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# Facile preparation of $Y_{2.9}Ce_{0.1}Al_5O_{12}$ nano-phosphors without photobleaching behavior

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ABSTRACT

$Y_{2.9}Ce_{0.1}Al_5O_{12}$ (YAG:$Ce^{3+}$) phosphors with $80 \pm 5$ nm are successfully prepared by hydrothermal processing followed by the post annealing process in Ar/15%$H_2$ atmosphere. The emission intensity of the as-prepared YAG:$Ce^{3+}$ nano-phosphor is as high as with that of the ~15 μm YAG:$Ce^{3+}$ commercial phosphor. Meanwhile, the YAG:$Ce^{3+}$ nano-phosphors prepared in both Ar/15%$H_2$ and air atmosphere show same stable emission intensity under continuous irradiation of blue excitation light, although this photobleaching behavior is easily observed for YAG:$Ce^{3+}$ nano-phosphors in the literatures. Photobleaching is probably suppressed by complete crystallinity due to the post annealing process and solid morphology due to the hydrothermal process in the present work.

## 1. Introduction

Yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG), activated with trivalent cerium $Y_{3-x}Ce_xAl_5O_{12}$, has been recognized as an excellent phosphor satisfactorily applied in white phosphor-based LED commercial market [1]. It had been found that for LED applications, nano-phosphor YAG was better than fine-powder phosphors with a larger particle size because nano-phosphors could reduce internal scattering when they were coated onto a bare LED surface [2,3]. In order to obtain pure YAG phase with nanometer particle size and narrow size distribution, various soft-chemical synthesis techniques have been used, such as the precipitation method, glycothermal method, sol–gel method, spray-pyrolysis, and the combustion process. One of the major problems in preparing nano-phosphors is that the preparation of nano-phosphors usually requires many additives and complicated processes, which are difficult to achieve in a large industrial scale [4]. Besides, several workers have also reported another problem in using nano-phosphor, which is that nanosized phosphors exhibit a peculiar photobleaching behavior, i.e., a decrease in the emission intensity under continuous excitation [3].

In this paper, $Y_{2.9}Ce_{0.1}Al_5O_{12}$ (YAG:$Ce^{3+}$) nano-phosphors were prepared by the hydrothermal method, and their microstructure and luminescence properties, especially photobleaching behavior were investigated. The hydrothermal method has been recognized as an effective, direct and low-temperature route for preparing ultrafine powders. By this method, heterogeneous powder formed from direct precipitation of metal salt and sodium hydroxide or ammonia is used as its precursor, and the as-prepared particles have a wide and uncontrollable size distribution. To improve the homogeneous precipitation process in this work we use the mixed solution of metal salt and urea as reactant. It is known that urea has been used as the ligand source for ammonia in a traditional homogeneous precipitation method. During urea hydrolysis, the precipitates with narrow size distribution are formed via homogeneous nucleation. Hence, homogeneous precipitation process using urea can provide dispersion comparable to the conventional precipitation using ammonia because of the homogeneous nucleation in urea precipitation. The homogeneous precipitation and the hydrothermal method is particularly suitable for large-scale production because it is a simple and inexpensive process for the preparation of ultrafine powders with narrow size distribution.

## 2. Experimental

The precursor solution was prepared by dissolving powders of yttrium nitrate ($Y(NO_3)_3 \cdot 6H_2O$, 99.99%), aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$, 98.0%) and cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$, 99.99%) into pure water. These metal salts were dissolved according to stoichiometric proportion of $Y_{2.9}Ce_{0.1}Al_5O_{12}$ and

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the total cation concentration was 1 mol/L. Then 4 mol/L urea was added into the above solution and then heated at 85 °C for 4 h to prepare a homogeneous precipitated hydroxide gel as the precursor for the hydrothermal process. The precursor gel was then transferred to a 500 L zirconium steel reactor. This reactor was sealed and heated at 240 °C for 20 h through hot oil heating system. The precipitated powders were filtered, washed, and dried at 100 °C. Finally, the powders were calcined at 1200 °C for 4 h in a furnace directly under Ar/15%$H_2$ atmosphere in order to obtain the YAG:$Ce^{3+}$ powders. For comparison, the YAG:$Ce^{3+}$ powders calcined under air atmosphere were also prepared.

The samples for characterization were obtained by using point-quarter sampling method to be representative. The phase development in the as-prepared powders was characterized by X-ray diffraction (XRD, Rigaku Geigerflex D/Max 2200) using Cu K$\alpha$ radiation. The morphology and size of the powders were checked using scanning electron microscopy (SEM, Philips XL 30S FEG). SEM samples were prepared by sonicating the as-prepared particles suspended in alcohol, and a few drops of the suspension were deposited onto an aluminum stud, dried, and sputter-coated with gold. Particle size and distribution were obtained by measuring the cross diagonals of ~50 particles from SEM images. The impurities in the powders were confirmed by chemical analysis and inductively coupled plasma atomic emission spectrometer (ICP–AES; Optima 3000). Specific surface area was measured using a BET surface area analyzer (Micromeritics Flowsorb 2300) with a gas mixture containing a 70:30 M ratio of helium to nitrogen. The optical properties of the phosphor powders were measured by spectrofluorophotometry (PerkinElmer LS50B, Norwalk, CT) under the excitation by blue light produced by a Xe flash lamp. The quantum efficiency (QE) was analyzed by an absolute photoluminescence quantum yield measurement system (C9920-02, Hamamatsu, Hamamatsu Electronic Press Co., Ltd., Shizuoka, Japan) at room temperature. The luminescence of the samples relative to that of the ~15 μm size YAG:$Ce^{3+}$ phosphor which was the commercial product prepared by solid-state reaction, were shown in the spectra.

## 3. Results and discussion

The XRD results as shown in Fig. 1(a) indicate that the powder calcined under Ar/15%$H_2$ atmosphere (for the sake of illustration, hereafter referred to as YAG : $Ce^{3+}_{Ar/15\%H_2}$) and the powder calcined under air atmosphere (YAG:$Ce^{3+}_{Air}$) are crystallized as a single-phase $Y_3Al_5O_{12}$, and no $CeO_2$ phase is detected. Fig. 1(a) also indicates that the unannealed YAG powder (YAG:$Ce^{3+}_{unannealed}$) is amorphous. The ICP and chemical analysis of the powders proves that there are no traces of other impurities. It was reported that YAG phase could be obtained at a temperature higher than 1600 °C in the conventional solid-state reaction for $Y_2O_3$–$Al_2O_3$ binary systems [5]. However, pure YAG phase is produced for samples prepared in this work at a calcination temperature of 1200 °C, about 400 °C lower than the conventional solid-state method. The SEM observations shown in Fig. 1(b) suggest that the YAG : $Ce^{3+}_{Ar/15\%H_2}$ powder has a particle size of $80 \pm 5$ nm, and the particle is quasi-spherical and solid. The particle size of YAG : $Ce^{3+}_{Ar/15\%H_2}$ powder, determined from the BET measurement, is 76 nm, which could be derived from the formula $6/(S_{BET} \cdot \text{density})$ [6]. These two particle sizes are close to each other, confirming that the YAG : $Ce^{3+}_{Ar/15\%H_2}$ powder is reasonably monodispersed and very solid. It must be noted that the intermediate product (YAG:$Ce^{3+}_{unannealed}$) and YAG:$Ce^{3+}_{Air}$ powder have the same particle size observed from SEM (Fig. 1(b)) and calculated from BET result as YAG : $Ce^{3+}_{Ar/15\%H_2}$ samples. Thus, the intermediate YAG:$Ce^{3+}_{unannealed}$ sample and the YAG:$Ce^{3+}_{Air}$ sample are also monodispersed and solid.

Fig. 2 shows the PLE and PL spectra of the YAG : $Ce^{3+}_{Ar/15\%H_2}$ sample, ~15 μm YAG:$Ce^{3+}$ commercial sample, the YAG:$Ce^{3+}_{Air}$ sample and the YAG:$Ce^{3+}_{unannealed}$ sample. The first three samples have the same excitation peaks at 345 and 450 nm in the PLE spectra and the same emission peak at 530 nm in the PL spectra, and the last sample has no excitation and emission peak. The YAG : $Ce^{3+}_{Ar/15\%H_2}$ sample has the nearly high PL intensity with the ~15 μm commercial sample and 5 times higher than the YAG: $Ce^{3+}_{Air}$ sample. The QE results also show the same tendency. The QE of the YAG : $Ce^{3+}_{Ar/15\%H_2}$ sample, YAG:$Ce^{3+}$ commercial sample and YAG:$Ce^{3+}_{Air}$ sample is 59%, 68% and 20%, respectively. It was found

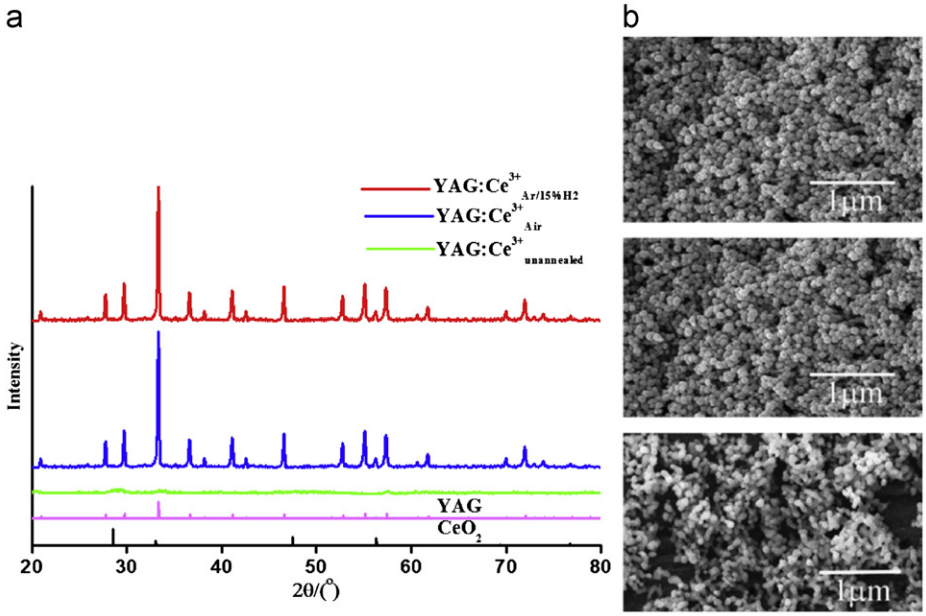

**Fig. 1.** XRD pattern (a) of the YAG : $Ce^{3+}_{Ar/15\%H_2}$; YAG:$Ce^{3+}_{Air}$; and YAG:$Ce^{3+}_{unannealed}$ nano-phosphors and their SEM image, and (b) top: YAG : $Ce^{3+}_{Ar/15\%H_2}$; middle: YAG:$Ce^{3+}_{Air}$; and bottom: YAG:$Ce^{3+}_{unannealed}$.