Synthesis of Y$_2$O$_3$:Eu$^{3+}$ micro- and nanophosphors by sol-gel process

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Abstract. In this paper, optical properties of Y$_2$O$_3$:Eu$^{3+}$ micro- and nanophosphors synthesized by sol-gel process are reported. Citric acid and tartaric acid were employed as chelating agents. Different factors effecting structures and properties of the phosphors, such as concentration of Eu$^{3+}$, sintered temperature and the ratio of metal ions to tartaric acid, were examined. Crystal structure of the particles was investigated by X-ray diffraction (XRD) technique. The results showed that the phosphor powders completely crystallized at 600°C. Morphology and particle size of the obtained phosphors were studied by scanning electron microscope (SEM) and transmission electron microscope (TEM). The particle size of the obtained phosphors varied from 1 to 6 μm (using citric acid as chelating agent) and from 20 to 30 nm (using tartaric acid as chelating agent). Photoluminescence measurements of the Y$_2$O$_3$:Eu$^{3+}$ particles showed red emission peaks at 610 - 612 nm (5D$_0$ → 7F$_2$). The optimal molar concentration to obtain the highest photoluminescent intensity for the phosphors was 7% of Eu$^{3+}$.

Keywords: Micro- and nanophosphors, sol-gel process, photoluminescent, optical properties.

1. Introduction

The red phosphor Y$_2$O$_3$:Eu$^{3+}$ has been studied and widely applied in fluorescent lamps because of its high quantum efficiency, and especially, it can be effectively excited by 254 nm radiation, the strongest emission of mercury vapor [1]. While in many applications, such as fluorescent lamps (FL), cathode ray tubes (CRT), plasma display panels (PDP), particle size of the phosphor is in the range of several micrometers [2, 3], nanoscaled Y$_2$O$_3$:Eu$^{3+}$ has been indicated to be one of the most promising red phosphors for field emission displays (FED) [4, 5]. Therefore, the studies on the preparation and luminescent properties of this phosphor attracted extensive interests.

Y$_2$O$_3$:Eu$^{3+}$ has been prepared by various methods. Vu et al. [6] used combustion reaction to synthesize the phosphor with the particle size estimated in the range of 10 to 20 nm. Nanocrystalline cubic Y$_2$O$_3$:Eu$^{3+}$ with an average particle size of only 10 nm was fabricated using chemical vapor technique by Konrad et al. [7]. A laser-heated gas condensation technique has also been employed to
prepare nanocrystalline $\text{Y}_2\text{O}_3: \text{Eu}^{3+}$ with the monoclinic crystal structure [8]. Zhang et al. [9] prepared the phosphor with the grain size in the range of 0.5 to 2 $\mu$m by sol-gel method which employed citric acid as a chelating agent. In these works, however, most of the authors have concentrated on studying synthesis process and photoluminescent properties of either nanoscaled materials or microphosphors. Many researchers have investigated the luminescent properties of bulk and nanocrystalline cubic yttrium oxide prepared by chemical vapor synthesis [7, 10], combustion synthesis [11], and fast thermal decomposition of metal nitrate solution [12].

In this work, we present structure and optical properties of $\text{Y}_2\text{O}_3: \text{Eu}^{3+}$ micro- and nanophosphors synthesized by sol-gel process. Citric acid and tartaric acid were employed as chelating agents in making sol. A general comparison of crystallite structure, morphology and optical properties of two kinds of phosphors was realized.

2. Experimental

2.1. Preparation of $\text{Y}_2\text{O}_3: \text{Eu}^{3+}$

Synthesis process of the phosphors is shown in figure 1. The initial rare earth oxides $\text{Y}_2\text{O}_3$ and $\text{Eu}_2\text{O}_3$ (99.99%, Aldrich, USA) with different atomic ratios were dissolved in a definite amount of diluted nitric acid (Merck) and stirred to obtain a transparent liquid. Next, chelating agent was fed on. The solution was constantly stirred for 12 hours at room temperature. Then, the mixture was heated at 80°C and a transparent sol was formed. In the process of heating at 100°C, the condensation reaction between –COOH groups occurred and led to the formation of water. The evaporation of water made the volume of the sol to be reduced quickly. When most of water was removed, the sol turned into a transparent gel and then a viscous resin was formed. Finally, further heating caused the combustion of the gel and the powder with a brownish color was obtained, which is called dry gel. The dry gel was then sintered at different temperatures to obtain the phosphors.

![Figure 1. Synthesis process of the phosphors.](image1)

2.2. Characterization of the phosphors

The IR spectra of the gels sintered at different temperatures were measured by using Nicolet 6700 FT-IR Spectrometer. X-ray diffraction images were studied with Brucker D8-Advance XRD meter using

![Figure 2. IR spectra of the nanophosphors before sintering and sintered at different temperatures.](image2)
Cu Kα radiation. The morphology and particle size of the phosphors were observed by using Hitachi S-4800 Field Emission Scanning Electron Microscope (FESEM) and JEOL JEM-1010 Transmission Electron Microscope (TEM). Photoluminescence measurements were performed using a continuous wave He–Cd laser (325 nm) as the excitation source.

3. Results and Discussion

3.1. Formation of Y2O3:Eu3+ phosphor in the sintering process

Figure 2 shows the IR spectra of Y2O3:Eu3+ powders before sintering and sintered at different temperatures. For the dry gel before calcination, the IR spectrum consists mainly of three parts: the first part with a peak at 3438.5 cm⁻¹ arises from the absorption of O–H vibration; the second part with the main peaks at 1418.3 and 1541.2 cm⁻¹ comes from citrate groups and the third part with a weak peak at 845.3 cm⁻¹ due to the absorption of small amount of CO3²⁻. After sintering at 600°C, the absorption peaks from the organic components decrease, and a new sharp peak at 560 arises due to the absorption of Y2O3. The absorption peak due to Y2O3 became stronger indicating the complete crystallization of Y2O3. The absorption of organic composition almost disappeared after sintering at 900°C.

A similar result was obtained for the nanophosphors using tartaric acid as chelating agent. XRD patterns of phosphors sintered at different temperatures are shown in figure 3. The powders completely crystallized when sintered at the temperature of 600°C. The difference in width of peaks indicates the difference in particle size.

3.2. The morphology of the phosphors

Figure 4 (a) shows SEM image of the micro-particles obtained by sintering the dry gel (using citric acid) at 900°C for 3 hours. It can be seen that nearly spherical particles are obtained and the mean particle size is estimated from 1 to 6 μm. On the other hand, nanophosphors were achieved in the case of tartaric acid was used (figure 4 (b) and figure 5). From these images we see that the particles are rather homogeneous and the grain size is in the range of 20 to 30 nm. Crystallite size of the nanophosphors can be calculated according to Scherrer formula [13]: 

\[ D = \frac{0.89\lambda}{\beta\cos\theta} \]

where D is the crystallite diameter (nm), \( \lambda \) the X-ray wavelength (0.15405 nm), \( \theta \) is the diffraction angle and \( \beta \) is the full-width at half-maximum (FWHM, in radian) of (222) peak. The results are summarized in the table 1. These results are in good agreement with the particle sizes obtained by FE-SEM and TEM. A slight
agglomeration of the particles occurs in both of cases. This can be explained as a consequence of high
temperature sintering process.

![Figure 4. SEM images of the microphosphors (a) and nanophosphors (b).](image)

![Figure 5. TEM image of the nanophosphor.](image)

**Table 1.** Crystallite size of the phosphors.

| Sample | Sintering temperature | Peak position | FWHM   | D (nm) |
|--------|-----------------------|---------------|--------|--------|
| 1      | 600°C                 | 29.03°        | 0.883° | 9      |
| 2      | 700°C                 | 29.12°        | 0.543° | 15     |
| 3      | 800°C                 | 29.12°        | 0.505° | 16     |
| 4      | 900°C                 | 29.15°        | 0.410° | 20     |

3.3. *The morphology of the phosphors*

Emission spectra of the phosphors with Europium atom concentration of 7% sintered at 800°C (nanophosphors) and 900°C (microphosphors) for 3 hours when excited by 325 nm beam are shown in figure 6.
It can be seen that the phosphors have an intensive fluorescence with sharp peaks at the wavelength of 611.5 nm (micro-particles) and 609.5 nm (nano-particles) corresponding to the transition between $^3D_0$ and $^7F_2$ levels of Eu$^{3+}$ ion. No significant difference in position of the peaks between two spectra, but there is a little difference in shape of the curves. The emission bandwidth of the nanophosphors is larger than that of the microphosphors. The increasing bandwidth results from the increase in the lattice relaxation energy of the excited state with decreasing particle size [10].

The emission intensity of the phosphors depends on the Eu$^{3+}$ concentration and sintering temperature as shown in figure 7. In both cases of the micro- and nanophosphors, the strongest emission intensity corresponds to the concentration of 7%. Higher concentrations caused the decrease in emission intensity. This effect may be attributed to the concentration quenching mechanism [14].

The effect of sintering temperature on photoluminescent intensity was investigated. The results showed that emission intensity increases with the raise of temperature. The optimal sintering temperature to produce high intensity is 800°C in the case of nanophosphors, while that of the microphosphors is 900°C. Higher sintering temperatures caused the decrease of emission intensity.
This can be explained that at higher temperatures, particles tend to move into clusters and, as a result, the emission intensity will be decreased.

From these results, we have a general comparison of emission intensities of two kinds of phosphors. It can be seen that the microphosphors have stronger emission intensity. Nanoscaled phosphors have lower quantum efficiency compared to microscaled particles. This is attributed to the large surface area, which amplifies quenching processes [15].

3.4. The effect of the ratio of metal ions to tartaric acid on particle size and luminescent properties of nanoparticles

In synthesis process of nanophosphors, different molar ratios of metal ions to tartaric acid (1:1, 1:2, 1:3, and 1:4) were studied. At the ratio of 1:1, the particles were in an inhomogeneous form (Fig. 9). Other ratios did not make an obvious change in particle size.

When the ratio of metal ion to tartaric acid was 1:2, the highest emission intensity was obtained. This can be explained that high tartaric acid concentration caused a higher carbon impurity left in the powder which decreased luminescent intensity while the lower tartaric acid amount accelerated the rate of hydrolysis in sol-gel process, as a result, the nanoparticles could not be homogeneous.

4. Conclusions

Y$_2$O$_3$:Eu$^{3+}$ micro- and nanophosphors have been synthesized by simple sol-gel process. The luminescent properties of Eu$^{3+}$ doped Y$_2$O$_3$ as a function of Eu concentration and sintering temperature have been investigated. The optimal Eu concentration is 7 at.%. The photoluminescent intensity increases with the decrease in sintering temperature up to 800°C and 900°C for the nanophosphors and microphosphors, respectively. Higher sintering temperatures reduce the emission intensity. The extension of emission bandwidth of the nanophosphors in comparison with that of the microphosphors was observed. The shape of the phosphor particles is nearly spherical, and particle size distribution is rather narrow.

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