

## UV pumped two color phosphor blend White emitting LEDs

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### Abstract

We have synthesized a  $\text{Eu}^{2+}$ -activated  $\text{Sr}_3\text{MgSi}_2\text{O}_8$  blue phosphor and  $\text{Ba}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4$  yellow phosphor investigated an attempt to develop white LEDs by combining it with a GaN blue LED chip. Three distinct emission bands from the GaN-based LED and the ( $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu} + \text{Ba}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4:\text{Eu}$ ) phosphor are clearly observed at 405nm, 455 nm and at around 540 nm, respectively. These three emission bands combine to give a spectrum that appears white to the naked eye. Our results show that GaN (405 nm chip)-based ( $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu} + \text{Ba}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4:\text{Eu}$ ) exhibits a better luminous efficiency than that of the industrially available product InGaN (460 nm chip)-based YAG:Ce.

### 1. Introduction

Remarkable progress can be observed in the development of white light-emitting diodes (LEDs) using GaN as well as InGaN chip [1,2]. Recently, especially, the white LEDs in which a blue LED is combined with a yellow YAG:Ce phosphor were investigated extensively due to their applications, such as back-lighting for liquid crystal displays (LCDs) and incandescent lamps. There have been some detailed studies on the integration of the blue LED and the yellow phosphor, as this creates white light from a combination of a blue LED emission (460 nm) and a broad-band yellow YAG phosphor [3]. The phosphor conversion of LED light for white light strongly depends on the strong absorption of the blue LED emission wavelength. The strong absorption can be expected from dipole-allowed electron

transitions in activated ions. The  $\text{Ce}^{3+}$  and  $\text{Eu}^{2+}$  ions are well known activated ions, which can be crystal field shifted in the spectral location of their absorption and emission lines. However, very few efficient new blue and yellow phosphors have actually been discovered, besides the YAG:Ce phosphor and the organic luminescent materials.

In the present work, we have synthesized an  $\text{Eu}^{2+}$ -activated  $\text{Sr}_3\text{MgSi}_2\text{O}_8$  blue phosphor and  $\text{Ba}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  yellow phosphor investigated in an attempt to develop white LEDs through the integration of the GaN blue LED chip ( $\lambda_{em}=405$  nm) and the ( $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu} + \text{Ba}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4:\text{Eu}$ ) phosphor into a single package.

### 2. Experiments

Powder samples with the general formula  $(\text{Sr}_{3-x}\text{Eu}_x)\text{MgSi}_2\text{O}_8$  and  $(\text{Sr}_{2-x-y}\text{Ba}_x\text{Eu}_y)\text{SiO}_4$  were prepared by solid-state reaction. The starting materials used in the preparation of this phosphor were powders greater than 99.9% pure of  $\text{SrCO}_3$ ,  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{BaCO}_3$ , and  $\text{Eu}_2\text{O}_3$ . Prewighed powders were mixed thoroughly in acetone in an agate mortar and dried at 130°C for about 24 h to drive off the solvent and successively heat-treated at several conditions of temperature and duration time, followed by an additional grinding and firing in a reduction atmosphere. At this time the gas flow was adjusted to yield a mixture of 4 vol nitrogen to 1 vol hydrogen.

The excitation and emission spectra of the fired samples were measured with a Perkin-Elmer LS-50 luminescence spectrometer with a xenon flash lamp ( $\Delta v^{1/2} = 10\mu\text{s}$ ). To

investigate the white luminescent LEDs of  $\text{Eu}^{2+}$  - doped  $\text{Sr}_3\text{MgSi}_2\text{O}_8$  and  $\text{Ba}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4$  phosphor, white luminescence conversion LEDs were fabricated. Based on standard LED technology, GaN-based  $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu} + \text{Ba}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  white LEDs were encapsulated in a transparent epoxy resin. The emission spectra of a GaN-based  $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu} + \text{Ba}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  under a forward bias of 20 mA were measured using a 50 cm single-grating monochromator.

### 3. Result and Discussions

#### 3.1 $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu}$ blue phosphor

Fig.1 shows the fluorescence spectra of  $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu}$  samples with different  $\text{Eu}^{2+}$  content. As seen from this figure, the emission spectra shows a broad-band character, and the broadness of the emission band indicates an interaction between the host and the activator, which can be attributed to the presence of an excited electron in an outer shell of the  $\text{Eu}^{2+}$  ion[4]. The emission band at about 455 nm shifts to a longer wavelength with an increase in  $\text{Eu}^{2+}$  concentration. This may be attributed to some increases of the probability of an energy transfer among  $\text{Eu}^{2+}$  ions as the  $\text{Eu}^{2+}$  concentration increases[5]. A non-radiative energy transfer from one  $\text{Eu}^{2+}$  ion to another  $\text{Eu}^{2+}$  ion usually occurs as a result of an exchange interaction, radiation reabsorption or a multipole-multipole interaction. In the case of the  $\text{Eu}^{2+}$  ion, the  $4f^7 \rightarrow 4f^6 5d^1$  transition is allowed, while the exchange interaction is responsible for the energy transfer of forbidden transitions and typical critical distance, which is about 5 Å [6]. It is indicated that the exchange interaction plays no role in the energy transfer between  $\text{Eu}^{2+}$  ions. Since the  $4f \rightarrow 5d$  transition of  $\text{Eu}^{2+}$  is allowed, the energy transfer in the present case will occur only as a result of an electric multipolar interaction. As an increased of  $\text{Eu}^{2+}$  concentration, the distance between  $\text{Eu}^{2+}$  ions becomes less, and the probability of energy transfer among  $\text{Eu}^{2+}$  ions increases. In other words, the probability of  $\text{Eu}^{2+}$  ions at higher levels of 5d which make an energy transfer to the lower 5d levels of  $\text{Eu}^{2+}$  ions, increases with an increase of  $\text{Eu}^{2+}$  concentration[5]. It

makes it possible to shift of emission peak to the longer wavelength with an increase of  $\text{Eu}^{2+}$  concentration.

#### 3.2 $\text{Ba}^{2+}$ co-doped $\text{Sr}_2\text{SiO}_4:\text{Eu}$ yellow phosphor

The fluorescence spectra of  $\text{Sr}_{2-x}\text{SiO}_4:\text{Eu}_x$  samples with different  $\text{Eu}^{2+}$  contents are shown in Fig. 2. As can be seen from this figure, the emission spectra show a broadband character, and the broadness of the emission band indicates an interaction between the host and the activator, which can be attributed to the presence of an excited electron in an outer shell of the  $\text{Eu}^{2+}$  ion[7]. The emission band at about 520 nm shifts slightly to a longer wavelength with an increase in  $\text{Eu}^{2+}$  concentration. This may be attributed to some changes in the crystal field around  $\text{Eu}^{2+}$  that increased the  $\text{Eu}^{2+}$  concentration. Although the 4f electrons of  $\text{Eu}^{2+}$  are not sensitive to a lattice environment due to the shielding function of the electrons in the outer shell, the 5d electrons are split by the crystal field, which may lead to a shift in its emission peak. The inset of Fig. 2 shows the shift of emission band of  $(\text{Sr}_{2-y}\text{Ba}_y)\text{SiO}_4:\text{Eu}_{0.1}$  with respect to the  $\text{Ba}^{2+}$  contents. When the amount of  $\text{Ba}^{2+}$  is increased in the composition of  $(\text{Sr}_{2-y}\text{Ba}_y)\text{SiO}_4:\text{Eu}_{0.1}$  the emission band shift gradually to shorter wavelength. In orthorhombic form of  $\text{Sr}_2\text{SiO}_4$ , the alkaline earth ions form chains along the c-axis[8]. It is indicated that a  $\text{Eu}^{2+}$  ion in these chains experiences positive charges due to cation neighbors in the chain direction, in addition to the negative charges of the nearest anion neighbors. The positive charges can orient one d-orbital preferentially. In other words, as the length of the c-axis increases by replacing part of the  $\text{Sr}^{2+}$  by  $\text{Ba}^{2+}$  ions, the effect of preferential orientation of a d-orbital in the chain direction decreases, so that the  $\text{Eu}^{2+}$  emission shifts to shorter wavelength[9].

#### 3.3 GaN-based White emitting LEDs

The relative emission spectra of the white emitting InGaN (460 nm chip)-based YAG:Ce LED and  $(\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu} + \text{Ba}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4:\text{Eu})$  LED are shown in Fig. 3. In the case of the InGaN-based YAG:Ce LED, two distinct emission bands

from the InGaN-based LED and the YAG:Ce phosphor are clearly resolved at 460 nm and at around 560 nm, respectively. Likewise the GaN-based ( $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu} + \text{Ba}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4:\text{Eu}$ ) LED shows three bands at 405 nm, 460 nm and 560 nm. The 405 nm emission band is due to a radiative recombination from a GaN active layer. This UV(405nm) emission was used as an optical transition of the  $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu} + \text{Ba}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  phosphor. The luminance of GaN-based  $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu} + \text{Ba}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  LED measured from these results is about  $158 \text{ cd/m}^2$ , which is higher than that of the industrially available InGaN-based YAG:Ce (in this case,  $200 \text{ cd/m}^2$ ).

The CIE chromaticity of GaN-based LED with different amounts of ( $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu} + \text{Ba}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4:\text{Eu}$ ) phosphor concentration are shown in Fig. 4. As the concentration of  $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu} + \text{Ba}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  increases, the color shifts from blue to white. In addition, the chromaticity coordinates are close to the straight lines interconnecting the points of the blue pump and white. The correlated color temperature (CCT) of a GaN-based  $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu} + \text{Ba}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  white LED packaged in a standard epoxy lamp configuration with a reflecting cup with a CIE chromaticity ( $x=0.31, y=0.32$ ) is 6493 K. On the other hand, industrially available InGaN-based YAG:Ce was shown 6609 K with a CIE chromaticity ( $x=0.31, y=0.31$ ).

#### 4. Conclusions

This UV(405nm) emission was used as an optical transition of the  $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu} + \text{Ba}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  phosphor. The luminance of GaN-based  $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu} + \text{Ba}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  LED measured from these results is about  $158 \text{ cd/m}^2$ , which is higher than that of the industrially available InGaN-based YAG:Ce (in this case,  $200 \text{ cd/m}^2$ ). The white GaN-based  $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu} + \text{Ba}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  developed in this work showed a higher luminance compared with the industrially available InGaN-based YAG:Ce.

#### 5. References

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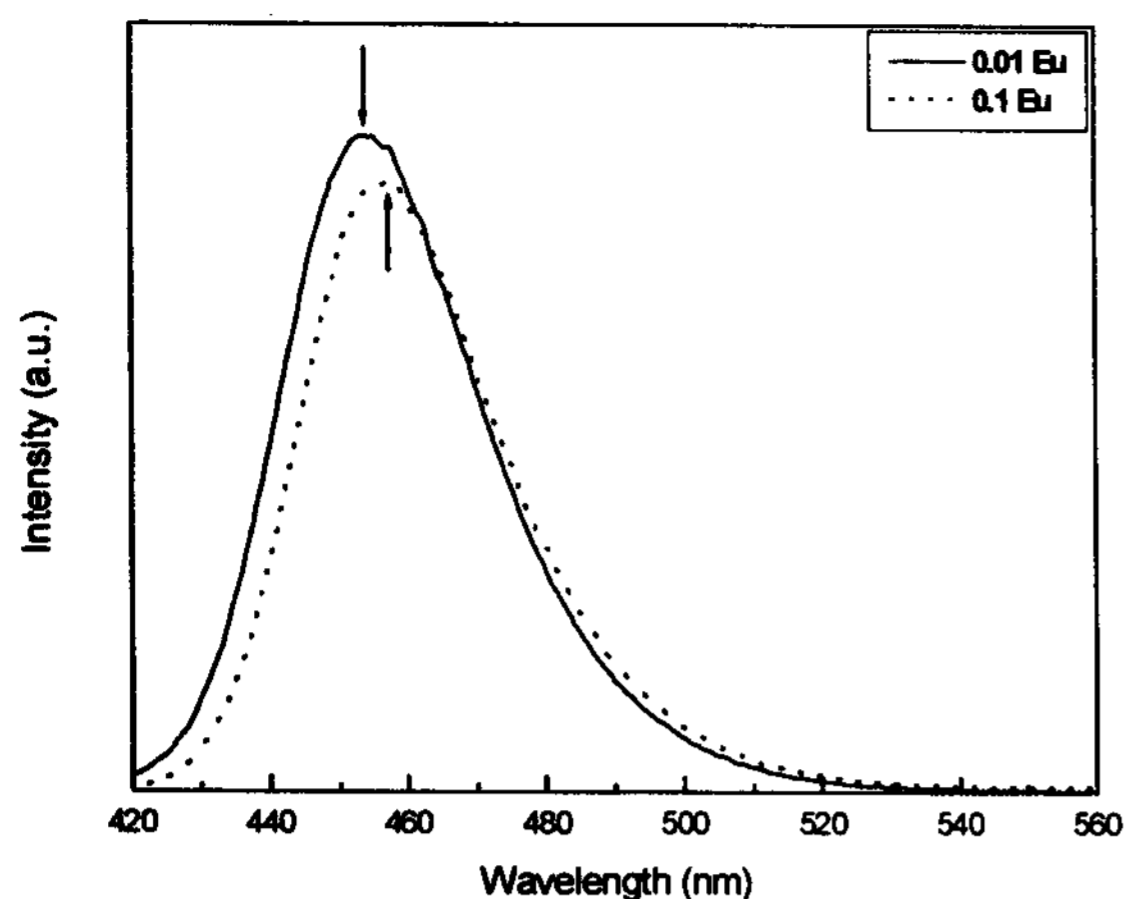


Fig. 1. The photoluminescence emission spectra of the  $\text{Eu}^{2+}$  in the  $\text{Sr}_3\text{MgSi}_2\text{O}_8$  system by the  $\text{Eu}^{2+}$  concentration under the 405 nm excitation wavelength.

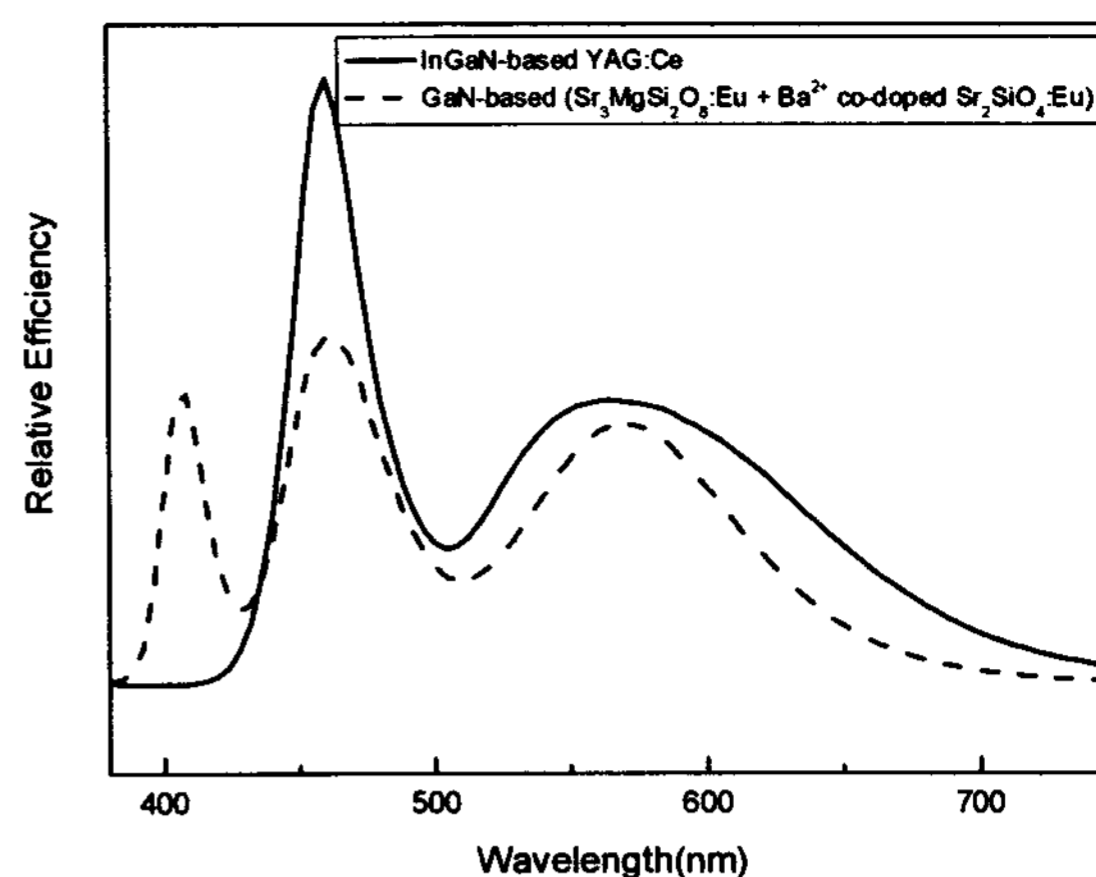


Fig. 3. Relative emission spectra of a white light-emitting InGaN-based YAG:Ce LED and GaN-based ( $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu} + \text{Ba}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4:\text{Eu}$ ) LED under a 20 mA drive current. Spectra were measured with a 50 cm single-grating monochromator under a forward bias of 20 mA.

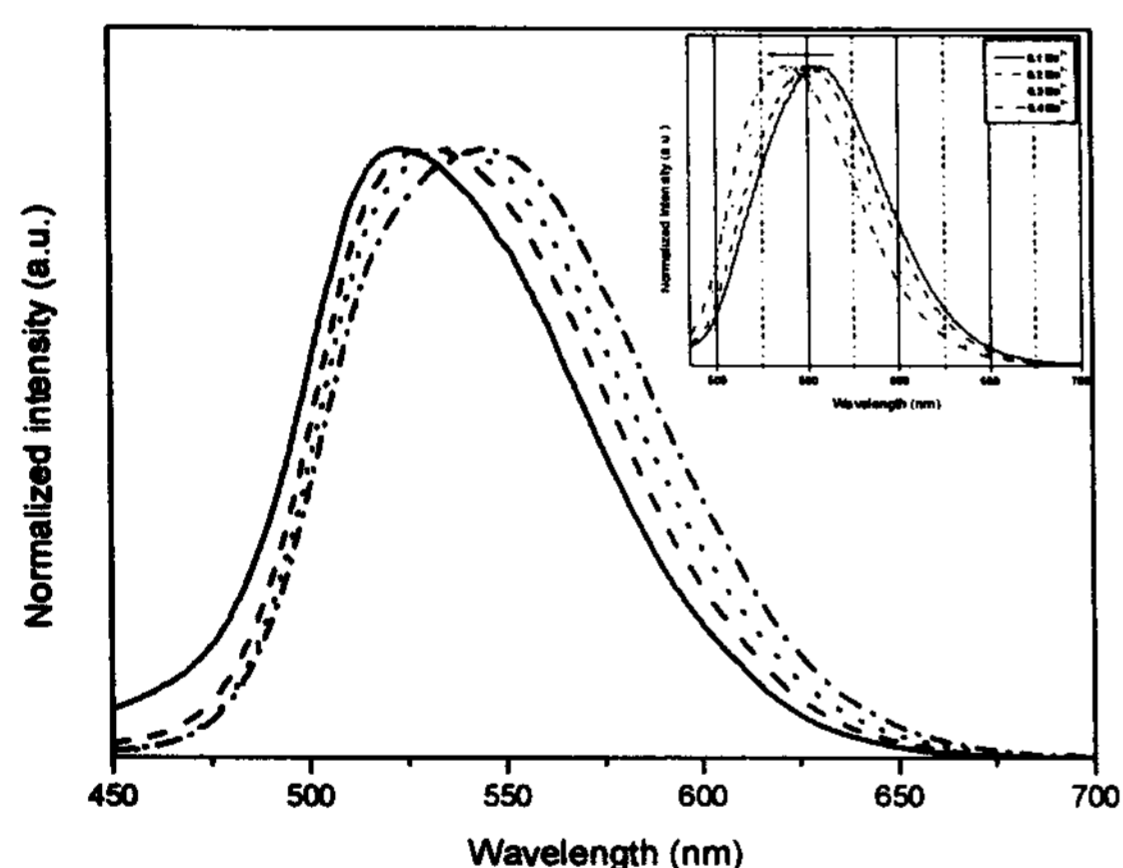


Fig. 2. Photoluminescence emission spectra of the  $\text{Eu}^{2+}$  in the  $\text{Sr}_2\text{SiO}_4$  system by varying the  $\text{Eu}^{2+}$  concentration under the 460 nm excitation wavelength. Solid line (0.01 mol  $\text{Eu}^{2+}$ ), dashed line (0.03 mol  $\text{Eu}^{2+}$ ), dotted line (0.07 mol  $\text{Eu}^{2+}$ ), and dashed-dotted line (0.1 mol  $\text{Eu}^{2+}$ ). The inset of this figure shows the  $\text{Ba}^{2+}$  co-doped effect on the emission bands of 0.1 mol  $\text{Eu}^{2+}$ .

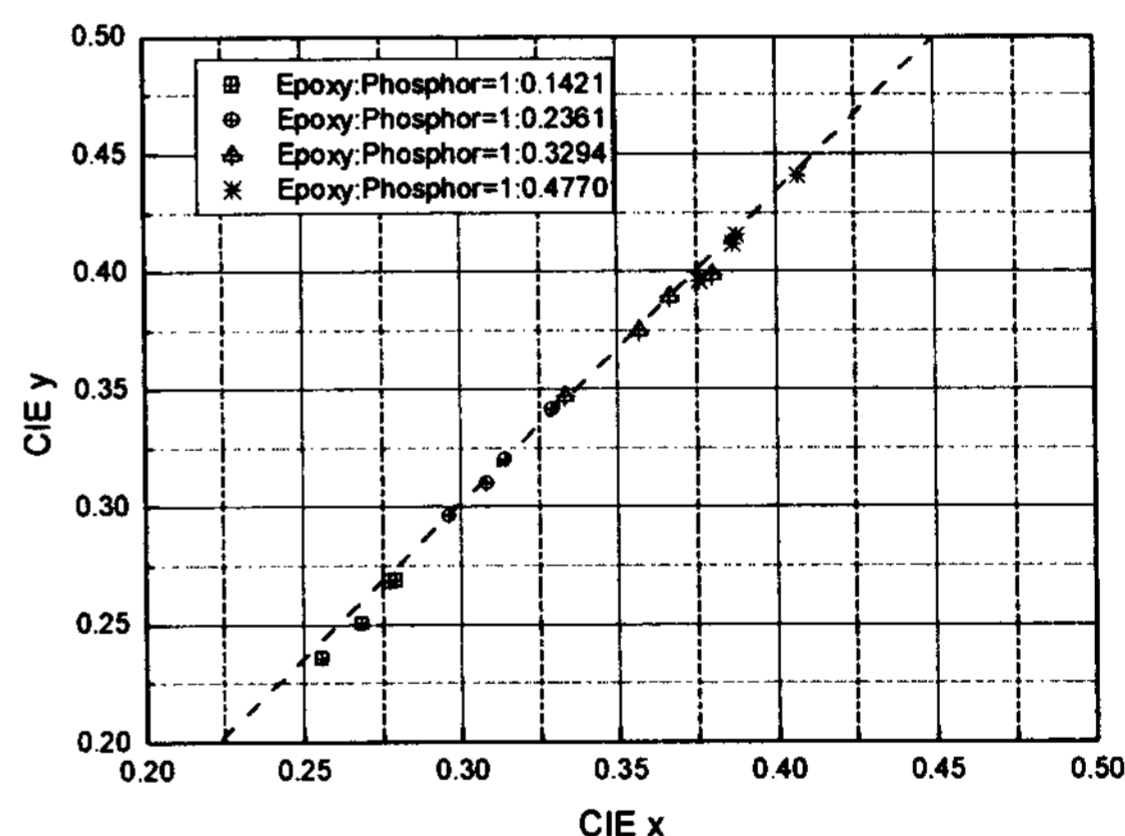


Fig. 4. CIE chromaticity points of GaN-based ( $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu} + \text{Ba}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4:\text{Eu}$ ) LED. The chromaticity points of GaN-based ( $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu} + \text{Ba}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4:\text{Eu}$ ) LED, produced by varying the ( $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu} + \text{Ba}^{2+}$  co-doped  $\text{Sr}_2\text{SiO}_4:\text{Eu}$ ) concentration, are on the straight line connecting the chromaticity point of GaN LED (marked by a closed circle).