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OPTICAL PROPERTIES OF Eu^{3+} DOPED Y_2O_3 NANOPHOSPHORS

Nguyen Vu, Man Hoai Nam, Tran Kim Anh, Le Quoc Minh,

Institute of Materials Science, VAST

Eric Tanguy

Universite de Nantes, LPIO 2 rue de la houssiniere 44322 Nantes, France

Abstract. Y_2O_3 : Eu is one of the phosphor materials in micrometer size scale which are mainly used for display technology. Recently the investigation of Y_2O_3 : Eu with nanometer size has attracted increasingly the interest of many research groups. In this paper we present the results of the study of Y_2O_3 : Eu nanophosphors prepared via combustion reaction between Glycine and Yttrium nitrate. The results of the DTA, TEM morphology, X-ray crystallogram, and luminescent spectra will be presented. The influence of the synthesis conditions was investigated for an effective nanophosphor Y_2O_3 : Eu.

I. INTRODUCTION

Trivalent Europium activated Yttrium Oxide (Y_2O_3) with micrometer size was used in red component, trichromatic lamps, and colour television. Commercially available micron-size powders have satisfactorily met the requirements for cathode-ray tubes. However, with the increasing need to reduce the size, weight, and power consumption of electronic devices, never low-voltage cathodoluminescent displays such as field- emission displays (FEDs) are being developed. FEDs operate at only a few hundred to few thousand volts, and have electron penetration depths of significantly less than $1\text{ }\mu\text{m}$ [1]. The fact that optical properties of nanocrystal and nanocrystalline materials differ from those of conventional materials and can be influenced by the particle size has initiated interest in this class of materials during the last few years [2]. The luminescent efficiency of the particles as a function of particle size it, also reported in [3]. It is interesting that under the excitation of the electron beam with the middle accelerating voltage ($\sim \leq 10\text{kV}$) the cathodoluminescent intensities of Y_2O_3 : Eu nanophosphor was higher than that of commercial microsize one [4].

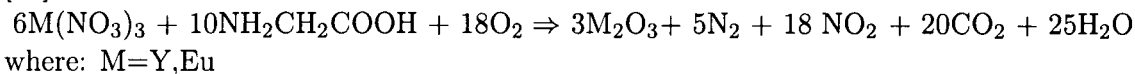
Many different techniques such as rapid exothermic reaction [5], spray pyrolysis [6], epitaxial growth [7], chemical vapour deposition [2,8] and co-precipitation [4,9] have been used in preparation of Y_2O_3 :Eu nano particles and thin films.

Preparation of Y_2O_3 : Eu nanophosphor via the combustion reaction between Urea and Yttrium nitrate were presented in previously studies [10]. In order to find the best agent for combustion reaction, in this research, we present the results of Y_2O_3 : Eu nanophosphors prepared via combustion reaction between Glycine and Yttrium nitrate.

The aim is to develop a process that would give information of the influence of various chemical parameters and temperatures on the structure and particle size of materials. We will study both optical properties and structure ones: luminescent spectra and treatment temperature will be compared and discussed.

2. EXPERIMENTAL

Nanostructured Yttria samples were prepared using a combustion synthesis. The Eu (III) concentration is 5 mole %. Reaction of an aqueous solution contain $\text{NH}_2\text{CH}_2\text{COOH}$, $\text{Eu}(\text{NO}_3)_3$ and $\text{Y}(\text{NO}_3)_3$. Glycine and salts are easily soluble. The synthesis reaction is [11]:



A glycine-to-metal nitrate molar ratio of 1:1, 1.2:1, 1.4:1, 1.6:1, 1.67:1 was employed to prepare the precursor solution. After combustion, the powder was fired a hour at 600°C in air. For the samples with glycine-to-metal nitrate molar ratio of 1.67:1, the treatment temperatures were chosen from 500°C to 700°C .

The morphology and particle sizes of $\text{Y}_2\text{O}_3:\text{Eu}$ were observed by using transmission electron microscopy (TEM). The $\text{Y}_2\text{O}_3:\text{Eu}$ powder was analysed by X-ray diffraction D5000 (Siemens). DTA, DTG were measured in order to find optimal conditions for synthesis and annealing samples. The DTA, DTG diagrams were measured in air at a heating rate of $10^\circ\text{C}/\text{min}$ from room temperature to 700°C by using Shimadzu-50 (Japan). The excitation and emission spectra were obtained on spectrometer (FL3-22) with double monochromater. The excitation source is Xenon lamp XBO 450w.

III. RESULTS AND DISCUSSION

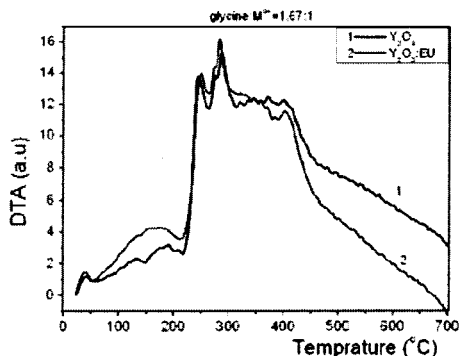


Fig. 1a. DTA diagram of Y_2O_3 (1) and $\text{Y}_2\text{O}_3:\text{Eu}$ (5mol%) (2) with the glycine-to-metal nitrate molar ratio = 1.67.

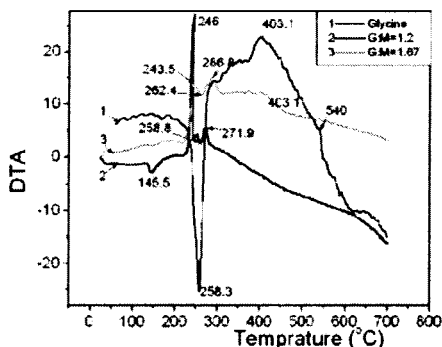


Fig.1b. DTA diagram of glycine (1) and Y_2O_3 with the different of glycine-to-metal nitrate molar ratio: 1.2 (2), 1.67 (3).

Fig. 1a presents the DTA diagram of Y_2O_3 precursor in comparison with $\text{Y}_2\text{O}_3:\text{Eu}$ (5mol%) precursor with the glycine-to-metal nitrate molar ratio equal of 1.67. Normalized, the

shape of the DTA curves in this case is almost same. Fig.1b shows DTA diagram of glycine and Y_2O_3 with the different of glycine-to-metal nitrate molar ratio ($\text{G}:\text{M}^{3+}$). The the DTA curves shape is not same. DTA spectrum of glycine has a strong endothermic peak at 258.3°C . This peak nearly disappear in two other onces because it is a weak peak in Y_2O_3 sample with $\text{G}:\text{M}^{3+}=1.2$ (258.8°C) and Y_2O_3 sample with $\text{G}:\text{M}^{3+}=1.67$ (262.4°C). DTA spectrum of glycine also has wide exothermic peaks from 286.8°C to 540°C (maximum at 403.1°C). It is nearly same for the sample with $\text{G}:\text{M}^{3+}=1.67$. Especially, the sample with $\text{G}:\text{M}^{3+}=1.2$ has a strong exothermic peak at 246°C and a exothermic peak at 271.9°C . This is treatment temperature for combustion effect of Y_2O_3 : Eu.

The transmission electron microscopic (TEM) and X-ray diffraction was measured for Y_2O_3 : Eu powder. Fig.2 shows the transmission electron microscopic (TEM) of the Y_2O_3 powder obtained by the calcinations at 600°C for 1h. We can see that the particles size is smaller than 50 nm.

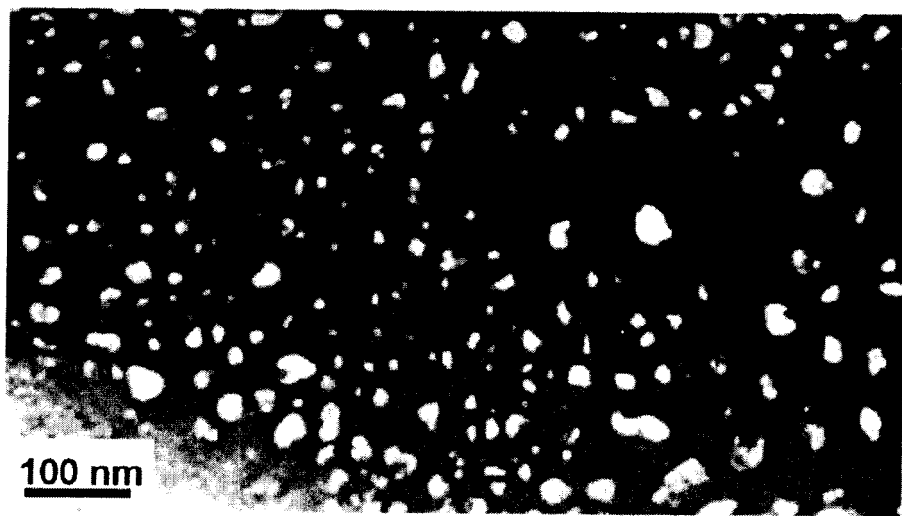


Fig. 2. The transmission electron microscopic (TEM) photograph of the Y_2O_3 powder ($\text{G}:\text{M}=1.67$), which was annealed at 600°C for 1h. in air.

Fig.3 displays the X- ray diffraction pattern of Y_2O_3 : Eu, Y_2O_3 samples annealed 600°C in hour and of standard sample. The X-ray pattern of prepared powders exhibits cubic symmetry Y_2O_3 as the reference powder. No additional lines indicating the presence of a monoclinic phase have been found. The breadth of the peaks of prepared powder suggests small particle size. However, the full width at half maximum (FWHM) of the diffraction peak at an ange of 2θ equal to 29.15° is narrower for powder prepared with glycine than for the powder prepared with urea, indicating the smaller crystalline size of the former than the latter. For the samples prepared with the glycine-to-metal nitrate molar ratio equal of 1.67, the peak FWHM of Y_2O_3 powder is narrower than Y_2O_3 :Eu (5 %) powder.

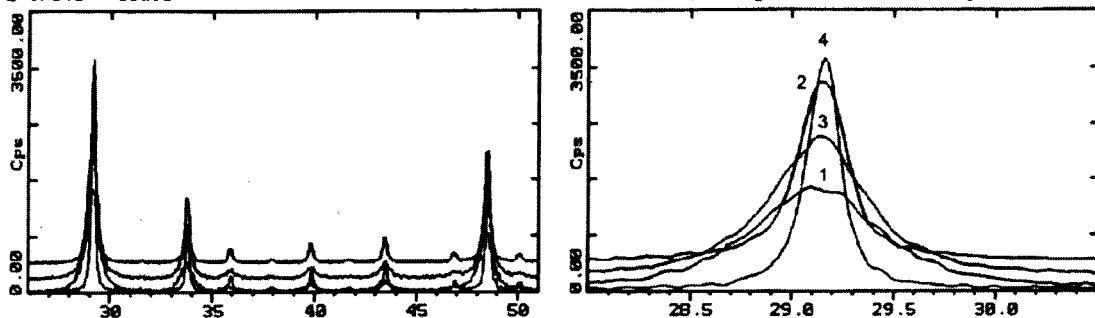


Fig. 3. X- ray diffraction pattern of Y_2O_3 , Y_2O_3 : Eu samples annealed $600^\circ C$ in hour and standard sample: 1- Y_2O_3 : Eu powder prepared with urea, 2- Y_2O_3 : Eu powder prepared with G: $M^{3+}=1.67$, 3- Y_2O_3 powder prepared with G: $M^{3+}=1.67$, 4- Y_2O_3 standard sample

The luminescent spectra of these nanophosphors in the visible region was studied. Fig.4 shows the emission spectra of the nano Y_2O_3 : Eu (5% Eu) with the different of glycine-to-metal nitrate molar ratio after excitation at a wavelength of 254 nm into the charge transfer state. The spectra are described by the well known $^5D_0 - ^7F_J$ line emissions ($J=0, 1, 2, \dots$) of the Eu^{3+} ion with the strongest for $J=2$ at 610 nm.

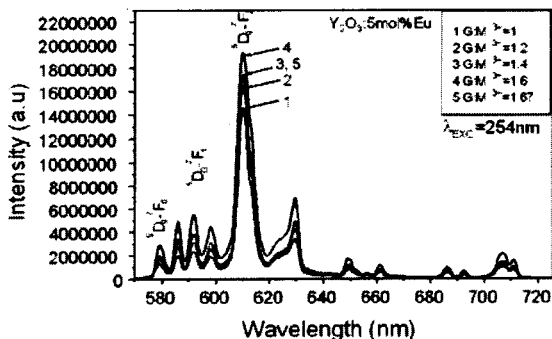


Fig. 4. Emission spectra of the nano Y_2O_3 : Eu (5 mol % Eu) with the different of glycine-to-metal nitrate molar ratio (G: M^{3+}), $\lambda_{EXC}=254$ nm.

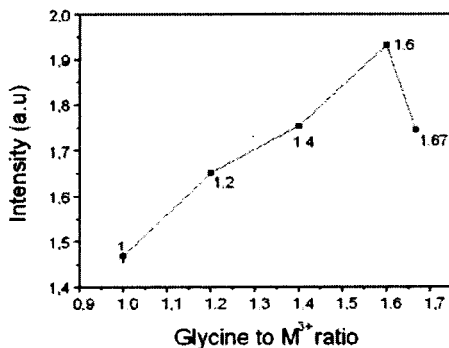


Fig. 5. Emission intensity at 610 nm with various glycine-to-metal nitrate molar.

In Fig.5, the influence of glycine-to-metal nitrate molar ratio on the fluorescence intensity at 610 nm was observed. The intensity is maximum for the sample with G: $M^{3+}=1.6$.

The excitation spectrum of the 610 nm line of nanocrystalline Y_2O_3 : Eu (5 mol% Eu), which is obtained by the calcination at $600^\circ C$ for 1 hour with G: $M^{3+}=1$, is presented in Fig.6. The strongest excitation position can be observed at about 399.5, 402.5, 469.5, 471.5, 537.5 nm, respectively.

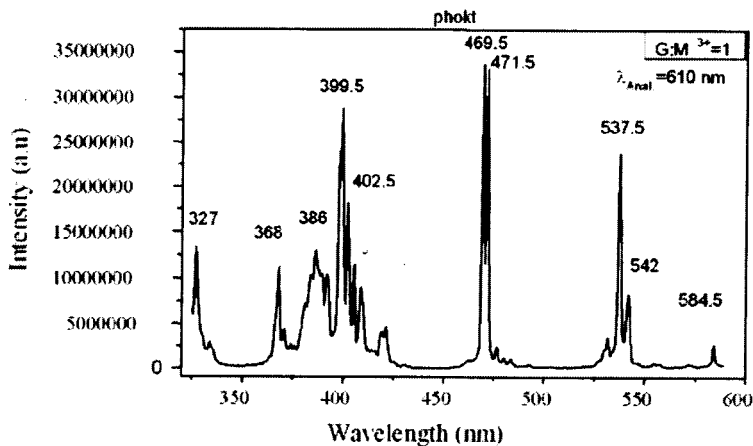


Fig. 6. Excitation spectrum of the nano $Y_2O_3:Eu$ (5 mol % Eu) with $G:M^{3+}=1$, obtained by the calcinations at $600^\circ C$ for 1h. $\lambda_{Anal.}=610$ nm.

The luminescent spectra of $Y_2O_3:Eu$ (5mol %) nanophosphors in the case of annealing $500^\circ C$, $600^\circ C$ and $700^\circ C$ for 1 h. and $G:M^{3+}=1.67$ were presented in Fig.7. Normalized, the fluorescent spectrum given by the samples has almost the same shape. The intensity increases as the annealing temperature increases.

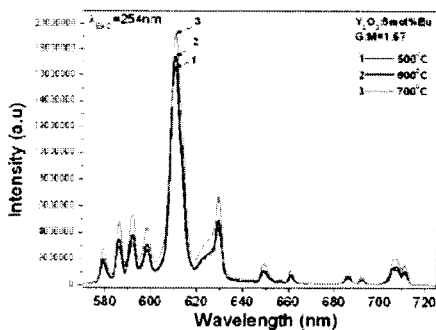


Fig. 7. Emission spectra of the nano $Y_2O_3:Eu$ (5 mol % Eu) with the $G:M^{3+}=1.67$, $\lambda_{EXC}=254$ nm, heat treatment at: 1: $500^\circ C$, 1hr; 2: $600^\circ C$, 1hr, 3: $700^\circ C$, 1hr

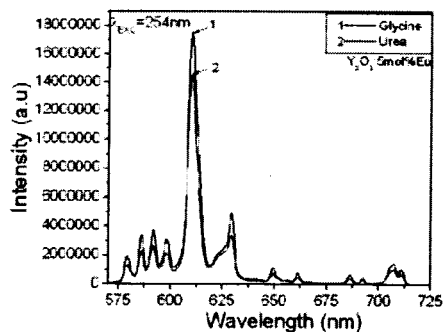


Fig. 8. Emission spectra of the nano $Y_2O_3:Eu$ (5 mol % Eu) prepared via combustion reaction between Glycine - Yttrium nitrate (1) and Urea - Yttrium nitrate (2)

Fig.8 shows the emission spectra of the nano $Y_2O_3:Eu$ (5 mol % Eu) prepared via combustion reaction between Glycine - Yttrium nitrate ($G:M^{3+}=1.67$) in comparison with the sample prepared by combustion reaction between Urea - Yttrium nitrate after excitation at a wavelength of 254 nm. Two samples were prepared at the same annealing condition ($600^\circ C$, 1 hour). We can see that the emission spectrum of two samples has almost the same shape but the intensity of the sample prepared via combustion reaction between Urea - Yttrium nitrate is higher than other once.

IV. CONCLUSION

The Y_2O_3 : Eu nanophosphors were prepared via combustion reaction between Glycine and Yttrium nitrate. The results of TEM images indicate that particles size is smaller than 50 nm. The optical properties of these materials were studied. The luminescent spectra were measured after excitation at a wavelength of 254 nm. The $^5\text{D}_0-^7\text{F}_j$ transitions were recorded in the all of samples. The excitation spectrum of the 610 nm line was measured for the nano Y_2O_3 : Eu (5 %), which is obtained by the calcination at 600°C for one hour with $\text{G:M}^{3+}=1$.

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