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Preparation and characterization of Y_2O_3:Eu phosphors by combustion process

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Abstract Europium-doped yttrium phosphors were successfully synthesized by combustion process using yttrium nitrate hexahydrate [$Y(NO_3)_3{\cdot}6H_2O$], europium nitrate [$Eu(NO_3)_3{\cdot}6H_2O$], and carbohydrazide [$CO(N_2H_3)_2$]. The process takes only a few minutes to obtain Y_2O_3:Eu phosphors. The resultant powders annealed at different temperature and were investigated by X-ray diffractometer (XRD), differential thermal analyzer/thermogravimeter (DTA/TG), Fourier transform infrared spectroscopy (FTIR), photoluminescence excitation and emission spectra (PL), and transmission electron microscopy (TEM). The results showed that the formation temperature of Y_2O_3 phase is significant low, compared to solid-state reaction route of constituent oxides. For luminescence property, the emission intensity of Y_2O_3:Eu phosphors synthesized by combustion process increases steadily with increasing europium amount from 1 mol% to 5 mol%.

Introduction

Inorganic luminescence materials are crystalline compounds that absorb energy and subsequently emit this absorbed energy as light [1]. Phosphors are composed of an inert host lattice and an optically excited activator, typically a 3d or 4f electron metal such as Ce^{3+}, Cr^{3+}, Eu^{3+}, and Tb^{3+}. Oxide phosphors were found to be suitable for field emission display (FED), vacuum fluorescent display (VFD), electroluminescent (EL) devices, and plasma panel display (PDP) devices. Luminescence efficiency increases as the size of the phosphor particle is decreased, the preparation process of phosphor powders become very important in the technological procedure [2].

The conventional way of producing these materials is by the solid-state reaction of oxide/carbonate with calcined at high temperature. Moreover, the grain size of phosphor powder prepared by solid-state reaction is in the range of 5–20 μm. The solid-state reaction method has some inherent disadvantages such as: (1) chemical inhomogeneity, (2) coarser particle size, and (3) introduction of impurities during ball milling [3]. To achieve better quality of small particle size powders, low temperature synthesizing is desired. In this study, we attempted a combustion synthesis process to produce Y_2O_3:Eu phosphors powders. The combustion synthesis process involves dissolving yttrium nitrate hexahydrate [$Y(NO_3)_3{\cdot}6H_2O$], europium nitrate [$Eu(NO_3)_3{\cdot}6H_2O$], and carbohydrazide [$CO(N_2H_3)_2$] in water [4], and then heating the solution on a hot plate. The carbohydrazide and metal nitrate decompose and release flammable gases such as NH_3, HNCO, and NO, respectively. After the solution reaches the point of spontaneous combustion, it begins burning. The combustion is not finished until all flammable substances are burned out and leaves loose substances which show voids, pores, and are highly friable, which are formed by the escaping gases during the combustion reaction. The whole process takes only a few minutes to yield powders of Y_2O_3:Eu phosphors powders. The Y_2O_3:Eu phosphors containing various europium amounts were further characterized by DTA/TG, XRD, FTIR, and PL measurements. The advantages of the combustion method are (1) simple process: all the reactions take only a few minutes, not like the other methods that require

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tedious processes, (2) simple equipment: complicated equipment is not needed in this method, (3) cheap sources: all the materials used in this method are cheap, unlike special materials needed in sol–gel process.

Experimental procedures

Sample preparation

The synthesis process involved the combustion of redox mixtures in which metal nitrate acted as an oxidizing reactant and carbohydrazide as a reducing one. The initial composition of the solution containing yttrium nitrate, europium nitrate, and carbohydrazide was based on the total oxidizing and reducing valences of the oxidizer and the fuel using the concepts of propellant chemistry [5].

A flowchart for the preparation of Y_2O_3:Eu phosphor powder is described in Fig. 1. Stoichiometric amounts of yttrium nitrate hexahydrate [$Y(NO_3)_3 \cdot 6H_2O$], europium nitrate [$Eu(NO_3)_3 \cdot 6H_2O$], and carbohydrazide [$CO(N_2H_3)_2$] were dissolved in 15 ml of deionized-distilled water in a cylindrical Pyrex beaker. The beaker containing the solution was heated on a hot plate. Initially, the solution boiled and underwent dehydration followed by decomposition with the evolution of a large amount of gases (NO, NH_3, and HNCO). After the solution reached the point of spontaneous combustion, it began burning and released lots of heat, the solution vaporized instantly and became a burning solid. The entire combustion process which produces Y_2O_3:Eu phosphors powders on a hot plate takes only 15 min. A stoichiometric combustion reaction of yttrium nitrate with carbohydrazide to form Y_2O_3 is, as follows:

$$
\begin{aligned}
&2.00\,Y(NO_3)_3 + 3.75\,CO(N_2H_3)_2 \rightarrow \\
&Y_2O_3 + 3.75\,CO_2 + 10.50\,N_2 + 11.25\,H_2O
\end{aligned}
$$

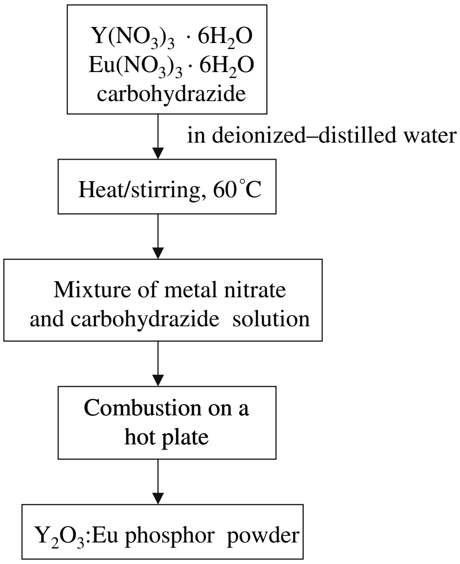

Fig. 1 Flowchart for the preparation of Y_2O_3:Eu phosphors powders prepared by combustion processing

Characterization

A computer-interface X-ray powder diffractometer (XRD) with Cu Kα radiation (Rigaku D/Max-II) was used to identify the crystalline phase. The particle shape, size, and microstructure were imaged by transmission electron microscopy (TEM, JEOL JEM-200CX) with an accelerating voltage of 200 kV. The emission spectra were obtained on a spectrofluorimeter (PL, Hitach F-4010) equipped with a 450 W xenon lamp as the excitation source. To obtain comparative phosphor performance data, specimens were prepared with an identical loading of 0.2 g/cm^3 of phosphor in a plastic sample holder. Therefore, the amount of phosphor materials is the same in all samples. Fourier transform infrared spectroscopy (FTIR, Nicolet Magna 550 FTIR) were used to measure Y_2O_3:Eu phosphors powder with the KBr pellet technique.

Results and discussion

Figure 2 shows the X-ray diffraction patterns of Y_2O_3:Eu powder with various europium concentrations. It is evident that the Y_2O_3:Eu powders contain only a single cubic phase with a space group Ia3, where Y^{3+} ions reside at 8b and 24d sites; O^{2-} ions are located at 48e sites. No obvious

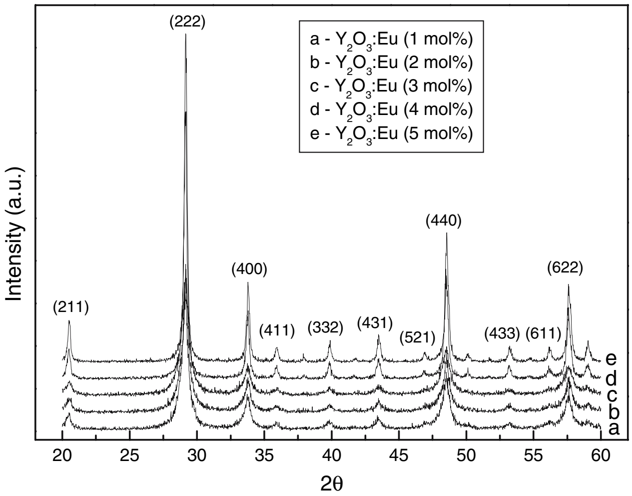

Fig. 2 XRD pattern of Y_2O_3:Eu phosphors powder with various europium concentration

difference can be found among the XRD patterns of Y_2O_3 with various europium concentrations. These results show that the formation of the Y_2O_3 phase using the combustion processing is rather low as compared to the conventional solid-state reaction. Much higher temperatures are required to prepare Y_2O_3 in a solid-state reaction of constituent oxide to form the Y_2O_3 phase. Table 1 summarizes the data of particle density, and crystallite size of the europium-doped Y_2O_3 powder with different europium contents, prepared by the combustion process. The particle size, D_{XRD} was calculated according to the Scherer equation [6]: $D_{XRD} = \frac{0.9\lambda}{B\cos\theta}$, where λ is the wavelength of the radiation, θ is the diffraction angle, and B is the corrected half-width of the diffraction peak, given by $B^2 = B_m^2 - B_s^2$. Here B_m is the measured half-width of the diffraction peak and B_s is the half-width of a standard Y_2O_3 with a crystal size greater than 100 nm. The particle size determined from the broadened peak is about 16–32 nm in europium-doped Y_2O_3 phosphor samples. The particle density was calculated according to the formula $D_x = \frac{16M}{Na^3}$, where M is the molecular mass, N is Avogadro's numder, and a is the lattice parameter which was calculated from the X-ray diffraction pattern.

Figure 3 plots the FTIR spectra of the Y_2O_3:Eu powders with various europium amounts. The peaks at 1636, 1384, and 1034 cm^{-1} represent the characteristic (Y–O) metal-oxygen vibrations, while the peak between 1580 and 1460 cm^{-1} may be due to residual nitrate and organic matter in Y_2O_3:Eu powders (1–3 mol%). This result is in correspondence with those observed in XRD, which the crystallinity increases in intensity with increasing europium concentration.

Figure 4 shows the luminescence properties of the Y_2O_3:Eu phosphors powder and specimens with various europium concentration. For photoluminescence measurements, Y_2O_3:Eu phosphors powder was excited with 260 nm wavelengths from a xenon lamp. The characteristic line at 611 nm appeared in the spectra of Y_2O_3:Eu phosphors powder with various europium concentration. The strong and narrow emission feature is an indication of the presence of Eu^{3+} in a highly crystalline cubic Y_2O_3 environment. From the luminescence spectrum, we can observe that the Y_2O_3:Eu phosphors powder shows a red emission. The emission of strong red emission at 611 nm is ascribed to the forced electric dipole transition ($^5D_o \rightarrow {}^7F_2$), which is allowed in this case as the europium does not occupy a center of symmetry in yttria [7]. According to previous reports, Y_2O_3 has a cubic space group T^7_h symmetry with two crystallographically different sites C_2 and C_{3i}. Eu^{3+} ions reside in both sites with equal probability. However, the strong red emission at about 611 nm caused the $^5D_o \rightarrow {}^7F_2$ transition of Eu^{3+} in the C_2 site [8].

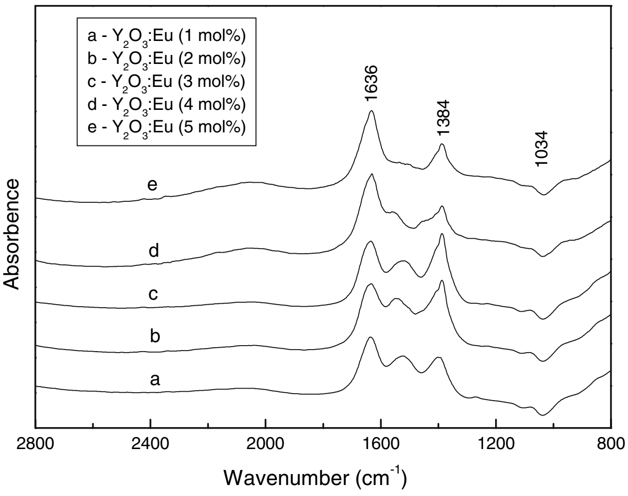

Fig. 3 Infrared spectra for Y_2O_3:Eu phosphors powder specimens with various europium concentration

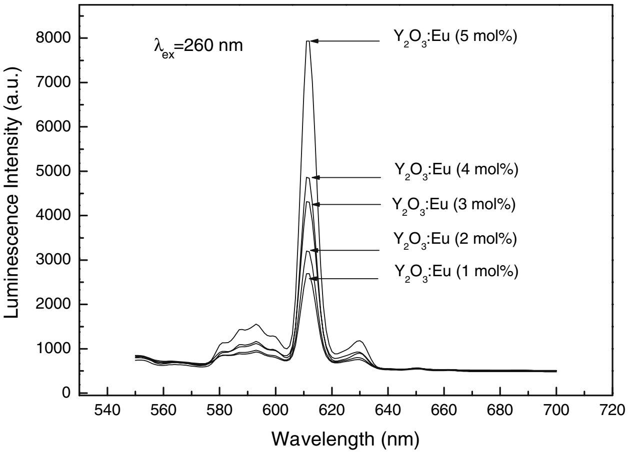

Fig. 4 Excitation spectra of Y_2O_3:Eu phosphors powder as a function of europium concentration

Table 1 Properties of Y_2O_3:Eu phosphor powder specimens

Eu-doped amount (mol%)	Particle density[a] (g/cm^3)	Crystallite size[b] (nm)
1	5.0116	17.9
2	5.0335	21.0
3	5.0398	16.2
4	5.0289	32.8
5	5.0377	39.7

[a] Particle density measured from X-ray diffraction pattern

[b] Crystallite size measured from XRD line broadening

Figure 5 displayed the excitation and emission spectra of Y_2O_3:Eu (1 mol%) phosphors powder. The excitation spectra are taken at an emission wavelength of 610 nm, the emission spectra are taken with an excitation wavelength of

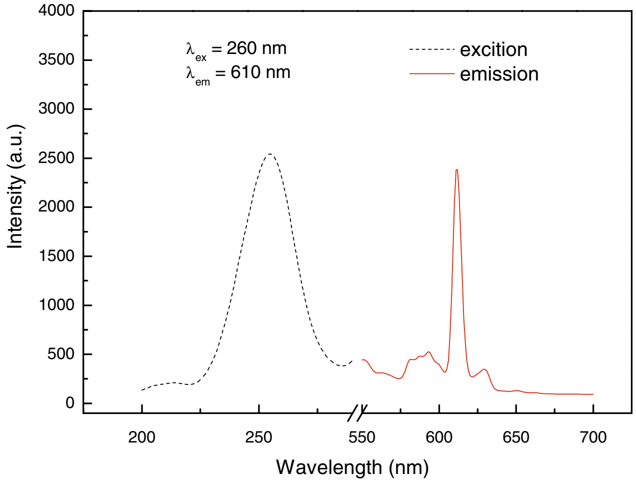

Fig. 5 Excitation (260 nm) and emission (610 nm) spectra from Y_2O_3:Eu (1 mol%) phosphors powder

260 nm. The board excitation band at 255 nm may be either ascribed to the pumping of Eu^{3+} d-orbitals or to a charge transfer transition. Figure 6 shows a plot of the emission intensity for Y_2O_3:Eu specimens versus europium concentration; the emission increases in intensity with increasing europium concentration, which indicates an optimum value of 5 mol% for the Y_2O_3:Eu phosphors. This value is referred to as the optimum europium concentration, and is consistent with the results given by another author [9]. The intensity of the PL spectrum may be ascribed to the increased crystallinity.

Figure 7 presents the morphology of the Y_2O_3:Eu (5 mol%) phosphors powders, revealing a uniform size around 50–60 nm. Noticeably, the crystals are structurally perfect. Moreover, the morphology of the Y_2O_3:Eu powders observed by SEM, showing the particle agglomerates of 1–3 μm in size. The surface of the powder shows voids and pores formed by the escaping gases during the combustion reaction. The particles of these specimens appear highly agglomerated with rough surfaces, as well as pores and cracks. These porous powders are highly friable which facilitates easy grind to obtain finer particles [10].

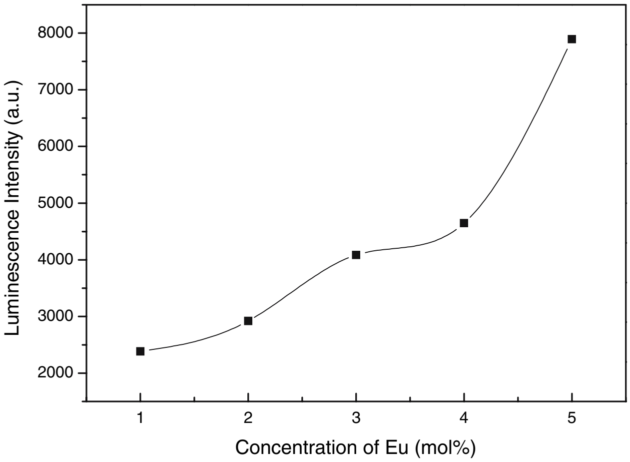

Fig. 6 Variation of luminescence intensity of Y_2O_3:Eu phosphors powder as a function of europium concentration

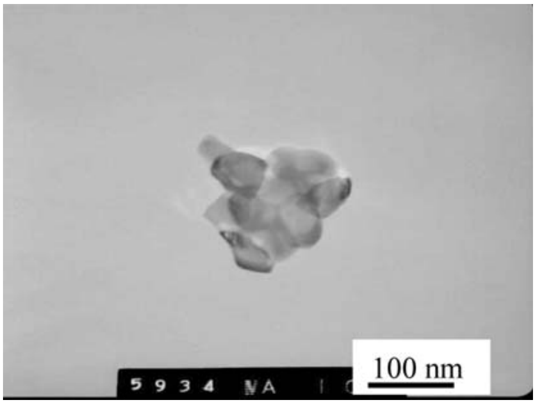

Fig. 7 TEM micrograph of Y_2O_3:Eu (5 mol%) phosphors powder prepared by combustion processing

Conclusion

Using yttrium nitrate hexahydrate, europium nitrate, and carbohydrazide as the starting materials, Y_2O_3:Eu powders have been synthesized successfully by combustion processing at low temperature. The formation temperature of Y_2O_3 phase is prominently low, compared to solid-state reactions. Furthermore, results of this study show that europium amounts greatly affect the luminescence properties of Y_2O_3:Eu powders. The emission intensity of Y_2O_3:Eu powder prepared by combustion processing can be significantly improved by adding the appropriate europium amount. The Y_2O_3:Eu powder prepared by combustion processing with 5 mol % europium concentration showed the maximum emission intensity. This method can be employed as a new route for synthesizing analogous phosphor materials.

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