The electrical properties of phosphors for plasma display panels

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The electric properties of porous phosphor layers for plasma display panels were studied, which generated typical RGB colors from vacuum ultraviolet light; red is \((\text{Y}, \text{Gd})\text{BO}_3 : \text{Eu}^{3+}\) (YGB), green is \(\text{Zn}_2\text{SiO}_4 : \text{Mn}^{2+}\) (ZSM), and blue is \(\text{BaMgAl}_{10}\text{O}_{17} : \text{Eu}^{2+}\) (BAM). Because the phosphors were not fully packed in cells of a plasma display panel (PDP), their electrical properties were measured using an appearance density of approximately 60%. There was only a slight difference in the dielectric constants of the RGB phosphors; however, the dielectric loss of the green phosphor was much larger than that of either the blue or red phosphors. The volumetric resistivity of the powders had increasingly lower values according to the emission wavelengths of the phosphors.

Key words: Phosphor, dielectric constant, conductivity, PDP.

Introduction

It is generally accepted that plasma display panels (PDPs) express the natural colors of the subject more realistically than other flat panel display devices. Most studies regarding materials used for discharge in PDPs have focused on the secondary electron coefficient and doping elements with MgO, because MgO is the most important material determining the discharge phenomena [1].

However, abnormal discharges have been shown in PDPs when they are operated at high or low temperatures or at high or low sustaining pulse frequencies. These mis-discharge phenomena of PDPs were not found in all RGB cells simultaneously, but rather in one or two specific color cells. It is generally believed that an improper balance of the three elements of the PDP, namely the cell design, the electric properties of the materials, and the driving waveform, induce these unbalanced discharges.

What is the reason for an unbalanced discharge in RGB cells? The shape of every cell and the driving waveform are fixed in the panel. However, with regard to materials, RGB cells contain phosphors with widely varying compositions, and it is reasonable to assume that these phosphors have different electrical properties.

Most studies on the use of phosphors in PDPs have concentrated on their reliability in a user environment. In particular, because of the degradation of the emission property of blue phosphor (the composition of BAM is \(\text{BaMgAl}_{10}\text{O}_{17} : \text{Eu}^{2+}\)), the blue phosphor composition and surface modification of BAM have been studied [2]. The phosphors used in PDPs were reviewed by Zhang [3, 4]. Despite many studies on PDPs, however, reports on the electrical properties of phosphors are difficult to find, with the exception of sulfides [5, 6].

In this study, phosphors used in PDPs were considered to be electrically inorganic materials in an electrically functional layer, instead of optical materials with emission properties. The dielectric constants and electrical conductivities of RGB phosphor materials were measured and compared.

Experiment

The specifications of the phosphor powders are shown in Table 1. The D50 of the powder was 2-4 µm.

Fig. 1 shows the microstructures of the phosphor layers in a cell. Phosphors in PDP cells are porous and their packing density cannot be measured directly, therefore we estimated that powder packing ranged between 30% and 60% [7]. The disk-type samples for measuring the dielectric properties were formed using a cold isostatic press (CIP) with 500 kgf/cm² (49 MPa) and sintered at various temperatures, depending on the phosphor type.

Table 1. The basic specifications of the red, green, and blue phosphors

<table>
<thead>
<tr>
<th>Color</th>
<th>Materials</th>
<th>D50</th>
<th>Specific gravity</th>
<th>Maker</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red</td>
<td>((\text{Y}, \text{Gd})\text{BO}_3 : \text{Eu}^{3+})</td>
<td>2.6 µm</td>
<td>5.1 g/cm³</td>
<td>Kasei</td>
</tr>
<tr>
<td>Green</td>
<td>(\text{Zn}_2\text{SiO}_4 : \text{Mn}^{2+})</td>
<td>3.2 µm</td>
<td>4.3 g/cm³</td>
<td>Nichia</td>
</tr>
<tr>
<td>Blue</td>
<td>(\text{BaMgAl}<em>{10}\text{O}</em>{17} : \text{Eu}^{2+})</td>
<td>2.1 µm</td>
<td>3.8 g/cm³</td>
<td>Samsung SDI</td>
</tr>
</tbody>
</table>

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Note: The electrical properties of phosphors for plasma display panels were studied, which generated typical RGB colors from vacuum ultraviolet light; red is \((\text{Y}, \text{Gd})\text{BO}_3 : \text{Eu}^{3+}\) (YGB), green is \(\text{Zn}_2\text{SiO}_4 : \text{Mn}^{2+}\) (ZSM), and blue is \(\text{BaMgAl}_{10}\text{O}_{17} : \text{Eu}^{2+}\) (BAM). Because the phosphors were not fully packed in cells of a plasma display panel (PDP), their electrical properties were measured using an appearance density of approximately 60%. There was only a slight difference in the dielectric constants of the RGB phosphors; however, the dielectric loss of the green phosphor was much larger than that of either the blue or red phosphors. The volumetric resistivity of the powders had increasingly lower values according to the emission wavelengths of the phosphors.
The weight and volume of the samples were measured to confirm an apparent packing density of approximately 60%.

During firing, the green and blue phosphor samples maintained their initial disk shape; however, it was impossible to sinter the red samples because of an abnormal expansion at approximately 900 °C, which was attributed to a phase transition of vaterite [(Y,Gd)BO$_3$]. Therefore, glass frit was used as a sintering additive for the red powder. The amount of glass frit was equivalent to 1/30 of the powder weight. The glass frit had a dilatometric softening point of 500 °C, a dielectric constant of 8.15 at 1 MHz, and a density of 2.75 g/cm$^3$. The dielectric properties of the red samples containing glass frit were measured after firing at 480 °C, which is the firing temperature for binder burn-out in the phosphor. The dielectric properties of the powders were measured using a precision LCR meter (Agilent, E4980A). The volumetric resistivity of the powders was measured using a 4-point probe system and hydraulic press (Mitsubishi Chemical Co., MCP-PD51).

**Results and Discussion**

Table 2 and Fig. 2 show the dielectric properties of the RGB powders. The dependencies of the frequency of the dielectric constants of the RGB phosphors were similar to those seen in sulfide phosphors [6].

The dielectric constant of the red powder was slightly

<table>
<thead>
<tr>
<th>Color</th>
<th>Dielectric constant ($\varepsilon_r$)</th>
<th>Dielectric loss (Tan$\delta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400 kHz</td>
<td>1 MHz</td>
</tr>
<tr>
<td>Red</td>
<td>5.14</td>
<td>5.12</td>
</tr>
<tr>
<td>Green</td>
<td>3.90</td>
<td>3.69</td>
</tr>
<tr>
<td>Blue</td>
<td>3.20</td>
<td>3.15</td>
</tr>
</tbody>
</table>

Fig. 1. Cross-section view of the packing shape of the RGB phosphors in PDP cells.

Fig. 2. Frequency-dependent variations in the dielectric constants of RGB phosphors with an appearance density of approximately 60%.
higher than that of the green and blue powders. Rao reported that ZSM has a higher dielectric constant than red or blue; however, there was no specific data in his report [8]. Even though it was difficult to locate studies on the dielectric properties of phosphors, we did find a few studies that included dielectric data for the host materials. Takada et al. studied the synthesis and microwave dielectrics of xRe$_2$O$_7$YB$_2$O$_3$ (Re, Lanthanide) for low temperature co-fired ceramics (LTCC). They reported that YBO$_3$, with a porosity of 15-30%, had a dielectric constant of approximately 6.5 [9]. In this study, the red samples had an apparent density of approximately 60%; therefore, we believe that their dielectric value was lower than that reported in Takada’s experiment because of the porosity.

Guo et al. reported that the dielectric constant of willemite (mineral name: ZnSiO$_3$) at a relative density of 93% was roughly 6.0 [10]. In this study, the dielectric constant of the green phosphor was 3.67. We believe that the porosity affected the green dielectric constant in much the same manner as it did for the red phosphor.

Unfortunately, it was difficult to find beta-alumina related to BAM, a type of hexaaluminate. However, Venkateshwaran et al. studied the dielectric properties of the magnetoplumbite family, another type of hexaaluminate [11]. They reported that the dielectric constant and loss of LaMaAl$_6$O$_{19}$ was approximately 10.5. It was assumed that the blue phosphor in the PDP cell had a very low dielectric constant in this study because of its microstructure.

As a result, we believe that there are differences in the dielectric constants of the RGB phosphors because the RGB phosphors in the PDP cells have a high porosity (over 40%) and because the host materials have low dielectric constants.

The loss observed for the green phosphor was much larger than the losses of the red and blue powders. Because the three phosphors have similar extrinsic contributions, such as a porous microstructure, the difference in loss observed was caused by a difference in intrinsic contributions, such as lattice vibration modes and ion occupation. Rao et al. attributed the dielectric loss of an alkali earth sulfide phosphor to an impurity defect in the complex [6]. However, it is difficult to believe that ZSM phosphors contain such impurity defects. We assume the loss of the ZSM was correlated with Zn$^{2+}$ ions occupying two non-equivalent sites and the presence of the four nearest neighbor oxygen ions in a slightly distorted tetrahedral configuration [12, 13].

In contrast, it is known that ZSM phosphors have long decay times (approximately 9 msec) and are less favorable for TV applications because of the reversal of a d-orbital electron in the Mn$^{2+}$ ion and $^{4}T_{1g}^{6}A_{1g}$ transition [12]. ZSM also has a negative surface charge, which reduces the wall charge and affects the margin of the green cell [8]. We thought it necessary to re-evaluate the problem of the wall charge on the green phosphor in lieu of the dielectric loss and surface charge because the delay time of the addressing current relates to the duration of the discharge current and discharge lag time.

Fig. 3 shows the volumetric resistances of the RGB phosphors. The volumetric resistivity of the powders had increasingly lower values according to the emission wavelengths of the phosphors; red was $5.65 \times 10^{11}$ cm, green was $2.18 \times 10^{11}$ cm, and blue was $2.24 \times 10^{10}$ cm. BAM approached the values seen in semiconductors. Mg-stabilized Ba-beta-alumina particles are used as solid electrolytes in chemical sensors with densities greater than 90% [14]. Therefore, we believe that the high conductivity of the blue phosphor induces the wall charge to disappear faster than for the other phosphors. In order to control the volumetric resistance of RGB phosphors, coating the phosphor surface or mixing the phosphor particles with a metal or metal oxide such as Al$_2$O$_3$ should be examined. There was no coating on the red and blue phosphor of this study. As a PDP panel, the firing voltage $V_{f\text{-}ya}$, which is the discharge voltage between address and y electrodes, delay time and wall charge loss will need to be measured and correlated with the dielectric loss and the volumetric resistance.

**Conclusions**

The electric properties of porous phosphors layers for plasma display panels were studied, which generated typical RGB colors by vacuum ultraviolet; red is (Y,Gd)BO$_3$:Eu$^{3+}$ (YGB), green is Zn$_2$SiO$_4$:Mn$^{2+}$ (ZSM), and blue is BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ (BAM). The phosphors had similar dielectric constants (red, 5.1; green, 3.7; blue, 3) at 1 MHz. However, the dielectric loss of the green phosphor was 6-33 times larger than the dielectric losses of the blue and red phosphors (green, 0.24; blue, 0.047; red, 0.007). The volumetric resistivity of the powders showed increasingly lower values according to the emission wavelength of the phosphors (red, $5.65 \times 10^{11}$; green, $2.18 \times 10^{11}$; blue, $2.24 \times 10^{10}$ cm).

It is necessary to understand the dielectric loss and volumetric resistance of phosphors, as well as their surface charge, to understand and address the basis of mis-discharges in RGB cells in PDPs and to design appropriate driving waveforms.

**Acknowledgement**

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