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Invited

Narrow-Band Emitters in LED Backlights for Liquid-Crystal Displays: Materials Design and Performance Optimization

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Keywords: light-emitting diodes; narrow-band emission; phosphor; quantum dot; liquid-crystal displays.

ABSTRACT

Narrow-band emitters are recognized as key enablers for LEDs backlights in LCDs by competing with state of the art and emerging display technologies. It is essential to explore narrow-band green/red luminescent materials with high quantum efficiency and excellent stability to optimize the performance of LED backlights.

1 INTRODUCTION

White light emitting diodes (WLED) currently as the backlight source in liquid-crystal display (LCD) is usually made by combination of a blue-emitting LED chip with one or several photoluminescent materials. Photoluminescent materials are mainly divided into doped inorganic phosphor materials, luminescent semiconductor quantum dots (QDs) and bulk metal halides, which are widely used in the field of lighting and display.[1] Inorganic luminescent materials with doped activators, also called phosphors, which are important components of phosphor-converted LED, have been researched for decades.[2-7] On the other hand, luminescent semiconductor quantum dots (QDs) including the II–VI, III-V compounds and the recent ABX_3 halide perovskite nanocrystals have been used as an alternative LCD backlight owing to high photoluminescence quantum yields (PLQY), narrow-band emission, and tunable emission spectra.[8-10] In addition, some Mn^{2+}-based bulk metal halides and layered halide perovskites with excellent optical properties were recently reported as potential candidates for use in LCD backlight applications.[11-13]

In this talk, we will present an overview of the significant progress in narrow-band emitters used in LED backlights for LCDs with the emphasis on the versatile materials databases from doped phosphors to luminescent II–VI, III-V semiconductor quantum dots, and the recent halide perovskites nanocrystals and bulk metal halides. Since our group contributed several recent interesting papers in the materials design and performance optimization of the narrow-band phosphors for LCDs, and we will specially analyze the correlation of structure-luminescence properties. Finally, our talk will summarize and compare the remarkable examples of outdated and new narrow-band luminescent materials as potential candidates in LED backlights, and the outlooks and challenges in discovering new narrow-band emitters will be also proposed.

2 STATE OF THE ART DISPLAY TECHNOLOGIES

Displays have been utilized in a great variety of products such as smartphones, computers, TV sets, and other electronic display devices. Presently, there are several display technologies on the market, namely LCDs, organic light emitting diode (OLED) displays, quantum dot LED (QLED) displays and micro LED displays. Presently, there are several display technologies on the market, including LCD mentioned above, organic light emitting diode (OLED) display, quantum dot LED (QLED) display, and micro LED display. From the current market point of view, micro LED and QLED displays are still in the research stage before slowly entering the market, OLED display is at the development stage, while LCD is at the mature stage and dominate the display market because of their various advantages such as high resolution, low power consumption, long life span, and low cost.

3 DOPED PHOSPHOR MATERIALS FOR LCD BACKLIGHT APPLICATION

Doped phosphor materials are typically composed of an inorganic host and one or several dopant ions as activator and/or sensitizer, which are usually rare earth (RE) and transitional metal (TM) ions. By adjusting the composition of the host and dopant, multi-color phosphors can be designed and applied. As for the RE ions, there are intraconfigurational 4*f*–4*f* transitions represented by Eu^{3+} and Tb^{3+}, and interconfigurational 4*f*-5*d* transition represented by Eu^{2+} and Ce^{3+}. As for TM ions, mainly including Mn^{2+} and Mn^{4+}, they exhibit *d-d* parityforbidden transitions, which can result in different spectral profiles and are strongly influenced by the crystal field. Many inorganic phosphors exhibiting 4*f*-5*d* and *d-d* transitions have been commercialized for lighting and backlight display.

3.1 The Outdated Phosphors in Commercial Devices

The simplest WLED for backlights is composed of a blue-emitting LED chip and $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce). However, due to the broad yellow emission spectrum

(full-width-athalf-maximum (FWHM) >100 nm), the color gamut is quite poor and covers only ~70% of the National Television Standard Committee (NTSC) standard. But it has been applied to many lower-end display products because of high efficiency and low cost. $SrGa_2S_4$:Eu, a green-emitting phosphor (FWHM = 47 nm), and CaS:Eu, a red-emitting phosphor (FWHM = 64 nm), can be used to realize a wide color gamut. However, they are sensitive to humidity, easy to deliquesce in moist air, which lead to the outgassing of corrosive hydrogen sulfide and the degradation of LED. $CaAlSiN_3$:Eu^{2+} is not a narrow-band phosphor (FWHM = ~ 86 nm), but it is usually used as a red component in LED backlights due to its low cost and high efficiency.

3.2 The Emerging Phosphors for LCD Backlight Applications

The most typical way for LED backlights is a combination of a blue-emitting LED chip, a narrow-band green phosphor and a narrow-band red phosphor. As a present commercial narrow-band green phosphor, *β*-SiAlON:Eu^{2+} is widely applied to fabricate wide color gamut backlights owing to its excellent luminescence properties with narrow emission band (FWHM ~ 55 nm), outstanding thermal stability (~10% emission loss at 150 ^{o}C), and high quantum efficiency. Subsequently, during the exploration of narrow-band green-emitting phosphors, our group conducted the pioneer work in this field and reported two oxide-based UCr_4C_4-type phosphors, namely $RbLi(Li_3SiO_4)_2$:Eu^{2+} (RLSO:Eu^{2+}) and $RbNa(Li_3SiO_4)_2$:Eu^{2+} (RN:Eu^{2+}). Both of them are reported as new narrow-band green emitters with excellent thermal quenching behavior and demonstrate potential in LED backlight for LCD. Eu^{2+}-doped RLSO exhibits an unprecedented narrow-band green emission peaking at 530 nm with an FWHM of 42 nm under 460 nm excitation. RN can be obtained by cation substitution for RLSO, in which the Li^+ ions in the *vierer* ring channels of RLSO are substituted by the Na^+ ions. RN:Eu^{2+} shows a narrow-band green emission at 523 nm with an FWHM of 41 nm under blue light excitation. In any case, compared with *β*-SiAlON:Eu2+, RLSO:Eu^{2+} and RN:Eu^{2+} both have a narrower emission band and a more suitable emission peak position, which is favorable for realizing a lager color gamut in LED backlights.

Mn^{2+}-doped narrow-band green phosphors have always been reported for application in LED backlights. Generally, Mn^{2+}- doped phosphors exhibit green emission when Mn^{2+} occupies tetrahedral sites and show red emission in octahedral sites. γ-AlON:Mn^{2+} is a typical Mn^{2+}-doped narrow-band green phosphor (λ_{em} = 512 nm, FWHM = 32 nm). Compared with *β*-SiAlON:Eu^{2+}, γ-AlON:Mn,Mg has a narrower emission band, indicating that γ-AlON:Mn,Mg can achieve a wider color gamut in LED backlights. However, the γ-AlON:Mn,Mg has a low absorption efficiency owing to the spin-forbidden transition of $3d^5$ electrons in Mn^{2+}, which results in a low external quantum efficiency. This is a common shortcoming of Mn^{2+}-doped phosphors.

Presently, the narrow-band red-emitting phosphors are classified into two groups: Eu^{2+}-doped nitride/oxynitrides phosphors and Mn^{4+}-doped fluoride phosphors. $Sr[LiAl_3N_4]$:Eu^{2+} is a narrow-band red-emitting nitride phosphor with UCr_4C_4-type structure, which shows a narrow-band red emission band centered at 654 nm (FWHM ~ 1180 cm^{-1}, ~50 nm). However, $Sr[LiAl_3N_4]$:Eu^{2+} suffers poor chemical stability, thus restricting commercial application. As the famous narrow-band red emitters, Mn^{4+} activated fluoride phosphor, KSF:Mn^{4+}, is the most promising and widely used narrow-band red phosphor, because they exhibit broadband excitation and sharp emission lines (FWHM = 3 nm) owing to its intraconfigurational $3d^3$ transitions.

In summary, there are still a few narrow-band green and red phosphors in Eu^{2+}-doped phosphors. However, Mn^{2+}-activated narrow-band green phosphors have low absorption efficiency and long lifetime values, and Mn^{4+}-doped narrow-band red phosphors suffer from poor moisture resistance. Considering the advantages and disadvantages of the current narrow-band phosphors, the only commercial narrow-band phosphors for LED backlight are *β*-SiAlON:Eu^{2+} (green) and KSF:Mn^{4+} (red). Therefore, the existing narrow-band phosphors should be optimized to meet the application conditions, and new narrow-band phosphors with excellent optical properties and high chemical/thermal stability should be actively explored.

4 LUMINESCENT SEMICONDUCTORS FOR LCD BACKLIGHT APPLICATION

Another way for LED backlights is a combination of a blue-emitting LED chip, a green quantum dots (QD) and a red QD or a red phosphor. Semiconductor QDs, have many unique optical properties, such as high luminescence efficiency, narrow-band emission, tunable emission spectra. These properties are important prerequisites for the application in display devices. Owing to the very narrow-band emission of NCs, the color gamut can reach at least 110% NTSC. Presently, QDs are divided into two types, namely II – VI , III – V QDs and ABX_3 perovskite QDs.

4.1 The Outdated II–VI and III–V QDs

In the long history of the development of QDs, the typical representative of the II-VI QDs is CdSe, which is the most widely used material in backlight technology (>100% NTSC), but toxicity of Cd limits the development of these materials. The III – V QDs are Cd-free. For example, InP is well known with established technologies and applications. Compared with CdSe QDs, the InP QDs have a slightly lower PLQY and a slightly broader emission band, which lead to smaller

color gamut.

4.2 Luminescent Halide Perovskites QDs

In recent years, ABX_3 type perovskite QDs have attracted extensive attention owing to their outstanding optical and electronic properties. There exist two types of semiconductors among the ABX_3 perovskite, namely organic–inorganic (hybrid) halide perovskites (e.g. $CH_3NH_3PbX_3$, X = Cl, Br, I) and inorganic metal halide perovskites (e.g. $CsPbX_3$). Their emission band are narrower than II – VI and III – V NCs and thus they can achieve a larger color gamut (>120% NTSC) in the LED backlight displays. However, their poor stability restricts its commercial applications. Several strategies, such as compositional engineering, surface engineering, matrix encapsulation and device encapsulation have been used to overcome these drawbacks.

5 BULK METAL HALIDES

Bulk metal halides have received great attention as the alternative narrow-band emitters for LED backlight with the development of narrow-band solid-state phosphors and emerging perovskite QDs, including some intrinsic metal halides and the Mn^{2+}-based bulk metal halides. Owing to tetrahedrally-coordinated Mn(II) showing green emission, some Mn^{2+}-based narrow-band green-emitting halides have been reported, including inorganic halide and hybrid halide. Our group firstly reported zero-dimensional (0D) alkali halides Cs_3MnBr_5, which exhibits narrow-band green emission centered at 520 nm with an FWHM of 42 nm. In addition, bulk layered halide perovskites represented by L_2PbX_4 (L = organic ligand, X = Cl, Br, I) act as another alternative for LCD backlights. The emission of the halide perovskites is surprisingly diverse, and the peak covers a range of colors (from near-UV to near-IR) and a range of widths (from narrow blue emission to broadband white-light emission). In summary, the development of the bulk metal halides with narrow-band emission will give more opportunities for backlighting of displays, but the poor stability is the fatal shortcoming of these metal halides.

6 CONCLUSIONS AND OUTLOOK

Inorganic luminescent materials ranging from doped phosphors to luminescent II–VI, III–V semiconductors and the recent halide perovskites and bulk metal halides are a key part of LED backlights for LCD. In past decades, the photoluminescent materials have been studied in detail to achieve narrow emission band, high PLQY, and excellent stability. In this talk, we summarize recent advances in the field of narrow-band emitters for display technologies, including outdated, state of the art narrow-band luminescent materials, and the potential new candidates, in relation to the crystal structure, optical performance, and future development. Despite the considerable progresses that have been made over the past few decades, challenges remain and there are also more opportunities for discovering new narrow-band luminescent materials for LED backlights Many research areas that need further work, include but are not limited to:

(1) Optimization of existed/reported narrow-band phosphors to obtain higher stability, higher PLQY, and narrower FWHM.
(2) Exploration of new rigid structural models for the discovery of phosphors with narrow-band emission.
(3) Further development of the composite of QDs and inorganic materials to achieve high stability for LED backlight applications.
(4) Design and discovery of new QDs and bulk metal halides with high stability for LED backlights.

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