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Combustion synthesis of $CaSc_2O_4:Ce^{3+}$ nano-phosphors in a closed system

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ABSTRACT

The $CaSc_2O_4:Ce^{3+}$ nano-phosphors were successfully prepared by a single-step combustion method at an ignition temperature as low as 200 °C in a closed autoclave using glycine as a fuel and PEG4000 as a dispersant. The samples were characterized by X-ray diffraction (XRD), photoluminescence (PL) spectroscopy, scanning electron microscopy (SEM) and transmission electron microscope (TEM). The results revealed that $CaSc_2O_4:Ce^{3+}$ nano-phosphors can be conveniently prepared at an ignition temperature as low as 200 °C, which was much lower than that in the ordinary combustion methods. The optimized ignition temperature was 220 °C. The $CaSc_2O_4:Ce^{3+}$ nano-phosphors give a uniform particle size in the range of 15–20 nm. The low ignition temperature and the addition of PEG4000 dispersant play important roles in the formation of small sized nanoparticles. The as-prepared nano-phosphors were incompact aggregates, but highly dispersed nano-phosphors can be obtained after further ultrasonic treatment. The $CaSc_2O_4:Ce^{3+}$ nano-phosphors give satisfactory luminescence characteristic benefiting from the closed circumstance, in which cerium atoms can be isolated from the oxidizing atmosphere and non-fluorescent Ce^{4+} ions can be ruled out. The present highly dispersed $CaSc_2O_4:Ce^{3+}$ nano-phosphors with efficient fluorescence are promising in the field of biological labeling, and the present low temperature combustion method is facile and convenient and can be applied as a universal process for preparing non-aggregate oxide nano-phosphors, especially those being sensitive to air at high temperature.

1. Introduction

Recently, rare-earth ions doped oxide nanophosphors have attracted much attention in the field of fluoroimmunoassay [1,2], cell detection [3], and solar cell [4] due to their stable physical and chemical properties [5] as compared to that of fluorides [6] and sulfides [7]. Highly fluorescent nano-phosphors with low particle size, even size distribution and good dispersity are needed to meet the requirements. Several techniques, such as co-precipitation [8,9], hydrothermal [10], sol–gel [11,12] and combustion method [13], have been used to prepare oxides nano-materials. Fluorescence of Ce^{3+} is usually highly efficient benefiting from its allowed *4f–5d* transitions and Ce^{3+}/Eu^{2+} doped phosphors formed a large category of commercial available phosphors. Although numerous Ce^{3+} doped nano-phosphors have been reported [14,15], serious aggregation of the nano-phosphors are always found and reports on highly dispersed Ce^{3+} doped nano-phosphors are seldom. This is because that Ce^{3+} doped phosphors are always achieved by treating the samples in reducing atmospheres at high temperature [16–20], since completely reducing of cerium to Ce^{3+} is very difficult at low temperature. This high temperature treatment always leads to serious aggregation of the nano-phosphors, which may severely limit their applications in fluoroimmunoassay and cell detection. In the present work, highly dispersed $CaSc_2O_4:Ce^{3+}$ nano-phosphors with efficient fluorescence were synthesized by a single-step combustion method at an ignition temperature as low as 200 °C. To the best of our knowledge, this is the lowest temperature reported in the combustion synthesis of Ce^{3+} doped phosphors. $CaSc_2O_4:Ce^{3+}$ was adopted in the present work since it has been reported as a very efficient phosphor and its excitation spectrum matches well with the emission spectrum of a blue GaN LED [21], which would offer facilities for many applications.

2. Experimental

2.1. Sample preparation

Samples of $CaSc_2O_4:Ce^{3+}$ were prepared with a combustion method in a closed autoclave at a temperature range of 200–250 °C. Fig. 1 presents a flowchart for the fabrication of $CaSc_2O_4:Ce^{3+}$ by the combustion process. The starting materials were Sc_2O_3 (99.99%), $Ce(NO_3)_3·5H_2O$ (99.99%), $Ca(NO_3)_2·5H_2O$ (A.R) and nitric acid (A.R). Solutions of $Ce(NO_3)_3$ (1.0 mol L^{-1}) and $Ca(NO_3)_2$ (2.0 mol L^{-1}) were prepared by dissolving the corresponding salts in distilled water. $Sc(NO_3)_3$ (2.0 mol L^{-1}) were prepared by dissolving Sc_2O_3 in nitric acid. These nitrate solutions were mixed with

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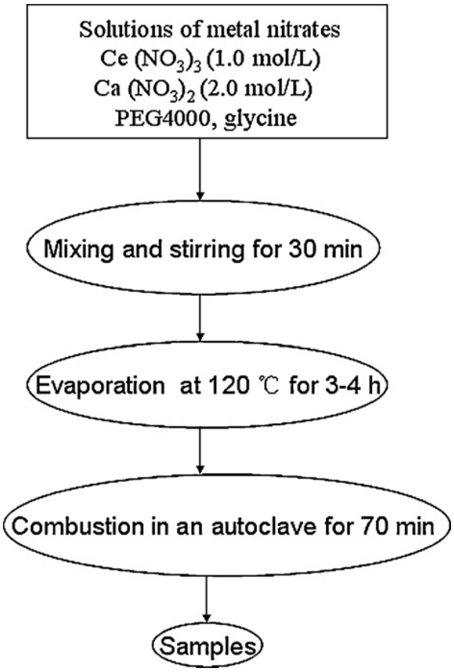

Fig. 1. Process for the fabrication of $CaSc_2O_4$:Ce^{3+} by the combustion method.

appropriate stoichiometric ratio, then appropriate amount of glycine and PEG4000 (10%) were added. The mixtures were stirred in a crucible for 30 min and heated at 120 °C for 3–4 h until gel precursors were obtained. The gel precursors were put into an autoclave and heated to a certain temperature for 70 min. A fluffy product was obtained after the combustion reaction. In the combustion reaction, glycine acted as a fuel and nitrate acted as an oxidizing reactant [22]. The glycine-to-nitrate molar ratio (G/N) was fixed at an optimized value of 5/8. The combustion reaction can be realized in the absence of PEG4000. However, it is important for the formation of small sized (less than 50 nm) nanoparticles to add PEG4000 as a dispersant. Samples of $CaSc_2O_4$:Ce^{3+} were also prepared with a co-precipitation method according to Ref. [23] for comparison.

2.2. Characterizations

The resultant phosphors were structurally characterized by X-ray diffraction (XRD) (Rigka, D/max-rB analysis with Cu Kα radiation operated at 36 kV and 20 mA. λ = 0.15406 nm, scanning speed 8°/min). Fluorescence spectra were measured using Hitachi F-4500 fluorescence spectrophotometer equipped with 150 W xenon lamps. Fluorescence decay curves were recorded with a 1 GHz oscilloscope (Agilent, model DSO6102) and samples were excited with the 337 nm lines from a pulsed N_2 laser (Stanford Research Systems, model NL100). Morphologies of samples were examined by scanning electron microscopy (SEM, XL-30, Philips), or transmission electron microscope (TEM, tecnai-10, Philips). The average particle size and particle size distribution were analyzed with a nano particle size analyzer (Zetasizer Nano-ZS). All measurements were conducted at room temperature.

3. Results and discussion

3.1. Crystal structure

Fig. 2 shows the XRD patterns of the products obtained after combustion reaction for 70 min at a temperature range of 200–250 °C. All diffraction peaks match well with those of the $CaSc_2O_4$ phase (JCPDS No. 72-1360) and no impurity peaks were detected. It indicates that doping Ce^{3+} ions do not cause any significant changes in the host $CaSc_2O_4$ structure and samples of $CaSc_2O_4$:Ce^{3+} can be prepared at an ignition temperature as low as 200 °C, which is much lower than the calcinations temperature of 1500 °C in solid state reaction [21] and 700 °C in co-precipitation method [23]. Besides glycine, citric acid, which is also a common used fuel in a combustion reaction, has also been attempted. However, no combustion reaction occurs even when the precursors were heated to 250 °C. The temperature of the combustion reaction has been optimized according to the fluorescence intensity of $CaSc_2O_4$:Ce^{3+} nano-phosphors. The optimized temperature of 220 °C was adopted in the following experiments. The crystallite size of the sample prepared at 220 °C was determined to be 20 nm from FWHM of the peak at $2\theta = 34.5°$ using Debye Scherrer formula.

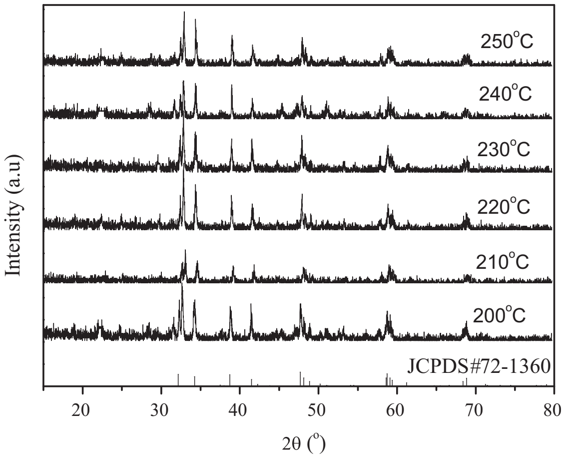

Fig. 2. XRD patterns of $CaSc_2O_4$:Ce^{3+} nano-phosphors prepared at different temperatures in comparison with that of $CaSc_2O_4$ (JCPDS#72-1360).

$$D = \frac{0.89\lambda}{\beta \cos\theta} \qquad (1)$$

where D is the average grain size of the crystallite, λ is the wavelength of CuKα (0.154 nm) radiation and β is the diffracted full-width at half-maximum (in radian) caused by the crystallites and θ is the Bragg angle.

3.2. Morphology characteristic

Combustion synthesis of inorganic compound has been extensively investigated [13,17,18,22]. The combustion process always involves the reaction between a fuel and the metal nitrate. The fuel is usually an organic compound such as glycine, urea and citric acid. The morphology of the resultant particles is greatly affected by this kind of fuel. Some dispersant such as PEG, oleic acid, and PVA may also be added to obtain special morphology. Our investigation on the morphology of $CaSc_2O_4$:Ce^{3+} nano-phosphors prepared by the combustion method also illustrated the effects of dispersant as shown in Fig. 3. It can be seen that the sample prepared in the absence of PEG4000 (Fig. 3c) is composed of aggregate particles with sizes ranging from 200 to 500 nm, and the grain size is larger than 100 nm, which is similar to the results of Ref. [23]. When PEG4000 was added in the combustion reaction, the grain size greatly decreased to 30–40 nm (Fig. 3b) for the sample sintered at 500 °C. The grain size can be further reduced to 15–20 nm (Fig. 3a) when the sample was prepared at 220 °C, which is closed to the size calculated from the XRD patterns. As we all know, PEG4000 is a nonionic surfactant, which can be absorbed onto the particles and prevent the agglomeration by reducing the surface tension. In addition, PEG4000 is also a polymer and can prevent particles from contacting with each other by steric-hindrance effect [24]. sharma et al. [25] also demonstrated particle size of Y_2O_3:Eu^{3+} would decrease in the presence of a surface modifier with appropriate content.

Although nano-phosphors with small grain size could be obtained with combustion reaction, non-aggregate nano-particles are difficult to achieve with this method since serious aggregation always occurs. To the best of our knowledge, the ignition temperature is always higher than 400 °C in the published results on combustion synthesis. However, we found the ignition

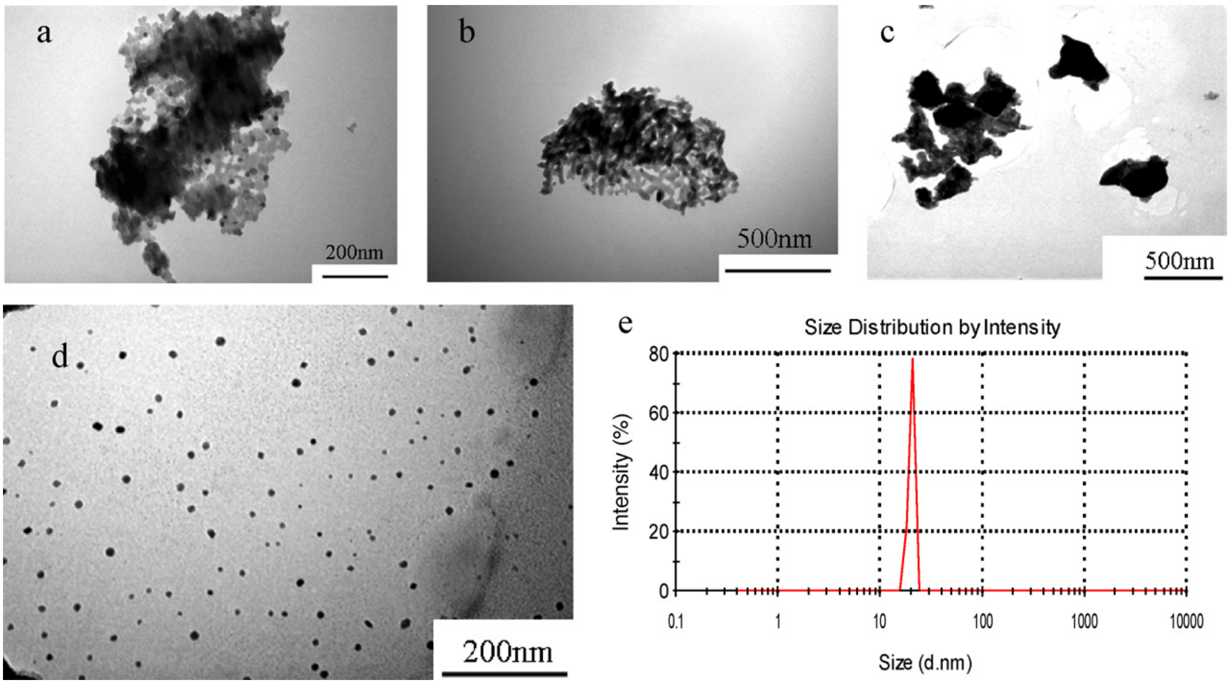

Fig. 3. TEM images of $CaSc_2O_4$:Ce^{3+} nano-phosphors prepared by the combustion method. (a) Sample with an ignition temperature of 220 °C and in the presence of PEG4000; (b) sample with an ignition temperature of 500 °C and in the presence of PEG4000; (c) sample with an ignition temperature of 220 °C and in the absence of PEG4000; (d) sample a after ultrasonic treatment; (e) Size distribution line of d.

temperature might be greatly reduced to as low as 220 °C when using glycine as a fuel. It was also noticed that the degree of aggregation for $CaSc_2O_4$:Ce^{3+} nano-phosphors may be alleviated by adopting a lower ignition temperature. As shown in Fig. 3a and b, the grain boundaries for the samples prepared at 220 °C are much clearer than those on 500 °C. Besides aggregate particles, some non-aggregate particles can also be found in Fig. 3a. It indicated that the bond strength among these nano-grains might be weaker in samples prepared at 220 °C than that prepared at 500 °C. This is reasonable since samples prepared at a lower ignition temperature would go through a much-shorted high temperature experience.

The lower degree of aggregation of $CaSc_2O_4$:Ce^{3+} nano-phosphors prepared on 220 °C can be further illustrated by the results of ultrasonic treatment. In the ultrasonic treatment, 0.05 g of the as-prepared samples was put into an ethanol solution of citric acid, and the mixture was ultrasonic treated for 2 h. After further standing for 1 h, the aggregate particles subsided on the bottom of the vessel, and the upper clear solution was used for TEM and particle size analysis. The results were shown in Fig. 3d and e. It can be seen from Fig. 3d that the particles after the ultrasonic treatment have a small size distribution, uniform morphology and good dispersity. They are basically spherical in shape and the mean size is less than 20 nm, which is in accord with the particle size distribution measured with the laser nano-particle size analyzer. Furthermore, after separating the clear solution, the aggregate particles precipitating on the bottom are dried and carefully weighted. By comparing with the initial weight of the as-prepared sample, the proportion of aggregate particles was determined to be 64% and that of non-aggregate part to be 36%. Similar treatments were also applied to $CaSc_2O_4$:Ce^{3+} nano-phosphors prepared at 500 °C, but almost no non-aggregate particles are obtained, indicating that ultrasonic treatment have no effect on these samples.

3.3. *Fluorescence properties of $CaSc_2O_4$:Ce^{3+} nano-phosphors*

Fig. 4 displays the excitation and emission spectra of $CaSc_2O_4$:Ce^{3+} nano-phosphors prepared by combustion method. It is noted that both the profiles and positions of the spectra are similar to $CaSc_2O_4$:Ce^{3+} phosphors prepared by co-precipitation method [23], which are also shown in Fig. 4. The $CaSc_2O_4$:Ce^{3+} nano-phosphors give the excitation band centered at 450 nm and the emission band peaked at 520 nm. Fluorescence decay curve of the $CaSc_2O_4$:Ce^{3+} nano-phosphor monitored at 520 nm was also presented as inset of Fig. 4. By fitting the fluorescence decay curve with an exponential function, a lifetime of 57.4 ns was determined. The lifetime value was in accordance with the typical range of Ce^{3+}: *d-f* transition [26], indicating that the emission originated from the *d-f* transition of Ce^{3+}.

As Zhang and Shimomura reported [21,23], fluorescence intensity of Ce^{3+} doped phosphor obtained from direct combustion reaction is usually unsatisfactory owing to the partial oxidation of Ce^{3+} ions. Re-calcinations in a reducing atmosphere at an elevated temperature are always required to get the satisfactory

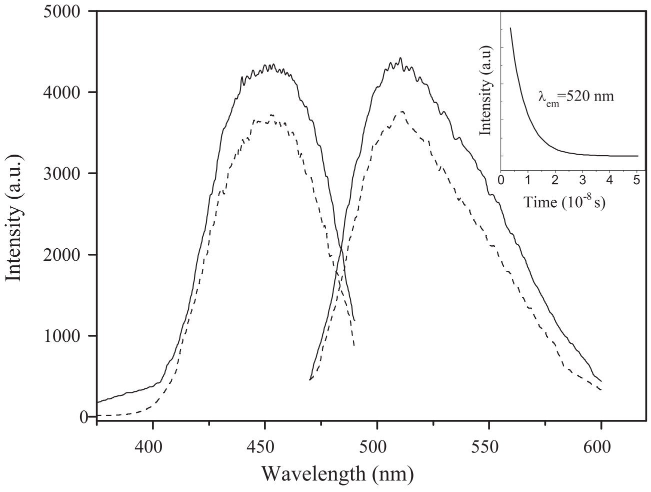

Fig. 4. Excitation (left, λ_{em} = 510 nm) and emission (right, λ_{ex} = 450 nm) spectra of $CaSc_2O_4$:Ce^{3+} prepared by combustion (——) and co-precipitation (……) methods. Inset: Fluorescence decay curve of the $CaSc_2O_4$:$0.01Ce^{3+}$ nano-phosphor.

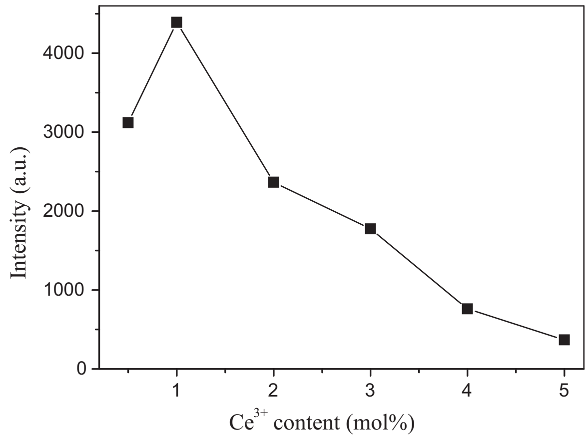

Fig. 5. Dependence of fluorescence intensity of $CaSc_2O_4:Ce^{3+}$ nano-phosphors on Ce^{3+} content.

fluorescence intensity. However, our result is different from these previous reports, and the fluorescence intensity of phosphors prepared by combustion method is slightly stronger than that by co-precipitation method. We suggest that the satisfactory fluorescence properties may benefit from the unique experimental setup in the present combustion reaction. The combustion reaction reported previously always occurred in an opened vessel and oxidation of Ce^{3+} by air was inevitable. But in our experiment, the samples were sealed in a closed autoclave all along the combustion reaction until they were cooled to room temperature. The local reducing atmosphere in the autoclave, which is essential for the formation of trivalent cerium ions, could be conveniently achieved and maintained by adjusting the ratio between the glycine and the metal nitrate.

The Ce^{3+} content in $CaSc_2O_4:Ce^{3+}$ nano-phosphors have also been optimized according to the fluorescence intensity as shown in Fig. 5. The optimized Ce^{3+} content is 1 mol% which was in accord with the result of co-precipitation method [23].

Fluorescence properties of $CaSc_2O_4:Ce^{3+}$ nano-phosphors after ultrasonic treatment were also investigated. The process of the ultrasonic treatment is identical to that described in Section 3.2. Fig. 6 shows the fluorescence spectra of both the colloidal water solution of $CaSc_2O_4:Ce^{3+}$ nano-phosphors before the ultrasonic treatment and the clear colloidal solution after the ultrasonic treatment. It can be seen that they have very similar spectrum profile in spite of the fluorescence intensity of the former is about 3.2 times of the later. The ratio between the two fluorescence intensities agrees well with the weight proportion of non-aggregate part after ultrasonic treatment, which has been determined to be 36%. This indicated that the fluorescence of the present $CaSc_2O_4:Ce^{3+}$ nano-phosphors were very stable in water even after long time ultrasonic treatment, which is very important for a bio-label application.

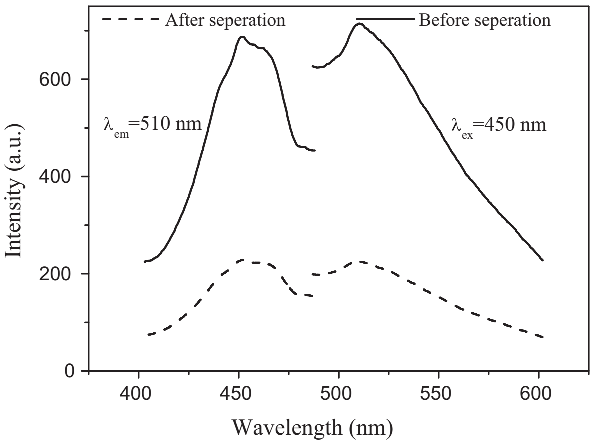

Fig. 6. The comparison of fluorescence intensity of samples before and after separation.

4. Conclusions

$CaSc_2O_4:Ce^{3+}$ nano-phosphors were successfully synthesized with a novel combustion method. The combustion reaction was carried out in a closed autoclave at an ignition temperature as low as 200 °C with glycine as a fuel and a reducing agent, metal nitrates as oxidizers and PEG4000 as a dispersant. The results reveal that the samples prepared at an ignition temperature of 220 °C and Ce^{3+} content of 1 mol% give the strongest luminescence. The XRD, PL, SEM and TEM results indicate that the present $CaSc_2O_4:Ce^{3+}$ nano-phosphors have a smaller grain size and less agglomeration than that of usual combustion methods. Non-aggregate $CaSc_2O_4:Ce^{3+}$ nano-particles with an average size smaller than 20 nm can be obtained after further ultrasonic treatment. The $CaSc_2O_4:Ce^{3+}$ nano-particles are also very stable in water and have satisfactory fluorescence properties, and are promising in application in the field of biological labeling. The present single-step combustion method is facile and convenient, and can be developed to a universal method for the preparation of nanosized oxide materials, especially those sensitive to oxygen in air.

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