Optical characteristics and longevity of quantum dot-coated white LED

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Abstract: For improving the light quality of a white LED, the feasibility of QDs was seriously considered and their longevity as well as efficiency was evaluated. For that purpose, the most similar combination of phosphors to the commercial light-converting system was selected and fabricated as the hybrid phosphor of $Lu_3Al_5O_{12}:Ce^{3+}$ and CdSe/ZnS QDs in remote type. To ensure competitive, a frame of reference with $Lu_3Al_5O_{12}:Ce^{3+}$ and $(Sr,Ca)AlSiN_3:Eu^{2+}$ was made and two cases were compared. When the hybrid phosphor with QDs was used, it was found that the luminous flux was increased by 20%, compared to the conventional combination of inorganic phosphor in commercial level. Also, CRI value can be controlled up to 90. But, the LED PKG reliability of a white LED with QDs in remote type still needs to be improved. The luminous flux of the hybrid phosphor with QDs was decreased to 91% within 1000 hours under the operating condition of 85°C and 85% of relative humidity, while that of conventional combination of inorganic phosphors was kept in stable luminescence. Substantial variation of color coordinates were observed. By tracking the changes of the R9 value over the time, it was found that the quantum structure had not been sustained during the operation. More work on the stability of QDs in phosphor plate should be done for device application.

OCIS codes: (160.2540) Fluorescent and luminescent materials; (160.5690) Rare-earth-doped materials; (250.5230) Photoluminescence; (270.0270) Quantum optics.

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1. Introduction

White Light Emitting Diodes (WLEDs) are superior to any other lighting source in luminous efficiency and have rapidly replaced the incandescent and fluorescent lamps. They have low power consumption, long life, and eco-friend. Besides, maintenance costs are low and the brightness can be adjustable [1, 2]. They are widely used as light source of backlight of LCD as well as the general lighting at department stores, public office building, and even art exhibition room at museum. In these existing application fields, they have not reached their full potential in terms of functionalities and performance. New application fields such as horticulture, biological-driven lighting, lighting in combination with daylight systems or projection systems for illumination are increasingly been explored.

White LEDs, based on Blue Chip of InGaN doped with a yellow emitting phosphor ($Y_3Al_5O_{12}$:Ce^{3+}), were first reported [3]. Since then, the significant improvements were made in the internal quantum efficiency and extraction efficiency in InGaN/GaN light emitting diode, which has enabled the fabrication of high-performance WLEDs [4–6]. Also, quality of light from the WLEDs has dramatically improved by selecting proper phosphors [7]. $Lu_3Al_5O_{12}$:Ce^{3+} phosphor of broad spectrum from green to orange light is one thing and another is red-emitting (Sr,Ca)$AlSiN_3$:Eu^{2+} phosphor [8]. The full potential in terms of efficacy is known to be around 190 lm/W for phosphor-converted LEDs [9]. With these big achievements, the main application of WLEDs is segmented into two sectors, i.e., general lighting and lighting source for liquid crystal display. Each application sector requires a little different attributes. Of course, they want higher efficiency as much as possible. In case of general lighting, more strict reliability under harsh environments such as high current injection and high humidity is required. Also, color rendering index (CRI) can be an important parameter to quantitatively measure the ability of a light source to reveal the colors of various objects faithfully in comparison with a natural light source. Accordingly, selection of proper phosphors and their thermal quenching are getting important. New phosphor system of the camera-module in recent iPhone shows the progress in picture quality. While color gamut is very important for back-lighting of LCD. For better color reproduction, light sources used as primaries need to be close to monochromatic (single wavelength) in deep level. However, they should be bright, so they are generally not close to monochromatic. From this point of view, the red-emitting (Sr,Ca)$AlSiN_3$:Eu^{2+} phosphor, which is most popular and even unique, is not good one for LCD backlighting. The solutions to be proposed are new red-emitting K_2SiF_6:Mn^{4+} phosphor and the quantum-dots (QDs) phosphor [10–12]. Using the Quantum-Dots (QDs) is known to be most promising. QDs are capable to adjust the emission energy by utilizing the quantum size effect [13]. In fact, in the past five years, important advances have been made in the synthesis of QD materials and the integration of QDs into the WLEDs. The QD-LEDs are often demonstrated on par with the commercialized organic LED technologies [2]. Among them, the CdSe/ZnS core/shell QD structure seems to be the most representative, as of now [12]. Note that typical commercial inorganic phosphor size is between 10μm and 20μm, while size of QDs is within the several nm order of magnitude. Accordingly, the surface degradation may be critical for device application. For instance, prolonged irradiation of blue light to QDs in WLEDs usually results in decrease in emission intensity and blue-shift in emission wavelength, which requires modification of QD-based inorganic nano-particles to ensure stability of photoluminescence. Typical approaches are the formation of nanocomposite particles and composite plates in remote type [14, 15]. However, reliability issue on QD for commercial application has rarely been reported so far.

In this study, we employed the hybrid type of $Lu_3Al_5O_{12}$:Ce^{3+} phosphor and CdSe/ZnS of QDs as a red light source. Then, color coordinate and luminous flux from the packaged white LED are investigated. All fabrications are made under consideration of lighting source for commercial application. More attention has been put on the examination for the reliability.

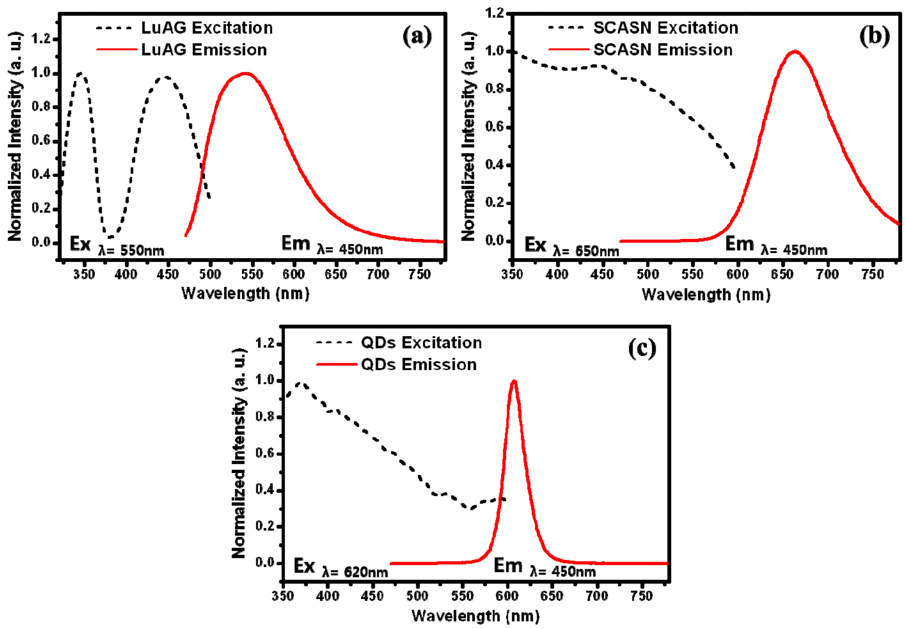

Fig. 1. Excitation and emission spectra of primary phosphors which are used in this experiment: (a) $Lu_3Al_5O_{12}$:Ce^{3+}, (b) (Sr,Ca)$AlSiN_3$:Eu^{2+}, and (c) CdSe/ZnS Quantum Dots.

2. Experimental

For investigating the optical characteristics and the longevity of QDs-coated WLEDs, the hybrid phosphor composite plate was fabricated in remote type, which reported to be most robust. The selected phosphors were the CdSe/ZnS QDs, $Lu_3Al_5O_{12}$:Ce^{3+}(LuAG), and (Sr,Ca)$AlSiN_3$:Eu^{2+}(SCASN) phosphors, which are typically used in commercial white LED. Their optical characteristics are shown in Figs. 1. The CdSe/ZnS QDs and the LuAG were mixed with silicone-based encapsulation material (OE6636 resin, Dow corning) and coated on the transparent glass substrate. Then, they are thermally cured at 150°C for 1 hours. The thickness and the diameter of glass substrate were 0.5 mm and 60 mm, respectively. As frame of reference, phosphor plate of LuAG and SCASN was also prepared on the same glass plate in remote type. Figure 2 shows the prepared color converting phosphor plates. Remote type of phosphor plate was mounted on the kit for down lighting, as shown in Figs. 3. Excitation source was prepared on the ceramic substrate by mounting 8 vertical chips, of which each size is 1,400 μm x 1,400 μm. The diameter of ceramic substrate was 70 mm. The whole set of lighting source was operated at 350 mA. The peak wavelength from the vertical blue chip was 450 nm.

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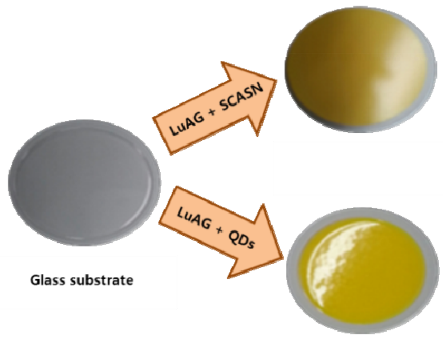

Fig. 2. Photograph of two sets of phosphor plate on glass substrate.

The excitation and emission spectra were measured by fluorescence spectrophotometer using a Xe lamp as the excitation source (Hitachi F7000). The photoluminescence, luminous flux (lm), chromaticity coordinates (Cx, Cy), and CRI of packaged WLED were recorded in the optical integrating sphere equipment (LMS-400, JNCTECH). For checking the reliability, the packaged WLEDs were loaded at the chamber and operated at high temperature and high humidity (85°C /85%). Then, the spectra, including the other optical properties, were monitored with time during 1000 hours.

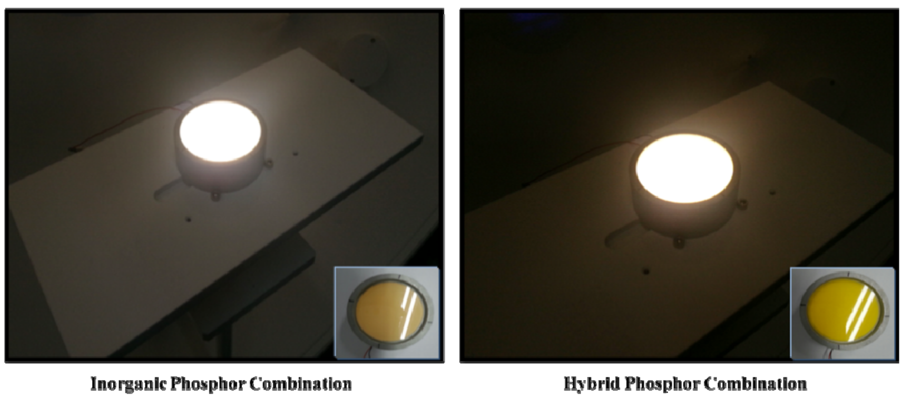

Fig. 3. Photograph of two sets of light-on white LEDs with phosphor plates.

3. Result and discussion

Purpose of this work was to check the possibility of replacing the conventional inorganic phosphor combination by QDs, which might be better in efficiency and color gamut. All the fabrication and measurement come with a reference, which is the most popular in industries and named as case-1. Optical spectrum from the packaged WLEDs are shown in Fig. 4. In case-1, the wide spectrum covers visible range over 500nm ~720nm region out of inorganic phosphor plate of LuAG and SCASN when they are excited by blue light from the LED chips. The full width at half maximum (FWHM) of a peak is 172 nm. While, in case-2, hybrid combination phosphor plate of LuAG and QDs gives much narrower spectrum at the region from 500nm to 670nm of which the FWHM is 123nm.

Each of color coordinates are presented in Fig. 5. Both of the color coordinates are positioned as Cx = 0.417, Cy = 0.399 and Cx = 0.437, Cy = 0.384, respectively. In case-1 and −2, the LMS Correlated Color Temperature (CCT) of each sample are 3300 and 2800 K. And, the CRI values are 88.6Ra with R9 = 62.5 and 88.9Ra with R9 = 15.7, respectively.

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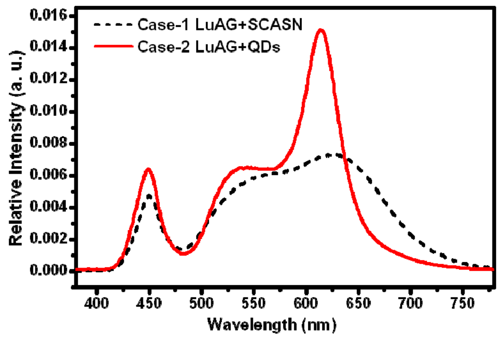

Fig. 4. Emission spectra of two sets of the white LEDs in integrating sphere.

The color temperature of a light source is the temperature of an ideal black body radiator that radiates light of comparable hue to that of the light source. Usually, white LED covers from 2700 K (warm) to 6500K (cool). The color rendering index (CRI), sometimes called color rendition index, is abbreviated variously as CRI or Ra. CRI is a measure of the degree to which the perceived colors of objects illuminated by the source conform to those of the same objects illuminated by a reference source for specified conditions. The introduction of this parameter is based on the fact that objects may look quite different in color under lamps which look quite alike in succession but are different in spectral distribution. When CRI is calculated, it can be rated on a scale from 0 to 100. The special CRI of R9 to R12 are very important to visual color rendering [16]. In particular, R9 can be a performance index to express red component and degradation of QDs, as shown later.

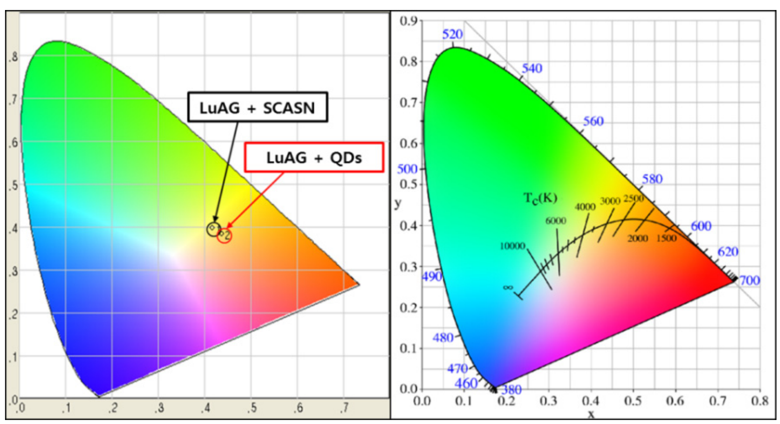

Fig. 5. Chromaticity coordinates and color temperature of each sample in Table 1.

Each luminous flux from both WLEDs are 406 lm and 512 lm, respectively. The hybrid type is better than conventional phosphor combination by 20%. But, note that color coordinates are different. Luminous efficiency is the performance index for the light source. The luminous efficiency of the light source is defined as the ratio of total Luminous flux (lumens) per power (watts equivalent). Each of luminous flux per power (lm/W) is about 63.5 and 81.4, respectively. The power can be either radiant flux of the output source, or the total electric power consumed by the source. The lumen is defined as 1/683 W of monochromatic green light at a wavelength of about 555 nm where the human eye is the most sensitive. This means that the theoretically attainable maximum value assuming complete conversion of energy at 555 nm would be 683 lm/W [2]. Generally, efficiency depends on the light spectrum which consists of white light. In case of red light such as SCASN phosphor, when

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moving far from the green part becomes deeper, efficiency is deteriorated because of absorption. In case-2, improve of the luminous efficiency must be due to the increased photons near green region as well as the decreased red component from 630nm to 750 nm, which causes the increase of reabsorption near visible light. The excitation spectra of inorganic phosphor combination and hybrid phosphor combination plates are shown in Figs. 6. Definitely, hybrid phosphor combination has far less reabsorption near green region. This experimental observation leads to the need to develop the phosphors which emit proper wavelength as well as prevent reabsorption, not like SCASN.

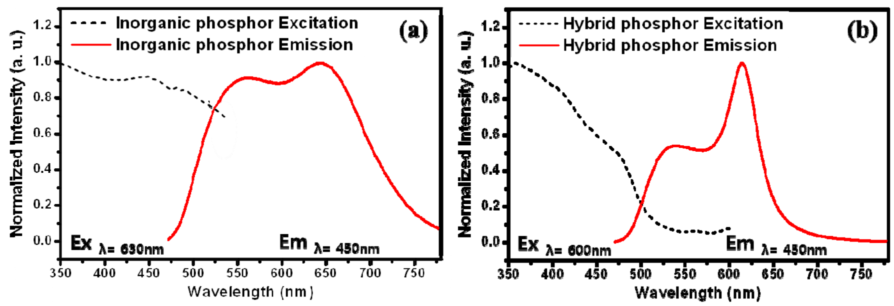

Fig. 6. Excitation and emission spectra of two set of phosphor plates: (a) Inorganic phosphor combination ($Lu_3Al_5O_{12}:Ce^{3+}$ + $(Sr,Ca)AlSiN_3:Eu^{2+}$) and (b) hybrid phosphor combination ($Lu_3Al_5O_{12}:Ce^{3+}$ + CdSe/ZnS QDs).

Reliability is the most important factor to be examined for device application. In particular, the longevity of quantum effects in device application has been wondered even with the intensive investigation for last decade due to the surface reactivity. Longevity over the time and thermal quenching are the general check points. The variation of luminous flux from the packaged WLED under the high-temperature of 85°C and high humidity of 85% condition is shown in Fig. 7.

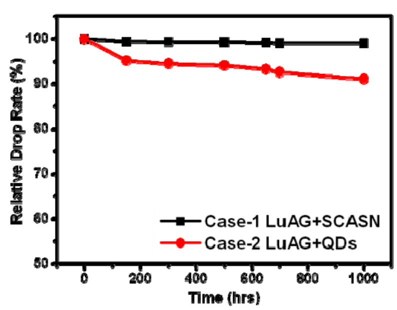

Fig. 7. Luminescence degradation of two sets of WLEDs during operation at 350 mA and 18V under environments of 85% and 85 °C.

The samples were derived at the current of 350mA and the voltage of 18V. The case-1, which is a conventional combination of inorganic phosphors, is very stable and experiences just 1% decrease in luminous flux during 1000hrs, while the luminous flux in case-2 is reduced by approximately 9%. During first 168 hours, initial drop of luminous flux is observed and continually being decreased till 1000 hours. Note that the allowable decrease in luminous flux is less than 1% within 6000 hours under longevity test of 85°C and 85% for commercial application. Hybrid phosphor combination including QDs is much inferior to the conventional combination in stability of luminous flux. We also examined color variation

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during test. Figure 8 shows the variation of the time-dependent Cx and Cy value. As expected, color coordinates are not changed during 1000 hours in case-1, while they are gradually moving to one direction in case-2. Color coordinate of Cy is gradually changed over time into the direction to that the luminous flux is decreased. Those variations are progressed fast and are saturated after 650 hours. Red component might be decreased over the time. The variation of Cx and Cy in case-2 may be due to the QDs. More details can be understood in Fig. 9, which shows the variation of spectrum over the time in case-2. Red region of the QDs was diminished with the time and was almost completely disappeared after 650hrs. This is in turn reconfirmed from the data in Table 1.

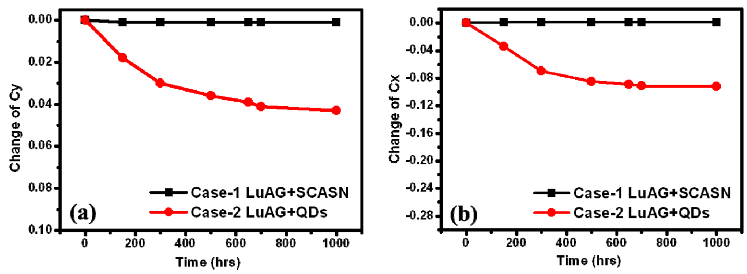

Fig. 8. Variation of the color coordinates of (a) Cx and (b) Cy over the time. The samples are the case of WLEDs presented in Fig. 7 under same conditions.

In case-1, Ra, R9 and CCT values are found to be kept in same over the time. Here, R9 value can be a good performance index in this experiments. When CRI is measured, the light source is tested against the first 8 (of the 14 possible) pigment color samples (R1-R8). R1-R8 are pastels, and the remaining 6 represent 4 saturated solids (R9-12) and 2 earth tones (R13 and R14). The current CRI scale does not cover the strong reds that are prevalent in skin tones, art work, clothing, and grocery store produce. LEDs can produce a spectral distribution that enhances the perception of these saturated colors, so although LEDs are achieving higher general CRI ratings, they have not been tested in the higher R-value saturated color ranges where they are prevalent [16]. This suggests that the R9 value, which produces strong reds and can have negative value in LEDs, should be considered in this particular experiment. As shown in case-2 of Table 1, Ra is reduced gradually over the time and the R9 value are going negative. By looking at the value, red component from QDs is decreasing and even gone. Also, the CRI has reduced the initial from 88.9 to 64.6 after 1000hrs. QDs is almost not contributed to the red component. A solid color from the LuAG-coated Blue Chip is getting dominant and CRI value of 65 is obtained [14]. Accordingly, warm color is gradually moving towards cool temperature in case-2.

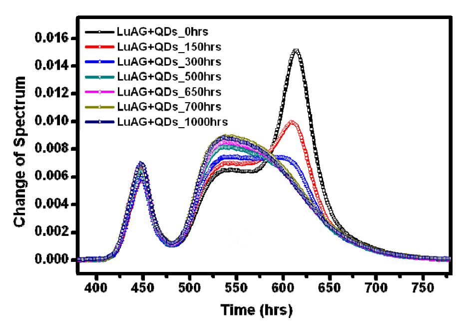

Fig. 9. Variation of spectra over the time from the WLED with hybrid type phosphor combination.

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Table 1. Variation of CRI, R9 and CCT over the time. All the data were obtained at WLED operating condition under 85% and 85 °C.

Index			Time (hrs)						
			0	**150**	**300**	**500**	**650**	**700**	**1000**
CRI & CCT	**Case-1 LuAG + SCASN**	**Ra**	88.6	88.6	88.6	88.5	88.5	88.5	88.5
		R9	62.5	62.5	62.4	62.4	62.4	62.3	62.3
		CCT	3300	3315	3317	3329	3334	3349	3359
	Case-2 LuAG + QDs	**Ra**	88.9	78.7	71.4	65.9	65.1	64.8	64.6
		R9	15.7	−19.3	−44.3	−67.8	−71.2	−73.3	−74.1
		CCT	2800	3577	4199	4717	4818	4826	4870

Based on these experimental observation, it is inferred that the quantum structure of QDs has been deformed within 168 hours and luminous flux could be decreased by 5% under the temperature of 85°C and the humidity of 85% while operating at 350 mA and 18V. Then, Deformation is progressing gradually up to 650 hours and saturated. This number is quite good, compared to the reported one. But, more stabilization of quantum structure in any media should be improved for commercial device application. This claim could be clearly supported in the variation of R9 value over the time in reliability teat of the WLEDs.

4. Conclusions

In summary, we are focusing on the optical efficiency and color rendering index and try to improve those properties by choosing proper phosphor properties. Based on the advanced technology as of now, color purity and the reabsorption of nitride phosphor up to yellow region were considered. By using the hybrid type of phosphor combination with QDs, the optical efficiency could be increased, as expected. This might be mainly due to the prevention of light reabsorption by nitride phosphor. The quantitative number that we improved was 20%, which is very substantial. However, the reliability of PKG LED characteristics was not stable in luminous flux. The variation of PL intensity of QDs could be confirmed by the variation of the color coordinates over the time with the value of R9. Our initial idea worked in improving the optical efficiency by controlling the excitation energy and emission energy of inorganic phosphors properly, of which case is the QDs. However, the QDs were unstable to the moisture and thermal properties over the time. The aging mechanism in phosphor composite should be clarified to overcome this problem. The basic mechanism to stabilize the quantum effects remains unsolved. The same aging test of QDs as that of the commercial WLEDs was applied. It showed that the longevity of QDs-coated WLEDs was not good enough to be applicable, even if excellent optical performance in hybrid type. QDs structure started being unstable just after 650 hours at operating condition under 85% and 85°C. More intensive work on the improvement of longevity of QDs structure under operation environments should be done for commercial application.

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