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Synthesis of Y_2O_3 phosphor by a hydrolysis and oxidation method

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Abstract: A novel and convenient hydrolysis and oxidation method was first used in preparation of carbon contained Y_2O_3 phosphor powders. The alloy was hydrolyzed in deionized water and the obtained $Y(OH)_3$ powders were heat treated in air atmosphere. The final products - Y_2O_3 powders were micron clusters which were aggregated by hundreds of nanoparticles with the size of about 5 nm. The chemical composition, structural and morphological features of the samples were characterized by means of X-ray powder diffraction (XRD) analysis, transmission electron microscopy (TEM), Fourier-transform infrared (FT-IR) spectra, X-ray photoelectron spectra (XPS) and carbon sulfur analyzer. The obtained powders showed good bluish-white photoluminescence (PL) emissions (ranging from 430 to 600 nm, peaking at 468 nm and 578 nm) under the xenon light excitation. The luminescent mechanism was ascribed to the carbon impurities in the Y_2O_3 host.

Keywords: yttrium oxide; hydrolysis and oxidation method; phosphors; optical properties; rare earths

Rare earth sesquioxide phosphor compounds have attracted considerable attention due to their important properties and potential applications in various devices, such as white light emitting diodes (WLED) phosphors, scintillation phosphors, upconversion phosphors, and laser medium[1]. Thereinto, Y_2O_3 phosphors are widely studied in industry and academia. It is known that Y_2O_3 is one of the multifunctional materials that give rise to many application areas and it continues to do so, thanks to its properties that can be tuned as needed[2]. In order to provide fine and cheap phosphor, extensive studies have been carried out on Y_2O_3, which has excellent optical properties and is easily obtained.

Although Y^{3+} is non-luminous, because of lack of 4f electrons, which plays a key role in the luminescence properties of rare earth materials, Y_2O_3 is a common luminescent host material due to its simple lattice structure, which makes other elements doped into Y_2O_3 lattice and perform excellent luminescent properties[3]. In particular, Eu^{3+}, Tb^{3+} and Dy^{3+} doped Y_2O_3 phosphors have been paid more attention because of their high luminous intensity and chemical stability[4–6]. These three ions doped Y_2O_3 phosphors emit red, green and yellow light, respectively. WLEDs are regarded as the fourth generation solid-state light, which have huge market. And blue emitting phosphors are an important group of the WLEDs[7]. But at present, compared to other color emitting materials, the studies of blue-emitting materials are relatively less, especially in Y_2O_3, although they have gained more and more attention recently. It was reported by Hao et al.[8] that Tm^{3+} doped Y_2O_3 phosphor exhibited good blue emission. Another report is that Bi doped Y_2O_3 phosphor also shows intense blue emissions[9]. Nowadays, the study of other elements doped Y_2O_3 blue-emitting phosphor become a research focus. It was reported by Lin et al.[10] that carbon contained Y_2O_3 phosphor prepared by sol-gel method has good luminescent property, showing an intense bluish-white emission. Another report is about flower-like Y_2O_3 phosphor fabricated by an ionic liquid-assisted method, which also has bluish-white photoluminescence properties[11].

Traditional processes for synthesis of Y_2O_3 phosphors mainly include: sol-gel[10], hydrothermal[12,13], precipitation[9] and spray pyrolysis[8]. Recently, a novel hydrolysis and oxidation method has been developed by our group to prepare CeO_2 nanopowers[14,15] and $La(OH)_3$ nanopowders[16]. Compared with other processes, the hydrolysis and oxidation method, which was considered as a "green" method without the usage of chemical agent[14], has many advantages, such as homogeneous mixing, large yield, easily applicable for industrial use, etc. However, this method has firstly been reported in the preparation of Y_2O_3 powders.

This paper described carbon contained Y_2O_3 powders successfully prepared via the hydrolysis and oxidation method. The obtained sample showed an intense bluish-

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white light emission (ranging from 430 to 600 nm, centered at 468 nm and 578 nm) under the xenon light excitation.

1 Experimental

1.1 Synthesis of Y_2O_3 powders

Pure yttrium (>99 wt.%) and graphite powders were put into a high density graphite crucible and melted in a vacuum induction melting (VIM) furnace. The mass ratio of carbon to yttrium was 12:1. Vacuum of the order of less than 6×10^{-2} Pa was created and then argon was purged in order to create an inert atmosphere inside the furnace. This process was carried out twice to remove the air in the furnace completely. And then the starting materials were heated until melting. Each time increase 10 kW and maintain for 5 min until up to 50 kW. After carbon was fully dissolved in the melt, the melt was cooled with fast rate in order to obtain the alloy yttrium carbide. The alloy was crushed into powders with particle diameter less than 1.0 mm. Then the alloy powder was transferred into deionized water with 1:20 mass ratios under agitation for 24 h at room temperature. After filtering, being washed three times by deionized water and then dried at 80 ºC for 8 h in an oven, brown powders were obtained. These powders were directly annealed in air atmosphere at various temperatures (200–1000 ºC) for 2 h to obtain Y_2O_3 powder samples. The samples prepared by the hydrolysis and oxidation process were denoted as Y*x* series, where *x* is the annealing temperature. Such as Y200 sample, where 200 means it was annealed at 200 ºC. We also denote Y00 as the sample without calcination.

1.2 Characterization

The phases of the synthesized products were analyzed by X-ray powder diffraction (D/max-rc, using Cu Kα radiation, λ=0.15405 nm). Transmission electron microscopy (TEM, JEOL, JEM-2010F, 200 kV) was performed to investigate the morphology of the powders. Thermal behavior of the sample was tested by means of thermogravimetry and a differential scanning calorimeter (TG-DSC, STA409PC). The optical properties of the synthesized products were analyzed by the photoluminescence spectrum (PL, F-70000) using a 355 nm xenon lamp as the excitation source. The infrared spectrum was obtained by means of Fourier transform infrared spectroscopy (FT-IR, VERTEX70). The X-ray photoelectron spectra (XPS) were recorded on an ESCALAB 250Xi X-ray photoelectron spectrometer. The carbon content was analyzed by a carbon sulfur analyzer (CS 600CR).

2 Results and discussion

2.1 XRD analysis

The XRD patterns of the samples calcinated at different temperatures are shown in Fig.1. The results show that the Y00 and Y200 are nearly amorphous. The crystallization peaks appear around 400 ºC and the sample crystallizes well at 600 ºC. These XRD data are entirely consistent with the PDF card No. 65-3178, which reveals that the samples are cubic Y_2O_3. No other phase is detected. With the increase of the calcination temperature, the diffraction peaks become sharp and high, which means better crystallinity for higher temperature annealing samples.

2.2 TEM and HRTEM analysis

Typical TEM and HRTEM images of Y400, Y600, Y800 and Y1000 are shown in Fig. 2. The samples of Y400, Y600, Y800 and Y1000 are all aggregated to form clusters of a few hundred nanometers, as depicted in Fig. 2(a), (b), (c) and (d), respectively. Each cluster is aggregated by hundreds of small particles due to their high surface free energy. Fig. 2(e) is the HRTEM lattice image corresponding to Fig. 2(a). As can be seen, these small particles are constituted by small grains and surrounding amorphous component. Fig. 2(f), (g) and (h) are the HRTEM lattice images corresponding to Fig. 2(b), (c) and (d), respectively. With the increasing temperature of heat treatment, the size of these crystalline grains become larger and larger, while the amorphous component disappears eventually. It means that the samples for higher annealing temperature have better crystallinity.

In Fig. 2(e), some interplanar distances are about 0.265 nm, which correspond to the (400) plane of the cubic Y_2O_3 phase and this reveals that the small grains are cubic Y_2O_3. In Fig. 2(f), some interplanar distances are about 0.228 nm and 0.263 nm, which correspond to the (332) and (400) plane of the cubic Y_2O_3 phase, respectively. This also reveals that these grains are cubic Y_2O_3 phase. The interplanar distances of 0.268 and 0.423 nm correspond to (400) and (211) plane of the cubic Y_2O_3 phase, respectively, as can be seen in Fig. 2(g) and (h). These results also reveal that these grains are cubic Y_2O_3 phase when the annealing temperature ranges from 400–1000 ºC.

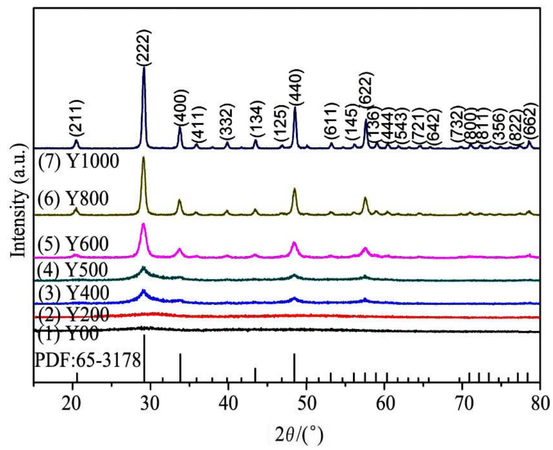

Fig. 1 XRD patterns of the samples