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Controlled peak wavelength shift of $Ca_{1-x}Sr_x(S_ySe_{1-y})$:$Eu^{2+}$ phosphor for LED application

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Abstract

The highly efficient red-orange-yellow-emitting phosphor $(Ca_{1-x}Sr_x)(S_{1-y}Se_y)$:$Eu^{2+}$ in combination with commercial green phosphor $SrGa_2S_4$:Eu^{2+} and blue LED are proposed for a three-band white LED. The luminescence mechanism and optimization parameters are discussed on the basis of proposed peak wavelength diagram.
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Keywords: Phosphor; Luminescence; LED

1. Introduction

The development of wide band gap III–V nitride compound semiconductors has led to the commercial production of high-efficiency LEDs [1,2]. The recent advent of blue InGaN technology has made it possible to produce a conventional white LED in which white light is obtained by coating a $Y_3Al_5O_{12}$:Ce (YAG) or $Tb_3Al_5O_{12}$:Ce (TAG) phosphor onto a blue LED chip [3–5]. In this device, known as a two-band white LED, white light is generated by additive color mixing of the blue light emitted by the blue LED and the yellow light emitted by the YAG or TAG phosphors. The development of a white LED is important because it opens the way for LED applications such as light bulbs and fluorescent lamps with high durability and low energy consumption. However, the spectral composition of the light produced by the conventional two-band white LED differs from that of natural white light, particularly in the red region. The color properties of conventional two-band white LEDs can potentially be improved by adding another component to create a white LED based on 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. Suitable phosphors must have a high efficiency of excitation at about 420–480 nm, and a wide chromaticity zone. 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.

Rare-earth (RE) calcium and strontium sulfides have been the object of increased interest in recent years [6–10]. One reason has been the low cost of these red phosphors and the good linear behavior. RE phosphors can be separated into two types: broad band emitting owing to the $5d$–$4f$ transition (Eu^{2+}, Ce^{3+}) or narrow band emitting owing to the transition between the $4f$ levels (Eu^{3+}, Tb^{3+}, Sm^{3+}). For white light in blue LED the broad band emitting phosphors are preferred. Eu^{2+}-doped CaS and SrS as well as CaSe and SrSe are currently under investigation as efficient phosphors for the emission of red-orange light for the LED application. To improve the luminescent properties and to receive the necessary spectra shift, the multi-compound phosphors are used. Some formulas can be considered: M_xM:Eu^{2+}, where M_x is variable Ca/Sr ratio as $Ca_{1-x}Sr_x$ and M is constant, for example, M is only sulfur [11–13] or only selenium [14].

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Other combination MM_y:Eu^{2+}, is also known from literature. Here M is constant, for example, M is Ca or Sr and M_y is variable $S_{1-y}Se_y$ [15].

In the present work we propose a new high efficiency phosphor described by general formula with two variable parameters M_xM_y:Eu^{2+}, where M_x can be $Ca_{1-x}Sr_x$, and M_y can be, for example, $S_{1-y}Se_y$. This phosphor $(Ca_{1-x}Sr_x)(S_{1-y}Se_y)$: Eu^{2+} emits in the deep red, orange or yellow range of spectra in dependence of x and y values. A mathematical diagram and algorithm is proposed to predict the peak wavelength shift and the luminescence properties. White light can be also achieved by combining a blue LED (460 nm) with $SrGa_2S_4$:Eu (green) and $(Ca_{1-x}Sr_x)(S_{1-y}Se_y)$: Eu^{2+} (red) phosphor.

2. Experimental details

Classical inorganic phosphors usually consist of a host lattice with activator ions doped into it in small concentrations, typically a few mole percent or less. Selection of optimum phosphor material (host, dopant and codopant) plus optimization the composition leads to color purity, high brightness, high efficiency and long-term stability. Right synthesis route and synthesis conditions give suitable powder characteristics.

One example of a phosphor composition for a three-band white LED comprises the green-emitting phosphor $SrGa_2S_4$:Eu^{2+} in combination with at least one of the following red-emitting phosphors consisting of $(Ca_{1-x}Sr_x)(S_{1-y}Se_y)$: Eu^{2+} , wherein x and y is a number from 0 to 1. All these phosphors can be synthesized by solid-state reaction. By combining the present red phosphor with green phosphor and blue LEDs, full color white light can be obtained.

The red-emitting phosphor can be prepared by combining the starting materials: CaS (99.99%, CERAC), SrS (99.99%, CERAC), EuS (99.9%, CERAC) with CaSe and SrSe. The host materials, CaSe and SrSe, can be prepared following the detailed description given by Yamashita et al. [16]. The phosphors can be synthesized by high temperature solid-state reaction. The stoichiometric amounts of the corresponding raw materials (CaS, SrS, CaSe, and SrSe) have to be thoroughly mixed by grinding in an agate mortar with EuS. Additional small amount of sulfur and ammonium chloride as flux were also used. The homogeneous mixture was calcined in an alumina tube furnace at 1000 °C for 2.5 h in a stream of reductive atmosphere ($95\%N_2+5\%H_2$). Fig. 1 shows morphologies (a) and particle distribution (b) of some of the prepared samples. The median diameter of powder particles is about 12 μm.

3. Results and discussion

Blue-emitting LEDs are generally known. Usually blue-emitting LED has an emission peak at 420–480 nm, optionally about 450–470 nm. A combination of two blue-excited phosphors (excited by the blue emission from LED), one emitting in the green and one emitting in the red, is used in place of the yellow-emitting yttrium aluminum garnet. Because these new emissions are close to peaks in the tristimulus functions in combination with the blue from the LED they produce light with higher luminous efficacy and better color rendering than the phosphors used in prior devices. These green and red phosphors are selected so that they are excited by the blue-emitting LED. The green color-emitting phosphor typically has an emission peak at 510–550 nm. The red color-emitting phosphor typically has an emission peak at 600–650 nm. To predict the properties and to receive the desirable color of emission, the careful analysis between x and y parameters needs to be carried out. From the literature data it is well known that there are no interstitials when strontium substitutes calcium in a rock-salt crystalline structure and selenium substitutes sulfur. Vegard's law states that there is a linear relationship between substitutional element concentration and the lattice parameter in cases where the solute and solvent have similar bonding properties. In these cases the lattice parameter is influenced only by the relative sizes of the atoms and has been shown to be valid in ionic salts and compounds such as CaSe or SrSe where sulfur substitutes for the selenium [17]. Conforming to the Vegard's law and the experimental linear dependence of wavelength peak versus

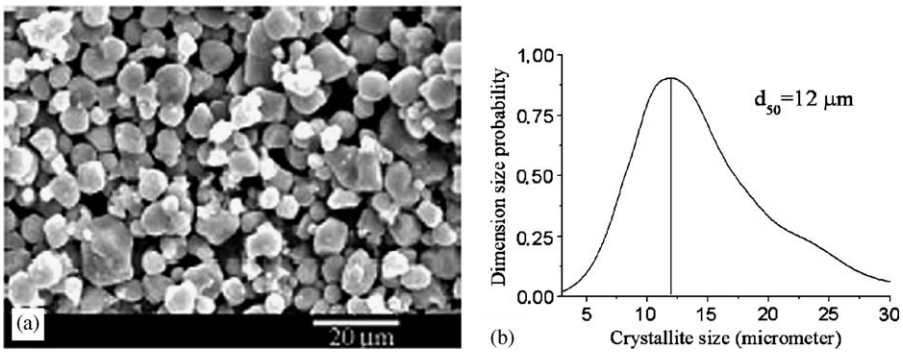

Fig. 1. (a) SEM micrographs and (b) particle distribution of $(Ca_{1-x}Sr_x)S$:Eu^{2+}.

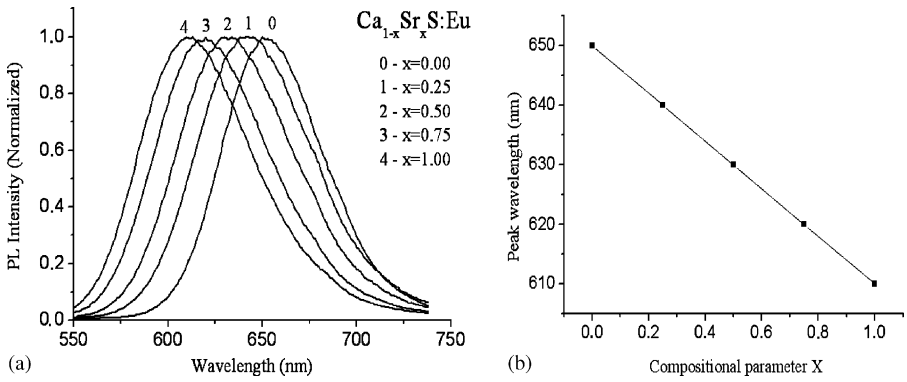

Fig. 2. The dependence of peak wavelength on the composition parameter x for $Ca_{1-x}Sr_xS:Eu^{2+}$ Excitation made by 460 nm light source.

compositional parameters (Fig. 2), a 3D diagram for multi-compound composition can be created (Fig. 3).

Similar linear dependences for other three-component compositions were obtained. Computer simulation for $(Ca_{1-x}Sr_x)(S_{1-y}Se_y):Eu^{2+}$ gives the plane surface for the peak wavelength versus compositional parameters (Fig. 3). Experimental data (black points) from different publications for CaS [11,12], SrS [13], CaSe [14] and SrSe [14] show very good agreement with our data and proposed model.

From this diagram it is evident that any peak shift from yellow to red color can be achieved in this system. Equation of the plane in space may be represented by

$$Z = Ax + By + C,$$

where Z means the peak wavelength, x and y are independent variable compositional parameters and A, B, C are coefficients, that can be determined from experimental data and boundary conditions (x,$y = 0$;1).

For our range:

$$0 \leqslant x \leqslant 1,$$

$$0 \leqslant y \leqslant 1$$

the peak position Z can be found as

$$Z = -40 \times -40y + 650.$$

Intersection of this plane with any Z = Const., gives a line, which projection determines the relation between compositional parameters x and y for every predetermined color. Using this equation, we find x and y data for different color ranges.

For red-emitting phosphor (650–600 nm):

$$0 \leqslant x + y < 1.25.$$

For orange-emitting phosphor (600–580 nm):

$$1.25 < x + y < 1.75.$$

For yellow-emitting phosphor (580–570 nm):

$$1.75 < x + y \leqslant 2.$$

To receive the phosphor with predicted properties, first we have to fix the desirable peak wavelength (Fig. 3). For

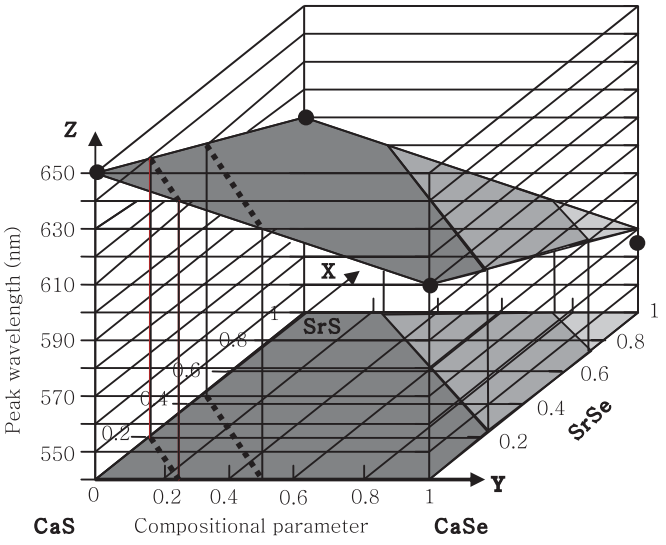

Fig. 3. Peak wavelength diagram for $(Ca_{1-x}Sr_x)(S_{1-y}Se_y):Eu^{2+}$.

example, for red-emitting phosphor with maximum emission at 630 nm we obtain from diagram $x+y = 0.5$. It means that if we want to substitute only Ca by Sr ($y = 0$, $x = 0.5$) the phosphor composition will be the next:

$$Ca_{0.5}Sr_{0.5}S : Eu^{2+}.$$

This phosphor was synthesized by above-mentioned solid-state reaction and the spectra are presented in Fig. 2a. The brightness of all our phosphors exceeds the commercial samples by about 20% (Fig. 4). Really, one can see the spectra shift from 650 nm ($CaS:Eu^{2+}$) spectrum 1 to 630 nm ($Ca_{0.5}Sr_{0.5}S:Eu^{2+}$) (Fig. 2a). Further substitution of Ca by Sr leads to subsequent spectra shift to 610 nm ($SrS:Eu^{2+}$). All these results are in good agreement with proposed diagram (Fig. 3).

As shown in Figs. 2 and 4, the emission spectra of phosphors as well as excitation, are very broad, this means the phosphors can be well excited by the visible light from 430 to 500 nm, fitting in with blue LED chip. The lowest excited state of $4f$ levels is located at about $28 \times 10^3\,cm^{-1}$ [18] and is higher than the $4f^6 5d^1$ level in most crystals, so

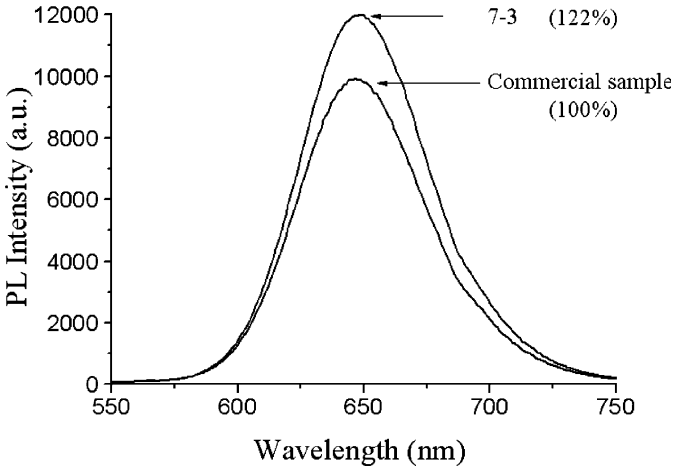

Fig. 4. Relative PL emission spectra of synthesized and commercial phosphors.

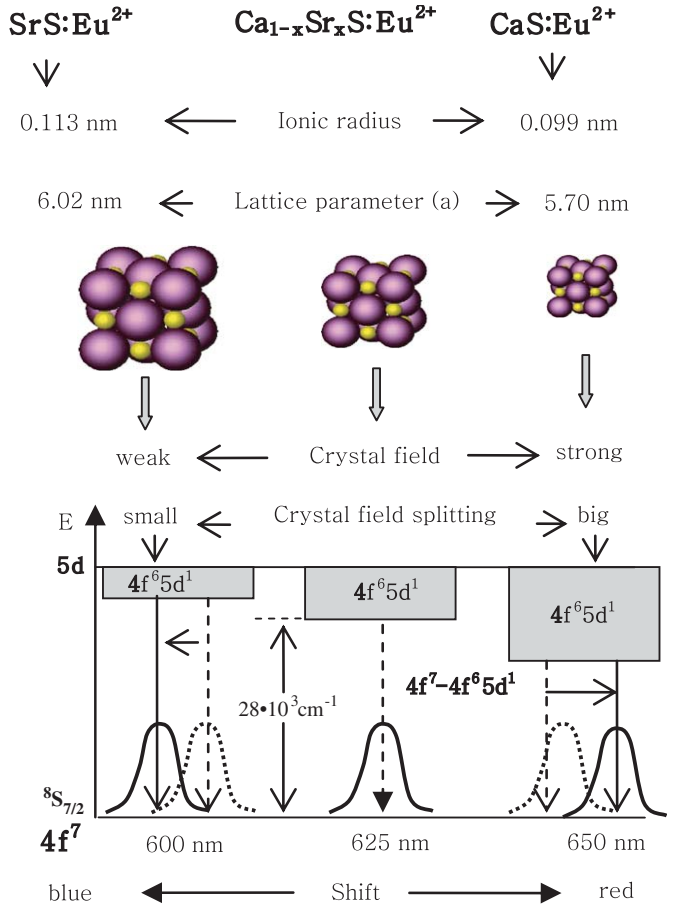

Fig. 5. Schematic illustration of crystal field splitting and spectra shift in $(Ca_{1-x},Sr_x)S:Eu^{2+}$ with a different Sr/Ca ratio.

that Eu^{2+} usually gives characteristic broadband emission due to transitions between the crystal field components of the $4f^6 5d^1$ excited state configuration and the $^8S_{7/2}$ ($4f^7$) ground state. The wavelength positions of the emission bands depend very much on hosts, changing from the near-UV to the red of the electromagnetic spectrum. This dependence is interpreted as the crystal-field splitting of the *5d* level, as shown schematically in Fig. 5.

With the increment of crystal-field strength, the emission bands shift to longer wavelength. As noted above, the $(Ca_{1-x},Sr_x)S:Eu^{2+}$ is a cubic rock-salt structure where Eu^{2+} is on Sr^{2+}/Ca^{2+} sites and is O_h symmetry and small, which result in the strong crystal field and lead to the red emission. In addition, as illustrated in Fig. 2, the emission of the phosphor shifts from 610 nm up to 650 nm by degrees with the Sr concentration (x) from 1 down to 0. Besides the dissimilarity in ionic radius between Sr^{2+} and Ca^{2+}, the energy gaps are 4.41 and 4.30 eV, respectively [19], therefore, the mixing of SrS and CaS makes for the change of the crystal field and energy gap, and accounts for the red shift of the emission wavelength. On this basis, one can vary the Sr/Ca ratio to obtain the desired wavelength.

4. Conclusions

As we gain a more detailed knowledge of the absolute placement of substitional ions within large band gap materials, we can better predict the behavior of these materials from different points of view including the consideration of the overall performance efficiency of luminescent materials.

The $(Ca_{1-x},Sr_x)S:Eu^{2+}$, $(Ca_{1-x},Sr_x)Se:Eu^{2+}$ as well as $(Ca_{1-x}Sr_x)(S_{1-y}Se_y):Eu^{2+}$ red-emitting phosphors were prepared by solid-state reaction at high temperatures in reductive atmosphere.

(1) These phosphors can be excited efficiently by visible light from 430 to 490 nm and emit red, orange and yellow light with broadband, which is in agreement with the blue LED chips.
(2) The luminescence originates from the doped Eu^{2+} that replaces the Sr/Ca sites in crystal and acts as the luminescence center.
(3) With the Sr/Ca ratio decreasing, the lattice parameters get lower, and the emission wavelength shows red shift. Suitable wavelength can be got by adjusting the Sr/Ca ratio.
(4) A mathematical peak wavelength diagram is in a good agreement with experimental data.

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