Recent progress in low-voltage cathodoluminescent materials: synthesis, improvement and emission properties

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Nowadays there are several technologies used for flat panel displays (FPDs) and the development of FPDs with enhanced energy efficiency and improved display quality is strongly required. Field emission displays (FEDs) have been considered as one of the most promising next generation flat panel display technologies due to their excellent display performance and low energy consumption. For the development of FEDs, phosphors are irreplaceable components. In the past decade, the study of highly efficient low-voltage cathodoluminescent materials, namely FED phosphors, has become the focus of enhancing energy efficiency and realizing high-quality displays. This review summarizes the recent progress in the chemical synthesis and improvement of novel, rare-earth and transition metal ions activated inorganic cathodoluminescent materials in powder and thin film forms. The discussion is focused on the modification of morphology, size, surface, composition and conductivity of phosphors and the corresponding effects on their cathodoluminescent properties. Special emphases are given to the selection of host and luminescent centers, the adjustment of emission colors through doping concentration optimization, energy transfer and mono- or co-doping activator ions, the improvement of chromaticity, color stability and color gamut as well as the saturation behavior and the degradation behavior of phosphors under the excitation of a low-voltage electron beam. Finally, the research prospects and future directions of FED phosphors are discussed with recommendations to facilitate the further study of new and highly efficient low-voltage cathodoluminescent materials.

1. Introduction

Currently, quite a few technologies are being developed for flat panel displays (FPDs), including plasma display panels (PDPs), electroluminescence (EL) devices, field emission displays (FEDs), liquid crystal displays (LCDs) and so on. Nowadays people have a larger need for image quality. Therefore, developing display panel technologies with enhanced energy efficiency and improved display quality is strongly required.\textsuperscript{3} Of these display technologies, in recent years, FEDs have been investigated for the development of full color flat panel displays, which are considered one of the most promising technologies for next generation FPDs due to their potential advantages in aspects of display quality (brightness, contrast ratio, angle of viewing and response time), power consumption, stability, lifetime, etc.\textsuperscript{2,4} The basis of an FED device is an array of aligned field emitter tips cathodes opposite to a phosphor anode, as shown in Scheme 1. Therefore, the development of FEDs mainly depends on the following aspects: field emitter arrays (namely electron-emitting microcathode arrays), the packaging of FED devices and luminescent materials.\textsuperscript{5} Field emitter arrays may be manufactured using a variety of materials (Mo, W, Ta, ZnO, silicon-based and carbon-based materials, etc.) by the photolithography technique with thin deposition and etching process.\textsuperscript{5} Moreover, cathode technology is sophisticated and its development affects the energy efficiency of FEDs. Because a number of issues exist in the packaging of FED devices, including frit seals, spacers to maintain cathode–anode distances, dielectric breakdowns, plasma discharge and vacuum generation and maintenance, the development of FED packaging is also necessary for the improvement of the display performance. Luminescent materials (or phosphors) are indispensable components of FED devices, whose luminescent efficiencies and properties not only determine the quality of the images but also affect the energy efficiency of the display devices.\textsuperscript{6–9} Therefore, the selection of phosphors for the anode is critical for FEDs. In order for FEDs to enter the market, it is clear that continued improvements are required in microcathode arrays and packaging technologies, especially for phosphors.
Consequently, in the past decade, the study and development of highly efficient low-voltage cathodoluminescent materials and the improvement of existing FED phosphors have become the focus of developing FED devices.16–22

The operation principle of FEDs is similar to that of conventional cathode ray tubes (CRTs) in which the images originate from the excitation of electrons in phosphors (Scheme 1). However, the requirements for phosphors in FEDs are greatly different from those used in CRTs due to the lower accelerating voltages and the higher current densities. Firstly, FED phosphors should decrease or avoid the release of gasses in the FED devices due to the progressive degradation of the vacuum in the display space, which affects its operating time.23–26 Secondly, for FED phosphors excellent cathodoluminescent properties, such as high emission intensity, high luminous efficiency, high saturation current density, high color purity and good stability and durability under low accelerating voltages (≤7 kV) and high current density (≥100 μA cm⁻²), are essential.27–29 Based on the above reasons, the selection of suitable hosts and luminescent centers is very important for the synthesis of FED phosphors.30 As activator ions, rare earth (RE) ions have been playing an important role in modern lighting and display fields due to the abundant emission colors in the whole visible light range owing to their 4f → 4f or 5d → 4f transitions.31 In addition, transition metal ion (Mn²⁺), Bi³⁺ ion and some groups (e.g. WO₄²⁻, MoO₄²⁻, GeO₄⁴⁻, SnO₂²⁻, TiO₂²⁻, NbO₂²⁻) are also efficient luminescent centers.32–39 For host materials, many efficient sulfide-based phosphors, such as Y₂O₂S:Eu³⁺, Gd₂O₂S:Tb³⁺, SrGa₂S₄:Eu³⁺/Ce³⁺, (Zn/Cd)S:Cu, Al, ZnS:Ag, Cl, etc., have so far been studied as efficient low-voltage cathodoluminescent materials.40–43 Unfortunately, sulfide phosphors are easily decomposed and emit sulfide gases under electron bombardment due to the dissociation of the cation–sulfur bonds, subsequently damaging the emission tips, shortening the device lifetime and simultaneously contaminating the environment, which impedes their practical application in FED devices.44,45 For the same reasons ZnS:Mn nanomaterials and CdSe–ZnS quantum dot composites need to be eliminated and the influence of other gasses on FED operation should also be avoided.46–48 To avoid the above mentioned defects, oxide-based phosphors, including rare-earth and transition metal ions doped garnets, oxides, silicates, phosphates, vanadates, perovskites, etc.,49–62 have gained increasing attention due to their better thermal stability, chemical stability and environmental friendliness compared to sulfides. However, most of these phosphors are insulators and negative loading is easy to accumulate on the grain surface in the phosphor layer, which decreases cathodoluminescence efficiency. That is why the electrical conductivity of FED phosphors should be high enough to avoid charge accumulation.27 In order to overcome this drawback, in recent years many semiconductor-based materials such as ZnO, Ga₂O₃, (Gd,Lu)Ga₂O₃, Zn(Ga,In)₂O₄, (Ca,Sr)In₅O₈, Zn₁Ta₂O₈, Zn₂GeO₅, GaGe₂O₇, Mg₂SnO₄, ZnGeN₂, etc., have been studied as low-voltage cathodoluminescent materials through the efficient doping of RE³⁺, Mn²⁺ and Bi³⁺ ions.63–75 Besides, current low voltage cathodoluminescent materials also suffer from rough surfaces, irregular shape and size distributions,

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poor adherence to substrates, poor preparation of phosphor screens (thin films) from phosphor powders, and the color saturation and color index need be further improved to enhance display quality.15,76,77 All of these considerations and the ever-growing demand for highly efficiently low voltage cathodoluminescent materials in FEDs have prompted researchers to reach an understanding that more attention should be paid to improve existing phosphors and develop newly efficient low voltage cathodoluminescent materials.

On another level, in modern chemistry and materials science, the tremendous advances in the synthetic control of morphology, size, dimensions and composition have allowed researchers to tailor the chemical and physical properties of materials and thus the rational control over these factors has motivated scientific and technological efforts in recent years.78–85 Morphology, size, composition, surface and crystallization can influence the cathodoluminescence properties of phosphors.27 To date many efforts have been made to research excellent approaches for the fabrication of a variety of inorganic luminescence materials to improve their performance. Among them, the soft-chemical methods are intensively pursued as effective and convenient approaches to prepare various inorganic cathodoluminescent materials with controllable shape, size, surface form, composition and luminescence properties.15,66,86–97 In this critical review, we summarize the recent progress in the chemical synthesis and improvement of existing and new phosphors including RE3+ ions and transition metal ions activated inorganic oxide-based luminescence materials, semiconductor-based luminescence materials, self-activated luminescent materials, etc. We discuss the modifications and optimizations in morphology, size, composition, conductivity of phosphors and their cathodoluminescence properties. Some emphases are also focused on the study of the selection of hosts and luminescent centers, enhancement of efficiency through energy transfer, adjustment and design of emission colors, improvement of color index and color gamut as well as color stability and degradation behavior of phosphors.

2. Improvement and development of FED phosphor powders

2.1 Improvement of phosphor powders

It is well known that the most common forms of phosphor powders, which are mixed with organic binders to spread on a substrate for display and lighting applications.6–8 Conventionally, phosphor powders are prepared by the solid reaction process, i.e. the direct mixing of precursor components (oxides, inorganic salts, etc.) and the sintering of them at high temperatures for a long time with a repeated grinding process. This process usually suffers from waste of energy (> 1000 °C, > 10 h in general), contamination from impurities and an inhomogeneous composition and morphology (> 3 μm particles with irregular shapes, wide size distributions and large aggregations) for the final phosphor products, which might result in a reduction of the luminescent performance of the phosphors.98 Because the morphology, size, composition, surface, and crystallization have great effects on the cathodoluminescence properties of phosphors, many efforts have been made to research suitable methods to control these factors for improving their cathodoluminescence performance, which has technological and fundamental scientific importance.15 Specifically, high-quality displays will require better low voltage efficiencies, chromaticity, saturation behavior and maintenance of phosphors. Some possible routes to achieve the above improvements are discussed in the following section.

2.1.1. Modification of particle morphology, surface and size. Usually, soft chemistry processes are utilized to design and synthesize inorganic nano/microstructures with various kinds of shape, size, and chemical composition for application as advanced functional and engineering materials.99,100 In recent years, a large number of synthetic methods have been developed for the generation and improvement of inorganic cathodoluminescent materials.15 After reviewing recent phosphors being developed in FED devices, advances in the soft chemistry synthesis of low-voltage cathodoluminescent materials (such as sol–gel, hydrothermal, spray pyrolysis, electrospinning, homogenous precipitation, high boiling solvent, combustion and microwave) are summarized and discussed.15,66,86–97 In general, soft chemistry synthesis can produce future generation phosphors with better morphologies and surface forms (more regular shapes, even spherical in some cases), and narrower size dispersions at moderate temperatures (< 1000 °C). These factors can decrease the light scattering and non-radiative transitions of phosphors, which is conducive to the enhancement of the cathodoluminescence performance. On the other hand, for FED phosphor powders, particle size is critical to loading on screens, which further influences their luminescent performance.27,101 It is known that the cathodoluminescence emission intensities and brightness of FED phosphors increases with increasing accelerating voltage and filament current of the anodes, which is attributed to the deeper penetration of the electrons into the phosphor body and the larger electron-beam current density. The electron penetration depth can be estimated using the empirical formula:

$$L[A] = 250 \left( \frac{A}{\rho} \right) \left( \frac{E}{\sqrt{Z}} \right)^n,$$

where $n = 1.2/(1 - 0.29lgZ)$, $A$ is the atomic or molecular weight of the material, $\rho$ is the bulk density, $Z$ is the atomic number or the number of electrons per molecule in the compounds and $E$ is the accelerating voltage (kV).86 The deeper the electron penetration depth, the more plasma will be produced, which results in CL intensity increases. However, according to the above empirical formula, the electron penetration depth into phosphors is generally tens of nanometers in FED devices due to the low excitation voltage (1–7 kV), which means that activator ions in the inner part of phosphor particles with large sizes (microsize) cannot be efficiently excited. So a reasonable particle size is important to improve their cathodoluminescence efficiencies. In addition, the resolution is a pivotal index for display quality, which is also closely related to the particle size of the luminescent materials.102 Although some theoretical and experimental considerations have suggested that the most efficient phosphors are spherical and submicron grain sized,103,104
nanoparticle phosphors might be more appropriate for low-voltage FED applications in terms of the following aspects: 15,27,101 (1) in some cases, the preparation of nanocrystalline phosphors requires much less temperature and time in comparison with conventional micr osized grains, which lower the synthesis cost; (2) the employment of such materials allows for the optimal packaging of grains, avoids cutting of the picture spot and decreases the scattering of the light-emitting layer, which enhances the efficiency of the phosphor layer and the quality of images; (3) at present, many optoelectronic devices trend to mini type, phosphor powders with a small grain size allow the fabrica tion of thin light-emitting films that could extend the display operating time and fundamentally decreased the total resistance of a phosphor layer. Based on the above reasons, recently, some researchers have paid more attention to optimizing nano or submicr osized low-voltage cathodoluminescent materials via various soft chemical synthesis processes for improving their luminescence efficiency.

Sol–gel process. The sol–gel technique is one of the most well-known soft chemistry processes, which can be generally divided into three types based on the different use of the precursors: 99 (a) sol–gel process under hydrolysis and condensation of molecular precursors; (b) gelation process under concentration of aqueous solutions into metal-chelates, namely the “chelate” route; (c) polymerization and complex process (called Pechini-type sol–gel process, and abbreviate as PSG). Most of the metal alkoxides suffer from high costs, unavailability, toxicity, and a fast hydrolysis rate that result in a difficult control of the homogeneity of different components during experimental processes, and thus the latter processes, especially the PSG processes, are frequently employed in the preparation of multicomponent metal oxide materials. The PSG process commonly uses metal salts as precursors, citric acid (CA) as a chelating ligand of metal ions and polyhydroxy alcohol, such as ethylene glycol (EG) or poly(ethylene glycol) (PEG), as a cross-linking agent to form a polymeric resin at the molecular level, which can ensure the compositional homogeneity and enhance the dispersion of particles. Since CA is a polybasic compound having three carboxylic acid groups and one alcoholic group in one molecule, rare earth ions and other non-monovalent cations can form very stable chelate complexes with CA. The potential ability of CA to solubilize a wide range of metal ions in a mixed solvent of EG/PEG and H2O is of prime importance, especially for systems involving cations that can be readily hydrolyzed to form insoluble precipitates in the presence of water. An advantage of the PSG process is that the viscosity and the molecular weight of the polymer can be tailored by varying the CA : EG(PEG) molar ratio. After a heat treatment at moderate temperatures (500–1000 °C) followed by the PSG process, the organic additives can be removed and a pure phase of multiple-components metal oxide is obtained. The final materials (including luminescent materials) can be made into powder, thin films and other forms (Scheme 2). It should be pointed out that the PSG process may be far from a green chemistry process due to the generation of a large amount of organic mass during the synthesis. So far, the PSG process has been extensively used for the synthesis of electric and magnetic materials. 105–108 By the PSG process, the physical properties of materials can be improved with respect to other routes such as the solid-state reaction process and amorphous citrate process, as suggested by Kakihana in a review article. 109 In the past decade, Lin’s group has derived multiformed cathodoluminescent materials from the PSG process, including nanocrystalline luminescent materials, monodisperse and spherical core–shell structured phosphors, one-dimensional (1D) nanostructures (combined with the electrospinning process), thin film phosphors (via dip-coating) and their patterning (combined with the soft-lithography process). The basic principle is shown in Scheme 2. The purpose is to gain a fine control of the material morphology, surface and size, and to find novel catho doluminescent materials and optimize their cathodoluminescence performance. A series of oxide-based nanocrystalline phosphors from tens of nanometers to several hundred of nanometers have been prepared through the PSG process for FEDs, including La2O3/LaOCl/LaGaO3/LaAlO3:RE3+,14,86,92,110–113 Lu3Ga5O12:RE3+,114 NaCaPO4:Mn2+,94 CaYAlO4:Tb3+/Eu3+,95 KNaCa2(PO4)2:A (A = Ce3+, Eu3+, Tb3+, Mn3+),115 K[Ca2Ba3(PO4)6]:RE3+/Mn2+ (RE = Ce, Tb, Dy, Eu, Tm),116,117 and so on. It was found that the nanocrystalline phosphor layer could be much thinner compared to that consisting of micr osized phosphor grains, which can influence both the total resistivity of the phosphor.
layer and the amount of residual gasses bounded between the grains.\textsuperscript{27,101} It further influences the efficiency of the light source, long time stability of the intensity of emitted light and the device lifetime. Psuja et al. investigated the effect of grain sizes on the emission yield of RE doped nanophosphors in the case of Eu\textsuperscript{3+}:Y\textsubscript{2}O\textsubscript{3}, Tb\textsuperscript{3+}:Y\textsubscript{2}O\textsubscript{3}, Tb\textsuperscript{3+}:Y\textsubscript{2}Al\textsubscript{5}O\textsubscript{12} (Tb:YAG), Ce\textsuperscript{3+}:YAG, and Tb\textsuperscript{3+}:YAG/Eu\textsuperscript{3+}:YAG.\textsuperscript{27} They found that the light-emitting efficiencies increase with grain size in the nanorange by comparing cathodoluminescence intensities of phosphor layer and powders, and that the Eu:Y\textsubscript{2}O\textsubscript{3} nanopowder (900 °C, 46 nm) was more efficient than commercially available micro-sized phosphor grains (3.5 μm). Moreover, the CIE chromatic coordinates did not change with phosphor grain sizes. Therefore, they suggested that the RE\textsuperscript{3+} doped nanocrystalline phosphors may effectively replace the microsized phosphors in FED devices. Xu et al. also demonstrated that these as-prepared nanocrystalline phosphors (Lu\textsubscript{2}Ga\textsubscript{5}O\textsubscript{12}:Tb\textsuperscript{3+}) by the PSG process can form a more compact phosphor screen, which exhibits an improved luminescent efficiency and stability under the bombardment of an electron beam.\textsuperscript{67} Wakefield et al. also confirmed that the nanocrystalline oxide based phosphors (Y\textsubscript{2}O\textsubscript{3}:Eu and Zn\textsubscript{2}SiO\textsubscript{4}:Mn) had better luminescence efficiencies than that of commercial FED phosphors, which shows promising properties for use in low voltage field emission displays.\textsuperscript{101}

Homogenous precipitation process. The homogenous precipitation process is a simple, effective solution-based method for a large-scale fabrication of novel inorganic nano/microstructured materials under template-free conditions. It is usually used to synthesize hydroxide materials under different precipitants using metal salts as precursors.\textsuperscript{87} After an annealing process at a moderate temperature, the obtained hydroxides can be transformed into oxide materials with maintaining the morphology.

Over the past several years, monodisperse nano and microstructures with controllable morphologies and sizes have been synthesized by homogenous precipitation process and their size-dependent luminescence properties have been investigated. Li et al. has reported the simple synthesis of monodisperse β-Ga\textsubscript{2}O\textsubscript{3}:Dy\textsuperscript{3+},\textsuperscript{66} La\textsubscript{2}O\textsubscript{3}/La\textsubscript{2}O\textsubscript{2}CO\textsubscript{3}:RE\textsuperscript{3+} (RE = Eu, Tb, Yb, Ho, Er, Tm),\textsuperscript{87} etc., with defined morphologies and narrow size dispersions (Fig. 1a–g) by optimizing the external experimental parameters. They demonstrated that the cathodoluminescence properties of the phosphors can be improved by improving the morphologies and sizes of the phosphor particles. As shown in Fig. 1h, the relative CL emission intensities of the β-Ga\textsubscript{2}O\textsubscript{3}:Dy\textsuperscript{3+} phosphors are different with different morphologies/sizes, which are attributed to the difference of surface defects. The more defects on a phosphor particles surface, the lower the luminescent efficiency, which is due to the increase of non-radiative transitions. A similar situation appears in the as-prepared La\textsubscript{2}O\textsubscript{3}/La\textsubscript{2}O\textsubscript{2}CO\textsubscript{3}:RE\textsuperscript{3+} (RE = Eu, Tb) phosphor particles with different shapes and sizes (Fig. 1i and j). Jung et al. also improved the luminance of Zn\textsubscript{2}SiO\textsubscript{4}:Mn phosphors by the homogenous precipitation process.\textsuperscript{110} The as-prepared Zn\textsubscript{2}SiO\textsubscript{4}:Mn phosphor particles present a uniform spherical shape and have an enhanced emission intensity compared to commercial Zn\textsubscript{2}SiO\textsubscript{4}:Mn bulk phosphors, as shown in Fig. 2(a–c). In addition, spherical sub-micrometre Y\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+} and cubic (Y, Gd)\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+} phosphor particles have been synthesized through a novel homogeneous precipitation method by Silver et al.\textsuperscript{121} These cubic-Y\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+} spherical phosphor particles (ca. 300 nm) will be ideal for FED devices as they can densely close-pack on screens (Fig. 2d) and they display a high luminous efficiency under low-voltage electron beam excitation (Fig. 2e). It is also confirmed that these particles are useful in voltage ranges up to 5000 V and perform well at such voltages compared to commercial phosphors. Therefore, it is concluded that the luminescent efficiencies of inorganic nano and microstructures are strongly related to their morphologies and sizes. Through the modification of morphology, size and surface, one can reduce surface defects and thus enhance the luminescent efficiencies of phosphors.

Hydro/solvothermal process. As a typical solution-based approach, the hydro/solvothermal process generally employs water or organic solvents under certain temperatures and pressures for the synthesis of various inorganic nano and/or microcrystals due to advantages including a relatively green synthesis, easily controllable reaction conditions, low reaction temperature (in general \textless 250 °C) and cost, high yield, and especially an easily controllable size,
structure and shape of the products. Shang et al. developed a water-based hydrothermal system to prepare Zn$_2$GeO$_4$:Mn$^{2+}$ phosphors with an irregular submicrorod shape. Fig. 3a shows a possible formation mechanism of the Zn$_2$GeO$_4$:Mn$^{2+}$ submicrorods, which is as follows: firstly, GeO$_2$ is hydrolyzed to form GeO$_3^{2-}$ ions, and then Zn$^{2+}$, Mn$^{2+}$ and GeO$_3^{2-}$ ions combine to form Zn$_2$GeO$_4$ nuclei in the presence of OH$^-$ ions. These nuclei further grow along the c-axis to produce Zn$_2$GeO$_4$:Mn$^{2+}$ nanorods and finally aggregate together to form Zn$_2$GeO$_4$:Mn$^{2+}$ submicrorod-like bundles. Annealing at different temperatures can remove H$_2$O and organic components on the surface, obtaining Zn$_2$GeO$_4$:Mn$^{2+}$ submicrorod phosphors. As shown in Fig. 3b–d, the Zn$_2$GeO$_4$:Mn$^{2+}$ submicrorod phosphor has a smooth surface, regular shape and narrow size distribution compared to the bulk material prepared by the solid state reaction method. Due to the optimal shape, size and surface of the particles, the cathodoluminescence efficiency of Zn$_2$GeO$_4$:Mn$^{2+}$ phosphor was enhanced.

During the process of hydro/solvothermal reaction, selecting an appropriate organic additive with functional groups is one of the promising and popular strategies to control shape and size. The organic additive generally acts as a complex agent or structure-directing agent. By using oleic acid in the reaction system, Shang et al. successfully prepared well-separated LaOF:RE$_{3+}$ (RE = Eu$^{3+}$, Ho$^{3+}$, Tm$^{3+}$, Dy$^{3+}$, Sm$^{3+}$, Tb$^{3+}$) nanoparticles with sizes of about 30–50 nm (Fig. 4A). The HRTEM image (inset in Fig. 4A) shows lattice planes with perfect crystallinity. Due to their excellent dispersion and crystallinity, these as-prepared LaOF:RE$_{3+}$ phosphor nanoparticles can also be compactly coated on a screen to improve the intensity of the emitted light and device lifetime. Doping RE$_{3+}$ ions into a LaOF host, emission colors from blue to red with a high color purity (4f–4f transition, Eu$^{3+}$, red; Ho$^{3+}$, green; Tm$^{3+}$, blue; Dy$^{3+}$, yellow; Sm$^{3+}$, orange in Fig. 4C) were obtained. Importantly, the green-emitting LaOF:Tb$^{3+}$ and blue-emitting LaOF:Tm$^{3+}$ with the CIE chromaticity coordinates LaOF:0.07Tb$^{3+}$ (0.2521, 0.5647) and LaOF:0.005Tm$^{3+}$ (0.1510, 0.0761) are more pure than those of ZnO:Zn (0.2053, 0.3879) and Y$_2$SiO$_5$:Ce (0.1651, 0.1568), respectively. For CL, the efficiency of a luminescent...
material includes the radiant efficiency ($\eta$) and the luminous efficiency ($L$, brightness),14 which can be compared roughly by their emission peak areas (integrated luminescence intensity) and the CL intensity (in height), respectively. It can be seen from Fig. 4D that under the same excitation conditions, although the emission peak areas of the LaOF:RE$^{3+}$ (RE = Tm$^{3+}$, Tb$^{3+}$, ZnO:Zn and $Y_2SiO_5$:Ce) phosphors are smaller than that of ZnO:Zn and $Y_2SiO_5$:Ce, the CL intensity (in height) and integrated area (Radiant efficiency) of the LaOF:RE$^{3+}$ (RE = Tm$^{3+}$, Tb$^{3+}$, ZnO:Zn and $Y_2SiO_5$:Ce) phosphors can be considered as potential full color LED phosphors.

In addition, the morphology and size of the products can also be well controlled and modified by a combination of water and organic solvents in the hydrothermal process. During these fabrication processes, organic solvents act as the “shape modifier” to either promote or inhibit crystal growth by modifying crystal growth dynamically and thus can adjust and control the morphology and size of the products. By using the above synthesis method, a series of cathodoluminescent materials such as $\beta$-Ga$_2$O$_3$:Dy$^{3+}$,66,124 Gd$_2$O$_3$:Eu$^{3+}$,125 and Lu$_2$O$_3$:RE$^{3+}$ (RE = Eu, Tb, Dy, Pr, Sm, Er, Ho, Tm)$^{126}$ with regular prism, rod or sphere shapes at the nano to microscale were synthesized, which not only improve the cathodoluminescence performances of the phosphors but also meet some of requirements in the minitype of FED devices.

**Electrospinning process.** Due to specific and fascinating luminescence properties, for example various emission lifetimes and increased luminescence efficiencies, etc., there is a growing interest in studying new luminescent materials in one-dimensional (1D) nanostructures.127–134 These one-dimensional luminescence nanomaterials possess diverse potential applications in nanoscale electronics, photonics, display and advanced bioanalysis.38 The electrospinning technique is an effective and simple method for preparing one-dimensional (1D) nanomaterials. It is a process that uses the strong electrostatic force from a high static voltage acting on a polymer solution placed in a container with a millimeter diameter nozzle. Under an applied electrical force, the polymer solution is ejected from the nozzle.38,127 After the solvents are evaporated during the course of jet spraying, the fibers are collected on a grounded collector. In the past few years, some researchers have combined the electrospinning technique with sol–gel process to prepare a rich variety of 1D luminescent nanomaterials.38,128–134 The electrospinning setup and formation process of 1D luminescent nano/microstructures is shown in Scheme 3. 1D nanomaterials synthesized by this method usually have an exceptionally long length, a uniform diameter and a diverse composition.

Through the electrospinning process a variety of RE$^{3+}$ ion doped 1D fiber, tube and belt-like cathodoluminescent materials, including LaOCl,15 CaTiO$_3$,129 VVO$_4$,130 GdVO$_4$,135 LaPO$_4$,136 $Y_2SiO_5$,137 Ca$_2$Y$_6$(SiO$_4$)$_6$O,139 Ca$_2$Gd$_6$(SiO$_4$)$_6$O$_2$,139 La$_{2}$Si$_3$(SiO$_4$)$_2$O$_2$,140 CaWO$_4$,141 Tb$_2$(WO$_4$)$_3$,142 Gd$_2$MoO$_6$,143 CaMoO$_4$,144 have been derived and/or optimized. In particular morphology- and size-dependent luminescence performances were investigated and the color tuning by doping different kinds of RE$^{3+}$ ions, changing RE$^{3+}$ ion concentrations, co-doping and/or energy transfer were designed. For example, the as-prepared LaOCl:Eu$^{3+}$ 1D nanofiber, nanotube and microbelt phosphors are all composed of nanoparticles with perfect crystallinity, as shown in Fig. 5a-c. The comparison of the CL spectra of LaOCl:Eu$^{3+}$ 1D nanomaterials with three different morphologies/sizes (here all the experimental conditions were kept identical) is shown in Fig. 5d, and it can be seen that the CL intensity (in height) and integrated area (Radiant efficiency) of the LaOCl:Eu$^{3+}$ 1D nanomaterials are smaller than that of the ZnO:Zn and $Y_2SiO_5$:Ce phosphors, which not only improve the cathodoluminescence performances of the phosphors but also meet some of requirements in the minitype of FED devices.

**Scheme 3** Schematic diagram of the electrospinning setup and the formation process of 1D luminescent nano/microstructures. (Reproduced with permission from ref. 15, copyright 2010, Wiley.)
be seen that the belt-like sample has a higher CL intensity than that of the fiber-like and tube-like samples. That is because the LaOCl:Eu$^{3+}$ nanofibers and nanotubes produce more surface defects than microbelts due to the smaller nanoparticles and larger surface area. However, defects have serious drawbacks for the luminescent intensity of phosphors as they provide non-radiative recombination routes for electrons and holes. The same morphology- and size-dependent luminescence performance appears in systems of YVO$_4$:RE$^{3+}$ (RE = Eu, Tb, Dy, Tm) 1D nanomaterials, and the corresponding CL spectra are shown in (d). The dependence of the CL intensities of LaOCl:RE$^{3+}$ 1D nanomaterials on the accelerating voltage (kV) and filament current (mA), respectively. (Reproduced with permission from ref. 15, copyright 2010, Wiley.)

Hydrolysis-sol–gel method. According to previous research, the emission performances can be improved in spherical phosphors with respect to the irregular ones, which are basically attributed to the high packing densities and low scattering of light. Therefore, there has been a growing interest in synthesizing inorganic phosphors with spherical morphologies in recent years. As one of the most well-known hydrolysis method, the Stöber method, which is based on the hydrolysis of tetraethylorthosilicate (TEOS) in an alcohol medium in the presence of water and ammonia, has been extensively employed to prepare monodisperse silica (SiO$_2$) spheres with sizes from nano to micrometers by a modified procedure. Lin’s group developed a combination of these monodisperse SiO$_2$ spheres and the PSG process by following suitable annealing temperatures to synthesize a series of monodisperse and spherical core–shell structured phosphors (Scheme 4). The size-dependent and/or tunable luminescence properties have also been extensively investigated. The concrete experimental process is extremely simple and is as follows: first, stir the as-formed SiO$_2$ particles in corresponding PSG precursor solutions of the phosphors (composed of metal ions, citric acid and PEG), then separate the SiO$_2$ particles by centrifugation following a heat treatment to obtain the final phosphor products. The size of the phosphor particles can be controlled by the ones of the silica cores and the number of coating cycles. By the above method, a variety of precursor solutions of phosphors can be coated on the surface of SiO$_2$ spheres to form the desired spherical phosphors. For example, the comparison of the TEM images of Fig. 6a and d clearly increase in electron energy and filament current are attributed to the deeper penetration of the electrons into the phosphor body and the larger electron-beam current density. However, a larger current density may result in the accumulation of excess electrons on the phosphor surface. If these electrons cannot be promptly transferred, the cathodoluminescence efficiency will be reduced due to a saturation behavior. Under low-voltage electron beam excitation, the CL emission intensities of 1D LaOCl:RE$^{3+}$ nanophosphors gradually elevate with increasing accelerating voltage and filament current without an obvious saturation behavior (Fig. 5g and h), which is beneficial in FED devices.

**Scheme 4** Hydrolysis-sol–gel synthesis of spherical core–shell-structured phosphors.
shows that the YVO₄:Eu³⁺ phosphor layer was formed on SiO₂ surface and the HRTEM and ED images also confirm the formation of the YVO₄:Eu³⁺ phase. The photoluminescence emission spectra of the as-formed SiO₂@YVO₄:Eu³⁺ phosphor exhibits excellent red emission of Eu³⁺ (618 nm, ⁵D₀ → ⁷F₂) in the YVO₄:Eu³⁺ system. More importantly, the luminescent properties of the core–shell structured phosphor particles can be tuned and optimized by changing the size of SiO₂ cores and thickness of the phosphor shells (Fig. 6f). Due to their low cost (silica is cheaper than most of the pure phosphor materials that often employ expensive rare earth elements as the activators and/or host components) and large scale synthesis, a series of spherical core–shell structured cathodoluminescent materials were prepared and the corresponding core–shell sizes and emission properties are collected in Table 1.¹⁴⁵,¹⁴⁷–¹⁶⁰

Spray pyrolysis process. Except for hydrolysis-sol–gel method, better spherical morphologies with a size around 0.5–3 μm for phosphors can be obtained by the spray drying process.⁹⁶ It needs a combination of PSG precursor solutions and a subsequent annealing process to obtain the final phosphor products. Shimomura et al.⁵⁷ obtained high luminance and a small-sized Y₂O₃:Eu³⁺ phosphor with little agglomeration by spray pyrolysis, as shown in Fig. 7a. The maximum luminance in this study was better than that of commercial Y₂O₃:Eu³⁺ phosphor synthesized by solid state reaction at the same median particle size (Fig. 7b). By loading the corresponding precursor solution in a spray drying apparatus and following this with an annealing process at a high-temperature (600–1200 °C), the representative red-emitting Y₂O₃:Eu³⁺,⁹⁹ green-emitting Y₂O₃: Tb³⁺,¹⁶¹ and blue-emitting Sr₂CeO₄:Ce³⁺⁹⁰ FED phosphors were also prepared as spherical particles with sizes ranging from 0.6 to 3.0 μm. It is demonstrated that the as-prepared spherical phosphors indeed improve their emission intensity over the other irregular ones, which is also due to the high packing densities and low scattering of light.⁹⁹,¹⁶¹ It is noticed that the disadvantage of phosphors prepared by spray pyrolysis is that the optimal heating temperature was generally higher than that for the solid-state reaction.⁵⁷ Moreover, it also has a bigger size distribution than that prepared by the homogenous precipitation or hydrolysis-sol–gel methods. Therefore, it will be further improved.

2.1.2 Modification of phosphor composition. For phosphors to produce luminescence, the substitution of cations in the host lattice with activator ions is often involved, which easily results in a mismatch of charge and crystal lattice due to different valence state and ion radius. These mismatches will generate many defects (vacancy, gap, crystal lattice distortion and strain) to decrease the luminescent efficiency of the phosphors, and as a result need to be avoided or reduced. By modifying the phosphor composition, the luminescent performance of the phosphors

Table 1 Characteristics of some core–shell structured phosphor particles prepared by the PSG process

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂ core–phosphor shell size (nm)</th>
<th>Emission colors</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂@Y₂O₃:Eu³⁺</td>
<td>500/60</td>
<td>Red (Eu³⁺)</td>
<td>148</td>
</tr>
<tr>
<td>SiO₂@YVO₄:Eu³⁺/Dy³⁺/Sm³⁺</td>
<td>500/60</td>
<td>Red (Eu³⁺); yellow (Dy³⁺); orange (Sm³⁺)</td>
<td>145</td>
</tr>
<tr>
<td>SiO₂@Gd₂(WO₄)₃:Eu³⁺</td>
<td>400, 500, 600, 700/50</td>
<td>Red (Eu³⁺)</td>
<td>149</td>
</tr>
<tr>
<td>SiO₂@NaGd(WO₄)₃:Eu³⁺</td>
<td>400/40</td>
<td>Red (Eu³⁺)</td>
<td>151</td>
</tr>
<tr>
<td>SiO₂@CaWO₄:Eu³⁺/Tb³⁺</td>
<td>500/50</td>
<td>Red (Eu³⁺) green (Tb³⁺)</td>
<td>152</td>
</tr>
<tr>
<td>SiO₂@LaPO₄:Ce³⁺/Tb³⁺</td>
<td>1200/60</td>
<td>Red (Eu³⁺); green (Ce³⁺,Tb³⁺)</td>
<td>153</td>
</tr>
<tr>
<td>SiO₂@CaMoO₄:Eu³⁺/Ce³⁺/Tb³⁺</td>
<td>385/50</td>
<td>Red (Eu³⁺); green (Ce³⁺,Tb³⁺)</td>
<td>154</td>
</tr>
<tr>
<td>SiO₂@Y₂SiO₅:Eu³⁺/Ce³⁺,Tb³⁺</td>
<td>385/50</td>
<td>Red (Eu³⁺); green (Ce³⁺,Tb³⁺)</td>
<td>155</td>
</tr>
<tr>
<td>SiO₂@La₂Mo₂O₇:Eu³⁺</td>
<td>500/50</td>
<td>Red (Eu³⁺)</td>
<td>156</td>
</tr>
<tr>
<td>SiO₂@YBO₃:Eu³⁺</td>
<td>300, 570, 950, 1200/100</td>
<td>Red (Eu³⁺)</td>
<td>157</td>
</tr>
<tr>
<td>SiO₂@Y₃Al₅O₁₂:Ce³⁺/Tb³⁺</td>
<td>500/100</td>
<td>Green (Tb³⁺)</td>
<td>158</td>
</tr>
</tbody>
</table>

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can be efficiently improved. Generally, composition modifications of phosphors mainly focus on two aspects: one is to conduct charge compensations for relaxing charge mismatches, and the other is to relieve crystal lattice strain by introducing other cations with a complementary radius. Based on the above consideration, representative Ca$_2$GeO$_4$:Eu$^{3+}$ and Zn$_2$GeO$_4$:Mn$^{2+}$ phosphors have been optimized and the effect of the composition modification on cathodoluminescence efficiencies of phosphors has been elaborately investigated. Fig. 8 shows the CL spectra of Mg-doped Zn$_{1.96}$GeO$_4$:0.04Mn$^{2+}$ samples show their maximum emission at 532 nm (green light with CIE chromaticity coordinates $x = 0.268$, $y = 0.644$) under the excitation of 3 kV accelerating voltage, which corresponds to the characteristic emission of Mn$^{2+}$ from $^4T_1$ to $^6A_1$, as shown in Fig. 8a. Moreover, the CL intensity increases with the replacement of Mg$^{2+}$ ions. The possible reason is the joining of Mg$^{2+}$ ions ($r = 0.57$ nm, Coordination Number (CN) = 4) decreases the crystal lattice strain due to the mismatched ions radius with Zn$^{2+}$ ($r = 0.60$ nm, CN = 4) and Mn$^{2+}$ ($r = 0.66$ nm, CN = 4) ions. The relaxing of the crystal lattice strain can efficiently suppress non-radiative processes and finally result in the improvement of cathodoluminescence efficiency. A similar situation appears in the Mg$^{2+}$, Ba$^{2+}$-doped Ca$_{1.99}$GeO$_4$:0.01Eu$^{3+}$ systems (Fig. 8b). The emission intensities of Mg-0.2 and Mg-1.0 doped Ca$_{1.99}$GeO$_4$:0.01Eu$^{3+}$ samples are comparable to or even higher than that of the Ca$_{1.99}$GeO$_4$:0.01Eu$^{3+}$ sample, but the emission drastically decreases in the Ba-1.99 sample. This may be because the radius of Mg$^{2+}$ ions is smaller than that of Ca$^{2+}$ ions, which allows Mg$^{2+}$ ions to enter more easily into the host lattice, introducing the smaller lattice distortion. While the doping of Ba$^{2+}$ ions increases the lattice distortion due to a larger ion radius than Ca$^{2+}$ ions, and thus decreases the luminescent intensity. For Ca$_{1.99}$GeO$_4$:0.01Eu$^{3+}$ systems, there is a charge mismatch between Eu$^{3+}$ and Ca$^{2+}$ ions. According to the electroneutrality theory, two Eu$^{3+}$ ions will replace three Ca$^{2+}$ ions to obtain charge balance, and as a result two positive defects of $[\text{EuCa}]^{2+}$ and one negative Ca$^{2+}$ vacancy of $[\text{V}_{\text{Ca}}]^{-}$ would form.
These defects and vacancies may capture excited electrons to proceed to non-radiative transitions and damage the luminous efficiency. Therefore, Shang et al. introduced Li⁺ ions or Al³⁺ ions to use as compensation for charge defects. Co-doping Li⁺ ions can help to incorporate Eu³⁺ ions into Ca²⁺ sites by compensating for the different charges between Eu³⁺ and Ca²⁺ ions and the red light emission intensity of Ca₁.₉₉L₁₀.₀₁Eu₀.₀₁GeO₄ is elevated with respect to Ca₁.₉₉Eu₀.₀₁GeO₄. In the Al³⁺ co-doped Ca₁.₉₉Eu₀.₀₁GeO₄ sample, the Al³⁺ ions may replace the Ge⁴⁺ ions, which can also maintain the charge compensation and reduce the luminescent efficiency. Unexpectedly, it exhibits a decrease in the crystal lattice strain. This is attributed to the electronegativity difference between Ge and O (Δχ = 1.43) being lower than that between Al and O (Δχ = 1.83). The compound composed of elements with small differences in electronegativity (X) should have a narrower band gap which leads to a higher conductivity, while the cathodoluminescence intensity is related to the conductivity of the phosphors and a narrow gap can lead to higher conductivity, which is beneficial to the cathodoluminescence. So the CL emission intensity of the Al³⁺-codoped sample is decreased compared with that of the un-codoped sample. An X-ray diffraction study by Shimomura et al. indicated that the highest luminescence Y₂O₃:Eu³⁺ phosphor obtained by the addition of a lithium salt had little strain in the crystal and its crystal growth was promoted by the additive. Therefore, the luminance improvement by Li composition modification originated from the acceleration of crystal growth and reduction of its strain. Similar research was carried out and reduction of its strain. Similar research was carried out.

A simple model to illustrate the possible increasing mechanism of luminescent efficiency by composition modification (charge compensations and crystal lattice strain relaxing).

Scheme 5 A simple model to illustrate the possible increasing mechanism of luminescent efficiency by composition modification (charge compensations and crystal lattice strain relaxing).

A simple model to illustrate the possible increasing mechanism of luminescent efficiency by composition modification is shown in Scheme 5. During the process of doping cations into the host lattice, if its valence state is higher than that of the host cations, cation vacancies will be produced, whereas oxygen vacancies will appear (Scheme 5a). These vacancies, namely crystal lattice defects, increase the probability of non-radiative transitions, and thus decrease luminescent efficiency. When introducing charge compensator ions into the host lattice, charge defects will be reduced and thus the luminescent performance will be improved. On the other hand, cationic replacements with a different radius in one matrix will result in crystal expansion or shrinkage. This will generate strain or many defects due to the distorted crystal lattice, which also increases the possibility of non-radiative transitions. By doping other ions with a complementary radius, it can relieve lattice strain and then decrease defects, which finally enhance the luminescence efficiency of the phosphor (Scheme 5b). In general, the cathodoluminescence efficiency of FED phosphors can be optimized by composition modification, including charge compensations and crystal lattice strain relaxing, which promotes a potential application of phosphors in field emission display devices.

2.1.3 Improvement of conductivity. It is well known that electron beam is used as the excitation source in field emission display technology. In order to realize a highly efficient field emission display, phosphors should be efficiently excited by low voltage electrons. Although the accelerating voltage employed in FEDs is much less than that worked in CRTs, its energy is still much higher than UV or visible light radiation, which is around a few thousand to thousands of eV. If not promptly transferred, these electrons very easily accumulate on the phosphor surface to recombine with holes/surface defects, which increase non-radiative transitions and thus decrease cathodoluminescence efficiency. In addition, excessive electrons staying on the phosphor surface also easily reach charge saturation. There is a tendency for the brightness to plateau even when the current is increased at a fixed electron voltage, this is a serious concern especially for FEDs since the voltage is normally low (<4 kV), requiring a high current for high power and brightness. Accordingly, an important question for FEDs is how to eliminate or weaken charging and surface recombination effects, and improve saturation. One of the most promising and efficient approaches is to improve the conductivity of FED phosphors. This approach can efficiently and opportunistically release the accumulated charges on phosphors and thus improve the saturation of phosphors and enhance their cathodoluminescence efficiency. Generally, there are two main routes to increase the conductivity of FED phosphors: one is the selection of semiconductor materials as the host lattice and the other is to mix transparent and conductive nanocrystalline powders with FED phosphors. For the selection of hosts, it is known that the compounds composed of elements with small differences in electronegativity have a narrower band gap.
The band gap of oxide-based phosphor systems is related to the crystal structures of the hosts. Generally, reticular acid radical-coordinated polyhedrons in hosts easily result in a narrow band gap host, while the band gap of the host has great effects on the conductivity and luminescent efficiency of phosphors. A narrow gap can lead to a higher conductivity which is beneficial to the cathodoluminescence. On the other hand, luminescence quenching will occur if the energy levels of the excited states of the activator ions are located among the conduction band of the host. Only when the excited states of activator ions are located below the conduction band of the host the phosphors present excellent luminescent performance. Therefore, appropriate hosts with reasonable band gaps should be considered during the study and design of novel FED phosphors, which could merge the luminescence performance and conductivity of phosphors.

According to the first route, a series of RE$^{3+}$ or Mn$^{2+}$ ion activated Ga$_2$O$_3$ (Ca,Sr)In$_2$O$_4$, La(Ga,In)$_2$O$_4$, Mg(Sn,Ti)O$_4$, (Zn,Mg,Ge)$_2$O$_4$, Li$_2$ZnGeO$_4$, etc., cathodoluminescent materials were derived, as summarized in Table 2. Except for the efficient transport of electrons, semiconductor hosts (emission from UV to bluish-green light region) generally have a sensitive enhancement for luminescent efficiency of RE$^{3+}$ ions. A simple model illustrating the luminescence mechanism of the representative phosphor example CaIn$_2$O$_4$:Dy$^{3+}$, Pr$^{3+}$, Tb$^{3+}$ is shown in Fig. 9a.

Under the excitation of electron beam, an electron moves freely around CB and finally relaxes to the donor band (oxygen vacancies). The recombination of the electron in the donor band with the acceptor (calcium vacancies or indium vacancies) yields a blue emission with a maximum wavelength at 450 nm. When Dy$^{3+}$ is present in the CaIn$_2$O$_4$ host lattices, the excitation energy can be non-radiatively transferred to Tb$^{3+}$, resulting in an enhanced emission of Dy$^{3+}$ (Pr$^{3+}$ or Tb$^{3+}$). Furthermore, after continuous electron beam excitation for half an hour, the CaIn$_2$O$_4$:0.015Dy$^{3+}$, Eu$^{3+}$, Dy$^{3+}$ (Pr$^{3+}$ or Tb$^{3+}$) is experimentally observed a 92% and 90% of their original intensity, but for the commercial Y$_2$O$_2$S:0.05Eu$^{3+}$ phosphor, it only keeps 80% of its original intensity value, as shown in Fig. 9a-d, respectively. The results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Emission peaks (nm)/main transition</th>
<th>Color</th>
<th>CIE chromaticity coordinates (x, y)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga$_5$O$_3$:Dy$^{3+}$</td>
<td>438/T$<em>{1g}$ -A$<em>1$ (GaO$<em>6$) 492, 580/F$</em>{9/2}$ to H$</em>{11/2}$ 6$^1$H$</em>{13/2}$ (Dy$^{3+}$)</td>
<td>Blue</td>
<td>(0.1837, 0.1602)</td>
<td>66</td>
</tr>
<tr>
<td>CaIn$_2$O$_4$:Eu$^{3+}$</td>
<td>431, 447, 467, 492, 512, 537, 588, 616/D$<em>{1g}$ -F$</em>{0,1,2,3}$ (Eu$^{3+}$); 588/D$<em>{1g}$ -F$</em>{2}$; 619/D$<em>{4g}$ -F$</em>{2}$ (Eu$^{3+}$)</td>
<td>White</td>
<td>(0.3237, 0.3232)</td>
<td>54</td>
</tr>
<tr>
<td>CaIn$_2$O$_4$:Dy$^{3+}$, Pr$^{3+}$, Tb$^{3+}$</td>
<td>493, 582/F$<em>{9/2}$ to H$</em>{11/2}$, 6$^1$H$<em>{13/2}$ (Dy$^{3+}$); 494/5P$</em>{0}$ -H$<em>{11/2}$ (Pr$^{3+}$); 487/D$</em>{2g}$ -F$<em>4$; 544/D$</em>{3g}$ -F$_3$ (Tb$^{3+}$)</td>
<td>Yellowish white</td>
<td>(0.3456, 0.3758)</td>
<td>71</td>
</tr>
<tr>
<td>SrIn$_2$O$_4$:Dy$^{3+}$, Pr$^{3+}$, Tb$^{3+}$</td>
<td>493/4F$<em>{9/2}$ -H$</em>{11/2}$, 487/4F$<em>{9/2}$ -H$</em>{11/2}$ (Dy$^{3+}$); 494/5P$<em>{0}$ -H$</em>{11/2}$ (Pr$^{3+}$); 487/D$_{2g}$ -F$<em>4$; 544/D$</em>{3g}$ -F$_3$ (Tb$^{3+}$)</td>
<td>Cyan</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>LaOCl:Sm$^{3+}$, Dy$^{3+}$, Sm$^{3+}$, Tb$^{3+}$, Eu$^{3+}$</td>
<td>485/D$<em>{2g}$ -F$<em>5$ (Sm$^{3+}$); 480, 571/F$</em>{9/2}$ to H$</em>{11/2}$, 6$^1$H$<em>{13/2}$ (Dy$^{3+}$); 565, 607, 650/G$</em>{5/2}$ -H$<em>{11/2}$, 6$^1$H$</em>{13/2}$ (Sm$^{3+}$); 584, 416, 437, 486, 543/D$_{3g}$ -F$<em>j$ (j = 6 - 0) (Tb$^{3+}$); 615/D$</em>{5g}$ -F$_5$ (Eu$^{3+}$)</td>
<td>Green</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>LaGaO$_3$:Tm$^{3+}$, Sm$^{3+}$, Tb$^{3+}$, Dy$^{3+}$, Eu$^{3+}$</td>
<td>458/D$<em>{2g}$ -F$<em>5$ (Tm$^{3+}$); 561, 597, 642/G$</em>{5/2}$ -H$</em>{11/2}$, 6$^1$H$<em>{13/2}$ (Sm$^{3+}$); 414, 437, 414/D$</em>{4g}$ -F$<em>{4}$ (Tb$^{3+}$); 480, 572/F$</em>{9/2}$ to H$<em>{11/2}$, 6$^1$H$</em>{13/2}$ (Dy$^{3+}$); 590, 614/D$_{5g}$ -F$_5$ (Eu$^{3+}$)</td>
<td>Blue</td>
<td>—</td>
<td>—</td>
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<tr>
<td>LaInO$_3$:Eu$^{3+}$</td>
<td>465, 491, 512, 534, 588, 610/D$<em>{0,1,2,3}$ -F$</em>{0,1,2,3}$ (Eu$^{3+}$); 588, 610/D$<em>{5g}$ -F$</em>{1}$ (Eu$^{3+}$)</td>
<td>Yellowish white</td>
<td>(0.3668, 0.4040)</td>
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<td>Mg(Sn,Ti)O$_4$:Mn$^{2+}$</td>
<td>465/SnO$_4$; 456/TiO$<em>4$; 499/T$</em>{1g}$ -A$_1$ (Mn$^{2+}$)</td>
<td>Yellowish white</td>
<td>(0.5740, 0.3451)</td>
<td>—</td>
</tr>
<tr>
<td>Li$_2$ZnGeO$_4$:Mn$^{2+}$</td>
<td>530/T$_{1g}$ -A$_1$ (Mn$^{2+}$)</td>
<td>Blue</td>
<td>(0.1780, 0.2449)</td>
<td>37</td>
</tr>
<tr>
<td>CaGeO$_3$:Eu$^{3+}$</td>
<td>631/D$_{2g}$ -F$_2$ (Eu$^{3+}$)</td>
<td>Blue</td>
<td>(0.1773, 0.2186)</td>
<td>37</td>
</tr>
<tr>
<td>CaYAlO$_4$:Tb$^{3+}$, Eu$^{3+}$</td>
<td>383, 416, 468, 538, 446/D$<em>{4g}$ -F$<em>j$ (j = 6 - 0) (Tb$^{3+}$); 593, 623/D$</em>{5g}$ -F$</em>{1}$ (Eu$^{3+}$)</td>
<td>Blue</td>
<td>(0.181, 0.123)</td>
<td>95</td>
</tr>
<tr>
<td>SrY$_2$O$_7$:Tb$^{3+}$, Sm$^{3+}$, Dy$^{3+}$</td>
<td>545/D$<em>{2g}$ -F$<em>5$ (Tb$^{3+}$); 455/D$</em>{2g}$ -F$<em>5$ (Sm$^{3+}$); 491, 581/F$</em>{9/2}$ to H$</em>{11/2}$, 6$^1$H$_{13/2}$ (Dy$^{3+}$)</td>
<td>Green</td>
<td>(0.278, 0.351)</td>
<td>97</td>
</tr>
</tbody>
</table>

Under the excitation of electron beam, an electron moves freely around CB and finally relaxes to the donor band (oxygen vacancies). The recombination of the electron in the donor band with the acceptor (calcium vacancies or indium vacancies) yields a blue emission with a maximum wavelength at 450 nm. When Dy$^{3+}$ (Pr$^{3+}$ or Tb$^{3+}$) is present in the CaIn$_2$O$_4$ host lattices, the excitation energy can be non-radiatively transferred to Dy$^{3+}$ (Pr$^{3+}$ or Tb$^{3+}$), resulting in an enhanced emission of Dy$^{3+}$ (Pr$^{3+}$ or Tb$^{3+}$). Furthermore, after continuous electron beam excitation for half an hour, the CaIn$_2$O$_4$:0.015Dy$^{3+}$, Eu$^{3+}$, Dy$^{3+}$ (Pr$^{3+}$ or Tb$^{3+}$) still keep 88%, 92% and 90% of their original intensity, but for the commercial Y$_2$O$_2$S:0.05Eu$^{3+}$ phosphor, it only keeps 80% of its original intensity value, as shown in Fig. 9a-d, respectively. The results
show that the CaIn\textsubscript{2}O\textsubscript{4}-based phosphors have better stability than the Y\textsubscript{2}O\textsubscript{2}S-based phosphors under the low-voltage excitation conditions. In general, the cathodoluminescence efficiency and electron beam-stimulated stability can be efficiently improved with the increase of conductivity of the phosphor due to the decrease of charge accumulation and the reduction of surface chemical reaction, respectively.

Another route towards increasing phosphor conductivity is a mixing of conductive nanocrystalline powders like In\textsubscript{2}O\textsubscript{3}, SnO\textsubscript{2}, ZnO, Au, Ag, and so on on.\textsuperscript{27,67,89,168–170} Zhang et al. encapsulated a In\textsubscript{2}O\textsubscript{3} layer on Y\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+} phosphor particles to form a Y\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+}@In\textsubscript{2}O\textsubscript{3} phosphor and found a positive effect on their cathodoluminescence performance.\textsuperscript{89} They found that the luminous efficiency of the Y\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+}@In\textsubscript{2}O\textsubscript{3} phosphor screens was obviously improved with respect to uncoated Y\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+}, as shown in Fig. 10a. Moreover, the luminous efficiency of the former improves much more than the latter with an increase in the accelerating voltage. This is attributed to the increased electrical conductivity of the Y\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+} phosphors with increasing In\textsubscript{2}O\textsubscript{3} coating (Fig. 10b), which is consistent with the previous reports.\textsuperscript{171,172} In addition, In\textsubscript{2}O\textsubscript{3}-coated Y\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+} phosphor screens have a better stability than the uncoated one under a 700 V accelerating voltage (Fig. 10c). This is because the conductive In\textsubscript{2}O\textsubscript{3} nanoparticles not only can reduce the surface charge accumulation but also may serve as protective layer on the phosphor surface to prevent chemical degradation caused by the direct electron beam bombardment. Finally, the aging rate of the low-voltage CL efficiency is suppressed and as a result the lifetime and stability of the phosphor screens are remarkably improved.\textsuperscript{171} They also observed the Commission International de l’Eclairage (CIE) chromaticity coordinates stability of Y\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+}@In\textsubscript{2}O\textsubscript{3} phosphors under electron beam radiation. Under an excitation of 700 V accelerating voltage, the Y\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+}@In\textsubscript{2}O\textsubscript{3} phosphors gives a bright red light, and its CIE values are nearly invariant (\textit{x} and \textit{y} keeps at about 0.575 and 0.375) with the changing accelerating voltage (Fig. 10d), which is suitable for applications in field emission displays. Similar improvement for cathodoluminescence efficiency and luminance appear in In\textsubscript{2}O\textsubscript{3}-coated ZnGa\textsubscript{2}O\textsubscript{4} and ZnGa\textsubscript{2}O\textsubscript{4}:Mn\textsuperscript{2+} phosphors.\textsuperscript{168,169} Therefore, employing some conductive materials on the surface of a phosphor can indeed reduce the accumulated electrons on the surface of the phosphor and improve the cathodoluminescence efficiency of the phosphors. This may also act as a bridge to drain the coulomb charge to the ITO substrate efficiently, which decreases the excited voltage and improves the lifetime, stability, and efficiency of the phosphor screen.

2.2 The development of new phosphors for FEDs

Due to a relatively severe operation environment (low voltage and high current density) in FEDs, future generation phosphors
should possess better low voltage efficiencies, chromaticity (high color purity and wide color gamut), saturation and degradation behavior, and maintenance. Possible routes to achieve these improvements include optimizing the morphology, size, surface and crystallization of phosphor grains, enhancing electrical conductivity of phosphors particles, modifying the composition of phosphors, enlarging the color gamut, designing energy transfers, and so on. On the basis of these approaches, in the past decade a series of novel FED phosphors has been developed, as collected in Table 2, which show excellent low-voltage cathodoluminescence properties and have promising applications in field emission display devices. Although most of the newly developed low-voltage cathodoluminescent materials commonly have the higher color purity and color stability than traditional FED phosphors, for examples, LaOCl:TM3+ and LaGaO3:Tb3+ than Y2SiO5:Ce (blue);86 LaOCl:Tb3+ than ZnO:Zn (green);92 (Zn,Mg)2GeO4:Mn2+ and Mg2SnO4:Mn2+ than Y2SiO5:Tb3+ (green);37,75 NaCaPO4:Mn2+ than (Zn,CdS):Ag+ (yellow),94 the luminescent efficiencies of the formers are still lower than the latters. Fortunately, the luminescent disadvantages of the newly developed low-voltage cathodoluminescent materials can be reduced or eliminated to some extent through process optimization, including improvements to the morphology, size and crystallization of phosphors. Therefore, it is very necessary to study appropriate preparation processes for these phosphors.

3. Phosphor thin films and patterning

Except for phosphor powders, phosphor thin films are the other important form to apply in display faceplates. Usually, phosphor thin films are formed by depositing a phosphor precursor on a substrate following a subsequent annealing. In the previous sections, the main discussion was focused on cathodoluminescent materials in powder forms prepared by various soft chemical methods. Phosphor thin films appear more attractive for field emission displays (FEDs) because they could be operated at lower voltage and endure much higher power densities without degradation than those with powder phosphors.99,173 In addition, phosphor thin films also offer advantages such as higher contrast and resolution, better thermal stability, superior thermal conductivity, a high degree of uniformity and better adhesion to the substrate, and reduced outgassing for FEDs compared with the conventional display screen prepared by the direct deposition of phosphor grains.174–178 In order to define a smaller pixel spot size and then achieve a higher resolution, thin film phosphors should possess uniform thickness, smoother surface form and small grain size. To date, phosphor thin films have been prepared by a variety of deposition techniques, such as chemical vapor deposition (CVD),179 physical vapor deposition (PVD),180 ion beam sputtering,181 filtered arc deposition,182 electrophoretic deposition (EPD),183 spray pyrolysis,11,12 and pulsed laser ablation.184 These techniques are time-consuming or need expensive and complicated equipment setups. Therefore, a simple and economical method for making high quality phosphor thin films is desirable. Lin’s group studied the facile preparation of oxide phosphor films by the PSG process and investigated their structure, morphology, and optical properties.185–188 The simple preparation process mainly involves three steps: the first step is the preparation of the precursor solution with a certain viscosity, including the dissolution of the starting materials, formation of metal chelates with citric acid (CA) and their polyesterification with PEG; the second step is the preparation of the amorphous precursor film by a dip-coating or spin-coating process on the desired substrates (silica glasses, silicon wafers, ITO and quartz plates, some ceramics slides, etc.); finally, crystalline phosphor films are produced by the postannealing process at moderate temperature (500–1000 °C) with a slow heating rate to avoid the cracking and peeling of the films. Generally, the phosphor thin films prepared via the PSG process are smooth and consist of nanocrystalline grains ranging from 100 to 500 nm, such as the previously reported YVO4:Eu3+ (Fig. 11a and b), GdVO4:Eu3+ (Fig. 11c and d) and LaVO4:Eu3+ (Fig. 11e and f).192 The as-prepared phosphor thin films via the PSG process have many advantages, as follows:185–188 (a) simple process and equipment; (b) low processing temperature, making it possible to prepare films on glass, semiconductor and integrated photo-electronic devices; (c) films can be coated on substrates with a large area, various shapes and different material compositions; (d) an easy control of homogeneity, constituents and microstructure; (e) a controllable thickness by adjusting the viscosity of the coating solution or the repeating number of the coating process.

![Atomic force microscope (AFM) images for YVO4:Eu3+ (a and b), GdVO4:Eu3+ (c and d), and LaVO4:Eu3+ (e and f) phosphor films prepared by the PSG dipcoating process. (Reproduced with permission from ref. 192, copyright 2005, American Institute of Physics.)](image-url)
It is noted that the thin film phosphors present similar luminescence properties to powder phosphors, but have lower emission intensity due to the light trapping inside the luminescent layer. Therefore, such films cannot presently compete with powder phosphors in applications that require high brightness. On the other hand, full-color displays generally need to deposit the three color modules (red, green, blue) on the desired regions to form pixels. Therefore, during the fabrication of display devices, patterning luminescent materials on screen to form pixel matrices is an essential and critical technique. An accurate patterning technology and screening process for phosphor screens has a vital effect on the resolution of display devices. For instance, pitches of phosphor lines for a supervideo graphics adapter with 800 × 600 lines, video graphics adapter with 640 × 480 lines, and quarter video graphics adapter with 320 × 240 lines in 6 in color displays are defined as 50.8, 63.5, and 127 μm, respectively. So far, electrophoretic deposition, screen printing, vacuum deposition, etc., based on photolithographic patterning technologies have been employed to fabricate flat panel display (FPD) devices. Unfortunately, these patterning techniques for a phosphor screen frequently require expensive photolithographic and etching equipment, a complicated layout, and excessive loss of expensive phosphor materials during the fabrication process. Based on these considerations, a growing interest has been focused on soft lithography patterning techniques, which has the potential of becoming a versatile and low cost method for creating submicrometer and micrometer sized structures. The soft lithography technique uses a soft and flexible poly(dimethylsiloxane) (PDMS) elastomer that can exactly replicate the feature of the stamp and form the pattern in this process is shown in Fig. 12 (left). First, polydimethylsiloxane (PDMS) stamp moulds (with different channel widths 5–50 μm) were fabricated by casting PDMS on masters having desired patterns. Then the PDMS moulds were placed in conformal contact with thoroughly cleaned silicon wafer substrates. The channels of the mode thus formed capillaries with the silicon wafer substrate. The phosphor precursor sol (via the PSG process) was then dropped at the open end with a transfer pipette. The capillary force made the sol flow into the mold. Then the moulds and substrates were dried at 100 °C overnight. After carefully removing the moulds, the resulting patterned gel films were heated to a high-temperature (500–1000 °C depending on the host compositions) with a slow heating rate (1 °C min⁻¹) and held for several hours. In this way, phosphor films with patterning were obtained. Fig. 12 (right) shows optical micrographs of the as-prepared patterned LaPO₄:Ce³⁺, Tb³⁺ gel films. The dark and white regions correspond to the film strips and spaces, respectively. It is clearly seen from Fig. 13a–d that film strips have widths of 5, 10, 20, and 50 μm, respectively, with smooth and perfect surfaces. Patterned phosphor films were formed after a subsequent annealing of these patterned gel films. According to the MIMIC technique, many other kinds of patterned phosphor films, such as Y₂O₃:Eu³⁺, Gd₂O₃:Eu³⁺, (Y,Lₐ,Gd)VO₄:Eu³⁺, etc., can be prepared, which are promising for applications of field emission displays.

3.1 Micromolding in capillaries (MIMIC)

As a soft lithography technique, MIMIC can pattern a material based on a low-viscosity solution. Phosphor thin films also can be patterned by the MIMIC technique. The basic principle of this process is shown in Fig. 12 (left). First, polydimethylsiloxane (PDMS) stamp moulds (with different channel widths 5–50 μm) were fabricated by casting PDMS on masters having desired patterns. Then the PDMS moulds were placed in conformal contact with thoroughly cleaned silicon wafer substrates. The channels of the mode thus formed capillaries with the silicon wafer substrate. The phosphor precursor sol (via the PSG process) was then dropped at the open end with a transfer pipette. The capillary force made the sol flow into the mold. Then the moulds and substrates were dried at 100 °C overnight. After carefully removing the moulds, the resulting patterned gel films were heated to a high-temperature (500–1000 °C depending on the host compositions) with a slow heating rate (1 °C min⁻¹) and held for several hours. In this way, phosphor films with patterning were obtained. Fig. 12 (right) shows optical micrographs of the as-prepared patterned LaPO₄:Ce³⁺, Tb³⁺ gel films. The dark and white regions correspond to the film strips and spaces, respectively. It is clearly seen from Fig. 13a–d that film strips have widths of 5, 10, 20, and 50 μm, respectively, with smooth and perfect surfaces. Patterned phosphor films were formed after a subsequent annealing of these patterned gel films.

3.2 Microtransfer molding (μTM)

Microtransfer molding (μTM) is one of the most popular and typical soft-lithography techniques. This technique can directly replicate the feature of the stamp and form the pattern in accordance with the geometry of the stamp. Wang et al. introduced YVO₄:Eu³⁺ as an example to illustrate the fabrication of...
light-emitting arrays via the \( \mu \)TM technique, as shown in the left of Fig. 13a.\(^{204}\) First, the PDMS stamps were fabricated by casting the PDMS prepolymer, a mixture of Sylgard silicone elastomer, and its curing agent over a relief master prepared by photolithography. The elastomer was degassed for 30 min at room temperature and cured at 65 °C for 4 h, then peeled gently from the master. In this way, PDMS stamps with microwells were obtained. Secondly, the quartz plates were made hydrophilic by immersing them in a piranha solution of concentrated sulfuric acid and hydrogen peroxide. Next, the YVO₄:Eu\(^{3+}\) precursor solution was cast on the patterned side of the PDMS mold and the excess solution was removed by scraping with a flat PDMS block. After spin-coating at 1500 rpm, the YVO₄:Eu\(^{3+}\) precursor solution was deposited into the recessed square regions of the PDMS mold, and the mold was brought into contact with the quartz substrate. Then, the mold and substrate were dried at 100 °C for 4 h. When the mold was peeled away carefully, patterned squares of the YVO₄:Eu\(^{3+}\) precursor gels were left on the surface of the quartz substrate. Finally, the patterned substrate was calcined at 700 °C for 3 h to pyrolyze the organic components and the precursor gel was transformed into crystalline YVO₄:Eu\(^{3+}\). The as-prepared YVO₄:Eu\(^{3+}\) precursor gel pattern by the \( \mu \)TM technique (Fig. 13b) exhibits ordered square arrays without obvious swelling or deformation (a high fidelity to the initial PDMS stamp). The estimated side length of the precursor gel square is 22.56 ± 1.37 \( \mu \)m. After calcination at 700 °C in air, the patterned YVO₄:Eu\(^{3+}\) crystalline film was formed on the quartz plate and the corresponding optical microscope image is shown in Fig. 13c. The white square is the final crystalline YVO₄:Eu\(^{3+}\) and the black is the bare substrate. A size-shrinkage of the square gels was observed after firing, which is attributed to the pyrolysis and evaporation of the organic compounds in the gel. The estimated side length of the crystalline square is 19.17 ± 2.05 \( \mu \)m, as observed in Fig. 13b and c. The calcination procedure did not modify the morphology of the printed feature in principle, and the aspect ratio of the square pattern is 1 : 1 before and after heat treatment. However, calcination reduces the size of the square gel spots owing to the pyrolysis and evaporation of the organic species, and the edges of the calcined square spots are not as clear as those of the uncalcined gel spots because of the shrinkage during the heat-treatment process. The red luminescence image (Fig. 13d) and CL spectrum (Fig. 13e) of the YVO₄:Eu\(^{3+}\) phosphor films indicate that the as-prepared YVO₄:Eu\(^{3+}\) phosphor films can be efficiently excited by UV light and a low voltage electron beam.

### 3.3 Microcontact printing (\( \mu \)CP)

Microcontact printing (\( \mu \)CP) is another of the most popular and typical soft-lithography techniques.\(^{204}\) In the contrast to \( \mu \)TM, the \( \mu \)CP technique prints the self-assembled monolayer (SAM) pattern on the substrate in the first step, which makes the substrate change from being chemically homogeneous into chemically heterogeneous. Then other functional materials can be grown or deposited on the desired patterned regions. Although \( \mu \)CP requires multiple steps and the final pattern formation depends on the chemical heterogeneity of the substrate’s surface, these techniques are continuously being developed and improved. For example, a self-assembled monolayer can be firstly transferred...
onto a substrate and its end group can then be modified through organic synthesis to generate well-defined surfaces with a broad range of characteristics. Moreover, μCP is an improved technique based on μTM. Fig. 14a shows the process of fabricating representative YVO₄:Eu³⁺ arrays of dots via μCP. This technique is based on the modification of the substrate surface and the selective deposition on desired regions. First, the PDMS molds and the quartz plates were subjected to the same treatment as μTM technique. The PDMS mold was subsequently flooded with 1H,1H,2H,2H-perfluorooctyltrichlorosilane (PFOTS) solution in n-octane (1 vol%) and blow dried with N₂, then the PDMS mold was placed in contact with the as-cleaned quartz substrate to print the self-assembled PFOTS monolayer (SAM). Next, the patterned substrate was used as a template for the selective deposition of the metal salts solution by spin-coating. During this spin-coating process, the precursor solution was selectively deposited on the hydrophilic regions because of the poor adhesion between the solution and the SAM. Finally, the substrate with the patterned gel was calcined at 700 °C for 3 h to obtain the crystalline YVO₄:Eu³⁺ film. Fig. 14b shows the optical microscope image of a YVO₄:Eu³⁺ precursor gel pattern (just spin-coating dried, without annealing) fabricated by the μCP technique. It can be seen that the ordered dot-patterned gel spots owing to the pyrolysis and evaporation of the organic species, and the edges of the calcined square spots are not as clear as that of the uncalcined gel spots because of shrinkage during the heat-treatment process. Under 254 nm UV light excitation, the patterned YVO₄:Eu³⁺ thin film phosphors show a bright red light emission, as shown in Fig. 14d. The CL spectrum of patterned YVO₄:Eu³⁺ films in Fig. 14e also shows the characteristic Eu³⁺ emission at 596 nm and 619 nm, which correspond to the Eu³⁺ transitions of ⁵D₀→⁷F₁, and ⁵D₀→⁷F₂, respectively. Except for YVO₄:Eu³⁺, many other kinds of patterned phosphor films, such as CaWO₄:Ln³⁺ (Ln = Tb, Eu), Gd₂(WO₄)₃:Ln³⁺ (Ln = Eu, Tb) were also prepared based on the μTM and μCP methods, indicating that soft lithography (μTM and μCP) techniques could be used for patterning inorganic rare-earth salts. These results demonstrate that the Pechini-type sol–gel process has a good compatibility with soft-lithography techniques for patterning inorganic phosphor materials, which holds potential for fabricating new-generation field-emission display devices. Moreover, these results can guide us in future research, and be helpful to others who have interest in these types of devices.

3.4 Inkjet printing (IP)

Recently, inkjet printing has attracted substantial interest as a pathway to make display devices, in which the material deposition and patterning can be performed within a single step by a fully digital driven process. This direct-writing technique has many advantages, such as simplicity, fast, large area, and low material consumption. There are many reports for the application of inkjet printing on the fabrication of polymer light-emitting diodes (PLED). The deposition of light-emitting polymers as pixels or conducting polymer PEDOT:PSS as the hole transportation layer can be carried out by inkjet printing. The CL spectrum of the patterned YVO₄:Eu³⁺ film (accelerating voltage: 4 kV; filament current: 100 mA). (Reproduced with permission from ref. 204, copyright 2011, Wiley.)
printing in the PLED fabrication process. The bottleneck of the inkjet printing technique in organic electronics is being exceeded and some prototypes of full-color organic light-emitting televisions have been demonstrated. The quantum dots are also considered excellent candidates for the inkjet printing route in fabricating a display device due to their good dispersibility in solvent and the size tunable light emission. Cheng et al. have made an attempt to pattern inorganic phosphor materials for the application of a field emission flat display by the inkjet printing technique. The principle of this process is shown in Fig. 15. Using YVO$_4$:Eu$^{3+}$ as a representative example, the patterning of phosphor thin films through inkjet printing technique can be realized. The inkjet printing system consists of a piezoelectric-type printing head with a nozzle diameter of 70 μm. The microdrops were squeezed out by applying a voltage to the glass capillary inside the dispenser head. A computer-controlled motorized translation stage can move along the x,y directions relative to the dispenser head which provide the patterns on the substrate such as dots and lines. Prior to the inkjet printing process, the ITO glass plates were first immersed into the saturated NaOH–ethanol solution for 5 h and then ultrasonically cleaned for 10 min to remove the organic contamination. Then the ITO glass substrates were rinsed by copious amounts of deionized water and dried under nitrogen flow to form a hydrophilic surface. Additionally, the hydrophobic ITO surface was obtained by putting the precleaned ITO glass plates into a 3 mM perfluorooctyltrichlorosilane (PFOTS, Aldrich) solution in hexane for 4 h to self-assemble the densely packed monolayer of PFOTS onto the ITO surface. After careful filtration with a polyvinylidene fluoride (PVDF) microporous filter, the ink solution was loaded onto the inkjet printing system to produce the dots or lines pattern on the ITO glass. The driven voltage and pulse width are 20 V and 34 μs, respectively. The inkjetting frequency is 100 droplets per second. After being dried at 100 °C for 20 min, the resulting pattern-formed substrates were baked at 600 °C with an increasing rate of 1 deg min$^{-1}$ and held there for 4 h in air in order to form the light-emitting YVO$_4$:Eu$^{3+}$ pixels. Fig. 16a, c and b, d show the microscope image of as-inkjet-printed dots array before and after annealing, respectively. Obviously, the as-inkjet-printed dots arrays are highly uniform before and after annealing. However, significant shrinking in the diameter of the dots due to the removal of the organic components was observed after annealing at 600 °C, although its shape was maintained. In addition, it can be seen from Fig. 16e that the crystalline YVO$_4$:0.05Eu$^{3+}$ is composed of fine particles with size between 20 and 120 nm (measured on the long axis) after 600 °C annealing.
The patterned YVO₄:0.05Eu³⁺ film shows the strong red emission under a hand-held UV light with 254 nm wavelength (Fig. 16f), which indicates the feasibility of printing inorganic nanophasor material for high-resolution screen application through the Pechini-type sol–gel and inkjet printing route. Under the excitation of a low voltage electron beam, the patterned YVO₄:0.05Eu³⁺ film can also give good red light emission centered at 614 and 619 nm due to the ⁵D₂→⁷F₂ transition, as shown in Fig. 16e. Moreover, the CL intensity increases quickly upon raising the accelerating voltage from 1 to 4 kV when the filament current is fixed on 105 mA, indicating that the light-emitting intensity of YVO₄:0.05Eu³⁺ is strongly dependent on the accelerating voltage, which is in line with the FED working principle. In summary, the preparation of patterning YVO₄:Eu³⁺ light-emitting pixels by a combination of inkjet printing and the PSG method shows a feasible scheme for patterning inorganic thin film phosphors by the inkjet printing route. This facile and quick method has the potential to be used in the fabrication of FED devices by continuing efforts to further improve the properties of the ink solution and prestructuring substrate, modifying the layout, and so forth.

4. Enlarge color-gamut and design white light emission

4.1 Enlarge color-gamut

The resolution is a vital parameter for display devices, which is highly related to color saturation, namely, the color gamut of the phosphor. Generally, the wider the color gamut of the phosphor, the higher picture quality can be achieved. The color gamut for phosphors is depicted by the location of their CIE chromaticity coordinates. The typical color gamut for FEDs is made up of a triangle region enclosed by three chromaticity coordinate points of trichromatic (Red, Green and Blue, RGB) FED phosphors, (0.647, 0.343) (Y₂O₃:Eu³⁺; red), (0.298, 0.619) (ZnS:Cu,Al; green) and (0.146, 0.056) (ZnS:Ag,Al; blue). In order to realize high-quality full-color FEDs, it is necessary to enlarge the color gamut of these phosphors. There are two main strategies to reach this goal. The one is to develop FED phosphors with higher color purity with respect to current trichromatic FED phosphors. The other one is to research some novel phosphors with their CIE chromaticity coordinates locating out of the above triangle area. According to the first strategy, Lin’s group has develop a series of RGB phosphors with high color purity. For example, blue-emitting Tm³⁺-doped La₂O₃, LaOCl, LaOF, LaGaO₃ and so on were prepared and investigated. These phosphors all demonstrate more higher color purities than the commercial FED blue phosphor Y₂SiO₅:Ce due to the main ¹D₂→³F₁ transition (around 458 nm) transition emission of Tm³⁺ ions (Table 2). In addition, some Tb³⁺-activated phosphors such as Tb³⁺-doped LaOCl, LaGaO₃, KNaCa₃(PO₄)₂, etc., can also give highly pure blue emissions through a low Tb³⁺-doping content due to the main ⁵D₁→⁷F₄ transitions emission of Tb³⁺ ions. As mentioned in the previous section, rare earth (RE) ions have been playing an important role in display fields due to their abundant emission colors based on their 4f→4f or 5d→5f transitions. For the 4f→4f transitions of RE ions, the emission spectra are narrow and the peak positions are basically stable in different hosts because the electrons in 4f orbits are strongly shielded by the outside 5s and 5p electrons. As a result, their luminescent properties (peak width and position) are not strongly dependent on the crystal structure of the host and can maintain a high color purity. For the 5d→5f transitions of RE ions, the energy level of the excited state 4f→5d is commonly lower than that of the lowest excited state in its 4f electron configuration, they generally presents broader band emissions than the 4f→4f transitions. The different coordination surroundings in a host that results in different crystal field strength have a prominent influence on its luminescence due to the 5d states of RE ions in the outer orbitals. Furthermore, the spectral position of the 4f→5d→4f transition is closely related to the nephelauxetic effect. The higher the charge and the smaller the radius of the ligand ion, the stronger the nephelauxetic effect appears, which will result in the lower position of the 5d energy level. So, the 4f→5d transitions of RE ions depends deeply on the host lattice, and the emission color from the 4f→5d→4f transition can be adjusted from the ultraviolet to the red light region. Hiroaki et al. realized a highly pure blue emission of Eu²⁺ in AlN host with CIE coordinate (0.139, 0.106). Under electron beam excitation, it showed a better saturation behavior, brightness and degradation behavior than that of Y₂SiO₅:Ce. So it is an excellent blue-emitting FED phosphor. For green-emitting phosphors, Mn²⁺-activated Mg₂SnO₄, (Zn,Mg)₂GeO₄ and Li₂ZnGeO₄ systems have promising properties for use in FEDs. Because the Mn²⁺ is a transition metal ion with 3d⁵ electronic configuration, its emission, corresponding to the ⁴T₁→⁴A₁ transition, consists of a broad band whose position depends strongly on the host lattices. If the crystal field around the Mn²⁺ ion is weak, the splitting of the excited energy levels in the d orbitals will be small resulting in Mn²⁺ emission with higher energy, whereas it will give lower energy emission. Due to the weak crystal field surroundings, the as-prepared Mn²⁺-activated Mg₂SnO₄, (Zn,Mg)₂GeO₄ and Li₂ZnGeO₄ phosphors give brilliant green emissions from 500 nm to 530 nm with a narrow bandwidth, which makes them have a higher green purity than commercial green ZnO:Zn phosphors (Table 2). While Mg₂Y₄(SiO₄)₆O₂:Ce³⁺/Mn²⁺ and Ca₄Y₆(SiO₄)₆O:Ce³⁺/Mn²⁺ show excellent red emission of Mn²⁺ due to the strong crystal field surroundings, which can be used for highly efficient red-emitting FED phosphors. In addition, other promising red-emitting phosphors like Ca₃GeO₄:Eu²⁺ and Ca₂TiO₃:Pr³⁺ also have potential application in FEDs due to their high color purity (Table 2). In general, these trichromatic phosphors have higher color purity than those of commercial RGB phosphors, resulting in potential applications in full-color FEDs. Developing phosphors with higher color purity than commercial RGB FED phosphors is also a feasible strategy to improve display quality.

On the other hand, the colors observed by the human eye are those depicted in the 1931 Commission International de l’Eclairage (CIE) chromaticity diagram according to the
colorimetry theory. In a four-color system, if four points are selected as red, yellow, green and blue (RYGB) or red, green, cyan and blue (RGCB), they would surround a larger color gamut than the three-color system. Therefore, these four-color systems will display more natural color than the RGB system, and thus better meet people’s individual requirements. Moreover, the four-color system has a higher “information density” (namely, the pixels per unit area) compared with the three-color system. Accordingly, the second strategy to enhance the display quality is to research suitable four-color (RYGB) or (RGCB) systems phosphors such as cyan- or yellow-emitting phosphors. As mentioned in the previous section, the emission of the Eu$^{2+}$ ion can vary from ultraviolet to red light depending on the host lattice. Therefore, the Eu$^{2+}$ ion can obtain cyan emission by selecting a suitable host. Xie and Wang et al. realized cyan emission of Eu$^{2+}$ ions in Li$_2$CaSiO$_4$:Eu$^{2+}$ (ref. 232) and BaZrSi$_3$O$_9$:Eu$^{2+}$ (ref. 233) systems, respectively, as shown in Fig. 17 and Table 3. We can obviously observe that the CL emission intensities increase in direct proportion to voltage and current of the anodes without saturation. The as-prepared BaZrSi$_3$O$_9$:Eu$^{2+}$ has a comparable emission intensity to that of the commercial blue phosphor (BAM) under the same excitation condition. Eu$^{2+}$-activated BaSi$_2$O$_2$N$_2$ can also be developed as a cyan-emitting FED phosphor due to its excellent stability and high color purity (Fig. 17 and Table 3). In addition, Li et al. designed a highly pure cyan light emission by mixing blue light (Ti$^{4+}$) and green light (Mn$^{2+}$) in Ti$^{4+}$:Mn$^{2+}$-codoped Mg$_2$SnO$_4$ system, as shown in Fig. 18a and b. The as-prepared cyan-emitting phosphors have good stability under low voltage electron beam excitation. After continuous electron beam excitation for an hour, it still keeps 92% of its original intensity, with little change of its CIE chromaticity coordinates. Therefore, it is a promising phosphor for use in FEDs. Based on the second strategy, NaCaPO$_4$:Mn$^{2+}$ shows bright yellow emission under electron beam excitation with the CIE chromaticity coordinates (0.428, 0.552), which has a higher color purity than the commercial yellow-emitting FED phosphor (Zn,CdS):Ag$,^+$ as shown in the inset of Fig. 18c and d. The corresponding CL spectra all consist of a broad emission from 500 to 650 nm with a maximum at 560 nm under different electron beam excitations, which is assigned to the $^4T_1(^6G) \rightarrow ^6A_1(6S)$ of Mn$^{2+}$. Under different voltages and continuous electron beam bombardment, its CIE chromaticity coordinates present a good stability. The luminance of the NaCaPO$_4$:3 mol% Mn$^{2+}$ phosphor screen increases with increasing accelerating voltage ($V_a$) and current density ($J_a$) and a luminance of 1510 cd m$^{-2}$ can be achieved when $V_a = 7$ kV and $J_a = 130$ µA cm$^{-2}$ (Fig. 17c). Moreover, there is no obvious saturation effect for the CL intensity of these phosphors with the increase of $V_a$ and $J_a$. So the as-prepared NaCaPO$_4$:Mn$^{2+}$ phosphor has the potential to be used as a yellow-emitting phosphor in four-color system (RBGY) FEDs due to its good color purity and stability. Other yellow-emitting LaGaO$_3$:Sm$^{3+}$, ZnGeN$_2$, LaAlO$_3$:Sm$^{3+}$, and Ca$_2$Gd$_6$(SiO$_4$)$_8$O$_2$:Ce$^{3+}$/Mn$^{2+}$ (ref. 231) also demonstrate excellent chromaticity coordinates and stability (Table 3), and are also potential RYGB system phosphors in FED devices. In general,
Table 3 The CIE chromaticity coordinates, emission colors of color-gamut enlarged phosphors under low voltage electron beam excitation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Color coordinates</th>
<th>Color</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$<em>{21-y}$Sn$</em>{1+y}$O$_2$C$_4$% Ti$^{4+}$, y% Mn$^{2+}$</td>
<td>(0.1409, 0.3185)</td>
<td>Cyan</td>
<td>37</td>
</tr>
<tr>
<td>x = 2.0, y = 0.01</td>
<td>(0.1637, 0.2574)</td>
<td>Cyan</td>
<td>37</td>
</tr>
<tr>
<td>x = 2.0, y = 0.025</td>
<td>(0.1647, 0.2819)</td>
<td>Cyan</td>
<td>37</td>
</tr>
<tr>
<td>Li$_3$CaSiO$_4$:Eu$^{2+}$</td>
<td>(0.119, 0.203)</td>
<td>Yellow</td>
<td>94</td>
</tr>
<tr>
<td>BaZrSi$_2$O$_7$:Eu$^{2+}$</td>
<td>Cyan</td>
<td>233</td>
<td></td>
</tr>
<tr>
<td>Ba$_2$Si$_2$O$_7$:Eu$^{2+}$</td>
<td>Cyan</td>
<td>233</td>
<td></td>
</tr>
<tr>
<td>NaCaPO$_4$:Mn$^{2+}$</td>
<td>(0.428, 0.552)</td>
<td>Yellow</td>
<td>94</td>
</tr>
<tr>
<td>LaGaO$_3$:0.5%Sm$^{3+}$</td>
<td>(0.4880, 0.4153)</td>
<td>Yellow</td>
<td>14</td>
</tr>
<tr>
<td>LaAlO$_3$:0.25%Sm$^{3+}$</td>
<td>(0.5133, 0.4625)</td>
<td>Yellow</td>
<td>111</td>
</tr>
<tr>
<td>Ca$_2$Gd$_8$(SiO$_4$)$_6$O$_2$:5%Ce$^{3+}$, 18%Mn$^{2+}$</td>
<td>(0.519, 0.414)</td>
<td>Yellow</td>
<td>231</td>
</tr>
<tr>
<td>Ca$_2$Gd$_8$(SiO$_4$)$_6$O$_2$:5%Ce$^{3+}$, 10%Mn$^{2+}$</td>
<td>(0.497, 0.401)</td>
<td>Yellow</td>
<td>14</td>
</tr>
<tr>
<td>Ca$_2$Gd$_8$(SiO$_4$)$_6$O$_2$:5%Ce$^{3+}$, 25%Mn$^{2+}$</td>
<td>(0.545, 0.415)</td>
<td>Yellow</td>
<td>111</td>
</tr>
</tbody>
</table>

Fig. 18 The CL spectra of (a) Mg$_3$SnO$_4$x mole% Ti$^{4+}$, y mole% Mn$^{2+}$ (x = 0–3.0, y = 0.01–0.1) and (c) NaCaPO$_4$:3 mole% Mn$^{2+}$ samples. The CIE chromaticity coordinates of (b) Mg$_3$SnO$_4$x mole% Ti$^{4+}$, y mole% Mn$^{2+}$ (x = 0–3.0, y = 0–0.1) and (d) NaCaPO$_4$:3 mole% Mn$^{2+}$ samples. The triangle and quadrangle in (b) and (d) show the typical and enlarged color gamut for FED phosphors, respectively.

The development of highly pure RGB phosphors and appropriate four-color system (cyan or yellow emitting phosphors) phosphors can efficiently enlarge the color gamut and improve color saturation, and further realize high-quality field emission displays.

4.2 Design of white light emission

It is well known that excellent white light emission can supply excellent backlights in display fields like LED, LCD, PDP and FED, which has a positive effect on display quality. 

In recent years, there is an increasing focus on obtaining a white light emission in a single-phase host due to some potential advantages in luminous efficacy, chromatic stability, color-rendering index and cost against the mixing of two or three different phosphors. Many excellent and tunable white light emitting materials for FEDs can be obtained via designing co-emission (mono- or co-doping RE$^{3+}$ ions) and energy transfer (from hosts or RE ions to RE ions or Mn$^{2+}$ ions) in single-phase hosts. The basic guiding principle mainly involves a complex of complementary luminescence such as blue and yellow light, red, green and blue light to obtain white light emission. A schematic illustration of the generation of white light via co-emission and energy transfer in a single-phase host is shown in Scheme 6. Due to the abundant emission colors from blue to red based on the 4f-4f transitions of trivalent RE$^{3+}$ ions, white light emission in co-emission systems can be realized through mono-doping Eu$^{3+}$ or Dy$^{3+}$ ions, and co-doping Tm$^{3+}$/Dy$^{3+}$, Tb$^{3+}$/Sm$^{3+}$, Tb$^{3+}$/Eu$^{3+}$, Tm$^{3+}$/Tb$^{3+}$/Eu$^{3+}$ ions, etc., into a single matrix (Scheme 6a). While white light emission in energy transfer systems mainly results from the Ce$^{3+}$ → Mn$^{2+}$ (Blue-Yellow light complex) and Ce$^{3+}$ → Tb$^{3+}$, Mn$^{2+}$ (Red-Green-Blue light complex) energy transfers, as shown in Scheme 6b. The summary of the luminescence properties for single-phase white-emitting phosphors via co-emission and energy transfer under low voltage electron beam excitation is shown in Table 4. It is noticed that the energy can also be transferred to the lower energy excited state among the RE ions, depending on the RE concentration, energy transfers rates and phonon energy. Moreover, the more energy transfer occurs among the RE ions, the lower the luminescence efficiency. Therefore, it is important to optimize RE ion doping concentrations and select suitable hosts. The elaborate discussions are shown as follows.

4.2.1 Singly doping RE$^{3+}$ ions like Eu$^{3+}$ or Dy$^{3+}$ into an appropriate single host. The trivalent Eu$^{3+}$ ion is well-known as a red-emitting activator due to its $^5$D$_0$–$^7$F$_2$ transitions ($J = 0, 1, 2, 3, 4$, usually ranging from 578 nm to 700 nm) based on 4f$^6$ configuration with the most prominent $^5$D$_0$–$^7$F$_2$ emission group around 610–625 nm. Except for the red emission, some other emission lines located in the blue-green region from higher $^5$D levels, such as $^5$D$_1$ (green), $^5$D$_2$ (green, blue), and $^5$D$_3$ (blue) can also appear at the low phonon frequencies of the host lattices and the low doping concentration of Eu$^{3+}$ (Scheme 6a). That is attributed to the avoidance of the multi-phonon relaxation and cross relaxation occurring among the energy levels of Eu$^{3+}$, respectively. If the phonon energy (highest vibration frequency, $\nu_{max}$) of the host lattice is high enough to cause multiphonon relaxation, it will quench the higher-level $5D_{2,3}$ emission of Eu$^{3+}$. Moreover, if the doping concentration of Eu$^{3+}$ is high, the $5D_{2,3}$ emission might be quenched by cross-relaxation between two neighboring Eu$^{3+}$ ions, such as Eu$^{3+}$(F$_0$) + Eu$^{3+}$(F$_0$) → Eu$^{3+}$(D$_2$) + Eu$^{3+}$(F$_3$) and Eu$^{3+}$(D$_3$) + Eu$^{3+}$(F$_3$) → Eu$^{3+}$(D$_2$) + Eu$^{3+}$(F$_3$) (Scheme 5a). So whether the emission can occur from higher excited states $^5D_{1,2,3}$, $^5D_2$, and $^5D_3$ or not for Eu$^{3+}$ ion depends critically upon the highest vibration frequencies ($\nu_{max}$) available in the host lattice and the doping concentration of Eu$^{3+}$. In other words, an appropriate selection...
of the host lattice and doping concentration of Eu$^{3+}$ is necessary to yield simultaneously the red emission from the $^5D_0$ energy level and the blue and green emissions from the higher $^5D_{1,2,3}$ energy levels of Eu$^{3+}$ with comparable intensity, thus generating a white light emission from Eu$^{3+}$-monodoped materials. It has been proposed by Blasse and Grabmaier that the radiative rate is approximately equal to the non-radiative rate if the energy gap in the non-radiative transition amounts to 4–5 times the maximum phonon frequency of the host lattices. For Eu$^{3+}$-doped CaIn$_2$O$_4$, the $\nu_{\text{max}}$ of CaIn$_2$O$_4$ is 475 cm$^{-1}$, whereas the energy gaps for $^5D_1 \rightarrow ^5D_0$, $^5D_2 \rightarrow ^5D_1$, and $^5D_2 \rightarrow ^5D_0$ of Eu$^{3+}$ are 1571, 2563, and 2948 cm$^{-1}$, respectively. Thus, the $\nu_{\text{max}}$ of CaIn$_2$O$_4$ is low enough and the numbers of phonons needed to bridge these neighboring excited levels are 4 ($^5D_1 \rightarrow ^5D_0$), 5 ($^5D_2 \rightarrow ^5D_1$), and 6 ($^5D_2 \rightarrow ^5D_0$), respectively. So it is reasonable that all of the emissions from the higher energy levels $^5D_{1,2,3}$ of Eu$^{3+}$ are present, apart from the lowest $^5D_0$ excited state in CaIn$_2$O$_4$ host lattice. Under low voltage electron beam excitation, the emission spectra of CaIn$_2$O$_4$:xEu$^{3+}$ consists of all the emission lines from the $^5D_{0,1,2,3}$ excited states to the $^7F_i$ ground states of Eu$^{3+}$, i.e. $^5D_{1,2,3} \rightarrow ^7F_0$ (418 nm), $^5D_2 \rightarrow ^7F_1$ (431 nm), $^5D_2 \rightarrow ^7F_2$ (447 nm), $^5D_2 \rightarrow ^7F_3$ (467 nm), $^5D_2 \rightarrow ^7F_4$ (492 nm), $^5D_2 \rightarrow ^7F_5$ (512 nm), $^5D_1 \rightarrow ^7F_1$ (537 nm), $^5D_1 \rightarrow ^7F_2$ (555 nm), $^5D_0 \rightarrow ^7F_1$ (588 nm), $^5D_0 \rightarrow ^7F_2$ (616 nm), and $^5D_0 \rightarrow ^7F_4$ (700 nm), as shown in Fig. 19a. These emission lines of Eu$^{3+}$ cover the whole visible spectral region and the relative intensities vary with the doping concentration of Eu$^{3+}$ based on the cross relaxation effects. At appropriate Eu$^{3+}$-doping concentrations at $x = 0.01$, the above emission lines of CaIn$_2$O$_4$:xEu$^{3+}$ have comparable intensities and give a brilliant white light emission (Fig. 19b). Moreover, a tunable white light emission can be obtained by precisely controlling the doping concentration of the Eu$^{3+}$ ions, as shown in Table 4. According to the same approach, LaInO$_3$:Eu$^{3+}$, LaOF:Eu$^{3+}$ and $\beta$-NaYF$_5$:Eu$^{3+}$ have been developed as single-phase white light emitting cathodoluminescent materials (Table 4).

![Diagram](image-url)

**Scheme 6** The schematic mechanisms of generation of white light via (a) co-emission (mono-/co-doping RE$^{3+}$ ions) and (b) energy transfer (from hosts or RE ions to RE ions or Mn$^{2+}$ ions) in single-phase host. A generation of white light through the complex of different colors, Blue-Yellow (BY) or Red-Green-Blue (RGB). Colored straight lines with arrows represent different luminescence. The horizontal braces with different colors represent different light emissions and white stars represent white light by the complex of different light emissions.

It is known that the emission spectrum of Dy$^{3+}$ can be mainly separated into two groups, the blue emission from 460 to 505 nm and the yellow emission from 570 to 600 nm accompanied by a group of weak lines in the red region from 650 to 700 nm based in its 4$^P$ configuration. These emissions correspond to the transitions from $^4F_{9/2}$ to $^6H_{15/2}$, $^6H_{13/2}$ and $^6H_{11/2}$ of Dy$^{3+}$ (Scheme 6a), respectively. The yellow-emitting $^4F_{9/2}$-$^6H_{13/2}$ transition is a hypersensitive transition, which is susceptible to the crystal environment. However, the blue emission is basically invariant with the surrounding environment. In composite oxides, the covalency between Dy$^{3+}$ and O$^2-$ has an important effect on the ratio of yellow to blue emission. Generally, the bigger covalency, the stronger yellow emission of Dy$^{3+}$ ion will be achieved. Moreover, the covalency of Dy$^{3+}$–O$^2-$ is different in the different host matrix due to the local variation of the symmetry and coordination environment of the crystal structure. Therefore, the ratio of the yellow to blue emission can be adjusted by doping into different host lattices, resulting in a possible white-light emission in Dy$^{3+}$-monodoped luminescent material. For example, for the SrIn$_2$O$_4$:0.015Dy$^{3+}$ phosphor, its CL spectrum (Fig. 19c) is made up of the characteristic emission lines of Dy$^{3+}$, i.e., $^4F_{9/2}$-$^6H_{15/2}$, 491 nm and $^4F_{9/2}$-$^6H_{11/2}$, 580 nm. It has a suitable yellow-to-blue intensity ratio, and thus appears as a white emission of Dy$^{3+}$ in SrIn$_2$O$_4$ with CIE chromaticity coordinates $x = 0.3019$ and $y = 0.3291$. The Dy$^{3+}$-doped CaIn$_2$O$_4$, LaGaO$_3$ and Ga$_2$O$_3$ are also considered as excellent single-phase white emitting FED phosphors with tunable chromaticity coordinates in the white light region, as shown in Table 4. Moreover, an enhanced cathodoluminescence performance is observed by host sensitization effects in the above mentioned Dy$^{3+}$-doped phosphors.

4.2.2 Co-doping different RE$^{3+}$ ions such as Tm$^{3+}$/Dy$^{3+}$, Tb$^{3+}$/Sm$^{3+}$, Tb$^{3+}$/Eu$^{3+}$, Tm$^{3+}$/Tb$^{3+}$/Eu$^{3+}$, etc., into a single matrix. Due to the abundant energy levels in 4f orbits of RE$^{3+}$ ions such as Tm$^{3+}$, Dy$^{3+}$, Tb$^{3+}$, Sm$^{3+}$, Eu$^{3+}$ ions, they produce various luminescence colors covering the whole visible light region.

The Tm$^{3+}$ ion mainly emits blue light around 458 nm due to the $^1D_2$-$^3P_0$ transition. The Dy$^{3+}$ ion usually exhibits two main emissions in the visible region: one in the blue region (470–500 nm) and one in the yellow region (570–600 nm), which originate from the $^4F_{9/2}$ $\rightarrow$ $^6H_{13/2}$ and $^4F_{9/2}$ $\rightarrow$ $^6H_{15/2}$ transitions of Dy$^{3+}$.
ions, respectively. The emission of the Eu\textsuperscript{3+} ion mainly appears in the red region with the maximum between 610 nm and 625 nm due to the \( \text{D}_0\text{-}F_2 \) emission. The emission of Sm\textsuperscript{3+} is situated in the orange spectral region and consists of transitions from the excited \( \text{G}_{5/2} \) level to the ground state \( \text{H}_{15/2} \) and higher levels \( \text{H}_J \) (\( J > 5/2 \)). The Tb\textsuperscript{3+} ion has a low-energy ground state \( \text{J}_F \) (\( J = 6, 7, ... \)) and excited states \( \text{D}_J \) and \( \text{D}_{J+1} \). Generally, with a low doping concentration of Tb\textsuperscript{3+} in the host matrix, the transitions of \( \text{D}_J \) to \( \text{F}_J \) dominate and produce the blue emissions. As the Tb\textsuperscript{3+} concentration increases, the cross relaxation from \( \text{D}_J \) to \( \text{D}_{J+1} \) occurs owing to the interaction between Tb\textsuperscript{3+} ions, which enhances the transitions of \( \text{D}_J \) to \( \text{F}_J \) with a green emission. Although these RE\textsuperscript{3+} ions generally are used as single activator in single host, they also generate highly efficient luminescence when coexisting in a single matrix. Accordingly, many RE\textsuperscript{3+} ions co-doped single-phase phosphor systems were designed to realize white light emission, for examples, Tb\textsuperscript{3+}/Dy\textsuperscript{3+}, Tb\textsuperscript{3+}/Sm\textsuperscript{3+}, Tb\textsuperscript{3+}/Eu\textsuperscript{3+}, Tb\textsuperscript{3+}/Tm\textsuperscript{3+}/Eu\textsuperscript{3+} systems, as shown in Table 4. Fig. 20 shows the CL spectra and corresponding luminescent photographs of co-doping phosphor systems. Under electron beam excitation, LaOCl:Tb\textsuperscript{3+} and LaOCl:Tm\textsuperscript{3+} emit blue light (458 nm, \( \text{D}_0\text{-}F_2 \)) and yellow light (571 nm, \( \text{F}_{0,1}\text{-}H_{15/2} \)), respectively. When co-doping Tb\textsuperscript{3+} and Dy\textsuperscript{3+} ions into the LaOCl host, it simultaneously gives blue and yellow emissions, which results in a white light emission (CIE coordinates, \( x = 0.318, y = 0.329 \)) by the blue and yellow lights complex (Fig. 20a and Table 4). For Tb\textsuperscript{3+}/Sm\textsuperscript{3+}-codoped LaGaO\textsubscript{3}, the white emission is realized by the complex of red, green and blue components. The red component comes from the characteristic transitions of Sm\textsuperscript{3+} (561, 597, 642 nm/\( \text{G}_{4/2}\text{-}6\text{H}_{5/2}, \text{G}_{5/2}\text{-}6\text{H}_{7/2}, \text{G}_{7/2}\text{-}6\text{H}_{9/2} \)), while the green and blue components result from the mixing emissions of 414, 437 nm/\( \text{D}_{4}\text{-}\text{F}_{4,5,6} \), 414, 437 nm/\( \text{D}_{5}\text{-}\text{F}_{5,6} \) at a moderate Tb\textsuperscript{3+} doping concentration (Fig. 20b and Table 4). Based on the same complex method, the LaOCl:Tb\textsuperscript{3+}/Eu\textsuperscript{3+}, LaOCl:Tb\textsuperscript{3+}/Sm\textsuperscript{3+}, LaOCl/Tb\textsuperscript{3+}/Eu\textsuperscript{3+}/Tm\textsuperscript{3+} phosphor systems also obtained excellent white light emission (Fig. 20c and Table 4). Fig. 20d intuitively shows the adjustment of emission colors in LaOCl:Tb\textsuperscript{3+}/Eu\textsuperscript{3+}/Tm\textsuperscript{3+} systems via precisely controlling the doping contents of RE\textsuperscript{3+} ions. Consequently, the CIE chromaticity coordinates and luminescent efficiencies of white light emission in co-doped systems can be optimized through the appropriate selection of various RE\textsuperscript{3+} doping contents. These advantages allow RE\textsuperscript{3+}-codoped single-phase white light emission to have potential application as backlights in FED devices.

4.2.3 Designing energy transfers from host or RE ions to RE ions or Mn\textsuperscript{2+} ions to a single host. It is well-known that energy transfer plays an important role in the optical properties
of luminescent materials both from a theoretical and a practical point of view, because it cannot only enhance the luminescent efficiency but also tune the luminescent color in the single-phase host. The Ce$^{3+}$ with the 4f$^1$ configuration in solids shows efficient broad band luminescence due to the 4f–5d parity allowed electric dipole transition. The Ce$^{3+}$ ion has a larger stokes shift than those of the other rare earth ions, because of the extended radial wave functions of the 5d state. Furthermore, the Ce$^{3+}$ ion can also act as an efficient sensitizer by transferring a better part of its excitation energy to coactivators. The transition metal ion Mn$^{2+}$ can give a broad band emission in the visible range owing to the d–d transition, and the emission color of Mn$^{2+}$ can vary from green to red depending on the crystal field. Because the d–d transition of Mn$^{2+}$ is forbidden and difficult to pump, the emission of Mn$^{2+}$ ions is generally excited by energy transfer from the host or the sensitizer. Caldin et al. reported the spectral overlap between the 5d$^1$ → 4f$^2$ ${\text{Ce}}^{3+}$ emission and the 6A$^1$ → 4T$^2$ _{2,3}$^{2+}$ absorption. So far, the Ce$^{3+}$ → Mn$^{2+}$ energy transfers have been reported in many inorganic hosts, such as fluorides, phosphates, and borates, and the corresponding mechanisms have been extensively investigated. In these systems, there is a common feature that Ce$^{3+}$ and Mn$^{2+}$ ions simultaneously substitute one or two lattice sites and the Ce$^{3+}$ ions serve as effective sensitizer ions for Mn$^{2+}$, transferring the energy from the 5D level of the Ce$^{3+}$ to the 4G level of the Mn$^{2+}$ by a process of resonance transfer via a spin exchange mechanism, which not only helps Mn$^{2+}$ ions to emit efficiently but also to tune their emission colors from blue to yellow or orange/red, crossing the whole white light region, as shown in Scheme 5b and Table 4. Generally, there are two main aspects responsible for the resonant energy-transfer mechanism: one is the exchange interaction and the other is the multipolar interaction. It is known that if the energy transfer results from the exchange interaction, the critical distance between the sensitizer and activator should be shorter than 4 Å. The critical distance $R_c$ for the energy transfer from the Ce$^{3+}$ to Mn$^{2+}$ ions can firstly be calculated using the concentration quenching method.
According to Blasse, the critical distance $R_C$ can be expressed by

$$R_C \approx 2 \left( \frac{3V}{4\pi XC N} \right)^{1/3}$$

where $N$ is the number of available sites for the dopant in the unit cell, $X$ is the total concentration of $\text{Ce}^{3+}$ and $\text{Mn}^{2+}$, and $V$ is the volume of the unit cell. The radiative emission from $\text{Ce}^{3+}$ prevails when $R_{\text{Ce-Mn}} > R_C$ and the energy transfer from $\text{Ce}^{3+}$ to $\text{Mn}^{2+}$ dominates when $R_{\text{Ce-Mn}} < R_C$. If the $R_C$ value is much longer than 4 Å, it indicates little possibility of energy transfer via the exchange interaction mechanism. Thus, the energy transfer between the $\text{Ce}^{3+}$ and $\text{Mn}^{2+}$ ions mainly takes place via electric multipolar interactions. On the basis of Dexter’s energy-transfer expressions of multipolar interaction and Reisfeld’s approximation, the following relation can be given: \(^\cite{247, 249, 252}\)

$$\frac{I_{S0}}{I_S} \propto C^{6/3}$$

where $\eta_{S0}$ and $\eta_S$ are the luminescence quantum efficiency of $\text{Ce}^{3+}$ in the absence and presence of $\text{Mn}^{2+}$ and $C$ is the sum of the content of $\text{Ce}^{3+}$ and $\text{Mn}^{2+}$. The $\eta_{S0}/\eta_S$ can be approximately calculated by the ratio of related luminescence intensities as \(^\cite{253, 254}\)

$$I_{S0}/I_S \propto C^{6/3}$$

The $n$ value can be obtained by observing the linear relationship of $I_{S0}/I_S - C^{1/3}$ plots and $n = 6, 8, 10$ corresponds to dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively. Under normal conditions, energy transfer from $\text{Ce}^{3+}$ to $\text{Mn}^{2+}$ is through the dipole–quadrupole interaction in most of the host materials. \(^\cite{236}\) The energy transfer probability $P_{SA}$ (in s$^{-1}$) from $\text{Ce}^{3+}$ to $\text{Mn}^{2+}$ for dipole–quadrupole interactions is given by the following formula: \(^\cite{255}\)

$$P_{\text{DQ}}^{\text{Ce-Mn}} = 3.024 \times 10^{12} \frac{f_d}{R_{\text{TS}}} \frac{F_S(E)F_A(E)dE}{E^4}$$

where $f_d$ is the oscillator strength of the involved absorption transition of the acceptor ($\text{Mn}^{2+}$), $\tau_S$ (in Å) is the wavelength position of the sensitizer’s ($\text{Ce}^{3+}$) emission, $\tau_d$ is the radiative decay time of the sensitizer (in seconds), $R$ is the sensitizer–acceptor average distance (in Å), $E$ is the energy involved in the transfer (in eV), and $F_S(E)F_A(E)/E^4dE$ represents the spectral overlap between the normalized shapes of the $\text{Ce}^{3+}$ emission $F_S(E)$ and the $\text{Mn}^{2+}$ excitation $F_A(E)$. The critical distance ($R_C$) of energy transfer from $\text{Ce}^{3+}$ to $\text{Mn}^{2+}$ is further defined as the distance for which the probability of transfer equals the probability of radiative emission of the donor, the distance for which $P_{\text{DQ}}^{\text{Ce-Mn}} = 1$. Hence, $R_C$ can be obtained from eqn (1) as \(^\cite{256}\)

$$R_C^8 = 3.024 \times 10^{12} \frac{f_d}{\lambda_S^2} \frac{F_S(E)F_A(E)dE}{E^4}$$

The oscillator strength of the $\text{Mn}^{2+}$ electric quadrupole transition ($f_d$) is about $10^{-16}$. So the critical distance $R_C$ of the energy transfer can be calculated by the spectra overlap method. If this result is in good agreement with that obtained using the concentration quenching method it further reveals that the mechanism of energy transfer from the $\text{Ce}^{3+}$ to $\text{Mn}^{2+}$ ions is mainly due to a dipole–quadrupole interaction. On the other hand, the trivalent $\text{ Tb}^{3+}$ are generally used as a green emitting activator, whose emission is mainly due to transitions of $^{5}D_{4} \rightarrow ^{7}F_j$ in the blue region and $^{5}D_{1} \rightarrow ^{7}F_j$ in the green region ($j = 6, 5, 4, 3, 2$) depending on its doping concentration. \(^\cite{193, 209}\) The $\text{Ce}^{3+}$ ion can also efficiently transfer energy to $\text{ Tb}^{3+}$ ions in a single host, and the $\text{ Ce}^{3+} \rightarrow \text{ Tb}^{3+}$ energy transfer has been extensively reported. \(^\cite{237, 258}\) Furthermore, a single-phase white-light-emitting phosphor utilizing energy transfer can avoid the reabsorption for blue or UV light by the red/green emitting phosphors and the mixing of RGB phosphors. Consequently, it can enhance the luminescence efficiency and color reproducibility of the white light source and reduce manufacturing costs. Some research groups have demonstrated the above situation in many $\text{Ce}^{3+}$–$\text{Mn}^{2+}$ (blue-yellow) or $\text{Ce}^{3+}$–$\text{Mn}^{2+}$–$\text{ Tb}^{3+}$ (blue-red-green) co-doped systems such as $\text{Mg}_2\text{Yd}_2\text{SiO}_5\text{O}_2$, $\text{Ca}_2\text{Yd}_2\text{SiO}_5\text{O}_2$, $\text{Ca}_2\text{Ca}_2\text{SiO}_5\text{O}_2$, $\text{Ca}_3\text{MgNa}_2\text{PO}_4\text{O}_2$, $\text{Ca}_2\text{Ca}_2\text{SiO}_5\text{O}_2$, $\text{Sr}_2\text{In}_2\text{PO}_4\text{O}_2$, $\text{Ca}_2\text{S}_2\text{Si}_2\text{O}_2\text{Ce}^{3+}$, $\text{Mn}^{2+}$, $\text{ Tb}^{3+}$, and so on (Table 4). For example, there is an efficient energy transfer from $\text{Ce}^{3+}$ to $\text{Mn}^{2+}$ in $\text{Ca}_2\text{Ca}_2\text{SiO}_5\text{O}_2\text{Ce}^{3+}$, $\text{Mn}^{2+}$, phosphor, and the energy transfer mechanism of the $\text{Ce}^{3+} \rightarrow \text{ Mn}^{2+}$ pair is dominated by an electric dipole–dipole interaction. This phosphor simultaneously emits the blue light of $\text{Ce}^{3+}$ ions (428 nm) and the yellow light of $\text{Mn}^{2+}$ ions (490 nm) (Fig. 21a), respectively. By changing the relative doping concentrations of $\text{Ce}^{3+}$ and $\text{Mn}^{2+}$, the ratio of blue to yellow is controllable and thus obtains an excellent white light emission (Fig. 21a) with CIE coordinates (0.342, 0.318). For $\text{Ce}^{3+}$–$\text{Mn}^{2+}$–$\text{ Tb}^{3+}$-codoped systems, there simultaneously exist two energy transfer processes of $\text{Ce}^{3+} \rightarrow \text{ Mn}^{2+}$ and $\text{Ce}^{3+} \rightarrow \text{ Tb}^{3+}$, which emit red light and green light, respectively (Fig. 21b), because these energy transfer processes can be controlled via tuning the relative doping concentrations of $\text{Ce}^{3+}$, $\text{T b}^{3+}$ and $\text{Mn}^{2+}$ ions. Therefore, the relative emission intensities of blue, green and red light can be adjusted in the single-phase phosphor, resulting in the controllable white light emission (Fig. 21c). In summary, by designing the efficient energy transfer process $\text{Ce}^{4+} \rightarrow \text{ Mn}^{2+}$ or $\text{Ce}^{3+} \rightarrow \text{ Mn}^{2+}$, $\text{ Tb}^{3+}$ in single host lattices, excellent white light emission with tunable chromaticity coordinates and high efficiency can be obtained, which is promising for field emission display backlights. Except for the above energy transfer processes, other energy transfer routes like from $\text{Eu}^{2+}$ to $\text{ Mn}^{2+}/\text{ Tb}^{3+}$ such as $\text{Ca}_2\text{Si}_2\text{O}_5\text{F}_2\text{Eu}^{2+}$, $\text{Mn}^{2+}$, $\text{ Tb}^{3+}$, $\text{Ca}_2\text{Y}_2\text{PO}_4\text{O}_2\text{Eu}^{2+}$, $\text{Mn}^{2+}$, $\text{Ca}_2\text{Gd}_2\text{PO}_4\text{O}_2\text{Eu}^{2+}$, $\text{Mn}^{2+}$, $\text{Ca}_2\text{Sc}_2\text{Si}_2\text{O}_2\text{Ce}^{3+}$, $\text{Mn}^{2+}$, $\text{ Tb}^{3+}$ (ref. 267) and $\text{BaMg}_2\text{Al}_8\text{Si}_4\text{O}_{20}\text{Eu}^{2+}$, $\text{Mn}^{2+}$, $\text{ Tb}^{3+}$ (ref. 268) from host or self-activated luminescent center to RE$^{3+}$ ions such as $\text{Ga}_2\text{O}_3\text{Dy}^{3+}$ (ref. 66) and $\text{CaMo}_2\text{O}_5\text{Eu}^{3+}$ (ref. 144) (Fig. 21d) also can gain excellent white light emission, as shown in Table 4.

5. Improvement of the electron-stimulated degradation behavior

It is known that most phosphors will degrade upon exposure to large doses of electrons (> 50 C cm$^{-2}$). The luminescent degradation property of phosphors under electron beam bombardment is very important for their LED application.
becomes slower with increasing In$_2$O$_3$ contents. The decay is
et al. Xu and to protect phosphors from irradiation damage. For example, when exposed to moisture and other atmospheric components, of coatings can also yield excellent stability to the phosphors
decomposing, two strategies can be employed: first, selecting
intensity of the FED phosphors. To prevent the phosphors from
deformation and hence the formation of the new layers has
negative effects on both the chemical stability and luminescent
beam irradiation commonly can decompose phosphors into
volatile atomic species through the surface chemical reaction
The origin of this degradation is now becoming clear, and is
generally considered to be related to the stability of the crystal
structures and electron stimulated surface chemical reaction of
phosphor grains; 77, 269, 270 This is because prolonged electron
beam irradiation commonly can decompose phosphors into
volatile atomic species through the surface chemical reaction
then and a possibly form new layers on the surface, while the
decomposition and hence the formation of the new layers has
negative effects on both the chemical luminance and luminescence
intensity of the FED phosphors. To prevent the phosphors from
decomposing, two strategies can be employed: first, selecting
hosts with excellent chemical stability under electron beam
irradiation; secondly, coating Al$_2$O$_3$, In$_2$O$_3$, Y$_2$O$_3$, ZnO, SiO$_2$, MgO,
and organic polymers on the phosphor surface. 271 The formers
require stable crystal phases and crystal structures for phosphors,
which can endure continuous electron beam irradiation. For example,
the rare earth ions activated semiconductor materials and (oxo)nitridosilicates are possible selections. 5, 13, 41, 272 The use of
coatings can also yield excellent stability to the phosphors
when exposed to moisture and other atmospheric components,
and to protect phosphors from irradiation damage. For example,
Xu et al. 67 investigated the degradation properties after mixing
the representative Lu$_2$Ga$_3$O$_{12}$:Tb$^{3+}$ phosphor with In$_2$O$_3$ nanosize. Fig. 22a shows that the degradation of the phosphor
film becomes slow after being mixed with In$_2$O$_3$. Moreover, is
becomes slower with increasing In$_2$O$_3$ contents. The decay is

Fig. 21 The CL spectra and corresponding luminescence photographs
of energy transfer phosphor systems: (a) Ca$_2$Ca$_8$(SiO$_4$)$_6$O$_2$:Ce$^{3+}$, Mn$^{2+}$
(b) Mg$_2$Y$_6$(SiO$_4$)$_6$O$_2$:Ce$^{3+}$, Mn$^{2+}$, Tb$^{3+}$. (c) The cathodoluminescence photo-
graphs of Mg$_2$Y$_6$(SiO$_4$)$_6$O$_2$:Ce$^{3+}$, Mn$^{2+}$, Tb$^{3+}$ with different Ce$^{3+}$, Mn$^{2+}$, Tb$^{3+}$
doping concentrations. (d) The emission spectra of CaMoO$_4$: x mol% Eu$^{3+}$
with the x values. Arrow A, B, C and D represent the co-doping of Eu/Tb (high Tb$^{3+}$ concentration), Eu/Tb (moderate Tb$^{3+}$ concentration), Eu/Tm and Tm/Sm in the LaOCl host, respectively. (Reproduced with permission from ref. 144, 229 and 231, copyright 2009, 2011, American Chemical Society and Royal Society of Chemistry.)

partially due to the charge-up of the phosphor. The improve-
ment of the conductivity of Lu$_2$Ga$_3$O$_{12}$:Tb$^{3+}$ phosphor film by
mixing with In$_2$O$_3$ eases the charge-up effect and thus a slower
decay can be observed. After stopping bombardment for a
while, however, the luminescence could not restore to the initial
value, indicating that besides the charge-up effect, permanent
damage to the phosphor occurs. According to X-ray photo-
electron spectroscopy analyses, they found that no obvious
change was observed for Lu 3d, Ga 2p, and Tb 3d peaks. However the intensity of the carbon 1s peak increased signifi-
cantly after bombardment. Therefore, the degradation of lum-
inance may be due to the accumulation of carbon at the surface
during electron bombardment. Accretion of graphitic carbon
during electron-beam exposure at high current densities is a
well-known effect. 273, 274 This carbon contamination will prevent
low-energy electrons from reaching the phosphor grains and also
exacerbate surface charging, and thus lower the luminescence. 275
Although the short time experiment indicates that the stability of
the phosphor is good, further experiments are needed to verify
the long term stability of In$_2$O$_3$-coated Lu$_2$Ga$_3$O$_{12}$:Tb$^{3+}$ phosphor. Other In$_2$O$_3$-coated FED phosphors also confront the same
problem and need to be overcome. In addition to the mixing
with semiconductive materials, Do et al. confirmed that coating
SiO$_2$ on phosphor surface can also efficiently improve their
electron-stimulated stability. 276 Fig. 22b shown the formation of
thin and uniform coatings on ZnS:Cu powders with a thick-
essence 5 nm. They found that the SiO$_2$-coated phosphors were
far more resistant to the loss of S species and to the formation
of an oxide dead layer. The CL aging study (Fig. 22c) showed that the co-doping of Eu/Tb (high Tb$^{3+}$ concentration), Eu/Tb (moderate Tb$^{3+}$ concentration), Eu/Tm and Tm/Sm in the LaOCl host, respectively. (Reproduced with permission from ref. 67 and 276, copyright 2010, American Vacuum Society and The Electrochemical Society.)
the development of commercial FEDs. On the other hand, the surface protective species need not necessarily to be externally applied, they can also originate from electron stimulated surface chemical reaction, which is attributed to surface disassociates partially of a phosphor compound. Pitale et al. found that a thermodynamically stable Al$_2$O$_3$ layer could be formed on the surface of lithium aluminate family like LiAl$_5$O$_8$:Tb as a result of the electron stimulated surface chemical reactions. Moreover, it generates a positive contribution to the CL stability of the LiAl$_5$O$_8$:Tb phosphor, as shown in Fig. 23. The time stability of the LiAl$_5$O$_8$:Tb phosphor under prolonged electron beam exposure suggests that it can be used in information displays. Therefore, it is necessary to develop phosphors from this family whose partial decomposition can form a protective layer such as Al$_2$O$_3$ during electron beam exposure to enhance the chemical stability without affecting the original properties of the phosphor itself. In general, the stable crystal structures and the surface protective species indeed can enhance the time stability of phosphors under electron beam irradiation to some extent. It is noticed that although the improvement can simply be attributed to the electron stimulated surface chemical reaction, the more exact degradation mechanism is not clear and needs to be further studied.

6. Summary and outlook

Field emission displays (FEDs) are a promising newcomer to the world of panel technologies due to their advantages in high-quality display performances and low energy consumption with respect to other display devices. Phosphors are irreplaceable components in FED devices and thus the development of FEDs inevitably requires the appearance of highly efficient low voltage cathodoluminescent materials. In the past decade, the study of highly efficient FED phosphors has become the focus of realizing high-quality field emission displays. In this review, we have discussed the importance of FED phosphors and the recent progress in chemical synthesis and improvement of existing and new phosphors including rare-earth and transition metal ions activated inorganic solid-state luminescent materials, semiconductor-based luminescence materials, self-activated luminescent materials, etc. We have also outlined the common strategies for the modifications and optimizations in morphology, size, composition, conductivity of phosphors and corresponding effects on their cathodoluminescence properties. Special emphases are mainly focused on the study of the selection of hosts and luminescent centers, enhancement of efficiency through energy transfer, adjustment and design of emission colors, improvement of color index and color gamut as well as color stability and degradation behavior of phosphors. Based on the above modifications and optimizations, cathodoluminescence performances like emission intensity, brightness, color purity and saturation behavior can be obviously improved. Simultaneously, conductivity and degradation behaviors of phosphors are also optimized. Therefore, improved low-voltage cathodoluminescent materials have potential applications in full-color FEDs. In addition, single-phase white light emitting FED phosphors with excellent emission properties and tunable CIE chromaticity coordinates have also been developed through designing co-emission and energy transfer between hosts or RE ions and RE ions or Mn$^{2+}$ ions, which are promising backlights in FED devices.

Although substantial and rapid progress has been made in the synthesis, properties, and applications of FED phosphors in
recent years, developing better synthetic routes to further improve their luminescent performances and more detailed fundamental studies on their luminescence properties and mechanisms have a level of urgency, thus there still remains much room for improvement in the future. First, despite the fact that the cathodoluminescence performances of FED phosphors can be improved by optimizing their morphology, size, surface state and crystallization, further and detailed investigations are still required to exactly study how the effects happen, and to develop better synthesis routes for highly efficient cathodoluminescent materials. Secondly, as the cathodoluminescence properties of phosphors are strongly related to the electrical conductivity of their matrix, how to make the matrix maintain a proper electrical conductivity is also a difficult issue to be addressed. Thirdly, although some possible degradation processes under electron beam bombardment have been depicted by many researchers, the exact degradation mechanism should be further investigated in order to develop highly efficient FED phosphors with better stabilities. Fourthly, to move forward, researchers with various backgrounds, like electronic technology and process optimization, may be needed to develop multicolor-system display units and color-gamut enlarged phosphors to improve the color saturation of FED devices. Finally, the methods through solely doping or multi-doping to obtain white light in a single-phase host material have a good controllability of emission colors, while the luminous efficiency and intensity are lower. Therefore, numerous efforts need be made to further develop single-phase white-emitting luminescence materials based on the energy transfer from sensitizer to activator to contain the advantages of a controllability of emission colors and high luminescent efficiency. In addition, processes and methods for preparing phosphor thin films and screens should be optimized to further enhance their cathodoluminescence performances in FED devices. From a long-term point of view, some emerging phosphors, like defect-related environment-friendly phosphors that have high luminous efficiency, should be actively researched to open the door to novel display applications. From the point of view of devices, the development of highly efficient low voltage cathodoluminescent materials might not only promote their application in daily display fields but also offer possibilities for FED devices incorporation in exploration, expedition, aviation, marine and military fields due to the perfect adaptation of these devices to some extremely harsh environments such as very cold or hot conditions. In summary, a large amount of new improvement methods and novel low voltage cathodoluminescent materials are still at the research stage. There is a long way still to go to achieve high-quality field emission displays and thus more efforts still need to be made.

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Notes and references
