Fast response time PDP phosphors for 3D display application

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Abstract

New phosphors that enable the 3D application of PDP have been developed. The decay times of $Y_3Al_5O_{12}$: Ce^{3+}, $(Y,Gd)Al_3(BO_3)_4$:Tb^{3+}, and $(Y,Gd)_2O_3$:Eu^{3+} were extremely shorter than those of conventional PDP phosphors. The color coordinates and intensities of the phosphors were also suitable for PDP. For the first time in PDP industry, 3D/2D switchable PDP has been commercially available by adopting the phosphors.

1. Introduction

The interest in 3D displays has grown steadily because of increasing needs for advanced image devices. Stereoscopic 3D displays using special glasses have been considered as most promising methods because of their high image quality and cost-effectiveness.[1] However, these methods undermine color reproduction efficiency or image resolution. To overcome such difficulties, one has to separate images for left and right eyes by dividing the scanning time period. Meanwhile, this type of 3D device requires high response time to prevent an overlap between left (or right) and the following right (or left) images. It is known that the response time of plasma display panel (PDP) is faster than liquid crystal display (LCD). However, it is still insufficient for 3D PDP. Therefore, fast-decaying PDP phosphors have to be developed.

The 1/10 decay time, determined from the first 10-folding time of phosphor luminescence, should be less than 4.0msec to prevent the cross talk between images. Conventional PDPs are mainly using $(Y,Gd)BO_3$:Eu^{3+}, Zn_2SiO_4: Mn^{2+} (or YBO_3:Tb^{3+}) and $BaMgAl_{10}O_{17}$:Eu^{2+} phosphors to generate red, green and blue colors, respectively.[2] The decay time of $BaMgAl_{10}O_{17}$:Eu^{2+} is extremely short (<1.0msec). However, those of Zn_2SiO_4:Mn^{2+}, YBO_3:Tb^{3+} and $(Y,Gd)BO_3$:Eu^{3+} are 7.3, 9.2 and 8.3msec, respectively. The Zn_2SiO_4:Mn^{2+} decay time decreases with Mn addition. However, it is impossible to decrease the decay time less than 4.0msec since the luminescence intensity of Zn_2SiO_4:Mn^{2+} also decreased with Mn addition.[3] For YBO_3:Tb^{3+} and $(Y,Gd)BO_3$:Eu^{3+}, one cannot efficiently control the decay times by changing the activator concentrations. Therefore, 3D image resolution can be deteriorated when PDP uses conventional phosphors.

This work is concerned with the development of fast-decaying green and red phosphors for 3D PDP. The luminescence properties of $Y_3Al_5O_{12}$:Ce^{3+}, $(Y,Gd)Al_3(BO_3)_4$:Tb^{3+}, and $(Y,Gd)_2O_3$:Eu^{3+} under vacuum ultraviolet (VUV) excitation were suitable for PDP applications. The decay time and CIE color coordinate values were adjusted by making a phosphor mixture.

2. Experimental

Phosphors of the present study were synthesized with a solid-state reaction. Commercial Zn_2SiO_4:Mn^{2+}, YBO_3:Tb^{3+}, $(Y,Gd)BO_3$:Eu^{3+}, and $Y(V,P)O_4$:Eu^{3+} were used as references.

Emission spectra were obtained by exciting the phosphors using a VUV light from Kr excimer lamp or Xe gas-discharge. Luminescence from the phosphors in the 380 ~ 780nm wavelength region were recorded using a CCD array coupled with a grating. Decay curves were measured using a Xe flash lamp (147nm) and a digital oscilloscope. Excitation spectra were measured at 130 ~ 300nm using deuterium lamp. The wavelength of excitation light was selected by using a vacuum monochromator. The

spectral response of the measurement system was calibrated using a light from sodium salicylate powder.

42" PDP adopting the developed green and red phosphors was also prepared with a standard PDP fabrication process.

3. Results and discussion

3.1. Fast-decaying Green Phosphors

Fig. 1 shows decay curves of $Y_3Al_5O_{12}:Ce^{3+}$ and $(Y,Gd)Al_3(BO_3)_4:Tb^{3+}$ under 147 nm excitation light. The decay profiles of conventional $Zn_2SiO_4:Mn^{2+}$ and $YBO_3:Tb^{3+}$ were also recorded. The 1/10 decay times of $Y_3Al_5O_{12}:Ce^{3+}$, $(Y,Gd)Al_3(BO_3)_4:Tb^{3+}$, $Zn_2SiO_4:Mn^{2+}$, and $YBO_3:Tb^{3+}$ were < 0.6 ± 0.3, 4.9 ± 0.3, 7.3 ± 0.3, and 9.2 ± 0.3msec, respectively. The decay times of rare-earth doped phosphors are relatively long because intra f-f electric dipole transition in rare-earth ion is forbidden due to the parity forbidden rule.[4] However, $Y_3Al_5O_{12}:Ce^{3+}$ generate green light by allowed 5d-4f transition.[5] The d-f transition rate was extremely high (> 10^6/sec) and this resulted in the fast decay of the luminescence from phosphor. The decay time of $(Y,Gd)Al_3(BO_3)_4:Tb^{3+}$ (4.9msec) was also shorter than that from same activators in YBO_3 (9.2msec). In $(Y,Gd)Al_3(BO_3)_4$ crystal, 4f energy levels of Tb^{3+} ions are distorted by non-centrosymmetrical crystal field.[6] This results in a partial breaking of the parity forbidden rule and also increases the electric dipole transition rates in Tb^{3+}.

Upon 147nm excitation, $Y_3Al_5O_{12}:Ce^{3+}$ and $Zn_2SiO_4:Mn^{2+}$ generated broad emissions centered at 510 and 550 nm, respectively. $(Y,Gd)Al_3(BO_3)_4:Tb^{3+}$ and $YBO_3:Tb^{3+}$ showed several sharp emission peaks due to 4f-4f intra transitions in Tb^{3+}. The most intense peaks were at ~550nm. Table 1 shows the luminescence properties of the green phosphors. The CIE color coordinate values of $Y_3Al_5O_{12}:Ce^{3+}$ and $(Y,Gd)Al_3(BO_3)_4:Tb^{3+}$ were worse than conventional phosphors. The relative luminance of $Y_3Al_5O_{12}:Ce^{3+}$ was only 60% of $Zn_2SiO_4:Mn^{2+}$ reference. However, the luminance of $Y_3Al_5O_{12}:Ce^{3+}$ significantly increased when the VUV from Xe gas-discharge was used as an excitation source.

Table 1. Luminescence properties of green phosphors

	Sample	CIE x	CIE y	Luminance
Conventional	$Zn_2SiO_4:Mn^{2+}$	0.26	0.70	100 %
	$YBO_3:Tb^{3+}$	0.34	0.61	85 %
New	$(Y,Gd)Al_3(BO_3)_4:Tb^{3+}$	0.34	0.59	95 %
	$Y_3Al_5O_{12}:Ce^{3+}$	0.42	0.56	60 %

Fig. 2 shows excitation spectra of the phosphors. The Xe gas-discharge generates both 147 and 173 nm VUV lights. The excitation efficiency of $Y_3Al_5O_{12}:Ce^{3+}$ was higher at 173nm wavelength than that of 147nm. This indicates that $Y_3Al_5O_{12}:Ce^{3+}$ can be efficiently excited by the PDP discharge. In addition, it was believed that the luminescence saturation properties of $Y_3Al_5O_{12}:Ce^{3+}$ was also responsible for the high efficiency. Under intense excitation, the light emitting efficiency of phosphor

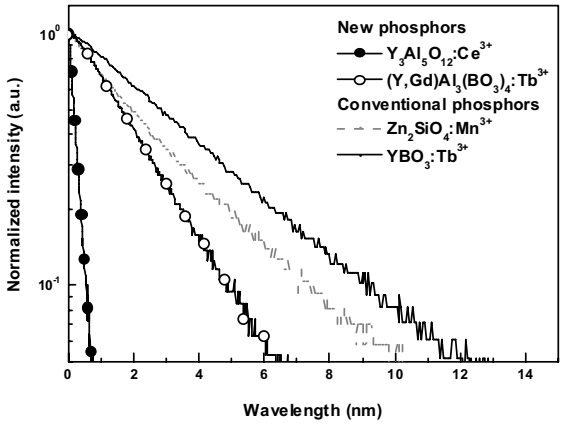

Fig. 1. Decay curves of green phosphors

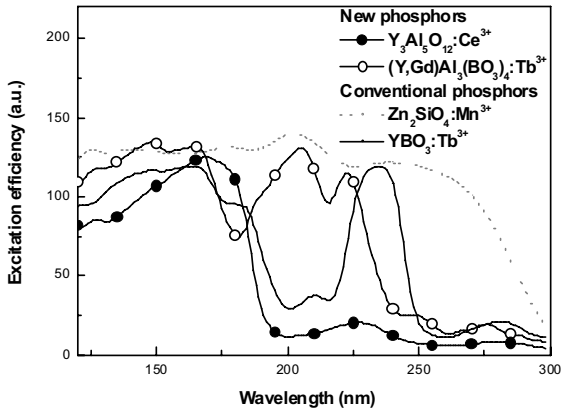

Fig. 2. Excitation spectra of green phosphors.

can be decreased.[7,8] However, the fast decay time of $Y_3Al_5O_{12}:Ce^{3+}$ represented its good light generation efficiency. $Y_3Al_5O_{12}:Ce^{3+}$ can generate emissions without losing energy by non-radiative quenching even under intense excitation. It is also reported that the saturation properties of Tb^{3+} activated phosphors are better than that of $Zn_2SiO_4:Mn^{2+}$.[9] Analyses on the luminescence saturation properties of the fast-decaying phosphors also revealed their enhanced saturation properties (data not shown).

3.2 Fast-decaying Red Phosphor

Fig. 3 shows decay curves of emissions from $(Y,Gd)_2O_3:Eu^{3+}$, $(Y,Gd)BO_3:Eu^{3+}$, and $Y(V,P)O_4:Eu^{3+}$. Decay times of $(Y,Gd)_2O_3:Eu^{3+}$, $(Y,Gd)BO_3:Eu^{3+}$, and $Y(V,P)O_4:Eu^{3+}$ were 3.4 ± 0.3, 8.3 ± 0.3, and 3.7 ± 0.3msec, respectively. The emission spectra of the phosphors were also measured (Fig. 4). The emission peaks from Eu^{3+} can be divided into two spectral regions, 590 ~ 605 (magnetic dipole) and 605 ~ 630 nm (electric dipole). The most intense peaks of $Y(V,P)O_4:Eu^{3+}$, and $(Y,Gd)_2O_3:Eu^{3+}$ were located at 605 to 630nm region. This indicates that the electric dipole transition rates were higher than those from magnetic dipole transitions.

The relation between the 1/10 decay time and transition rates is as follows.

$$\frac{1}{\tau_{10}} = 0.434(A_{ed} + A_{md}) \qquad (1)$$

Here, τ_{10} represents 1/10 decay time. A_{ed} and A_{md} is electric dipole and magnetic dipole transition rates, respectively.

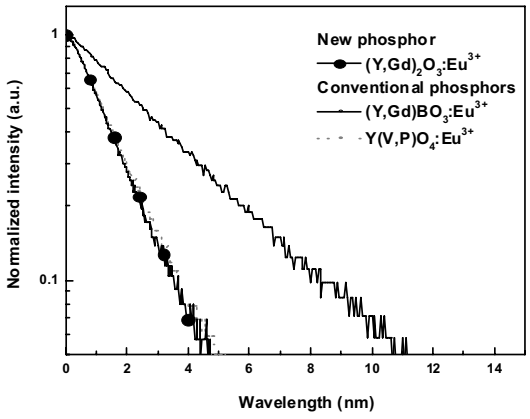

Fig. 3. Decay curves of red phosphors

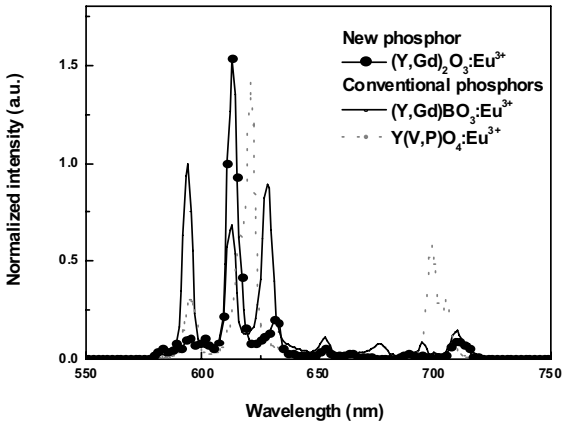

Fig. 4. Emission spectra of red phosphors

Therefore, decay time of phosphor decreases as the transition rate increases. The strength of electric dipole transition can be enhanced when Eu^{3+} are occupying a site without inversion symmetry, while that of magnetic dipole transition is independent from the site symmetry. Eu^{3+} ions are located at a site without inversion symmetry (D_{2d}) in $Y(V,P)O_4$ crystal. In $(Y,Gd)_2O_3$, Eu^{3+} ions occupy C_2 (non-centro symmetry) or S_6 (centrosymmetry) site. However, the red emission is mainly originated from Eu^{3+} ions in non-centrosymmetric C_2 site symmetry due to the energy transfer between Eu^{3+} ions.[10] Thus, the intense electric dipole transition of Eu^{3+} resulted in fast decay of excited Eu^{3+} ions in $(Y,Gd)_2O_3$.

Table 2 shows the luminance properties of the red phosphors. The CIE coordinate values of the phosphors were suitable for PDP. However, the luminance values of $Y(V,P)O_4:Eu^{3+}$ and $(Y,Gd)_2O_3:Eu^{3+}$ were 70 and 75% compared to that of $(Y,Gd)BO_3:Eu^{3+}$, respectively. Meanwhile, PDPs are using Ne-cut filter to attenuate 590nm light from PDP discharge. Therefore, the luminance of red phosphor can be greatly decreased because of absorbed emissions at ~590nm. However, $(Y,Gd)_2O_3:Eu^{3+}$ have weak peaks at the wavelength region resulting in only a slight luminance decrease. The luminance of $(Y,Gd)_2O_3:Eu^{3+}$ reached up to 90% of $(Y,Gd)BO_3$ after the attachment of Ne-cut filter.

3.3 Luminescence characteristics of 3D PDP

Table 3 shows the luminescence properties of phosphors in 42" PDPs. Changes in color coordinates of phosphors were negligible (data not shown). The luminance of $Y_3Al_5O_{12}:Ce^{3+}$ was enhanced in PDP due

Table 2. Luminescence properties of red phosphors

	Sample	CIE x	CIE y	Luminance
Conventional	$YBO_3:Eu^{3+}$	0.65	0.35	100 %
	$Y(V,P)O_4:Eu^{3+}$	0.67	0.33	70 %
New	$(Y,Gd)_2O_3:Eu^{3+}$	0.66	0.34	75 %
Conventional (with filter)	$YBO_3:Eu^{3+}$	0.67	0.33	100 %
	$Y(V,P)O_4:Eu^{3+}$	0.68	0.32	85 %
New (with filter)	$(Y,Gd)_2O_3:Eu^{3+}$	0.67	0.33	90 %

Table 3. Luminescence properties of phosphors in PDP

	Sample	Luminance (under 147nm)	Luminance (in PDP)
Conventional	$Zn_2SiO_4:Mn^{2+}$	100 %	100 %
New	$Y_3Al_5O_{12}:Ce^{3+}$	60 %	110 %
	$(Y,Gd)Al_3(BO_3)_4:Tb^{3+}$	95 %	110 %
	Phosphor mixture	85 %	95 %
Conventional	$YBO_3:Eu^{3+}$	100 %	100 %
New	$(Y,Gd)_2O_3:Eu^{3+}$	75 %	90 %

to its luminescence saturation property and the high emission efficiency at ~173nm region. The luminance reached up to ~110% of $Zn_2SiO_4:Mn^{2+}$. Meanwhile, the broad green emission of $Y_3Al_5O_{12}:Ce^{3+}$ deteriorated green color reproduction of PDP. The use of $(Y,Gd)Al_3(BO_3)_4:Tb^{3+}$ was also limited since its decay time exceeded 4.0msec. To achieve suitable luminescence properties, green phosphor mixture was prepared with $Zn_2SiO_4:Mn^{2+}$ (50wt%), $(Y,Gd)Al_3(BO_3)_4:Tb^{3+}$ (25wt%), and $Y_3Al_5O_{12}:Ce^{3+}$ (25wt%). It should be noted that Zn_2SiO_4 containing large amount of Mn was used to make the mixture. The decay time and relative luminance of the phosphor were 5.5 ± 0.3msec and 85%, respectively.

3D PDP generate 3D image by making left and right images in one TV field (16.7msec). Shutter glasses were used to select the images for each eye. To prevent the cross-talk, the decay time of phosphor should be less than 4.0msec. In a plasma display panel, the decay times slightly increased compared to those under 147 nm pulse excitation. The high frequency of sustain pulse (>100 kHz) generates a stream of visible lights in PDPs. In this case, a slow-decaying tails of light can be overlapped with the latter light. This can result in a slight increase in decay time. However, the increases in decay times were less than 1.0msec. The decay times of developed phosphor (or phosphor mixture) were significantly shorter than conventional phosphors. The cross-talk between images was not detected by human eyes. 3D PDP adopting the phosphors supports both 2D and 3D operation modes and the performance of 2D mode was similar to that of conventional PDP.

4. Summary

Fast-decaying phosphors were developed for 3D PDP applications. As green phosphors, $Y_3Al_5O_{12}:Ce^{3+}$ and $(Y,Gd)Al_3(BO_3)_4:Tb^{3+}$ selected since they have significantly short decay times compared to conventional green phosphors. The luminance values of the phosphors were increased in PDP due to their 173nm excitation efficiency or saturation properties. To adjust color reproduction efficiency of green phosphors, conventional $Zn_2SiO_4:Mn^{2+}$ were added into the green phosphor mixture. For red phosphor, emission properties of $(Y,Gd)_2O_3:Eu^{3+}$ were investigated. The phosphor has short decay time and relatively high luminance. By the use of the fast-decaying phosphors, commercialization of 3D PDP has been realized for the first time in PDP industry.

5. References

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