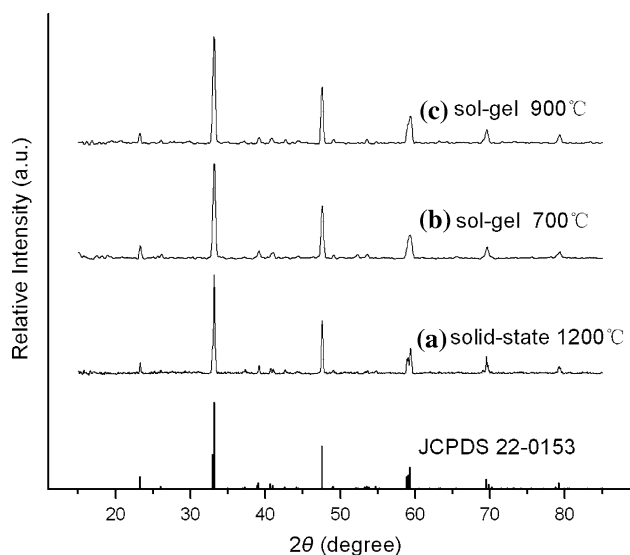
The thermal decomposition behavior of the dried gel was examined by TG in static air with the heating rate of 10 °C/min. The TG/DTG results for the dried gel prepared by magnetic stirring are shown in Fig. 1. It shows the total weight loss of about 70%. At the temperature below 400 °C, the weight loss of about 40% corresponds to the solution and part of organic compounds. At the temperature range 400–700 °C, the main weight loss corresponds to the decomposition of citrate and other organic compounds. As the temperature above 700 °C, the curve is stationary. This means that at 700 °C the resin combustion is almost complete and crystallization of the  $\text{CaTiO}_3$  has occurred. This result is in agreement with the XRD patterns of the sample prepared at 700 °C as follows.

### Phase formation and particle size analysis

The XRD patterns of nominal composition  $\text{CaTiO}_3: 0.1\%\text{Pr}^{3+}, 0.1\%\text{Al}^{3+}$  samples prepared by the solid-state reaction and the sol-gel method are presented in Fig. 2. The results indicate that the diffraction peak positions and the relative intensities of the prepared samples are well matched with the standard powder diffraction file (JCPDS 22-0153), and the co-doped Pr and Al ions have little influence



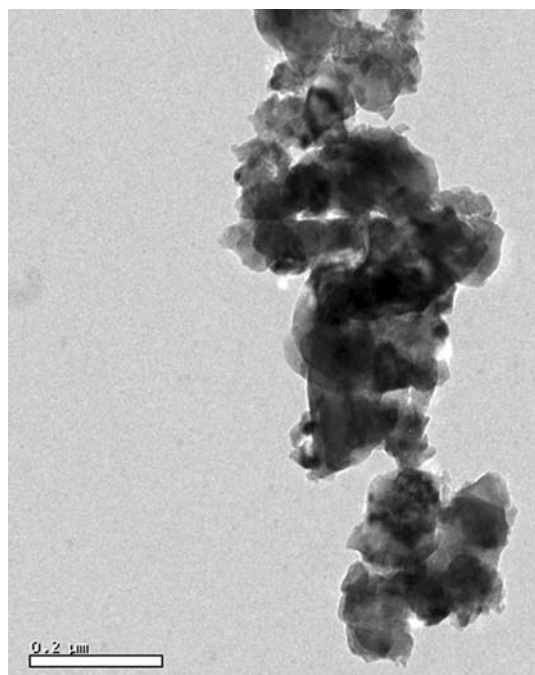
**Fig. 1** TG-DTG curves of xerogel performed at the heating rate of 10 °C/min



**Fig. 2** XRD patterns of  $\text{CaTiO}_3:0.1\%\text{Pr}^{3+}, 0.1\%\text{Al}^{3+}$  synthesized by solid-state reaction and sol-gel method

on the host structure. Phase-pure crystalline  $\text{CaTiO}_3$  can be obtained at 700 °C, a much lower temperature than conventional solid-state reaction to form phase-pure  $\text{CaTiO}_3$ . It is ascribed to that the citric acid can chelate metal atoms and these metal atoms disperse at molecular level, showing high activity as the bonds between metal atoms and ligands are broken.

Figure 3 displays a typical transmission electron micrograph of the phosphors synthesized via sol-gel pro-



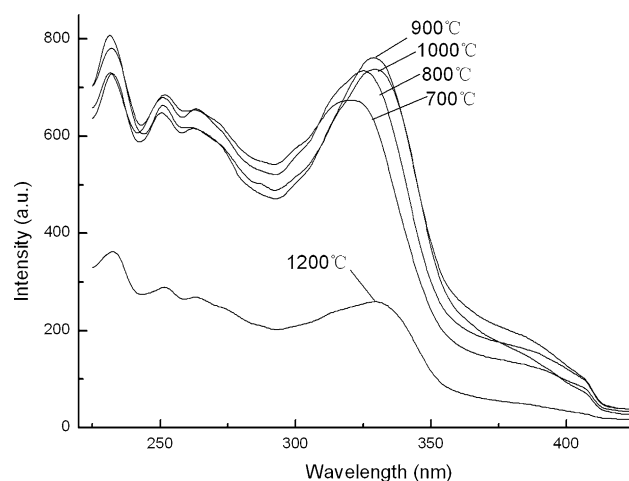
**Fig. 3** TEM photograph of particles prepared by sol-gel method (scale bar of 0.2  $\mu\text{m}$ )

cess at 700 °C. The electron micrograph reflects the basic particle morphology, where the smallest particle could be identified with the crystalline and/ or their aggregates. It reveals that the particles are nearly uniform size range about 100 nm.

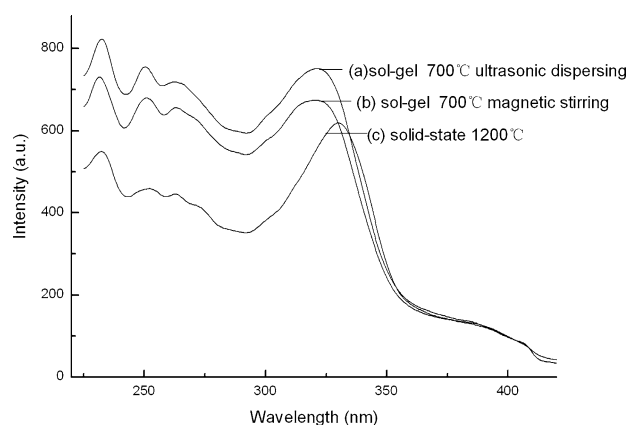
#### Luminescence properties

The excitation and emission spectra at room temperature of  $\text{CaTiO}_3: \text{Pr}, \text{Al}$  phosphors prepared by the sol-gel and the solid-state reaction methods are shown in Figs. 4–6, respectively. Figure 4 shows that the main peaks of excitation spectra of phosphors synthesized by sol-gel method at different sintering temperatures shift to shorter wavelength (from 332 to 320 nm) as the phosphors particle size decrease due to the sintering temperature from 1,200 to 700 °C. This may be associated with the quantum size effect of the nanometer phosphors, which increased the kinetic energy of the electrons and resulted in large band gap, and thus need higher energy to excite the long after-glow powders [20]. When the sintering temperature is up to 1,200 °C, the excitation strength decreases drastically. It may be due to excessive sintering and aggregation of particles.

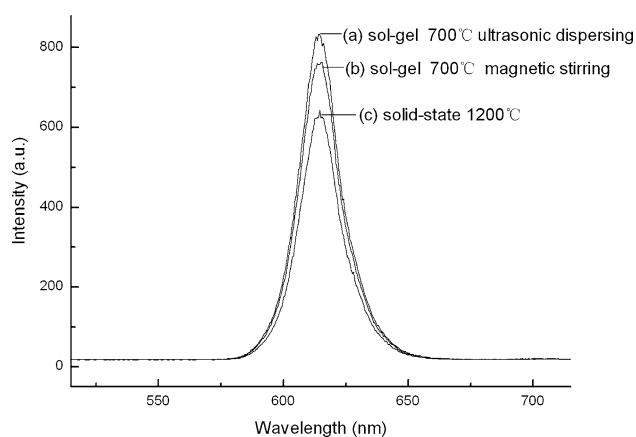
Figure 5 presents the excitation spectra of samples synthesized by different processes show dissimilar characteristics. It can be seen that by sol-gel method, the excitation peak around 330 nm shift to shorter wavelength (from 332 to 320 nm). Moreover, compared with the sample obtained by solid-state reaction method, the absorptions at short-wavelength sides are greatly increased due to different synthesis methods. The detailed reasons need to be further investigated. In addition, compared with the sample prepared using magnetic stirring by the sol-gel



**Fig. 4** Excitation spectra of  $\text{CaTiO}_3: 0.1\%\text{Pr}^{3+}, 0.1\%\text{Al}^{3+}$  prepared by sol-gel method at different sintering temperatures monitoring at 614 nm



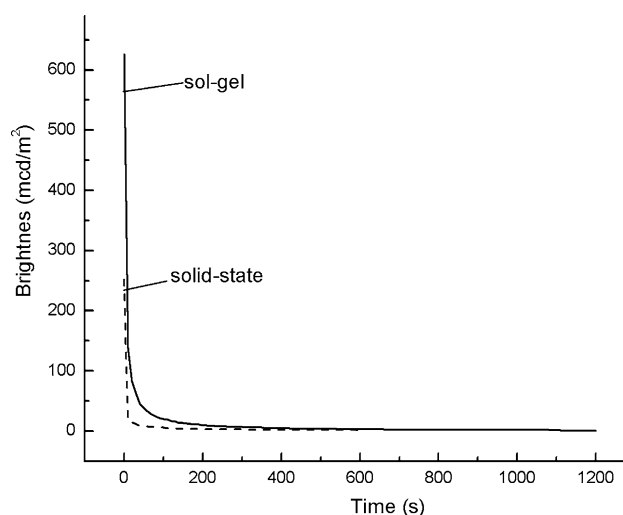
**Fig. 5** Excitation spectra of  $\text{CaTiO}_3: 0.1\%\text{Pr}^{3+}, 0.1\%\text{Al}^{3+}$  prepared by solid-state reaction and sol-gel method monitoring at 614 nm



**Fig. 6** Emission spectra of  $\text{CaTiO}_3: 0.1\%\text{Pr}^{3+}, 0.1\%\text{Al}^{3+}$  prepared by solid-state reaction and sol-gel method exciting at the wavelength of 327 nm

process, the excitation strength of the sample prepared using ultrasonic dispersing technique increases. As shown in Fig. 6, although the synthesis processes are different, all of the samples show the emission peak at the same position centered at 614 nm, corresponding to the characteristic  $^1\text{D}_2 \rightarrow ^3\text{H}_4$  transition of  $\text{Pr}^{3+}$  [1].

Figure 7 shows comparative decay behavior of the phosphor samples prepared by a sol-gel method (900 °C) and a solid-state reaction (1,200 °C). For measurement of long afterglow properties, a 9 W conventional tricolor fluorescent lamp was used to irradiate the samples for 15 min and then the lamp was switched off. After the light source was cut off, all of the phosphors showed a rapid decay and subsequently long lasting phosphorescence. From the decay curves of the phosphors shown in Fig. 7, it is observed that the initial luminescent intensity and decay time of phosphors are different from each other. The observed enhancement of initial intensity and decay time of samples prepared by sol-gel method can be attributed to



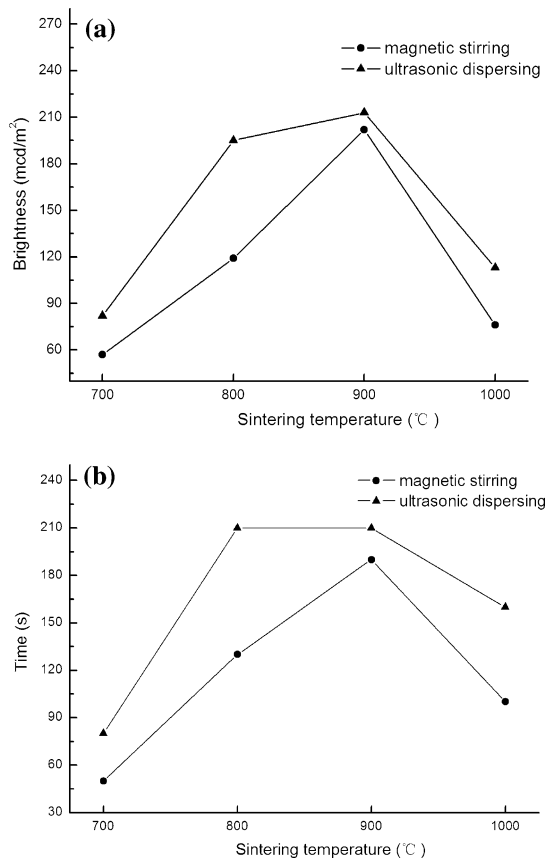
**Fig. 7** Decay curves of  $\text{CaTiO}_3: 0.1\%\text{Pr}^{3+}, 0.1\%\text{Al}^{3+}$  prepared by solid-state reaction and sol-gel method

that the sol-gel processes improve the homogeneity of the atomic repartition and thus facilitate intergranular migrations of Ca and Ti atoms, even at lower temperatures than in the solid state [16].

The relationship between red long afterglow properties of samples at room temperature and sintering temperature is shown in Fig. 8. At 10 s after the light source was switched off, the brightness of samples synthesized using magnetic stirring and ultrasonic dispersing by sol-gel processes are shown in Fig. 8a. When the brightness of the samples decreased to 10  $\text{mcd}/\text{m}^2$ , the afterglow durations are shown in Fig. 8b. Figure 8 implies that the long afterglow properties of samples prepared using the ultrasonic dispersing technique have been enhanced at various sintering temperatures. With the sintering temperature increasing from 700 to 900 °C, the intensity and decay time increase due to the improvement of the crystallinity. This result is consistent with the literature [17]. And, a high sintering temperature improves the intensity of the red luminescence because it favors densification of the submicrometer-size powders and contributes, to some extent, to remove some residual hydroxyl groups from the structure [16]. However, the intensity and decay time decrease drastically at the sintering temperature of 1,000 °C. It may be due to that excessive sintering and aggregation of particles have led to decreasing of the long afterglow properties.

## Conclusions

Using ethanol as solvent and citric acid as chelating agent, red long afterglow  $\text{CaTiO}_3: \text{Pr}, \text{Al}$  phosphors have been successfully synthesized by sol-gel method at the sintering temperature of 700 °C, which is about 500 °C lower than



**Fig. 8** Brightness (a) and decay time (b) of  $\text{CaTiO}_3: 0.1\% \text{Pr}^{3+}, 0.1\% \text{Al}^{3+}$  prepared by sol-gel method using magnetic stirring and ultrasonic dispersing at different sintering temperatures

the conventional solid-state reaction. Analytical results show the phosphors have formed pure  $\text{CaTiO}_3$  phase at 700 °C, the average particle size was about 100 nm and the red shift of main peaks of excitation of the phosphors occurred along with the increasing of the sintering temperature. Compared with the solid-state reaction, the luminescence properties of the samples were significantly improved. In addition, the luminous properties of the long

afterglow phosphors were enhanced via using ultrasonic dispersing technique.

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