# Development of Phosphor film for Ultra-thin, High-brightness LCDs

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**ABSTRACT**

*In recent years, mini-LEDs and local dimming have been used in direct-type backlight units (BLUs) in LCDs to realize thinner LCD designs and higher contrast, so as to compete with OLEDs. A phosphor film with a green-emitting $SrGa_2S_4$:Eu phosphor, red-emitting $K_2SiF_6$:Mn phosphor and dichroic filter was developed and commercialized and is described in this paper. An LCD with a phosphor film and blue mini-LEDs in a direct-type BLU can realize a thinner design, higher contrast, higher luminance and higher uniformity. A smaller particle size is required for the $SrGa_2S_4$:Eu phosphor to improve the uniformity of the phosphor film, but the fluorescence of the phosphor tends to degrade during aging. A new surface coating for the $SrGa_2S_4$:Eu phosphor was found to improve its reliability.*

## 1 Introduction

LCDs and OLEDs are well represented in the market. OLEDs are thinner than LCDs and have higher contrast since OLEDs are emissive displays. LCDs have higher luminance than OLEDs since there is less limitation to the electric power input for LCDs. In recent years, mini-LEDs and local dimming have been used in direct-type backlight units (BLUs) in LCDs to realize a thinner design and higher contrast in order to compete with OLEDs. However, it is difficult to employ conventional white LEDs including blue LED chips and red- and green-emitting phosphors in the BLU with mini-LEDs because of fluctuations in the luminescence and chromaticity for many white LEDs, and it is difficult to control the angular light distribution to realize a thinner design. A phosphor film and a BLU with a phosphor film had been proposed, and the advantages of this configuration have been discussed [1-3]. It is very useful to employ a phosphor film in a BLU with blue mini-LEDs. The phosphor layer thickness affects the luminance and chromaticity. The phosphor film can easily provide more uniform luminance and chromaticity than white LEDs since uniform phosphor layers can be easily achieved by roll-coating. The phosphor film is remote from the blue LEDs in the BLU. It is much easier to design the angular light distribution of blue LEDs to achieve thinner BLUs than for white LEDs, where the phosphors are in contact the blue LEDs. A direct-type BLU with a phosphor film causes problems with chromaticity uniformity when it is driven with local dimming since the chromaticity in areas where the blue emission intensity is large becomes different from that in areas where the emission intensity is small due to local dimming. In this paper, we will first review the use of a dichroic filter to solve the chromaticity uniformity problem. Another advantage of having the phosphor film remote from the blue LEDs is that phosphors that react with moisture and/or oxygen can be employed because they can be sandwiched between moisture- and/or oxygen-barrier substrates. For example, it is possible to employ thiogallate, sulfide, CdSe QD, InP QD and perovskite phosphors in the phosphor film, though it is difficult to employ them in white LEDs [2-7]. A green-emitting $SrGa_2S_4$:Eu phosphor is useful for realizing a wide color gamut because its emission peak has a narrow full width at half maximum (FWHM) of around 48 nm [1]. This material was introduced in the current phosphor film [2-3]. A small particle size is required for $SrGa_2S_4$:Eu phosphors in order to improve the uniformity of an LCD with a phosphor film. However, $SrGa_2S_4$:Eu phosphors with smaller particles exhibit more fluorescence degradation during aging than those with larger particles. This paper will also review the improvement in reliability achieved by high-temperature annealing after surface coating of the phosphors.

## 2 Structure of phosphor film and BLU

Figure 1(a) shows a schematic of a direct-type conventional BLU with white LEDs, and Figure 1(b) shows a schematic of a direct-type BLU with a phosphor film and blue LEDs. For a conventional BLU with white LEDs, the phosphor-containing resin is coated directly onto blue LEDs. The phosphor film in Figure 1(b) consists of a phosphor-containing resin layer and PET or gas barrier films. The BLU with the phosphor film has the following characteristics. (I) The phosphor is remote from the blue LEDs, which are emission and heat sources; (II) The phosphor can be protected by barrier films. Characteristics (I) and (II) allow the utilization of phosphors that react with moisture and oxygen, and it is much easier to design the angular light distribution for blue LEDs to achieve thinner BLUs than for the conventional design with white LEDs, in which the phosphors are in contact with the blue LEDs. Therefore, the phosphor film can contribute to the realization of thinner BLUs. A green-emitting $SrGa_2S_4$:Eu phosphor and a red-emitting $K_2SiF_6$:Mn phosphor were selected for the phosphor films. Table 1 shows the properties of these phosphors, which are generally reactive to moisture. However, their narrow emission FWHM makes it possible to achieve a wide color gamut, and the peak wavelength for $K_2SiF_6$:Mn at 633 nm can provide higher luminance for the BLU since it is shorter than that for other red-emitting phosphors.

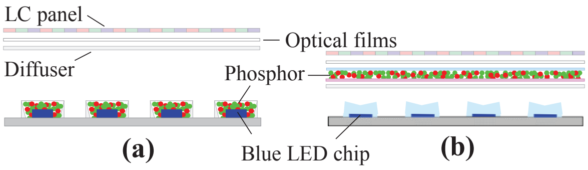


**Fig. 1 Typical schematics of a conventional BLU and a BLU using a phosphor film (a) conventional BLU with white LEDs (b) BLU with a phosphor film and blue LEDs**

**Table 1 Phosphor emission properties and their reactivity with moisture**

| Phosohor | $Y_3Al_5O_{12}$ :Ce | $(Si,Al)_6(O,N)_8$ :Eu | $SrGa_2S_4$ :Eu | $CaAlSiN_3$ :Eu | CaS :Eu | $K_2SiF_6$ :Mn |
|---|---|---|---|---|---|---|
| Peak wavelenght (nm) | 565 | 542 | 539 | 630 | 654 | 633 |
| FWHM (nm) | 128 | 53 | 48 | 89 | 65 | 11 |
| Reactivity with moisture | non | non | Reactive | non | Reactive | Reactive |

Emission spectra of powders were measured by spectrofluorometer

## 3 Effect of dichroic filter on phosphor film

The concept of local dimming is explained below. A large number of blue LEDs are placed on a printed circuit board (PCB) in a direct-type BLU. The electric current is varied for each blue LED or each LED segment depending on the image signals, with larger currents representing brighter areas. Therefore, higher luminance is achieved in bright areas than in dark areas. In this way, higher contrast can be realized with local dimming than without it. However, a direct-type BLU with a phosphor film has problems with chromaticity uniformity when it is driven with local dimming. Figure 2(a) shows a schematic of blue emission from blue LEDs, green and red emissions converted by phosphors in a direct-type BLU with a phosphor film implementing local dimming, and a color image of the BLU. There are two blue LEDs at the bottom of the BLU. The left LED is turned on and the right LED is turned off. The phosphor above the left LED (ON area) absorbs the blue light and emits green and red light. A fraction of the blue, green and red emissions is backscattered toward the blue LEDs and reaches the phosphor above the right LED (OFF area). The backscattered blue emission that reach the phosphor in the OFF area is converted to green and red emissions, and the backscattered green and red emissions penetrate the phosphor in the OFF area. The ratio of red and green emissions to blue emissions in the OFF area is larger than that in the ON area. These green and red emissions are perceived as yellow light leakage and cause nonuniform chromaticity. In order to solve this problem, a phosphor film with a dichroic filter was introduced. Figure 3 shows the spectral transmittance of the dichroic filter. The filter transmits blue light but reflects most green and red light. Figure 2(b) shows a schematic of the blue emissions from the blue LEDs, green and red emissions converted by phosphors in the direct-type BLU containing a phosphor film with dichroic filter under local dimming, and a color image of the BLU. The left LED is turned on and the right LED is turned off. The phosphor in the ON area that absorbs the blue light and emits green and red light. The green and red emissions are not backscattered, because they are reflected by the dichroic filter. A fraction of the blue emission is transmitted through the dichroic filter and is backscattered toward the LEDs, and a part of the emissions reaches the phosphor in the OFF area. The backscattered blue emissions that reach the phosphor in the OFF area are converted to green and red emissions. The ratio of red and green emissions to blue emissions in the OFF area is almost the same as that in the ON area. The dichroic filter can thus reduce yellow light leakage and solve the problem of chromaticity nonuniformity. Furthermore, the dichroic filter can increase the luminance efficiency of the BLU with the phosphor film. The dichroic filter reflects green and red emissions, and they are not backscattered toward the blue LEDs. The dichroic filter can eliminate absorption of green and red light by the reflective sheet on the PCB where the blue LEDs are mounted. The luminance efficiency improvement depends on the absorbance of the reflective sheet and the other materials in the BLU. It is possible to achieve a luminance efficiency improvement of 25%, for example. Improving the luminance efficiency is one of the most important issues for LEDs. Thus, it is concluded that the phosphor film with the dichroic filter is especially advantageous. Patents were obtained for the novel direct-type BLU with local dimming, phosphor film, and dichroic filter [8].

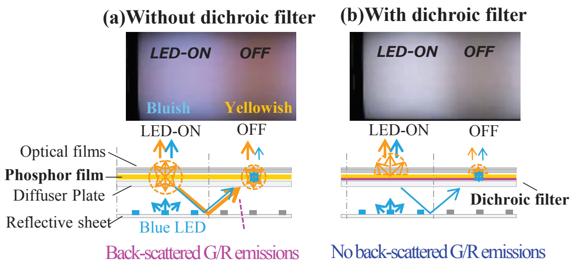


**Fig. 2 Schematic diagrams of blue emissions from blue LEDs and green and red emissions converted by phosphors in direct-type BLU with phosphor film implementing local dimming (a) without dichroic filter and (b) with dichroic filter**

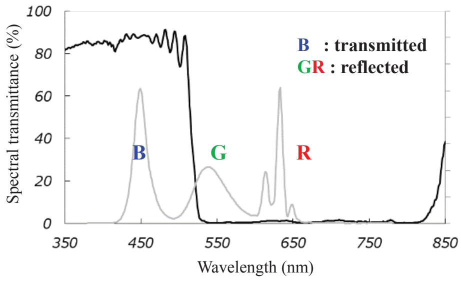


**Fig. 3 Spectral transmittance of dichroic filter**

## 4 Improvement of reliability for $SrGa_2S_4$:Eu phosphors with smaller particles

### 4.1 Dependence of phosphor film appearance on particle size for $SrGa_2S_4$:Eu phosphor

Table 2 shows the appearance of the phosphor film as a function of the particle size for a $SrGa_2S_4$:Eu phosphor. It can be seen that a smaller particle size improves the phosphor film appearance, since it increases the uniformity of the LCD emission.

**Table 2 Dependence of phosphor film appearance on particle size for $SrGa_2S_4$:Eu phosphor**

| Median diameter $D_{50}$ (μm) | 5.3 | 9.2 | 19.3 |
|---|---|---|---|
| Film appearance (uniformity) |  |  |  |

The powder particle was measured using an LA960 laser-scattering particle-distribution analyzer (HORIBA Corp.)

### 4.2 Dependence of phosphor reliability on particle size of $SrGa_2S_4$:Eu phosphor

The dependence of the phosphor reliability on the particle size of the $SrGa_2S_4$:Eu phosphor was investigated because smaller particles, which provide a larger overall phosphor surface area, may undergo accelerated fluorescence degradation due to moisture. Aluminum substrates 20 mm x 20 mm in size with no Ag content were utilized in order to avoid discoloration by sulfide gas during aging. Blue LED chips (650 μm x 650 μm) with a peak emission wavelength of 448 nm were mounted on the substrates. Four types of uncoated $SrGa_2S_4$:Eu phosphors were prepared. The median diameters (D50) for these phosphors were 2.5, 4.9, 5.5 and 21.3 μm. Silicone resin containing each of the $SrGa_2S_4$:Eu phosphors was coated directly on the blue LED chips, and was thermally cured at 150°C for 1 hr. The substrates were placed in a chamber at 70°C and 85% RH and the blue LEDs in these substrates were energized at If=140 mA in the chamber for 168 h. The chromaticity for the samples was measured using an integrating sphere before and after aging, and the chromaticity change Δu'v' between 0 and 168 h was evaluated. Figure 4 shows the dependence of Δu'v' during aging on the particle size of uncoated $SrGa_2S_4$:Eu phosphors. It was found that more fluorescence degradation occurred for a smaller particle size. In other words, there is a trade-off between emission uniformity and reliability. We therefore considered additional annealing of the phosphors at high temperature in an inert atmosphere to resolve this problem.

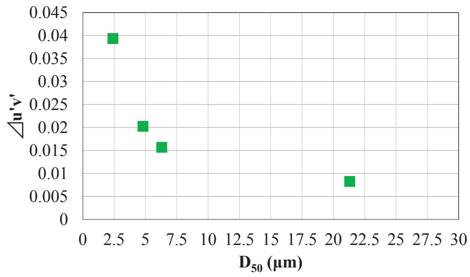


**Fig. 4 Particle size dependence of chromaticity change Δu'v' during aging for uncoated $SrGa_2S_4$:Eu phosphors**

### 4.3 Synthesis of $SrGa_2S_4$:Eu phosphors with surface coating

The precursor for the $SrGa_2S_4$:Eu phosphors was prepared by the coprecipitation method [9]. After dissolving the initial raw materials in an aqueous solution, the precursor was precipitated by a neutralization reaction, and the precipitate was filtered and dried. To obtain the bulk material, the dried precursor was sintered at 850-1000°C under a $H_2S$ gas atmosphere. The sintered bulk phosphors were ground in a ball mill to obtain materials with the target average particle sizes. The phosphor particle surfaces were treated with a protective coating using the sol-gel method. Ethyl orthosilicate (TEOS) was selected as the raw material to coat the surface of the particles [10]. Ethyl alcohol was used as the solvent and aqueous ammonia solution was used as the reaction catalyst and initiator. Experiments showed that by varying the conditions used during the surface treatment, it was possible to control the surface coating thickness from about 10 to 100 nm. However, as shown in Figure 5, progressive agglomeration between particles was observed as the thickness of the surface coating increased.

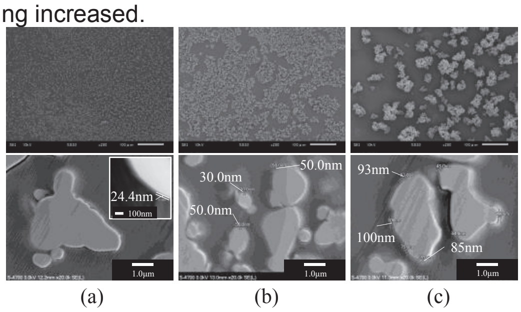


**Fig. 5 Top-view (upper) and cross-sectional SEM (lower) images of $SrGa_2S_4$:Eu particles with (a) thin coating (b) medium-thickness coating and (c) thick coating**

### 4.4 Effect of additional high-temperature annealing of surface-coated $SrGa_2S_4$:Eu phosphors with different particle sizes in inert atmosphere on reliability

Additional annealing of the surface-coated $SrGa_2S_4$:Eu phosphors was next investigated. The samples are shown in Figure 5(a). The median particle diameter in the samples was 5.3 μm, as shown in Table 2. Samples were placed in a tube furnace under a nitrogen atmosphere and annealed at various temperatures for 2 h. The annealing temperatures were set at 600, 700, 800 and 900°C. In cases where the annealed particles were agglomerated, the samples were crushed in a mortar for evaluation. In this study, only the particles annealed at 900°C needed to be crushed due to slight agglomeration. Substrates on which the samples were coated onto blue LEDs were prepared using the same procedure as detailed in section 2 and placed in a chamber at 70°C and 85% RH, and the LEDs were energized at If=140mA in the chamber for 504 h. The Δu'v' value between 0 and 504 hours was then determined. Figure 6 shows Δu'v' during aging as well as the particle size for the phosphors as a function of the temperature employed for additional annealing. Small particle sizes could be maintained during annealing at temperatures from 200 to 800°C. Only the sample annealed at 900°C showed an increase in particle size after annealing. It was found that Δu'v' decreased with increasing annealing temperature up to 800°, and then increased for an annealing temperature of 900°C. Thus, we were successful in improving the reliability while maintaining a smaller particle size. The result indicates that setting an appropriate annealing temperature can both prevent an increase in particle size and improve phosphor reliability.

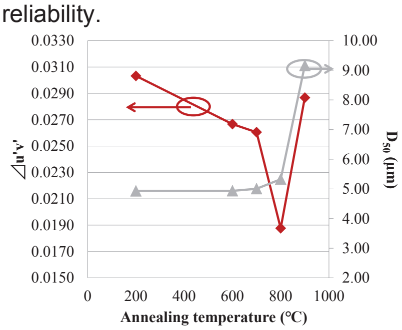


**Fig. 6 Particle size for $SrGa_2S_4$:Eu phosphors and chromaticity change Δu'v' during aging as function of annealing temperature**

### 4.5 Discussion

The particle size for the surface-coated $SrGa_2S_4$:Eu phosphors annealed at 900°C was around 9 μm, which was much larger than those annealed at lower temperatures, and these larger particles could not satisfy the phosphor reliability requirement. The particles were therefore crushed by a mortar in order to reduce the particle size. It is thought that damage to the particle surface during the crushing process increased Δu'v'. The crushing treatment is not appropriate, and it is very important to prevent the phosphor particles from fusing together during annealing. The increase in particle size after annealing at 900°C suggests that thermal diffusion occurs between the surface coating and the $SrGa_2S_4$ at temperatures of 900°C and higher. The surface-coated $SrGa_2S_4$:Eu phosphors annealed at 800°C or less could maintain particle sizes less than 6 μm without the need for crushing treatment, which meant that both the phosphor film appearance requirement and the phosphor reliability requirement could be satisfied. The phosphor reliability was improved by higher annealing temperatures up to 800°C. It is thought that annealing at higher temperatures under an inert atmosphere accelerated the densification of the surface coating. It is very important to determine the best annealing temperature in order to prevent the phosphor particles from fusing together during annealing, and to use an inert atmosphere in order to protect the phosphors from thermal oxidation. This additional annealing process succeeded both in maintaining a smaller particle size and achieving reliability. Thus, the trade-off between uniformity and reliability for $SrGa_2S_4$:Eu phosphors with smaller particle size could be eliminated. Consequently, we were able to commercialize a novel phosphor film to realize LCDs with a thinner design, higher contrast, higher luminance and good chromaticity uniformity.

## 5 Conclusion

A new phosphor film with a dichroic filter, green-emitting $SrGa_2S_4$:Eu phosphor and red-emitting $K_2SiF_6$:Mn phosphor has been developed and commercialized. The dichroic filter can improve the chromaticity uniformity of the LCDs with local dimming and enhance their luminance. Additional annealing of the $SrGa_2S_4$:Eu phosphors in an inert atmosphere led to good reliability and a smaller particle size to satisfy the requirement of good chromaticity uniformity. The phosphor film can contribute to realizing LCDs with a thinner design, higher contrast, higher luminance and good chromaticity uniformity. Employing the new phosphor film in a direct-type BLU with blue mini-LEDs in LCDs is expected to allow such devices to compete with OLEDs.

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