Optical characteristics and longevity of the line-emitting $K_2SiF_6:Mn^{4+}$ phosphor for LED application

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Abstract: Optical properties of the line-emitting $K_2SiF_6:Mn^{4+}$ phosphor were investigated for LED application. The color coordinate on the CIE chromaticity diagram, photoluminescence (PL), excitation characteristics and decay time of the $K_2SiF_6:Mn^{4+}$ phosphor were measured and compared with those of the $CaAlSiN_3:Eu^{2+}$ red phosphor. Then, a set of white LEDs were fabricated based on these two red phosphors. The $K_2SiF_6:Mn^{4+}$-loaded white LED is found to have big advantages over the $CaAlSiN_3:Eu^{2+}$-loaded white LED in the luminous flux and the color gamut. Its longevity and the color variation are inferior to its counterpart at 85°C, 85% relative humidity test. However, it is demonstrated in this work that they are improved much by blending two phosphors for white LED application while keeping its performance. Also, it is discussed on how longevity of the $K_2SiF_6:Mn^{4+}$ phosphor is improved.

OCIS codes: (160.2540) Fluorescent and luminescent materials; (230.3670) Light-emitting diodes; (250.5230) Photoluminescence.

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1. Introduction

White light-emitting diode (LED) has already been popular as the light source for general lighting as well as various electronic devices, i.e., head and tail light of automobiles, flash lights, and indoor lighting for exhibition arts. Its efficiency and light quality has been improved through new selection of phosphors. In the existing application fields, they have not yet reached their full potential in terms of functionalities and performance. New application fields such as horticulture, biologically-driven lighting, and lighting for the art exhibition are increasingly being extended [1]. However, the main application of LEDs is segmented into two sectors in terms of market volume: general lighting and lighting source for the liquid crystal display. Each application sector requires different attributes and wants higher efficiency in common. In case of general lighting, strict reliability under harsh environments such as high current injection and high humidity is required. Furthermore, 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, while the color gamut is one of the most important attributes in display application.

Recently, Cree and Philips have both announced the development of luminaire prototypes that have achieved efficacies of 200 lm/W, demonstrating the feasibility of reaching these performance levels. However, the trade-off between luminous efficacy and acceptable color quality in conventional phosphor-converted white LEDs should be addressed for a given phosphor system [2]. As well known, Nichia's pioneering work on a white LEDs was $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce^{3+}) yellow emitting phosphor on a blue diode chip, which lead to the

2014 Nobel laureates in physics. The $YAG:Ce^{3+}$ is an excellent phosphor for blue-chip excitation with high photoluminescence quantum yield and good thermal stability. However, due to the lack of red light component in the emission of $YAG:Ce^{3+}$, it is not a proper candidate for display application. In addition, it is difficult to make warm white LEDs with high color-rendering index using the material. This difficulty has been overcome by adding suitable phosphors in packaged LEDs, depending on the application sector. Such phosphors are $Lu_3Al_5O_{12}:Ce^{3+}$, β-SiAlON:Eu^{2+} ($Si_{6-z}Al_zO_zN_{8-z}$, where z represents the number of Al–O pairs substituting for Si–N pairs) [3] and $CaAlSiN_3:Eu^{2+}$ [4]. They are field-proven phosphors in optical properties as well as in longevity for commercial application. It is worth noting that only a few materials are available for device application in commercial level, even though many scientists and engineers have proposed many phosphors for the last two decades, including oxynitride compounds. As of now, $CaAlSiN_3:Eu^{2+}$ is the unique red-emitting phosphor which has been used in the commercial market. It is very stable and proper for blue-chip excitation with relatively high quantum yield. Also, it does not show any saturation behavior at high photon excitation. Its emission spectrum is very broad (full-width at half maximum: ~80 nm), which can cover the full wide range of visible spectrum and is favorable to general lighting application. However, the $CaAlSiN_3:Eu^{2+}$ phosphor is not known to be perfect for the present blue-chip based white LEDs. A large part of the spectrum is beyond 650 nm in wavelength and insensitive to human eyes. This portion therefore does not contribute to the luminous efficiency of radiation. Also, since the absorption of the phosphor covers the spectral range of ~400 to 600 nm, serious re-absorption will take place when this phosphor is mixed with other green or yellow phosphors, which causes color change and lower luminous efficacy of LEDs. Our previous work shows that this effect is dominant when compared to the other phosphor system, like quantum dot [1]. The red-emitting phosphors such as $K_2SiF_6:Mn^{4+}$ can provide a very good solution for the maximum luminous efficacy by minimizing the spillover of light in the deep red wavelength [5]. Another disadvantage of $CaAlSiN_3:Eu^{2+}$ is the manufacturing cost. The rigorous synthetic conditions of nitride compounds increase its production cost. Generally, $CaAlSiN_3:Eu^{2+}$ phosphor is prepared at high temperature (1600 ~1800 °C) under high nitrogen pressure. The production yield is relatively poor. The portion of the red phosphor constitutes 40% of the total phosphor market, despite its relatively small volume. The selection of conversion phosphors for white LED application was well reviewed by Smet et al. [6].

A red-emitting phosphor, $K_2SiF_6:Mn^{4+}$, patented by GE, might be another candidate to produce the broad gamut in display application and maximize the luminous efficacy in solid state lighting application [7, 8]. The efficient Mn^{4+} emission in fluorine coordination was well reported by Paulusz [9]. Continuously, its optical properties were well investigated by Brik and Srivastava [10]. Comparing to the oxides, the octahedral coordination may be preferred in fluoride, such as SiF_6^{2-} and PF_6^{-}. It may be a steric effect (the F^- ion is slightly smaller than O^{2-}) as well as the greater electronegativity difference between the central ion and the ligands. In these conditions, Mn^{4+} can be easily compressed into a small lattice site in fluorophosphates and fluorosilicate. Also, the small size and instability of the manganese ion in theses compound makes them quite stable without contacting water. As of now, well known hosts for octahedrally coordinated Mn^{4+} as an activator are Na_2SiF_6, K_2SiF_6, K_2TiF_6, K_2GeF_6, K_2SnF_6, Na_2SnF_6 and Cs_2SnF_6 [11–13]. Among these systems, the most actively researched phosphor is $K_2SiF_6:Mn^{4+}$. The emission spectrum of Mn^{4+} surrounded octahedrally by F^- ions in K_2SiF_6 solid is dominated by the spin-forbidden ^2E_g-$^4A_{2g}$ transition which is very narrow (~2 nm of FWHM) and emission peak wavelength of 632 nm under 450 nm excitation, while the excitation bands corresponding with the $^4A_{2g}$-$^4T_{2g}$ and $^4A_{2g}$-$^4T_{1g}$ (^4F) are spin-allowed and relatively broad. Furthermore, the tight compression of Mn^{4+} ions in K_2SiF_6 host may lead to the narrow inter-nuclear separation between the ground state and the excited state. Consequently, the emission efficiency is very high at room temperature and the thermal quenching is low at high temperature.

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Currently, the most widely used phosphor for red emission is the $CaAlSiN_3:Eu^{2+}$, which is thermally and chemically stable [14]. The spectrum from Eu^{2+} is relatively broad due to the energy transitions between the $4f^7$ ground level and the $4f^65d^1$ excited state [15]. Even though the optical characteristics of $K_2SiF_6:Mn^{4+}$ phosphor are superior to those of field-proven $CaAlSiN_3:Eu^{2+}$ phosphor, ionic bonding based-fluoride phosphor of $K_2SiF_6:Mn^{4+}$ remains unclear for commercial application. In this work, white LEDs are fabricated with $K_2SiF_6:Mn^{4+}$ phosphor and their optical characteristics are investigated from the application point of view. The purpose of this work is to understand the advantages and the problems of the line emitting $K_2SiF_6:Mn^{4+}$ red phosphor, compared to those of the $CaAlSiN_3:Eu^{2+}$ phosphor.

2. Experimental

For the purpose of fabricating the white LED, the $K_2SiF_6:Mn^{4+}$ and $CaAlSiN_3:Eu^{2+}$ red-emitting phosphors were purchased from the Mitsubishi Co., Ltd., Japan and the green-emitting β-$SiAlON:Eu^{2+}$ powder phosphor was purchased from Denka Co., Ltd., Japan. In the experiment, more attention was put on the red emitting phosphors for comparison. The room temperature photoluminescence emission (PL) and excitation (PLE) spectra of those samples were recorded using a PMT and xenon lamp (PSI, Korea). To investigate the temperature-dependent PL characteristics, purchased samples were mounted on a thick copper block with a resistive heating attachment and the optical properties with respect to different temperatures were measured using CAS 140 CT spectrometer (PSI, Korea). Phosphor-converted white LEDs were fabricated using green-emitting β-$SiAlON:Eu^{2+}$ phosphor blended with $K_2SiF_6:Mn^{4+}$ red phosphor or $CaAlSiN_3:Eu^{2+}$. The blending ratio of green phosphor to the respective red phosphor ($K_2SiF_6:Mn^{4+}$ or $CaAlSiN_3:Eu^{2+}$) was optimized to obtain the white point as close as possible in each case. Those phosphors blended with epoxy resin were deposited onto the blue chip by using a conventional phosphor dispensing method. The packaged LED device (LG Innotek 7020 series/type 450nm) was placed into an integrating sphere coupled into a spectrograph and its optical properties were measured. Also, to investigate the reliability, a series of packaged white LEDs were operated at 210 mA in a chamber for a given time, where the environments were kept at 85 C and 85% RH. Then, the optical characteristics of the aged white LED samples were measured.

3. Result and discussion

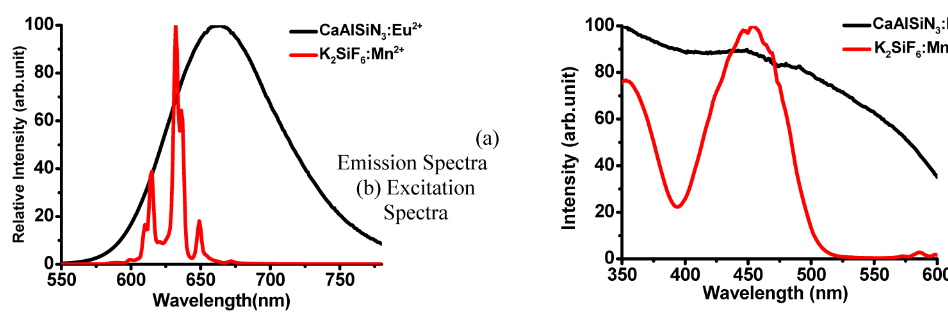


Fig. 1. Normalized excitation and emission spectra of $K_2SiF_6:Mn^{4+}$ and $CaAlSiN_3:Eu^{2+}$.

The optical properties of the sample phosphors used for experiments are shown in Fig. 1. For comparing luminescence properties of two samples, the emission and the excitation intensities are normalized. Also, the absolute emission intensities in an integrating sphere are presented in Table 1. The emission spectrum of $K_2SiF_6:Mn^{4+}$ is very sharp due to the spin-forbidden ^2E_g-$^4A_{2g}$ transition, as shown in Fig. 1. But, note that the quality of the spectrum is not precise as much as that of the literature value [16]. This is due to the slit width of the detector used in

#253657 Received 9 Nov 2015; revised 20 Jan 2016; accepted 21 Jan 2016; published 10 Feb 2016

our measuring system. The emission spectra were obtained at the excitation of 450 nm. The measured absorption efficiencies of $K_2SiF_6:Mn^{4+}$ and $CaAlSiN_3:Eu^{2+}$ were 74% and 93%, respectively. The internal and external quantum efficiency of $K_2SiF_6:Mn^{4+}$ were 78% and 58%, respectively, while those of the $CaAlSiN_3:Eu^{2+}$ were 85% and 79%. The excitation spectra were obtained at the maximum emission peak of each phosphor. One can notice that the emission peak of $CaAlSiN_3:Eu^{2+}$ phosphor is smooth and the absorption region is extended to yellow region. The absolute luminescence properties of two selective phosphors are summarized in Table 1.

Table 1. Optical properties of $CaAlSiN_3:Eu^{2+}$ and $K_2SiF_6:Mn^{4+}$

	$CaAlSiN_3:Eu^{2+}$	$K_2SiF_6:Mn^{4+}$
Color Coordinate(CIE 1931)	CIE x : 0.683 CIE y : 0.316	CIE x : 0.692 CIE y : 0.308
Dominant Wave Length (nm)	660	632
Max Peak (arb. unit)	2421	13691
Integrated Emission Spectrum (arb. unit)	10018	1139

The key attributes of a device are very important and must be a prerequisite for proper phosphor selection [6]. Thermal behavior, color purity, efficiency, dominant wavelength, decay time, longevity and stability are the important properties of phosphor in common. Table 1 demonstrates that $K_2SiF_6:Mn^{4+}$ is very good at color reproduction and brightness due to the limited photon waste above 650 nm.

First, thermal behavior of two phosphors is measured, as shown in Fig. 2. As commented earlier, the $K_2SiF_6:Mn^{4+}$ shows excellent thermal behavior. The temperature dependence of luminescence is determined by intersection of the configuration curves and the energy difference between the configuration curve minimum of the excited state and its intersection with the ground state, through which a transition to ground state can be made without luminescence. The good thermal behavior of $K_2SiF_6:Mn^{4+}$ may be attributed to its stable structure. A tight binding of Mn^{4+} ions to octahedral coordination in fluoride seems to minimize the interatomic distance at the excited state from the equilibrium of the ground state, which prompts greater room for cross intersection of the configuration curves. $K_2SiF_6:Mn^{4+}$ exhibits steady luminescent intensity up to around 125 °C, but decreases significantly around the 150 °C mark. It is quite allowable for device application when one considers that the junction temperature of LED is less than 150 °C.

The decay time is another important factor to be considered for the device application of a phosphor. Because of its parity-forbidden nature, the decay time of the Mn^{4+}-related light emission is very slow, in the milliseconds region [18]. Decay time is typically defined as the time required to decay to a fraction of the initial intensity equal to 1/e ($\tau_{1/e}$) and/or to 1/10 ($\tau_{1/10}$).

Figure 3 shows luminescence decay characteristics of our samples to be investigated. Those numbers are inserted in Fig. 3.

The issues related to the decay time of phosphor are the motion blur, the flickering and the photo-saturation at high excitation flux. Long decay time may have negative effect on the picture quality of LCD due to the motion blur. It usually is due to the slow response time of liquid crystal, which is known to be 4~5 milliseconds. The liquid crystal is unable to change its orientation and transmission rapidly enough when the picture changes from one frame to the next. Since the standard video rate is 60 frames per second, a pixel is expected to be able to fully update its light transmission opacity within 16.7 milliseconds (1/60 second).

#253657 Received 9 Nov 2015; revised 20 Jan 2016; accepted 21 Jan 2016; published 10 Feb 2016

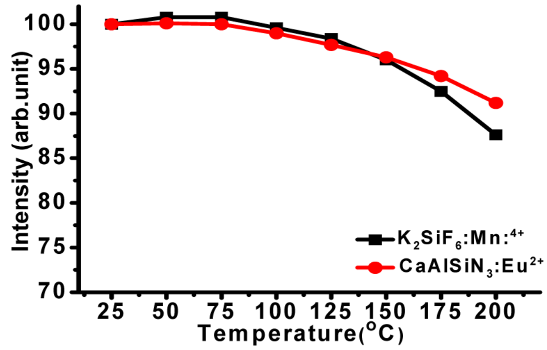
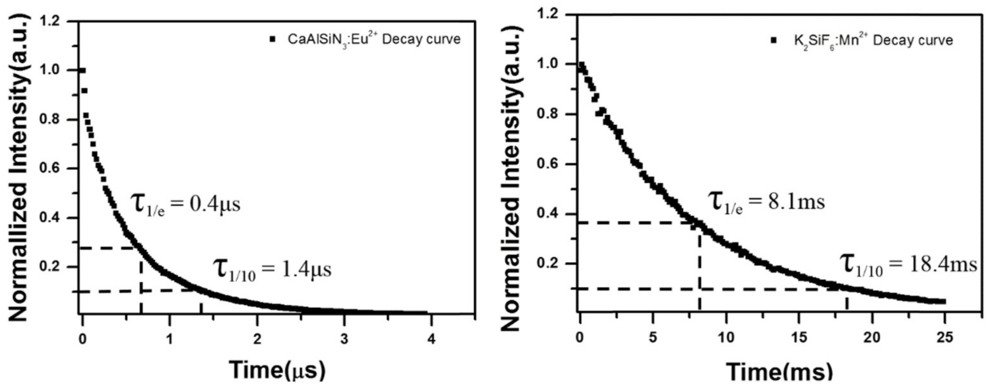


Fig. 2. Thermal quenching of K_2SiF_6:Mn^{4+} and $CaAlSiN_3$:Eu^{2+}.



(a) Decay characteristic of $CaAlSiN_3$:Eu^{2+} (b) Decay characteristic of K_2SiF_6:Mn^{2+}

Fig. 3. Luminescence decay characteristics of K_2SiF_6:Mn^{4+} and $CaAlSiN_3$:Eu^{2+} measured at room temperature. The phosphor samples were excited at λex = 450 nm and monitored at λem = 632 and 660 nm for K_2SiF_6:Mn^{4+} and $CaAlSiN_3$:Eu^{2+}, respectively.

If it takes any longer than that then the image shows some degree of lag, which appears as a trailing smear or blur whenever there is motion. To solve this problem, higher 120 Hz and 240 Hz screen refresh rates are adopted in commercial product. In these cases, residual light after refreshed screen after 8.3, and even 4.2 milliseconds, respectively, can affects the visibility of the leading portions of moving objects. The plasma display panel has suffered from this issue because of the long decay time of Mn^{2+}-doped green phosphor [24, 25]. Other issues are flickering and photo-saturation. All light sources that ultimately derive their power from the AC mains are likely to flicker. LEDs react quickly to current variation. At 120 Hz, phosphor-converted white LEDs have plenty of time to completely stop photon generation during the "off" part of the waveform. However, phosphor that exhibits a long decay time, such as K_2SiF_6:Mn^{4+}, still emits some photons during the "off" part of the cycle. It may have a chance to relax the flickering. However, more quantitative analysis remains unclear and inconclusive on this effect. Also, long decay lifetime causes photo-saturation and leads to photo-bleaching where the excited ion cannot absorb blue photons. This is not favorable to Mn^{4+}-doped phosphor at high excitation flux.

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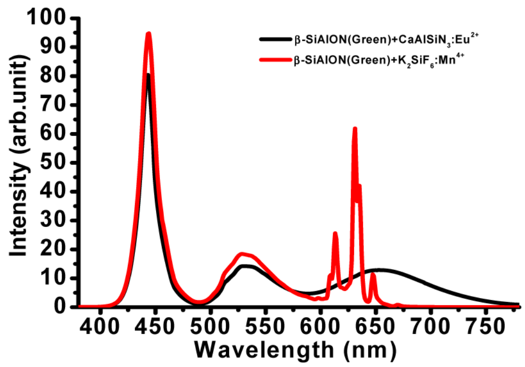


Fig. 4. Emission spectra of phosphor-converted white LED. The green emitting β-SiAlON:Eu^{2+} phosphor and two red phosphors are used: $CaAlSiN_3$:Eu^{2+} (black-line) and K_2SiF_6:Mn^{4+} (red-line).

Figure 4 shows the light spectra from the white LED in cases that the K_2SiF_6:Mn^{4+} and $CaAlSiN_3$:Eu^{2+} phosphors are used with green emitting β-SiAlON:Eu^{2+} phosphor. The optical characteristics of each red phosphor are well demonstrated in this experiment. The blue light absorption of the K_2SiF_6:Mn^{4+} phosphor is well centered near 450 nm and excites the β-SiAlON:Eu^{2+} phosphor effectively. Red emission is well confined near 630 nm. In Table 2, the device characteristics of each white LED are summarized. Note that the two chips are packaged in type 7020, which is popular in the B/L unit of a liquid crystal display.

Table 2. Device characteristics of the white LEDs

Phosphor		Luminous Flux*		Cx	Cy	Coverage	
Red	Green	(lm)	(%)			NTSC (%)	sRGB (%)
$CaAlSiN_3$:Eu^{2+}	β-SiAlON:Eu^{2+}	34.7	100	0.249	0.192	86.5	133.2
K2SiF_6:Mn^{4+}		42.1	121.5	0.248	0.192	89.9	137.0

*Operating current: 160 mA

In Table 2, it can be observed that the white points of two white LEDs were similar enough to compare $CaAlSiN_3$:Eu^{2+} and K_2SiF_6:Mn^{4+}. The luminous flux of K_2SiF_6:Mn^{4+}-loaded white LED is superior to that of $CaAlSiN_3$:Eu^{2+}-loaded white LED by 21.5%. The coverage of color reproduction can be increased by 3.4% and 4.8% in NTSC and sRGB basis, respectively. The expansion of color reproduction coverage is due to the color purity of the K_2SiF_6:Mn^{4+} phosphor due to its narrow emission spectrum. The enhancement of luminous flux in case of the K_2SiF_6:Mn^{4+}-loaded white LED was much higher than expected. It may be understood by examining the excitation and emission spectra of the $CaAlSiN_3$:Eu^{2+} phosphor. Its excitation spectra are extended to the yellow range, which causes the reabsorption of green light. As shown in Fig. 4, the emission intensity near the green region is a little weak for the $CaAlSiN_3$:Eu^{2+}, compared to the K_2SiF_6:Mn^{4+}. Also, eye sensitivity is dramatically decreased over the 650 nm region. In case of the $CaAlSiN_3$:Eu^{2+}-loaded white LED, a substantial portion of photons over 700 nm does not contribute to the luminous flux.

Apart from the device performance, the reliability issue is one of the most important factors when it comes to its application. The purpose of this work is to quantitatively understand the characteristics of K_2SiF_6:Mn^{4+} phosphor and apply its excellent properties to a device. Its line-emitting characteristics at proper peak emission wavelength and clean energy absorption near 450 nm region are favorable to wide color gamut, high CRI, and even high energy efficiency. But, reliability issue remains unclear. The reliability test usually carries out at the accelerated operating condition under the relative humidity of 85%. Besides the $CaAlSiN_3$:Eu^{2+}-loaded white LED (case-1) and the K_2SiF_6:Mn^{4+}-loaded white LED (case-2),

#253657 Received 9 Nov 2015; revised 20 Jan 2016; accepted 21 Jan 2016; published 10 Feb 2016

two red phosphors that were blended with the β-SiAlON:Eu^{2+} phosphor were coated on the blue chip. The mixing ratio of β-SiAlON:Eu^{2+}, K_2SiF_6:Mn^{4+} and $CaAlSiN_3$:Eu^{2+} was 30: 66: 4 in weight % (case-3). Three samples were operated at 210 mA under HTHH (85 °C/85% RH) environments and the values of luminous flux and color coordinate were taken every 250 hour. Table 3 shows the luminous flux over the time. Also, the variation of luminous flux over the time is shown in Fig. 5.

Table 3. Relative luminous flux of white LEDs for each phosphor combination

Index	Phosphor combination	Relative Flux (Avg. in %)				
		0hr	250hr	500hr	750hr	1000hr
Case-1	β SiAlON:Eu^{2+}+CaAlSiN3:Eu^{2+}	100	96.6	94.8	90.1	84.4
Case-2	β SiAlON:Eu^{2+}+K_2SiF_6:Mn^{4+}	100	96.5	93.7	87.7	76.2
Case-3	β SiAlON:Eu^{2+}+K_2SiF_6:Mn^{4+}+$CaAlSiN_3$:Eu^{2+}_4%	100	96.4	93.7	88.9	82.3

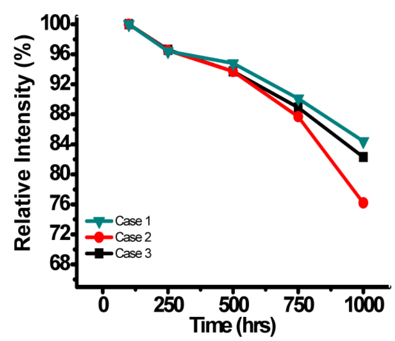


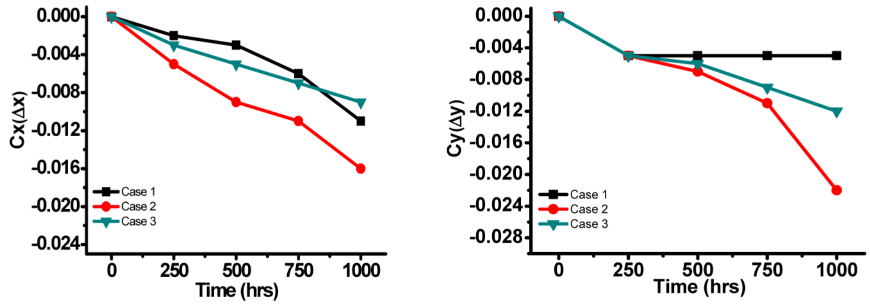
Fig. 5. Variation of luminous flux over the time under 85 °C and 85% RH.

Light output after 1000 hours decreased to 84.4% in case-1, in which $CaAlSiN_3$:Eu^{2+} was used as red phosphor. It decreased to 76.2% when K_2SiF_6:Mn^{4+} was used. It was 82.3% in case-3. Interestingly, light degradation was found to be relatively steady when the two red phosphors were used (case-3). The color change was also monitored during operation under HTHH environments. The color change for each case is summarized in Table 4 and depicted in Fig. 6.

Table 4. Color change of the white LEDs for each phosphor combination

Index	Phosphor combination	Change of Cx (Δx)					Change of Cy (Δy)				
		0hr	250hr	500hr	750hr	1000hr	0hr	250hr	500hr	750hr	1000hr
Case-1	β SiAlON:Eu^{2+} +$CaAlSiN_3$:Eu^{2+}	0	-0.002	-0.003	-0.006	-0.011	0	-0.005	-0.007	-0.009	-0.014
Case-2	β SiAlON:Eu^{2+} +K_2SiF_6:Mn^{4+}	0	-0.005	-0.009	-0.011	-0.016	0	-0.005	-0.007	-0.011	-0.022
Case-3	β SiAlON:Eu^{2+} +K_2SiF_6:Mn^{4+} +$CaAlSiN_3$:Eu^{2+} _4%	0	-0.003	-0.005	-0.007	-0.009	0	-0.005	-0.006	-0.009	-0.012

#253657 Received 9 Nov 2015; revised 20 Jan 2016; accepted 21 Jan 2016; published 10 Feb 2016



(a) Change of Cx over time (b) Change of Cy over time

Fig. 6. Color change of the white LEDs for each phosphor combination.

The variation of color change in each case shows similar to that of luminous flux. More color change in case-2 is observed than that in case-1. Here again, some relaxation of color change is observed in case-3. One may expect that the $K_2SiF_6:Mn^{4+}$ phosphor, of which the ionic characteristics are dominant, may be weaker than the strong covalent bonding-based $CaAlSiN_3:Eu^{2+}$. In Fig. 2, thermal behavior of $K_2SiF_6:Mn^{4+}$ phosphor is found to be good.

Degradation may be due to low moisture resistance of the $K_2SiF_6:Mn^{4+}$. To do a simple moisture test, phosphor powders were put into hot water and boiled for 1 hour. Then, the body color of phosphors and SEM image were examined. Figure 7 shows the body color of two red phosphors before/after boiling.

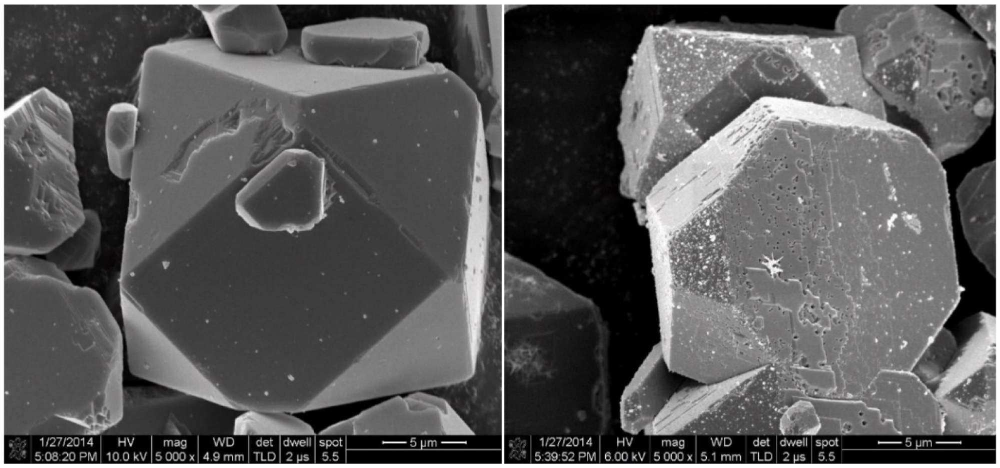
(a) Before Boiling (b) After Boiling

Fig. 7. Body color of two red phosphors before/after boiling.

The surface of the $K_2SiF_6:Mn^{4+}$ phosphor was obviously changed due to the hydrolysis on the surface. Once they are exposed to the boiling water, a lot of tiny pores on surface are observed in SEM image, as shown in Fig. 8. Relatively, $K_2SiF_6:Mn^{4+}$ must be weak to moisture. This simple experiment indicates that the longevity of $K_2SiF_6:Mn^{4+}$ phosphor can be improved by surface protection with proper materials.

This reliability experiment shows that the luminous flux and the color coordinate of the $K_2SiF_6:Mn^{4+}$-loaded white LED are more easily degraded during operation at high temperature and humid environment. The SEM analysis shows that this degradation is mainly due to the surface change of $K_2SiF_6:Mn^{4+}$ phosphor which is caused by moisture. Recently, very comprehensive work on this issue was reported [19]. However, it is found that the blending of two red phosphors can take some advantages of higher luminous flux and less color change at HTHH. The reliability trend follows the $CaAlSiN_3:Eu^{2+}$ phosphor, which is very beneficial to device performance. The change of emission spectrum after aging is shown in Fig. 9. It does not show any significant abnormal variation. Close surface analysis should be done in the future. Extra experiments are currently being conducted for further understanding.

#253657 Received 9 Nov 2015; revised 20 Jan 2016; accepted 21 Jan 2016; published 10 Feb 2016



(a) as-received (b) after boiling

Fig. 8. SEM image of $K_2SiF_6:Mn^{4+}$ phosphor: (a) as-received and (b) after boiling.

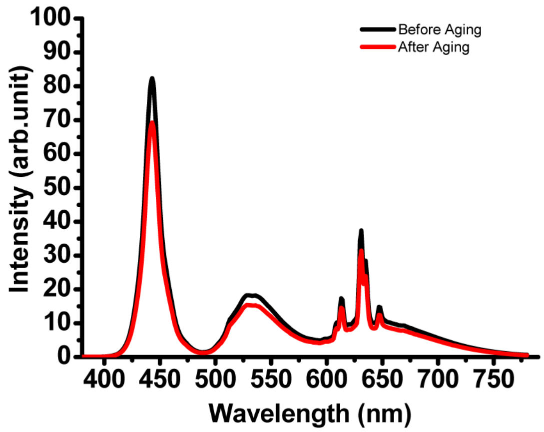


Fig. 9. Variation of emission spectrum of white LEDs after aging. It was operated under 85 °C and 85% RH at 200 mA for 1000 hours.

4. Summary

For device application, the optical properties of a $K_2SiF_6:Mn^{4+}$phosphor were examined. As a reference, the red-emitting $CaAlSiN_3:Eu^{2+}$phosphor was taken. It is quantitatively confirmed that the $K_2SiF_6:Mn^{4+}$phosphor is very suitable for a white LED application. However, the $K_2SiF_6:Mn^{4+}$ red phosphor has a long decay time. The times required to decay to a fraction of the initial intensity equal to 1/e ($\tau_{1/e}$) and1/10 ($\tau_{1/10}$), are 18.4 milliseconds and 8.1 milliseconds, respectively. When one considers that the commercial LCD-TV products on market are operated at 120 Hz (8.3 milliseconds/frame) and the response time of liquid crystal is less than 5 millisecond, the application of $K_2SiF_6:Mn^{4+}$ to LCD backlight units may be limited due to the image blur. However, long lifetime can be favorable to less flickering, which is increasingly important to lighting application.

The line-emitting characteristics of $K_2SiF_6:Mn^{4+}$ phosphor with a proper peak emission wavelength are found to guarantee the wide color gamut and the effective luminous flux. When the $K_2SiF_6:Mn^{4+}$phosphor was used with a green emitting β-SiAlON:Eu^{2+} phosphor, the color gamut of a white LED reached 89.9% of NTSC coverage. However, it was 86.5%

#253657 Received 9 Nov 2015; revised 20 Jan 2016; accepted 21 Jan 2016; published 10 Feb 2016

under same conditions when $CaAlSiN_3:Eu^{2+}$ was used. The color reproduction coverage increased by 3.4%. Also, the luminous flux out of the white LED with a $K_2SiF_6:Mn^{4+}$phosphor is much superior to that of the white LED with $CaAlSiN_3:Eu^{2+}$. Our experimental data show that the luminous flux can be increased by 21.5% under the same color coordinate. It is due to the optical property of $K_2SiF_6:Mn^{4+}$phosphor, of which the absorption cut-offs above 510 nm and the emission confines under 650 nm, which is favorable to brightness because of eye sensitivity.

The reliability issue of $K_2SiF_6:Mn^{4+}$has been controversial because of its ionic bonding characteristics. Obviously, the longevity of the $K_2SiF_6:Mn^{4+}$-loaded white LED are inferior to that of the $CaAlSiN_3:Eu^{2+}$-loaded white LED. Fortunately, the cause of failure on the longevity test at high temperature and high humidity was well defined, which might be due to the low moisture resistance of the $K_2SiF_6:Mn^{4+}$phosphor. In this work, we demonstrated that the longevity as well as the color change of the white LED was improved by loading the $K_2SiF_6:Mn^{4+}$ phosphor with small portion of $CaAlSiN_3:Eu^{2+}$ (~4% in weight percentage). By using two red phosphors, the longevity and luminous flux of the white LED are found to be improved.

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