

Development of Special LEDs Using Phosphors Emitting Near-infrared Light

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Abstract Near-infrared light has been considered unnecessary in lighting and displays for its difficulty of invisibility in human eyes. However, it is important in the fields of plant growth and spectroscopic analysis, and is considered to be applied in such fields as LEDs. This paper covers our development of various LEDs using phosphors that emit near-infrared light.

1. Introduction

White LEDs are an achievement accomplished by the development of blue LEDs as well as by the development of phosphors. In the visible light region, white LEDs suitable for lighting and LCD backlighting have been developed by controlling the emission spectrum using phosphors emitting light from green to red. In particular, white LEDs for general lighting applications have been spread rapidly since the Great East Japan Earthquake of 2011, and luminous efficiency approached the theoretical limit.

However, from perspective of the near-infrared (NIR) region, there are still some fields where the conversion of existing lamps to LEDs is lagging behind.

As for examples of NIR emitting LEDs, there are LEDs used as sensors for remote controls for audio-visual equipment and opening and closing of automatic doors, as LEDs emitting light at around 840nm or 940nm are used for those applications. In those applications, LEDs with a small full width at half maximum (FWHM) are easy to use, but on the other hand, light sources with a broad band emission in the NIR region are needed.

OCT (optical coherence tomography) is used in ophthalmologic procedures such as glaucoma because it's nondestructive, first and also enables high-resolution observation. A light source with a broad band emission spectrum in the NIR region is needed, and studies have been conducted using blue LEDs and phosphors that emit NIR light¹⁾.

NIR spectroscopy is widely used to sort fruit sugar content and to brand Japanese black beef branding, etc., since it can observe the optical absorption of functional groups such as O-H, C-N, and C-H and analyze various components²⁾. Near-infrared spectroscopy requires a light source with a broad emission spectrum from 700 to 2,500nm, and NIR phosphors have been reported to emit NIR emission from 650 to 1,400nm³⁾.

The characteristics and emission spectra of NIR phosphors and LEDs are shown in Table 1 and Figure 1. According to the Table 1, the FWHM of LEDs has a narrow band of less than 50nm, whereas the FWHM of phosphors is wider than 80nm.

Table 1: Characteristics of NIR Phosphors and LEDs

	Abbreviation	composition	Emission peak	FWHM
Phosphor	CASN	CaAlSiN ₃ :Eu	650nm	90nm
	YGG	Y ₃ Ga ₅ O ₁₂ :Cr ³⁺	711nm	80nm
	SBO	ScBO ₃ :Cr ³⁺	811nm	138nm
	CCSO	CaCuSi ₄ O ₁₀ ⁶⁾	921nm	109nm
LED	AlGaAs	(Al,Ga)As	840nm	40nm
	GaAs	GaAs	936nm	48nm

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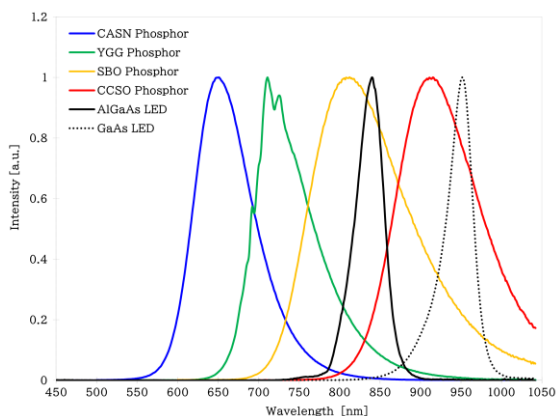


Figure 1: Emission Spectra of NIR Phosphors and LEDs

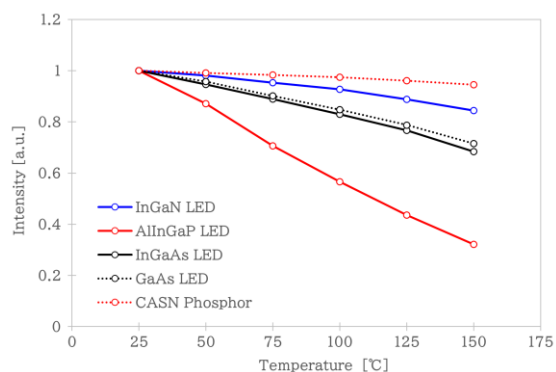


Figure 2: Temperature Dependence of Emission Intensity of LEDs and CASN Phosphor

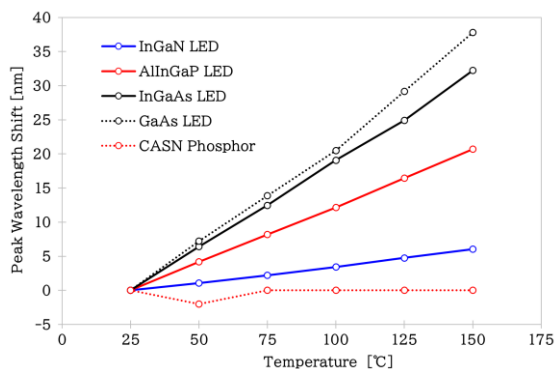


Figure 3: Temperature Dependence of Peak Wavelength Shift of LEDs and CASN Phosphor

Although NIR LEDs have a small decrease in emission intensity output by increasing temperature (Figure 2), they have a large change in emission spectra (Figure 3), which is a major issue.

Most phosphors are composed of a crystal line host matrix and activators, and it is known that the decrease in emission intensity due to temperature rise can be improved by the amount of activators⁷. There are also phosphors, such as CASN phosphors, whose emission spectra change little by increasing temperature (Figure 3).

Based on the above, we developed special LEDs using phosphors with broad band emission spectrum and excellent temperature characteristics.

2. LEDs for Plant Growth

$\text{LiAlO}_2\text{:Fe}$ phosphors that emit light at around 740nm have been long-standing component of fluorescent lamps for plant growth⁸). However, $\text{LiAlO}_2\text{:Fe}$ phosphors cannot be excited by blue light. Although these cannot be applied in blue LEDs.

$(\text{Ba,Sr,Ca})_3\text{MgSi}_2\text{O}_8\text{:Eu,Mn}$ phosphors can be excited by visible light. And it emits deep red light⁷). The blue luminescence from Eu^{2+} and the red luminescence from Mn^{2+} overlap sufficiently with the photosynthetic action spectrum of chlorophyll, so they are expected to be used for plant growth⁹).

In addition, since the light absorption of phytochrome is located around 650nm and 730nm, LEDs with increased deep red light for plant growth have been developed¹⁰).

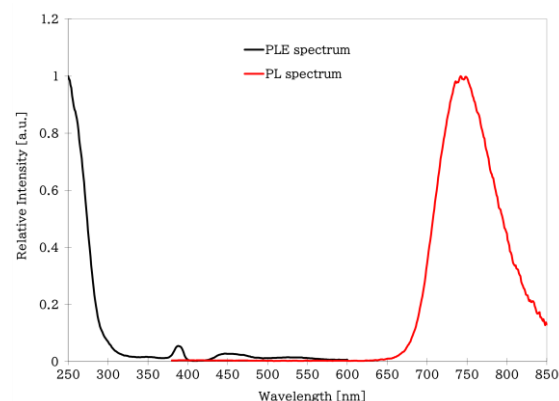


Figure 4: Photoluminescence(PL) Spectrum and Photoluminescence Excitation(PLE) Spectrum of $\text{LiAlO}_2\text{:Fe}$ Phosphors

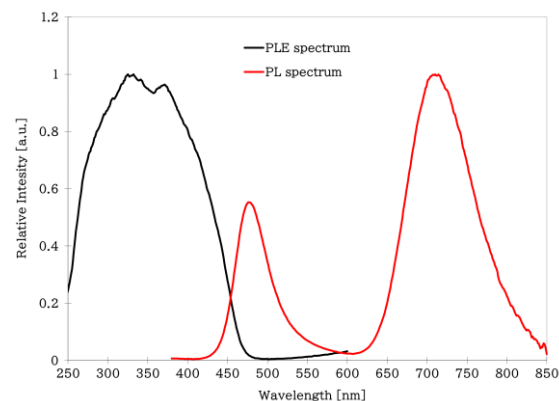


Figure 5: Photoluminescence(PL) Spectrum and Photoluminescence Excitation(PLE) Spectrum of $\text{Ca}_3\text{MgSi}_2\text{O}_8\text{:Eu,Mn}$ Phosphors

Sunlight has sufficient light with wave lengths above 800nm, but artificial light such as that from fluorescent lamps or white LEDs does not.

The NIR spectroscopy described above uses absorption bands of molecular bonds. The absorption band attributed to the O-H stretching vibration is around 970nm, and the

absorption band attributed to the C-H stretching vibration is around 920nm¹¹⁾. Therefore, water molecules and sucrose molecules are thought to cause optical absorption of these NIR lights. By making water molecules and sucrose molecules oscillate, we can expect vigorous circulation of nutrients in the plant, which may promote growth.

In this study, we focused on the NIR region from 920nm to 970nm. As mentioned earlier, the emission of NIR LEDs (GaAs) around 920nm decreases due to the shift in emission to longer wavelengths as the temperature increases. For this reason, we developed a special LEDs for plant growth using phosphors that emit NIR light.

The CCSO phosphors in Table 1 were used to obtain NIR light from 920nm to 970nm. CCSO phosphors have a strong excitation band around 600nm, but cannot be excited by blue light. To obtain NIR light from CCSO phosphors, the first step would be to excite them with a red LEDs. However, as shown in Figures 2 and 3, the current AlInGaP-based red LEDs have poor temperature dependency, resulting in a decrease in light output and a change in the emission spectra.

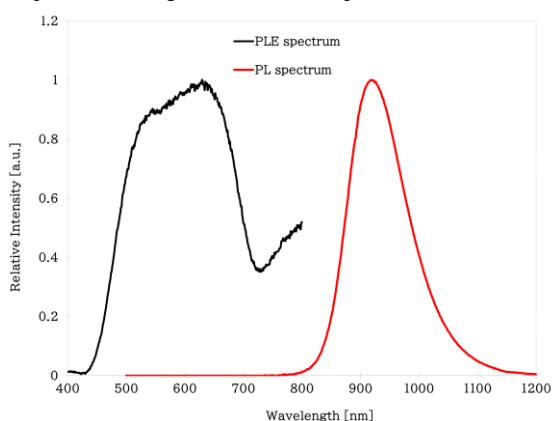


Figure 6: Photoluminescence(PL) Spectrum and Photoluminescence Excitation(PLE) Spectrum of CCSO Phosphors

Therefore, we tried to excite (Sr,Ca)AlSiN₃:Eu(SCASN) red phosphors with a blue LEDs, so that its red light emission would cause a CCSO phosphors to emit NIR light.

As a comparison, the emission spectrum of an LED combining a red LED and CCSO phosphor (red LED excitation), and the emission spectrum of an LED combining a blue LED, SCASN phosphor, and CCSO phosphor (blue LED excitation) that we developed, are shown below.

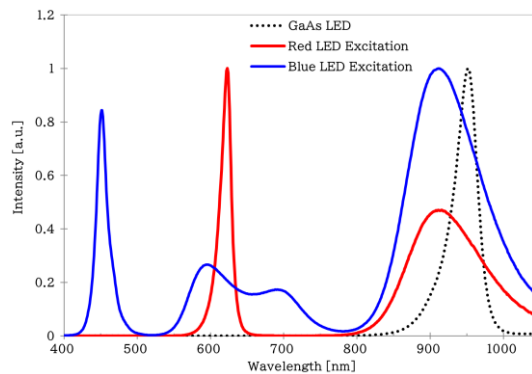


Figure 7: Emission Spectra of LEDs for Plant Growth

Since NIR light is invisible to the human eye, we used *WPE* (Wall Plug Efficiency) to compare luminous efficiency. *WPE* is expressed by the following equation.

$$WPE (\%) = (\text{Light output } W) / (\text{Input power } W) \\ = (\text{Light output } W) / \{(\text{current } A) \times (\text{voltage } V)\}$$

For measurements of emission spectra, we used CAS-140 (Instrument Systems GmbH). The *WPE* calculation was based on the sum between 380nm and 1,042nm ($\Sigma_{380-1042}$) for using this spectrometer. Visible light output is the sum between 380nm and 780nm ($\Sigma_{380-780}$), and NIR light output is the sum between 781nm and 1,042nm ($\Sigma_{781-1042}$). The results are shown in Table 2.

Table 2: Characteristics of LEDs for Plant Growth

	Current [mA]	Voltage [V]	Input Power [W]	$\Sigma_{380-780}$ [mW]	$\Sigma_{781-1042}$ [mW]	$\Sigma_{380-1042}$ [mW]	WPE [%]
Red LED Excitation	65.0	2.15	0.14	5.2	14.8	20.0	14
Blue LED Excitation	65.0	2.75	0.18	13.3	25.4	38.7	22

The NIR emission ($\Sigma_{781-1042}$) light output and *WPE* were higher for the blue LED excitation than for the red LED excitation.

The graph of the temperature dependence on the NIR light ($\Sigma_{781-1042}$) is shown in Figure 8. The blue LED excitation has less decrease in light output at high temperatures.

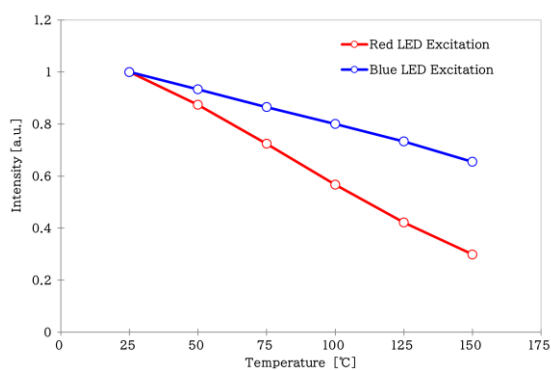


Figure 8: Temperature Dependence of LEDs for Plant Growth

From the above, it was found that the blue LED excitation is superior because it produces strong NIR luminescence and has little output decreasing even at high temperatures¹².

Although it is not known how NIR light around 920-970nm affects plant growth, it contains blue and red Lights necessary for photosynthesis, so we have high expectations for experiments using LEDs for plant growth.

3. LEDs for Halogen Lamp Replacement

Broad band lights are used for spectrophotometers. Which lights has 200nm to 1,000nm spectrum. The phosphors in Figures 4 and 5, are measured by spectrophotometer manufactured by FP-6500 (JASCO Corporation). This spectrophotometer has a 150W xenon lamp, and a 20W halogen lamp valued from 350nm to 900nm, enabling measurements in the wavelength range of 220nm to 900nm. The luminescence of xenon lamps does not stabilize after using lighting time of more than 1,000 hours, so it is recommended to use less than 1,000 hours.

Light sources for spectroscopic analysis require correction of the device and measurement of calibration curve each time the lamp is replaced. In addition, LEDs are desired for reasons such as miniaturization, power saving, and minimum heat emission.

The required emission spectra differs depending on the application, but since the luminous efficiency of LEDs is low in the ultraviolet (UV) region from 220 to 350nm, the target wavelength for this work is from 360 to 1,000nm, and we have developed three types of LEDs (Types (a) to (c)) as halogen lamps replacement.

Details of the LEDs and phosphors (a) to (c) are shown in Tables 3 and 4. Emission spectra shown in Figure 9 is comparing ultra-high color rendering LED¹³, and a halogen lamp.

Table 3: Configuration of LEDs

	UV Region		Visible light Region			NIR Region		
Type (a)	-	-	Blue LED	Phosphor A	Phosphor B	Phosphor C	-	-
Type (b)	-	-	Blue LED	Phosphor A	Phosphor B	Phosphor C	Phosphor D	Phosphor E
Type (c)	UV-LED	Phosphor F	Blue LED	Phosphor A	Phosphor B	Phosphor C	Phosphor D	Phosphor E

Table 4: List of Material Characteristics of Used for Type(a) to (c) LEDs

	Composition	Emission peak	
UV-LED	InGaN	363nm	UV Region
Phosphor F	(Sr,Mg) ₂ P ₂ O ₇ :Eu ²⁺	397nm	
Blue LED	InGaN	435nm	Visible light Region
Phosphor A	Lu ₃ (Al,Ga) ₅ O ₁₂ :Ce ³⁺	486nm	
Phosphor B	(Sr,Ca)AlSiN ₃ :Eu ²⁺	642nm	
Phosphor C	ScBO ₃ :Cr ³⁺	810nm	NIR Region
Phosphor D	Y ₃ Ga ₅ O ₁₂ :Cr ³⁺ ,Nd ³⁺	878nm, 1,067nm	
Phosphor E	Y ₃ Ga ₅ O ₁₂ :Cr ³⁺ ,Yb ³⁺	1,030nm	

Table 5: WPE of LEDs (Types (a), (b))

	Current [mA]	Voltage [V]	Input Power [W]	$\sum_{380-780}$ [mW]	$\sum_{781-1042}$ [mW]	$\sum_{380-1042}$ [mW]	WPE [%]
Ultra-high color rendering LED	32.5	5.45	0.18	91.0	0.4	91.4	51
Type (a)	65.0	2.85	0.19	42.5	9.5	52.0	28
Type (b)	65.0	2.85	0.19	26.2	14.1	40.3	22

The sharp emission spectrum above 850nm caused by phosphors D and E is due to the 4f-4f transition of rare earth ions Nd³⁺ and Yb³⁺, and the emission peak changes extremely small compared to the NIR LED in Figure 3 because of the 4f inner shell transition.

As shown in Figure 10, phosphor D has sharp spectra around 1,067nm due to Nd³⁺ ion. Light whose peak wavelength is above 1,042nm cannot be measured by this spectrophotometer. Considering that Type (b) also emits light with wavelengths above 1,042nm, the WPE of Type (b) is even higher than that of Table 5.

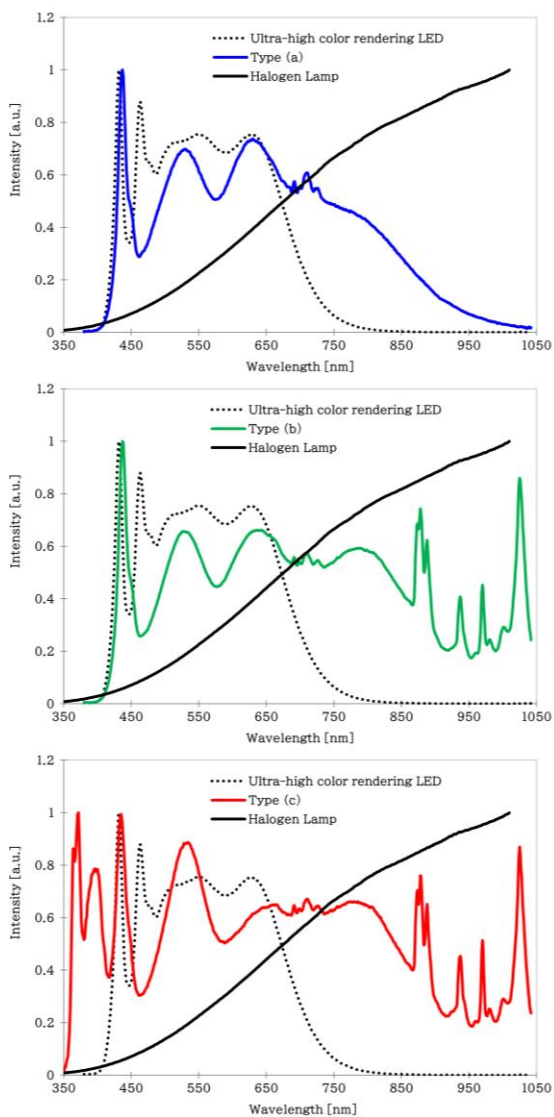


Figure 9: Emission Spectra of Type(a) to (c) LEDs Comparing Ultra-high Color Rendering LED, and Halogen Lamp

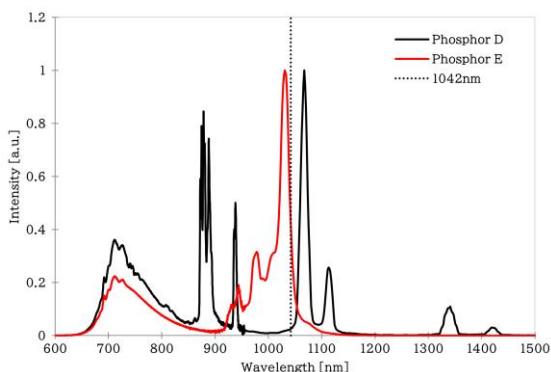


Figure 10: Photoluminescence(PL) Spectra of Phosphor D and E

Although there is a concavity in the emission spectrum in Figure 9, the emission intensity is more than 10% of the main peak in the targeted wavelength region¹⁴). The emission spectra can be adjusted by changing type and amount of phosphors, making it possible to create LEDs that meet market needs. We expect those to be used for spectroscopic analysis.

4. LEDs for Vehicle Paint Inspection and Stage Lighting

Sunlight contains a large amount of NIR light, but fluorescent lamps and white LEDs contain almost no NIR light. Artificial lighting has been improved to reduce intensity of light from red region to NIR region, because these emission have poor visual sensitivity^{15, 16, 17} .

For the lighting used in painting process of automobile bodies, replacement with LEDs is not progressed, because the objects illuminated by artificial lighting are not be shown similarly comparing to ones with sunlight

To make human facial color and expression be reflected, NIR (far-red) light is necessary, although its visual sensitivity is poor. Halogen lamps are used persistently in stage lighting for it's ability to realistically reflect facial expressions.

We have now developed LEDs emphasizing NIR (far-red) light as LEDs for vehicle paint inspection and stage lighting. We used YGG phosphor, of which emission peak is 711nm, as shown in Table 1,

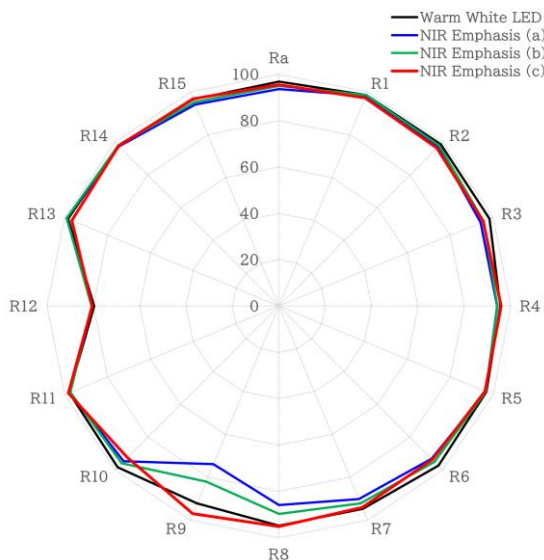


Figure 11: Color Rendering Index of LEDs for Vehicle Paint Inspection and Stage Lighting

Unlike the LEDs for replacement of halogen lamps mentioned above, light used for lighting also needs to have the same color rendering index as well as chromaticity (color

temperature, deviation), because illuminated objects are seen by human eyes.

The developed LEDs are adjusted to almost the same chromaticity (color temperature, deviation) as the warm white LEDs, and have almost the same color rendering index except for R9. (Table 6, Figure 11) R9 is an index for red, which is affected by the intensity of NIR (far-red) light. With comparing the 4 LEDs, although there are small differences in R9, there are clear differences between 4 LEDs in the intensity of NIR (far-red) light, as shown in Figure 12.

The values of spectral luminous efficiency function above 700nm are almost 0, but the spectrum multiplied 50 times shows that brightness can be sensed up to around 750nm. Therefore, objects illuminated by the developed LEDs are expected to be shown the same with those illuminated by sunlight.

For the poor visual sensitivity of NIR, the luminous efficiency of the developed LEDs was decreased by about half, while their *WPE* was decreased by about 30%. Since there is a trade-off relationship between these efficiencies and the

intensity of the NIR light, it is preferable to adjust the intensity of the NIR light as necessary.

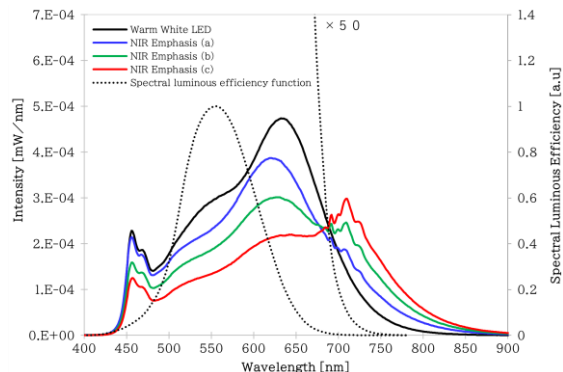


Figure 12: Emission Spectra of LEDs for Vehicle Paint Inspection and Stage Lighting

In this study, NIR light was emphasized by targeting the warm white light, but it can be applied to daylight white and other color temperatures as well. For this reason we have high expectations for LEDs for vehicle paint inspection and stage lighting.

Table 6: Characteristics of LEDs for Vehicle Paint Inspection and Stage Lighting

	Luminous Efficiency		Light Output $\sum_{380-1042}$		WPE	x	y	Color Temperature [K]	Deviation [duv]
	[lm/W]	Ratio	[mW]	Ratio					
Warm White LED	127	109%	82.3	100%	45%	0.439	0.411	3022	0.002
NIR Emphasis (a)	108	93%	75.1	91%	41%	0.435	0.402	3006	-0.001
NIR Emphasis (b)	86	74%	68.3	83%	38%	0.437	0.405	3012	0.001
NIR Emphasis (c)	62	53%	60.5	74%	33%	0.434	0.400	3010	-0.001

5. Conclusion

Using NIR emitting phosphors, we have developed special LEDs for plant growth, spectroscopic analysis, vehicle paint inspection, and stage lighting. They have a unique emission spectrum from the NIR phosphors, and changes in their emission peak can be kept small. Since their luminous efficiency is at a practical step, we would like to move to demonstration experiment of each LEDs to confirm their usefulness.

We thank Dr. Yasushi Nanai of the National Defense Academy for his cooperation in measuring the emission and excitation spectra of NIR phosphors.

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