

Phosphors in phosphor-converted white light-emitting diodes: Recent advances in materials, techniques and properties

S. Ye, F. Xiao, Y.X. Pan, Y.Y. Ma, Q.Y. Zhang*

MOE Key Lab of Specially Functional Materials and Institute of Optical Communication Materials, South China University of Technology, Guangzhou 510641, PR China

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ABSTRACT

Phosphor-converted white light-emitting diodes (pc-WLEDs) are emerging as an indispensable solid-state light source for the next generation lighting industry and display systems due to their unique properties including but not limited to energy savings, environment-friendliness, small volume, and long persistence. Until now, major challenges in pc-WLEDs have been to achieve high luminous efficacy, high chromatic stability, brilliant color-rendering properties, and price competitiveness against fluorescent lamps, which rely critically on the phosphor properties. A comprehensive understanding of the nature and limitations of phosphors and the factors dominating the general trends in pc-WLEDs is of fundamental importance for advancing technological applications. This report aims to provide the most recent advances in the synthesis and application of phosphors for pc-WLEDs with emphasis specifically on: (a) principles to tune the excitation and emission spectra of phosphors: prediction according to crystal field theory, and structural chemistry characteristics (e.g. covalence of chemical bonds, electronegativity, and polarization effects of element); (b) pc-WLEDs with phosphors excited by blue-LED chips: phosphor characteristics, structure, and activated ions (i.e. Ce^{3+} and Eu^{2+}), including YAG:Ce, other garnets, non-garnets, sulfides, and (oxy)nitrides; (c) pc-WLEDs with phosphors excited by near ultraviolet LED chips: single-phased white-emitting phosphors (e.g. Eu^{2+} – Mn^{2+} activated phosphors), red-green-blue phosphors, energy transfer, and mechanisms involved; and (d) new clues for designing novel high-performance phosphors for pc-WLEDs based on available LED chips. Emphasis shall also be placed on the relationships among crystal structure, luminescence properties, and device performances. In addition, applications, challenges and future advances of pc-WLEDs will be discussed.

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* Corresponding author. Tel.: +86 20 87113681; fax: +86 20 87114204.

E-mail address: qyzhang@scut.edu.cn (Q.Y. Zhang).

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Nomenclature

A	acceptor
A.R.	analytical reagent
CCT	correlated color temperature
CIE	commission Internationale de l'Eclairage
CR	cross-relaxation
CRI or R_a	color rendering index
CTB	charge transfer band
CTS	charge transfer state
D	donor
$d-d$	dipole–dipole
$d-q$	dipole–quadrupole
$q-q$	quadrupole–quadrupole
λ_{ex}	excitation wavelength
λ_{em}	emission wavelength
η_T	energy transfer efficiency
ΔE	energy difference between different energy levels
EL	electroluminescence
ET	energy transfer
LE	luminous efficacy
LED	light-emitting diode
MPR	multiphonon relaxation
NUV	near ultraviolet
pc-WLEDs	phosphor-converted white light-emitting diodes
PAT	phonon-assisted transfer
PL	photoluminescence
PLE	photoluminescence excitation
QE	quantum efficiency
RE	rare-earth
Ref.	reference
RGB	red–green–blue
RT	room temperature
SEM	scanning electron microscopy
SSL	solid-state lighting
TM	transition metal
UV	ultraviolet
WLED	white light-emitting diode
W_{NR}	nonradiative transition rate
XRD	X-ray powder diffraction
YAG	yttrium aluminum garnet

1. Introduction

1.1. Overview

The increasing demand for fossil fuels and the environmental impact of their use are continuing to exert pressure on an already-stretched world energy infrastructure [1]. Conventional incandescent and fluorescent lamps rely on either heat or discharge of gases. Both phenomena are associated with large energy losses that occur because of the high temperatures and large Stokes shifts involved [2]. In 1996, a totally new lighting device was invented by Nichia Chemical Co. by means of a blue InGaN LED chip coated with yttrium aluminum garnet yellow phosphor ($Y_3Al_5O_{12}:Ce$, YAG:Ce) [3]. A schematic of this phosphor-converted white light-emitting diodes (pc-WLEDs) is shown in Fig. 1. When the chip is driven under certain current, blue light is emitted by the InGaN chip through electron–hole recombination in the p–n junctions. Some of the blue light from the LED excites the YAG:Ce phosphor to emit yellow light, and then the rest of the blue light is mixed with the yellow light to generate white light. This lighting style based on LED is the so-called solid-state lighting (SSL). Advantages of SSL are high luminous efficiency, energy savings, environment-friendliness, small volume, and long persistence [4–8]. Until now, the conventional white light sources have almost reached their physical limit of efficiency, as shown in Fig. 2, while white LEDs have not. For the conventional incandescent lamps and fluorescent lamps, a large amount of energy is consumed as heat radiation for

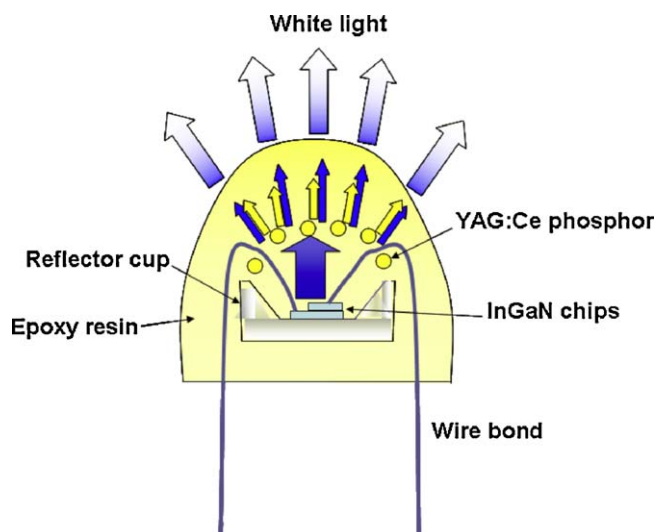


Fig. 1. Schematic structure of dichromatic pc-WLEDs.

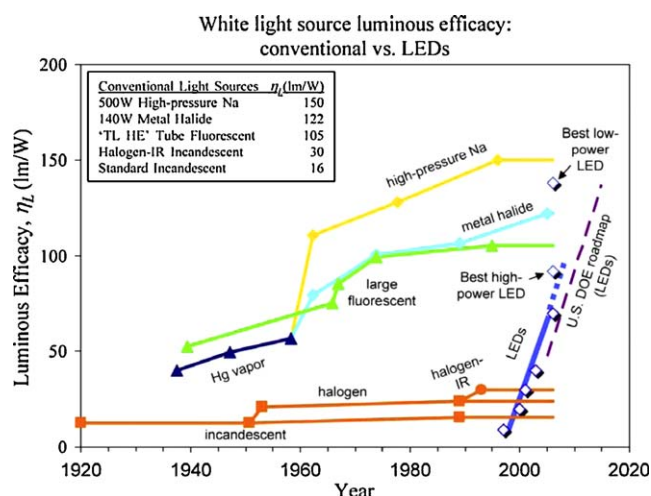


Fig. 2. Evolution of luminous efficacy performance of white light sources. Commercially available high-power LED performance is indicated by the points along the solid blue curve [7]. Reproduced from J. Display Technol. 3 (2007) 160. Copyright © 2007, IEEE.

high-temperature tungsten filament lamps and mercury vapor discharge lamps. The luminescence efficiency of semiconductor-based white LEDs can be greatly improved by reducing the nonradiative recombination of electron-hole pairs in the p-n junctions and designing a new structure to enhance external quantum efficiency. Based on the physical principles, the luminous

efficiency of white LEDs can approach 200 lm/W by the year of 2020 [6], which will be far greater than that of incandescent lamps and fluorescent lamps. It can be seen in Fig. 3 that the costs of white light generated by LEDs have been decreasing continually, which makes white LEDs more competitive for the future. It is believed that LED-based SSL is the next generation lighting source for common illumination [4–8].

Generally, there are three different approaches which can be used for generating white light based on LEDs as shown in Fig. 4: (1) by mixing reds, greens, and blues, i.e. red-green-blue (RGB) LEDs, (2) by using an ultraviolet (UV) LED to stimulate RGB phosphors, and (3) by using a blue-emitting diode that excites a yellow-emitting phosphor embedded in the epoxy dome; the combination of blue and yellow light makes a white-emitting LED. Today's commercial pc-WLEDs normally use a 450–470 nm blue GaN LED chip covered by a yellowish phosphor coating, which is usually made of YAG:Ce. However, pc-WLEDs made by means of blue-LED + YAG:Ce yellow phosphors suffer some weaknesses, such as poor color rendering index and low stability of color temperature [4,5]. Since the white light is generated by the combination of blue light emitted by an LED chip and yellow light emitted by YAG:Ce phosphors, deterioration of the chip or YAG:Ce phosphors would cause some significant color changes [4,5]. The instability of color temperature also exists for RGB LEDs as the degradation of different color LEDs or variations of driving current. Additionally, RGB LEDs require different driving currents for different color LEDs, complicating their fabrication [6]. White UV-LEDs fabricated by UV-LED chips coated with white light-emitting single-phased phosphors or RGB tri-color phosphors [5,10–13]

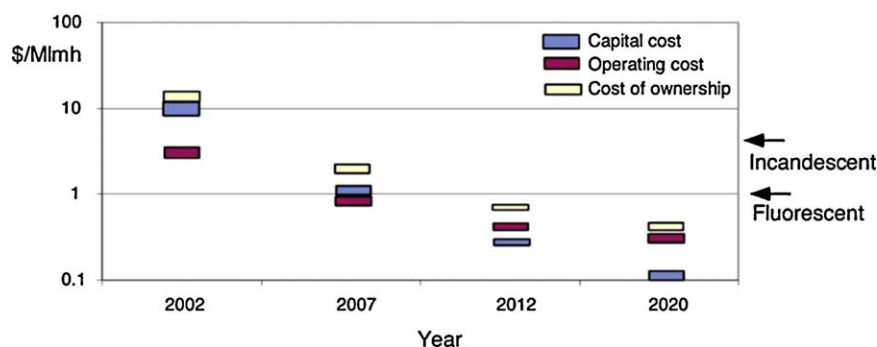


Fig. 3. Projected cost of light. Arrows show the present cost of ownership for incandescent and fluorescent lighting [6], data from [9]. Reproduced from Proc. IEEE 93 (2005) 1691. Copyright © 2005, IEEE.

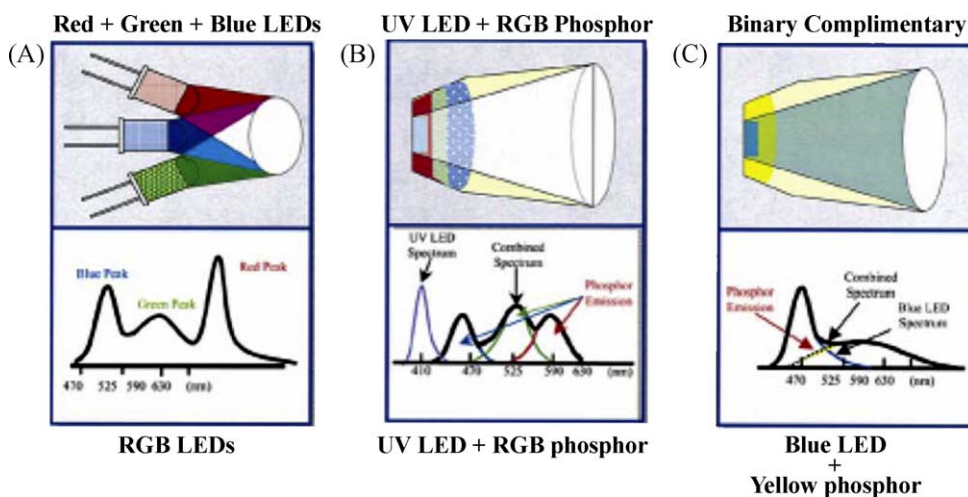


Fig. 4. Three methods of generating white light from LEDs: (a) red + green + blue-LEDs, (b) UV-LED + RGB phosphors, and (c) blue-LED + yellow phosphor [4]. Reproduced from IEEE J. Sel. Top. Quant. 8 (2002) 310. Copyright © 2002, IEEE.

Table 1
Comparison of white light based on the blue-LED+yellow phosphors and UV-LED+RGB phosphors.

LEDs	Advantages	Disadvantages
Blue-LED + yellow phosphors	Low cost, easy fabrication	Relatively low efficiency, low CRI, low chromatic stability under different driving currents
UV-LED + RGB phosphors	High efficiency, high CRI, high chromatic stability under different driving currents, tunable color temperature	Complex blending of different phosphors, lack of efficient red phosphor

might conquer the aforementioned pitfalls owing to the invisible emission of the LED chip. Despite the variation of driving current, white UV-LEDs are optically much more stable. It is considered that white UV-LEDs might be the direction of SSL development for their high efficiency and easy fabrication [5]. Table 1 summarizes the advantages and disadvantages of white light based on the blue-LED + yellow phosphors and UV-LED + RGB phosphors.

Fig. 5 depicts the bandgap of III–V semiconductors vs. lattice constant. The bandgaps of InN, GaN, AlN (bulk, at room temperature) are 2.4 eV (~520 nm), 3.4 eV (~362 nm), and 6.2 eV (~200 nm), respectively [14]. For the GaN-based UV-LED chips, the emitting efficiency declines dramatically when the emission wavelength moves to the short side, compared to the InGaN blue chip (~460 nm) [15–21]. Short wavelength emission of the chips requires more Al, which would cause many defects due to a mismatch of crystal lattice between the sapphire substrate and the nitride membrane. Difficulty would be encountered in fabrication when using other substrates like AlN [15–21]. Additionally, the short wavelength emission of the GaN-based chips leads to strong self-absorption of GaN. Accordingly, the UV emission with relatively high efficiency in a GaN-based system would probably be located at long wavelength (365–410 nm, NUV) [4–8,10].

On the other hand, phosphors have been considered as key and technologically important components of the functionality and success of many lighting and display systems over the past several

years. At present, rare-earth (RE)-based phosphors with efficiencies close to the theoretical maximum (100%) are employed in different fluorescent tubes, X-ray imaging, and color televisions. Such applications depend on the luminescent properties of RE ions, e.g. sharp lines, high efficiency, and high lumen equivalence [24,25]. However, a good phosphor for electronic or X-ray excitation is not necessarily a good choice for excitation by semiconductor LED chips. Most previously indentified phosphors for general illumination have been developed for Hg discharge lamps (fluorescent lamps), which are designed to fit the excitation of 254 nm (low-pressure Hg lamps) or 365 nm (high-pressure Hg lamps) UV light. By far, most of the commercial phosphors for lighting are oxide-based materials, and only a few of them can be excited efficiently by blue InGaN chip (λ_{ex} = 420–480 nm), such as YAG:Ce and other garnet phosphors [26]. Additionally, the temperature-quenching of YAG:Ce is a big challenge for white LED applications [2]. Accordingly, a new hot topic of nitride and oxynitride phosphors has recently attracted much attention [2,27,28]. Commercial phosphors for white UV-LED applications (λ_{ex} = 365–410 nm) are also scarce, especially red phosphors [29–37]. Much effort has been dedicated to the phosphors in pc-WLEDs, which could be excited efficiently by blue [2,26–28,38–42] or NUV lights [10–13,29–37,43–52].

RE ions and transition metal (TM) ions are the most frequently used phosphor activators [10–13,29–37]. The white LEDs require phosphors with efficient absorption bands in the blue region (λ_{ex} = 420–480 nm) or NUV region (λ_{ex} = 365–410 nm). Generally the $4f \rightarrow 5d$ transition of some RE ions or charge transfer state (CTS) of some transition metal ion-anions groups can meet the requirements [2,10–13,28,32–40,42]. The $d \rightarrow d$ transitions of TM ions are normally less efficient in NUV-blue region, due to the parity-forbidden nature of this kind of transition [32,33,36]. Thus, TM ions used as activators are normally accompanied by sensitizers. Owing to the exposure of the d orbital to the crystal coordination environment, the $4f \rightarrow 5d$ transition of RE ions is strongly affected by the nephelauxetic effect and crystal field splitting [53–57]. The nephelauxetic effect and crystal field splitting are primarily used to describe the $d \rightarrow d$ transition of TM ions. For RE ions, the nephelauxetic effect is linked to the

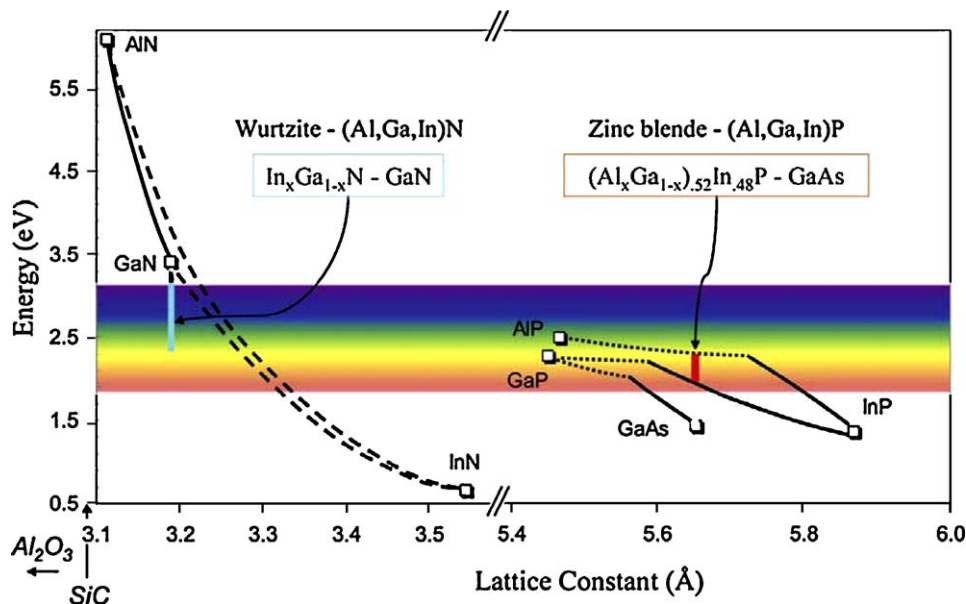


Fig. 5. Energy bandgap vs. lattice constant for III-nitride and III-phosphide semiconductor alloy systems employing Al, In, and Ga [22,23]. Solid lines indicate directbandgap alloys, dotted lines indicate indirectbandgap alloys, and dashed lines are estimates (due to relative uncertainty in bowing parameters for high InN-fraction alloys). The InGaN system is grown pseudomorphic to GaN, and strain and alloy miscibility issues have, to date, limited the useful emission wavelength range from UV (~365 nm) to deep green (~550 nm) [7]. Reproduced from J. Display Technol. 3 (2007) 160. Copyright © 2007, IEEE.

centroid shift, which is the shift of the average of the $5d$ levels relative to the free ion value. Crystal field splitting is defined as the energy difference between the maxima of the highest and the lowest broad vibronic $5d$ bands appearing in excitation or absorption spectra [55]. The nephelauxetic effect usually includes anion polarizability, electronegativity of ions, and covalency between cations and anions [53,54,56,57]. The crystal field splitting based on a point charge electrostatic model correlates to the crystalline environment, which involves the coordination number of RE ion polyhedra, the negative charge of the ligands, and the distance between RE ion and ligands [55]. The polarizability and electronegativity of ions also have strong effects on CTS of TM ion-anions groups [14,58]. All these effects offer ways to tune the properties of phosphors to fit different excitation wavelengths. Phosphors presented in this contribution will be discussed mainly according to these effects.

1.2. Challenge and objectives

An overwhelming contribution has been made to the development of phosphors in pc-WLEDs with the advent of science and technology, such as micro- and nano-solid material synthesis, functionalization and characterization of materials, as well as the emergence of novel luminescent materials. Major challenges in pc-WLEDs until now have been to achieve high luminous efficacy, high chromatic stability, brilliant color-rendering properties, and price competitiveness with fluorescent lamps, which rely critically on the phosphor properties. An intensive understanding of the nature and limitations of phosphors and the factors dominating the general trends in pc-WLEDs is essential for advancing technological applications.

The main objective of this contribution is to present the very recently-made advances in the synthesis and application of phosphors for pc-WLEDs with emphasis specifically on: (a) materials, techniques, and developments in the fields of pc-WLEDs and the mechanism involved, including phosphors excited by blue-LED chips and phosphors excited by NUV-LED chips; (b) principles to tune the excitation and emission spectra of phosphors: prediction according to crystal field theory and structural chemistry characteristics; and (c) new clues for designing novel high-performance phosphors for pc-WLEDs based on available LED chips. Emphasis shall also be placed on the relationships among crystal structure, luminescence properties, and device performances. In addition, applications, challenges, and future advances of pc-WLEDs will be discussed.

2. Fundamental aspects of phosphors-converted white LEDs

2.1. Basic concepts

2.1.1. Photoluminescence

Luminescence is defined as the emission of electromagnetic radiation in excess of thermal radiation [59]. Luminescence differs from incandescence, which is a process in which solids emit light by reason of their high temperatures [60]. Luminescence arises when atoms of a solid become energized in some way without appreciably heating the bulk material. These atoms then release the excess energy in the form of ultraviolet, visible, or infrared radiation [61]. This contribution will focus on the inorganic phosphors for white LED applications. Since these phosphors are excited by the radiative emission of LED chips, the luminescence of the phosphors is expressed as photoluminescence (PL) [62]. Herein, phosphors generally consist of a host and an activator (also called a luminescent center).

The PL in a material usually involves the following processes [61]:

- (i) excitation of the activator to a higher energy state (10^{-11} s);
- (ii) relaxation of the activator ion to the lowest energy level of the excited state (10^{-8} s); and
- (iii) emission of a lower-energy photon as the activator ion returns from its excited state to the ground state (10^{-9} – 10 s).

The configurational coordinate diagram is usually used to describe the PL mechanism of an activator [14,61]. As shown in Fig. 6, the total energy E of the activator is plotted as a function of r , the distance between metal cations and anions in the lattice. The horizontal dashed lines in ground state and excited state curves denote the vibrational states. r_0 and r_1 represent the equilibrium distances of the ground-state activator and the excited state activator, respectively. When the activator absorbs some radiation light, an expansion of the lattice occurs in the vicinity of the activator ion and the activator is raised to the excited state [63]. The excitation (EX) and emission (EM) processes are illustrated by vertical arrows, showing that the nucleus of the activator stays at approximately the same position during these processes. This is the so-called Franck–Condon principle, which is based on the fact that an atomic nucleus is 10^3 – 10^5 times heavier than an electron, and an electron moves much faster than a nucleus [14]. The energy difference between EX and EM is known as the Stokes shift. When the temperature of the phosphor exceeds some certain value, the vibrational energy makes the excited activator reach the Q point of the excited state curve and then the activator returns to ground state without radiation, which is called temperature-quenching.

The principal localized luminescent centers can be classified by their electronic transitions as follows (below, an arrow to the right indicates optical absorption and to the left, emission) [14]:

- (i) $1s \rightleftharpoons 2p$; an example is an F center.
- (ii) $ns^2 \rightleftharpoons nsnp$; this group includes Ga^+ , In^+ , Tl^+ , Ge^{2+} , Sn^{2+} , Pb^{2+} , As^{3+} , Sb^{3+} , Bi^{3+} , Cu^- , Ag^- , Au^- , etc.
- (iii) $nd^{10} \rightleftharpoons nd^9(n+1)s$; (it is $3d^{10} \rightleftharpoons 3d^94s$ in the book); examples are Cu^+ , Ag^+ and Au^+ . Acceptors in IIB–VIA (It is VIB in the book) compounds are not included in this group.
- (iv) $3d^n \rightleftharpoons 3d^n$, $4d^n \rightleftharpoons 4d^n$; the first and second TM ions form this group.

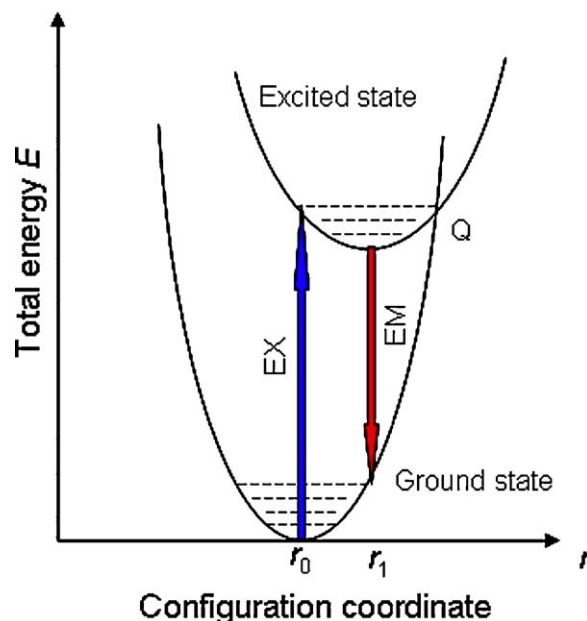


Fig. 6. A schematic illustration of a configurational coordinate model. r denotes the distance between metal cations and anions in the lattice. The two curves represent ground state and excited state of the activator, the vertical blue and red lines indicate the excitation and emission process, respectively.

- (v) $4f^n \Leftrightarrow 4f^n$, $5f^n \Leftrightarrow 5f^n$. RE and actinide ions.
- (vi) $4f^n \Leftrightarrow 4f^{n-1}5d$. Examples are Ce^{3+} , Sm^{2+} , Eu^{2+} , Tm^{2+} and Yb^{2+} .
- (vii) A charge transfer transition or a transition between an anion p electron and an empty cation orbital. Examples are intramolecular transitions in complexes such as VO_4^{3-} , MoO_4^{2-} and WO_4^{2-} . Transition from anion p orbitals to Eu^{3+} or TM ions are observed only as absorption processes [14].

RE and TM ions are most frequently used in phosphors. The $4f$ – $4f$ transitions of RE ions are line-shaped, and the energies of the levels involved in transition are well-defined and changeless in different hosts, due to the shielding of $4f$ orbitals by the filled $5s^2 5p^6$ sub-shells [64]. The selection rules of parity-forbidden $4f$ – $4f$ transitions are derived under some hypotheses which are not always completely fulfilled in reality. For instance, the $4f$ wavefunctions are not totally pure and the symmetries of crystal lattice sites in which RE ions stay have some effects on the parity of $4f$ wavefunctions, while the $4f$ – $5d$ transition of RE ions are parity-allowed and can be efficient [64]. The d – d parity-forbidden transitions of TM ions are also strongly influenced by the host lattice phonon, resulting in parity-permitted transitions. Both the $4f$ – $5d$ transitions of RE ions and the d – d transitions of TM ions are broadband-shaped and can be tuned by variation of coordination environment.

2.1.2. Energy transfer

ET between ions finds wide application in sensitizing solid-state lasers and infrared quantum counters, as well as infrared to visible converters [65,66]. ET between ions also plays an important role in pc-WLEDs. In this section, the basic processes of ET and their applications to pc-WLEDs are presented. Before going on with this section, it is better to introduce some terms which are frequently used in this section, such as donor/acceptor and sensitizer/activator. A donor is some species which gives out protons, electrons or energy, etc. while, an acceptor is some species that accepts protons, electrons or energy given by a donor. In terms of phosphors, ET is a very common phenomenon. Thus, the donor is the ion or group which absorbs energy in the form of light or exciton, etc. Then the donor transfers the energy to another ion or group called the acceptor, which could emit light and terminate the whole process. The ions or groups as luminescent centers in phosphors are also called activators. When ET occurs between activators, those who give out energy are sensitizers. In the ET process, a sensitizer sensitizes the activator, and the activator

emits aimed light. Hence, donor/acceptor and sensitizer/activator are almost the same for phosphors with impurity luminescent centers. Aside from ET by movement of charge transportation, there remain four basic mechanisms involved in ET processes between ions: (a) resonant radiative transfer through emission of sensitizer and reabsorption by activator; (b) nonradiative transfer associated with resonance between sensitizer and activator; (c) multiphonon-assisted ET; and (d) cross-relaxation (CR) between two identical ions. A schematic diagram to illuminate the different ET processes between two ions is presented in Fig. 7 [67]. The efficiency of radiative transfer (Fig. 7a) depends on how efficiently the activator fluorescence is excited by the sensitizer emission. It requires a significant spectral overlap between the emission spectrum of the sensitizer and the absorption spectrum of the activator. If radiative ET takes place predominantly, then the decay time of sensitizer fluorescence does not vary with the activator concentration. In contrast to the radiative ET (Fig. 7b), the nonradiative ET accompanies the significant decrease in decay time of sensitizer fluorescence with the activator concentration. Because of the requirement for a considerable absorption capability of activator, the radiative ET can usually be neglected relative to nonradiative ET in most inorganic systems. Only in a few cases, the requirements for radiative ET are satisfied [68]. ET may occur if the energy difference between the ground- and excited state of the donor (or sensitizer) is equal to that of the acceptor (or activator) and there exists a suitable interaction between systems [68]. Non-resonant ET can also take place with the assistance of a phonon unless the difference between the ground- and excited state of donor and acceptor is large.

The mechanism involved in this review is mostly resonant energy transfer. Sketches of the two types of interaction for resonant energy transfer are depicted in Fig. 8. For the electrostatic interaction, it appears to be multipole interaction, which can be categorized as dipole–dipole (d – d) interaction, dipole–quadrupole (d – q) interaction, quadrupole–quadrupole (q – q) interaction, etc. according to the transition characteristic of donor (D) and acceptor (A). The transfer probability, P_{DA} , between D and A could be expressed by the following formula [14]:

$$P_{DA} = \frac{2\pi}{\hbar} |\langle D^*, A | H_{DA} | D, A^* \rangle|^2 \int g_D(E) g_A(E) dE \quad (1)$$

where $\langle D^*, A |$ and $| D, A^* \rangle$ represent initial state and final state, respectively; H_{DA} is the Hamiltonian of interaction and $\hbar$ is Planck constant; $\int g_D(E) g_A(E) dE$ denotes the integral of spectral overlap

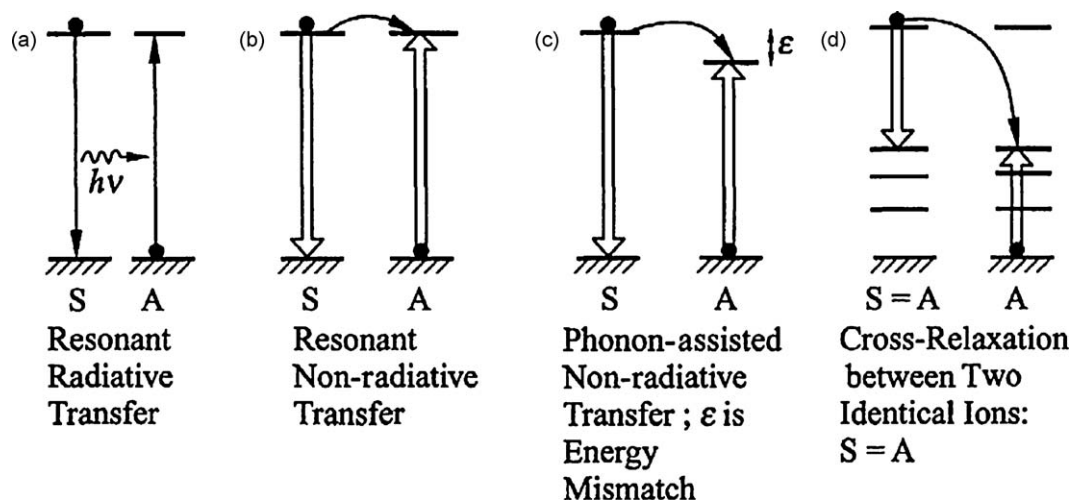


Fig. 7. A schematic diagram to illuminate the different ET processes between two ions: (a) resonant radiative transfer through emission of sensitizer (S) and reabsorption by activator (A); (b) non-radiative transfer associated with resonance between sensitizer and activator; (c) multiphonon-assisted ET; and (d) CR between two identical ions [67]. Reproduced from *Spectroscopic Properties of Rare Earths in Optical Materials*, 2005, Copyright © 2005, Springer.

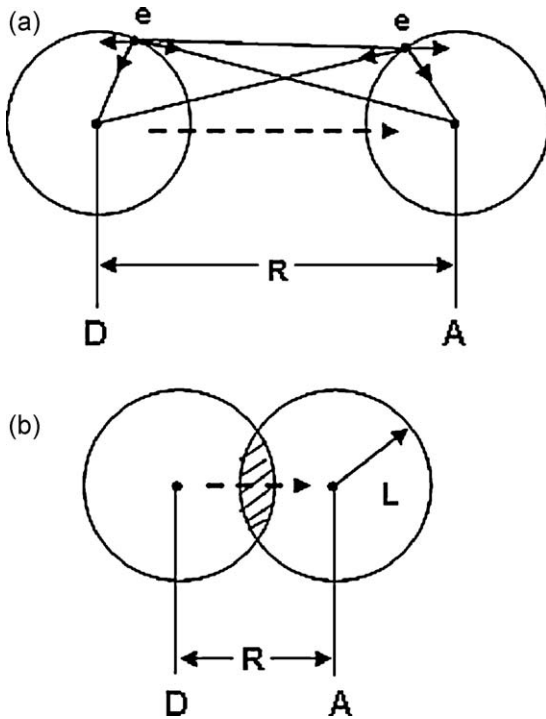


Fig. 8. Sketches of (a) electrostatic interaction; (b) quantum mechanical exchange interaction, hatching represents the overlap of wavefunction between D and A. R , e , L denote distance between D and A, electron and effective Bohr radii, respectively [14]. Reproduced from *Phosphor handbook*, 1999, Copyright © 1999, CRC press.

between D and A. For d - d , d - q and q - q interactions, transfer probability is inversely proportional to R^6 , R^8 , and R^{10} , respectively.

When D and A are close enough and their wavefunctions are overlapped, the ET mechanism from D to A can be exchange interaction. The transfer probability $P_{\text{ex}}(R)$ can be expressed by [14]:

$$P_{\text{ex}}(R) = \frac{2\pi}{h} K^2 \exp\left(-\frac{2R}{L}\right) \int F_D(E) F_A(E) dE \quad (2)$$

in which K^2 is constant; R is the distance between D and A; L denotes the average radius of excited state D and ground-state A; and the integrated item represents spectral overlap.

The ET mechanisms in phosphors are generally the result of many competitive interactions, which is dominant depends on the characteristic transition of D and A, and the distance between D and A.

If two ions have different excited states, the probability for ET should drop to zero, where the overlap integral $\int g_D(E) g_A(E) dE$ vanishes [67], as shown in Fig. 7c. However, it is experimentally found that ET could take place without phonon-broadened electronic overlap, which suggests that overall energy conservation is maintained by production or annihilation of phonons with energies approaching $k\Theta_d$, where Θ_d is the Debye temperature of the host matrix [69]. For small energy mismatch ($\approx 100 \text{ cm}^{-1}$), ET assisted by one or two phonons can take place [70]. However, in ET between RE ions, energy mismatches as high as several thousand reciprocal centimeters are encountered. This is much higher than the Debye cut off frequency found in normally encountered hosts, so that multiphonon phenomena must be considered. This was done by Miyakawa and Dexter [71,72]. In their theoretical analysis of multiphonon processes, Miyakawa and Dexter derived a comparative relaxation analogue of the multiphonon gap dependence. According to their theory, the probability of phonon-assisted transfer (PAT) is expressed by:

$$W_{\text{PAT}}(\Delta E) = W_{\text{PAT}}(0) e^{-\beta \Delta E} \quad (3)$$

where ΔE is the energy gap between the electronic levels of donor and acceptor ions and β is a parameter determined by the strength of electron-lattice coupling as well as by the nature of the phonon involved. The above equation has the same form as that for the energy gap dependence of the multiphonon relaxation (MPR) rate, which is also given by the Miyakawa–Dexter theory as:

$$W_{\text{MPR}}(\Delta E) = W_{\text{MPR}}(0) e^{-\beta \Delta E} \quad (4)$$

It is further indicated that the parameter α is given by:

$$\alpha = \frac{1}{h\omega} \left[\ln \left\{ \frac{N}{g(n+1)} \right\} - 1 \right] \quad (5)$$

where α and β are connected with each other as: $\beta = \alpha - \gamma$, and $\gamma = (1/h\omega) \ln(1 + g_S/g_A)$, where g is the electron-lattice coupling constant, suffixes S and A are sensitizer and activator ions respectively, n is the number of phonons excited at the temperature of the system, $h\omega$ is the phonon energy which contributes dominantly to these multiphonon processes, and N is the number of phonons emitted in the processes, namely, $N = \Delta E/h\omega$. Non-resonant phonon-assisted ET between various trivalent RE ions in yttrium oxide crystals was thoroughly studied by Yamada et al. [73]. In their experiments the energy gap between the sensitizer and activator systems varied in a wide range of energies up to 4000 cm^{-1} . The probability of phonon-assisted ET was observed to obtain the exponential dependence on energy gap predicted by the Miyakawa–Dexter theory [71,72]. It was revealed that the phonons of about 400 cm^{-1} , which produce the highest intensity in the vibronic side bands of yttrium oxide, contribute dominantly to the phonon-assisted process [72].

Cross-relaxation (CR) terminology usually refers to all types of downconversion ET between identical ions. In such a case the same kind of ion is both a sensitizer and an activator. As shown in Fig. 7d, CR may give rise to the diffusion process already considered between sensitizers when the levels involved are identical or to self-quenching when they are different. In the first case there is no loss of energy, whereas in the second there is a loss or a change in the energy of the emitted photons [67].

2.1.3. CIE chromaticity coordinates and color temperature

To characterize and express “color”, some terms are used frequently. The Commission Internationale de l’Eclairage (CIE) system is the most common method to describe the composition of any color in terms of three primaries, as shown in Fig. 9 [74,75]. Artificial “colors”, denoted by X, Y, Z , also called tristimulus values, can be added to produce real spectral colors. By a piece of mathematic legerdemain, it is necessary only to quote the quantity of two of the reference stimuli to define a color since the three quantities (x, y, z) are made always to sum to 1 [76]. The x, y, z , i.e. the ratios of X, Y, Z of the light to the sum of the three tristimulus values, are the so-called chromaticity coordinates [77]. (x, y) is usually used to represent the color.

Color temperature (Kelvin) is the absolute temperature at which a blackbody radiator must be operated to have a chromaticity equal to that of the light source [77]. The light of an incandescent bulb is thermal radiation and the bulb is very close to an ideal black-body radiator, so its color temperature is the temperature of the filament. Many other light sources, such as fluorescent lamps, emit light by ways other than thermal radiation. Color temperature values associated with light sources other than incandescent lamps are correlated color temperature (CCT) and not true color temperatures. Correlated color temperature is the temperature of a blackbody whose chromaticity most nearly resembles that of a light source [77]. Therefore, the color temperature values of pc-WLEDs in this review all refer to the correlated color temperature. Low color temperature implies

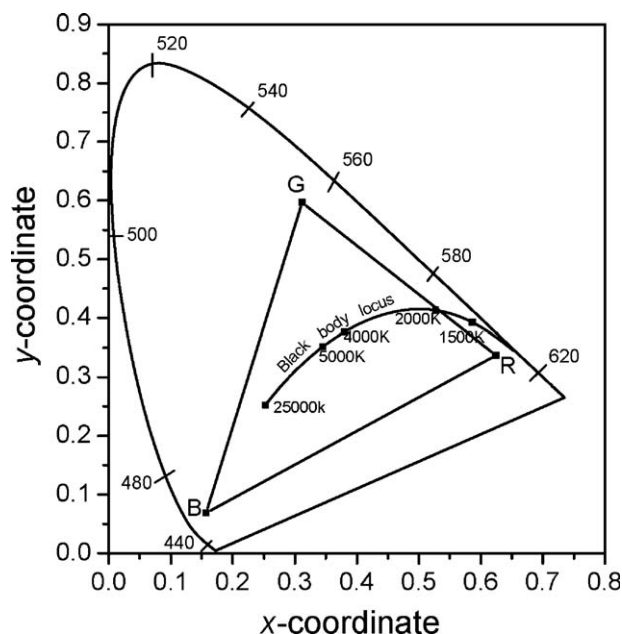


Fig. 9. CIE chromaticity coordinates and CCT (R, G, B: CRTs coordinates).

warmer (more yellow-red) light, while high color temperature appears to be a colder (more blue) light. Daylight has a rather low color temperature near dawn, and a higher one during the day. It correlates with human feelings. Therefore it can be useful to install an electrical lighting system that emits warm or cool color light when needed. Lamps for general-purpose illumination are designed to fall on or in the proximity of the blackbody locus as shown in Fig. 9.

2.1.4. CRI and luminous efficacy

Color rendering index is a unitless index, abbreviated variously as CRI or R_a . CRI is a measure of the degree to which the perceived colors of objects illuminated by the source conform to those of the same objects illuminated by a reference source for specified conditions [77]. The introduction of this parameter is based on the fact that objects may look quite different in color under lamps which look quite alike in succession but are different in spectral distribution. When CRI is calculated, it can be rated on a scale from 0 to 100. A CRI of 100 would represent that all color samples illuminated by a light source in question would appear to have the same color as those same samples illuminated by a reference source.

Luminous efficacy is a figure of merit for light sources. The luminous efficacy of a light source is defined as the ratio of the total luminous flux (lumens) to the power (watts or equivalent) [77]. Depending on context, the power can be either the radiant flux of the source's output, or the total electric power consumed by the

source. The lumen is defined as $1/683$ W of monochromatic green light at a frequency of 540×10^{12} Hz (corresponding to a wavelength of about 555 nm where the human eye is most sensitive). This means that the theoretically attainable maximum value assuming complete conversion of energy at 555 nm would be 683 lm/W. The luminous efficacies that can actually be attained vary depending on the lamps, but always remain far below this ideal value.

The luminous efficacy is always in contradiction with CRI, because a high CRI value requires proper spectral dispersion over all the visible range, which would make the luminous efficacy far below 683 lm/W. Thus, balanced values of these two parameters are adopted for different lighting occasions.

2.2. Experimental description: materials synthesis and fabrication

It is well known that materials' performances are closely related to the ways that they are processed [78]. The synthesis method of phosphors has played a significant role in determining the microstructure, luminescence properties, and quantum efficiency of phosphors. Phosphors were synthesized conventionally via a solid-state reaction process, using powdered raw materials as the starting materials. Due to their relatively rough grains, these phosphors require relatively high sintering temperature to obtain phosphors with designed compositions and desired performances. For non-oxides phosphors, they are very likely to undergo changes in their properties during the sintering at high temperatures, due to the high volatility and unstable chemical properties. To reduce the sintering temperature, it is necessary to use powders of phosphor compounds in a very small grain size and a narrow size distribution. For this purpose, submicron or even nanosized products have been synthesized by various wet-chemistry methods over the past several years, including hydrothermal synthesis, chemical co-precipitation, sol-gel process, combustion synthesis, etc. Table 2 gives a comparison of synthesis methods in terms of the particle sizes, required temperatures, cost, and limitations. Although significant progress has been achieved, there are problems, for example, the sol-gel process uses metal alkoxides as the starting materials normally, which are very expensive and extremely sensitive to environmental conditions such as moisture, light, and heat. Moisture sensitivity makes it necessary to conduct the experiment in dry boxes or clean rooms. Co-precipitation processes involve repeated washing to eliminate the anions coming from the precursor salts used, making the process complicated and very time-consuming. Furthermore, it is difficult to produce large batches by using most of the wet-chemical solution processing routes. Therefore, exploring alternative methods for the preparation of phosphors is still of technological as well as scientific significance.

2.2.1. Solid-state reaction

The solid-solid reaction, which occurs between powders in the solid state, has been used partly to synthesize inorganic materials

Table 2
Comparison of synthesis methods in terms of the particle sizes, morphology control, required temperatures, cost and limitations.

Synthesis methods	Particle size	Morphology control	Homogeneity of composition	Required temperatures	Cost	Limitations
Solid-solid reaction	Micrometer-scale	Bad	Bad	High	Low	No
Hydrothermal synthesis	Nanometer- to micrometer-scale	Good	Good	Low	Medium	Soluble raw materials
Sol-gel synthesis	Nanometer- to micrometer-scale	Medium-good	Good	Medium	High	Soluble raw materials organometallic compounds
Chemical co-precipitation	Nanometer- to micrometer-scale	Medium	Medium	Medium	Medium	Soluble raw materials
Combustion synthesis	Nanometer- to micrometer-scale	Medium	medium-good	Medium	Medium	Soluble raw materials
Spray pyrolysis	Nanometer- to micrometer-scale	Good	Medium-good	Medium	Medium	Soluble raw materials

because of the facile operation. Up to now, this method has been the most widely and intensively used approach for the preparation of phosphors including oxides, (oxy)nitrides, and fluorides because it is comparatively simple and very suitable for mass production. Because of the refractory nature of alumina and RE oxides, conventional solid–solid reaction synthesis of oxide-based phosphors like YAG requires temperature higher than 1000 °C. The solid-state reaction is controlled by atom diffusion between different raw materials. Hence, repeated grinding and repeated heating are required. Furthermore, a controlled atmosphere is necessary to master the valence of the activator and the stoichiometry of the host lattice. The synthesis of some phosphors, such as (oxy)nitride phosphors, needs additional high pressure. The particle size of the phosphor prepared by this method is relatively large and less controllable.

There are several limitations in the synthesis of LED phosphors by a conventional solid-state method. Firstly, this process often results in poor homogeneity and requires high calcination temperature. Secondly, the grain size of phosphor powders prepared by this method is several tens of micrometers. Phosphors of small particles could be obtained by grinding the larger phosphor particles. Furthermore, preparation of a single phase compound is somewhat difficult by the conventional solid-state method. This process easily introduces additional impurities and defects which would greatly reduce luminous efficacy [24].

2.2.2. Solution-based chemical synthesis

Solution-based chemical synthesis, namely wet-chemical methods, are defined as techniques which do not comprise of the normal mixing, calcinations, and grinding operations [79,80]. In fact, solution-based chemical synthesis such as hydrothermal, sol–gel, chemical co-precipitation, and combustion have received considerable attention since they offer the possibilities for controlling homogeneity, purity of phase, size distribution, surface area, and microstructural uniformity of the phosphors. Hydrothermal and sol–gel methods have been successfully employed to synthesize various phosphors.

Hydrothermal synthesis: hydrothermal synthesis refers to the preparation by chemical reaction of a substance in a sealed heated solution above ambient temperature and pressure. The hydrothermal method is a promising synthetic route which can be better-controlled from the molecular precursor to the reaction parameters, such as the reaction time and temperature, to give highly pure and homogeneous products. The technique allows low reaction temperature, and controllable size, phase, and morphology of the products [81–86]. Recently, efforts have been made to develop non-oxide-based phosphors through hydrothermal synthesis [87,88]. These experimental results have shown that the critical factors for the pure products are dependent on the pH value, the initial composition, and the reaction temperature, while a controlled atmosphere is not necessarily required [88].

Sol–gel synthesis: the beginning of the sol–gel methods dates back to as early as 1846 when Ebelenen discovered the formation of SiO₂ gel by hydrolyzing Si(OEt)₄. Only in the 1930 s did this method begin its further development. The basic processing steps of this method can be summarized as follows: solution → hydrolysis → reactive monomer → condensation → sol gelation → gel → further heat treatment. Based on this synthetic route, variations of precursors, solvents, ligands, different addition sequences of compounds, and further treatment as well as other changes in sol–gel methods have been reported and widely applied in the preparation of, e.g. glasses, ceramics, inorganic fillers, and coatings. An intense level of research activity has provided a special focus on the development of luminescent materials via the sol–gel method in the past years [89–95].

Chemical co-precipitation: chemical co-precipitation has also been used to fabricate oxide-based and fluoride-based phosphors [24,85,96]. All the raw materials can be dissolved in solutions and all the cations are co-precipitated by adding some certain reagent. The precipitates are separated, heat-treated to decompose the precursor and finally annealed to crystallize the powder. Co-precipitation synthesis may be regarded as an attractive method for the preparation of complex fluorides, because it does not require expensive high-purity RE fluorides as starting materials, and results in smaller grains and more homogeneous distribution of dopant ion. However, co-precipitation processes involve repeated washing to eliminate the anions coming from the precursor salts used, making the process complicated and very time-consuming. And calcination is usually required to get fine crystalline phosphors.

Combustion synthesis: solution combustion synthesis is another wet-chemical method, which has been proved to be an excellent technique for preparing several grams micro/nanocrystalline phosphors due to its short processing time, low processing temperature, low cost, and high yield, as well as good ability to achieve high purity in making single or multiphase complex oxide powders at the as-synthesized state [97–100]. This technique is based on exothermic redox reactions that undergo self-sustaining combustion. Mixtures of oxidizer (usually metal nitrides) and reducer (e.g. urea, citric acid or glycine as fuel) undergo spontaneous combustion under heating, and the chemical energy from the exothermic reaction heats the precursor mixture to high temperatures. Such a high temperature leads to formation and crystallization of phosphor materials. In comparison with other methods, the products obtained by the combustion synthesis method are generally more homogeneous, have less impurity, and have higher surface areas than powders prepared by conventional methods. Until now, this technique has been employed to produce a variety of materials such as oxides, borates, silicates, and aluminates [97,101–106].

Spray pyrolysis: spray pyrolysis is a powerful technique to synthesize a wide variety of high-purity and homogeneous ceramic powders. The basic principle of this method is that when a droplet of the spray solution reaches the hot substrate, fine powders would be deposited due to the pyrolytic decomposition of the solution [107]. The morphology of the particles produced by spray pyrolysis can be controlled to some degree by the choice of precursors, concentration, droplet size, and the residence time in the furnace. Oxide powders with homogeneous particle size less than 100 nm may be produced by this method, which allows for continuous operation and offers opportunity to tailor materials on a nano-scale. For instance, well-dispersed commonly used LED yellow phosphors YAG:Ce can be synthesized by this method [108,109].

3. Phosphors excited by blue-LED chips

3.1. Garnet phosphors: materials, technique and properties

3.1.1. Crystal structure of YAG

YAG, which is one of the garnet family compounds, is a well-known commercial yellow phosphor host for pc-WLEDs. The garnets usually have a general formula of [A]₃{B}₂(C)₃O₁₂, where [], { }, and () denote dodecahedral, octahedral, and tetrahedral coordination, respectively. YAG has a cubic structure with Ia-3d symmetry [110]. Fig. 10 shows the crystal structure of YAG, where Y³⁺ is coordinated with eight oxygen ions, some Al³⁺ are six-fold coordinated and others are four-fold coordinated. Each AlO₆ octahedron is connected to six AlO₄ tetrahedrons, and each AlO₄ tetrahedron is connected to four AlO₆ octahedrons by sharing the corners. Y³⁺ locates at the space inside the AlO_x framework.

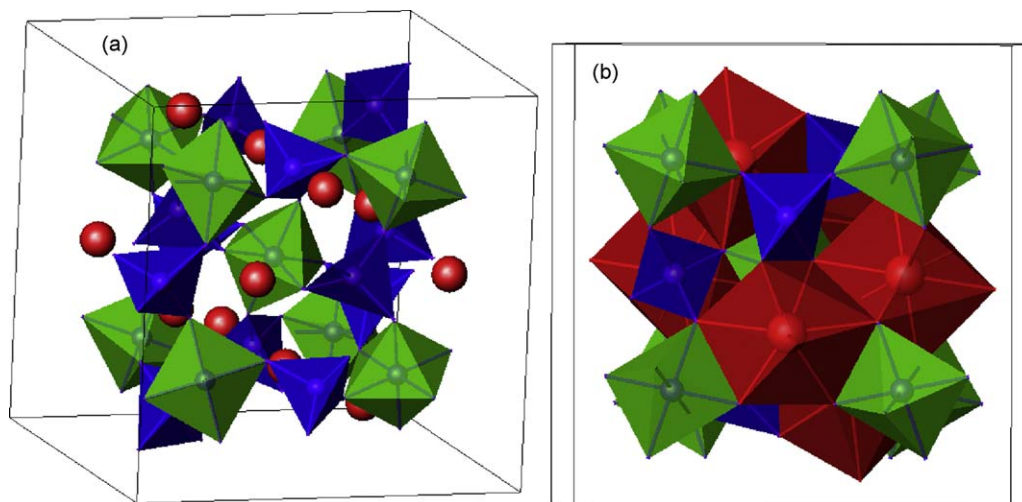


Fig. 10. Crystal structure of YAG. Red, green, blue polyhedrons represent YO₆ dodecahedron, AlO₆ octahedron, and AlO₄ tetrahedron, respectively. (a) shows the corner sharing between AlO₆ and AlO₄; (b) shows the edge sharing among YO₆, AlO₆ and AlO₄ (data quoted from ICSD 280104).

3.1.2. Composition dependent structure and properties of YAG:Ce

In 1967, Blasse et al. made a systematic spectroscopic investigation on YAG:Ce [111]. They found that the YAG:Ce³⁺ phosphor had special long wavelength of the excitation (~460 nm) and emission (~530 nm) bands [53], ascribed to the strong crystal field splitting of the 5d energy level of Ce³⁺ [111]. Recently, Wu et al. summarized the structure–property correlations in Ce-doped garnet phosphors [26]. They gave a sketch of the 4f5d energy level of the Ce³⁺ under the cubic crystal field (yttrium site), as shown in Fig. 11. The strong crystal field of the garnet structure lowered the

lowest 5d orbital energy. It is of great significance to tune the excitation and emission bands of YAG:Ce to fit the different wavelength excitation of blue InGaN chips or improve CRI due to the lack of a red component [6,26]. Previously, an empirical rule was that with increasing the radii of the ions on the dodecahedron site or decreasing the radii of the ions on the octahedron site, the emission of Ce³⁺ in garnets shifts to a longer wavelength [112]. Wu et al. investigated the structure–property correlations from another point of view, the emission of Ce³⁺ as a function of the distortion around RE ions [26]. The distortion of cubic symmetry at the RE ion site can be represented by a ratio of the O–O bond distances d_{88} and d_{81} (i.e. d_{88}/d_{81}), where d_{88} denotes the O–O bond distance that is shared with an adjacent dodecahedron and d_{81} denotes the O–O bond distance shared with an adjacent tetrahedron, as shown in Figs. 12 and 10(b). Fig. 13 shows the excitation and emission maxima of Ce³⁺-doped Y₃Al_{5-x}Ga_xO₁₂ and

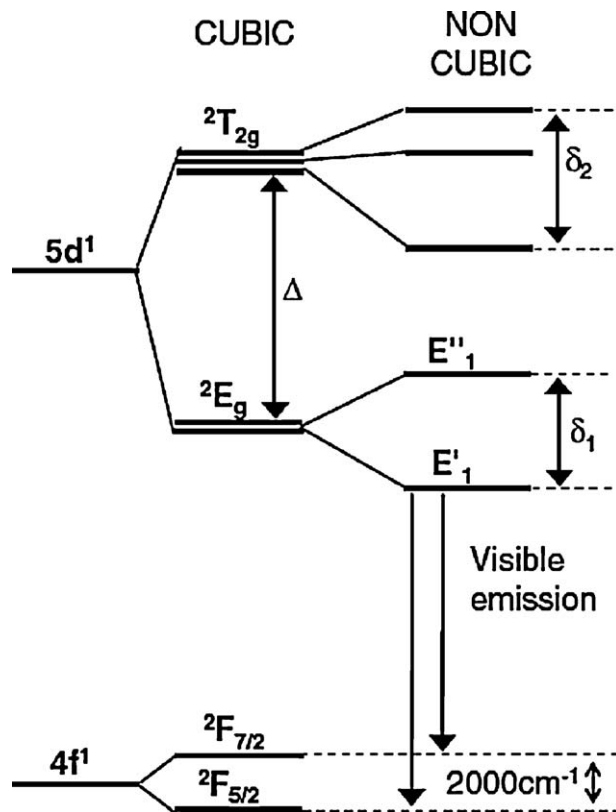


Fig. 11. Energy level diagram showing the lowest energy ground-state components and the first excited 5d states of Ce³⁺ in garnets. The cubic crystal field splitting is indicated by Δ and noncubic splitting by δ [26]. Reproduced from Chem. Phys. Lett. 441 (2007) 250. Copyright © 2007, Elsevier B.V.

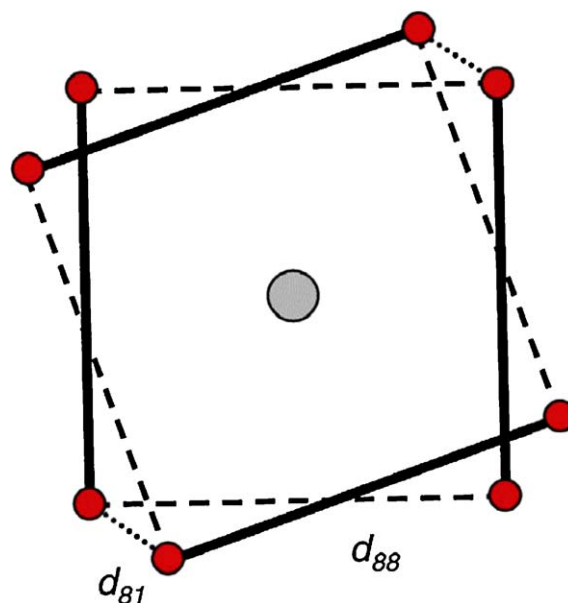


Fig. 12. Schematic representing the eight-fold cubic coordination of Ln³⁺ in garnets. Oxygen atoms are located at the corners and the Ln³⁺ in the center of the distorted cube. Solid lines indicate shared edges with other Ln–O dodecahedra, dashed lines indicate shared edges with M–O octahedra and dotted lines indicate shared edges with M–O tetrahedra [26,113]. Reproduced from Chem. Phys. Lett. 441 (2007) 250. Copyright © 2007, Elsevier B.V.

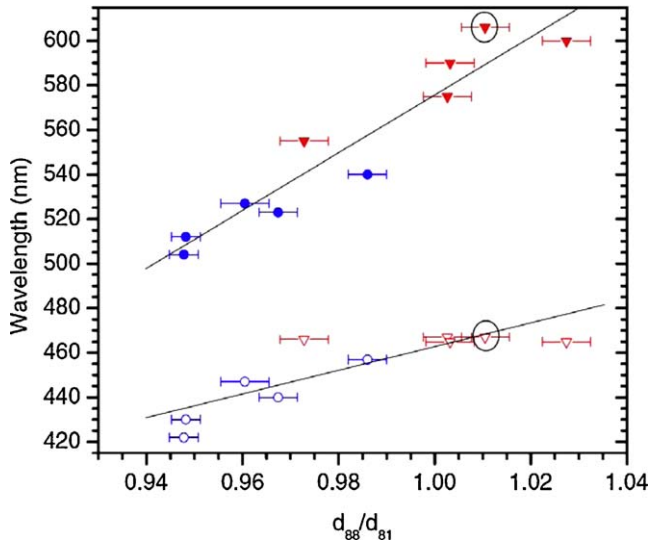


Fig. 13. Excitation (open) and emission (filled) maximum of Ce^{3+} -doped $\text{Y}_3\text{Al}_{5-x}\text{Ga}_x\text{O}_{12}$ (blue circles), $0 \leq x \leq 5$ and $\text{Mg}_3\text{Y}_{2-y}\text{Gd}_y\text{Ge}_{3-z}\text{Si}_2\text{O}_{12}$ (red triangles), $0 \leq y \leq 2$, $z = 0, 1$ as a function of the ratio of the bond distances d_{88} and d_{81} (d_{88}/d_{81}). The points for the Si-doped inverse garnets are circled [26]. Reproduced from Chem. Phys. Lett. 441 (2007) 250. Copyright © 2007, Elsevier B.V.

$\text{Mg}_3\text{Y}_{2-y}\text{Gd}_y\text{Ge}_{3-z}\text{Si}_2\text{O}_{12}$ as a function of the ratio of the bond distances d_{88} and d_{81} (d_{88}/d_{81}). An increase in the ratio d_{88}/d_{81} implies the compression of the cubic polyhedron. The results in Fig. 13 indicate that with an increase in the ratio, both the excitation and emission of Ce^{3+} shift to a longer wavelength. Table 3 summarizes the spectroscopic and structural properties of Ce^{3+} -doped garnets.

Due to the lack of a red component, the CRI of WLEDs fabricated with blue InGaN chips and YAG:Ce phosphors is low. It is reported that the CRI of pc-WLEDs could be improved by incorporating some other activators such as Cr^{3+} , Pr^{3+} , and Sm^{3+} [40,114–116] or non-luminescent ions [112,116–119]. Herein, we give some illustrations of pc-WLED performances fabricated with YAG:Ce phosphors and derivatives, as shown in Fig. 14. Pr^{3+} or Tb^{3+} can result in an enhancement of red emission when co-doped in YAG:Ce, due to the emission of Pr^{3+} or crystal field splitting of Ce^{3+} modified by Tb^{3+} [116]. Adjustable lighting parameters could be obtained, as listed in Tables 4 and 5, by co-doping Pr^{3+} or Tb^{3+} . By increasing the quantity of Pr^{3+} , a high R_a of 83 can be obtained, while both the emission intensity (see Fig. 14) and the luminous efficiency (see Table 4) of white LEDs decline noticeably. For the Tb^{3+} co-doped systems, the high R_a could be obtained without distinct decrease of luminous efficiency (see Table 5), which indicates that co-doping with Tb^{3+} benefits the balance of CRI and luminous efficiency. It can

Table 3
Spectroscopic and structural properties of Ce^{3+} -doped garnets [26].

Host composition	λ_{ex} (nm)	λ_{em} (nm)	d_{88}/d_{81}	Lattice constant (Å)
$\text{Y}_3\text{AlGa}_4\text{O}_{12}$	422	504	0.9478	12.2123
$\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$	430	512	0.9482	12.1552
$\text{Y}_3\text{Al}_3\text{Ga}_2\text{O}_{12}$	440	523	0.9674	12.0926
$\text{Y}_3\text{Al}_4\text{GaO}_{12}$	447	527	0.9605	12.0432
$\text{Y}_3\text{Al}_5\text{O}_{12}$	457	540	0.986	12.0062
$\text{Mg}_3\text{Y}_2\text{Ge}_3\text{O}_{12}$	466	555	0.9728	12.2526
$\text{Mg}_3\text{YGdGe}_3\text{O}_{12}$	467	575	1.0026	12.2934
$\text{Mg}_3\text{Y}_{0.25}\text{Gd}_{0.75}\text{Ge}_3\text{O}_{12}$	465	590	1.0032	12.3173
$\text{Mg}_3\text{Gd}_2\text{Ge}_2\text{SiO}_{12}$	467	606	1.0105	12.2257
$\text{Mg}_3\text{Gd}_2\text{Ge}_3\text{O}_{12}$	464	600	1.0274	12.3293

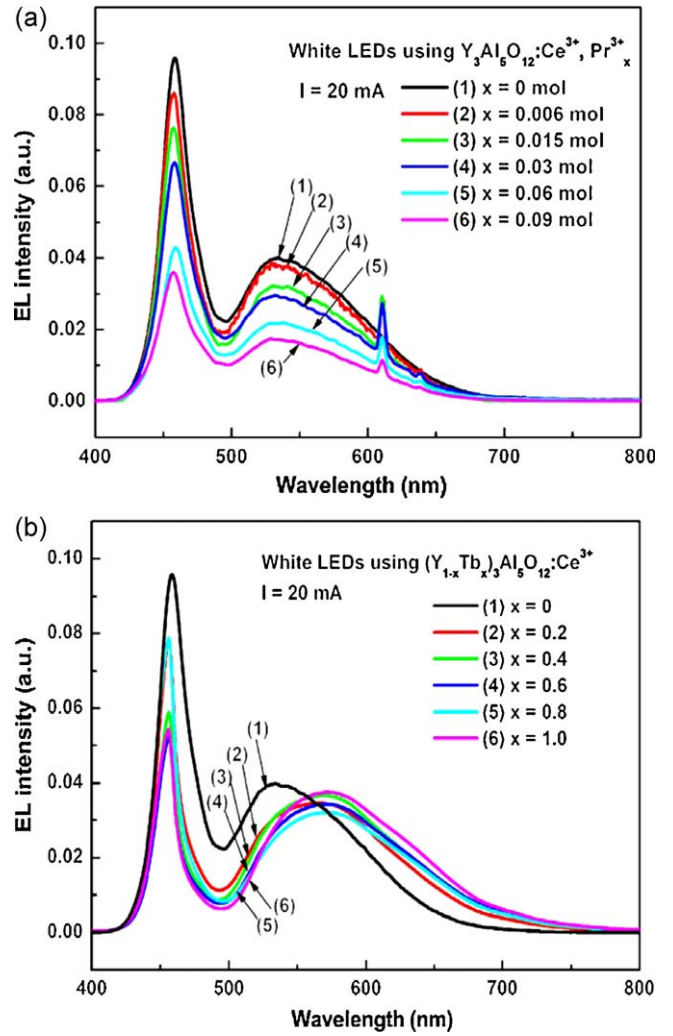


Fig. 14. EL spectra of the white LEDs using both InGaN-based blue-LEDs and (a) $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}, \text{Pr}^{3+}$ phosphors with varying the amount of Pr^{3+} and (b) yellow-emitting $(\text{Y}_{1-x}\text{Tb}_x)_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ phosphors with varying the amount of Tb^{3+} [116]. Reproduced from J. Lumin. 126 (2007) 371. Copyright © 2006, Elsevier B.V.

Table 4
Optical properties of white LEDs using $\text{Y}_{2.94-0.06}\text{Al}_5\text{O}_{12}:0.06\text{Ce}^{3+}, u\text{Pr}^{3+}$ [116].

Pr amount (u)	CIE coordinates		R_a (CRI)	Efficiency (lm/W)
	x	y		
0	0.290	0.317	71	32.7
0.006	0.292	0.318	76	26.5
0.015	0.303	0.330	78	21.7
0.03	0.299	0.324	82	19.0
0.06	0.296	0.322	83	13.7
0.09	0.300	0.337	77	10.8

Table 5
Optical properties of white LEDs using $(\text{Y}_{1-u}\text{Tb}_u)_3\text{Al}_5\text{O}_{12}:0.06\text{Ce}^{3+}$ [116].

Tb amount (u)	CIE coordinates		R_a (CRI)	Efficiency (lm/W)
	x	y		
0	0.290	0.317	71	32.7
0.2	0.298	0.319	76	30.8
0.4	0.315	0.330	72	31.7
0.6	0.335	0.353	73	29.2
0.8	0.322	0.326	80	27.8
1	0.331	0.328	72	29.3

Table 6
Methods for preparation of YAG:Ce.

Methods	Temperature (°C)	Particle size	Refs.
Solid-state reaction method	1500	Micrometer-scale	[120]
Co-precipitation method with ammonium bicarbonate (NH_4HCO_3)	above 1000	Nanometer-scale	[120]
Sol-gel method	1000–1100	Nanometer-scale	[120,127]
Combustion method with urea ($\text{CO}(\text{NH}_2)_2$)	1000	Micrometer-scale	[120]
Precipitation method with different aluminum sources	850	Nanometer-scale	[124]
Pechini technique	900–1000	Nanometer-scale	[126]
Spray pyrolysis	1000	Submicrometer-scale	[108]
Flame-assisted spray pyrolysis	1100	Submicrometer-scale	[109]
Salted sol-gel method	800	Nanometer-scale	[128]
Glycothermal method	300	Nanometer-scale	[129,130]
Sol-gel pyrolysis method	1000	Nanometer-scale micrometer-scale	[131,132]
Emulsion route	1000	Nanometer-scale	[133]
Microwave assisted synthesis	600	Nanometer-scale	[134]
Sonochemistry	900	Nanometer-scale	[135]
Solvothermal method	300	Nanometer-scale	[136]

also be concluded from Tables 4 and 5 that high R_a and high luminous efficiency are always conflicting.

3.1.3. YAG:Ce phosphor: materials synthesis, characterization and properties

The synthesis method, particle size, morphology, and annealing treatment also influence the PL properties of YAG:Ce [120–123]. Table 6 summarizes the synthesis methods, the temperature required for each method, and the results of particle size. It can be seen that all the nano-scale YAG:Ce phosphors are synthesized by solution-based methods at relatively low temperature.

Chiang et al. [124] synthesized the YAG:Ce phosphor via different aluminum sources and precipitation processes. It was

found that the best performance of YAG:Ce phosphors was obtained by using aluminum nitrate combined with a normal strike precipitation method. Li et al. [125] used a polyacrylamide gel method to synthesize YAG:Ce phosphors and studied the structure evolution of powders during the annealing process. It was found that some intermediate phases would appear and the pure YAG phase could be formed directly when calcining polyacrylamide gel with $\alpha\text{-Al}_2\text{O}_3$ as the seed crystal. Zych et al. [126] prepared nanocrystalline powders of YAG:Ce by using the Pechini technique and precipitation with urea. They found that heating YAG:Ce powders in a reducing atmosphere of nitrogen–hydrogen mixture at 1000 °C would cause a redshift of the Ce^{3+} emission by about 20–25 nm. The effect was stronger for the

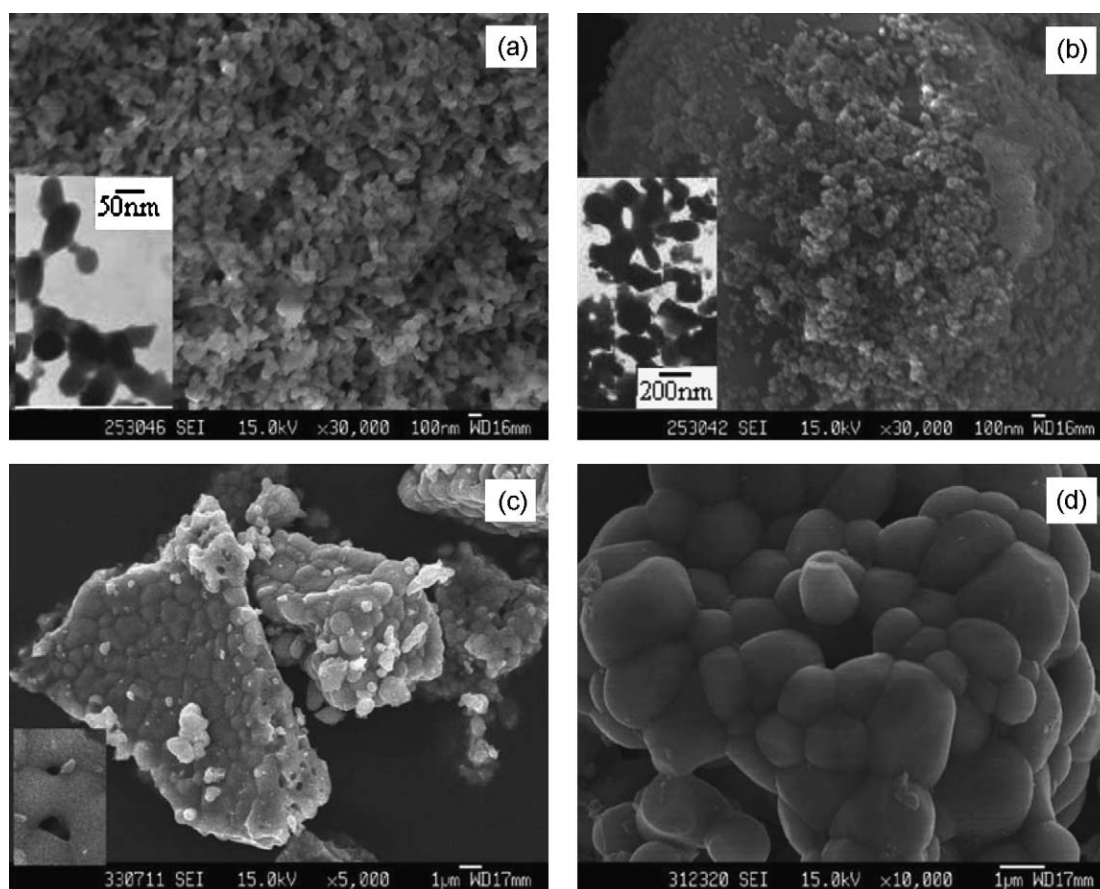


Fig. 15. SEM images of YAG:Ce prepared by (a) co-precipitation, (b) sol-gel, (c) combustion, (d) solid-state synthesis [120]. Reproduced from Mater. Sci. Eng. B 106 (2004) 251. Copyright © 2003, Elsevier B.V.

powder prepared with urea. It was also found that this powder had a longer Ce^{3+} emission decay time, which implies that treatment at a reduced atmosphere diminishes the nonradiative relaxation probability of the excited electrons.

Pan et al. performed a comparative investigation of YAG:Ce synthesis by different methods: solid-state reaction, co-precipitation with ammonium bicarbonate, sol-gel with citric acid, and combustion with urea [120,121]. The crystallization, morphologies, particle size, and luminescent character of the phosphors were obtained under different experimental conditions. A temperature as high as 1500 °C was needed for crystallization of YAG:Ce by solid-state reaction, and the particles were large with irregular shapes. However, a lower temperature gained good crystallinity for combustion, co-precipitation, and sol-gel methods, which gave rise to spherical particles with nanometer size as shown in Fig. 15. Redshift of the Ce^{3+} emission occurred for the products derived from the combustion method and the solid-state reaction compared with those prepared by the sol-gel and co-precipitation methods. The smaller particles obtained by the latter two methods have higher surface tension than that of the bulk derived from the former two methods, as shown in Fig. 16. Similar blueshift from bulk to nanocrystals and redshift for higher Ce concentration were reported by Jia et al. [128]. Both emission and excitation spectra of YAG:Ce nanocrystals synthesized by a salted sol-gel method and sol-gel combustion show blueshift compared to the counterpart of the bulk phosphors due to lower crystal field effects of nanocrystals [128]. A reducing atmosphere of CO, increasing Ce^{3+} concentration, or substituting Y^{3+} with Gd^{3+} would lead to redshift of the emission band [121]. The fluxes used in a solid-state reaction or substituting part of Al^{3+} with In^{3+} or Ga^{3+} led to blueshift of the emission band. The modified garnet derivatives showed better emission power distribution in red, but had sacrificed energy efficiency.

Mancic et al. [108] reported a spray pyrolysis synthesis of highly spherical submicronic particles of YAG:Ce at 1000 °C, which is a much lower temperature than that applied in solid-state reaction synthesis. As shown in Fig. 17, most of the particles were in submicrometer size and the mean particle size was about 0.9 μm . However, the targeting garnet structure of YAG was mixed with YAlO_3 and $\text{Y}_4\text{Al}_2\text{O}_9$ in the sample annealed at lower temperature or for short residence time. Furthermore, the CeO_2 phase was even present in the sample annealed for 6 h at 900 °C. The phases other than cubic YAG did not contribute to but rather decreased the luminescence intensity of the phosphor YAG:Ce. Lee et al. [137] prepared YAG:Ce phosphor powders with mean size of 1.73 μm by spray pyrolysis from the spray solutions with BaF_2 flux. BaF_2 flux

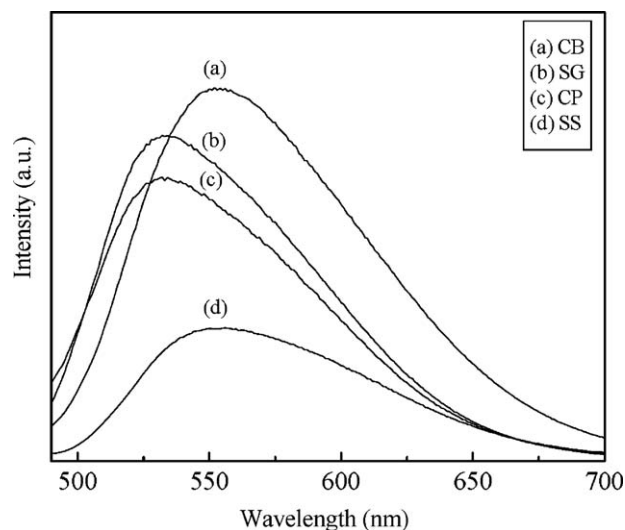


Fig. 16. Emission spectra of 4 mol% Ce-doped YAG prepared by (a) combustion, (b) sol-gel, (c) co-precipitation, (d) solid-state synthesis [120]. Reproduced from Mater. Sci. Eng. B 106 (2004) 251. Copyright © 2003, Elsevier B.V.

improved the morphological and optical properties of the YAG:Ce phosphor powders.

Purwanto et al. reported flame-assisted spray pyrolysis synthesis of agglomerate-free YAG:Ce submicrometer particles [109]. SEM shown in Fig. 18 demonstrated that crystals annealed at 1100 °C for a time shorter than eight hours were agglomerate-free spheres. Higher annealing temperature and longer time led to a necking phenomenon and even agglomeration among particles with rougher surfaces. The brightness of YAG:Ce phosphor increased with annealing temperature and time because of the improved crystallization.

To prepare well-dispersed YAG:Ce nanocrystals with size of 10–20 nm, Isobe et al. [129,130] applied glycothermal method synthesis with polyethylene glycol (PEG), and Lu et al. [131,132] used sol-gel pyrolysis with urea and polyvinyl alcohol (PVA). In the former, PEG did not change the crystallite size or the lattice distortion, but enhanced the luminescence of YAG:Ce significantly due to the surface passivation effect of PEG through preferential coordination to the YAG:Ce nanocrystals and the prevention of oxidation of Ce^{3+} to Ce^{4+} . In the latter, urea and PVA played the role of fuel and dispersing matrix, which made the synthesis temperature as low as 1000 °C and the YAG:Ce nanocrystals exhibited single-crystal like features. The crystal size can vary with the ratio of PVA to urea.

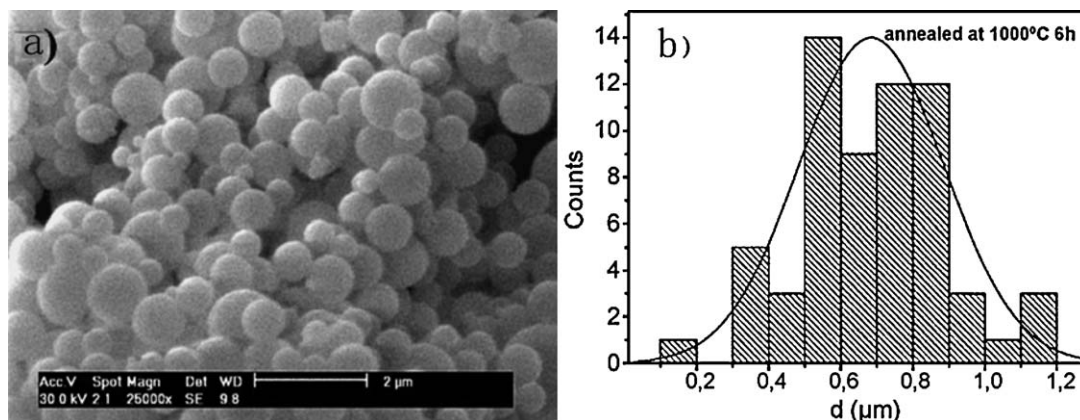


Fig. 17. SEM photomicrographs of as-prepared particles annealed for 6 h at 1000 °C (a) and particle size distribution curve, together with the histogram obtained through the raw size data processing for powder annealed at 1000 °C for 6 h (b) [108]. Reproduced from J. Eur. Ceram. Soc. 27 (2007) 4329. Copyright © 2007, Elsevier Ltd.

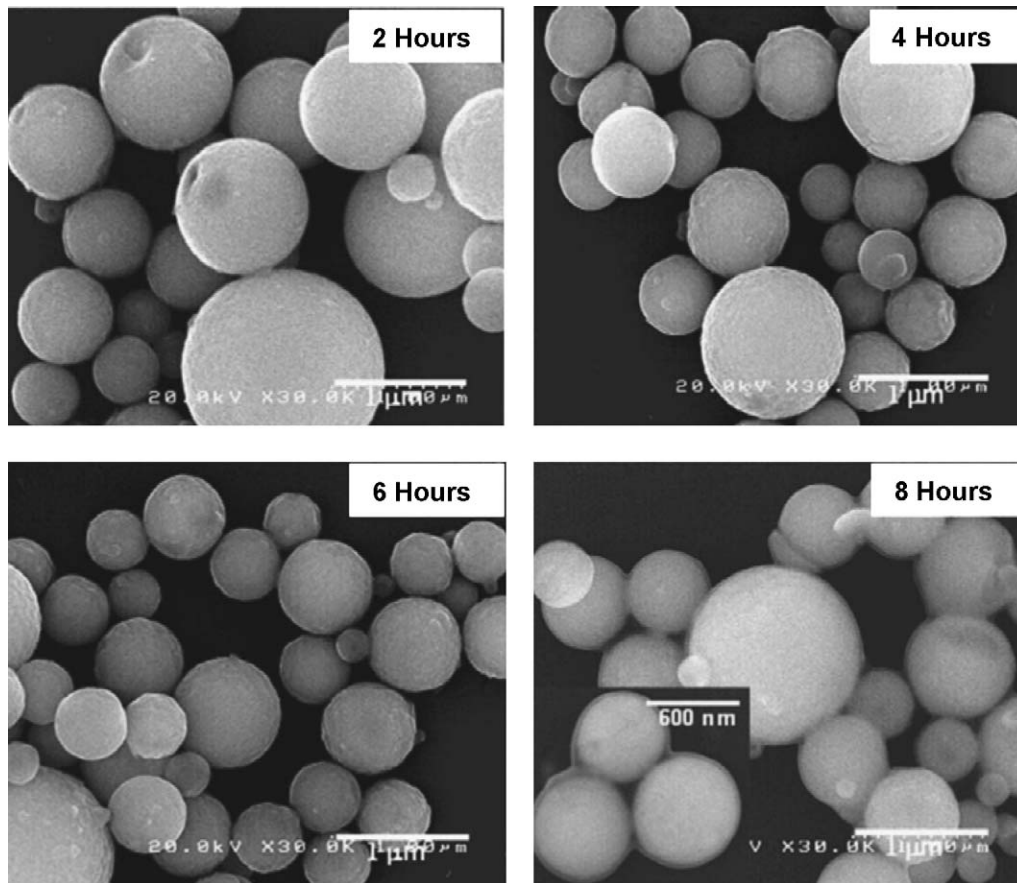


Fig. 18. FE-SEM images of powder post-treated at 1100 °C for various treatment times [109]. Reproduced from J. Electrochem. Soc. 154 (2007) J91. Copyright © 2007, The Electrochemical Society.

3.1.4. Packaging performance of YAG:Ce phosphor

The packaging of YAG:Ce phosphors on LED chips is of great importance to obtain high yield of light output. Commonly available commercial packages of YAG:Ce phosphors on LED chips are epoxy-encapsulated [138]. Huang et al. investigated the effect of particle size distribution of YAG:Ce phosphors on packaging performance in white LED applications [139]. The YAG:Ce phosphors with different particle sizes were packaged in white LEDs using different amounts of each phosphor, and it was found that smaller particle sizes required a minimal amount of phosphor material for efficiency similar to that exhibited by commercially available YAG:Ce phosphors. Yum et al. obtained good quality white light ($x = 0.2994$, $y = 0.3272$) by coating $Y_3Al_5O_{12}:0.05Ce^{3+}$ phosphor particles on flexible indium tin oxide-coated polyethylene terephthalate, using electrophoretic deposition to achieve a uniform and high-packed coating [140].

Optical ray-tracing analysis is a convenient tool to investigate novel concepts of pc-WLEDs, including light transmission, reflection, and absorption properties. A laboratory study was conducted by Zhu et al. [141] to quantify at different wavelengths of light the optical properties of a medium made by mixing YAG:Ce phosphor into epoxy. At a phosphor density suitable for creating a balanced white light, the amount of back-transferred and forward-transferred light, including blue and yellow light, were 53% and 47%, respectively. Nearly equal amounts of green and red radiant energy were transferred in the backward and forward directions at the similar phosphor density.

Recently, Pan et al. [142] measured backscattering and transmitted luminescence from YAG:Ce powder phosphor diluted in a layer of optical epoxy resin and pasted on a piece of glass as shown in Fig. 19. The data were recorded using a 475 nm blue-LED

excitation. The ratio of backscattering vs. transmission was approximately 4–1. The intensity of the yellow luminescence was about the same in both sides and the transmitted blue light was reduced by adjusting the thickness of the sample. However, the blue-LED light was strongly scattered back to the LED side and counted for 60% of the total light from the sample. Furthermore, backscattering was stronger for the blue light than for the longer wavelength luminescence light. Due to backscattering, absorption, and reabsorption of the powder phosphor particles, a significant

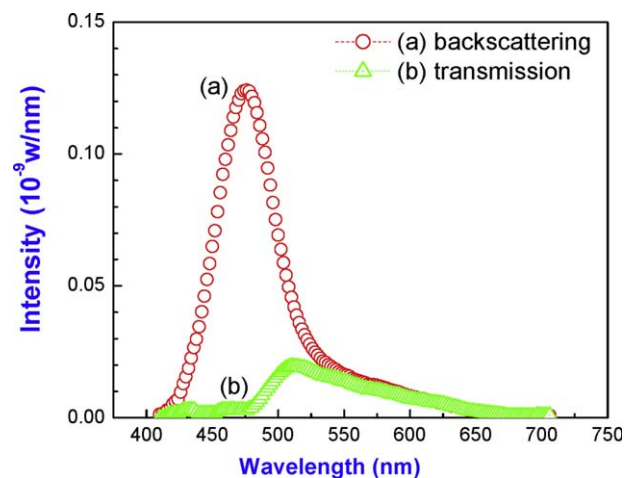


Fig. 19. Backscattering (a) and transmitted luminescence (b) from $Y_{2.97}Al_5O_{12}:Ce_{0.03}$ nanocrystal phosphor with size about 50 nm diluted in a layer of optical epoxy pasted on a piece of glass.

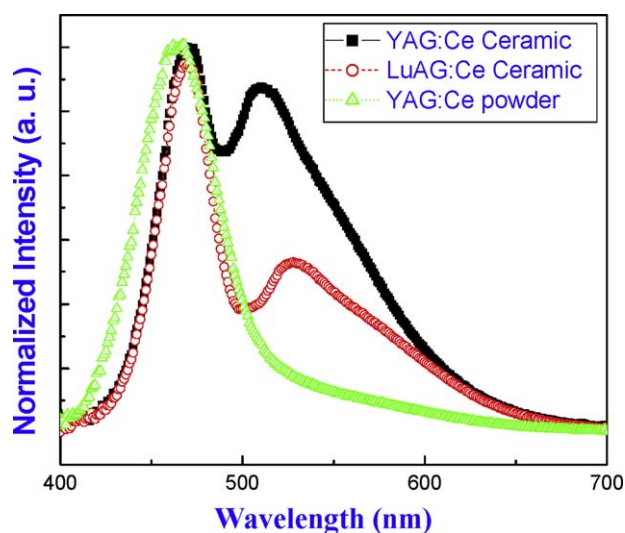


Fig. 20. Comparison of transmitted luminescence of Ce^{3+} activated garnet luminescent powder phosphor and ceramics.

portion of blue light from the LED and yellow light from the phosphor layer were ultimately lost within the package.

The scattering coefficient depends upon particle size and the micrometer particles showed stronger scattering than either smaller or much larger particles. Theoretically decreasing the size of phosphor particles to several nanometers should eliminate scattering because their sizes are much shorter than the excitation light wavelength. However, most RE doped nanophosphors show poor luminescent properties due to increased surface defects of

nanosized particles and aggregation was unavoidable, particularly in glue and resin.

Compared with the powder phosphor, transparent YAG:Ce and LuAG:Ce luminescent ceramics show much higher efficacy due to elimination of backscattering as shown in Fig. 20. The spectra of the phosphor layer and transparent ceramic are normalized into the peak intensity of the blue light. It is clearly observed that the yellow light transmitted from the phosphor layer is much lower than that from ceramics. Low efficacy of converting blue light into yellow light will lead to low efficacy of the overall extraction. The lost energy ultimately converts into heat that will not only quench the luminescence of the phosphors but will also decrease the efficacy of the LED chips. Moreover, the excitation and emission bands of some phosphors can shift with increasing device temperature.

Fig. 21 shows scheme and photographs of the transparent color conversion films composed of a highly concentrated YAG:Ce nanoparticles fabricated by Kasuya et al. [143] using the glycothermal method. The film was 200 μm thick and its luminescence was doubled by putting a mirror on the back side of the film because the transmitted emission light of the phosphor can be reflected. In addition, YAG:Ce nanoparticles transparently dispersed in the film can suppress the scattering loss and improve the conversion efficiency significantly.

Tanabe et al. [144–146] developed a glass-ceramic material of $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3\text{--SiO}_2$ glasses containing a single phase of YAG:Ce microcrystals which could be backward-excited by blue-LEDs to give white emission. Experiments revealed that the composite of the glass-ceramic and a blue-LED chip gave high luminous efficiency comparable to that of commercial white LEDs working at the same current power. The color coordinate (x, y) of the spectra increased owing to the increase in the ratio of yellow to blue bands,

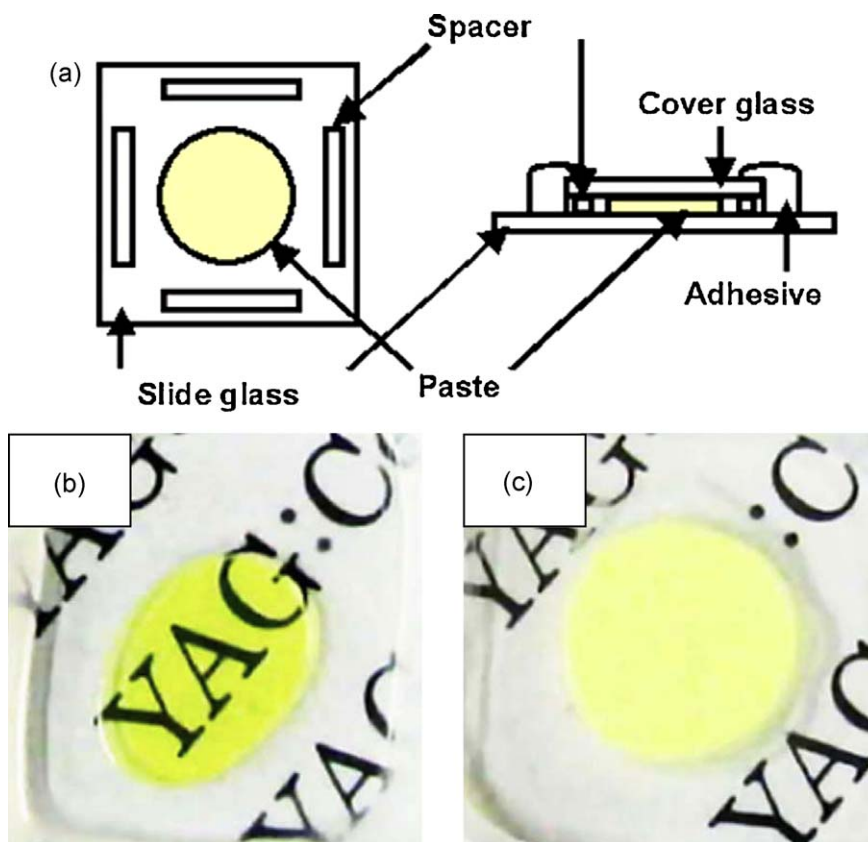


Fig. 21. Scheme and photographs of the color conversion film. (a) Top view (left) and side view (right) of the prepared film; (b) the 200 μm thick film containing YAG:Ce $^{3+}$ nanoparticles. The solid content estimated by TG curve was 70.7 wt.%; (c) the 200 μm thick film containing commercial micron sized YAG:Ce $^{3+}$. The solid content was 61.6 wt.% [143]. Reproduced from Appl. Phys. Lett. 91 (2007) 111916. Copyright © 2007, American Institute of Physics.

and the CCT changed from 8000 to 5000 K with increasing glass-ceramic thickness. The variation of color coordinate locus in the CIE chromaticity diagram followed nearly that of the Planckian locus for black-body radiation. With this glass-ceramic plate, the problems of the current packaged white LEDs, i.e. degradation of organic resin and difficulty in packaging of powder phosphors might be avoided.

3.1.5. Temperature-quenching of YAG:Ce

The temperature-quenching of the PL of YAG:Ce phosphors was reported by many researchers [2,119,138,147–149]. The white LEDs fabricated with YAG:Ce and blue InGaN chips were also quenched with increasing temperature, as shown in Fig. 22. Thus, the chromaticity of white LEDs varied with the temperature of the device. The temperature-quenching behavior limits the application of current garnets and semiconductors in high-power white LEDs. Recently, Bachmann et al. figured out that the intrinsic quenching temperature of Ce^{3+} emission in YAG could reach 700 K [150]. Fig. 23 demonstrates that for high dopant concentrations of Ce^{3+} (3.33%), the temperature-quenching of YAG:Ce was almost the same under different wavelength excitations, while for low Ce^{3+} concentrations (0.033%), the temperature-quenching was quite different under different wavelength excitations. To understand the different temperature-quenching behavior of YAG:Ce with different Ce^{3+} concentrations, lifetime measurements of Ce^{3+} emission with various Ce^{3+} contents in YAG as a function of temperature were performed and the results are illustrated in Fig. 24. Generally, the lifetime of an allowed transition does not change significantly with temperature. The lifetimes for the samples with high Ce^{3+} content show strong decrease at high temperature, which means there is a concentration quenching effect. The lower quenching temperatures reported in previous literature were ascribed to the thermally activated concentration quenching (for high dopant concentration) and the temperature dependence of the oscillator strength (for low dopant concentra-

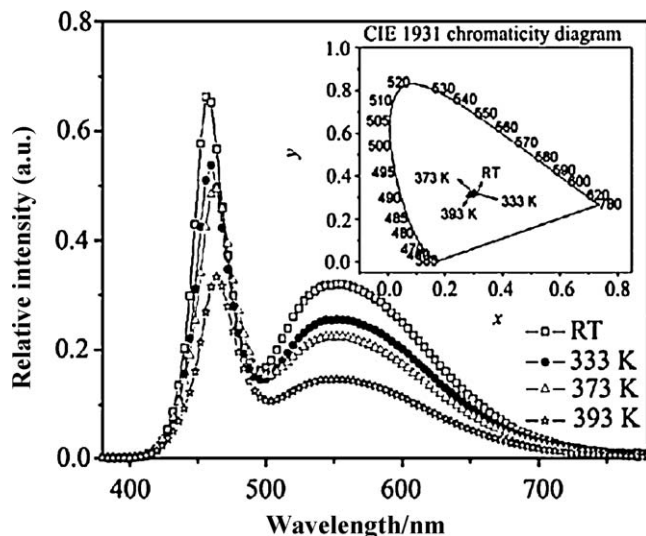


Fig. 22. Temperature-dependent emission spectra of the white LED with as-prepared phosphors. Inset shows the temperature dependence of CIE chromaticity of white light from the white LEDs [148]. Reproduced from J. Rare Earth 26 (2008) 446. Copyright © 2007, Elsevier.

tions). Thus, the YAG:Ce phosphors could be utilized for high-power white LED applications when the Ce^{3+} doping concentrations are low.

3.1.6. Other garnets

There are other garnet phosphors, including $\text{Tb}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ [151–157], $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ [158], $\text{Lu}_2\text{CaMg}_2(\text{Si,Ge})_3\text{O}_{12}:\text{Ce}$ [158], and $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}$ [159–161], which have similar PL behavior to that of YAG:Ce. Chen et al. investigated the different flux effects on the preparation of $\text{Tb}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ and found that the mixture of H_3BO_3 and LiF was an excellent flux to lower the synthesis temperature

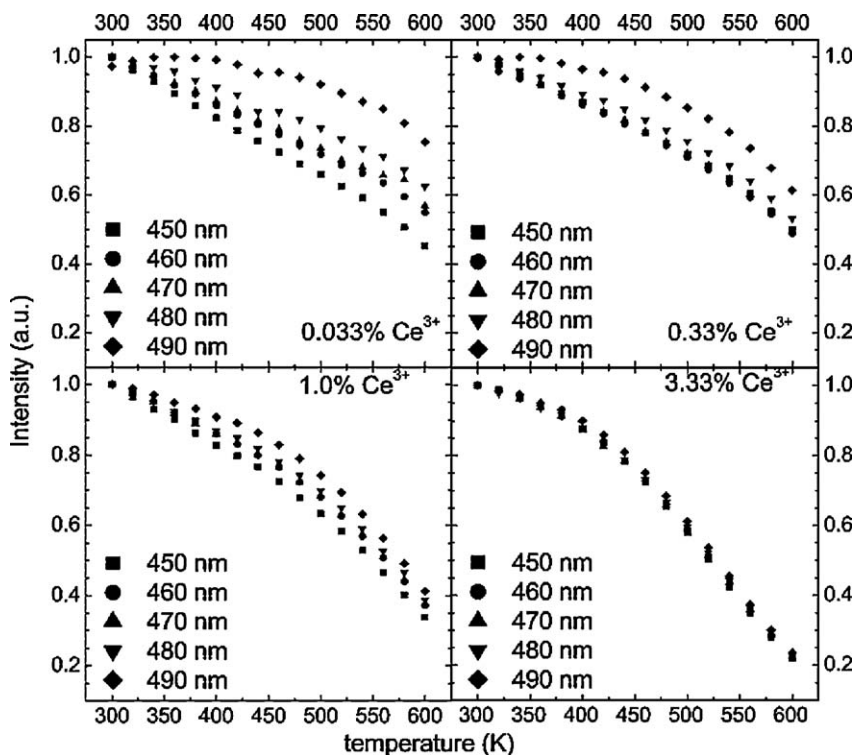


Fig. 23. Temperature dependence of the integrated emission intensity for YAG:Ce 0.033%, 0.33%, 1.0%, and 3.33% taken at the five excitation wavelengths indicated [150]. Reproduced from Chem. Mater. 21 (2009) 2077. Copyright © 2009, American Chemical Society.

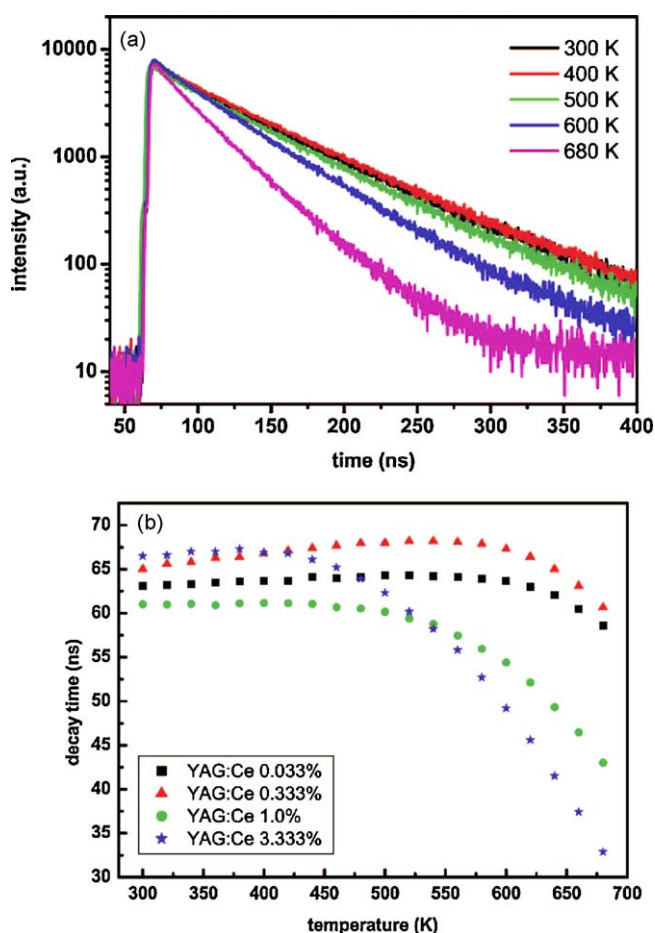


Fig. 24. (a) Luminescence decay curves of YAG:Ce 3.33% for $\lambda_{\text{ex}} = 406$ nm and $\lambda_{\text{em}} = 580$ nm, taken at the temperatures indicated; (b) decay times determined from single-exponential fits of the luminescence decay as a function of temperature for YAG:Ce 0.033%, 0.33%, 1.0%, and 3.33% [150]. Reproduced from Chem. Mater. 21 (2009) 2077. Copyright © 2009, American Chemical Society.

and improve the morphology, as well as to enhance the PL of $\text{Tb}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ [152]. When co-doping Ce^{3+} and Eu^{3+} in $\text{Tb}_3\text{Al}_5\text{O}_{12}$, energy transfer from Tb^{3+} to Ce^{3+} and Eu^{3+} , and from Ce^{3+} to Eu^{3+} was noted [155–157]. It is reported that the $\text{Lu}_2\text{CaMg}_2(\text{Si},\text{Ge})_3\text{O}_{12}:\text{Ce}$ has quantum efficiency comparable to that of a typical YAG:Ce phosphor [158]. The high quantum efficiency of the $\text{Lu}_2\text{CaMg}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$ phosphor combined with its minimal reabsorption effects in the yellow-green spectral region should lead to good performance in LED-based lamps as shown in Fig. 25. It is especially desirable for lower CCT and higher CRI light sources.

In $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}$, the Ce^{3+} replaced the Ca^{2+} position according to X-ray diffraction refinement, and the phosphor had smaller thermal quenching effects at 150 °C than the YAG:Ce [159]. Additionally, the introduction of Mg^{2+} in $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}$ made the emission of Ce^{3+} move toward longer wavelength, and the Mg^{2+} probably substituted the Sc^{3+} to compensate for the substitution of Ca^{2+} by Ce^{3+} , which resulted in more Ce^{3+} moving into the lattice [160]. The spectral shift was also observed by adding Na^+ or Li^+ as compensators, therefore, the spectral modification was due primarily to the increase of Ce^{3+} contents [160].

3.2. Non-garnet oxide-based phosphors

To improve the CRI and PL dependence on temperature of YAG:Ce, and to avoid the issues associated with intellectual property, much scientific effort has been made in the development of non-garnet yellow phosphors. Ce^{3+} or Eu^{2+} in some non-garnet

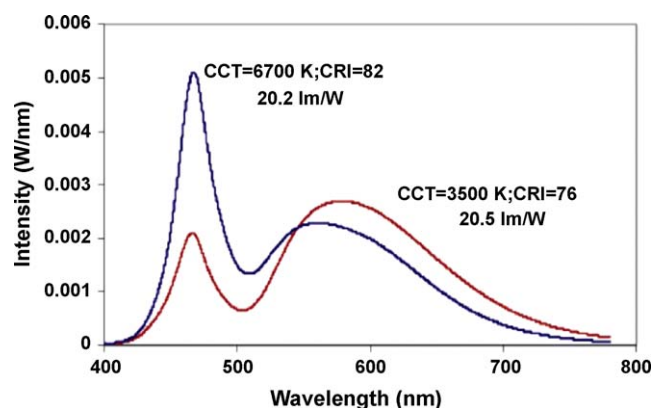


Fig. 25. Spectra of LED-based lamps with high CCTs that use solely typical YAG:Ce garnets (blue line) and low CCTs using blends of typical YAG:Ce garnets with $(\text{Lu}_{0.94}\text{Ce}_{0.06})_2\text{CaMg}_2\text{Si}_3\text{O}_{12}$ (red line) [158]. Reproduced from Chem. Mater. 18 (2006) 3314. Copyright © 2006, American Chemical Society.

hosts can give yellow emission when excited by blue light. Most of these hosts are silicates and aluminates, which are just a few members of the extremely large silicate and aluminate families. They are $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ [162–170], $\text{Sr}_3\text{SiO}_5:\text{Eu}^{2+}$ [39,41,164,171,172], $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ [173,174], $\text{Li}_2\text{SrSiO}_4:\text{Eu}^{2+}$ [42], $\text{LaSr}_2\text{AlO}_5:\text{Ce}^{3+}$ [175–177], haloborate $\text{Ca}_2\text{BO}_3\text{Cl}:\text{Eu}^{2+}$ [178], and haloaluminates $\text{Sr}_3(\text{Al}_2\text{O}_5)_2\text{Cl}_2:\text{Eu}^{2+}$ [179]. The long-wavelength emissions of $\text{Ce}^{3+}/\text{Eu}^{2+}$ in these non-garnet oxide compounds result primarily from large crystal field splitting. Poort et al. [180] summarized the luminescence of Eu^{2+} in some alkaline earth silicates with chain arrangement of alkaline earth ions and concluded that the long-wavelength emission of Eu^{2+} was due to preferential orientation of one d orbital of Eu^{2+} . There is also other research work [181] on the Eu^{2+} doped alkaline earth borates with low emission energy of Eu^{2+} , such as $\text{Ba}_2\text{Mg}(\text{BO}_3)_2$, $\text{Ba}_2\text{LiB}_5\text{O}_{10}$, $\text{Sr}_3(\text{BO}_3)_2$, and $\text{Sr}_2\text{Mg}(\text{BO}_3)_2$. The study showed that those compounds in which an oxygen anion was coordinated by at least three heavy alkaline earth ions such as Sr^{2+} and Ba^{2+} produced long-wavelength emission of Eu^{2+} .

There are two forms of Sr_2SiO_4 which can give long-wavelength emission of Eu^{2+} , α' - Sr_2SiO_4 [167,168,170] and beta- Sr_2SiO_4 [168]. The XRD patterns of the two forms are similar [168], making the study of their individual luminescences difficult. The incorporation of Mg^{2+} in α' - $\text{Sr}_{1.98}\text{SiO}_4:0.02\text{Eu}^{2+}$ shifts the Eu^{2+} emission from 535 nm to 564 nm [167]. The phase transmits from beta to α' in $\text{Sr}_2\text{SiO}_4:\text{xEu}^{2+}$ when the concentration of Eu^{2+} increases, the single beta phase is obtained as $x \leq 0.005$ and changes to α' phase when $x > 0.01$ [168]. Some research [170] indicates that co-doping Ba^{2+} in Sr_2SiO_4 favors the crystallization of α' - Sr_2SiO_4 .

Both Ce^{3+} and Eu^{2+} in Sr_3SiO_5 have long-wavelength emissions of ~530 and 570 nm, respectively, as shown in Figs. 26 and 27. Usually the $d \rightarrow f$ transition energy of Ce^{3+} is higher than that of Eu^{2+} due to the difference in intrinsic electronic configurations [182]. This difference suggests that Ce^{3+} and Eu^{2+} could replace each other to meet different demands on some occasions. Fig. 26 also demonstrates that with an increase of Ba^{2+} contents substituting Sr^{2+} in Sr_3SiO_5 , the emissions of Eu^{2+} show redshift. When $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ is fabricated with different LED chips [173], white LEDs could be obtained for 460 nm LED chip + $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ and 405 nm LED chip + $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$, as shown in Fig. 28(a) and (b). These two white LEDs show luminous efficiency of 31.7 and 25.0 lm/W, respectively, while the luminous efficiency for white LEDs using commercial YAG:Ce phosphors is only 23.5 lm/W. The CIE chromaticity coordinates and R_a of the two white LEDs are ($x = 0.3086$, $y = 0.3176$), 81 and ($x = 0.3173$, $y = 0.3103$), 69, respectively. The low R_a of the 405 nm LED chip-based white LEDs is due to the lack of emission in the 430–465 nm range.

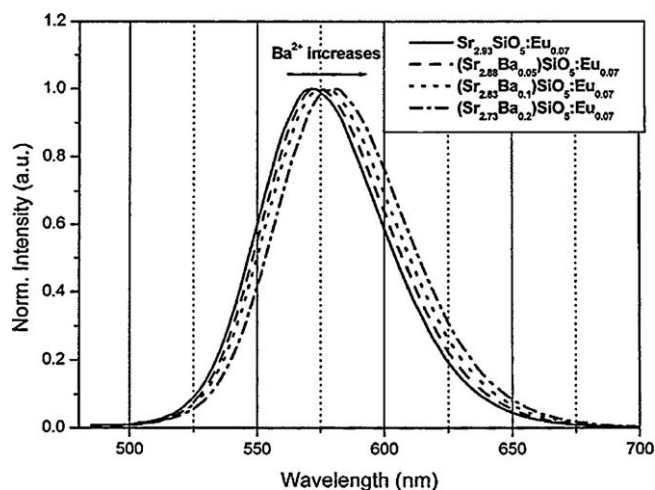


Fig. 26. Emission spectra of $\text{Sr}_{2.93}\text{SiO}_5:\text{Eu}_{0.07}$ phosphor as a function of Ba^{2+} concentration (~ 460 nm) [171]. Reproduced from Appl. Phys. Lett. 88 (2006) 043511. Copyright © 2006, American Institute of Physics.

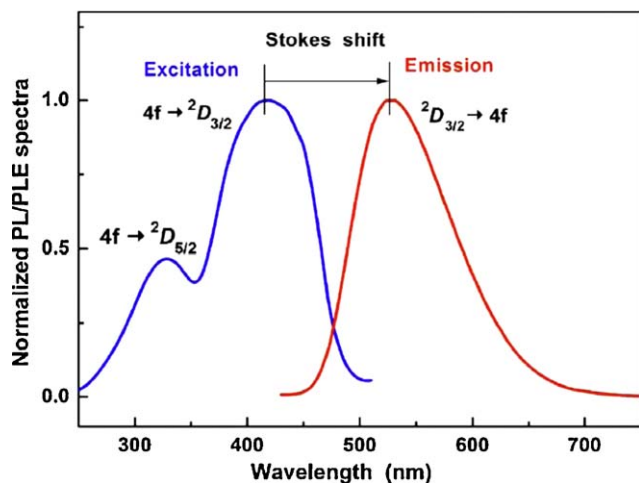


Fig. 27. Normalized PL and PLE spectra of $\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+},\text{Li}^+$ [173]. Reproduced from Appl. Phys. Lett. 90 (2007) 41906. Copyright © 2007, American Institute of Physics.

Im et al. reported a new yellow phosphor, $\text{LaSr}_2\text{AlO}_5:\text{Ce}^{3+}$, but its quantum efficiency ($\sim 42\%$) was lower than that of the YAG:Ce reference ($\sim 75\%$) [177]. They studied the solid solutions of $\text{LaSr}_2\text{AlO}_5$ and Sr_3SiO_5 with similar structure to tune the luminescence properties [175]. With careful investigation of structure, spectra, energy level of Ce^{3+} 5d orbitals, and isovalent substitutions of all three cations in $\text{LaSr}_2\text{AlO}_5:\text{Ce}^{3+}$, the authors found that the $5d \rightarrow 4f$ transition energy of Ce^{3+} varied considerably in accordance with the Ce–O distance and crystal field splitting [176]. The authors calculated the electronic structure of phosphor to understand and design the new phosphor host. A similar idea was used in our work [35,37]. Im et al. [176] also showed that Gd-substitution for La effectively increased the crystal field splitting and, hence, efficiently enhanced the red emission of $\text{LaSr}_2\text{AlO}_5:\text{Ce}^{3+}$. With Tb- and Ba-substitutions, crystal lattice covalence played an additional role over crystal field splitting.

3.3. Sulfides

The electronegativity of S is smaller than that of O, and S could be polarized easily. Thus, the nephelauxetic effect in sulfides is generally larger than that in oxide-based compounds, which results in large centroid shift of Ce^{3+} or Eu^{2+} [56]. The Ce^{3+} and Eu^{2+}

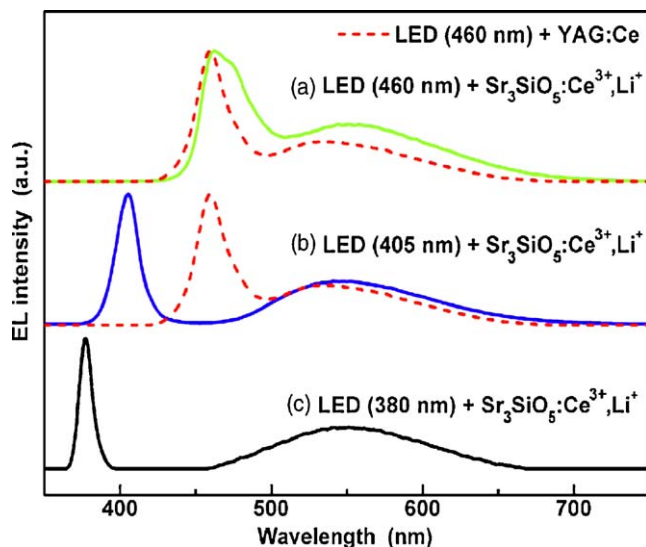


Fig. 28. EL spectra of white LEDs using (a) 460 nm chip and (b) 405 nm chip and (c) a yellow LED using 380 nm chip measured under a forward bias of 20 mA [173]. Reproduced from Appl. Phys. Lett. 90 (2007) 41906. Copyright © 2007, American Institute of Physics.

in alkaline earth sulfides can absorb blue light and give green to red light emissions [183–189]. Fig. 29 gives the spectra of alkaline earth sulfide phosphors excited by 450 nm blue-LED chips. Co-doping Ce^{3+} into $\text{SrS}:\text{Eu}^{2+}$ and $\text{CaS}:\text{Eu}^{2+}$ leads to the enhancement of Eu^{2+} emission due to ET from Ce^{3+} to Eu^{2+} [187]. The analogous phenomenon was observed in Ba_2ZnS_3 [186]. Nazarov et al. [185] investigated the luminescence of Eu^{2+} -doped CaS – SrS solid solution and found that the emission of Eu^{2+} varied linearly with alkaline earth–sulfur distance, i.e. the crystal field strength. A schematic diagram is given in Fig. 30 [185]. The effects of crystal field splitting (associated with cation–anion distance) in solid solution $(\text{Ca}_{1-x}\text{Sr}_x)(\text{S}_{1-y}\text{Se}_y):\text{Eu}^{2+}$ on Eu^{2+} emission can be seen clearly in Fig. 31 [185].

Guo et al. investigated the effects of different flux and cations incorporated in $\text{CaS}:\text{Eu}^{2+}$ phosphor on the luminescence properties [183]. The authors found that both the addition of flux NH_4F and

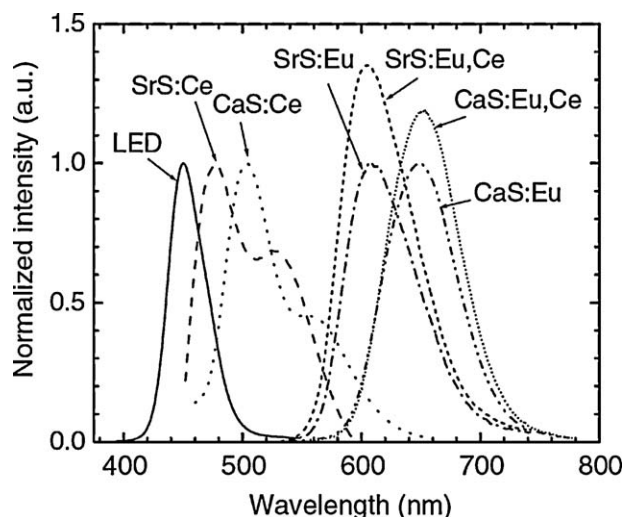


Fig. 29. Emission spectra of the alkali earth sulfide phosphors excited by 450 nm blue-LEDs. Emissions from Eu^{2+} , Ce^{3+} co-doped samples are normalized to emissions of Eu^{2+} singly doped in CaS and SrS , respectively. LED emission is also shown there as a reference [187]. Reproduced from Opt. Mater. 30 (2007) 375. Copyright © 2006, Elsevier B.V.

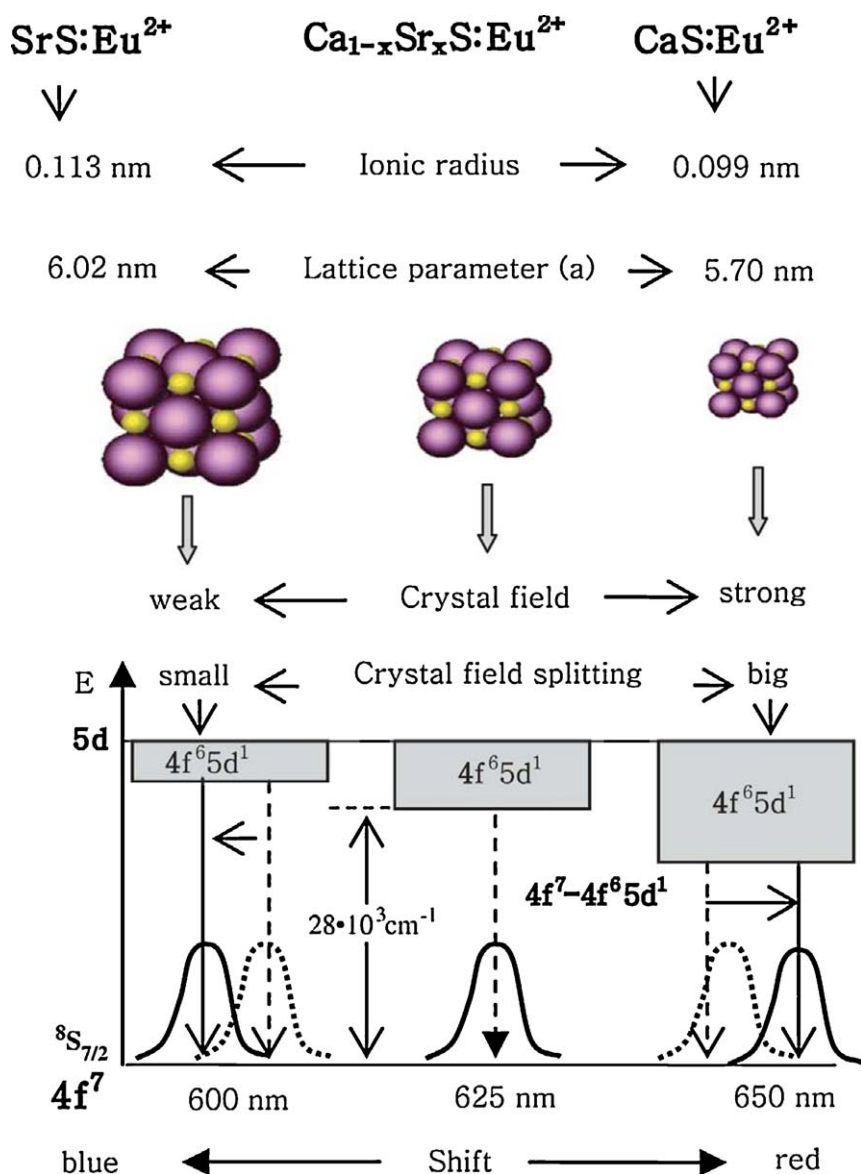


Fig. 30. Schematic illustration of crystal field splitting and spectra shift in $(\text{Ca}_{1-x}\text{Sr}_x)\text{S}:\text{Eu}^{2+}$ with a different Sr/Ca ratio [185]. Reproduced from J. Solid State Chem. 179 (2006) 2529. Copyright © 2006, Elsevier Inc.

the introduction of Er^{3+} , Sr^{2+} or Mg^{2+} could enhance the emission of Eu^{2+} . The incorporation of Sr^{2+} also shifted the excitation band of Eu^{2+} to fit different excitation wavelengths of blue-LED chips.

Some Ce^{3+} - or Eu^{2+} -doped thiosilicates, such as Ca_2SiS_4 , BaSi_2S_5 , and Ba_2SiS_4 , can have deep blue to red emissions [190], which make them applicable in pc-WLEDs. For instance, combining the $\text{Ca}_2\text{SiS}_4:\text{Eu}^{2+}$ phosphor with a blue-LED chip (450 nm) give white light with CCT ~ 3000 K and CRI ~ 67 , as shown in Fig. 32. The commercially available Luxeon III star LED [190] has a CCT of 5600 K and a CRI of 72. The low CRI of a blue-LED chip (450 nm) + $\text{Ca}_2\text{SiS}_4:\text{Eu}^{2+}$ phosphor is due to the lack of green emission. Table 7 gives a summary of the performance of some phosphors other than YAG:Ce (nitrides and oxynitrides are listed alone in the next section) which could be excited by blue-LED chips. However, in general sulfide phosphors are thermally unstable and sensitive to moisture, which would degrade the luminescence of pc-WLEDs. The lack of the green emission component when excited by blue-LED chip is another problem of the sulfide phosphors, which results in low luminous efficacy and low CRI of the pc-WLEDs. Exploring new types of sulfides with good thermal stability such as thiogallates might be a new

direction. Moreover, sulfides with different cation sites may give the solution of wide spectral dispersion in the green and red region.

3.4. Nitrides and oxynitrides

Nitride and oxynitride phosphors are newly developed members of the phosphor family. Until now, most of the nitride and oxynitride phosphors applicable for excitation of blue-LED chips were Ce^{3+} - or Eu^{2+} -doped silicon-based compounds, due to the high covalency of the crystal lattices and strong crystal fields of the host lattices [2]. Ce^{3+} - or Eu^{2+} -doped nitride and oxynitride phosphors usually have longer wavelength excitation and emission bands than those of oxide phosphors because of the smaller electronegativity of N^{3-} over O^{2-} . The smaller electronegativity causes stronger nephelauxetic effect (covalency) and the higher negative charge of N^{3-} makes the crystal field splitting of the d orbital of Ce^{3+} or Eu^{2+} larger, according to crystal field theory. Evidence shows that the emission of Eu^{2+} in O^{2-} -containing oxynitrides is normally found in blue to yellow region, as seen with $\text{MSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) [27,50,193–197], $\text{Ba}_3\text{Si}_6\text{O}_{12}\text{N}_2:\text{Eu}^{2+}$ [198], $\text{SrSi}_5\text{AlO}_2\text{N}_7:\text{Eu}^{2+}$ [199], and $\text{SrSiAl}_2\text{O}_3\text{N}_2:\text{Eu}^{2+}$ [199]. Where-

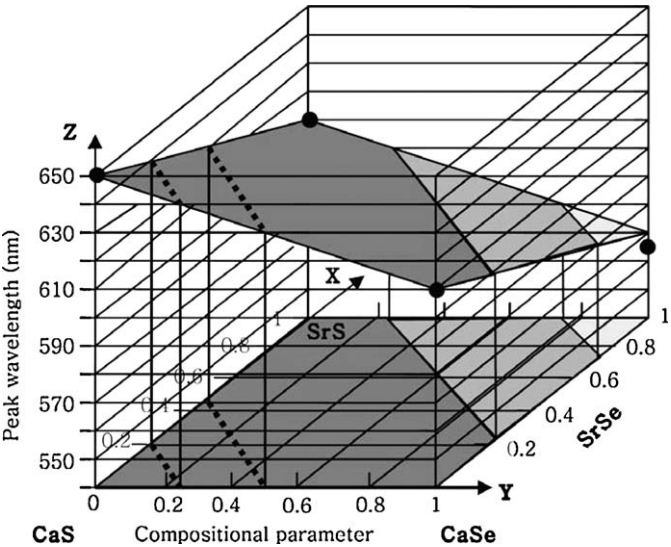


Fig. 31. Peak wavelength diagram for $(\text{Ca}_{1-x}\text{Sr}_x)(\text{Si}_{1-y}\text{Se}_y):\text{Eu}^{2+}$ [185]. Reproduced from J. Solid State Chem. 179 (2006) 2529. Copyright © 2006, Elsevier Inc.

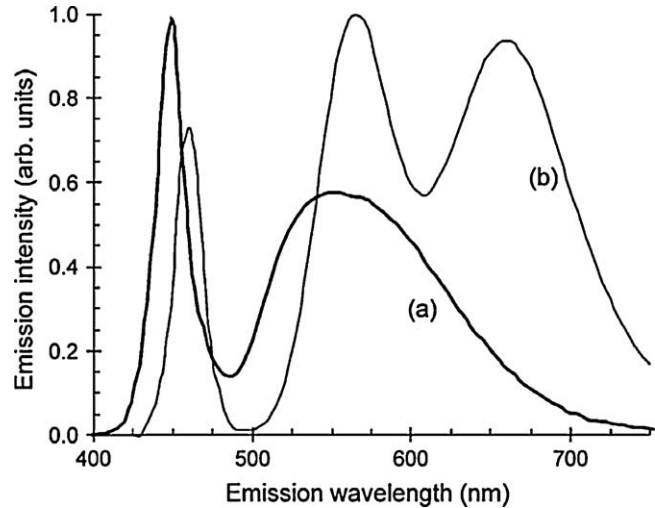


Fig. 32. Emission spectrum of (a) Luxeon Star 3 Watt white-emitting LED and (b) the combination of a 450 nm blue-LED and $\text{Ca}_2\text{SiSi}_4:\text{Eu}$ powder [190]. Reproduced from Mater. Sci. Eng. B 146 (2008) 264. Copyright © 2007, Elsevier B.V.

as the emission of Eu^{2+} in nitrides is generally found in the yellow to deep-red region, as is the case with $\text{CaAlSiN}_3:\text{Eu}^{2+}$ [200–203], $\text{M}_2\text{Si}_3\text{N}_8:\text{Eu}^{2+}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) [204–211], $\text{MSiN}_2:\text{Eu}^{2+}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) [212,213], $\text{LiSi}_2\text{N}_3:\text{Eu}^{2+}$ [214], $\text{SrAlSi}_4\text{N}_7:\text{Eu}^{2+}$ [215] and $\text{Ba}_2\text{AlSi}_5\text{N}_9:\text{Eu}^{2+}$ [216]. Other examples include the incorporation of Si–N in

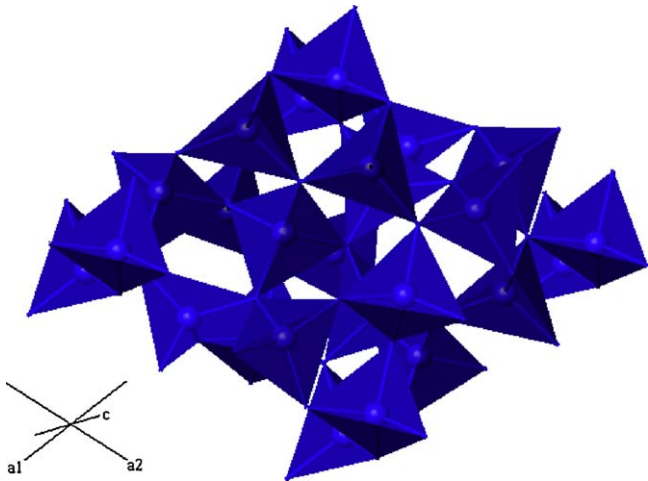


Fig. 33. The structure of $\alpha\text{-Si}_3\text{N}_4$, the blue tetrahedron represents the SiN_4 (data quoted from ICSD 92156).

$\text{YAG}:\text{Ce}$ [119] or $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ [217], which shifts the emission of $\text{Ce}^{3+}/\text{Eu}^{2+}$ towards longer wavelengths.

Chemically, the crystal structures of nitrides (simple binary compounds to complex) are fully described in previous works [2,218–220]. The basic units of the SiN_4 tetrahedron form a three-dimensional network of Si_3N_4 through sharing the corners, as shown in Fig. 33, that is, one N^{3-} is covalently bonded by three Si^{4+} [221]. The introduction of alkaline earth ions or RE ions breaks up the SiN_4 networks, so the degree of cross-linking of the SiN_4 network can be judged by the ratio of metal ions to silicon or silicon to nitrogen [2,222]. Highly condensed nitrides normally have high chemical and thermal stability, which makes them favorable for the host lattices of phosphors [2,222]. Si–N in nitrides can be substituted by Al–O; one of these well-known materials is sialon ceramic phosphor [199,223–232]. Accordingly, Al–O in aluminates can also be replaced by Si–N [119,217,233].

The information on chemical and electronic structures of (oxy)nitride compounds is fundamental and would be helpful in better understanding the luminescent properties of (oxy)nitride phosphors. A good knowledge of the chemical structures is theoretically the base for calculating the electronic structure, bond valence, and Madelung partial lattice energy [208,213,214,216,243]. The electronic structure usually reflects the characteristics of some chemical bonds in (oxy)nitrides [213,214] or the net positive charge of activators in certain environments [235]. The bond valence and Madelung partial lattice energy would give some information on site occupation by different atoms such as $\text{N}^{3-}/\text{O}^{2-}$ or $\text{Al}^{3+}/\text{Si}^{4+}$ etc., which would have considerable effects on luminescence for the derived phosphors but could hardly be determined by XRD, due to their similar scattering factors [243]. Schmidt et al. studied the

Table 7
Characteristic of some phosphors other than YAG:Ce for pc-WLEDs excited by blue-LED chips (nitrides and oxynitrides are not included).

Phosphor	Excitation	Emission	CIE (x, y)	LE (lm/W)	CCT (K)	CRI	Refs.
$\text{Tb}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$	460	545–555	(0.3681, 0.3691) (0.3359, 0.3255)	9.29, 18.31, 22.51	4305, 4404, 5339	80.6, 81.0, 85.8	[152]
$\text{Lu}_2\text{CaMg}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$	466	605	–	20.5	3500	76	[158]
$\text{Sr}_3\text{SiO}_5:\text{Eu}^{2+}$	460	570	(0.37, 0.32)	20–32	–	64	[191]
$\text{Sr}_3\text{SiO}_5:\text{Ce}^{3+}, \text{Li}^+$	460	465–700	(0.3086, 0.3176)	31.7	6857	81	[173]
$\text{Ca}_2\text{BO}_3\text{Cl}:\text{Eu}^{2+}$	450–470	573	(0.33, 0.36)	–	–	–	[178]
$\text{Sr}_3(\text{Al}_2\text{O}_5)_2\text{Cl}_2:\text{Eu}^{2+}$	420, 460	610	–	–	2447, 3546, 4300	76, 66, 90	[179]
$\text{Li}_2\text{SrSiO}_4:\text{Eu}^{2+}$	420	562	(0.3346, 0.3401)	35	–	–	[42]
$\text{LaSr}_2\text{AlO}_5:\text{Ce}^{3+}$	450	556	(0.34–0.36, 0.33–0.36)	20	4200–5500	81–85	[177]
$\text{Y}_3\text{Mg}_2\text{AlSi}_2\text{O}_{12}:\text{Ce}^{3+}$	450	600	–	–	–	–	[192]
$\text{Ba}_2\text{ZnS}_3:\text{Ce}^{3+}, \text{Eu}^{2+}$	420	498, 655	–	–	–	–	[186]
$\text{Ca}_2\text{SiSi}_4:\text{Eu}^{2+}$	450	560, 660	–	–	3000	67	[190]

structure–property relations of Eu^{2+} -doped $\text{M}_2\text{Si}_5\text{N}_8$ and $\text{MSi}_7\text{N}_{10}$ ($\text{M} = \text{Sr}, \text{Ba}$) via examination of the local activator environment in combination with net positive charge calculations for Eu^{2+} by means of extended Hückel method [235]. A high charge density between Eu^{2+} and its ligand sphere, i.e. the more covalent $\text{Eu}-\text{N}$ bond and the lower net positive charge of Eu^{2+} , would redshift the emission of Eu^{2+} since a decrease of the net positive charge of Eu^{2+} reduces the energy separation between the $4f$ and $5d$ orbitals. Electronic structure calculations of anionic model clusters in $\text{M}_2\text{Si}_5\text{N}_8$ and $\text{MSi}_7\text{N}_{10}$ shows that Eu^{2+} sites in $\text{MSi}_7\text{N}_{10}$ have a higher net positive charge than those in $\text{M}_2\text{Si}_5\text{N}_8$, and the emission wavelength of Eu^{2+} in $\text{MSi}_7\text{N}_{10}$ is shorter than that in $\text{M}_2\text{Si}_5\text{N}_8$, which is in accordance with the experimental data (the former is 484 nm emission and the latter is 655 nm for $\text{M} = \text{Ba}$) [235].

The adjustment and control of emission and absorption properties of phosphors is the most demanding task in phosphor design for pc-WLEDs [235]. Take $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ and $\text{MSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) phosphors, for example. Li et al. [208] found that the replacement of Sr by Ca in $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ could result in a spectral shift from 620 to 643 nm for Eu^{2+} emission, while the excitation spectrum is hardly modified. The peak position of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ series varied from 618 to 690 nm with increasing Eu^{2+} ion concentration [206]. A green-yellow emission peaking from 530 to 570 nm was observed for $\text{SrSi}_2\text{O}_{2-\delta}\text{N}_{2+2/3\delta}:\text{Eu}^{2+}$, depending on the exact value of δ [27]. The emission color of $\text{MSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ can also be tuned by changing Eu^{2+} concentration and by substitution of the host lattice cation Sr^{2+} with either Ca^{2+} or Ba^{2+} [196]. Increasing the Eu concentration above 2 mol.% makes the emission of Eu^{2+} redshifted, which is explained by energy migration and energy transfer to Eu^{2+} ions. Partial substitution of Sr^{2+} by either Ca^{2+} or Ba^{2+} also resulted in the redshift of Eu^{2+} emission. In the case of Ca^{2+} substitution, the redshift is explained by an increased crystal field splitting for Eu^{2+} on the smaller Ca^{2+} site vs. the Sr^{2+} site, but the reason of the redshift for Ba^{2+} substitution remains unknown [196]. There is literature on the correlations between structures [2] or compositions [234] and the luminescence properties of (oxy)nitride phosphors.

Another example is $\text{Ca}-\alpha\text{-SiAlON}:\text{Eu}^{2+}$ [236]. $\alpha\text{-SiAlON}$, which is isostructural with $\alpha\text{-Si}_3\text{N}_4$, has a solid solution composition of $\text{M}_x\text{Si}_{12-(m+n)}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n}$ ($x = m/v$, x and v are the solubility and valence of the M ion, respectively). The PL spectra are presented in Fig. 34. The excitation spectrum consists of two broad bands

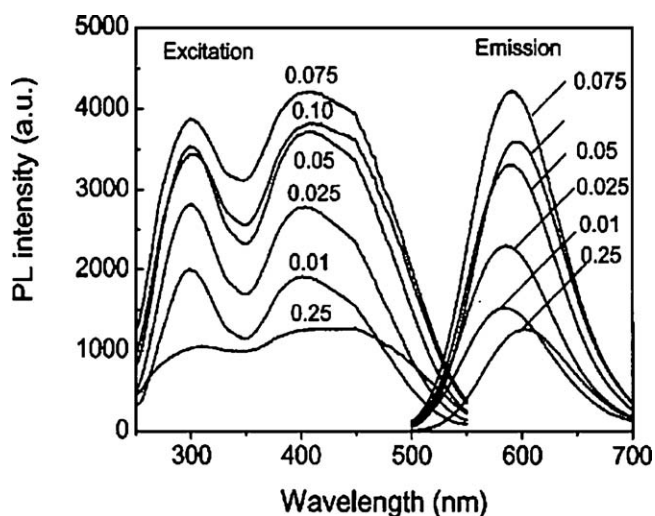


Fig. 34. Excitation and emission spectra of $\text{Ca}-\alpha\text{-SiAlON}:\text{Eu}^{2+}$. ($\lambda_{\text{ex}} = 450$ nm for emission and $\lambda_{\text{em}} = 590$ nm for excitation) [236]. Reproduced from Appl. Phys. Lett. 84 (2004) 5404. Copyright © 2004, American Institute of Physics.

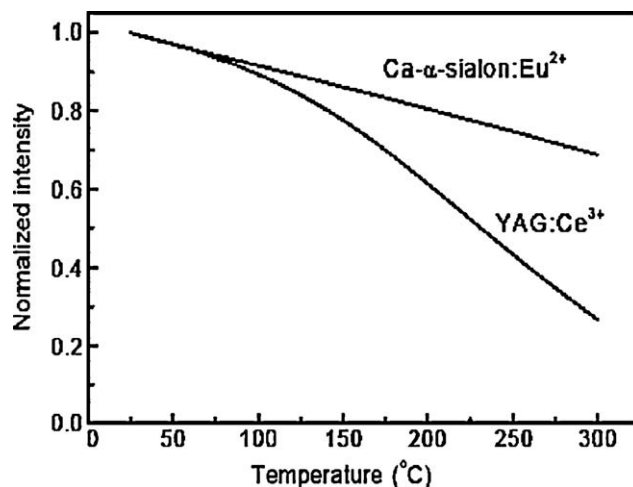


Fig. 35. Temperature dependence of emission intensities of $\text{Ca}-\alpha\text{-sialon}:\text{Eu}^{2+}$ and $\text{YAG}:\text{Ce}^{3+}$ [2]. Reproduced from Sci. Technol. Adv. Mater. 8 (2007) 588. Copyright © 2007, NIMS and Elsevier Ltd.

ranging from the UV to the visible spectral region, which are assigned to absorption of the host lattice (peak at ~ 300 nm) and $f \rightarrow d$ transition of Eu^{2+} (peak at ~ 400 nm), respectively. The intense emission band from 583 to 603 nm with a peak at 590 nm is ascribed to the $d \rightarrow f$ transition of Eu^{2+} . The long wavelengths of the excitation and emission bands of $\text{Ca}-\alpha\text{-SiAlON}:\text{Eu}^{2+}$ indicate that this nitrogen-rich oxynitride lowers the center of gravity of Eu^{2+} $5d$ orbitals and causes a large crystal field splitting [236]. The spectra also show that the $\text{Ca}-\alpha\text{-SiAlON}:\text{Eu}^{2+}$ has more saturation in red than $\text{YAG}:\text{Ce}$. Moreover, the temperature-quenching performance of $\text{Ca}-\alpha\text{-SiAlON}:\text{Eu}^{2+}$ is better than that of $\text{YAG}:\text{Ce}$ [2], as shown in Fig. 35, possibly due to the rigidity (high covalency) of the nitride phosphor.

Xie et al. [237,238] have fabricated white LEDs by using a single $\text{Ca}-\alpha\text{-SiAlON}:\text{Eu}^{2+}$ or $\text{Li}-\alpha\text{-SiAlON}:\text{Eu}^{2+}$ yellow phosphor combined with a blue-LED chip ($\lambda_{\text{em}} = 450$ nm), as demonstrated in Fig. 36. The CCT, luminous efficacy and CRI of $\text{Ca}-\alpha\text{-SiAlON}:\text{Eu}^{2+}$ -converted white LED are 2830 K, 55 lm/W, and 58, respectively [239]. The luminous efficacy is about three times higher than that of

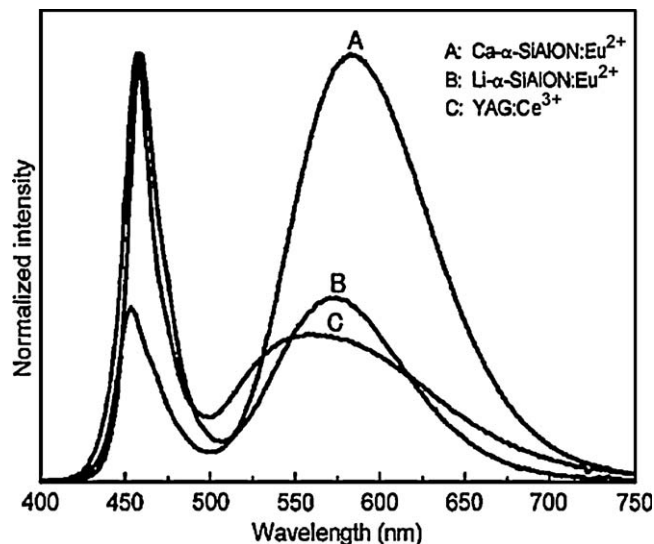


Fig. 36. EL spectra of white LEDs using $\text{Ca}-\alpha\text{-SiAlON}:\text{Eu}^{2+}$ [238], $\text{Li}-\alpha\text{-SiAlON}:\text{Eu}^{2+}$ and $\text{YAG}:\text{Ce}^{3+}$, measured under a forward-bias current of 20 mA at room temperature [237]. Reproduced from Appl. Phys. Lett. 88 (2006) 101104. Copyright © 2006, American Institute of Physics.

Table 8
Synthesis methods of nitrides and oxynitride phosphors.

Synthesis method	Phosphors	Raw materials	Temperature (K)	Pressure (MPa, N ₂ –H ₂)	Refs.
Solid-state reaction	CaAlSiN ₃ :Ce	Ca ₃ N ₂ , α-Si ₃ N ₄ , AlN, Li ₃ N, CeN	1973	0.48	[243]
	Ba ₂ AlSi ₅ N ₉ :Eu	Ba, Eu, Si ₃ N ₄ , AlN	1873	Ambient pressure	[216]
Gas-pressure sintering	Ca-α-SiAlON:Ce, Sm, Dy	α-Si ₃ N ₄ , AlN, CaCO ₃ , rare-earth oxides	2023	1.02	[244]
Gas-reduction nitridation	LaSi ₃ N ₅ :Ce	La ₂ O ₃ , CeO ₂ , SiO ₂	1723	Ambient pressure (NH ₃ –CH ₄ atmosphere)	[245]
	Ca-α-SiAlON:Eu	Si ₃ N ₄ , AlN, SiO ₂ , CaO	2023		[246]
Spray pyrolysis	SrSi ₂ O _{2–3} N _{2+2/3δ} :Eu	Si ₃ N ₄ , Sr(NO ₃) ₂ , Eu ₂ O ₃	1573	Ambient pressure	[247]
	CaSrSi ₅ N ₈ :Eu	SrCO ₃ , Si ₃ N ₄ , Eu ₂ O ₃ , CaCN ₂	1823		[248]
Calcium cyanamide reduction					
Self-propagating high-temperature synthesis	CaAlSiN ₃ :Eu	Si, Ca, Al, Eu	1823	Ambient pressure	[202]
One-Pot synthesis	M ₂ Si ₅ N ₈	Nanocrystalline silicon, M(NH ₂) ₂ M = Sr, Ba, Eu	1673	30	[249]
Carbothermal reduction and nitridation	Sr ₂ Si ₅ N ₈ :Eu	SrCO ₃ , Si ₃ N ₄ , Eu ₂ O ₃ , C	1773	Ambient pressure	[206]
Alloy method + nitride mixture + hot isostatic pressing	Sr _x Ca _{1–x} AlSiN ₃ :Eu	Sr, Ca, Al, Si, Eu, Ca ₃ N ₂ , α-Si ₃ N ₄ , AlN	2173	190	[250]

incandescent bulbs (16–18 lm/W), and the CRI is lower than that of WLED using YAG:Ce but close to that of fluorescent lamps ($R_a = 60$) [232]. The Li-α-SiAlON:Eu²⁺-converted LED offers CCT in the range of 4000–8000 K with R_a varying from 63 to 74 and luminous efficacy from 40 to 44 lm/W, depending on the variation of the Li-α-SiAlON:Eu²⁺ composition. The CCT and CRI values are higher than those of Ca-α-SiAlON:Eu²⁺-converted white LEDs. The luminous efficacy is close to that of YAG:Ce-based white LED, but the R_a is lower [237]. There are also many pc-WLEDs using more than one (oxy)nitride phosphor with better performance [2,239–242].

Nitride and oxynitride phosphors, however, suffer drawbacks such as their critical synthesis condition (high temperature, high N₂ pressure, and air-sensitive raw materials), the lack of general synthetic routes and the limited understanding of their crystal structures as a result of the difficulties in crystal growth [2]. Over the past several years, much research effort has been devoted to the development of some relatively simple techniques to synthe-

size nitrides and oxynitrides with high purity, good crystallinity and narrow size distribution. Table 8 summarizes the synthesis methods of nitride and oxynitride phosphors presented in literature recently.

Table 9 shows the properties of (oxy)nitride phosphors which could be excited by blue light. As seen in Table 9, most of the phosphors applicable for blue-LED chips are nitrides, which imply the important role of N^{3–}. Generally, the rigidity of the covalenced silicon-based nitride or oxynitride compounds causes a small Stokes shift of Ce³⁺ and Eu²⁺ [2]. Thus, those nitride or oxynitride phosphors that emitted yellow to red lights usually absorb blue to green lights, which favors their application in blue-LED chips for generating white light. Nevertheless, the intense absorption of green light for the red phosphors will unavoidably sacrifice luminous efficacy, although it would improve the CRI of the white LEDs.

Although much work on (oxy)nitride phosphors has been reported, there are few data on phase diagram of (oxy)nitrides. It is

Table 9
Properties of (oxy)nitride phosphors.

Phosphors	Excitation (nm)	Emission (nm)	CIE (x, y)	CRI	CCT (K)	LE (lm/W)	Refs.
CaAlSiN ₃ :Eu ²⁺	400–470	649	(0.647, 0.347)	–	–	–	[202]
CaAlSiN ₃ :Ce ³⁺	460	580	(0.389, 0.345)	70	3722	50	[243]
Sr ₂ Si ₅ N ₈ :Eu ²⁺	400–460	625	(0.621, 0.368)	–	–	–	[206]
			(0.669, 0.322)				
Sr ₂ Si ₅ N ₈ :Ce ³⁺	370–450	553	–	–	–	–	[251]
Ba ₂ Si ₅ N ₈ :Eu ²⁺	460	572–650	(0.521, 0.472)	50–70	2700–4000	–	[205]
			(0.668, 0.327)				
Ba ₂ AlSi ₅ N ₉ :Eu ²⁺	450	584	–	–	–	–	[216]
SrAlSi ₄ N ₇ :Eu ²⁺	450	632, 500	–	–	–	–	[215]
SrSi ₂ O ₂ N ₂ :Eu ²⁺	450	535–554	(0.337, 0.619)	–	–	–	[196]
SrSiN ₂ :Eu ²⁺	300–530	670–685	–	–	–	–	[213]
CaSiN ₂ :Ce ³⁺	450–550	625	–	–	–	–	[212]
Ca-α-SiAlON:Eu ²⁺	450	500–700	(0.492, 0.495)	58	2600–3500	55	[239,246]
			(0.538, 0.456)				
Li-α-SiAlON:Eu ²⁺	460	573	–	72	6150	43	[237]
γ-AlON:Mn–Mg	445	512	(0.217, 0.706)	–	–	–	[252]
MgSiN ₂ :Mn ²⁺	370–450	550–800	–	–	–	–	[253]
LaAl(Si _{6–z} Al _z)(N _{10–2O₂}):Ce ³⁺	405	460–500	–	95	2830	20	[254]
CaSi ₂ O _{2–3} N _{2+2/3δ} :Eu ²⁺	460	534–562	(0.3396, 0.3474)	74	5223	20	[255]

thus of high scientific importance and worth great efforts to draw the phase diagram and find new members of (oxy)nitrides with detailed structural data from fundamental and practical points of view. Tuning or adjusting the excitation and emission spectra of (oxy)nitride phosphors via compositional variation according to phase diagram to satisfy a diversity of demands also makes these efforts rewarding. Accurately controlling and determining the compositions of O/N in (oxy)nitrides is also of significance since the O/N ratio has a large effect on the emissions properties of (oxy)nitride phosphors. There has been no general route to characterize the O/N ratio with high accuracy for (oxy)nitrides, which usually contain impurities. Morphology with desired size and shape is an essential issue for integrating these (oxy)nitride phosphors in pc-WLEDs. Generally, the critical synthesis conditions (high temperature, air-sensitive raw materials, etc.) make it difficult to control the crystal growth.

4. Phosphors excited by NUV-LED chips

4.1. Single-phased white-emitting phosphors in pc-WLEDs

pc-WLEDs made by means of blue-LED + yellow phosphor suffer weaknesses such as poor color rendering index and low stability of the color temperature, due to deterioration of the chip or the phosphors. RGB LEDs might also encounter instability of color temperature for the degradation of different color LEDs or variation of driving current. Moreover, since RGB LEDs require different driving current for different color LEDs, the fabrication is rather complicated. However, white UV-LEDs fabricated by UV-LED chips coated with white light-emitting single-phased phosphors or RGB tri-color phosphors could conquer the aforementioned pitfalls owing to the invisible emission of the LED chip.

In oxide-based luminescent materials, Ce^{3+} or Eu^{2+} could efficiently absorb NUV light and give blue to green broadband emissions [53,56]. To give proper energy dispersion in the visible region, co-doping activators are required for single-phased white-emitting phosphors such as Eu^{2+} - Mn^{2+} [10–13,46,256–262] and Ce^{3+} - Mn^{2+} [263]. Because the $5d$ - $4f$ transition energy of Ce^{3+} is higher than that of Eu^{2+} , Ce^{3+} - Eu^{2+} paired ions are also designed for white light generation through energy transfer from Ce^{3+} to Eu^{2+} [163,264,265]. In general, the components of white light are normally contributed by different activators or by one kind of activator at different crystal sites in a single phase [13,259,263,264]. Thus, a proper crystal field at the substitution sites for these activators is necessary to generate white light.

$\text{Ba}_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+},\text{Mn}^{2+}$ [10] is a typical example of a single-phased white-emitting phosphor, which shows three emission bands at around 442, 505, and 620 nm as shown in Fig. 37. There are three different Ba sites in a unit cell: 12-coordinated Ba(I) sites with Ba–O bond length of 2.50 Å, 10-coordinated Ba(II) sites with Ba–O bond length of 1.05 Å, and 10-coordinated Ba(III) sites with Ba–O bond length of 1.00 Å. Electron paramagnetic resonance measurement demonstrates that Eu^{2+} ions occupy three different Ba^{2+} sites. The 442 nm emission peak is assigned to the $5d \rightarrow 4f$ transition of Eu(I) in Ba(I) sites due to weaker crystal field strength (longer bond length), whereas the 505 nm emission peak is assigned to the $5d \rightarrow 4f$ transition of Eu(II)/Eu(III) in Ba(II)/Ba(III) sites due to stronger crystal field strength (shorter bond length). Accordingly, the 620 nm emission peak is ascribed to the $d \rightarrow d$ transition $^4T_1 \rightarrow ^6A_1$ of Mn^{2+} .

Another example is $\text{SrZn}_2(\text{PO}_4)_2:\text{Eu}^{2+},\text{Mn}^{2+}$ [13]. A typical spectrum of $\text{SrZn}_2(\text{PO}_4)_2:\text{Eu}^{2+},\text{Mn}^{2+}$ is illustrated in Fig. 38. There are one seven-coordinated Sr^{2+} site and two four-coordinated Zn^{2+} sites. Considering the ion radii of Eu^{2+} (1.20 Å), Mn^{2+} (0.66 Å), Sr^{2+} (1.21 Å), and Zn^{2+} (0.60 Å), Eu^{2+} and Mn^{2+} prefer Sr^{2+} and Zn^{2+} sites, respectively. Therefore, the 416 nm blue emission band is assigned

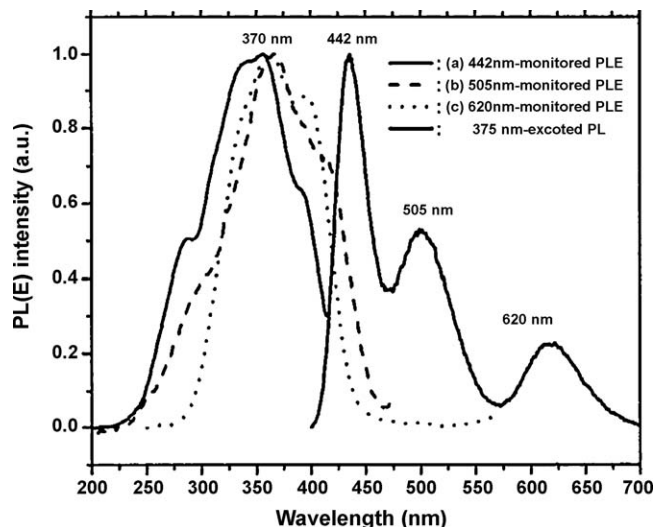


Fig. 37. PLE spectra monitored at (a) 442 nm, (b) 505 nm, and (c) 620 nm and PL spectrum excited at 375 nm of $\text{Ba}_3\text{MgSi}_2\text{O}_8:0.075\text{Eu}^{2+}, 0.05\text{Mn}^{2+}$ [10]. Reproduced from Appl. Phys. Lett. 84 (2004) 2931. Copyright © 2004, American Institute of Physics.

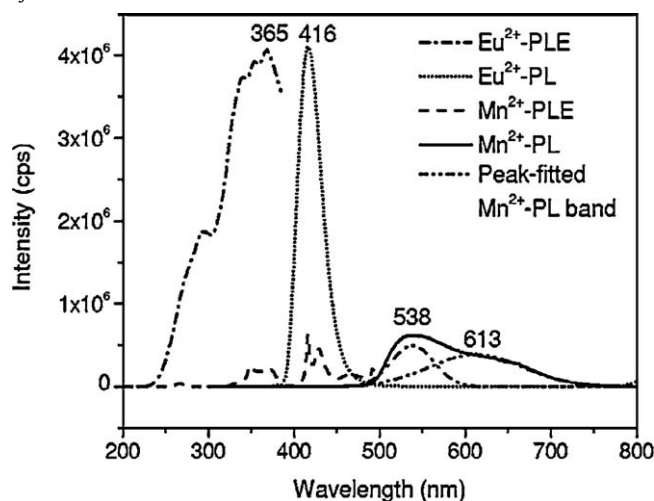


Fig. 38. PL and PLE spectra for $(\text{Sr}_{0.99}\text{Eu}_{0.01})\text{Zn}_2(\text{PO}_4)_2$ ($\lambda_{\text{ex}} = 365$ nm and $\lambda_{\text{em}} = 416$ nm) and $\text{Sr}(\text{Zn}_{1.96}\text{Mn}_{0.04})(\text{PO}_4)_2$ ($\lambda_{\text{em}} = 538$ nm and $\lambda_{\text{ex}} = 416$ nm) and peak-fitting spectra for luminescence band of $\text{Sr}(\text{Zn}_{1.96}\text{Mn}_{0.04})(\text{PO}_4)_2$ [13]. Reproduced from Appl. Phys. Lett. 88 (2006) 101903. Copyright © 2006, American Institute of Physics.

to the emission of Eu^{2+} in Sr^{2+} sites and the 538 nm and 613 nm emission peaks are assigned to the emission of Mn^{2+} in two different crystallographic Zn^{2+} sites.

Jong et al. [261] systematically studied the luminescence properties of Eu^{2+} - and Mn^{2+} -co-doped $\text{M}_3\text{MgSi}_2\text{O}_8$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$). All the blue and green bands of Eu^{2+} emission and the red band of Mn^{2+} emission were shifted to longer wavelengths when cation M was substituted with smaller cations in the order of Ba, Sr, and Ca. This can be explained by the stronger crystal field strength and the covalence effects [261].

Xiao et al. recently investigated Eu^{2+} - Mn^{2+} co-doped $\text{Ba}_2\text{Ca}(\text{B}_3\text{O}_6)_2$ phosphor, which exhibited a tunable color emission from blue to white and finally to red under UV light, by adjusting the ratio of Eu^{2+} and Mn^{2+} appropriately [262]. Fig. 39 presents the PL spectra of $\text{Ba}_2\text{Ca}(\text{B}_3\text{O}_6)_2:0.04\text{Eu}^{2+}, y\text{Mn}^{2+}$ phosphors with varied Mn^{2+} concentrations. The effective ET from Eu^{2+} to Mn^{2+} was observed by the significant decrease of blue emission intensity of Eu^{2+} with increasing concentration of Mn^{2+} . The energy transfer efficiency (η_{T}) as a function of Mn^{2+} concentration (y) was found to

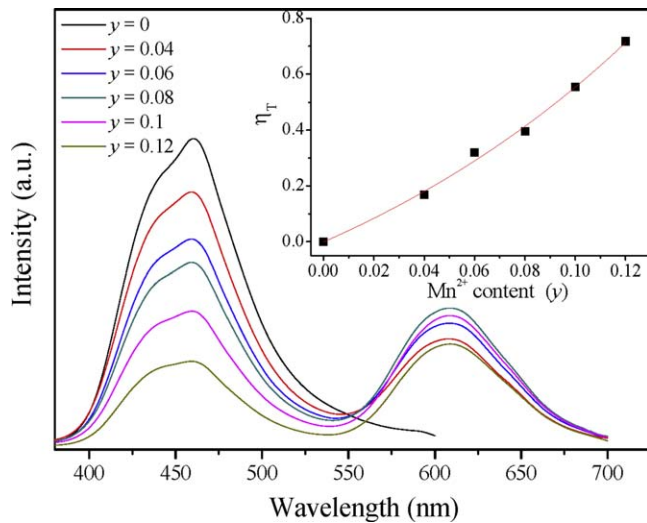


Fig. 39. PL spectra of $\text{Ba}_2\text{Ca}(\text{B}_3\text{O}_6)_2:0.04\text{Eu}^{2+}, y\text{Mn}^{2+}$ phosphors ($\lambda_{\text{ex}} = 330 \text{ nm}$). Inset shows the dependence of the energy transfer efficiency η_T on the Mn^{2+} contents (y) [262]. Reproduced from *Physica B* 405 (2010) 891. Copyright © 2009, Elsevier B.V.

increase gradually as shown in the inset of Fig. 39. Corresponding CIE chromaticity coordinates of the series example were calculated and are presented in Fig. 40. The optimal $\text{Ba}_2\text{Ca}(\text{B}_3\text{O}_6)_2:0.04\text{Eu}^{2+}, 0.12\text{Mn}^{2+}$ phosphor could generate warm white light with CIE coordinates of ($x = 0.37, y = 0.25$) and CCT of 2654 K, implying its potential application for pc-WLEDs.

There are many other phosphors co-doped with Eu^{2+} and Mn^{2+} that could be used to realize white light emission, including $\text{Ca}_2\text{MgSi}_2\text{O}_7$ [266], $\text{CaAl}_2\text{Si}_2\text{O}_8$ [12], $\text{La}_{0.827}\text{Al}_{11.9}\text{O}_{19.09}$ [267], and $\text{Ba}_2\text{SiO}_3\text{Cl}_2$ [260].

The energy transfer mechanism from Eu^{2+} to Mn^{2+} can be determined by the following relation according to Dexter's energy transfer formula of multipolar interaction [65,66]:

$$\frac{\eta_0}{\eta} \propto C^{n/3} \quad (6)$$

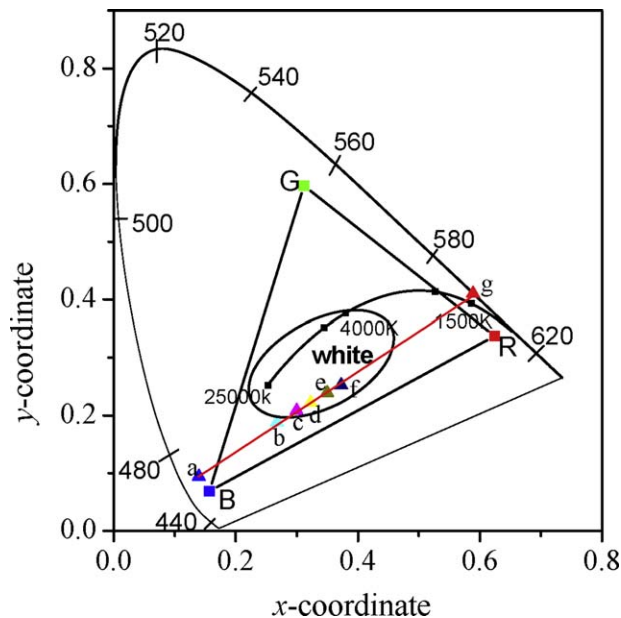


Fig. 40. CIE chromaticity coordinates of $\text{Ba}_2\text{Ca}(\text{B}_3\text{O}_6)_2:x\text{Eu}^{2+}, y\text{Mn}^{2+}$ phosphors represented as color dot (a, b, c, d, e, f, g) ($x = 0.04$ excited at 330 nm, $x = 0$ excited at 402 nm) [262]. Reproduced from *Physica B* 405 (2010) 891. Copyright © 2009, Elsevier B.V.

where η_0 and η are the luminescence quantum efficiency of Eu^{2+} in the absence and presence of Mn^{2+} , respectively; C is the sum content of Eu^{2+} and Mn^{2+} ; $n = 6, 8$, and 10 , corresponding to $d-d$, $d-q$ and $q-q$ interactions, respectively. Experimentally, I_0 and I , which are luminescence intensity of Eu^{2+} in the absence and presence of Mn^{2+} , can be used to represent η_0 and η approximately. n determines the interaction type. Evidence shows that energy transfer from Eu^{2+} to Mn^{2+} is through the $d-q$ mechanism [12,13]. The transfer probability $P_{\text{Eu-Mn}}^{dq}$ is given in the following equation [65,268]:

$$P_{\text{Eu-Mn}}^{dq} = 0.63 \times 10^{28} \times \frac{f_q \lambda_s^2 Q_A}{\tau_{s0} R_{\text{Eu-Mn}}^8 f_d E_s^4} \int F_S(E) F_A(E) dE \quad (7)$$

where $Q_A = 4.8 \times 10^{-16} f_d$, which is the absorption cross section of Mn^{2+} ; $f_d = 10^{-7}$ and $f_q = 10^{-10}$, which are the oscillator strengths of the dipole and quadruple electrical absorption transitions for Mn^{2+} , respectively. λ_s (in Å) and E_s (in eV) are the emission wavelength and emission energy of Eu^{2+} ; $\int F_S(E) F_A(E) dE$ is the spectral overlap of the Eu^{2+} emission $F_S(E)$ and the Mn^{2+} excitation $F_A(E)$; $R_{\text{Eu-Mn}}$ is the distance between Eu^{2+} and Mn^{2+} ; and τ_{s0} is the lifetime of Eu^{2+} in the absence of Mn^{2+} . According to Eq. (7), the energy transfer efficiency is correlated with $R_{\text{Eu-Mn}}$ and the spectral overlap. The energy transfer efficiency η_T can also be calculated by Eq. (8) [269]:

$$\eta_T = 1 - \frac{\tau_s}{\tau_{s0}} \quad (8)$$

where τ_s is the lifetime of Eu^{2+} in the presence of Mn^{2+} . The critical distance for energy transfer from Eu^{2+} to Mn^{2+} in phosphors can be calculated according to Eq. (7) and is approximately 10 Å [12,13,32].

Recently, Setlur et al. reported the Eu^{2+} - Mn^{2+} co-doped phosphor saturation phenomenon in pc-WLEDs [270]. The 5 mm LED lamps were fabricated by combining 405 nm LED chips and $\text{Ca}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$ (4%), Mn^{2+} (9%) halophosphate phosphors. The saturation, evidenced by pulsed LED measurements, was due to high light flux incident on the phosphors in these lamps. A pulse with frequency of $\sim 5 \text{ Hz}$ and variable pulse length of 0.5–110 ms was used. To prevent excited state buildup over multiple pulses, the pulse length had to be significantly shorter than the pulse period.

Fig. 41 depicts the variation of integrated Eu^{2+} and Mn^{2+} emission efficiencies with pulse length (5 Hz pulse period). The reduction of Eu^{2+} and Mn^{2+} emission efficiencies is caused by

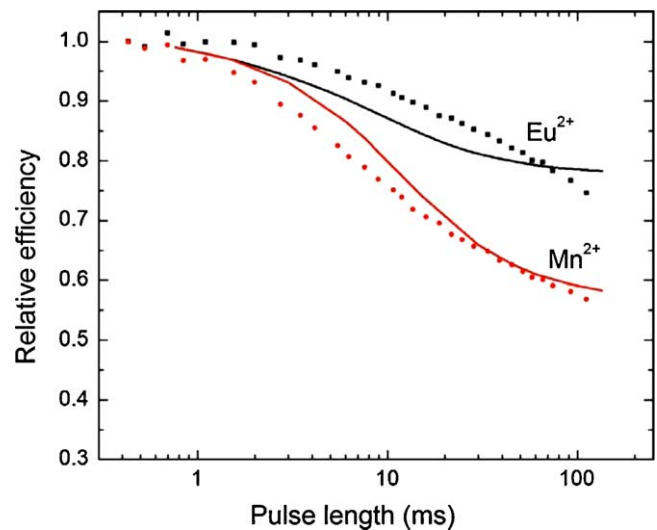


Fig. 41. Integrated Eu^{2+} emission and Mn^{2+} emission efficiencies in a $\text{Ca}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$ (4%), Mn^{2+} (9%) coated pc-LED vs. pulse length with a 5 Hz pulse period. The solid lines are the calculated efficiencies using the integrated solution to equations in Ref. [270]. Reproduced from *Appl. Phys. Lett.* 92 (2008) 081104. Copyright © 2008, American Institute of Physics.

saturation and the temperature effects are excluded. The quenching of Mn^{2+} emission at long pulse length is owed to the long lifetime of Mn^{2+} emission (~ 11.3 ms). The Eu^{2+} emission is not supposed to quench at long pulse length due to the fast radiative rate of Eu^{2+} (~ 580 ns), but Fig. 42(a) clearly shows that a decrease of Eu^{2+} intensity occurs over ~ 20 ms timescale and is directly correlated with increased population of Mn^{2+} excited states. Additionally, the Mn^{2+} decay profile in Fig. 42(a) has additional nonradiative components which are not present at lower intensity, suggesting that there exists ET between the excited Mn^{2+} ions [270]. Using the equations [270] based on the ground-state depletion [271,272] and ET between excited Mn^{2+} ions [272] and between Eu^{2+} – Mn^{2+} dual ions (excited), the calculation results with saturation coincide with the experimental results, as shown in Fig. 42(b). The conclusion is that the ET between excited Mn^{2+} ions, $\text{Eu}^{2+} \rightarrow \text{Mn}^{2+}$ energy transfer, and Mn^{2+} ground-state depletion is responsible for the quenching of $\text{Ca}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$, Mn^{2+} in the LEDs lamps. Phosphors with shorter lifetimes or lamps with relatively low incident flux on Eu^{2+} – Mn^{2+} phosphors are recommended for practical applications [270].

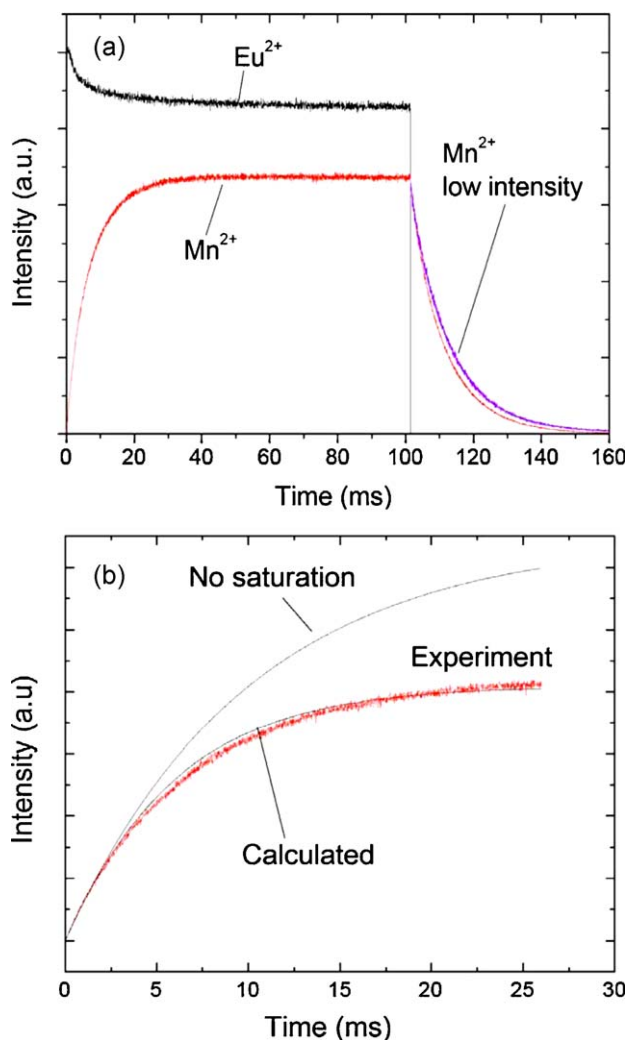


Fig. 42. (a) Luminescence intensity of Eu^{2+} (~ 470 nm) and Mn^{2+} (~ 600 nm) in a $\text{Ca}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$ (4%), Mn^{2+} (9%) pc-LED with a 100 ms pulse length. The Mn^{2+} decay in the pc-LED is compared to the Mn^{2+} decay in a low intensity spectrometer measurement. (b) Mn^{2+} luminescence buildup (600 nm) in a $\text{Ca}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$ (4%), Mn^{2+} (9%) pc-WLED using a pulse period of ~ 2.5 Hz and pulse length of 30 ms vs. a calculated buildup curve from the integrated solution to equations and in the absence of saturation [270]. Reproduced from Appl. Phys. Lett. 92 (2008) 081104. Copyright © 2008, American Institute of Physics.

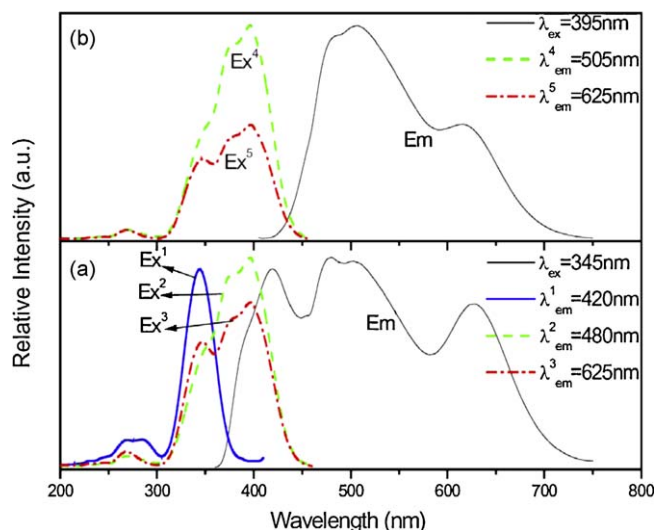


Fig. 43. The PL and PLE spectra of $\text{Ba}_{1.94}\text{Ce}_{0.03}\text{Na}_{0.03}\text{Ca}_{0.97}\text{Mn}_{0.03}(\text{BO}_3)_2$ [263]. Reproduced from J. Electrochem. Soc. 155 (2008) J310. Copyright © 2008, The Electrochemical Society.

$\text{Ba}_2\text{Ca}(\text{BO}_3)_2:\text{Ce}^{3+},\text{Mn}^{2+}$ phosphors are presented as an example of Ce^{3+} – Mn^{2+} codoped white light phosphors [263]. Three emission bands located at 420, 480 and 625 nm are obtained under the excitation of 345 nm as shown in Fig. 43(a). Additionally, upon excitation with 395 nm light, two emissions peaked at 505 and 625 nm are observed, as shown in Fig. 43(b). The blue and green lights are obtained by the two types of Ce^{3+} which occupy $\text{Ba}^{2+}[\text{Ce}^{3+}(1)]$ and $\text{Ca}^{2+}[\text{Ce}^{3+}(2)]$ sites, respectively, while, Mn^{2+} ions could enter the Ca^{2+} sites and emit red light. ET from $\text{Ce}^{3+}(1) \rightarrow \text{Ce}^{3+}(2)$, $\text{Ce}^{3+}(1) \rightarrow \text{Mn}^{2+}$, and $\text{Ce}^{3+}(2) \rightarrow \text{Mn}^{2+}$ are observed in this host. The warm white lights with R_a of 95.43 ($\lambda_{\text{ex}} = 345$ nm) and of 86.37 ($\lambda_{\text{ex}} = 395$ nm) are obtained by combining selected phosphors with UV or violet LEDs.

$\text{Sr}_3\text{B}_2\text{O}_6:\text{Ce}^{3+},\text{Eu}^{2+}$ phosphors are illustrated for white-emitting phosphors with Ce^{3+} – Eu^{2+} pairs [273]. The emission spectrum gives two emission bands with peaks at 434 and 574 nm, as shown in Fig. 44, which are ascribed to the emissions of Ce^{3+} and Eu^{2+} , respectively. The energy transfer mechanism is dominated by an electric dipole–dipole interaction. In addition, a tunable color from blue through white to red is obtained by adjusting the ratio of $\text{Ce}^{3+}/\text{Eu}^{2+}$.

To investigate the possible application of phosphors for WLEDs, there are some auxiliary characteristics of white light that need to be considered, including CIE chromaticity diagram, CCT, CRI, and LE. Frequently, blends of different phosphors gain better performance for pc-WLEDs. Fig. 45 presents the luminescence spectra of $\alpha\text{-Ca}_2\text{P}_2\text{O}_7:\text{Eu}^{2+},\text{Mn}^{2+}$ blue-orange phosphor and $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ green phosphor, and pc-WLEDs combined by NUV-GaN chip with these

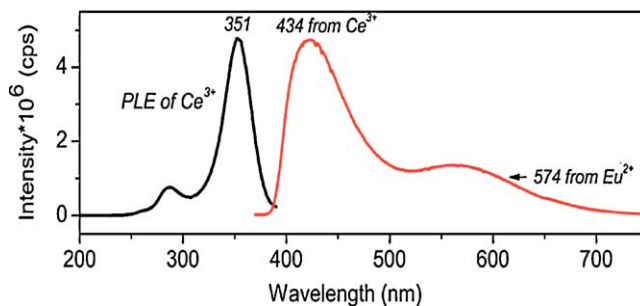


Fig. 44. PL ($\lambda_{\text{ex}} = 351$ nm) and PLE ($\lambda_{\text{em}} = 434$ nm) spectra of $\text{Sr}_3\text{B}_2\text{O}_6:\text{Ce}^{3+},\text{Eu}^{2+}$ [273]. Reproduced from Appl. Phys. Lett. 91 (2007) 081902. Copyright © 2007, American Institute of Physics.

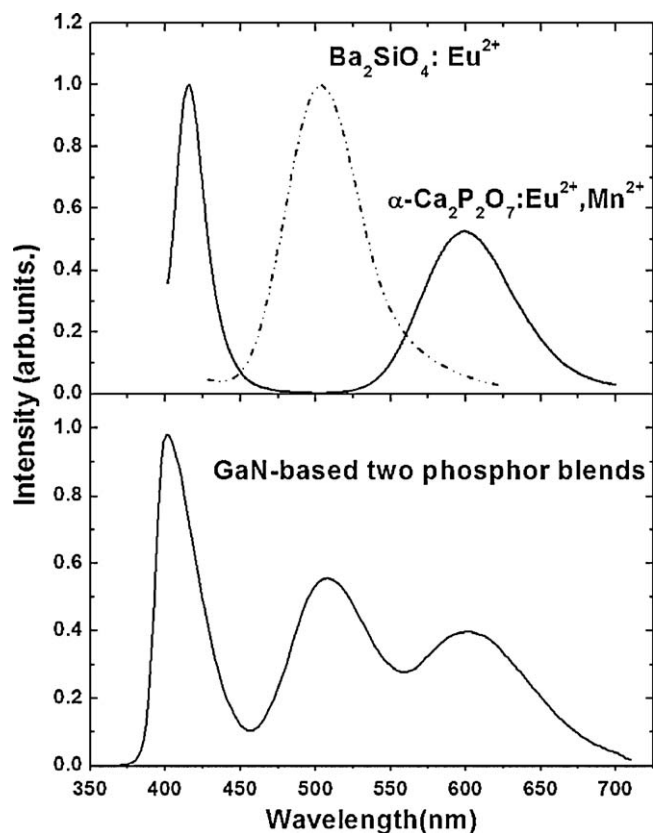


Fig. 45. Luminescence spectra of $\alpha\text{-Ca}_2\text{P}_2\text{O}_7:0.04\text{Eu}^{2+}, 0.12\text{Mn}^{2+}$ and $\text{Ba}_2\text{SiO}_4:0.03\text{Eu}^{2+}$ phosphors (a) and the UV-pumped white LED with the blends of $\alpha\text{-Ca}_2\text{P}_2\text{O}_7:0.04\text{Eu}^{2+}, 0.12\text{Mn}^{2+}$ and $\text{Ba}_2\text{SiO}_4:0.03\text{Eu}^{2+}$ phosphors under the forward-bias currents of 20 mA (b) [46]. Reproduced from Appl. Phys. Lett. 90 (2007) 261113. Copyright © 2007, American Institute of Physics.

two phosphor blends. The pc-WLEDs exhibit good characteristics with CIE coordinates of $(x = 0.27, y = 0.30)$, CRI of 78, and LE of 9 lm/W upon the forward-bias current of 20 mA [46]. The dependence of CIE chromaticity coordinates and CRI on the forward-bias currents of the pc-WLEDs is shown in Fig. 46, indicating the low color-point

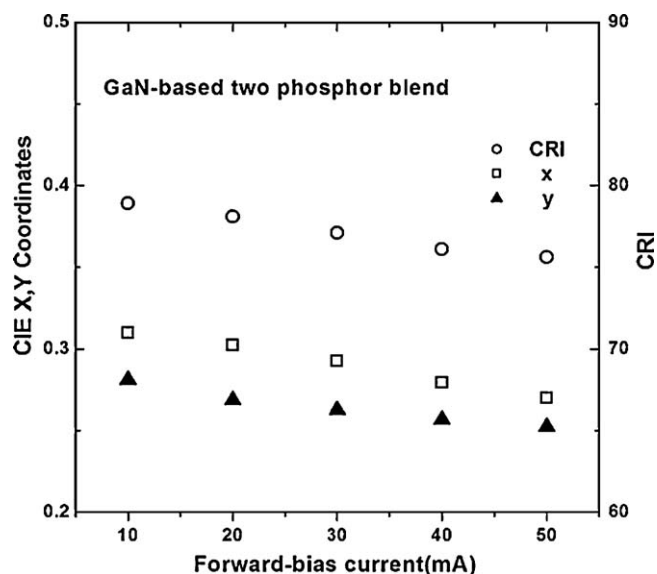


Fig. 46. CIE chromaticity coordinates and CRI of UV-pumped white LED with $\alpha\text{-Ca}_2\text{P}_2\text{O}_7:0.04\text{Eu}^{2+}, 0.12\text{Mn}^{2+}$ and $\text{Ba}_2\text{SiO}_4:0.03\text{Eu}^{2+}$ phosphors with increasing forward-bias currents from 10 to 50 mA [46]. Reproduced from Appl. Phys. Lett. 90 (2007) 261113. Copyright © 2007, American Institute of Physics.

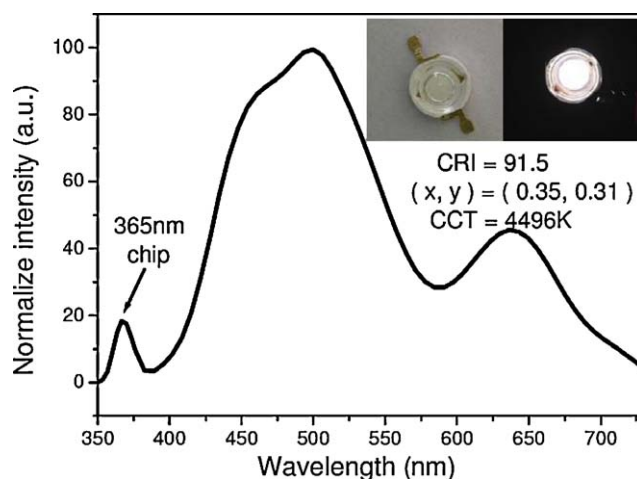


Fig. 47. EL spectrum of a white LED lamp fabricated using a UV-chip (365 nm) and a phosphor blend of $(\text{Ca}_{0.98}\text{La})_9\text{La}(\text{PO}_4)_7:0.005\text{Eu}^{2+}, 0.015\text{Mn}^{2+}$ and $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ under a forward bias of 350 mA [276]. Reproduced from Opt. Express 18 (2010) 5089. Copyright © 2010, Optical Society of America.

variation properties, which is a very important element for the application. An excellent CRI of 98 has been obtained from $\text{Ca}_{6-x-y}\text{Mg}_{x-z}(\text{PO}_4)_4:\text{Eu}^{2+}, \text{Mn}^{2+}$ mixed with $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ green-emitting phosphors integrated with NUV-LED [274].

To make WLEDs for interior lighting applications, pc-WLEDs with high CRI of 84 and 92 were fabricated by using 375 nm emissive chips with white light-emitting phosphors $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}$ and $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}, \text{Mn}^{2+}$, respectively [275]. Most recently, Chen's group developed a warm WLED, as shown in Fig. 47, with CIE chromaticity coordinates of $(x = 0.35, y = 0.31)$, superior CRI of 91.5, and lower CCT of 4496 K by combining a 365 nm NUV-InGaN chip with a mixed phosphor blend of yellow-emitting $(\text{Ca}_{0.98}\text{Eu}_{0.005}\text{Mn}_{0.015})_9\text{La}(\text{PO}_4)_7$ and blue-emitting $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ [276].

There are some other co-doping ion pairs which could generate white light, such as $\text{Ce}^{3+}\text{-Tb}^{3+}$ in $\text{Ca}_2\text{Al}_2\text{SiO}_7$ [277], $\text{Bi}^{3+}\text{-Eu}^{3+}$ in $\text{Y}_4\text{MgSi}_3\text{O}_{13}$ [278], and $\text{Dy}^{3+}\text{-Ce}^{3+}$ in $\text{GdAl}_3(\text{BO}_3)_4$ [279,280]. Eu^{3+} singly-doped phosphors with the excitation of UV light can also realize white light, such as $\text{BaY}_2\text{ZnO}_5:\text{Eu}^{3+}$ [281] and $\text{CaIn}_2\text{O}_4:\text{Eu}^{3+}$ [282,283]. In these cases, the concentration of Eu^{3+} should remain low to reduce cross-relaxation, which would result in blue and green emission from $^5\text{D}_3$, $^5\text{D}_2$, and $^5\text{D}_1$ levels of Eu^{3+} . Table 10 gives a summary of single-phased white-emitting phosphors applicable for pc-WLEDs. As seen in Table 10, only a few phosphors are suitable for NUV excitation. For the development of pc-WLEDs as the next generation lighting system, finding suitable white-emitting phosphors which have broad absorption in NUV region with good auxiliary characteristics, i.e. CIE chromaticity coordinates, CCT, and CRI, is a significant research subject.

4.2. Tri-color phosphors

It is considered that NUV-LED + RGB phosphors is one of the best approaches to generate white light for both high luminous efficiency and high CRI [292,293]. The blue and green phosphors, such as $\text{Ca}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$, $\text{BaMgAl}_{14}\text{O}_{23}:\text{Eu}^{2+}/\text{Mn}^{2+}$, $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}/\text{Mn}^{2+}$, etc. are commercially available and could meet the requirements of NUV excitation in terms of spectra. The newly developed (oxy)nitride phosphors could also be efficient blue or green phosphors [2,234]. However, the identified red phosphors for NUV white LED application are scarce. The reported nitride-based red phosphors that absorb not only the NUV lights but also the blue-green lights are excluded here because the absorption of visible light would decrease the total luminous efficiency. Additionally, the preparation of the nitride-based phosphors is

Table 10

Summary of some single-phased white-emitting phosphors applicable for pc-WLEDs.

Phosphor	Excitation (nm)	Emission (nm)	CIE (x, y)	LE (lm/W)	CCT (K)	CRI	Refs.
Sr ₃ MgSi ₂ O ₈ :Eu ²⁺	375	470, 570	(0.32, 0.33)	–	5892	84	[275]
Sr ₃ MgSi ₂ O ₈ :Eu ²⁺ , Mn ²⁺	375	470, 570, 680	(0.35, 0.33)	–	4494	92	[275]
Ba ₃ MgSi ₂ O ₈ :Eu ²⁺ , Mn ²⁺	400	442, 505, 620	–	–	5200–6000	85	[10]
Ca ₂ MgSi ₂ O ₇ :Eu ²⁺ , Mn ²⁺	381	528, 602	(0.45, 0.44)	–	–	–	[266]
CaMgSi ₂ O ₆ :Eu ²⁺ , Mn ²⁺	365	450, 580, 680	–	–	4845–9180	71–88	[284]
Ca ₅ MgSi ₃ O ₁₂ :Eu ²⁺ , Mn ²⁺	353	430, 500, 548	(0.29, .34)	–	7659	–	[285]
Sr ₂ LiSiO ₄ F:Ce ³⁺ , Eu ²⁺	350	360–620	–	–	–	–	[264]
CaAl ₂ Si ₂ O ₈ :Eu ²⁺ , Mn ²⁺	354	425, 568	(0.33, 0.31)	–	–	–	[12]
Y ₄ MgSi ₃ O ₁₃ :Bi ³⁺ , Eu ³⁺	350	485, 614	(0.31, 0.31)	–	6907	–	[278]
Sr ₃ Y ₂ (BO ₃) ₄ :Dy ³⁺	370	488, 575, 665	(0.2997, 0.3142)	–	5896	–	[286]
GdAl ₃ (BO ₃) ₄ :Dy ³⁺ , Ce ³⁺	400	480, 575, 620	(0.31, 0.33)	5	6480	78	[279]
Sr ₃ B ₂ O ₆ :Ce ³⁺ , Eu ²⁺	351	434, 574	(0.31, 0.24)	–	–	–	[273]
Ba ₂ Ca(BO ₃) ₂ :Ce ³⁺ , Mn ²⁺	345	420, 480, 625	(0.33, 0.31)	–	5861	72.84	[263]
	395	505, 625	(0.35, 0.41)	–	5088	86.37	
Ba ₂ Ca(B ₃ O ₆) ₂ :Eu ²⁺ , Mn ²⁺	330	459, 608	(0.37, 0.25)	–	2654	–	[262]
Ca ₂ BO ₃ Cl:Ce ³⁺ , Eu ²⁺	349	421, 575	(0.326, 0.334)	–	–	–	[287,288]
La _{0.827} Al _{1.19} O _{19.09} :Eu ²⁺ , Mn ²⁺	385	450, 525, 660	(0.40–0.43, 0.40–0.41)	–	3100–3600	–	[267]
Sr ₃ (Al ₂ O ₅)Cl ₂ :Ce ³⁺ , Eu ²⁺	330	444, 609	(0.35, 0.32)	–	–	–	[265]
SrZn ₂ (PO ₄) ₂ :Eu ²⁺ , Mn ²⁺	365	416, 538, 613	(0.32, 0.31)	–	–	–	[13]
α-Ca ₂ P ₂ O ₇ :Eu ²⁺ , Mn ²⁺	330	416, 600	(0.27, 0.30)	9	10,465	78	[46]
α-Sr(PO ₃) ₂ :Eu ²⁺ , Mn ²⁺	323	404, 625	–	–	–	–	[289]
Ca ₂ Al ₂ SiO ₇ :Ce ³⁺ , Tb ³⁺	352	419, 542	(0.316, 0.336)	–	–	–	[277]
Ca ₁₀ K(PO ₄) ₇ :Eu ²⁺ , Mn ²⁺	347	467, 634	(0.35, 0.24)	–	–	81	[290]
Ca ₉ Y(PO ₄) ₇ :Eu ²⁺ , Mn ²⁺	365	486, 638	(0.31, 0.33)	–	7200	76	[291]
Sr ₂ SiO ₄ :Eu ²⁺	400	550	(0.39, 0.41)	3.8	–	68	[162]

still a challenge for their application in industrialization for pc-WLEDs [2,234]. Ce³⁺-, Eu²⁺-, or Mn²⁺-doped sulfide phosphors, however, suffer the problems of absorption of visible light and poor stability when exposed to air and high temperature. Much more effort is necessary to develop red phosphors. This section will focus on oxide-based tri-color phosphors, which are excited by NUV-LED chips for pc-WLEDs, with emphasis on red phosphors.

4.2.1. Blue phosphors

For the tunable $4f \rightarrow 5d$ transition of Ce³⁺ or Eu²⁺ due to the exposure of 5d electrons to a crystal environment, the centroid shift of the 5d levels of Ce³⁺ or Eu²⁺ is easily tuned to fit the NUV excitation with blue emissions in oxide-based phosphors. Examples include the recently reported blue-emitting phosphors including CaLaGa₃S₆O:Ce³⁺ [48], (CaCl₂/SiO₂):Eu²⁺ [294], Sr₃MgSi₂O₈:Eu²⁺ [295], Ba₂Si₃O₈:Eu²⁺ [296], Ba₅SiO₄Cl₆:Eu²⁺ [297], LiSrPO₄:Eu²⁺ [298], etc. [299–303].

Wu et al. reported the blue-emitting phosphor LiSrPO₄:Eu²⁺. Only a small amount of Eu²⁺ can be doped into the host due to the smaller ionic radius of Eu²⁺ than Sr²⁺, which would result in the distortion of the hexagonal structure [298]. The phosphor exhibits intense emission peaked at 450 nm as shown in Fig. 48. The emission intensity of the blue-emitting phosphor LiSrPO₄:Eu²⁺ is higher than that of the commercial blue phosphor BaMgAl₁₀O₁₇:Eu²⁺ upon excitation by 396 nm light. A bright blue-LED was fabricated by combining LiSrPO₄:Eu²⁺ with a 397 nm InGaN chip, and the CIE color coordinates were calculated to be (x = 0.160, y = 0.062).

Ce³⁺-doped CaLaGa₃S₆O phosphors prepared by a two-step solid-state reaction were studied by Yu et al. [48]. Under 398 nm excitation, a broad emission band appeared at 442 nm, along with a shoulder at 478 nm. A blue-LED with CIE chromaticity coordinates (x = 0.147, y = 0.089) was fabricated by precoating CaLaGa₃S₆O:Ce³⁺ phosphor onto a 398 nm-emitting InGaN chip at I_F = 20 mA.

4.2.2. Green phosphors

Mn²⁺ and Tb³⁺ are frequently used ions for green emissions with Eu²⁺ or Ce³⁺ sensitization. The recently reported green phosphors include Ca₃Sc₂Si₃O₁₂:Ce³⁺ [159], CaAl₂S₄:Eu²⁺ [304], Sr₆BP₅O₂₀:Eu²⁺ [45], BaMgSiO₄:Eu²⁺ [305], Ca₃Y₂(Si₃O₉)₂:Ce³⁺, Tb³⁺ [306], Ca_{2(1-x)}Sr_{2x}Al₂SiO₇:Eu²⁺ [307], Ca₃SiO₄Cl₂:Eu²⁺ [47],

(Sr,Zn)Al₂O₄:Eu²⁺, B³⁺ [308], Ca₂MgSi₂O₇:Eu²⁺, Mn²⁺ [266], etc. [309–313].

As an example, SrAl₂O₄:Eu²⁺ phosphor showed bright green emission peaked at ~520 nm when excited by NUV [308]. The phosphors were synthesized by spray pyrolysis. It was found that 10–50% Sr atoms substituted by Zn greatly enhanced the 520 nm green emission, especially for the excitation wavelength range from 380 to 420 nm, as shown in Fig. 49. A new blue emission (λ_{em} = 460 nm) was observed at high Zn concentration (x > 0.7). The excitation spectrum of (Sr_{1-x}, Zn_x)(Al_{1.98}, B_{0.02})O₄:Eu²⁺ phosphor (x ≤ 0.7) overlapped well with the 460 nm blue emission. Thus, it was concluded that the new blue emission center played the role of sensitizer for the energy transfer, which was responsible for the enhancement of the green emission intensity. The optimized (Sr_{0.6}, Zn_{0.4})_{0.9}(Al_{1.98}, B_{0.02})O₄:0.1Eu²⁺ phosphor could be a promising green phosphor for NUV-LED applications.

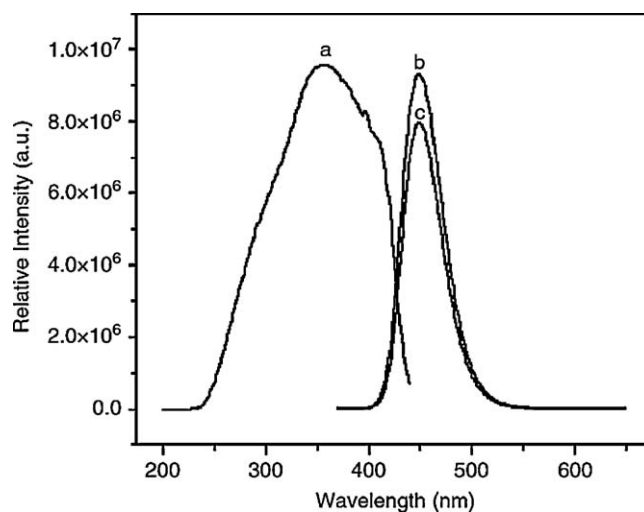


Fig. 48. PL spectra of LiSr_{0.95}PO₄:0.05Eu²⁺: (a) excitation spectrum (λ_{em} = 450 nm), (b,c) emission spectra (λ_{ex} = 356 and 396 nm, respectively) [298]. Reproduced from J. Solid State Chem. 179 (2006) 2356. Copyright © 2006, Elsevier Inc.

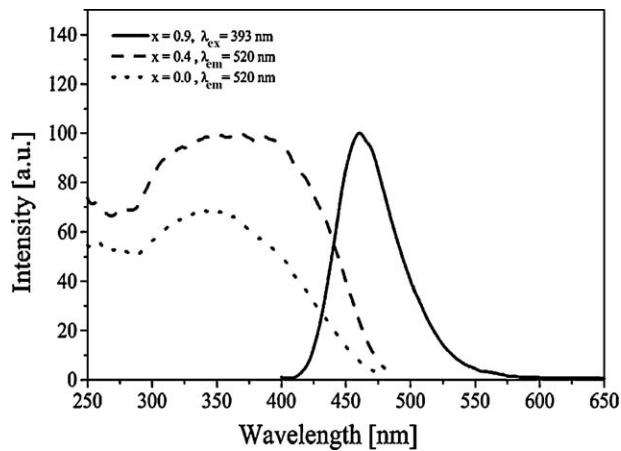


Fig. 49. Emission and excitation spectra of $(\text{Sr}_{1-x}, \text{Zn}_x)(\text{Al}_{1.98}, \text{B}_{0.02})\text{O}_4:\text{Eu}^{2+}$ [308]. Reproduced from Chem. Mater. 18 (2006) 2249. Copyright © 2006, American Chemical Society.

4.2.3. Red phosphors

4.2.3.1. Mn^{2+} as luminescent center. Since the excitation efficiency of the existing red-emitting phosphors such as $\text{YVO}_4:\text{Eu}^{3+}$ and $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ declines dramatically in the NUV region, exploring new red phosphors is a prerequisite for NUV-LED applications. Mn^{2+} ion could have red emission due to the ${}^4\text{T}_1({}^4\text{G}) \rightarrow {}^6\text{A}_1({}^6\text{S})$ transition as aforementioned, however, this kind of transition is spin- and parity-forbidden, and the emission of Mn^{2+} is usually very weak under NUV excitation. But there are a few exceptional cases. Recently, Duan et al. reported a novel red phosphor $\text{CaZnOS}:\text{Mn}^{2+}$ [314]. For $\text{CaZnOS}:\text{Mn}^{2+}$, there are relatively strong excitation bands in the wavelength range of 350–500 nm as shown in Fig. 50(a), which are ascribed to the $d \rightarrow d$ transitions of Mn^{2+} . While for $\text{BaZnOS}:\text{Mn}^{2+}$ in the same wavelength region, the excitation efficiency of Mn^{2+} is quite low (Fig. 50(b)). Table 11 compares the luminescence properties for phosphors doped with Mn^{2+} . The strong excitation band of Mn^{2+} in CaZnOS is uncommon. The explanation given by the authors is that the lifting of spin and parity prohibitions of Mn^{2+} $d-d$ transition in CaZnOS host lattice is due to the deviation from pure tetrahedral symmetry as a consequence of mixed MnS_3O coordination [314]. It is suggested that manipulating coordination of the Mn^{2+} ion by mixing different anions is one way to enlarge opportunities for designing novel Mn^{2+} -doped phosphors with unconventional properties for white LED applications [314].

Owing to the weak excitation bands of Mn^{2+} , sensitizers with high transition efficiency such as Eu^{2+} or Ce^{3+} with the $4f-5d$ allowed transition, are normally used to improve the intensity of Mn^{2+} emission [32,33,36,322,323]. Since not all of the energy absorbed by Eu^{2+} transfers to Mn^{2+} , the residual emission energy of Eu^{2+} would cause poor color purity of red emission. Thus, the match of energy levels of $\text{Eu}^{2+}/\text{Mn}^{2+}$ involved in the ET process and

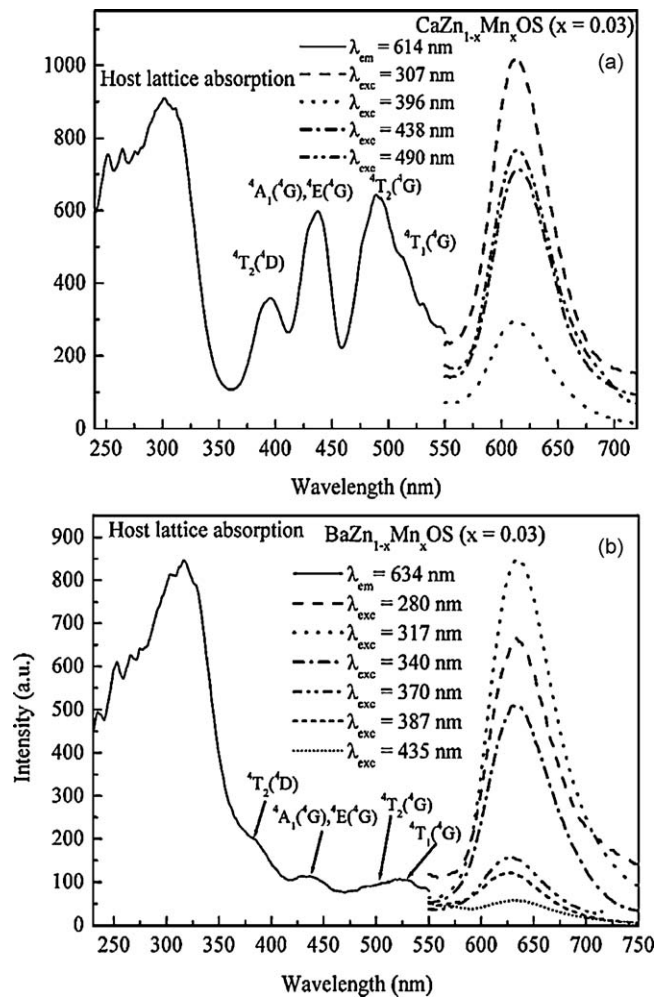


Fig. 50. Typical excitation and emission spectra of $\text{MZn}_{1-x}\text{Mn}_x\text{OS}$ ($x = 0.03$) phosphors: (a) $\text{M} = \text{Ca}$, (b) $\text{M} = \text{Ba}$ [314]. Reproduced from Chem. Mater. 21 (2009) 1010. Copyright © 2009, American Chemical Society.

the emissions of $\text{Eu}^{2+}/\text{Mn}^{2+}$ correlated with a crystal environment should be calculated. It was found that the emissions of both Eu^{2+} and Mn^{2+} show redshift under strong crystal field [36]. When comparing the ET efficiency from Eu^{2+} to Mn^{2+} in monoclinic $\text{SrAl}_2\text{Si}_2\text{O}_8$, hexagonal $\text{BaAl}_2\text{Si}_2\text{O}_8$, and $\alpha\text{-Sr}_2\text{P}_2\text{O}_7$ at a comparative distance between Eu^{2+} and Mn^{2+} , results show that an overlap of the Eu^{2+} emission with the lowest excitation level of Mn^{2+} is required to get higher ET efficiency [32,36]. The energy absorbed by Eu^{2+} could be efficiently transferred to Mn^{2+} in some hosts. Taking $\text{CaSiO}_3:\text{Eu}^{2+}, \text{Mn}^{2+}$ for example [33], the emission of Eu^{2+} almost vanishes and the emission of Mn^{2+} is greatly enhanced, as shown in Fig. 51. The favorable ET efficiency may be ascribed to the formation of a $\text{Eu}^{2+}\text{-Mn}^{2+}$ cluster (short distance between Eu^{2+} and

Table 11

Characteristics of Mn^{2+} -doped MZnOS ($\text{M} = \text{Ca}, \text{Ba}$) phosphors as compared to those of typical Mn^{2+} -doped phosphors at room temperature [314].

Phosphors	$\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$	$\text{Ba}_2\text{ZnSi}_3:\text{Mn}^{2+}$	$\text{ZnS}:\text{Mn}^{2+}$	$\text{BaZn}_{1-x}\text{Mn}_x\text{OS}$ ($0 \leq x \leq 0.2$)	$\text{CaZn}_{1-x}\text{Mn}_x\text{OS}$ ($0 \leq x \leq 0.2$)
Crystal system	<i>RH</i>	<i>Pnam</i>	<i>P6₃mc</i>	<i>Cmcm</i>	<i>P6₃mc</i>
Body color	Gray-white	Gray-white	Gray-white	Light yellow to pink	White to pink
Host excitation bands (nm)	175, 250 (strong)	360 (strong)	332 (strong)	295–340 (strong)	290–310 (strong)
Mn^{2+} excitation bands (nm)	360, 380, 425, 440 (very weak)	410, 510 (very weak)	466, 498, 530 (very weak)	396, 438, 490 (very weak)	396, 438, 490 (strong)
Emission peak center (nm)	520	625	585	634	50
Full width at half maximum (nm)	40	60–70	63	60	50
Refs.	[315]	[316–318]	[319,320]	[314,321]	[314]

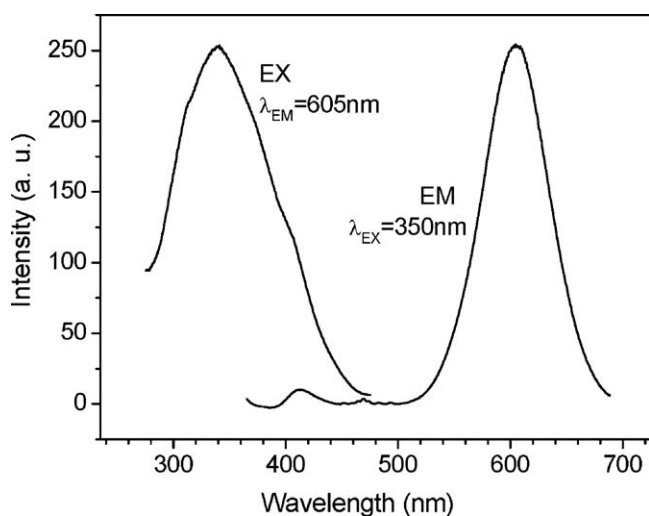


Fig. 51. Excitation and emission spectra of $\text{Ca}_{0.88}\text{SiO}_3:0.02\text{Eu},0.10\text{Mn}$ [33]. Reproduced from J. Electrochem. Soc. 155 (2008) J143. Copyright © 2008, The Electrochemical Society.

Mn^{2+}) due to ion size compensation, the one-dimensional arrangement of Ca^{2+} ($\text{Eu}^{2+}/\text{Mn}^{2+}$) cations or a better match between the lowest excitation level of Mn^{2+} and the emission level of Eu^{2+} [33]. Additionally, the ET processes of $\text{Ce}^{3+} \rightarrow \text{Eu}^{2+}$, $\text{Eu}^{2+} \rightarrow \text{Mn}^{2+}$, and $\text{Ce}^{3+} \rightarrow \text{Mn}^{2+}$ are observed in CaSiO_3 [33]; these ET processes in some $\text{Ce}^{3+}\text{--Eu}^{2+}\text{--Mn}^{2+}$ co-doping systems could enhance the red emission of Mn^{2+} .

Table 12 summarizes the emission wavelengths of Mn^{2+} in different hosts. Besides the long-wavelength red emission of Mn^{2+} , the green emissions of Mn^{2+} are also common.

Table 12

Emission wavelengths of Mn^{2+} in different hosts.

Emission wavelength (>550 nm)			Emission wavelength (≤550 nm)		
Hosts	Emission wavelength (nm)	Refs.	Hosts	Emission wavelength (nm)	Refs.
$\text{Ba}_3\text{MgSi}_2\text{O}_8$	620 (Ba)	[11]	CaAl_2O_4	525	[324]
$\text{CaAl}_2\text{Si}_2\text{O}_8$	568 (Ca)	[12]	$\text{SrZn}_2(\text{PO}_4)_2$	538 (Zn(II))	[13]
$\text{SrZn}_2(\text{PO}_4)_2$	613 (Zn(I))	[13]	ZnGa_2O_4	508 (Zn)	[325]
$\text{CaMgSi}_2\text{O}_6$	580 (Mg), 680 (Ca)	[284]	$\text{BaMgAl}_{10}\text{O}_{17}$	517	[326]
$\text{Ca}_2\text{MgSi}_2\text{O}_7$	602 (Mg)	[266]	$\text{Ta}_2\text{Zn}_3\text{O}_8$	514	[327]
$\text{BaMg}_2\text{Si}_2\text{O}_7$	620 (Mg), 675 (Mg)	[323]	$\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2$	540	[328]
$\alpha\text{--LiZnPO}_4$	550–560 (Zn)	[329]	Zn_2SiO_4	525	[328]
MgSiO_3	661	[324,330]	CaSb_2O_6	510	[328]
Mg_2SiO_4	644	[330]	CaF_2	495	[14]
ZnSiN_2	620	[331]	MgGa_2O_4	510	[328]
Ba_2ZnS_3	625	[317]	Zn_2GeO_4	540	[332]
SrB_4O_7	640	[333]	LiAl_5O_8	505–518	[334]
$\beta\text{--Zn}_3(\text{PO}_4)_2$	616	[335]	$\gamma\text{--AlON}$	520	[252]
$\text{La}_{0.827}\text{Al}_{11.9}\text{O}_{19.09}$	660 (Al,T)	[267]	$\text{La}_{0.827}\text{Al}_{11.9}\text{O}_{19.09}$	525 (Al,O)	[267]
$\text{Ca}_3\text{SiO}_4\text{Cl}_2$	570	[47]	$\text{LaAl}_{11}\text{O}_{18}$	517	[14]
$\text{Ba}_2\text{SiO}_3\text{Cl}_2$	608	[336]	Mg_2SnO_4	499	[337]
$\text{CaZnGe}_2\text{O}_6$	648	[338]	$\text{Ca}_2\text{Al}_2\text{SiO}_7$	550	[324]
$\text{Cd}_2\text{Ge}_7\text{O}_{16}$	585	[339]	$\text{Sr}_3\text{Gd}_2\text{Si}_6\text{O}_{18}$	550	[340]
$\text{Ca}_5(\text{PO}_4)_3\text{Cl}$	580	[328]	$\text{SrAl}_{12}\text{O}_{19}$	515	[341]
$(\text{La},\text{Y},\text{Gd})\text{MgB}_5\text{O}_{10}$	630	[328]	$\text{BaAl}_2\text{Si}_2\text{O}_8$	518	[36]
$\text{Cd}_2\text{B}_2\text{O}_5$	620	[328]			
$\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}$	575	[342]			
$\text{Ca}_{19}\text{Mn}_2(\text{PO}_4)_{14}$	636				
$\alpha\text{--Sr}_2\text{P}_2\text{O}_7$	585	[32]			
$\beta\text{--CaSiO}_3$	605	[33]			
$\text{SrAl}_2\text{Si}_2\text{O}_8$	564	[36]			
$\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$	665				
$\text{Ba}_2\text{Ca}(\text{BO}_3)_2$	625	[263]			
$\alpha\text{--Sr}(\text{PO}_3)_2$	625	[289]			
$\text{Ca}_{10}\text{K}(\text{PO}_4)_7$	634	[290]			
CaZnOS	614	[314]			

Note: The emission wavelength of Mn^{2+} refers to the maximum of Mn^{2+} emission band. The elements in parentheses mean that the site substituted by Mn^{2+} in references, T and O denote tetrahedron and octahedron at which Mn^{2+} locates. All the data are corresponding to some certain concentration of Mn^{2+} , the emissions of Mn^{2+} vary at different Mn^{2+} concentrations. The data with no references are from the author's unpublished work.

4.2.3.2. Eu^{3+} as luminescent center. Eu^{3+} is another commonly used and efficient ion for red phosphors with perfect color purity of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition ($\lambda_{\text{em}} = 615 \text{ nm}$). Many of the present works on Eu^{3+} -doped phosphors focus on phosphors with high-valenced transition metal groups, such as $\text{CaMoO}_4:\text{Eu}^{3+},\text{Li}^+$ [29–31], $\text{Gd}_2\text{Mo}_3\text{O}_9:\text{Eu}^{3+}$ [343], $(\text{Li}_{0.333}\text{Na}_{0.334}\text{K}_{0.333})\text{Eu}(\text{MoO}_4)_2$ [344], $\text{Na}_5\text{Ln}(\text{MoO}_4)_4:\text{Eu}^{3+}$ ($\text{Ln} = \text{La}, \text{Gd}$ and Y) [345], $\text{BaGd}_2(-\text{MoO}_4)_4:\text{Eu}^{3+}$ [346], $\text{CaWO}_4:\text{Eu}^{3+}$ [347], etc. [348–359]. There are also some phosphors without high-valenced transition metal groups [360–365]. All of them have narrow line-shaped excitation peaks at NUV ($\lambda_{\text{ex}} = 365\text{--}410 \text{ nm}$), which are not desirable for different types of NUV-LED chip applications with different emission wavelength. An example is given in Fig. 52. Furthermore, these line-shaped excitation peaks are ascribed to the parity-forbidden $4f\text{--}4f$ transitions, which normally are not efficient enough. To improve the absorption efficiency in the NUV region, Sm^{3+} is co-doped with Eu^{3+} in phosphors [350,356,359,366–368]. But the absorption of Sm^{3+} at NUV is limited because of the parity-forbidden $4f\text{--}4f$ absorption transitions of Sm^{3+} . Another way to improve the excitation efficiency of $4f\text{--}4f$ transition is to lower the site symmetry of Eu^{3+} , which makes the transition parity partially permitted [31,49,369–372].

To broaden the excitation bands at the NUV region, Bi^{3+} is also used in phosphors such as $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ [373], $\text{CaMoO}_4:\text{Eu}^{3+}$ [369], $\text{YVO}_4:\text{Eu}^{3+}$ [359], $\text{LiEuMo}_2\text{O}_8:\text{Eu}^{3+}$ [37], etc. [374,375]. Fig. 53 gives an illustration of $\text{LiEuMo}_2\text{O}_8:\text{Eu}^{3+}, \text{Bi}^{3+}$ [37]. It was found that both the polarization effect of Bi^{3+} on the charge transfer state (CTS) of MoO_4 and the $6s \rightarrow 6p$ transition of Bi^{3+} play roles in the redshift of the absorption band at UV region. Moreover, the incorporation of Bi^{3+} could also enhance the red emission intensity of Eu^{3+} efficiently upon NUV excitation.

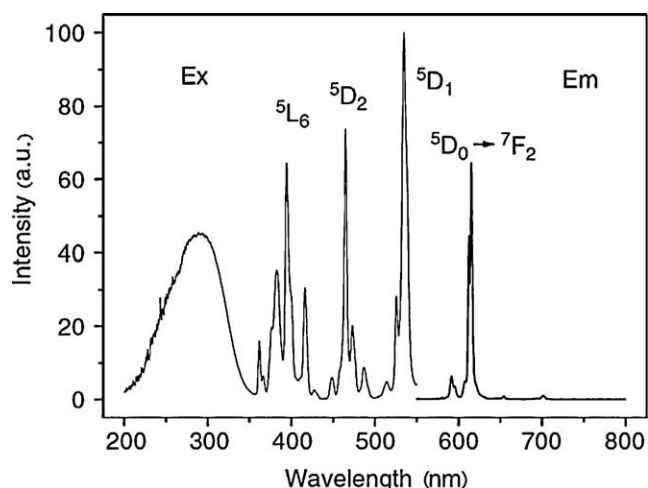


Fig. 52. Excitation and emission spectra of $\text{LiEuMo}_2\text{O}_8$ [31]. Reproduced from J. Lumin. 121 (2006) 57. Copyright © 2005, Elsevier B.V.

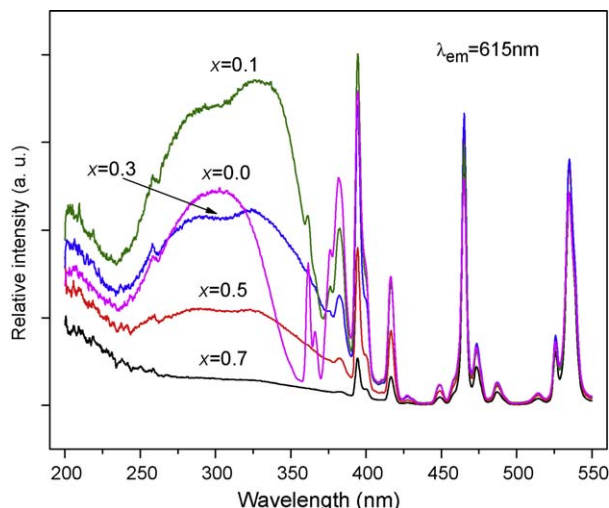


Fig. 53. Excitation spectra of the $\text{LiEu}_{1-x}\text{Mo}_2\text{O}_8:x\text{Bi}$ series [37]. Reproduced from J. Electrochem. Soc. 156 (2009) J121. Copyright © 2009, The Electrochemical Society.

It has been reported by Sivakumar and Varadaraju that ordered double perovskite $(\text{Ba,Sr})_2\text{CaMoO}_6:\text{Eu}^{3+}$, Li^+ phosphors have an intense broad absorption band at 200–450 nm, contributed primarily by the CTS of MoO_6 groups [51,376]. Recently, Ye et al. investigated this system further, and found that Eu^{3+} prefers the B site (Ca^{2+}) in this double perovskite system (general formula ABO_3 for simple perovskite), and the linear Mo-O-Eu configuration for Eu^{3+} at the B site benefits the ET from the CTS of MoO_6 to Eu^{3+} through an exchange mechanism [34,35]. A strong quenching among the CTS of MoO_6 groups was also found, which results in little CTS energy transfer to Eu^{3+} . According to the changes of the local crystal structure characterized by Raman spectra, the theoretical calculation of the electronic structure as well as the detailed PL and PLE spectra [34,35], some interesting results could be obtained, which show that the introduction of WO_6 groups and the tilting of BO_6 framework can reduce the quenching of CTS of MoO_6 groups and lead to more energy transferred to Eu^{3+} under NUV excitation. The effects of WO_6 groups on the excitation spectrum of $\text{Ba}_2\text{Ca}_{0.80}\text{Li}_{0.10}\text{Eu}_{0.10}\text{Mo}_{1-y}\text{W}_y\text{O}_6$ are shown in Fig. 54. A schematic summarizing the ET mechanism of this phosphor series is shown in Fig. 55. The WO_6 groups block the energy quenching among MoO_6 groups, and the tilting of the BO_6

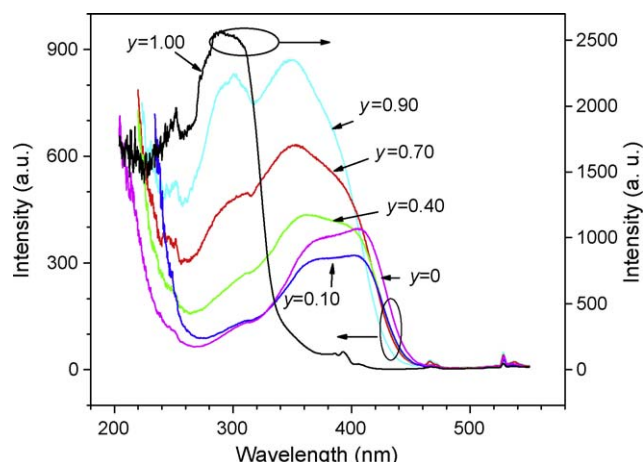


Fig. 54. Excitation spectra of $\text{Ba}_2\text{Ca}_{0.80}\text{Li}_{0.10}\text{Eu}_{0.10}\text{Mo}_{1-y}\text{W}_y\text{O}_6$ ($\lambda_{\text{em}} = 595 \text{ nm}$) [35]. Reproduced from Appl. Phys. B 91 (2008) 551. Copyright © 2008, Springer-Verlag.

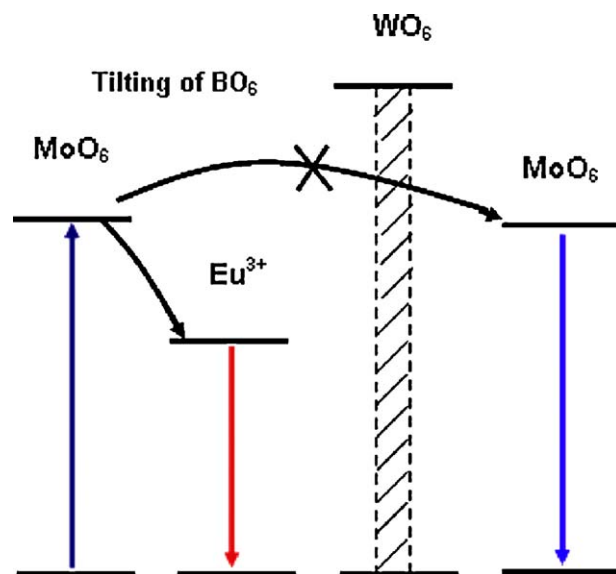


Fig. 55. Schematic of energy transfer in $\text{Ba}_{2-x}\text{Sr}_2\text{Ca}_{0.80}\text{Eu}_{0.10}\text{Li}_{0.10}\text{Mo}_{1-y}\text{W}_y\text{O}_6$.

framework based on the Raman spectra reveals that it benefits the ET from MoO_6 to Eu^{3+} .

Table 13 gives a summary of the absorption edge of different absorbing groups which contain high-valenced d^0 transition

Table 13

The absorption edge of some absorbing groups.

Compound	Absorbing group	Absorption edge (nm)
^a $\text{Gd}_2\text{Ti}_2\text{O}_7$	TiO_6	310
^a YVO_4	VO_4	320
^a $\text{Ca}_2\text{NaMg}_2\text{V}_3\text{O}_{12}$	VO_4	340
^a YNbO_4	NbO_4	260
^a GdTiNbO_6	TiO_6 and NbO_6	300
^a $\text{La}_2\text{LiNbO}_6$	NbO_6	300
^a Y_2MoO_6	MoO_6	350
^a La_2MoO_6	MoO_4	300
^a GdTiTaO_6	TiO_6 and TaO_6	320
^a Gd_2WO_6	WO_6	300
^a Y_2WO_6	WO_4	310
^b CaMoO_4	MoO_4	320
^b Ba_2CaWO_6	WO_6	325
^b $\text{Ba}_2\text{CaMoO}_6$	MoO_6	430

^a Data are from Ref. [377].

^b Data from author's work.

metals. It can be seen that MoO_6 groups in a perovskite compound show unique long-wavelength absorption, possibly caused by the weak bonding of O–Mo in MoO_6 (compared to MoO_4 in scheelite CaMoO_4) and the three-dimensional framework of $(\text{Mo}/\text{Ca})\text{O}_6$, which could lower the d energy level of Mo^{6+} for the CTS of $\text{O}^{2-} \rightarrow \text{Mo}^{6+}$. This may offer a clue for designing new red phosphors for NUV-LED applications.

5. Concluding remarks and perspectives

Major advances have been made recently by many research groups around the world in fabricating new phosphors, developing high efficiency pc-WLEDs, and the mechanism involved. There are still many areas that need additional work, including but not limited to:

- (1) For phosphors excited by blue-LED chips, YAG:Ce phosphor is the commonly used commercial phosphor. The special long-wavelength emission of Ce^{3+} results from the strong crystal field splitting on the $5d$ level of Ce^{3+} . According to Bachmann [150], the temperature-quenching of YAG:Ce is caused by the high doping concentration of Ce^{3+} . Therefore, the application of YAG:Ce phosphor with low Ce^{3+} concentration in high-power white LEDs is possible. The capacity of accommodating different ions in the YAG:Ce lattice makes the excitation and emission spectra of the phosphor tunable. The packing of YAG:Ce phosphor in pc-WLEDs is a significant issue to extract emission light, which deserves both technological and scientific concern. The particle size of phosphor, dispersion of phosphor and microstructure of the package play roles in the light-extraction efficiency of pc-WLEDs. New yellow-emitting oxide-based phosphors are still attractive to replace YAG:Ce. The phosphors of sulfides and (oxy)nitrides could be developed because of the strong nephelauxetic effects and/or strong crystal field on the $4f$ – $5d$ transition of $\text{Ce}^{3+}/\text{Eu}^{2+}$. The sulfide phosphors should conquer the problem of chemical stability, while the (oxy)nitride phosphors should be easily prepared for industrialization at relatively low cost. Most of the (oxy)nitride phosphors reported contain Si–N and/or Al–N; there is more room in B–N–, Ga–N– and Ge–N–based phosphors [218]. Furthermore, incorporating some other anions [218] such as S^{2-} , C^{4-} , and halogen anions in nitrides might enlarge the families of the phosphors.
- (2) For phosphors excited by NUV-LED chips, there are big challenges in both the chips and the red phosphors. Primarily, NUV-LED chips suffer much lower efficiency than the blue InGaN chips, which results in low luminous efficacy of pc-WLEDs. pc-WLEDs with single-phased white-emitting phosphors have the advantage of easy fabrication, but theoretically may suffer relatively poor performance in the balance of the high CRI and the high luminous efficacy compared with the NUV-LED + RGB phosphors. For red phosphors, the $\text{Ce}^{3+}/\text{Eu}^{2+}$ in phosphors which absorb NUV and efficiently emit red light with large Stokes shift (no absorption of blue or green lights) are normally scarce. Red (oxy)nitride phosphors doped with $\text{Ce}^{3+}/\text{Eu}^{2+}/\text{Yb}^{2+}$ usually absorb not only NUV light but also visible light, which is unfavorable when blended with blue/green phosphors for white light generation. Therefore, energy transfer between different luminescent centers is required to design this kind of red phosphor. Efforts on Ce^{3+} – Mn^{2+} or Eu^{2+} – Mn^{2+} co-doping systems are still needed to improve the performance. For Eu^{3+} -doped red phosphors, the sensitizers such as Eu^{2+} , or hosts with strong absorption of NUV, such as some absorbing groups with high-valenced d^0 transition metal, could be utilized to sensitize the Eu^{3+} to enhance red emission. Eu^{3+} -doped polysulfide phosphors are also possible for the NUV

pc-WLED applications due to the low charge transfer energy from the small electronegative ion S^{2-} to Eu^{3+} .

- (3) A motivation for the design and synthesis of new phosphors is driven by the possibility to exploit high-performance phosphors with low cost, high purity, good crystallinity, and narrow size distribution. The local environment of activator ions such as Ce^{3+} or Eu^{2+} is essential for the performance of phosphors. Therefore, in the first place bottom-up strategies could be considered to design phosphors computationally. Firstly, the energy levels of a specifically selected activator ion in the designed coordination environments (based on empirical data) could be obtained through theoretical calculation. The activator ion and its coordination environment can be viewed as a “cluster”. Then the assembly rule for the “cluster” could be established via different arrangements, i.e. space group symmetry, to build up the target phosphor according to chemical thermodynamics. Finally, the target phosphor could be chemically synthesized. It is also possible to find existing materials with the same characteristic as the designed coordination environments in the structure database.
- (4) Although some kinds of pc-WLEDs for general illumination are commercially available, there is plenty room for improvement of lumen efficiency, and price competitiveness against fluorescent lamps. The lumen efficiency depends on quantum efficiency of semiconductor chips, photoluminescence properties of phosphors, and the external efficiency of the lamps structure. The development and application of phosphors for white LEDs are stimulated significantly by the advance of LED chips, especially the NUV-LED chips for the NUV-LED + RGB phosphors lighting style.

A great number of newer concepts and novel materials are still in the research stage. Some of them may lead to much higher efficiency and lower cost in the coming decades. There is a long way ahead in achieving the goal from efficient phosphors for pc-WLEDs. However, the prospects of reaching this goal have been found to be satisfactory and more interesting against the backdrop of the emergence of different and promising materials and concepts. The overwhelming replacement of incandescent lamps and fluorescent lamps by pc-WLEDs remains to be seen. Surely novel phosphor materials and LED chips will trigger each other in the future.

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