

Protective Metal Oxide Coatings on Zinc-sulfide-based Phosphors and their Cathodoluminescence Properties

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We investigated the high-excitation voltage cathodoluminescence (CL) performance of blue light-emitting (ZnS:Ag,Al,Cl) and green light-emitting (ZnS:Cu,Al) phosphors coated with metal oxides (SiO₂, Al₂O₃, and MgO). Hydrolysis of the metal oxide precursors tetraethoxysilane, aluminum isopropoxide, and magnesium nitrate, with subsequent heat annealing at 400 °C, produced SiO₂ nanoparticles, an Al₂O₃ thin film, and MgO scale-type film, respectively, on the surface of the phosphors. Effects of the phosphor surface coatings on CL intensities and aging behavior of the phosphors were assessed using an accelerating voltage of 12 kV. The MgO thick film coverage exhibited less reduction in initial CL intensity and was most effective in improving aging degradation. Phosphors treated with a low concentration of magnesium nitrate maintained their initial CL intensities without aging degradation for 2000 s. In contrast, the SiO₂ and the Al₂O₃ coverages were ineffective in improving aging degradation.

Key Words: ZnS:Ag,Al,Cl, ZnS:Cu,Al, Metal oxide coating, Cathodoluminescence, Aging degradation

Introduction

Field emission display (FED) shows great potential for use in a flat panel display manufacturing. The FED operating mechanism is very similar to that of a conventional cathode ray tube (CRT) display, i.e. the phosphors are bombarded by streams of electrons. However, FED uses an array of emitters directly opposite the color pixels instead of a single source used in CRT display. FED combines the advantage of CRT displays (e.g., high resolution, fast response time, wide viewing angles, and high contrast levels) with the flatness and the thinness of plasma display panel (PDP) and liquid crystal display (LED). Currently, blue and green zinc sulfide-based phosphors (ZnS; P22B and P22G), and red yttrium oxysulfide-based (Y₂O₃S:Eu³⁺; P22R) phosphors are used in FED technology. When these phosphors are irradiated with an electron beam, they experience fast degradation, decreasing the luminous efficiency, and generate harmful gases such as SO_x.^{1,2} To avoid these problems, phosphor surfaces have been coated with metal oxides, such as SiO₂, MgO, ZnO, Al₂O₃ and In₂O₃.³⁻¹⁰ Intrinsic luminous efficiencies and aging effects of metal-oxide-coated phosphors have been investigated for accelerating voltages lower than 10 kV.

Carbon nanotubes (CNT) are being investigated as electron field emitters for FED¹¹⁻¹⁶ and flat lighting device.¹⁷⁻¹⁹ For a CNT-FED, the applied voltage should be higher than 10 kV to obtain reliable luminance.²⁰⁻²¹ For a green P22G phosphor, the luminance decreased suddenly at 1.3 kV when the space distance between the CNT emitter and the phosphor was 0.2 mm.²² For a lighting device with a CNT emitter, phosphors fabricated on anode side must be tolerant of an accelerating electron beam higher than 10 kV. We coated blue P22B and green P22G phosphors with SiO₂, Al₂O₃ and MgO using various methods for testing in a CNT lighting device. The effect on cathodoluminescence (CL) from coating the phosphors was investigated as a function of an accelerating voltage, particularly focusing on degradation behavior under CL excitation.

Experimental

Blue light-emitting P22B and green light-emitting P22G phosphors were purchased from IRICO Group Corp. (Beijing, China). The SiO₂ coating process used tetraethoxysilane (TEOS; 98%, Sigma-Aldrich, St. Louis, MO, USA) as the precursor material. Varying amounts (by percent weight of the phosphor) of TEOS were dissolved in 6 mL of a 1:1 solvent mixture of ethanol and water. Phosphor powder (1.0 g) was then added to the precursor solution. After adjusting the pH to 9 using diluted NH₄OH, the mixture was refluxed at 80 °C for 2 h. The slurry was dried and then heat-treated in a box furnace at 400 °C for 3 h.

Two precursors, aluminum nitrate hexahydrate (AN; 99%, Sigma-Aldrich) and aluminium isopropoxide (AI; 99 %, Sigma-Aldrich), were used to create Al₂O₃-coated phosphors. Varying amounts (by percent weight of the phosphor) of AN were dissolved in 50 mL of H₂O, and 1 g of phosphor powder was dispersed in each solution. After adjusting the pH to 11 using dilute NH₄OH, the mixture was stirred at 40 °C for 1 h. The resulting mixture was dried and then heat-treated in a box furnace at 400 °C for 3 h. Similarly, varying amounts (by percent weight of the phosphor) of AI were dissolved in 50 mL of H₂O, and 1 g of phosphor powder was dispersed in each solution. The mixture was heated at 90 °C for 24 h with continuous stirring. After cooling to room temperature and adjusting the pH to 4.5 using dilute HNO₃, the mixture was ultrasonicated until becoming viscous, then dried and annealed at 400 °C for 3 h in a box furnace. Basic pH condition and ultrasonic treatment resulted in a highly uniform, thin Al₂O₃ film. MgO-coated phosphors, using magnesium nitrate hexahydrate (99%, Sigma-Aldrich) as a precursor, were created using the same process as described for AN.

Phase information and surface morphology of coated phosphors were characterized by field emission scanning electron microscopy (FE-SEM) and energy dispersive spectroscopy (EDS). FE-SEM micrographs and EDS spectra were acquired using a JSM-7000F FE-SEM (JEOL, Tokyo, Japan).

For the fabrication of CL device, a viscous binder was prepared by dissolving ethyl cellulose (5 wt %) in α -terpineol, heating at 70–80 °C for 2 h, and then phosphor powders were mixed with the binder at 10:6 wt ratio. Each mixture was casted on a glass using a YP-450HP printer (Yuil System, Seoul, Korea). Castings were annealed by multi-step heating, going from 280 °C for 2 h to 460 °C for 1 h. CL intensity was measured using a BM-7 Luminance Colorimeter (Topcon, Tokyo, Japan) under high vacuum (5.0×10^{-6} torr) with an electrongun (PSI, Seoul, Korea).

Results and Discussion

Surface morphology. Figure 1 shows the surface morphologies of uncoated and SiO₂-coated blue and green phosphors. The surface of uncoated blue phosphor was smooth and clean, but some particles adhered to the uncoated green phosphors. After treatment with 1 wt % of TEOS precursor, blue phosphor surfaces were covered with SiO₂ nanoparticles (the sizes of the isolated particles are shorter than ~ 100 nm), and the density increased with increasing amounts of the TEOS precursor (Figure 1a). Green phosphor surfaces were not completely covered with SiO₂ nanoparticles below a 10 wt % TEOS concentration (Figure 1b). EDS was used to analyze the surface element for all blue and green phosphors treated with 10 wt % precursor solutions. As shown in Figure 2, Si and O peaks in the surface concentration were observed at 2.5 and 0.5 keV, respectively. The results of the EDS analyses are listed in Table 1.

Blue phosphor surfaces were uniformly covered with a thin, transparent Al₂O₃ thin film when treated with a 10 wt % AN precursor (Figure 3a), while green phosphor surfaces had only a few isolated Al₂O₃ islands (Figure 3b). Even at the highest precursor concentrations, only a small portion of green phosphor surfaces were covered by Al₂O₃ islands. Use of Al as a precursor resulted in both blue and green phosphor surfaces being fully coated with an Al₂O₃ thin film (Figure 4). Use of ultrasonic irradiation during solution processing produced a more uniform surface Al₂O₃ thin film even with low concentrations of Al.

Some portion of both blue and green phosphor surfaces were covered with MgO scale-type films after treatment with a 1 wt % magnesium nitrate precursor, and film thickness increased with increasing magnesium nitrate, resulting in thick coverage at higher concentrations (Figure 5). The degree of MgO coverage for blue and green phosphors was proportional to the amount of precursor.

CL performance. Coating effects on relative CL intensities

Table 1. Element compositions (wt %) of metal oxide(M)-coated phosphors from EDS analysis

	SiO ₂		Al ₂ O ₃		MgO	
	blue	green	blue	green	blue	green
O	30.8	25.5	16.0	6.4	8.6	10.1
M	6.3	7.3	7.0	2.6	3.8	6.0
S	17.0	19.3	24.9	38.8	27.6	26.0
Zn	43.9	48.0	52.0	52.3	60.0	57.9

for both blue and green coated phosphors were investigated at an accelerating voltage of 12 kV, $1.6 \mu\text{A cm}^{-2}$. As shown in Figure 6, the CL intensities of the coated phosphors decreased with increasing precursor concentration. Metal oxides may act as insulators, impeding electron beam penetration into the semi-

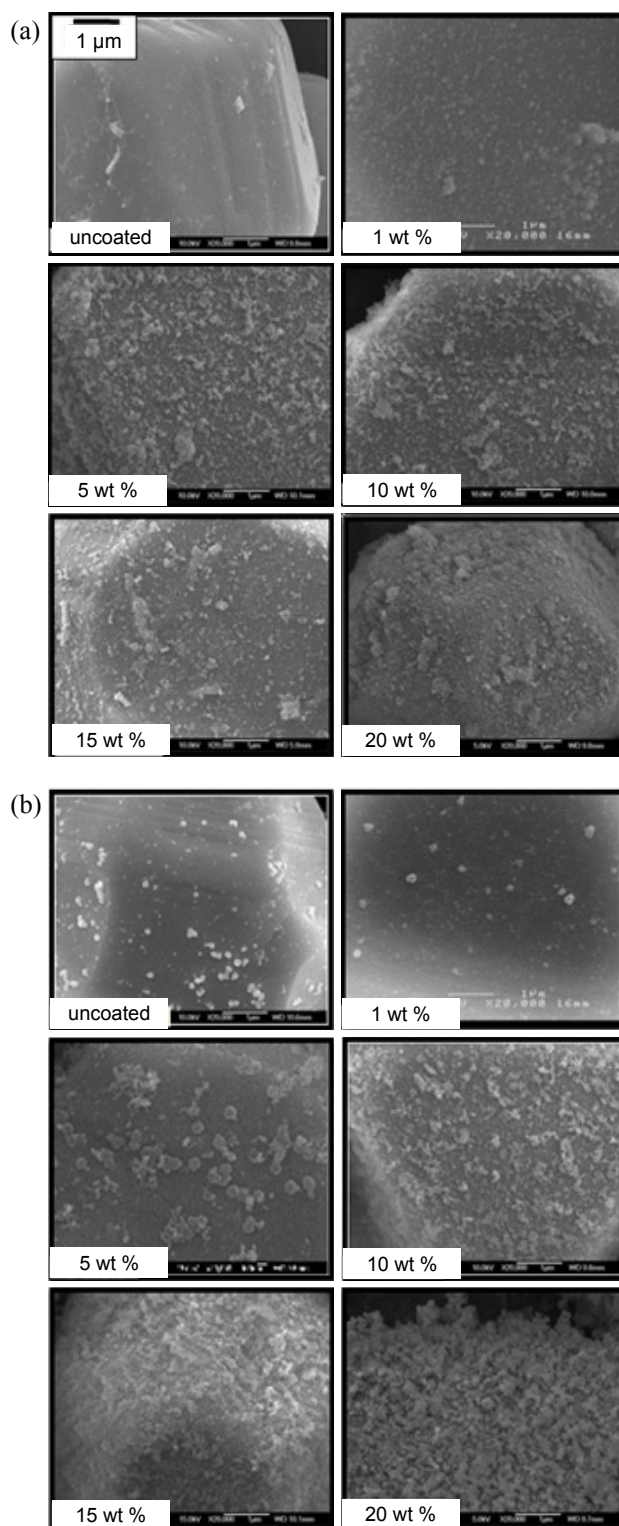


Figure 1. FE-SEM images of uncoated and SiO₂-coated blue (a) and green (b) phosphors treated with various concentrations of the tetraethoxysilane precursor.

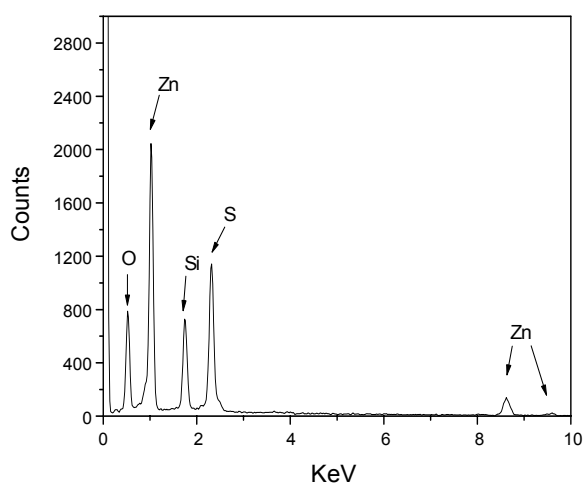


Figure 2. EDS spectrum of SiO₂-coated blue phosphor.

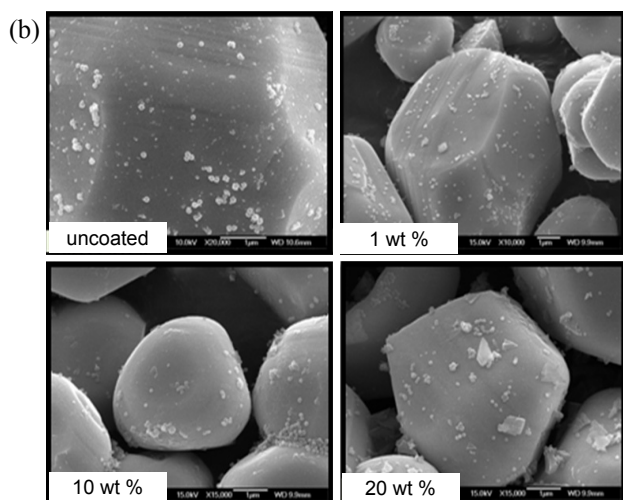
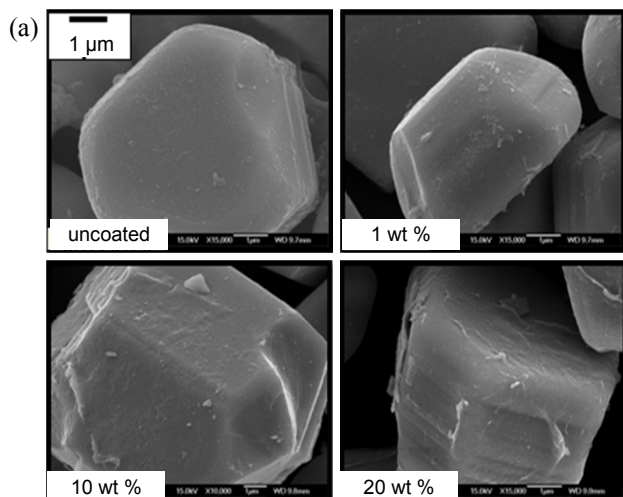


Figure 3. FE-SEM images of uncoated and Al₂O₃-coated blue (a) and green (b) phosphors treated with various concentrations of the aluminum nitrate precursor.

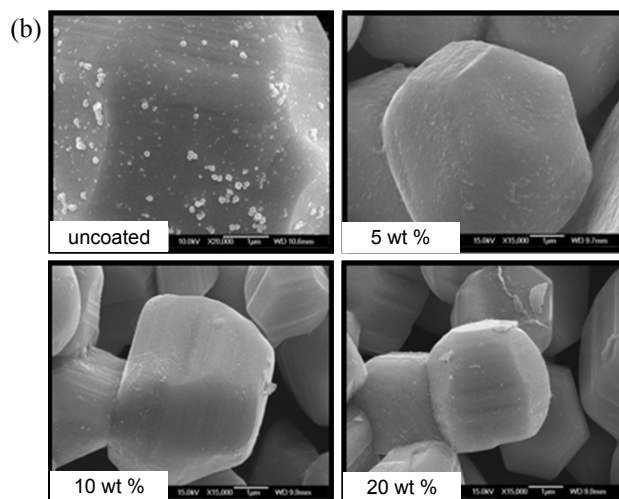
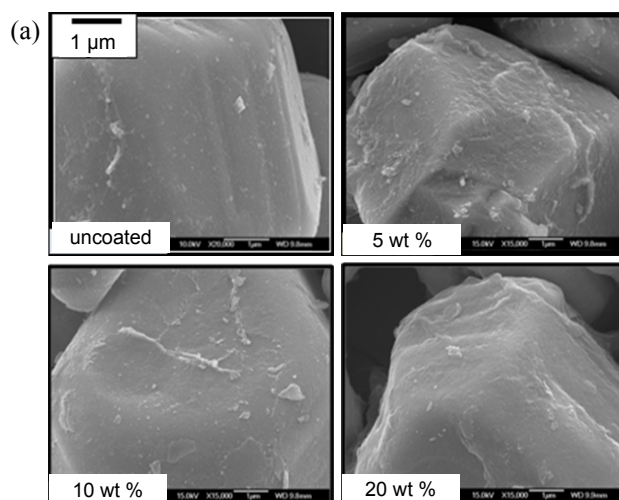


Figure 4. FE-SEM images of uncoated and Al₂O₃-coated blue (a) and green (b) phosphors treated with various concentrations of the aluminum isopropoxide precursor.

conductor phosphors, resulting in reduced CL intensity. SiO₂ nanoparticle coatings resulted in the greatest CL intensity reductions, almost 20% for the 20 wt % TEOS solution. Morphologically, the SiO₂ coated onto phosphor surfaces were nanoparticles instead of thin films; nanoparticles might produce a more diffused reflection of the incident beams than would a thin film.

Aging degradation of the uncoated was evaluated by measuring the loss of CL intensity with time under high-energy electron bombardment (Figure 7). For uncoated blue and green phosphors, CL intensity decreased by approximately 30% after 1000 s. For SiO₂-coated blue phosphors, aging degradation decreased with increasing precursor concentration. Although blue phosphor surfaces were completely coated by SiO₂ using a 20 wt % TEOS solution, CL intensity decreased by about 10% after 1200 s. SiO₂ coatings were more effective at reducing aging degradation in green phosphor. Green phosphor surfaces with 15 and 20 wt % precursor concentrations maintained initial CL intensity, with only minor fluctuation, for 1500 s. The diffe-

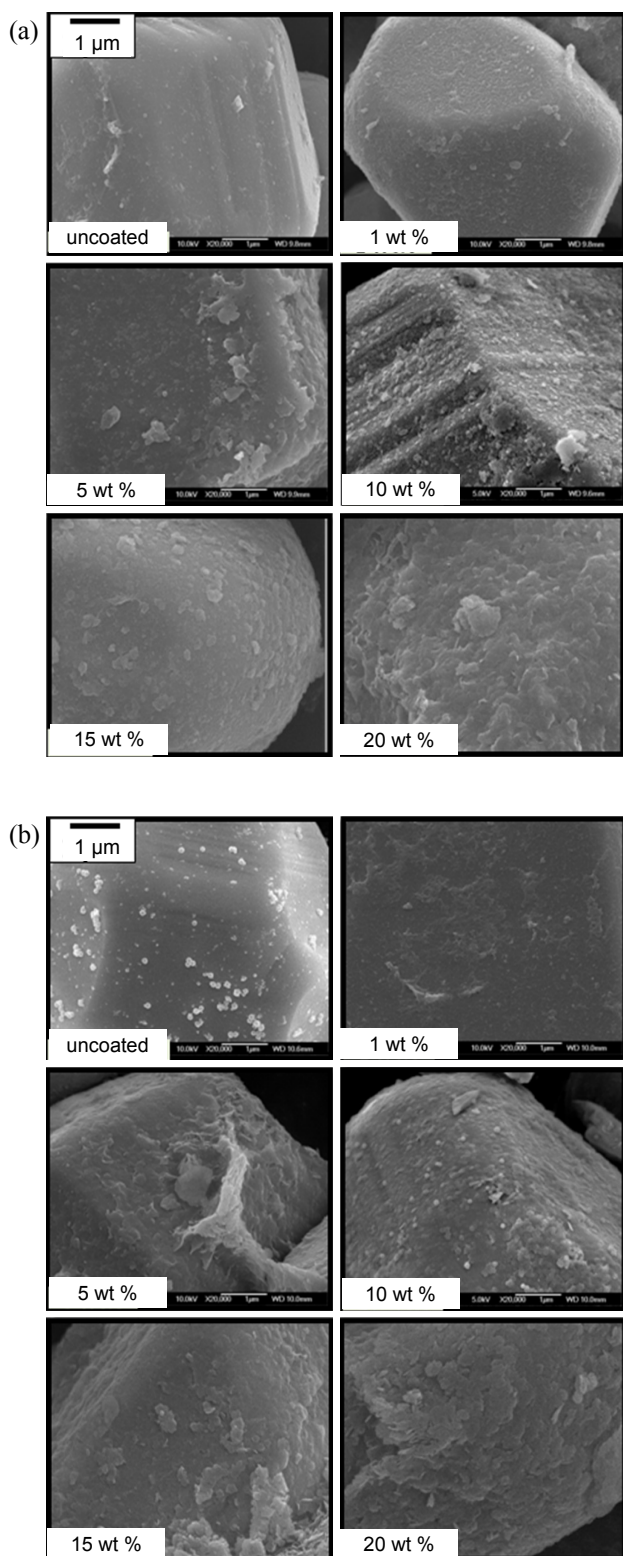


Figure 5. FE-SEM images of uncoated and MgO-coated blue (a) and green (b) phosphors treated with various concentrations of the magnesium nitrate precursor.

rence in the aging behaviors between the blue and the green phosphors can be attributed to the nature of dopants in the phosphors, since the host materials of both is zinc sulfide. The blue phosphor contains Ag, Al and Cl ions as dopants, and the green

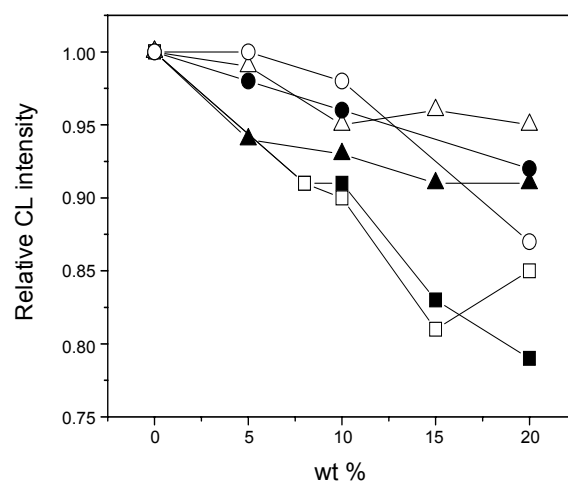


Figure 6. Relative CL intensities of coated blue (solid symbols) and green (open symbols) phosphors excited at 12 kV, $1.6 \mu\text{A cm}^{-2}$ (squares: SiO₂, triangles: Al₂O₃, circles: MgO).

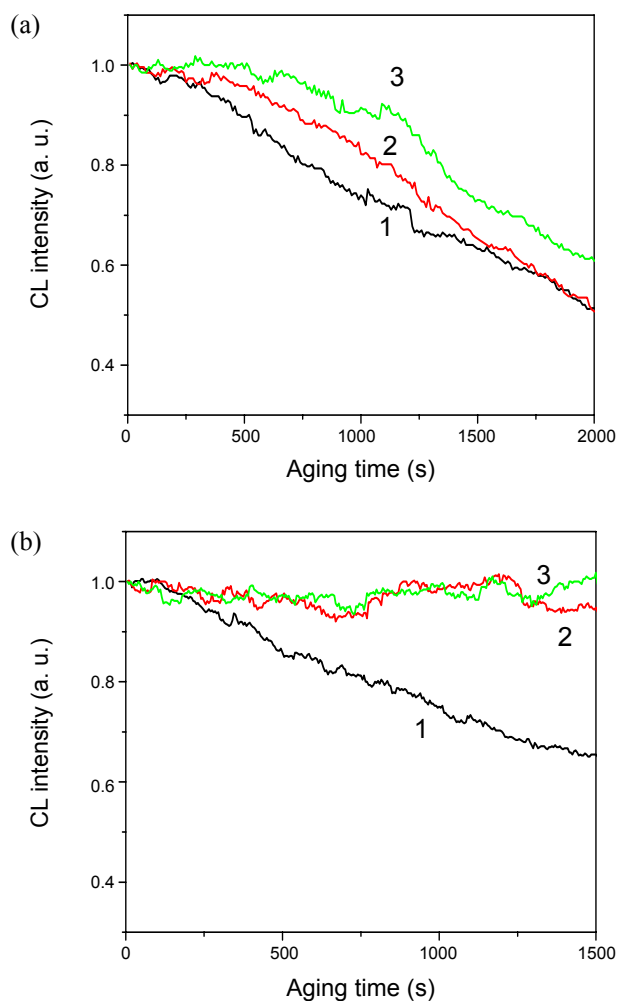


Figure 7. Aging behavior of uncoated and SiO₂-coated blue (a) and green (b) phosphors treated with various concentrations of the tetraethoxysilane precursor (1: uncoated, 2: 10 wt %, 3: 20 wt %). Accelerating voltage was 12 kV and $1.6 \mu\text{A cm}^{-2}$.

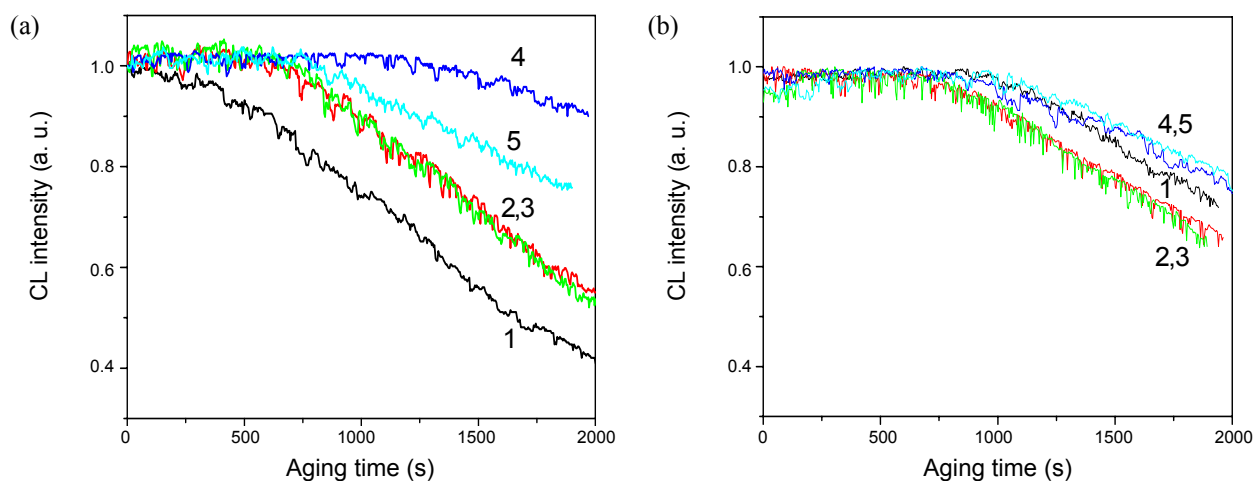


Figure 8. Aging behavior of uncoated and Al_2O_3 -coated blue (a) and green (b) phosphors treated with various concentrations of the aluminum isopropoxide precursor (1: uncoated, 2: 5 wt %, 3: 10 wt %, 4: 15 wt %, 5: 20 wt %). Accelerating voltage was 12 kV and $1.6 \mu\text{A cm}^{-2}$.

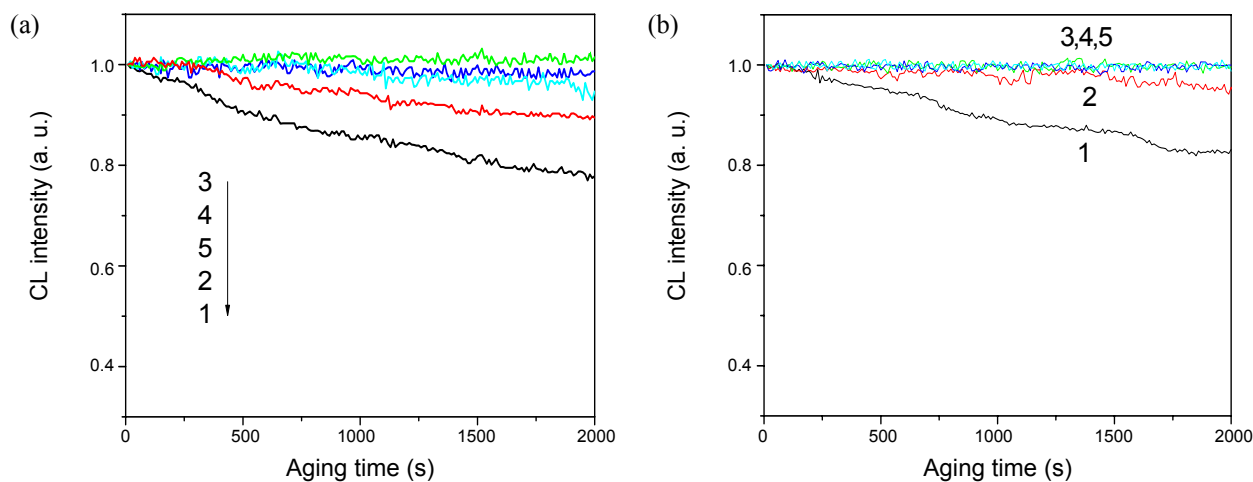


Figure 9. Aging behavior of uncoated and MgO-coated blue (a) and green (b) phosphors treated with various concentrations of the magnesium nitrate precursor (1: uncoated, 2: 5 wt %, 3: 10 wt %, 4: 15 wt %, 5: 20 wt %). Accelerating voltage was 12 kV and $1.6 \mu\text{A cm}^{-2}$.

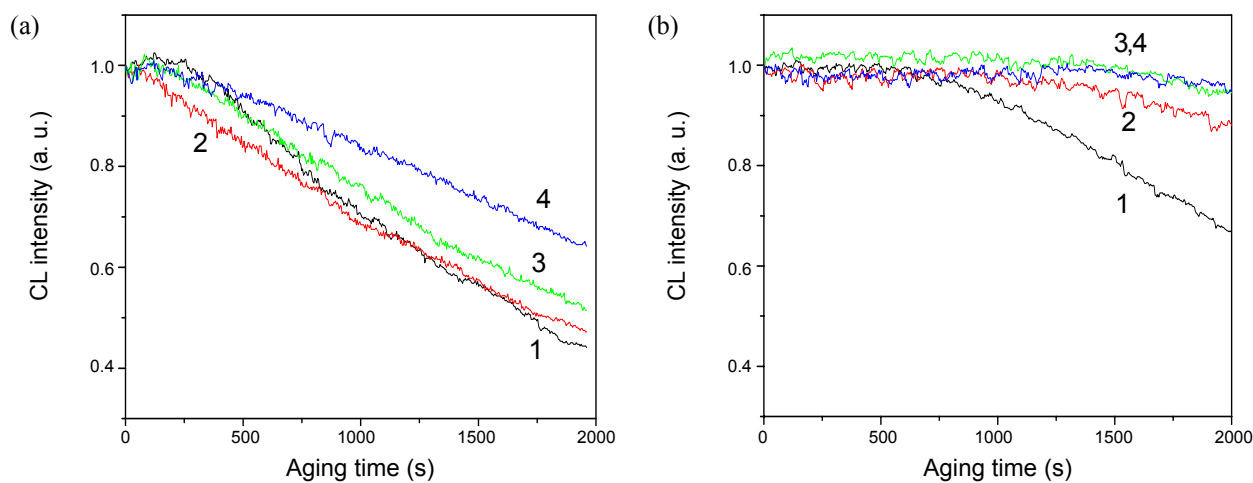


Figure 10. Aging behavior of uncoated and MgO-coated blue (a) and green (b) phosphors treated with various concentrations of the magnesium nitrate precursor (1: uncoated, 2: 5 wt %, 3: 10 wt %, 4: 20 wt %). Accelerating voltage was 15 kV and $1.6 \mu\text{A cm}^{-2}$.

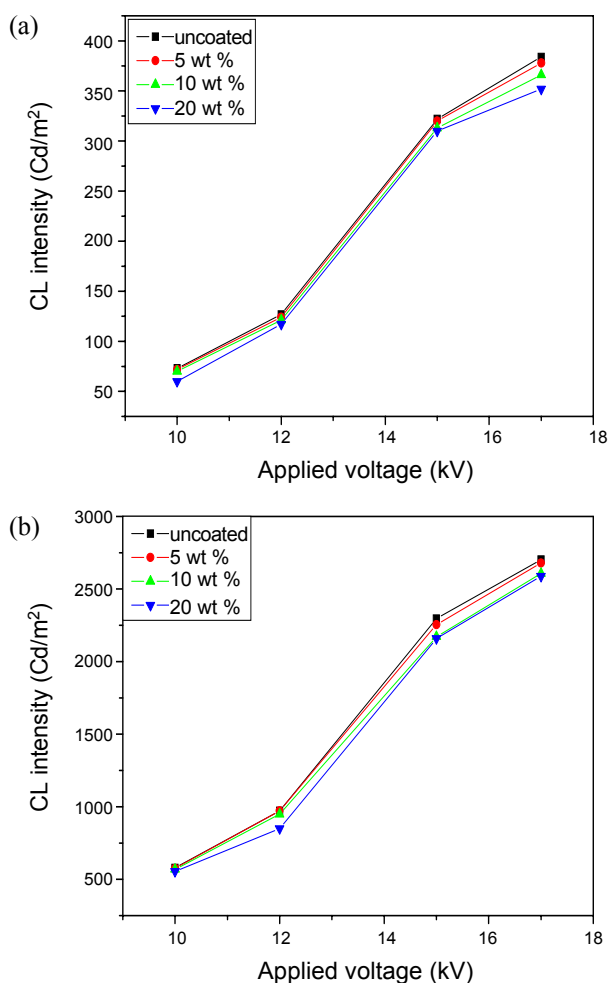


Figure 11. CL intensities of uncoated and MgO-coated blue (a) and green (b) phosphors measured in the high voltage range of 10 to 17 kV.

Table 2. Chromaticity index (x, y) of uncoated and MgO-coated phosphors (applied voltage: 12 kV)

	blue	green
uncoated	0.1425, 0.0465	0.2994, 0.5895
5 wt %	0.1421, 0.0504	0.2916, 0.5963
10	0.1424, 0.0511	0.2945, 0.5969
15	0.1433, 0.0508	0.2955, 0.5981
20	0.1435, 0.0519	0.2964, 0.6004

phosphor contains Cu and Al ions as dopants. By the excitation of the high-voltage electron beam, the light Cl ion with a negative charge is more affected than the heavy metal ions with positive charges. The Cl ion may result in the blue phosphor less stable.

Aging properties of Al₂O₃ film-coated phosphors using the Al precursor were measured (Figure 8), but due to poor coating of blue phosphors, those prepared using the AN precursor were not analyzed. Even though both blue and green phosphor surfaces were completely covered by a very uniform and thin Al₂O₃ film, aging degradation occurred rapidly, regardless of the precursor concentration.

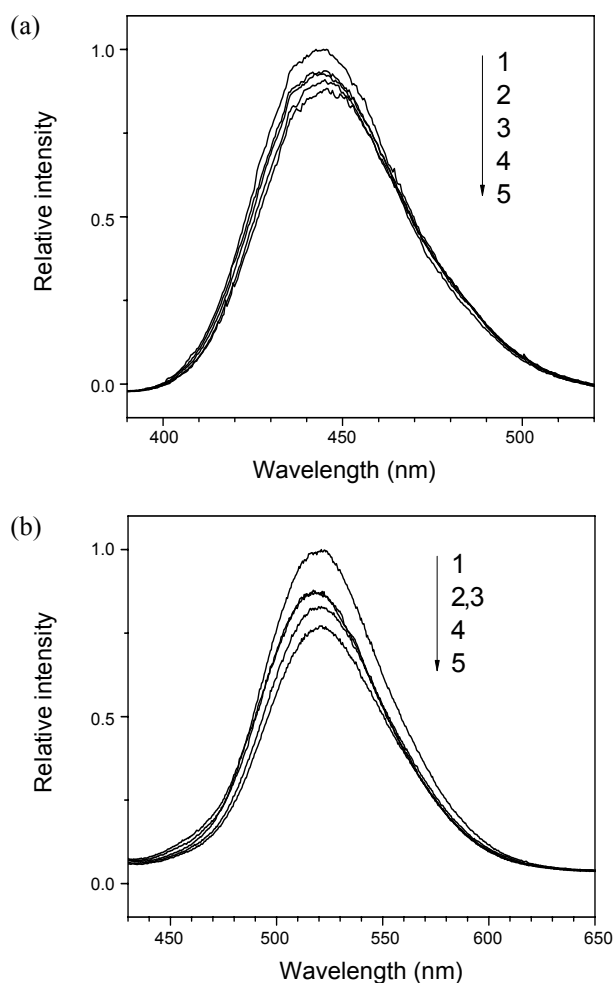


Figure 12. PL spectra of uncoated and MgO-coated blue ($\lambda_{\text{exn}} = 368$ nm) (a) and green ($\lambda_{\text{exn}} = 410$ nm) (b) phosphors.

The MgO coating effectively protected both blue and green phosphors from aging degradation (Figure 9). For blue phosphors treated with a 5 wt % precursor concentration, CL intensity decreased only about 10% after 2000 s. At greater precursor concentrations, CL intensity remained very stable for 2000 s. MgO-coated green phosphors treated with a 5 wt % precursor concentration experienced only a 5 wt % degradation after 2000 s. The optimum concentration of magnesium nitrate precursor was 10 wt % for both blue and green phosphors (Figure 9), experiencing only a 3% reduction in initial CL intensity due to MgO coating. Aging degradation of MgO-coated blue phosphors degraded quickly when irradiated with a 15 kV (1.6 $\mu\text{A cm}^{-2}$) accelerating electron beam (Figure 10). In contrast, MgO-coated green phosphors maintained initial CL intensity for approximately 1200 s, followed by a very slight aging degradation after 2000 s. Thus, critical voltage was below 15 kV for MgO-coated blue and green phosphors.

The metal oxide coating materials act as insulators, and the band gaps of SiO₂, α -Al₂O₃ and MgO were 9.0, 8.8 and 8.7 eV, respectively.^{23,24} Insulator coatings may build up charge potential on the surface and result in an additional CL intensity reduction. CL intensity of uncoated and MgO-coated phosphors

was investigated as a function of applied electron-beam voltage in the 10 - 17 kV range. As shown in Figure 11, CL intensity of uncoated and MgO-coated phosphors gradually increased with increasing voltage, and slopes for coated phosphors were parallel to those of uncoated phosphors. The CL intensities of the 10 wt % MgO-coated blue and green phosphors were evaluated as $45.6 (\pm 5.5)$ and $309.1 (\pm 30.1)$ $\text{Cd m}^{-2} \text{ kV}^{-1}$, respectively. As listed in Table 2, the CIE 1931 chromaticity of the phosphors was almost unaffected by MgO coating. The scale-type MgO-coating effect on the CL intensity is extraordinary, compared with the case for the PL intensity. As shown in Figure 12, the PL intensity of the coated phosphor apparently decreased with increasing the amount of the precursor. These indicate that no extra energy loss occurred due to insulator-related, built-up charge potential on the phosphor surface.

Conclusion

Relatively simple methods were used to coat blue P22B and green P22G phosphors. Hydrolysis of tetraethoxysilane, aluminum isopropoxide, and magnesium nitrate precursors, with subsequent heat annealing, produced SiO_2 nanoparticles, an Al_2O_3 thin film, and MgO scale-type films, respectively, on phosphor surfaces. At 12 kV, the Al_2O_3 thin film and MgO films resulted in less decrease in CL intensity as compared with SiO_2 nanoparticles. This can be attributed to greater incident beam diffraction by SiO_2 nanoparticles. Aging degradation of uncoated phosphors during excitation at 12 kV was profound, with a decrease in CL intensity of about 20% after 2000 s, presumably due to degradation of the uncoated phosphors under high-energy electron bombardment. Significant aging degradation occurred in all concentrations of the SiO_2 -coated blue phosphor and the Al_2O_3 -coated blue and green phosphors. The MgO multilayered films were most effective for reducing aging degradation. Blue and green phosphors treated with a 10 wt % (or greater) magnesium nitrate solution maintained their initial CL intensities for 2000 s.

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