Full Spectrum White LEDs of Any Color Temperature with Color Rendering Index Higher Than 90 Using a Single Broad-Band Phosphor

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A new phosphor alloy Ca1−xSr1−xGa2S3F2:Ce3+, Eu2+ with \( x = 0.04 \) exhibits a full spectrum emission in the entire visible wavelength range from 420 to 700 nm when excited by a LED chip with 400 nm emission. By simply depositing varying thicknesses (amount) of this phosphor powder on a 400 nm excitation LED source, white LEDs with correlated color temperatures (CCT) between 1700 K and 20,000 K and \((x,y)\) chromaticity coordinates lying on the Planckian locus of the CIE chromaticity diagram have been demonstrated. To the best of our knowledge, this is the first report on the demonstration of a single full spectrum phosphor based white LEDs exhibiting the entire gamut of white light color temperature with CRI exceeding 90. Specifically CRI greater than 95 is reported for the CCT range of 2200 K – 8500 K.

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Humans have evolved over centuries using natural sources of lights originating from natural and artificial blackbody sources, namely, sunlight and fire. Thus one can expect that the properties of light that they have been exposed must have played a significant role in the development of the biological system in addition to other environmental factors. Today, however, in the quest for creating energy efficient and environmentally friendly artificial light sources such as using LEDs, the basic characteristics of light that we are being exposed have changed drastically. New studies are slowly emerging on the health impacts of artificial lighting on human health. Recreating the blackbody like sources using LEDs is cumbersome and expensive. This paper reports a new approach that provides the pathway to create LED based lighting sources with blackbody characteristics.

One of the key attributes of LED based solid state lighting is its potential for delivering tailored full spectrum lighting. Tailored and full spectrum white light emitting diodes (WLEDs) of high optical power and high energy efficiency are needed for a wide gamut of emerging applications. Full spectrum artificial lighting mimicking natural sunlight is anticipated to have beneficial impacts on cognitive psychology, physiological health of human beings, safety, work place productivity, education, art and architecture, farming, industrial bio-chemical processes, etc. The phosphor converted white LED (pc-WLED) is the most suitable architecture for creating these miniaturized solid state light sources with the desired emission spectrum. Since pc-WLEDs are fabricated using single emission wavelength GaInN blue or near UV LEDs (the excitation source), it requires significantly simpler electrical driver and control circuits compared to white LED packages fabricated using direct emission LED chips of multiple colors. Therefore, pc-WLEDs provide the most economical solution for full spectrum lighting.

Spectrum tuning in a phosphor converted LED is currently done by varying weight ratios of phosphor powders of different emission wavelengths. This is also referred to as “Phosphor Blends” in the industry. The emission spectrum (color) and the color temperature of a pc-WLED can be tailored by mixing phosphor powders of green, yellow, orange and red emission wavelengths in various weight ratios. Figure 1 depicts the variation in the \((x,y)\) chromaticity coordinate of the light emitting from the LED as a result of mixing different phosphors or by varying the thickness of a single phosphor layer. Both these processes lead to linear shift in the \((x,y)\) coordinates between the end points of the individual chromaticity points as explained below. In this paper, we report a nonlinear shift in the chromaticity coordinate by using a full spectrum phosphor alloy instead of phosphor blends.

Referring to Figure 1, the \((x,y)\) coordinate B corresponds to the peak emission wavelength around 460 nm of a typical GaInN blue LED chip. The \((x,y)\) coordinates G, Y, O and R correspond to peak emission wavelengths of typical green, yellow, orange and red phosphors, respectively. By increasing the thickness (the quantity) of the phosphor powder on the blue LED chip, the emission intensity ratio of the blue versus the phosphor emission peak decreases. Thus the emission color of the LEDs can be continuously tuned with \((x,y)\) coordinates shifting linearly along the direction of the arrows on the straight dashed lines connecting the points BG, BY, BO and BR in Figure 1. By dispensing appropriate amounts of a yellow or an orange phosphor on a blue LED chip, one could create a cool white (CW) LED with CCT around 6000 K or a warm white LED (WW) with CCT around 3000 K (Figure 1). Though it is desirable to have the \((x,y)\) coordinate of the pc-WLEDs on the Planckian blackbody locus (curve shown in Figure 1 with equivalent blackbody temperatures in Kelvin), it is practically difficult to develop and use a multitude of phosphor compounds for fabricating LEDs with different color temperatures. Furthermore, for achieving high color rendering index (CRI) necessary for many applications, the emission spectrum must be tuned using two or more phosphors. Over the last two decades since the advent of candelaria class blue GaInN LEDs, there has been wide-spread global research and development of phosphor compounds that could meet a host of stringent criteria for pc-WLED packages. Today, CW and WW pc-WLEDs are fabricated by mixing two or three selected phosphors in optimized (but different) weight ratios (different phosphor blends).

Spectrum tuning by mixing phosphors is a tedious process. Slight variations in the individual phosphor quantity in the mixture (blends) can shift the \((x,y)\) coordinate away from the desired point. To the best of our knowledge, there are no reported fixed weight ratio of phosphor compounds that could be used to fabricate both CW and WW pc-WLEDs. This paper reports a single phosphor alloy that could be used to fabricate a wide range of pc-WLEDs with \((x,y)\) coordinate always lying on the Planckian locus by simply varying the thickness of the phosphor layer on the 400 nm excitation LED source. The shift in the \((x,y)\) coordinates is shown by the arrows along the Planckian locus in Figure 1. At the same time, high CRI (>90) is maintained throughout the color temperature range.

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The phosphor compound (alloy) used in this study was selected from a general composition space of Ca$_{1-x}$Sr$_x$Ga$_2$S$_3$: Ce$^{3+}$, Eu$^{2+}$ with ($0 \leq x \leq 1$, $0 \leq y \leq 2$, $0 \leq z \leq 3$) activated with Ce$^{3+}$ and Eu$^{2+}$. By varying the x, y and z and the activator species, the emission spectrum of pre-synthesized powders of SrS:Eu$^{2+}$ and Ca$_{1-x}$Sr$_x$In$_2$S$_3$:Ce$^{3+}$, Eu$^{2+}$ was kept at 2 mole%. The precursor compound was obtained from a specific full spectrum phosphor alloy with x = 0.04, y = 2 and z = 3. The process of arriving at this final composition based on series of experiments will be summarized below. The full spectrum phosphor was synthesized by alloying the necessary mole fractions of pre-synthesized powders of SrS:Eu$^{2+}$, SrS:Ce$^{3+}$, Na$^+$, Ca$_2$S:Eu$^{2+}$, Ca$_2$F$_2$:Eu$^{2+}$ and Ga$_2$S. Sodium sulfide (Na$_2$S) was used for Na$^+$ charge compensation. The concentration of each activator/dopant species (Eu, Ce, Na) in the starting precursor was kept at 2 mole%.

Figure 1. CIE 1931 (x,y) chromaticity diagram presenting the general linear shift in color coordinates (along the direction of the arrows) with increasing layer thickness (quantity) of green (G), yellow (Y), orange (O) and red (R) phosphors on a blue LED chip (B). The non-linear shift and traverse of the (x,y) coordinates for the reported full spectrum phosphor is shown by the arrows along the Planckian locus. The (x,y) coordinates corresponding to various emission wavelengths and the Planckian blackbody curve was plotted using the data in Reference 5.

Figure 2. Powder XRD pattern of Ca$_{1.04}$Sr$_{0.96}$Ga$_2$S$_3$F$_2$: Ce$^{3+}$, Eu$^{2+}$.
One of the most intriguing observations from this study was the realization of the universal nature of the full spectrum phosphor for delivering high CRI in a wide range of color temperature. Once the full spectrum was optimized to provide CRI greater than 95 for cool white LEDs around 6500 K, the same phosphor could be used in different quantities with the same excitation source to create white LEDs across the entire color temperature gamut (1700 K – 20,000 K) with CRI greater than 90. Another unique attribute was that all these high CRI LEDs exhibited color coordinates on the Planckian locus. Figure 5 presents the emission spectra of the LEDs covering the entire visible range. The narrow peak at 400 nm is due to the excitation source. The weak peak around 420 nm is attributed to a phase rich in CaF$_2$: Eu$^{2+}$. The peaks around 450 nm and 490 nm were found to be due to the Sr-rich phase of the Sr$_{1-x}$Ca$_x$Ga$_2$S$_3$: Ce$^{3+}$ alloy. The peak around 550 nm is due to Ca-rich phase of the Ca$_{1-x}$Sr$_x$Ga$_2$S$_3$: Eu$^{2+}$ compound. Finally, the peak around 630 nm is due to the Sr-rich phase of the Sr$_{1-x}$Ca$_x$S: Eu$^{2+}$ compound. It must be pointed again that the different spectrum presented in Figure 5 were not created by mixing different ratios of various phosphors (which is typically done to change the spectrum of phosphor LEDs). Rather the variations in the spectra occurred naturally as the thickness of the phosphor...
To understand the interactions between the luminescence centers, we analyzed the excitation spectrum of the phosphor for various emission wavelengths as shown in Figure 6. The intensity of the individual curves has been normalized for the sake of presentation. A preliminary analysis of the intensity of each excitation spectrum and its effect on the absorption and down conversion wavelengths was found to consistently explain the natural evolution and the trend observed in the change of shapes of the emission spectrum (shown in Figure 5). As the thickness of the phosphor layer is increased, the peak intensity of longer wavelength components such as the 630 nm emission increases more rapidly than the other peaks due to absorption of the shorter wavelength emission as evident from the excitation spectra. While the absorption and down conversion processes in a full spectrum phosphor ensemble might appear trivial for the shift in color coordinates that naturally falls on the Planckian locus and with high CRI, the compromise on lumen efficiency for the full spectrum source can be easily traded with other desirable features of the light quality for various applications. In summary, a new single phosphor alloy has been reported that provides full spectrum emission in the visible range. Most interestingly, this phosphor has demonstrated white LEDs with color coordinates that naturally falls on the Planckian locus and with high CRI (exceeding 90) for the entire white light color temperature. This is a first of a kind phosphor composition reported in the literature. The general shapes of the spectra (excluding the 400 nm LED peak) were found to match with the sunlight spectra.

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References

1. United States Department of Energy and related websites: http://energy.gov/eesl/solid-state-lighting.
2. S. Ye, F. Xiao, Y. X. Pan, Y. Y. Ma, and Q. Y. Zhang, *Mat. Sci. Eng. R.*, 71, 1 (2010).
3. J. Silver and R. Withnall. *Color Conversion Phosphors for LEDs*, Chapter 3, in *Luminescent Materials and Applications*, Edited by A. Kitai, John Wiley & Sons Ltd. (2008).
4. E. F. Schubert, *Light Emitting Diodes*, Second Edition, Cambridge University Press (2006).
5. G. Wyszecki and W. S. Stiles, *Color Science: Concepts and Methods, Quantitative Data and Formulas*, Wiley, New York, 1967, pp. 48-49, p. 240.
6. G. Fasol and S. Nakamura, *The Blue Laser Diode: GaN Based Blue Light Emitters and Lasers*, Springer, Berlin (1997).
7. W. M. Yen, S. Shionoya, and H. Yamamoto, *Phosphor Handbook*, CRC Press, Boca Raton, FL, USA (2007).
8. W. M. Yen and M. J. Weber, *Inorganic Phosphors: Compositions, Preparation and Optical Properties*, CRC Press (2004).
9. S. Shionoya and W. M. Yen, *Phosphor Handbook*, CRC Press (1999).
10. P. S. Dutta, U.S. Pat. 8974695 (2015).
11. A. Zukauskas, R. Vaicekauskas, P. Vitta, A. Tuzikas, A. Petrulis, and M. Shur, *Optics Express*, 20, 5356 (2012).