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Surface characteristics of $Y_3Al_5O_{12}$:Ce^{3+} phosphor with greatly enhanced photoluminescence after chemical defect-selective etching

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Abstract: The surface of a commercial $Y_3Al_5O_{12}$:Ce^{3+} phosphor was modified by 99% NH_4F+CH_3COOH solution in a supersonic bath with water temperature of 80 ºC for 4 h. The scanning electron microscopy (SEM) results showed that the edge angles were not as sharp as the unmodified particles and the flat surfaces turned rough with many micro-structures covered. Positron lifetime measurements quantitatively showed that surface defects were removed away by more than 50%. As a result, the photoluminescence determinations showed that the backscatter loss was reduced by 4.2% and the emission power was enhanced by 5.6% after the surface modification. The conversion efficiency was greatly improved from 47.3% to 51.1%, as presented by the fluorescence images. Therefore, it would be greatly helpful for the improvement of efficiency, transparency and stability of pc-LED. Moreover, this method was significantly suitable for mass production due to its easy operation and low cost.

Keywords: YAG phosphor; surface modification; wet etching; solid state reaction; rare earths

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Nowadays, the phosphor converted light emitting diode (pc-LED) still leads the development of solid state lighting which will be the next generation of lighting. Since 20% of electricity generation in the world is consumed for illumination every year[1], raising the efficiency of pc-LED is vital for energy conservation. As we know, the popular pc-LED is made of blue LED chip and YAG:Ce^{3+} phosphor[2], so the efficiency of a pc-LED is mainly determined by the one of the blue LED chip as well as the YAG:Ce^{3+} phosphor. Currently, because of advantages of mass production and low cost, the solid state reaction method is used to prepare YAG:Ce^{3+} phosphor in industry. However, in order to achieve micro-size particles, it is necessary to repeat the process of milling and grinding, which brings many edge angles in the surface and damages surface crystal lattice structure and causes surface defects[3]. As a result, it decreases the conversion efficiency of phosphor and increases the scattering loss. In order to avoid the milling and grinding process, extensive researches to fabricate phosphors in laboratories were studied, such as spray pyrolysis[4], co-precipitation (CP)[5], sol-gel (SG)[6,7], combustion (CB)[8,9], hydrothermal[10] and chemical wet etching[11,12] methods. Although it was reported that phosphors prepared by some of those methods showed a higher efficiency, more spherical particles or smaller size than those by solid-state reaction[13], none of those methods is brought into the industrial manufacture due to the low yield rates, severe agglomeration or high cost. Surface modification is a promising method to improve the feature of phosphors. For instance, Nien et al.[3] reported an improved photoluminescence of YAG:Ce^{3+} phosphor by silica coating. The increased emission intensity resulted from the inhibition of excitation energy transferred to quenching centers or surface states and higher light extraction from the encapsulating layer (SiO_2) on the surface of luminescent YAG:Ce^{3+} powders. Nevertheless, the coated particles still contained many defects which are critical to the luminescent intensity and thermal stability of phosphors. That is why many researchers have investigated the interactions between Ce^{3+} and defects in YAG both by theory[14,15] and experiments[16–18] for years.

In this paper, the chemical defect-selective etching method was used to modify the surface of commercial YAG:Ce^{3+} phosphor particles with a typical size of 15 μm. After the surface modification, the phosphor presents a higher photoluminescence (PL) and less backscatter due to the removal of surface defects and less sharp edge angles. These features can greatly improve external quantum efficiency and stabilization of pc-LED. Moreover, this method is remarkably appropriate for mass commercial production due to its easy operation and low cost.

1 Experimental

The experimental procedure was as follows: 1 g of YAG phosphor was added into 200 mL of 99% NH_4F+ CH_3COOH (1:1) aqueous solution. The mixture was then

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incubated in a supersonic water bath with water temperature kept at 80 ℃. Four hours later, the phosphor particles were filtered and washed by deionized water followed by ethyl alcohol. Finally, the phosphors were dried in an oven at 120 ℃ for three hours. Phosphor samples before and after modification were named as Y_a and Y_m, respectively.

The field emission scanning electron microscopy (FE-SEM) measurement was carried out to observe the morphology of the phosphor particles by using a field-emission gun scanning electron microscope (FEG-SEM) Hitachi S4800. The Cu Kα X-ray diffraction (XRD) (Bruke, D8 ADVANCE) was performed on the phosphor powders, scanning from $20° \le 2\theta \le 80°$ with step width of 0.01°, to analyze the crystalline quality and phase of phosphor particles before and after surface modification. Positron lifetime measurements were performed to probe the density of surface defects of YAG:Ce^{3+} phosphor particles before and after the modification using a conventional fast-slow coincidence system consisting of two BaF_2 scintillator detectors (PALS, Public Technology Service Center, Institute of High Energy Physics, Chinese Academy of Sciences). The prompt time resolution of the system using a ^{60}Co source with ^{22}Na gate was 191.196 ps. Two of the same samples were tightly clamped in on both sides of ^{22}Na radioactive sources, forming a sandwich structure. The lifetime spectra were de-convoluted using the code LT 9.0 software[19]. Appropriate source correction was made (subtract source component: 382ps, 24.558%).

The fluorescence of phosphor particles before and after the defect-selective wet etching were visualized with the fluorescence optics of an Axio ScopeA1 microscope (Zeiss, Oberkochen, Germany) at magnification times of 200× and under excited light with wavelength of 470 nm. The images were captured using an AxioCam digital camera interfaced with a computer.

PL spectra were recorded in the wavelength range from 380 to 780 nm by a spectrometer connected with an integrating sphere. The sketch of the PL system is shown in Fig. 1. The compact phosphor samples with a thickness of 1 mm were prepared by using a standard mask. Phosphor samples were positioned in the center of the integrating sphere. The solid state laser has the wavelength of 440 nm with full width at half maximum (FWHM) of 3 nm and the luminous power of 28.8 mW with power stability of less than 1%. The spectrum of the laser is shown in the inset of Fig. 1.

2 Results and discussion

Fig. 2 shows the SEM images of the shape of the YAG phosphor particles before and after the surface modification. Firstly, comparing Fig. 2(a) and (d), there is no obvious difference in typical size of the phosphor particles, which suggests that only a thin layer on the surface of phosphor particle is etched away by 99% NH_4F+ CH_3COOH aqueous solution during 4-hour incubation in a supersonic water bath of 80 ℃. Secondly, the edge angles of the modified particles are less sharp than that of unmodified particles which is shown clearly in Fig. 2(b) and (e). Thirdly, another observation presented in Fig. 2(c) and (f) is that the smooth surface of the phosphor particles turns rough after the surface modification.

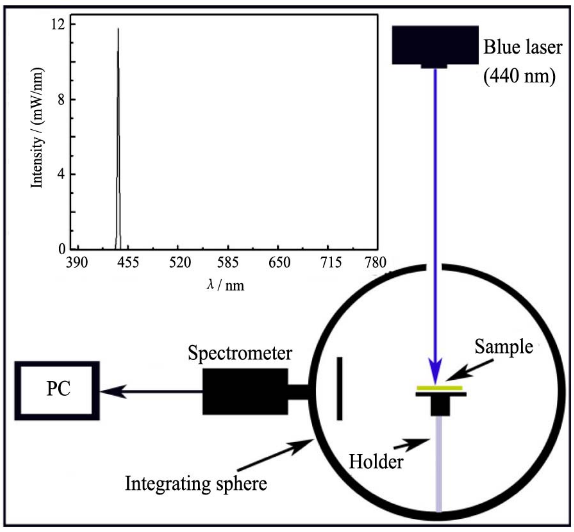

Fig. 1 Sketch of PL system (the inset is spectrum of the blue laser)

NH_4F and CH_3COOH solutions are widely used for surface modification of materials due to their defect-selective etching ability[20,21]. It is established that the edge angles of particles contain many kinds of defects, so they are more easily etched by the solution and become less sharp than that of particles without modification. As we know, some surface crystal structures are damaged in the milling and grinding process. Therefore, these damaged regions which contain bad crystal lattices are more easily etched by the solution than the undamaged parts of the surface, as seen in Fig. 2(f). The SEM results indicate that NH_4F+CH_3COOH solution has a very low etching rate and good defect-selective etching ability for YAG phosphor. The chemical etching process can be demonstrated through the following reaction function.

$$Y_xAl_yO_z+3(x+y)NH_4F \rightarrow xYF_3+yAlF_3+3(x+y)NH_3+zH_2O \qquad (1)$$

The chemical formula $Y_xAl_yO_z$ stands for defective parts of YAG phosphor particle surface. The reaction products YF_3 and AlF_3 are removed away from the surface under the supersonic effects and dissolved into CH_3COOH solution. Therefore, NH_4F+CH_3COOH solution can totally etch $Y_xAl_yO_z$ parts away without damaging the good crystal surface with a suitable reaction time.

Fig. 3 shows the XRD spectra of the YAG phosphor before and after the surface modification. Comparing the two XRD spectra, no different peaks are found. The spectra show only diffraction peaks different from

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