

MULTIEXCITED PHOSPHORS IN UV AND BLUE LED DEVICES

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(Received 31 October 2007)

Abstract

This study is devoted to multiexcitation of phosphors in LED devices. A new model of double and triple excitation of phosphors in UV chip and double excitation in blue chip was proposed and discussed. The suitable phosphor candidates were synthesized and investigated. A LED devices with an n-UV Ga(In)N chip as well as blue InGaN chip and multiexcited phosphors were designed and constructed. These LEDs show better quantum yield of green and red phosphors, higher total brightness and improved color rendering index (CRI).

1. Introduction

Since the commercial blue light emitting diodes (LEDs) was first reported by Nichia chemical Co. in 1994, much progress has been achieved on GaN-based LEDs [1–6]. Blue and near-UV light GaN-based LEDs can be used to excite longer wavelength emitting phosphor to realize white light emission. Nakamura pioneered this approach at Nichia Chemical Co. and the first white light emitting diodes became commercially available in 1997 [7–9]. The white light was obtained by combining a 465 nm blue light from the GaN-based LED and yellow light from the phosphor YAG:Ce. However, this light combination has exposed some drawbacks: firstly, the degradation rates of LEDs and phosphor are not isochronous; thus, the white light point in the color coordinates scheme shifts with working time. Secondly, the “white” light from this combination route has an undesirable color balance, the deficiency of the red light in the visible spectra (around 600 nm) results in a low color rendering index [10]. So a novel red emitting phosphor for compensating the red component is needed in order to obtain white light with higher color rendering index. There are two different ways to improve the color properties of the device. First of them is based on adding another component to create a white LED with three emission bands (a three-band white LED). Blue LEDs have been combined with phosphors to convert part of the blue light to red and green light, to produce white light. Another approach for obtaining white light is to combine a near-UV LED (around 370–410 nm) with tri-color phosphors. The white light consists of the red, green, and blue light emitted from the tri-color phosphors while excited by the near-UV LEDs [11, 12]. In this case, the float of white color point can be eliminated because all the visible lights come from the tri-color phosphors. In order to realize this type of white LEDs, novel phosphors are required, since most of commercially applicable phosphors were developed on different purposes of applications and do not meet the white LEDs applications. The phosphors for LED applications that need to be excited effectively by the near-UV light are lacking, especially the red one.

In order to improve the color properties of the LED devices, in this work we propose one new nontraditional way – to excite the red phosphor not only by UV source, but also by the emission of blue phosphor (double excitation) as well as by green phosphor (triple excitation). Nowadays, the commercially applicable red emitting phosphors for white LED are divalent Eu ion activated sulfides. These sulfide phosphors are chemically unstable when exposed in the moisture environment. Therefore, there is an urgent demand upon the superior red emitting phosphors for white LEDs applications. Eu^{3+} -doped materials, especially those in which the Eu^{3+} ions occupy a non-centrosymmetric site in the host, have been widely used as the red emitting phosphors due to their intense $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission in the red spectral region. Previous investigations [10, 13] have shown that Eu^{3+} -doped phosphors exhibited relatively strong absorption in the near-UV region and intense red emission with good color purity. The search for stable inorganic rare-earth-based red phosphors with high absorption in the near UV/blue spectral region is, therefore, an attractive research task. The requirement of a suitable red-emitting UV/blue phosphor is that it should have a stable host, exhibit strong and broad absorption around 400 nm (LED emission wavelength) and good absorption around 440-480 nm (emission of blue phosphor) with the chromaticity coordinates near the National Television Standard Committee (NTSC) standard values. The blue, green, and red phosphors that satisfy these criteria were developed and synthesized on the basis of our patents [14-16, 28] and are presented in this contribution.

2. Experimental

A luminescent material absorbs energy in one region of the electromagnetic spectrum and emits radiation energy in another region of the spectrum. Typically, the energy of the photons emitted is lower than the energy of the photons absorbed. Most useful phosphors emit radiation in the visible portion of the spectrum in response to the absorption of radiation, which is outside the visible portion of the spectrum. Thus, the phosphor converts electromagnetic radiation to which the human eye is not sensitive into electromagnetic radiation to which the human eye is sensitive.

However, it is very difficult to find three suitable phosphors equally excited by UV in the green, blue, and red regions to obtain really a white light. Usually, the quantum yield of red phosphor is very weak in comparison with green and blue phosphors. The present article is directed to overcoming or at least reducing the problem set forth above.

In order to resolve this problem we propose a white light illumination system comprising a radiation source, a first luminescent material (blue phosphor), having a peak emission wavelength of about 420 to about 480 nm, a second luminescent material (green phosphor), having a peak emission wavelength of about 490 to about 550 nm and a peak absorption wavelength of about 350 to about 480 nm, which is different from the first luminescent material, and a third luminescent material (red phosphor), having a peak emission wavelength of about 580 to about 620 nm and a peak absorption wavelength of about 350 to about 550 nm, which is different from the first and second luminescent material. At least one first blue phosphor can be selected from the following:

- a) $(\text{Sr}, \text{Ca})_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$,
- b) $\text{La}_{2.99}\text{Ce}_{0.01}(\text{SiS}_4)_2\text{I}$ [17],
- c) $\text{Ce}_3(\text{SiS}_4)_2\text{X}$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) [17];

a second green phosphor can be selected from:

- a) $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$,
- b) $(\text{Ba Sr})_2\text{SiO}_4:\text{Eu}^{2+}$,

- c) $\text{Sr}_2\text{Si}_3\text{O}_8\text{SrCl}_2:\text{Eu}^{2+}$ [18],
- d) $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}$ [18],
- e) $\text{Y}_2\text{SiO}_5:\text{Ce}^{3+}, \text{Tb}^{3+}$ [18],
- f) $\text{BaYSi}_4\text{N}_7:\text{Eu}^{2+}$ [19];

and a third red phosphor:

- a) $\text{K}_5\text{Eu}_{2.5}(\text{WO}_4)_{6.25}:\text{Sm}$,
- b) $\text{Li}(\text{WO}_4)_{1.25}:\text{Eu}, \text{Sm}$,
- c) $\text{Ca}_{0.76}\text{MoO}_4:\text{Eu}_{0.24}^{3+}$ [20],
- d) $\text{Ca}(\text{Eu}_{0.5}\text{La}_{0.5})\text{Si}_3\text{O}_{13}$ [21],
- e) $\text{Sr}_x\text{Ca}_{1-x}\text{S}:\text{Eu}^{2+}, \text{Cl}$.

In such a combination of proposed phosphors we can achieve a double and a triple excitation of the red phosphors by UV LED, a first phosphor and a second phosphor. The second phosphor can also be double excited by UV LED and first phosphor.

Some of these cited phosphors were used as commercial phosphors and others were synthesized in Samsung Co.

2.1. Synthesis

The synthesis of $(\text{Sr}, \text{Ca})_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$, $(\text{Ba}, \text{Sr})_2\text{SiO}_4:\text{Eu}^{2+}$, $\text{K}_5\text{Eu}_{2.5}(\text{WO}_4)_{6.25}:\text{Sm}$, and $\text{Li}(\text{WO}_4)_{1.25}:\text{Eu}, \text{Sm}$ phosphors was performed by traditional solid state reaction method. Polycrystalline $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ and some improved modification of thiogallate samples were synthesized by original method. SrS and Ga_2S_3 sulphide powders were mixed in stoichiometric composition and annealed at 900 -1000°C with a carbon reduction atmosphere for 4 h (instead of gas atmosphere). The doping ions were introduced in the form of EuS . This preparation method does not apply toxic H_2S gas [22-24], as well as any other gas atmosphere [25-27], and differs from that reported in above-mentioned literature. The method presented here provides powder samples with good crystalline properties as shown by X-ray diffraction measurements. Powder samples with 6 mol % Eu^{2+} concentration were prepared and studied. The thiogallate samples exhibit a deep green color with peak maximum at 535 nm. This peak maximum and the full width at half maximum (FWHM) can be changed on a large scale.

The red emitting phosphor $\text{Sr}_x\text{Ca}_{1-x}\text{S}:\text{Eu}^{2+}$ was prepared by solid state reaction by combining the starting materials: $\text{Sr}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and Eu_2O_3 . The element S of the phosphor is introduced from SrS/CaS . In alternative method we used CaS , SrS , and EuS as raw materials and additional amount of NH_4Cl was used as a flux. The annealing was carried out at 1000°C about 3 hours with a carbon reduction atmosphere. In this case the luminescence intensity of $\text{Sr}_x\text{Ca}_{1-x}\text{S}:\text{Eu}^{2+}, \text{Cl}$ was about 5-10% higher in comparison with $\text{Sr}_x\text{Ca}_{1-x}\text{S}:\text{Eu}^{2+}$.

All phosphor samples were characterized by crystalline structure and luminescence properties.

2.2. Sample characterization

2.2.1. X-ray diffraction measurement – The crystal structures of the prepared samples were determined by X-ray diffraction measurement using goniometer (PANalytical, X'Pert pro MPD with $\text{Cu-K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 30 mA. The scan speed was 3 seconds per step (0.02° step – 2θ) and covered the range between 10° and 90° .

2.2.2. EDS (Energy Dispersive Spectroscopy) and EPMA (Electron probe micro analysis) – Qualitative and Quantitative non-destructive elemental analysis was performed with

EPMA machine, model SX-100 (the electron acceleration was 20 kV, beam current 10 nA, and the diameter of electronic beam was 50 μm , DT:0.3 S). It is the most precise and accurate micro-analysis technique available, and all the elements from Beryllium to Uranium can be analyzed.

2.2.3. Photoluminescence (PL) measurement – Optical spectroscopy and PL characteristics were estimated on the basis of emission and excitation spectra registered at room temperature (Xe 500 W lamp) with DARSA PRO 5100 PL System (Professional Scientific Instrument Co, Korea). Excitation spectra were corrected for the energy distribution of the Xe-lamp. The excitation was performed with a 460 nm radiation, which usually used in blue LED.

2.2.4. Raman spectroscopy - Raman scattering spectra of SrGa_2S_4 , CaGa_2S_4 , and BaGa_2S_4 were measured by a Renishaw 3000 spectrometer with a He-Ne laser (excitation wavelength of $\lambda = 633$ nm and $\lambda = 785$ nm) and a photomultiplier counter at room temperature in back scattering configuration. The spectral resolution of spectrometer is about 4 cm^{-1} at 633 nm and 1 cm^{-1} at 785 nm.

2.2.5. Morphology and size measurement – Particle sizes and morphologies of the investigated phosphors were determined by scanning electron microscope (SEM) Hitachi-S-3000N. In order to control the particle size and to find the size distribution the Laser diffraction was carried out using HELOS particle size analysis system.

3. Results and discussion

Classical UV LED scheme of a white light illumination system is presented in Fig. 1:

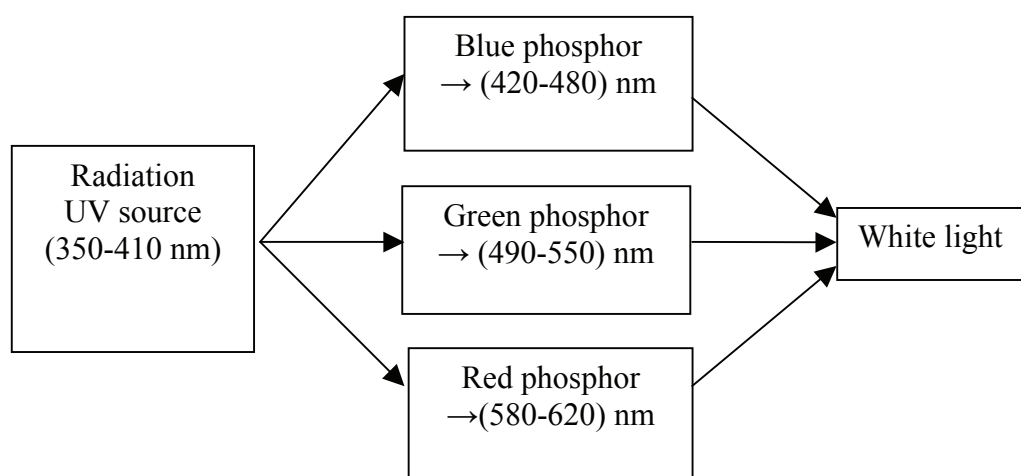


Fig. 1. Classical UV LED scheme.

Disadvantage of this scheme is in very weak quantum yield of red phosphor in comparison with green and blue phosphors. The double and triple excitation of red phosphor is proposed to increase the quantum yield of red phosphor.

3.1. Double excitation in UV LED

Schematically illustration of double excitation of red phosphor is shown in Figs. 2 and 3.

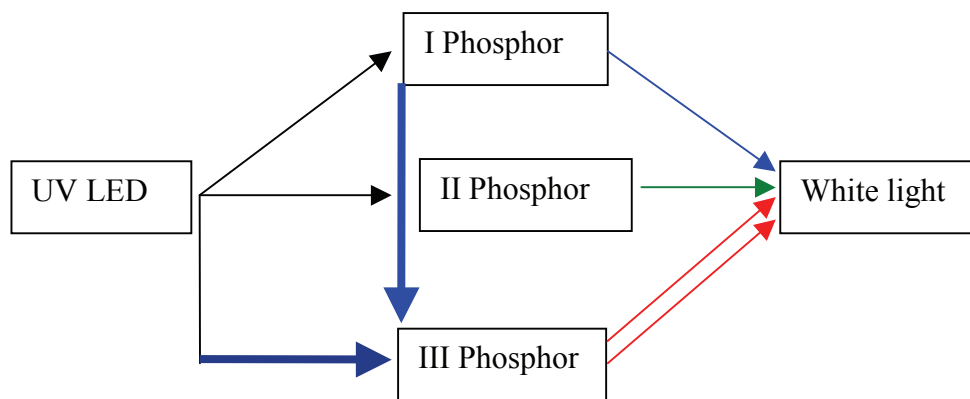


Fig. 2. Proposed scheme of a white light illumination system with a double excitation of third (red) phosphor.

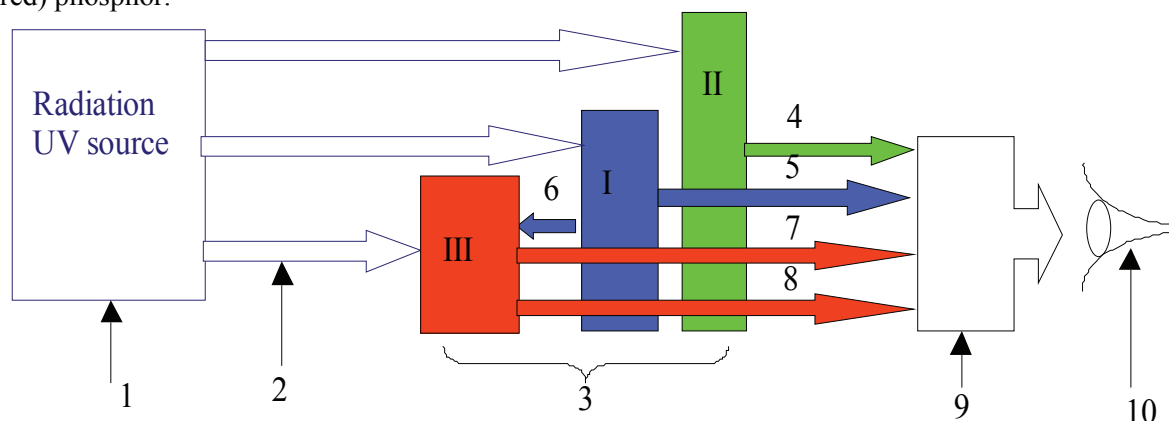


Fig. 3. Schematic illustration of a white light illumination system with a double excitation of red (III) phosphor.

In Fig. 3, a radiation source 1, such as an LED, emits radiation 2 incident on three luminescent materials 3, such as first phosphor I, second phosphor II, and third phosphor III. The three phosphors I, II, and III may be blended together (3) or separated (as shown in Fig. 3) and may comprise discrete overlying layers.

Radiation 2 may have a wavelength to which the human eye is not sensitive, such as 420 nm and below. After absorbing the incident radiation 2, second phosphor II emits green light 4 having a peak emission wavelength between 490 and 550 nm, first phosphor I emits blue light 5 and 6 having a peak emission wavelength between 420 and 480 nm, while third phosphor III emits red light 7 and 8 having a peak emission wavelength between 580 and 620 nm and a peak absorption wavelength of about 350 to about 480 nm. Red light 7 is the light emitting by third phosphor III due to absorption of radiation 6 of second phosphor II and light 8 is due to absorbing incident radiation 2 of source 1. Human observer 10 perceives the combination of green 4, blue 5 and red 7, 8 light as white light 9. Figure 3 schematically illustrates that green light 4, blue light 5, 6 and red light 7, 8 emanates from discrete phosphor areas to illustrate the concept of color mixing. However, it should be understood that the green, blue and red light may be emitted from the same area if first, second and third phosphors I, II, and III are blended together to form a single blended phosphor layer.

In order to realize in practice this double excitation of red phosphor by UV source and blue phosphor let us consider the energy transfer between the first (blue) and third (red) phosphors, presented in Fig. 4

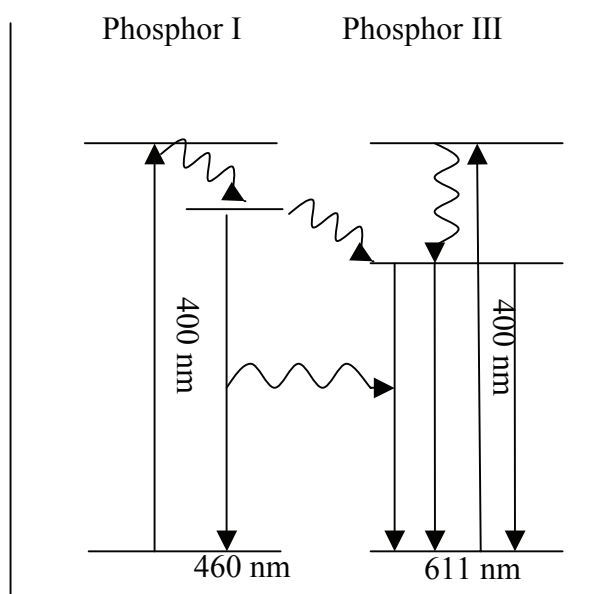


Fig. 4. Energy transfer between the first (blue) and third (red) phosphors.

First blue phosphor I is excited by UV source (400 nm, for example) and emits a blue light at 460 nm. If third red phosphor III is capable to absorb this wavelength as well as 400 nm from UV source, it will be double excited. Quantum yield and brightness will increase. All the proposed phosphors from the above mentioned list fit these criteria. Two high efficient candidates as phosphor III may be $\text{Ca}_{0.76}\text{MoO}_4:\text{Eu}_{0.24}^{3+}$ and $\text{K}_5\text{Eu}_{2.5}(\text{WO}_4)_{6.25}:\text{Sm}$.

The excitation and absorption spectra of these phosphors are shown in Figs. 5 and 6.

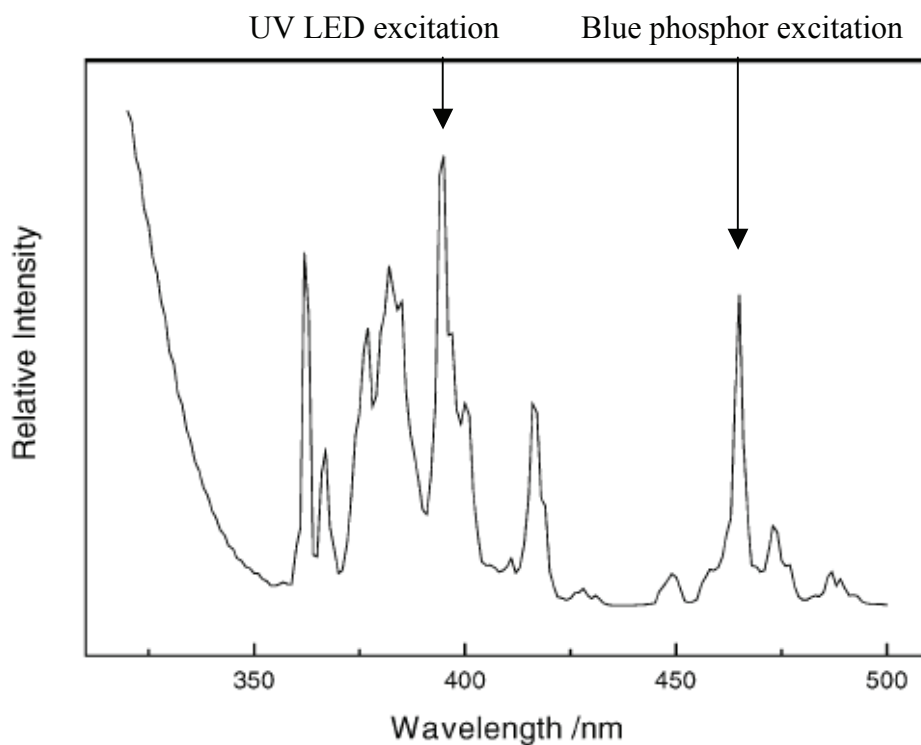


Fig. 5. Excitation spectrum of $\text{Ca}_{0.76}\text{MoO}_4:\text{Eu}_{0.24}^{3+}$ phosphor (monitored in wavelength 616 nm).

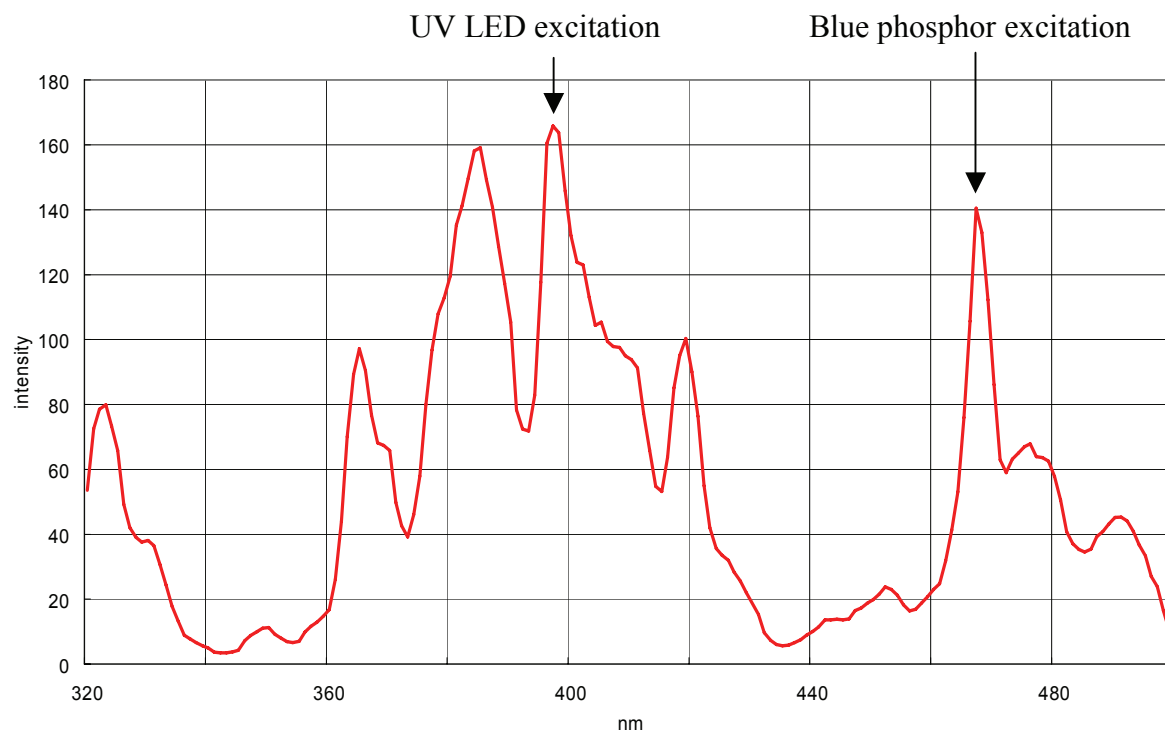


Fig. 6. Absorption spectra of $\text{K}_5\text{Eu}_{2.5}(\text{WO}_4)_{6.25}:\text{Sm}$.

From these figures one can see that both phosphors can be excited by UV LED (400 nm) and blue light (460 nm).

As example of blue phosphor we can take $\text{La}_{2.99}\text{Ce}_{0.01}(\text{SiS}_4)_2\text{I}$ and $\text{Ce}_3(\text{SiS}_4)_2\text{X}$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$). Their spectra are shown in Figs. 7 and 8. All these phosphors are properly excited by UV source (400 nm) and emit a blue light with high intensity at 460 nm.

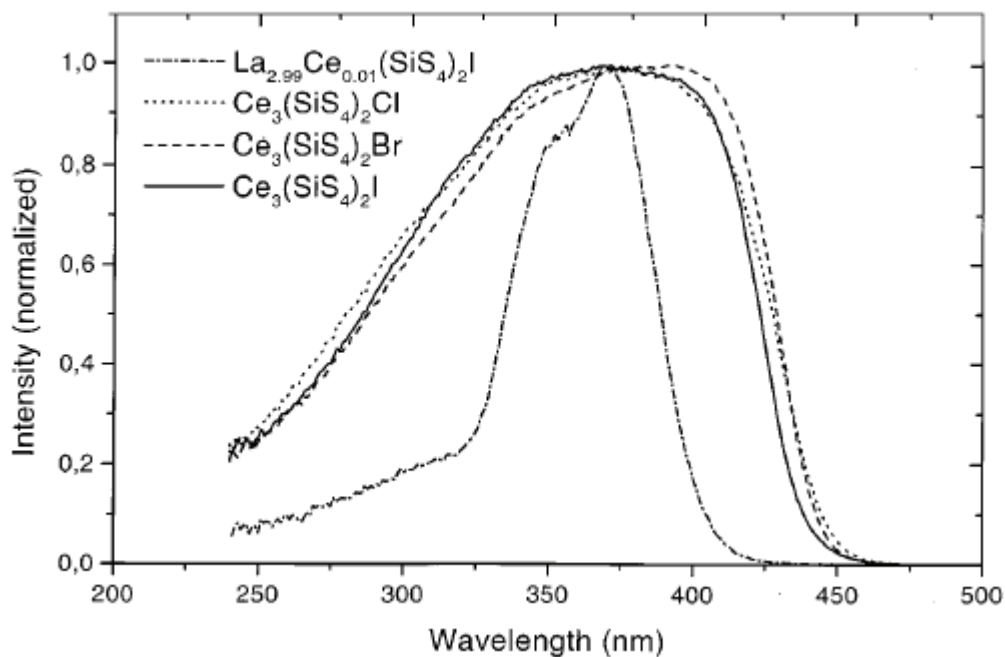


Fig. 7. Excitation spectra at 300 K ($\lambda_{\text{em}} = 500 \text{ nm}$) of $\text{La}_{2.99}\text{Ce}_{0.01}(\text{SiS}_4)_2\text{I}$ and $\text{Ce}_3(\text{SiS}_4)_2\text{X}$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$).

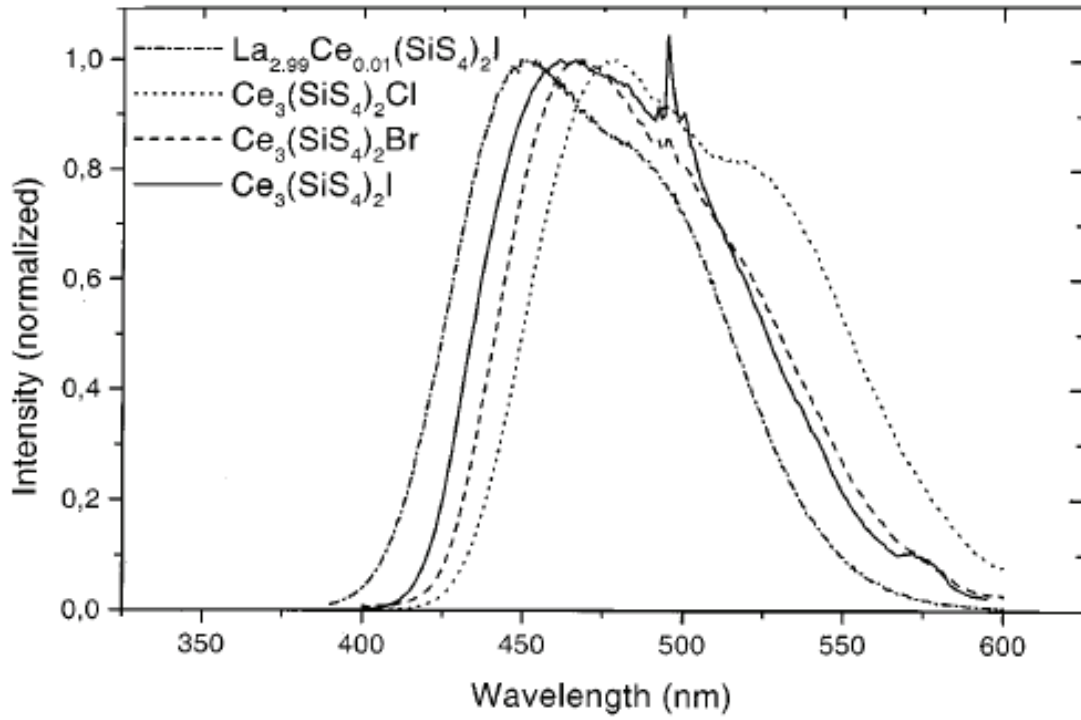


Fig. 8. Emission spectra ($\lambda_{\text{exc}} = 372$ nm) of $\text{La}_{2.99}\text{Ce}_{0.01}(\text{SiS}_4)_2\text{I}$ and $\text{Ce}_3(\text{SiS}_4)_2\text{X}$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) at 300 K. The lines around 495 nm are due to traces of praseodymium in cerium starting materials.

3.2. Triple excitation in UV LED

The model of a white light illumination system with a double excitation of second (green) phosphor and a triple excitation of third (red) phosphor is shown in Figs. 9 and 10.

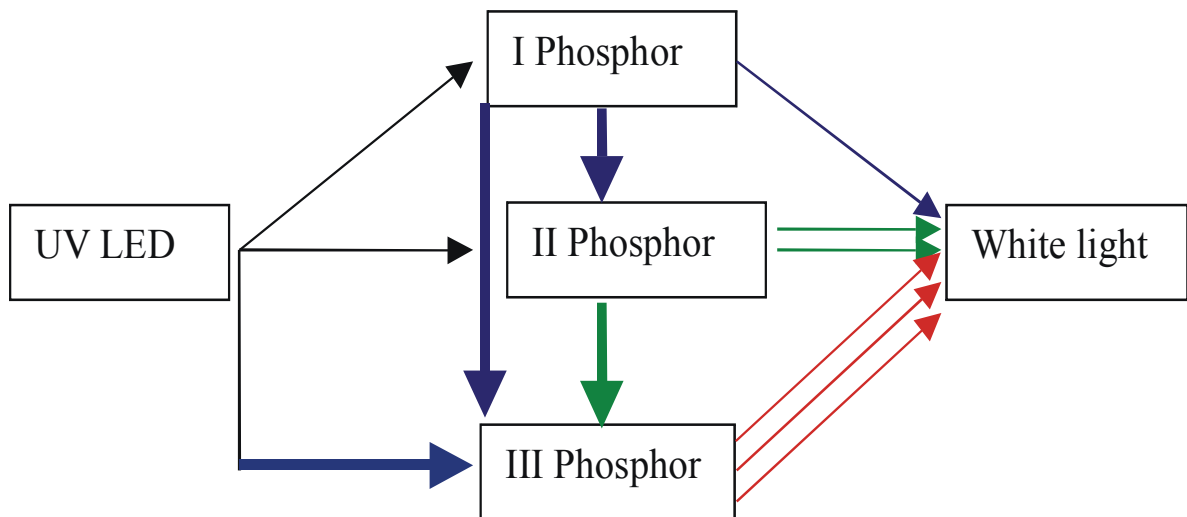


Fig. 9. Proposed scheme of a white light illumination system with a double excitation of second phosphor and a triple excitation of third phosphor.

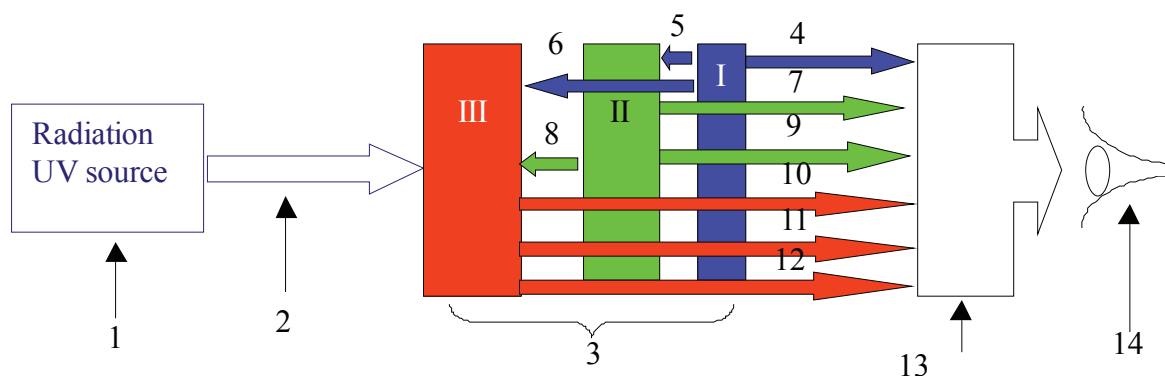


Fig. 10. Schematic illustration of a white light illumination system with a double excitation of green phosphor and a triple excitation of red phosphor.

Figs. 9 and 10 schematically illustrate a double excitation of green phosphor and a triple excitation of red phosphor. In Fig. 10, radiation source 1, such as an LED, emits radiation 2 incident on three luminescent materials 3, such as first (blue) phosphor I, second (green) phosphor II, and third (red) phosphor III. The principal difference of this model in comparison with Fig. 3 consists in important choice of green phosphor. It must be excited by UV LED and blue phosphor and excite the red phosphor. The energy transfer scheme between the first, second, and third phosphor is given in Fig. 11.

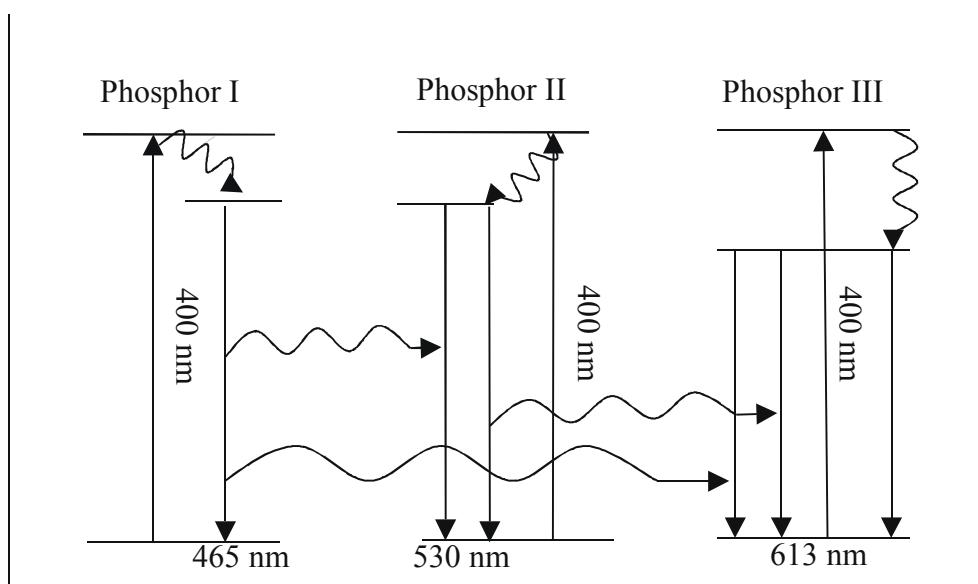


Fig. 11. Energy transfer scheme between the first, second, and third phosphor.

The first luminescent material may be the same as in the previous case, for example, $\text{La}_{2.99}\text{Ce}_{0.01}(\text{SiS}_4)_2\text{I}$ or $\text{Ce}_3(\text{SiS}_4)_2\text{X}$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$). Its spectra are shown in Figs. 7 and 8.

The second luminescent material may be any phosphor II, which in response to incident radiation 2 from radiation source 1, emits visible light having a peak emission wavelength between 490 and 550 nm and a peak absorption wavelength of about 350 to about 480 nm. For example, the following phosphors fit these criteria:

- a) $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$,
- b) $(\text{Ba Sr})_2\text{SiO}_4:\text{Eu}^{2+}$.

The $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ phosphor is preferred because it has a quantum efficiency of at least 90% for incident radiation having a wavelength of 350 to 500 nm, has little or no selective absorption of the visible light and strong excitation at 465 nm. Therefore, the Sr thiogallate with improved properties was carefully prepared by modified chemical route. PL characteristics of $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ are shown in Fig. 12.

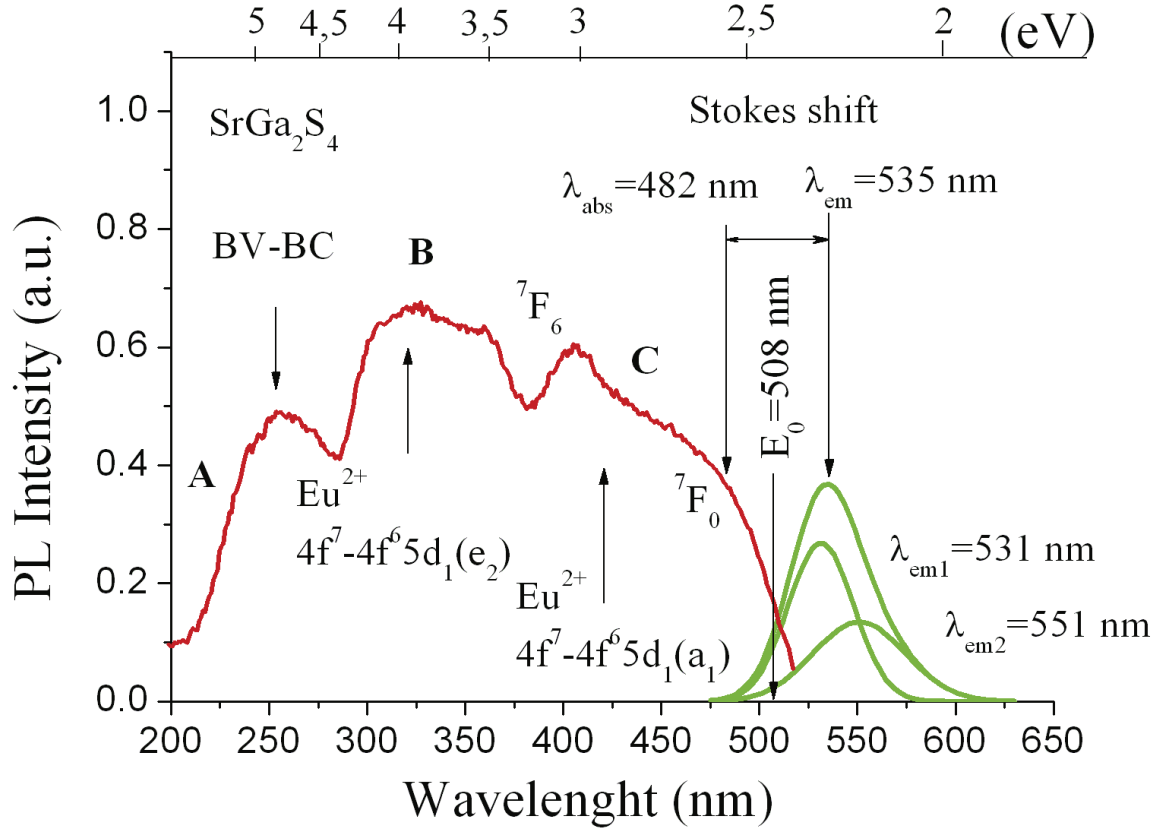


Fig. 12. Excitation and emission spectra of the $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ (6 mol %) powder at 300 K.

The emission spectra under excitation at 460 nm consist of a broad band in the visible range. The maximum wavelengths of the band is 535 nm, FWHM is 49 nm. No additional band due to the emission of Eu^{2+} in investigated $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ is observed, which indicates that no secondary phase is present in our sample. The emission is ascribed to the dipole-allowed transition from the lower $4f^6(^7F)5d$ state to the $4f^7(^8S_{7/2})$ fundamental state of the Eu^{2+} ions [24]. $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ excitation spectrum is composed of three large bands in the UV–visible range. The excitation band (A) (maximum at 254 nm) is ascribed to the transitions between the valence band and the conduction band of the SrGa_2S_4 host matrix. The two excitation bands (B) and (C) are ascribed to the $4f^7(^8S_{7/2})$ – $4f^6(^7F)5d$ transitions in Eu^{2+} electronic levels.

The high efficient red phosphor $\text{Ca}(\text{Eu}_{0.5}\text{La}_{0.5})\text{Si}_3\text{O}_{13}$ may be proposed as a candidate of phosphor III with a triple excitation. Excitation and emission spectra of $\text{Ca}(\text{Eu}_{0.5}\text{La}_{0.5})\text{Si}_3\text{O}_{13}$ are shown in Fig. 13.

This phosphor may be triply excited by incident radiation 2 from radiation source 1 and by incident radiation 6 from first phosphor I and radiation 8 from second phosphor II (Figs. 9, 10, and 11). Quantum yield of phosphor III, brightness of device, and color rendering index will increase.

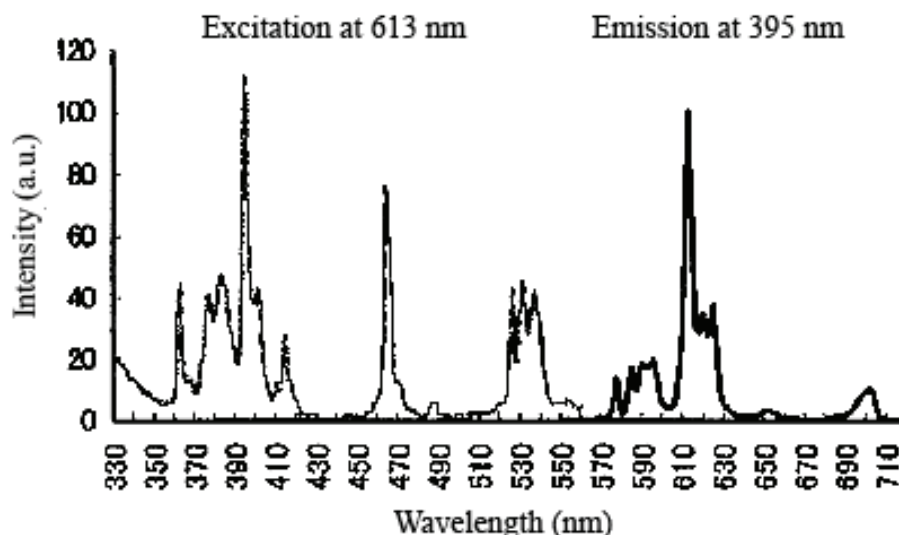


Fig. 13. Excitation at 613 nm (left) and emission at 395 nm (right) spectra of $\text{Ca}(\text{Eu}_{0.5}\text{La}_{0.5})\text{Si}_3\text{O}_{13}$ phosphor (monitored in wavelength 613 nm).

3.3. Double excitation in blue LED

The white light in blue LED is obtained usually by combining a 465 nm blue light from the GaN-based LED and yellow light from the phosphor $\text{YAG}:\text{Ce}$. However, the “white” light from this combination route has an undesirable color balance, the deficiency of the red light in the visible spectra (around 600 nm) results in a low color rendering index. Another approach for white light obtaining is to combine a blue LED (around 460 nm) with green and red phosphors. The white light consists of the blue light of the chip and red and green light, emitted from the two-color phosphors while excited by the blue LEDs. So, a novel red emitting phosphor with double excitation by blue LED and by green phosphor for compensating the red component is needed in order to obtain white light with higher color rendering index.

We can use the scheme proposed in Figs. 2 and 3 for a white light illumination system with a double excitation of red phosphor. The $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ as a green phosphor is preferred in this case. This phosphor is properly excited as by UV (400 nm) as well as by blue light (460 nm) (Fig. 12, excitation spectra). Moreover, it has highest possible quantum efficiency about 90% for incident radiation having a wavelength of 400 to 480 nm and has little or no selective absorption of the visible light.

The second (red) phosphor is capable of absorbing one part of blue light from the diode at 460 nm and simultaneously another part of green light from the first green phosphor ($\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$, for example) between 490 and 550 nm, and emitting light having a peak emission wavelength between 580 and 650 nm. Fig. 14 schematically illustrates the above principle.

One of the most efficient candidates as red phosphor may be proposed $\text{Sr}_x\text{Ca}_{1-x}\text{S}:\text{Eu}^{2+}, \text{Y}$ (wherein x is a number of from about 0.3 to 0.8, and Y is one or more halogens, in either their atomic or ionic forms). This proposed phosphor may be double excited by the incident radiation from the radiation source and by incident radiation from the green phosphor. Quantum yield and brightness will increase. The synthesis route and luminescence properties of $\text{Sr}_x\text{Ca}_{1-x}\text{S}:\text{Eu}^{2+}, \text{Cl}$ red phosphor were examined in detail in our previous works [28, 29]. The excitation and emission spectra of $(\text{Ca}_{1-x}, \text{Sr}_x)\text{S}:\text{Eu}^{2+}$ with a different Sr/Ca ratio, satisfying the above principle, are shown in Fig. 15.

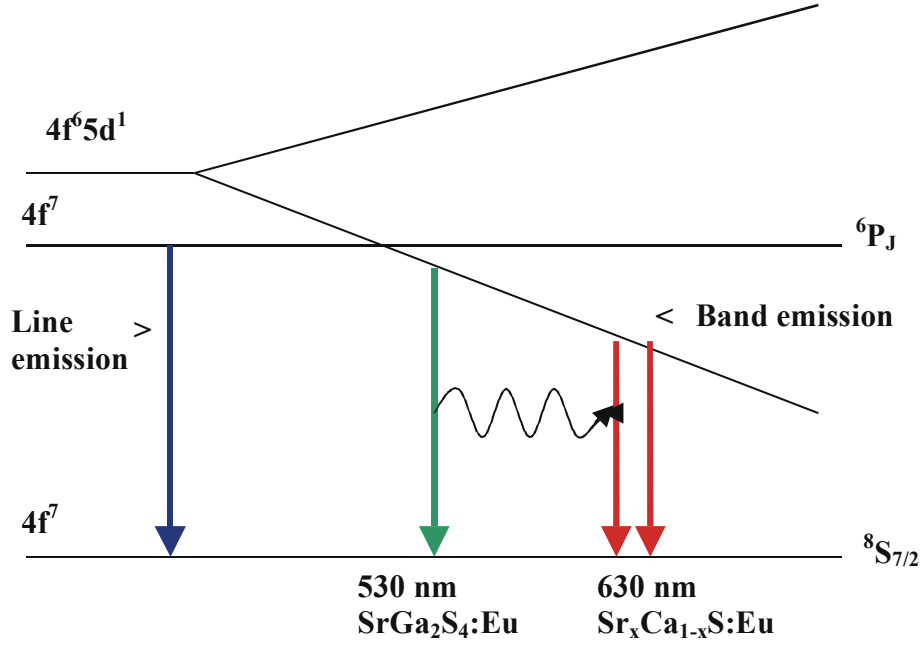


Fig. 14. Energy transfer between the first (green) and second (red) phosphor.

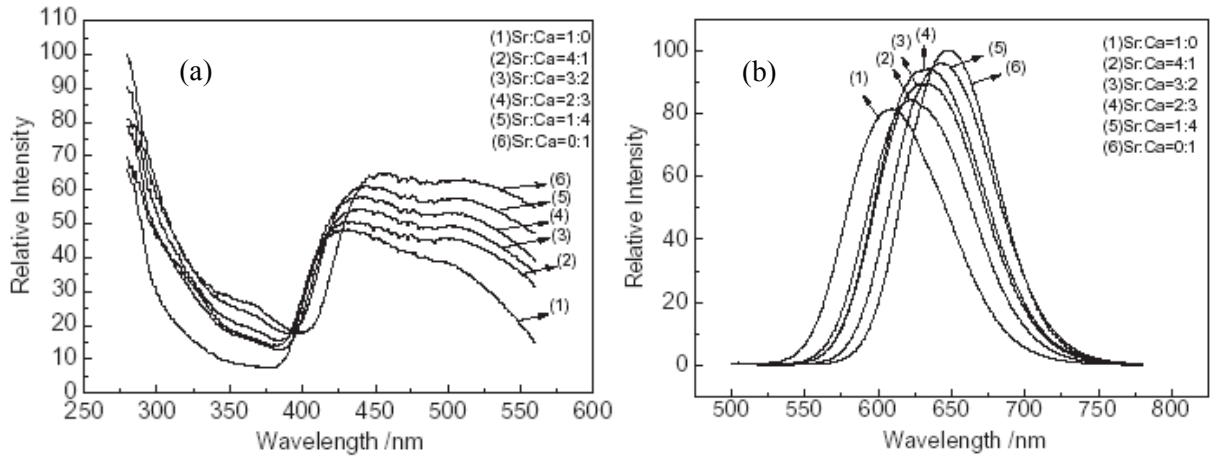


Fig. 15. The excitation (a) and emission (b) spectra of $(\text{Ca}_{1-x}\text{Sr}_x)\text{S}:\text{Eu}^{2+}$ with a different Sr/Ca ratio (excitation made by 460 nm light source).

The proposed multiexcited phosphors were combined in a LED device with an n-UV Ga(In)N chip and blue InGaN chip. For this purpose, a 395-nm UV Ga(In)N chip and 460 nm blue InGaN chip were used to fabricate the white-color LEDs based on different combinations of multiexcited phosphors. Compared with previous results, these phosphors show much more emission intensity in our experiments.

4. Conclusions

A new idea of multiexcitation phosphors in LED was proposed and discussed. The suitable phosphor candidates were synthesized and investigated. A LED devices with an n-UV Ga(In)N chip and blue InGaN chip with multiexcited phosphors were designed and con-

structed. Quantum yield of green phosphor was increased by about 5-10%. Quantum yield of red phosphor was increased by about 15-20%. The total brightness of device was increased by about 15-20%. CRI was improved by about 15-20%.

Acknowledgements

This work was supported by BK21 Program funded by the Ministry of Science and Technology of Korean government.

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