Direct Synthesis and Intense Luminescence of Y_2O_3:Eu Nanophosphors by Complexation Combustion

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In this paper, we report the synthesis of high-luminance Y_2O_3:Eu nanocrystal through a citrate–nitrate complexation combustion method at a low temperature of 200–280 °C. The as-combusted Y_2O_3:Eu phosphors are almost equiaxed crystallites with an average size of 30–40 nm, and have an intense red luminescence. The present fuel-deficient method suggests that by control of the ratio of citric acid to nitrates, it is valuable for the fabrication of Y_2O_3 nanoparticles without heat treatment. This process should be applicable to a wide range of nanocrystal oxides.

Eu-doped Y_2O_3 phosphor is a well-known red phosphor used in luminescence lamps and cathode-ray tubes (CRT), and it is also a candidate for red phosphor used in displays such as plasma display panels (PDP) and field emission displays (FED).[1] In the past few years, a number of different techniques, such as the sol–gel method,[2] combustion synthesis,[3,4] and coprecipitation technique,[5] have been developed to synthesize Y_2O_3 nanocrystals. In particular, combustion synthesis is attractive due to direct crystallization of small-sized particles, low process temperature, and reduced time consumption.[6,7] However, few papers have been reported on the fabrication of Y_2O_3 powders by citric acid combustion method. Citric acid is widely used as a complexation agent for sol–gel. It can increase the solubility of metal cations, thereby preventing preferential crystallization as water in the precursor solution evaporates.[8] Unfortunately, formation of an amorphous material is favored when citric acid is used.

In the present paper, a complexation combustion method for the preparation of Y_2O_3:Eu nanophosphors is reported, and Y_2O_3 nanophosphors can be synthesized directly through the combustion without heat treatment.

In a typical preparation procedure, aqueous solution of $Eu(NO_3)_3$ was prepared by dissolving 1.32 g of Eu_2O_3 with HNO_3 and 50 mL of neat water. 54.57 g of $Y(NO_3)_3 \cdot 6H_2O$ was also dissolved in 200 mL deionized water. The above solutions mixed were continuously stirred at 80 °C for 120 min, and an appropriate amount of citric acid was added to the solution. The ratio of citric acid to nitrates (C/N) in the present work is 0.3, 0.5, and 0.75. When the gel was introduced into an oven and the temperature was fixed at 200–280 °C, it started to foam and eventually auto-combusted. The as-combusted powders were sintered at temperatures from 400 to 800 °C in air. The three precursors are identified based on the ratio of citric acid to nitrates as $0.3Y_2O_3$, $0.5Y_2O_3$, and $0.75Y_2O_3$.

The X-ray diffraction data (XRD) was collected using the Rigaku D/MAX-2550-18KW powder diffractometer with Cu Kα-radiation. The transmission electron microscope (TEM) images were characterized by a JEOL JEM-200CX. The emission spectra were obtained by a JASCO FP-6500 fluorescence spectrophotometer.

The synthesis of Y_2O_3:Eu^{3+} phosphor is based on combusting the mixture of metallic nitrates and citric acid. The stochiometric combustion reaction to form $(Y_{1-x}Eu_x)_2O_3$ can be represented as:

$$6(1-x)Y(NO_3)_3 + 6xEu(NO_3)_3 + 5C_6H_8O_7 \rightarrow 3(Y_{1-x}Eu_x)_2O_3 + 9N_2 + 30CO_2 + 20H_2O. \tag{1}$$

The gases produced per moles of $(Y_{1-x}Eu_x)_2O_3$ is about 20 moles and the ideal ratio of citric acid to metal ions should be 5/6. The 0.3–$0.75Y_2O_3$ samples correspond to fuel-deficient systems.

The as-combusted $0.3Y_2O_3$ and $0.75Y_2O_3$ samples are yellow and black, respectively. The XRD patterns of the Y_2O_3:Eu^{3+} phosphors are shown in Figure 1. The as-combusted $0.75Y_2O_3$ powders were black in color, indicating the presence of carbon, and were essentially amorphous. For the Y_2O_3:Eu^{3+} phosphors sintered at 500 °C, all diffraction peaks are consistent with the cubic Y_2O_3 phase, but there is a great deal of disorder phase due to the remained organic group. When the sintering temperature is 600 °C, the powders have crystallized completely into Y_2O_3 phase.

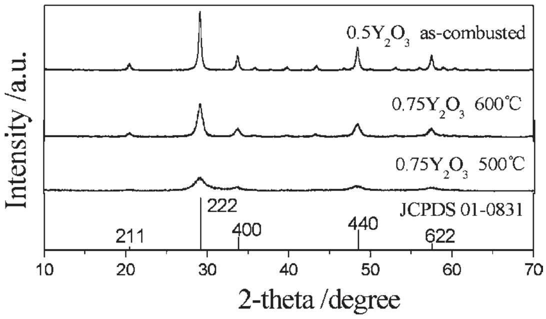

Figure 1. XRD patterns of Y_2O_3:Eu nanophosphors.

However, the as-combusted $0.5Y_2O_3$ powders are colorless. All diffraction peaks of Y_2O_3:Eu^{3+} as-combusted powders are consistent with the cubic yttria phase, which indicates the crystallization of yttria for the as-combusted phosphors. The TEM image of as-combusted $0.5Y_2O_3$:Eu^{3+} nanophosphor is presented in Figure 2. The particle is made up of some large and faceted crystallites. The crystallites are almost equiaxed and have an average size of 30–40 nm, which is close to the estimated size (20–30 nm) by Scherrer's formula. Sintering below 800 °C hard-

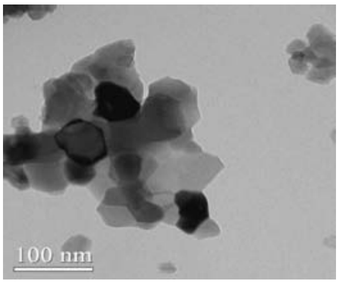

Figure 2. TEM image of $0.5Y_2O_3$:Eu nanophosphors.

ly leads to an increase of diffraction peak intensity.

The flame temperature during the combustion reaction is critical to the crystallization and particle size. The flame temperature can be increased through increasing the fuel/oxidizer molar ratio. The exothermic reaction in the $0.5Y_2O_3$ precursor could raise the local temperature enough to increase the crystallization of Y_2O_3, compared with $0.3Y_2O_3$. Thus, $0.75Y_2O_3$ should also crystallize due to the higher flame temperature than $0.5Y_2O_3$. However, $0.75Y_2O_3$ doesn't crystallize completely until sintered at 600 °C. At temperature below 600 °C, the remained carbon prevented complete crystallization of Y_2O_3 through increasing diffusion distances of the metallic cations. In the precursors, citric acid is the main carbon source. It is also observed that the inhibition of Y_2O_3 crystallization is more accentuated under higher content of citric acid. This is the major reason for the direct crystallization of $0.5Y_2O_3$ instead of $0.75Y_2O_3$. Previous works has also found that a high concentration of citric acid can retard the phase evolution.[9,10]

For the $0.5Y_2O_3$ precursor, the used fuel is less than the required amount of fuel. In general, amount of citric acid should be more than metallic nitrate in order to complex of citric acid and nitrate sufficiently. In fact, each monomer of citric acid has four functional groups. Particularly in solution of weak acid, citric acid has strong complex ability. Therefore, $0.5Y_2O_3$ can form a polymeric network, which will lead to a more homogeneous mixing of cations and reduce the diffusion length of crystallization. Under such conditions, the product formation is through two parallel reactions–simple decomposition of nitrates and gel combustions. The precursors started to foam during the stirring and solution drying process. The foam was caused during generation of NO_2 gas due to the decomposition of the nitrates. This simple decomposition of nitrates is endothermic, and can be represented as:[11]

$$4Y(NO_3)_3 \rightarrow 2Y_2O_3 + 12NO_2 + 3O_2. \qquad (2)$$

The gas of O_2 and NO_2 from reaction (2) may react with citric acid, which can be shown as:

$$C_6H_8O_7 + 9/2O_2 \rightarrow 6CO_2 + 4H_2O, \qquad (3)$$

$$C_6H_8O_7 + 7/2NO_2 + O_2 \rightarrow 6CO_2 + 4H_2O + 7/4N_2. \qquad (4)$$

The reaction (3) and (4) are exothermic, and a great deal of heat produced improves the temperature of system greatly. Once the temperature of system reach ignition, the propellant combustion occur as reaction 1. The generation of heat during an instant of combustion can form crystalline in appropriate case.

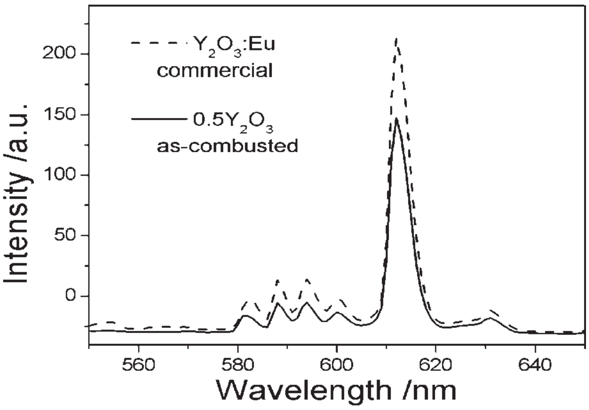

Figure 3. The luminescence spectra of $0.5Y_2O_3$:Eu nanophosphors and commercial Y_2O_3:Eu phosphors excited at 240 nm.

Figure 3 illustrates the emission spectra of $0.5Y_2O_3$:Eu nanophosphors and commercial Y_2O_3:Eu phosphors. The emission spectra consist of sharp lines from 500 to 700 nm, which are corresponding to the transitions from the excited $^5D_0$ level to the ^7F_J ($J = 1, 2, 3$, and 4) levels of Eu^{3+} ions. The strongest peak at 612 nm is due to the $^5D_0 \rightarrow {}^7F_2$ transition in C_2 symmetry for Eu^{3+} doped in Y_2O_3. The emission intensity of as-combusted phosphors reaches close to that of commercial Y_2O_3:Eu phosphors. Their emission quantum efficiency reaches about 67% (assuming that the value for the commercial Y_2O_3:Eu phosphor is 90%). It confirms that the as-combusted Y_2O_3:Eu nanophosphors are intensely luminescent.

In conclusion, high-luminance Y_2O_3:Eu nanophosphors have been successfully prepared by a simple complexation combustion method. The crystallization and grain size of Y_2O_3:Eu nanocrystals were found to depend on the ratio of fuel to nitrates (C/N). This method might be extendible to other oxide nanostructure materials.

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