Al₂O₃ Nanoencapsulation of BaMgAl₁₀O₁₇:Eu²⁺ Phosphors for Improved Aging Properties in Plasma Display Panels

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We studied the aging characteristics of the plasma display panel (PDP) containing Al₂O₃-coated BaMgAl₁₀O₁₇:Eu²⁺ blue phosphors and the thermal characteristics of coated phosphors. The nanoscale Al₂O₃ coatings on BaMgAl₁₀O₁₇:Eu²⁺ phosphors were obtained by the sol-gel method for an Al₂O₃ concentration of 2.0 wt %, pH values from 2 to 4, and a solution temperature of 50°C. Transmission electron microscopy measurements confirmed the formation of nano and uniform coatings on BaMgAl₁₀O₁₇:Eu²⁺ powders with the thickness of ~8 nm. An optical enhancement (~15%) was reported in the PDP containing Al₂O₃-coated BaMgAl₁₀O₁₇:Eu²⁺ phosphors after a 3000 h longevity test of PDP (a discharge voltage of 170 V and an average current of 2.06 A). We proposed that this improvement originated from both the enhanced thermal stability of coated phosphors and the enhanced operating stability of PDP containing coated phosphors.


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Experimental

The Al₂O₃ coatings on BaMgAl₁₀O₁₇:Eu²⁺ were synthesized by the sol-gel method using aluminum sec-butoxide (Akros, 99.9%) as the precursor material. Aluminum sec-butoxide was first dissolved in an acetylacetone(acac)/ethanol/water solution. The solution was then refluxed at an elevated temperature to ensure the completion of the hydrolysis reaction. The concentration of Al₂O₃ depended upon the precursor concentration, pH value, and the temperature of the solution. Our experimental results indicated that optimum performance was obtained for an Al₂O₃ concentration of 2.0 wt %, pH values from 2 to 4, and a solution temperature of 50°C. Figure 1 shows the normalized PL spectrum of uncoated and 2.0 wt % Al₂O₃-coated BaMgAl₁₀O₁₇:Eu²⁺ at 147 nm excitation. The results clearly indicate that the CIE chromaticity coordinates remained un-

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The Al₂O₃ coatings on BaMgAl₁₀O₁₇:Eu²⁺ are easily oxidized into Eu³⁺ because of its high luminance efficiency under vacuum ultraviolet (VUV) light excitation. However, when it is heated, the efficiency of the BaMgAl₁₀O₁₇:Eu²⁺ phosphor decreases while the CIE color coordinates of x and y increase. This poses a critical problem in PDP manufacturing, which requires heating to 500-600°C. Previous publications investigated the deterioration mechanism of BaMgAl₁₀O₁₇:Eu²⁺ phosphor by thermal processes and have indicated that Eu³⁺ ions in the BaMgAl₁₀O₁₇:Eu²⁺ crystal are easily oxidized into Eu³⁺ ions by heat-treatment in air. There are two possible physical ways to increase maintenance properties of the BaMgAl₁₀O₁₇:Eu²⁺ phosphor. First, by increasing the surface crystallinity of BaMgAl₁₀O₁₇:Eu²⁺ phosphor, the thermal stability or longevity could be improved to a regime where a longer lifespan of BaMgAl₁₀O₁₇:Eu²⁺ phosphor can be utilized. Second, the surface coating and encapsulation of phosphors could be another important technique to improve chemical and thermal stability of PDP phosphors. Our previous reports have indicated that coatings could also reduce the surface degradation (such as oxidation) associated with display fabrication processes in field emission display (FED) phosphors, thus reducing the surface dead-layer thickness. To study the change of thermal stability and longevity of BaMgAl₁₀O₁₇:Eu²⁺ phosphor, we investigated the effects of the nano and continuous coating of Al₂O₃ on the surface of BaMgAl₁₀O₁₇:Eu²⁺ phosphor as a protective layer. Al₂O₃ was used as the coating material because it has a wide bandgap and exhibits minimal losses in VUV penetration. Therefore, it is the aim of this paper to present optical and morphological analysis of nano and continuous coating of Al₂O₃, which increases the thermal stability or longevity of the phosphors by encapsulating the phosphor particles.

Results and Discussion

The properties of the coatings were found to be critically dependent upon the precursor concentration, pH value, and the temperature of the solution. Our experimental results indicated that optimum performance was obtained for an Al₂O₃ concentration of 2.0 wt %, pH values from 2 to 4, and a solution temperature of 50°C. Figure 1 shows the normalized PL spectrum of uncoated and 2.0 wt % Al₂O₃-coated BaMgAl₁₀O₁₇:Eu²⁺ at 147 nm excitation. The results clearly indicate that the CIE chromaticity coordinates remained un-
changed after coating and that the observed spectrum was not due to the introduction of new luminescent centers. The luminous intensity of both emission and excitation spectra of coated samples decreased with the increase of Al$_2$O$_3$ concentration on phosphors. Furthermore, we selected the coating conditions to simultaneously satisfy the minimum decrease of intensity and the formation of nanocapsulation. In this section, 2.0 wt % Al$_2$O$_3$-coated BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ phosphors are utilized as a standard sample in order to characterize the aging properties in this test.

The SEM pictures of coated and uncoated phosphors indicate that the surfaces of uncoated and Al$_2$O$_3$-coated BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ look nearly the same, although the coated phosphor has slightly smoother corners and edges. This indicates that no particle-like Al$_2$O$_3$ coating was formed on the surface of any BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ phosphor. However, an SEM picture is not direct evidence of a thin and uniform Al$_2$O$_3$ coating on BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$. To further characterize the nature of the coatings, TEM analysis was performed on several coated and uncoated samples. Figure 2 shows TEM cross-sectional images of 2.0 wt % Al$_2$O$_3$-coated BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ phosphors. It shows that thin and uniform coatings of Al$_2$O$_3$ were obtained on BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ phosphors by the sol-gel technique. The coating thickness was estimated to be ~8 nm, which is below a theoretical upper limit for Al$_2$O$_3$ coating. Therefore, TEM analysis has confirmed the encapsulation of BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ particles by Al$_2$O$_3$. This morphological analysis of coated and uncoated samples clearly indicates that the Al$_2$O$_3$ layer completely encapsulated the BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ particles, which provided a protective layer. Coulter counter measurements were used to compare the particle size distribution of uncoated and coated BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ phosphors. From these measurements, uncoated and Al$_2$O$_3$-coated BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ looked similar in shape and size, indicating little agglomeration after coating. This result means that the particle size and shape of Al$_2$O$_3$-coated BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ phosphors are suitable for application of the typical screen printing process in PDPs.

Previous papers reported that the origin of the aging process could be attributed to the oxidation reaction of Eu$^{2+}$ occurring at phosphor surfaces.$^{9,11}$ Therefore, a surface coating that could prohibit a surface chemical reaction would improve the phosphor longevity and thermal stability. The thermal stability of the coated phosphor was investigated first. The most important factor in the application of BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ phosphor in the PDPs is the thermal degradation, because a series of heating processes are performed to fabricate the PDP panels. As mentioned previously, Al$_2$O$_3$ coatings are expected to reduce phosphor surface degradation (such as oxidation) associated with the display fabrication processes. In order to investigate the thermal stability after Al$_2$O$_3$ coating, Al$_2$O$_3$ coated and uncoated phosphors were heated simultaneously to 500, 600, 700, and 800°C for 1 h in air. Then PL measurements were performed to evaluate the degree of thermal degradation in Al$_2$O$_3$-coated and uncoated BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ phosphors. Figure 3 shows the normalized spectral sum of the PL spectrum as a function of firing temperature under 147 nm VUV excitation. The normalized spectral sum of PL spectrum is defined as the ratio of the normalized spectral sum of heat-treated samples to that of the standard samples. The results indicated that the Al$_2$O$_3$-coated samples maintained the original efficiency up to 600°C before suffering a moderate decrease at 700°C. The uncoated sample shows a continuous gradual decrease. After heat-treating at 600°C for 1 h in air, the spectral sum of PL spectrum is 74% of its original value for the 2.0 wt % Al$_2$O$_3$-coated samples and 61% for the uncoated samples, respectively. Figure 4 compares the normalized PL spectrum of uncoated and Al$_2$O$_3$-coated BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ phosphor after heat-treating at 480°C for 1 h in air and at 350°C for 20 h under vacuum. The PL spectrum of uncoated phosphors is shifted to the longer wavelength range as compared to Al$_2$O$_3$-coated samples. This red shift of uncoated BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ phosphor is attributed to the oxidation reaction occurring at phosphor surfaces. To confirm the improved thermal stability of Al$_2$O$_3$-coated BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ phosphor, we fabricated a 42 in. PDP panel that includes coated and uncoated blue phosphors, side by side, on different stripes of the same panel. Table I summarizes the optical properties of uncoated and Al$_2$O$_3$-coated BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ phosphor in the same 42 in. PDP panel. As
expected, we observed a blue shift of Al₂O₃-coated BaMgAl₁₀O₁₇:Eu²⁺ phosphors. Therefore, we can conclude that the Al₂O₃ coatings protect the phosphor surface by prohibiting further oxidation during the firing process. This enhances the thermal stability of the phosphors, which is critical in PDP manufacturing. Even with the lower brightness of the coated samples, the spectral sum of Al₂O₃-coated BaMgAl₁₀O₁₇:Eu²⁺ phosphor is slightly higher than that of uncoated samples. Additionally, the CIE color coordinates of Al₂O₃-coated BaMgAl₁₀O₁₇:Eu²⁺ phosphor are purer than those of uncoated samples. The higher efficiency and deeper color coordinates of the coated samples confirm that coatings can be used to improve thermal stability of BaMgAl₁₀O₁₇:Eu²⁺ phosphors in real PDPs.

The other important factor regarding Al₂O₃ coatings on BaMgAl₁₀O₁₇:Eu²⁺ phosphors for application on PDPs can be studied by the aging measurements of PDPs, which were carried out at 170 sustained volts on phosphor screens printed on a 42 in. PDP. These samples were aged simultaneously with uncoated phosphors as a reference. Therefore, we tested longevity properties of coated and uncoated phosphors under equivalent discharge conditions.

Table I. The optical properties of uncoated and 2.0 wt % Al₂O₃-coated BaMgAl₁₀O₁₇:Eu²⁺ phosphor in the same 42 in. PDP panel.

<table>
<thead>
<tr>
<th></th>
<th>Uncoated</th>
<th>2.0 wt % Al₂O₃ coated BaMgAl₁₀O₁₇:Eu²⁺</th>
<th>BaMgAl₁₀O₁₇:Eu²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aging time (h)</td>
<td>0</td>
<td>3000</td>
<td>3000</td>
</tr>
<tr>
<td>Luminance (cd/m²)</td>
<td>142</td>
<td>133</td>
<td>115</td>
</tr>
<tr>
<td>Relative spectral sum</td>
<td>100</td>
<td>70</td>
<td>107</td>
</tr>
<tr>
<td>(efficiency)</td>
<td>80</td>
<td>76</td>
<td>70</td>
</tr>
<tr>
<td>CIE color coordinate</td>
<td>0.159</td>
<td>0.163</td>
<td>0.156</td>
</tr>
<tr>
<td>x</td>
<td>0.161</td>
<td>0.161</td>
<td>0.161</td>
</tr>
<tr>
<td>CIE color coordinate</td>
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<td>0.111</td>
<td>0.088</td>
</tr>
<tr>
<td>y</td>
<td>0.098</td>
<td>0.098</td>
<td>0.098</td>
</tr>
</tbody>
</table>

Figure 4. The normalized PL spectrum of uncoated and Al₂O₃-coated 2.0 wt % BaMgAl₁₀O₁₇:Eu²⁺ phosphor after heat-treating at 480°C for 1 h in air and 350°C for 20 h under vacuum.

Figure 5. The relative PL spectral sum and CIE y coordinate as a function of time under 170 V discharged with an average current of 2.06 A for uncoated and 2.0 wt % Al₂O₃-coated BaMgAl₁₀O₁₇:Eu²⁺ phosphors. The results indicate that the total amount of efficiency enhancement (~15%) is reported in the PDP containing 2.0 wt % Al₂O₃-coated BaMgAl₁₀O₁₇:Eu²⁺ phosphors after 3000 h longevity test (a discharge voltage of 170 V and an average current of 2.06 A). We believe this improvement originates from enhanced operating stability from the aging of PDP containing coated phosphors, as well as enhanced thermal stability of coated phosphors before the aging process.

The morphology and aging results of Al₂O₃-coated BaMgAl₁₀O₁₇:Eu²⁺ indicate that the nano and uniform Al₂O₃ encapsulation is an excellent protective layer that decreases the surface oxidation under PDP operation. In addition to the improved thermal stability of BaMgAl₁₀O₁₇:Eu²⁺ phosphor with Al₂O₃ coating, under PDP operating conditions the aging characteristics of the Al₂O₃-coated BaMgAl₁₀O₁₇:Eu²⁺ sample are also improved with a nano and uniform SiO₂ coating prepared by the sol-gel technique.

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