

## Improved methods for the preparation of $(Y_{1-x}Eu_x)_2O_3:MX$ and $(Y_{1-x-y}Gd_xEu_y)_2O_3:MX$ as red phosphor materials

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### Abstract

Substantially improved methods for the preparation of europium-doped yttrium oxide red phosphor with the inclusion of alkali metal halides having a general formula  $(Y_{1-x}Eu_x)_2O_3:MX$  where  $0.025 \leq x \leq 0.2$  and MX is alkali halide in the mole ratio 0.025 to 0.6, more preferably between 0.05 to 0.2 mole, are reported. Another series of the red phosphor materials with general formula  $(Y_{1-x-y}Gd_xEu_y)_2O_3:MX$  where

$0.05 \leq x \leq 0.40$  and  $0.025 \leq y \leq 0.20$  and MX is alkali halide in the mole ratio 0.025 to 0.5, more preferably between 0.1 to 0.2 mole, has also been presented. The inclusion of alkali halide greatly increase the luminance of the materials. The materials are very soft with fine particle size less than 100nm. The phosphorescent materials have good luminance in VUV region.

### 1. Introduction

Phosphors are used for the display of information since the invention of cathode ray tube (CRT) by Karl Ferdinand Braun in 1897 [1]. Most of the advancement in phosphor came in the last 30 years with the development of color television. Today the primary focus of the research in this field is the phosphor development and improvement for the low-voltage emissive flat-panel displays. Flat-panel display includes the electro-luminescent displays(EL), field emission displays(FEDs), plasma display panels(PDPs) and vacuum fluorescent displays(VFDs). The FED is the most promising candidate among information display systems.

Europium-doped yttrium oxide phosphors are well known photo- and cathodo-luminescent materials that are used in fluorescent lamps and cathode ray tube(CRT) displays for television or laptop computer etc. These materials luminesce with a red color with  $\lambda_{em}$  at 611nm when excited with high

energy electrons, the electronic transition is mainly due to  $4f \rightarrow 4f$  transition of the  $Eu^{3+}$  ions.

Disadvantages of Cathode ray tube for many applications are due to its size and power consumption. However field emission display(FED) solves many problems of the conventional CRT displays. The power consumption of FED is very low and has been applied in many display system like laptop computers, head-mounted displays etc. Stating briefly the technicalities of the FED system, very small particle size of phosphorescent material is required instead of larger particles since small particles have more surface area per unit weight and having good packing properties for flat panel displays. Comparatively thinner phosphor screens are required in order to increase the light transmission with improved spatial resolution and reduced saturation effects.

Most of the red phosphor emit red color between 500V to 1kV. The maximum efficiency reported for a powder at 1kv is 7.5 lm/W for  $Y_2O_2S:Eu$  followed by 7 lm/W for  $Y_2O_3:Eu$  in

1997 [2]. Also, the most efficient screen is 6.5 lm/W from  $Y_2O_3:Eu$  at 1kV [2]. This high and aggregation of particles takes place increasing the size of the particles which is not suitable for systems like field emission display or flat panel display systems. People working in this field are well aware with these problems.

Many difficulties are encountered in the preparation of europium-doped yttrium oxide materials. Usually the preparation requires a multi-step processes and many workers in this field have presented their own methods [1, 3, 4]. In all these processes, heating at a high temperature usually above 1100°C for many hours is required. During the process of heating, the phosphor particles grow in big-sized particles and when these are milled usually loose the luminescence characteristics.

## 2. Experimental

The first method is based on the facile combustion process [5], in which nitrates (appropriate amounts of yttrium nitrate, europium nitrate etc.) are decomposed with stoichiometric amounts of urea (2.5 moles of urea for one mole of trivalent metal ion) at 400°C, producing a mixture of combustible gases like oxides of nitrogen, ammonia, HCNO etc. The clear concentrated solution boiled immediately, resulting in the formation of a gel. The gel then formed a white gel foam which expanded to fill the quartz vessel. Shortly thereafter, the reaction initiated with the flame on the surface and spread over the entire volume, leaving a white powder with an extremely porous structure. The resulting mixture was powdered in a mortar and then placed in a plastic bottle containing glass beads of 2.5 mm diameter and water was added to make a slurry and then milled for about an hour at 100 rpm. The powder was washed thoroughly with water and then dried in an oven at 110-120°C.

In the second method, a microwave oven (Sam-sung RE-CM 160S with specifications 2450 MHz and output 1600 Watt) was used to propagate the above-said reaction instead of the heating in a furnace. Thoroughly mixed concentrated solutions of yttrium nitrate and europium nitrate were boiled first to convert into a gel and placed in the microwave oven adjusting its

maximum intensity for different time intervals. Within a minute, a bright white flame appeared that made the white powder with an extremely porous structure.

The materials with general formula  $(Y_{1-x}Eu_x)_2O_3:MX$  ( $0.05 < x < 0.2$ ) were prepared by dissolving yttrium nitrate with europium nitrate (alternatively taking oxides and converting them to nitrates) and  $(Y_{1-x-y}Gd_xEu_y)_2O_3$  ( $0.05 < x < 0.04$ ,  $0.025 < y < 0.2$ ) were prepared by dissolving a mixture of yttrium and gadolinium oxide/nitrate in pure water and preparing the phosphor materials as stated above.

## 3. Results and discussion

Inclusion of alkali halide between 0.025 mole to 0.6 mole with respect to the phosphor material in the above-said series, while dissolving the metal nitrates greatly increased the luminance of the materials. It was noticed that the most preferable amounts of alkali halides should be between 0.05 to 0.2 mole, where luminance is more than double. Lower amounts than 0.05 mole gave less luminance, while luminance was maximum in some cases when taken above 0.25 mole of some alkali halides, but the material lost its softness. The most compromisable amounts thus were between 0.05 to 0.2 mole of alkali halide per mole of the phosphorescent material, where the material formed was very soft. After grinding the particle size of the material was found to be about 100 nm without losing luminance.

The phosphor samples prepared by the present methods were characterized by the X-ray diffraction (XRD) spectrometer performed by a Rigaku spectrometer model D/Max 2000-Ultima (Japan) with a  $CuK\alpha$  radiation. Fig. 1 is the XRD patterns obtained for the red phosphor compositions (a)  $(Y_{0.95}Eu_{0.05})_2O_3$  without adding any alkali halide and (b)  $(Y_{0.95}Eu_{0.05})_2O_3:0.1NaCl$ , when prepared in the preheated furnace maintained at 500°C and heating for 20 minutes.

Powder morphology of the phosphors were determined by the scanning electron microscope using a Philips XL series model and elemental compositions were also checked by EDAX using the Philips EDAX PV 9900 series.

Fig.2 SEM photographs of the  $(Y_{0.95}Eu_{0.05})_2O_3:0.1NaCl$  phosphor composition prepared in the furnace (a) and microwave(b)

#### 4. Conclusion

The present methods are extremely simple, time saving and energy saving processes removing difficulties of in conventional method in the preparation of the said red phosphors. Soft and fine-particle sized phosphor materials are obtained with the present methods.

#### 5. References

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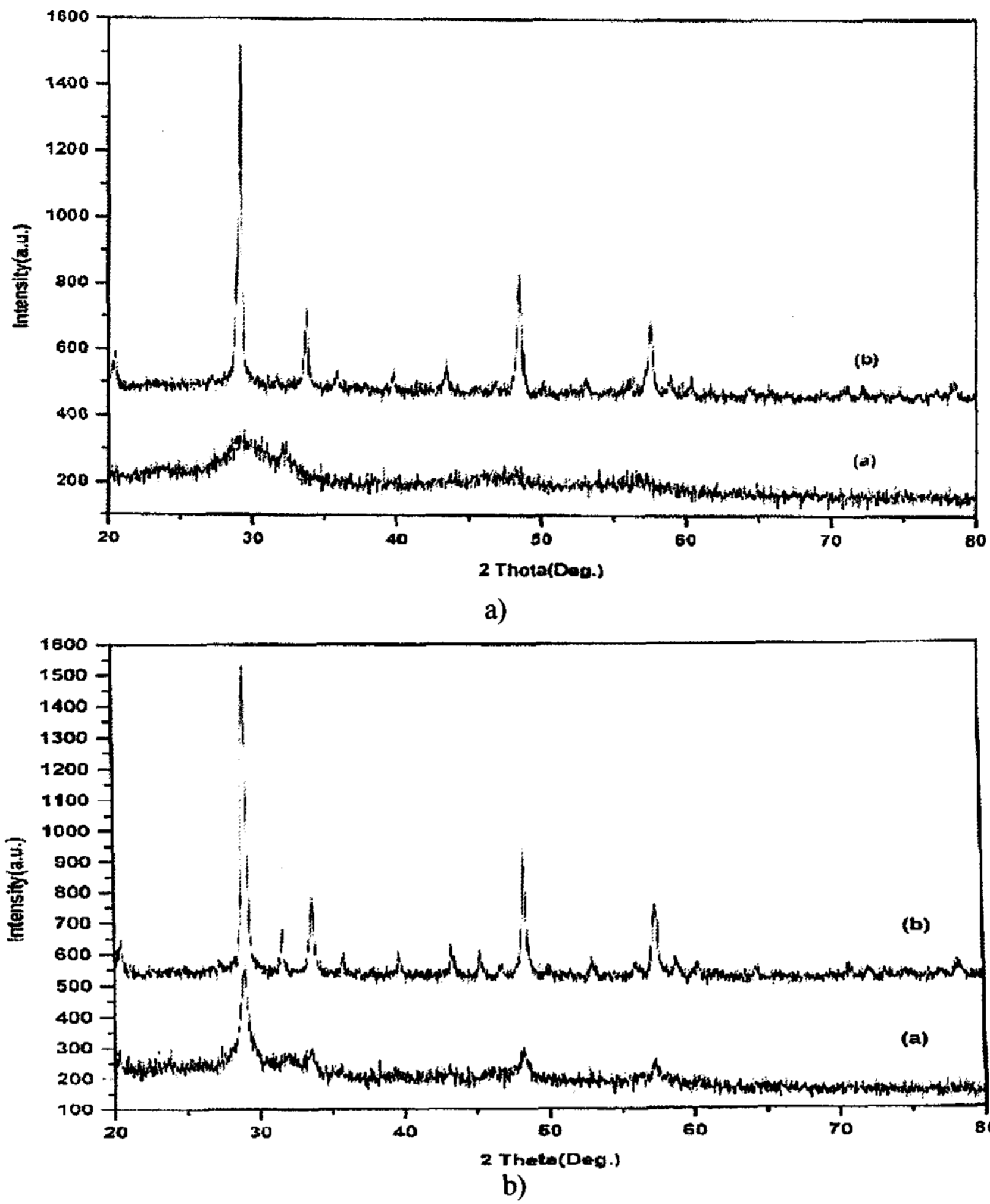


Figure 1 XRD patterns obtained for the red phosphor compositions:  
(a)  $(Y_{0.95}Eu_{0.05})_2O_3$ , (b)  $(Y_{0.95}Eu_{0.05})_2O_3:0.1NaCl$

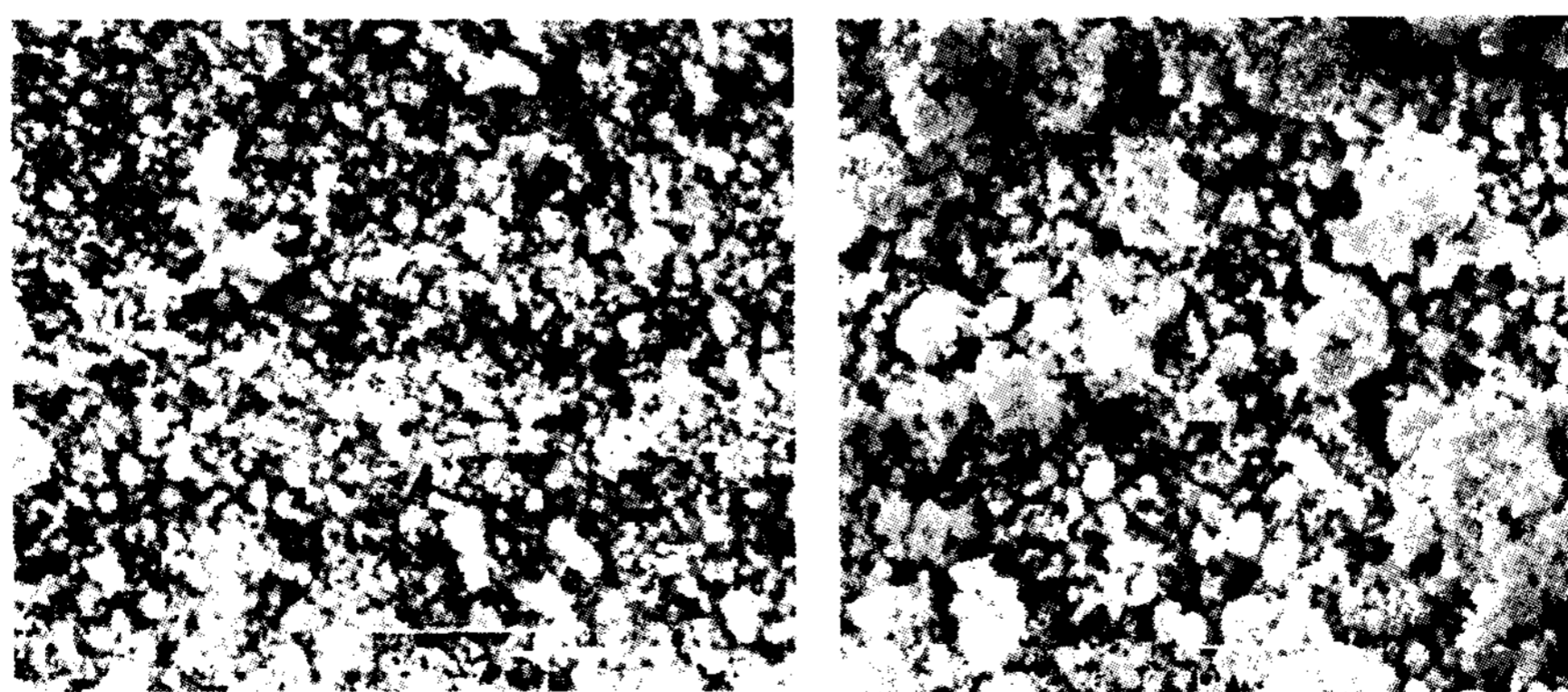


Figure 2 SEM photographs of the  $(Y_{0.95}Eu_{0.05})_2O_3:0.1NaCl$  phosphor composition prepared in the furnace (a) and microwave (b)