

# Synthesis and Luminescence Characterization of $\text{Eu}^{3+}$ Doped $\text{Gd}_2\text{O}_3$ Phosphors by Combustion Method

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Europium-doped gadolinium oxide ( $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ ) phosphors have been prepared by combustion method using urea [ $\text{H}_2\text{NCONH}_2$ ] or carbonylhydrazide [ $\text{H}_2\text{NNHCONHNH}_2$ ] as fuel materials in a preheated furnace at  $500^\circ\text{C}$ . The phosphors obtained were fired at  $1200^\circ\text{C}$  for 3 hours to get better luminescent properties. The combustion method used was found to be a simple and fast method for the preparation of fine-sized particles. The influence of the fuel/oxidant (urea or carbonylhydrazide/nitrate) mole ratio on the phosphor has been investigated and the optimum values for various parameters have been determined. By this method, phosphor that has better brightness and smaller size particles than that obtained by conventional method has been prepared.

*Keywords* :  $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$  phosphor, Combustion, Urea, Carbonylhydrazide, Luminescence

## 1. INTRODUCTION

The light emitting compounds of full color are called phosphor, which are composed of host lattice and optically excited activator(s), traditionally 3d or 4f metal(s)[1,2]. For practical phosphor applications, it is desirable that synthesized materials must have small particle size, thermal stability, radiation resistance and chemical purity for optimum chromaticity and brightness.

The luminescence of  $\text{Eu}^{3+}$  doped  $\text{Gd}_2\text{O}_3$  phosphor has attracted considerable attention because of its high brightness, atmospheric stability and importance in producing red emitting phosphors for various applications, e.g. fluorescent lamps (FL), cathode ray tubes (CRT)[3-5]. Recently, it has been applied widely to low voltage displays such as flat panel displays (FPD).

Traditionally, the  $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$  phosphors are prepared by heating up to  $1400\text{-}1600^\circ\text{C}$  for several hours by solid state method. The phosphors synthesized through this conventional method form inhomogeneous agglomerates with large particle size. Therefore, these must be ground or milled to get further smaller particles. Both the crystallinity and morphology of the phosphors are

greatly damaged during this process, resulting in the loss of luminescence efficiency[6-8].

However, by using combustion method, it is possible to synthesize phosphor powders with high surface area because it forms small-size particles in comparison with those from conventional method. The combustion method involves the exothermic reaction between metal nitrate and fuel. Generally, oxidizers such as metal nitrates, ammonium nitrate and ammonium perchlorate are used, and urea ( $\text{CH}_4\text{N}_2\text{O}$ ), glycine ( $\text{C}_2\text{H}_5\text{NO}_2$ ), and oxylydihydrazide play an important role as organic fuels[9-14].

In continuation of our previous studies on phosphor materials, we now report the properties of  $\text{Eu}^{3+}$ -doped gadolinium oxide phosphors which have been prepared by combustion process using urea or carbonylhydrazide as fuel.

## 2. EXPERIMENTAL

High grade chemicals from Aldrich Chemical Co. were used for experiments. As starting materials, gadolinium oxide ( $\text{Gd}_2\text{O}_3$ ) and europium oxide ( $\text{Eu}_2\text{O}_3$ ) were used with ethylenediaminetetraacetic acid (EDTA)

described as the best chelating materials in the previous report. Urea or carbohydrazide was taken as a fuel for experiments. The mixture was reacted thoroughly with diluted nitric acid to make aqueous solution and then dried stirring at  $100^\circ\text{C}$  on the hot plate. The amounts of urea and carbohydrazide were calculated using total oxidising and reducing valencies as reported by Ekambaram and Patil[15-17]. Weights corresponding to 1.66 moles of urea and 1.25 moles of carbohydrazide for divalent metals(2.50 moles of urea and 1.875 moles of carbohydrazide for trivalent metals) were added to completely decompose the metal nitrates to their corresponding metal oxides in a preheated furnace at  $500^\circ\text{C}$ , and then these phosphors were fired again at  $1200^\circ\text{C}$  for 3 hours to increase the brightness.

The photoluminescence (PL) and color coordinates (C.E) were measured using spectroradiometer(Minolta CS-1000). The morphology and size of particles were investigated by SEM(Philips XL30) and EDAX(PV99).

### 3. RESULTS AND DISCUSSION

The combustion reaction was initiated in a muffle furnace at  $500^\circ\text{C}$ . The compound containing metal nitrates in stoichiometric ratios was decomposed on heating with urea or carbohydrazide. On heating at about  $500^\circ\text{C}$ , the metal nitrates were decomposed into metal oxides. The product obtained was white, voluminous, and foamy powder which occupied the entire volume of the reaction crucible. The phosphors, when further heated at  $1200^\circ\text{C}$  for 3 hours, were observed to have better intensity and smaller-sized particles compared to conventional synthesis method. By this method, it was definitely possible to synthesize phosphor having suitable crystallinity and fine particle size because the chemical energy released from the exothermic reaction between the metal nitrates and fuel could rapidly heat the system to high temperatures without any external heat source and the large amount of gases simultaneously formed dissipated the heat leaving voluminous fine powder. The advantage of applying the present fuels to phosphor preparation is that they are completely decomposed around  $500^\circ\text{C}$  producing sufficient heat to primarily prepare the phosphor, and that the escaping gases prevent the oxides from sintering. The effect of urea or carbohydrazide on the preparation of  $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$  phosphor is reported in this paper from the viewpoint of luminescence and morphology.

For comparison,  $\text{Eu}^{3+}$  doped gadolinium oxide phosphors with general formula  $(\text{Gd}_{1-x}\text{Eu}_x)\text{O}_3$  where  $0.03 \leq x \leq 0.18$  were prepared by conventional method.  $\text{H}_3\text{BO}_3$  (2 wt%) was added as a flux material in the mixture so as to decrease the synthesis temperature. The powder was milled for 2 hours in water and the prepared

paste was dried and then fired at  $1200^\circ\text{C}$  for 3 hours.

Figure 1 shows the brightness of  $(\text{Gd}_{1-x}\text{Eu}_x)\text{O}_3$  phosphor as a function of  $\text{Eu}^{3+}$  concentration when the phosphor was prepared by combustion method. As shown in this Figure, the brightness of the phosphor by combustion method showed a maximum value when  $\text{Eu}^{3+}$  concentration was approximately 0.05 mole( $x=0.05$ ).

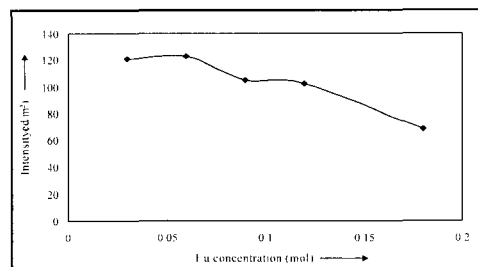
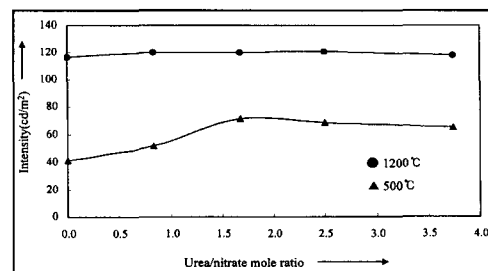
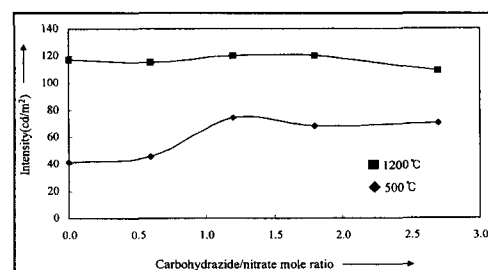


Fig. 1. Emission intensity(brightness) vs  $\text{Eu}^{3+}$  concentration for the  $(\text{Gd}_{1-x}\text{Eu}_x)\text{O}_3$  phosphor prepared by combustion method.

By observing Fig. 2 and Fig. 3 together, it is found that at  $500^\circ\text{C}$ , the emission intensity of  $(\text{Gd}_{1-x}\text{Eu}_x)\text{O}_3$  phosphor prepared by combustion method is increased by exothermic reaction between organic fuels and nitrates, compared to that from conventional method. But, when they were fired at  $1200^\circ\text{C}$ , the three phosphors showed almost the same emission intensity due to the termination of redox reaction.



(a) Urea



(b) Carbohydrazide

Fig. 2. Emission intensity(brightness) vs fuel/nitrate mole ratio for the  $(\text{Gd}_{1-x}\text{Eu}_x)\text{O}_3$  phosphor prepared by combustion method (fuel : (a) urea, (b) carbohydrazide).

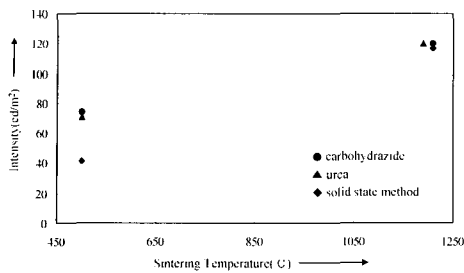


Fig. 3. Emission intensity vs sintering temperature for the  $(Gd_{1-x}Eu_x)O_3$  phosphor synthesized by combustion method (fuel:carbohydrazide/urea) and solid state method (conventional method).

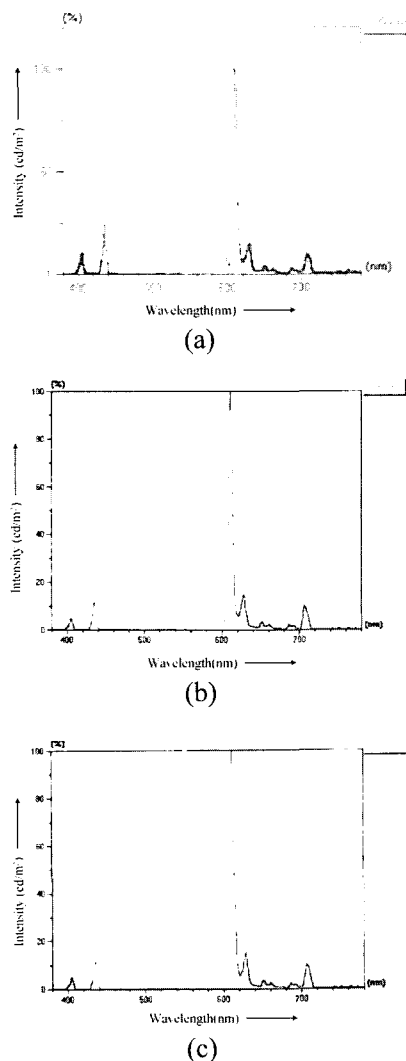


Fig. 4. Emission spectra of  $Gd_2O_3:Eu^{3+}$  phosphors prepared at  $1200^\circ C$ . (a) by conventional method ( $H_3BO_3$  2wt% as flux), (b) by combustion method (fuel : urea), (c) by combustion method (fuel : carbohydrazide).

Figure 4 and 6 show the emission spectra and color

coordinates of the phosphors prepared from different synthesis method (combustion method and conventional method) when they were fired at  $1200^\circ C$ , while Fig. 5 shows only emission spectra of the phosphors prepared at  $500^\circ C$ . From both Fig. 4 and Fig. 5, it is found that the phosphors (fuel : urea/carbohydrazide) synthesized by the combustion method display less emission intensities (lower peaks) than conventional method, at several wavelengths except 612nm (at 612nm, the peak intensities of (a), (b), and (c) in Figures 4 and 5 are almost the same), indicating better color purity. From Fig. 6, it is definitely shown that the color coordinates for combustion method ((b) and (c)) were more red-shifted than conventional method (a), backing up the above results and realizing improved red color purity.

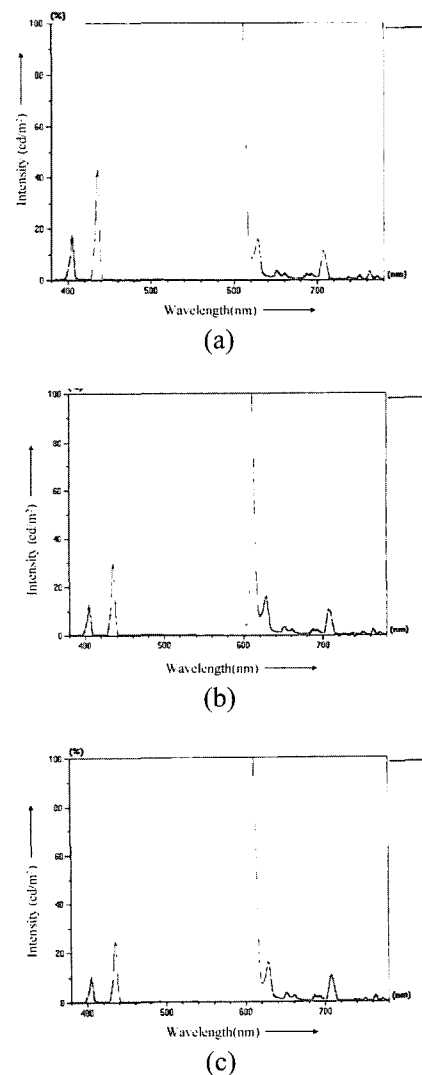


Fig. 5. Emission spectra of  $Gd_2O_3:Eu^{3+}$  phosphors prepared at  $500^\circ C$ . (a) by conventional method, (b) by combustion method (fuel : urea), (c) by combustion method (fuel : carbohydrazide).

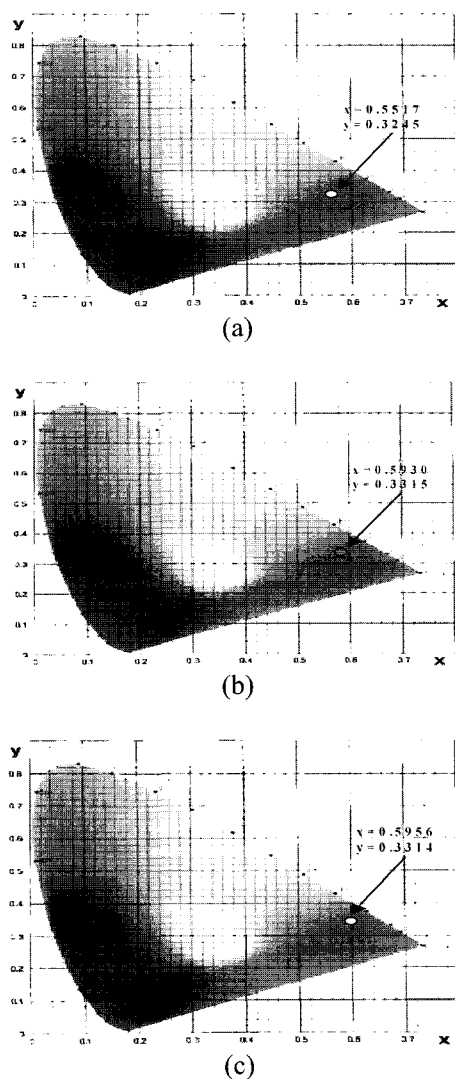


Fig. 6. Color coordinates of  $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$  phosphor prepared at  $1200^\circ\text{C}$ . (a) by conventional method ( $\text{H}_3\text{BO}_3$  2wt%), (b) by combustion method (fuel : urea), (c) by combustion method (fuel : carbonylhydrazide).

Figure 7 is the SEM (Scanning Electron Microscope) photos taken for combustion method ((b) and (c)) and

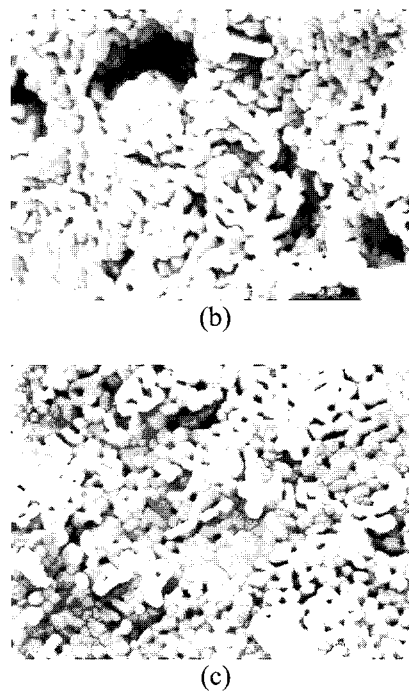
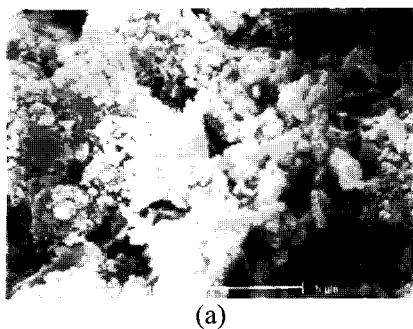


Fig. 7. SEM photos of  $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$  phosphor prepared at  $1200^\circ\text{C}$ . (a) by conventional method ( $\text{H}_3\text{BO}_3$  2wt% as flux), (b) by combustion method (fuel : urea), (c) by combustion method (fuel : carbonylhydrazide).

conventional method (a). From these SEM photos, it is found that the phosphors synthesized by the combustion method have more even particle size than the conventional method (solid state method), resulting in better emission intensity.

#### 4. CONCLUSION

By combustion method, it is possible to synthesize homogeneous and fine-size particles of  $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$  phosphors emitting in the red color range of 612nm. Combustion method makes it possible to synthesize  $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$  phosphor with better emission properties because fuel is completely decomposed with nitrate around  $500^\circ\text{C}$ , producing sufficient heat and flame to prepare the phosphor.

In this study, it was observed that the combustion synthesis method using carbonylhydrazide as a fuel is an ideal method to come up as a quick, straightforward preparation process to produce a homogeneous, finely sized, and crystalline europium-activated gadolinium oxide phosphor with no intermediate decomposition or firing steps.

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