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The study on Luminescent properties of Red Emitting phosphor for plasma display panel

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PDP용 적색형광체의 발광특성에 관하여

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Abstract

PDP용 적색형광체는 penning가스(Ne 및 5% Xe혼합가스)에 의해 방출되는 147nm파장에서 쉽게 여기되어 높은 양자효율을 주는 물질로 이루어지는데 본 실험은 발광효율을 높이기 위하여 Y_2O_3:Eu, $(Y,Gd)_2O_3$:Eu 및 $(Y,Gd)BO_3$:Eu를 공침법으로 합성하여 부활제인 Eu^{3+}의 농도, Flux첨가에 따른 미시조직의 변화등을 여기·방출 스펙트럼을 통해 발광효율을 조사하여 다음과 같은 결론을 얻었다.

Y_2O_3:Eu 형광체 합성시 최적조정은 Y_2O_3에 대한 Eu_2O_3의 몰비는 5:1, $BaCO_3$ 첨가시 몰비는 15:1로 나타났으며 2차 소성시 1200℃이상에서 1~3㎛의 구형입상이 형성되었으며 입자의 크기, 형상은 발광특성에 영향을 미쳤다. 또 Eu^{3+}농도는 7wt%가 최적조건으로 나타났다.

1. Introduction.

Phosphors are materials that efficiently generate steady-state photoluminescence through some form of excitation energy conversion, which it was used in fluorescent lamps, lasers, digital radiographys, high definition TV screen, fiber optics and solar concentration[1, 2].

Phosphors for CRT are excited by accelerated electron beam in brown tube. Phosphors for PDP must be efficiently excited by the 147nm wavelength which radiate from penning gas (Ne-5% Xe mixing gas) discharge[3] and then emit light through energy transfer after absorbing the incidence energy in sensitizer as in Fig. 1.

The development of phosphors with high conversion efficiency and color purity is required[4] for the products of various kind of flat panel display such as liquid crystal display, light emitting diode display, laser fluorescent display, elecroluminescent display, plasma display panel and field emission display.

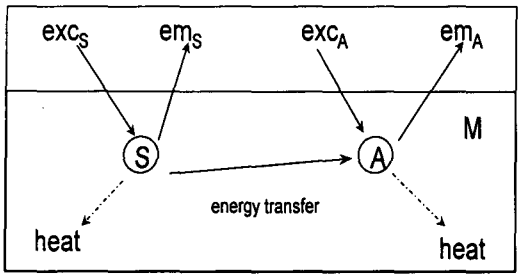


Fig. 1. Schematic diagram of emission process.
It s composed of matrix, activator and sensitizer.
M : It is crystal grain (not absorbed radiation)
A : activator, S : sensitizer, exc ; excitation
em : emission

Table 1 shows typical PDP phosphor materials[5]. Although these are highly efficient phosphors now in use, there is still a need for improving a chromaticity in red and green phosphors that uses faster activators like Eu and Mn. In fact, it is very important to attain longer lifetime for all of the phosphors used in a plasma display.

In this paper, the characterization of photoluminescence and crystallization was observed from red phosphors such as Y_2O_3 : Eu, $(Y,Gd)_2O_3$: Eu and $(Y,Gd)BO_3$: Eu which it was made by firing mixed composition of Y_2(oxalate)$_3$and Gd_2(oxalate)$_3$with a flux of ($BaCO_3$). Scanning electron microscopy, X-ray Diffraction method and IR spectrometry have been used to investigate the effect of concentration, added flux, shape and size of particles.

Table 1. PDP Phosphor

Red	Green	Blue
Y_2O_3 : Eu	Zn_2SiO_4 : Mn	$CaWO_4$: Pb
Y_2SiO_5 : Eu	$BaAl_{12}O_{19}$: Mn	Y_2SiO_5 : Ce
$Y_3Al_5O_{12}$: Eu	$BaMgAl_{14}O_{23}$: Mn	$BaMgAl_{14}O_{23}$: Eu
$Zn_2(PO_4)_2$: Mn	$SrAl_{12}O_{19}$: Mn	
YBO_3 : Eu	$ZnAl_{12}O_{19}$: Mn	
$Y_{0.65}Gd_{0.35}BO_3$: Eu	$CaAl_{12}O_{19}$: Mn	
$GdBO_3$: Eu	YBO_3 : Tb	
$ScBO_3$: Eu	$LuBO_3$: Tb	
$LuBO_3$: Eu	$GdBO_3$: Tb	
$ScBO_3$: Tb	$Sr_4Si_3O_8C_{14}$: Eu	

2. Experiment.

Phosphors for PDP with the composition [Y_2O_3 : Eu, $(Y,Gd)_2BO_3$: Eu, $(Y,Gd)_2O_3$: Eu] were prepared by firing intimate mixtures of MCO_3 and $(Y,Gd : Eu)_2(CH_3CO_2)_3$. Y_2O_3, Gd_2O_3 and Eu_2O_3 were dissolved in acetic acid to get co-precipitation with the oxalic acid. Materials obtained were mixed with same flux ($BaCO_3$, $SrCO_3$) after the 1st calcining. The mixture was fired at 1350℃ in alumina crucibles for 3 hours in the air.

Fig. 2 is the flow chart of co-precipitation process of red phosphors, [Y_2O_3 : Eu, $(Y,Gd)BO_3$: Eu]. The phosphor powder was pulverized into fine powder of 3㎛ diameter. The excitation spectra between 200 and 400㎛ were obtained with a OG 530 filter on excitation slit 0.28㎛ and emission slit 0.9㎛ by spectrofluorimeter under light

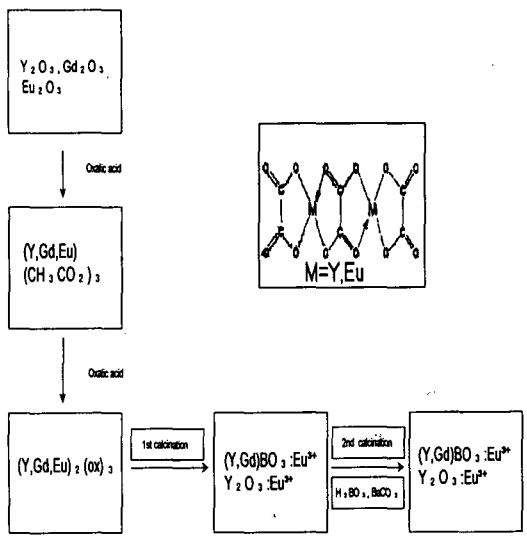


Fig. 2. The flow chart of co-precipitation

source of 150W for selective irradiation. The emission spectra were collected by spectrofluorimeter as a function of excitation wavelength. Products were examined by chemical analysis, X-Ray diffraction and scanning electron microscopy.

3. Result and discussion.

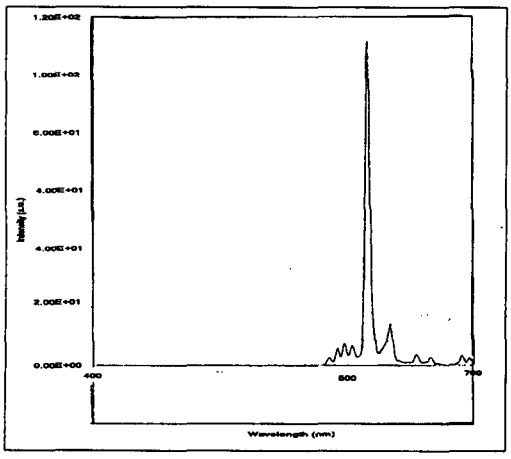
Phosphor efficiency is based on the quantum yield of a material, which is ultimately determined by the existence of other non-radiative pathways that compete with luminance[6]. Concentration usually extracts potential emission by radioactively transferring its energy to the adjacent chromaphors[7]. Then it is important to investigate the characterization related to the synthesize mechanism of phosphor materials.

3. 1. The effect of flux.

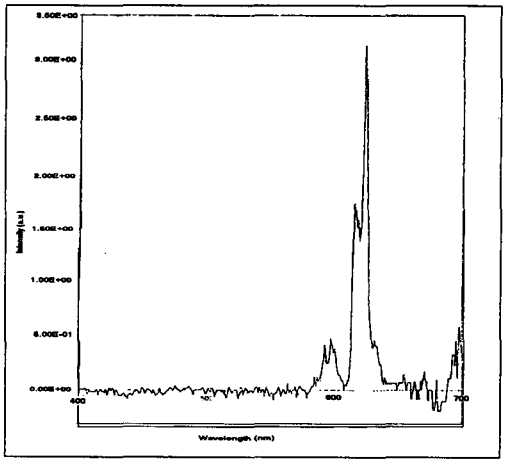
Fig. 3 shows the dependence of emission spectra of Y_2O_3 : Eu phosphor on the used flux. The peaks occurred at 254nm both, but more sharp peak was obtained by adding $BaCO_3$. It seems the results the dependence of oxalate process and crystal characterization by adding flux[8] ($BaCO_3$ mole fraction was 15 : 1).

Fig. 4 shows the XRD Patterns of Y_2O_3 : Eu phosphor on using flux with increasing temperature. Sharpened and high intensity in the XRD patterns shall indicate a well ordered structure and is necessary to obtain information on formation of homogeneous compound[9]. In optimum condition, 1mole % $Eu_2O_3$and 5mole% $Y_2O_3$was carried into oxalic acid in adding flux, $BaCO_3$ mole fraction was 15 : 1

Photo 1 is the Scanning Electron Micrographs of Y_2O_3 : Eu phosphor. It shows the change of crystal structure that adding flux and increasing temperature was processed from plate of 10㎛ to spheroidal shape of 1㎛ fine particle. It means that the number of nuclei per unit volume is increased enormously and solid state reaction was increased.

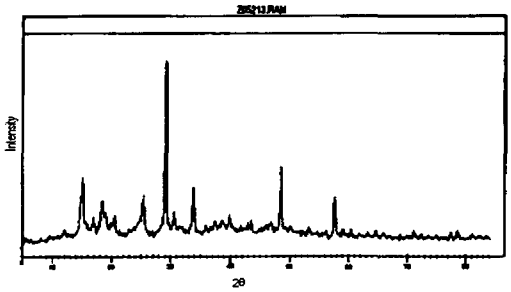


a) Emission spectra of Y_2O_3 : Eu which is produced at 800℃ for 3hr after addition of $BaCO_3$

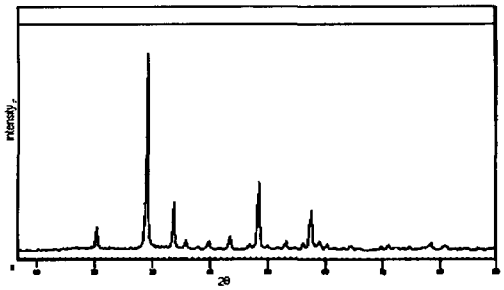


b) Emission spectra of Y_2O_3 : Eu whcih is produced to oxalic acid compound.

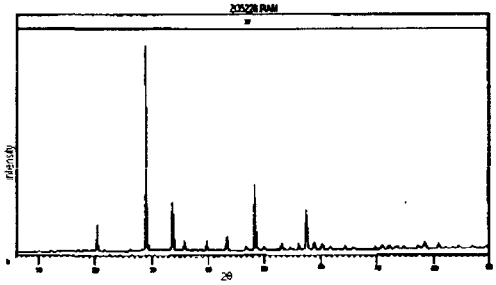
Fig. 3. Emission spectra of Y_2O_3 : Eu



a) Oxalate treated

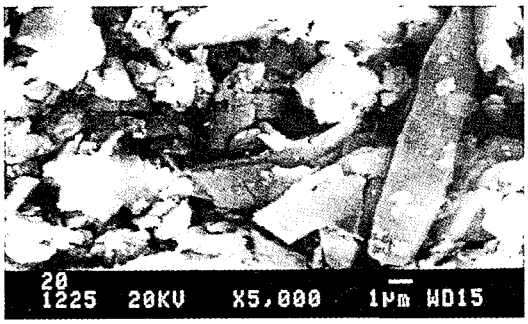


b) Firing at 800℃ for 3hr (added $BaCO_3$)

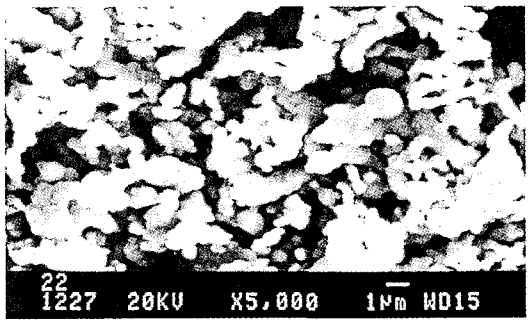


c) Firing at 1350℃ 3hr (added $BaCO_3$)

Fig. 4. XRD patterns of Y_2O_3 : Eu



a) Not added flux (firing at 800℃, 2hrs)



b) $BaCO_3$added (firing at 1350℃, 2hrs)

Photo 1. The SEM micrographs of Y_2O_3 : Eu phosphor

3. 2. The characterization of phosphor materials.

Fig. 5 is normalized emission spectra of red emitting phosphors for bring excited by 147nm ultraviolet ranges. The wavelength of maximum emission intensity is 591nm for $(Y,Gd)BO_3$: Eu, 611nm for $(Y,Gd)_2O_3$: Eu. The longer and narrower maximum emission peak is advantage for application of display due to the wide color gamut[10]. In three kinds of red emitting phosphor [Y_2O_3 : Eu, $(Y,Gd)_2O_3$: Eu and $(Y,Gd)BO_3$: Eu],

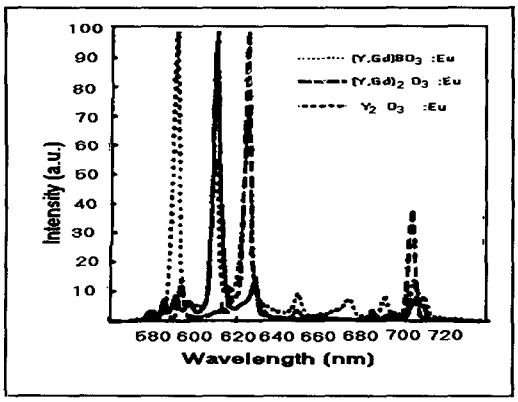


Fig. 5. Normalized emission spectra of red emitting phosphors.

it shows that $(Y,Gd)_2O_3$: Eu is better ($\triangle Y$: -0.01) than color coordinator of Y_2O_3 : Eu. It shows the crystalline field change and the width of the emission spectra is broadened by the Gd substitution of Yttrium site in Y_2O_3 : Eu.

3. 3. The effect of Eu^{3+} concentration.

Fig. 6 shows the effect of Eu^{3+} concentration with selective irradiations. In the emission intensity of $(Y0.9Gd0.1)_{1-x}BO_3$: Eu_X obtained from the 255nm, 277nm and the 320nm luminescent source. Under the 255nm and 320nm, maximum

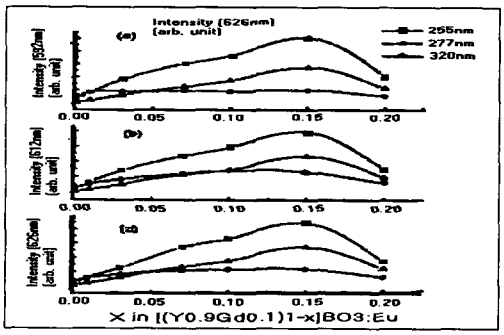


Fig. 6. Luminance vs. Eu concentration of (Y, Gd)$_2O_3$: Eu under the 147nm and 254nm excitation (Y : Gd=5 : 4)

intensity shows 0.15mole fraction of Eu^{3+} concentration. It's effect of Gd^{3+} which are due to transition from the higher crystal field levels of the $^6P_{1/2}$ level[11]. The emission of Eu^{3+} usually consists of lines in the red spectral area, which these lines correspond to the transitions from the exited $^5D_0$ level to the $^7F_5$ levels of the $^4f_6$ configuration[12].

Fig. 7 shows the change of Luminescences vs. Eu concentration of $(Y,Gd)_2O_3$: Eu under the 254nm and 147nm excitation. High concentration Eu shows high luminescence in 254nm, where as maximum luminescence was represented about 7wt% of Eu concentration under 147nm. That is, there were limited value of Eu concentration for luminescence

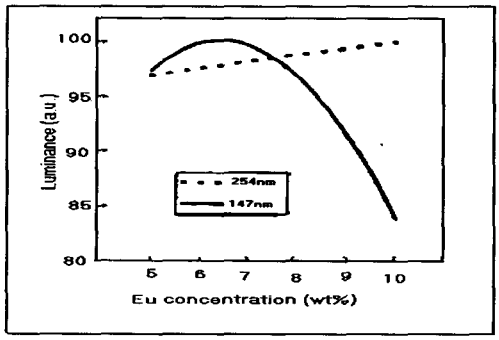


Fig. 7. Luminance Vs. Eu concentraion of (Y, Gd)$_2O_3$: Eu under the 147nm and 254nm exitation (Y : Gd=5 : 4)

4. Conclusion

Red emitting phosphor with 3 formulas of Y_2O_3 : Eu, $(Y,Gd)_2O_3$: Eu and $(Y,Gd)BO_3$: Eu for plasma display has been synthesized by co-precipitation method. The effect of adding flux, temperature and Eu^{3+} concentration was investigated by the emission spectra, excitation spectra and lumi-

nescence.

1) Quantum efficiencies are high where the $BaCO_3$ mole ratio for Y_2O_3 : Eu is 0.067.

2) Particles were changed from coarse plate shape to fine spheroidal by adding flux.

3) The crystal field change and the width of the emission spectra was broadened by the Gd substitution of yttrium site in Y_2O_3 : Eu.

4) In the emission intensity for luminance under the 147nm, optimum mole fraction of Eu_3^{3+} concentration was 7wt%.

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