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Simple route to the synthesis Y_2O_3 :Eu³⁺ nanoparticles like-spheres

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ABSTRACT

In the present work, $Y_2O_3:Eu^{3+}$ nanoparticles like-spheres have been synthesized via simple method. Synthesis conditions such as calcination temperature and the additive 2,3-dihyrosybutanedioic acid are played a role for synthesizing $Y_2O_3:Eu^{3+}$ nanoparticles with superior optical properties. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies have been carried out to understand surface morphological features and the particle size. The as-obtained nanoparticles have average crystallite size ranging between 25 to 45 nm. Crystal structure of the nanoparticles has been investigated by X-ray diffraction (XRD) technique. The incorporation of Eu^{3+} activator in these nanoparticles has been checked by luminescence characteristics, establishing that the main emission peak located at 613 nm corresponds to the hypersensitive forced electric dipole transition between 5D_0 and 7F_2 level of Eu^{3+} ions.

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Introduction

We are interested in luminescent materials that include lanthanide elements. One of them is Eu^{3+} doped Y₂O₃, which is known to be a good red phosphor. Eu^{3+} doped Y_2O_3 phosphor is used for high-efficiency cathode ray tubes and high fieldemission displays [1]. Nowadays, high-definition display has been one of the most interesting topics in flat-panel display (FPD) industry. To increase the resolution of a screen, the pixel size of the screen has been continuously reduced. Recent advances in high-definition display have placed some requirements on the development of corresponding phosphors. For application in high-definition displays with small-sized pixels, phosphors with a small size and narrow size distribution are required. A uniform size for the phosphor particles helps to form a uniform thickness of a phosphor layer, and thus their luminescence distribution can be uniform on a whole phosphor screen [2,3]. In addition, phosphor particles should have a spherical shape and high luminescence efficiency. Phosphor particles with a spherical shape are capable of minimizing light scattering on their surfaces. Consequently, the efficiency of light emission and the brightness of a phosphor screen are expected to be improved [4,5] Another feature of spherical phosphor particles is they can be packed more densely than ones with a different shape so that a dense phosphor layer can be formed by using the spherical phosphor particles [6-8].

On the other hand, shape and size, and thus luminescent properties, of phosphor particles are strongly affected by the synthesis methods used. It is difficult to control the shape and size of phosphor particles with a conventional solid-state reaction method that requires a high-temperature firing process for a long time as well as mechanical milling processes. Commercially available Eu³⁺ doped Y₂O₃ phosphor particles are prepared by high-temperature solid-state reactions or precipitation methods, resulting in large particles and agglomerates in the size range of 3 - 10 µm without regular shapes and surface damage, which act as a nonradioactive transition center and cause a decrease of luminescence efficiently [8,9]. Because, phosphor particles with regular shapes are generally known to have the highest efficiencies [9]. Recently, a spray-pyrolysis method has been recommended as a promising method with which to prepare fine, spherically shaped phosphor particles. However, the sizes of the phosphor particles prepared with a spray-pyrolysis method are not uniform and have a hollow structure [10]. The hollow structure of the phosphor particles is harmful to mechanical stability and luminescence efficiency [10-11] .Recent progress in a flame spray-pyrolysis method made it possible to prepare solid and nano-sized phosphor particles [12].

In the present work, we synthesized nano-sized particles made of $Y_2O_3:Eu^{3+}$ like spheres by using a simple process. In addition, because the $Y_2O_3:Eu^{3+}$ phosphor is a well known, highly efficient red-emitting phosphor for use in low-pressure florescent lamps and FPDs such as plasma display panels and conventional cathode ray tubes, it is worthwhile to study the optical properties of as-synthesied $Y_2O_3:Eu^{3+}$ nanoparticles [7-12].

Experimental

The starting materials include Y₂O₃ and Eu₂O₃, were of commercial grades and used without further purification. The synthesis process of the product is shown in diagram1. An appreciated amount of Y_2O_3 and Eu_2O_3 with atomic ratio 8% Eu were dissolved in a definite amount of diluted nitric acid and stirred for several minutes to obtain a transparent liquid. Next, 2,3-dihyrosybutanedioic acid was fed on as chelating agent. Always, the transparent fluid under magnetic stirring, was heated at 80 °C on a hot magnetic plate to form a liquid-sol. In the process of heating at 105 °C, the condensation reaction occurred and led to the formation of water. Thus, 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 gel and then a viscous resin was formed. Finally, further heating caused the combustion of the gel and the precursor powder of a chocolate color was obtained, which is called dry gel.

After then, the precursor powder (dry gel) was placed in an alumina boat located in alumina tube, which was mounted in the traditional resistance-heated furnace in air condition at different reaction temperatures of 620 °C 850 °C and 1150 °C in order to obtain nanostructures Y_2O_3 : Eu phosphors.



Diagram 1: Shows the synthesis process of Y₂O₃: Eu product

The crystal structure and phase purity of the product were examined by means of X-ray diffraction (XRD, D/max-RB) analysis with Cu kα radiation. The overview of the sample morphology was identified by scanning electron microscopy (SEM, JEOL JSM-6700F), equipped with the system of energydispersive X-ray (EDX) analysis. Sample powder was also ultrasonically dispersed in ethanol solution and dropped onto a carbon coated copper grid for transmission electron microscopy (TEM, JEM-210F, JEOL), with a micro-analysis system of energy dispersive spectroscopy (EDS). Photoluminescence measurements were performed using a continuous wave He-Cd laser (325 nm) as excitation source

Results and discussion

Figure 1a shows the XRD patterns of as-synthesized Y_2O_3 :Eu³⁺ samples. All diffraction peaks of the pattern obtained after heating the precursor powder at 620 °C for sample 1, 850 °C for sample 2 and 1150 °C for sample 3. As can be seen that the pattern for all the samples 1,2 and 3 (Fig. 1), can be well indexed to pure cubic Y_2O_3 corresponding to the JCPDS No. 65-3178. Furthermore, no additional peaks were detected, indicating that the Eu³⁺ ions were effectively built into the host lattice. Interestingly, the stronger and much intense XRD peaks appeared for the sample calcined at 1150 °C, indicates enhancement in crystallinity when compared to samples calcined at 620 °C and 850°C. This can be explained as a consequence of high temperature process.

Table 1 lists the main peak (222) positions, the FWHMs (full widths at half maximum) of the (222) peaks of the samples. The intensities of the main peaks (222) of the samples prepared from precursor powder (sample 1 through sample 3) increased with increasing the calcinations temperature, whereas, the FWHM of the (222) peaks of the samples decreased with increasing reaction temperature (table 1). Depending on Scherrer's equation (1) ,[13], the FWHM of the (222) peak is inversely proportional to the lattice parameter. This means that the grain size of the samples heated at low temperature is smaller than that heated at high temperature.

$$D = \frac{k\lambda}{\beta cos\theta} \qquad (1)$$

Where θ is the Bragg angle of diffraction lines, K is a shape factor taken as 0.89, λ is the wavelength of incident X-rays (λ =0.154056 nm), and β is the full-width at half maximum (FWHM). The average crystallite sizes obtained using Debye-Scherrer"s equation were ~25 nm for sample calcined at 620 °C, whereas, 1150 °C calcined sample shows ~40 nm. These computational results were found consistent with SEM and TEM observations (Fig. 2).

 Table 1: (222) peak positions and the FWHMs of the XRD patterns for the studies samples.

Sample No	(222) peak position (20)	FWHM of (222) peak	
1 (620 °C)	29.082	0.375	
2 (850 °C)	29.1	0.256	
3 (1150 °C)	29.11	0.201	



Figure 1: (a) shows XRD patterns of Y₂O₃:Eu³⁺ samples, calcined at 620 °C, 850 °C and 1150 °C for sample 1, 2 and 3 respectively; (b) EDX spectra of Y₂O₃:Eu³⁺ nanoparticles for sample 3.

Figure 2 shows the low magnification SEM images of the Y_2O_3 :Eu³⁺ nanoparticles calcined at (a) 620 °C (b) 1150 °C respectively. As can be seen , the SEM images confirmed that the as-synthesized Y_2O_3 :Eu³⁺ formed nanoparticles like-spheres. The average particle sizes were around ~25 nm for sample calcined at 620 °C; whereas, for sample calcined 1150 °C shows an average size of about ~45 nm. These results are in good agreement with the particle sizes obtained by Scherrer's equation. Interestingly, the SEM morphology established the majority of the as-obtained Y_2O_3 :Eu³⁺ nanoparticles are combined together in uniform shape like chains. The inset image 2c in Fig. 2 b depicts the transmission electron microscope image (TEM) of as-synthesized Y_2O_3 :Eu³⁺ nanoparticles

calcined at 1150 °C. The TEM morphology agree well with the SEM observations. Figure 1b shows the representative EDX spectrum of $Y_2O_3:Eu^{3+}$ nanoparticles calcined at 1150 °C. The Yttrium :Europium ratio found to be 79.8:19.09 weight %. ,this a clearly evidence that almost all the europium ions were incorporated in the $Y_2O_3:Eu^{3+}$ host.



Figure 2: shows SEM images of the as-synthesized Y_2O_3 :Eu³⁺ samples ; (a) SEM image for sample calcined at temperature 620 °C; (b) SEM image for sample calcined at temperature 1150 °C: The inset (c) shows the TEM image at 1150 °C.

Photoluminescence (PL) spectra of all the samples were recorded using an excitation wavelength of 325 nm. The emission spectra of the as-obtained Y₂O₃:Eu³⁺ nanoparticles calcined at 850 °C and 1150 °C for 3.5 hours are depicted in Figure 3a and 3b respectively. The PL spectra consists of a number of broading peaks ranging from 575 nm to 650 nm. The PL spectra consisted of the ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ line emissions (j = (0,1,2,3) of the Eu³⁺ ions. As can be seen, the main emission peak located at a wavelength of 613 nm corresponds to the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ hypersensitive forced electric dipole transition, leading to the red/orange light. Whereas the other dominant broading peak positioned at 591 nm is due to the magnetic dipole transition of ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$, which leading to the orange light emitted by the as obtained Y₂O₃:Eu³⁺ nanoparticles. Actually, the magnetic dipole transition of ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ is permitted and the electric dipole transition of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ is forbidden by the parity selection rule [14,15]. Also there are weak peaks recorded at 630 nm , corresponds to ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ transition and 600 nm peak was due to ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition of Eu3+. However, in most cases, local environment of the Eu³⁺ ions does not have inversion symmetry, and the parity-forbidden transition is partially permitted. This relaxation of the selection rule occurs in non-inversion symmetry sites, occupied by the Eu^{3+} ions in Y_2O_3 [16]. When the Eu^{3+} ions occupy the inversion symmetry sites, such as S_6 sites in Y₂O₃, the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition will appear relatively strong [14, 16 -18]. Because the crystallinity of the phosphor increased with an increase of the reaction temperature (Fig.1), the PL intensity also increased, indicating stronger luminescence for the reaction temperature of 1150 °C rather that 850 °C. The relative PL intensity among the emission peaks depends on the

temperature of the local environment of the Eu^{3+} activator ions, and it can be described in terms of Judd–Ofelt theory [14,17].



Figure 3: Represents the emission spectra of the samples calcined at ; (a) 850°C ; (b) 1150°C .

Conclusion

In summary, spherical nanoparticles of Y_2O_3 :Eu³⁺ with cubic phase has been synthesized by simple process, using 2,3-dihyrosybutanedioic acid as chelating agent. The results from SEM and TEM revealed that the as-synthesized Y_2O_3 :Eu³⁺ samples were uniform nanoparticles like-spheres. Moreover, the 1150 °C calcined sample yield intense red luminescence correspond to the ${}^5D_0 \rightarrow {}^7F_2$ hypersensitive forced electric dipole transition, suggesting them to be one of the most possible candidate for red phosphor and grab great potential in flat panel displayed application, which underlying the important of the current work.

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