

Advances in oxide thin-film phosphors for field emission displays

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Abstract

Advances in non-sulfur-containing phosphors from low-temperature synthesis of thin-films suitable for glass substrates are discussed. The effects of preparation process on the properties of a variety of rare-earth-doped oxide hosts are reviewed. Cathodoluminescent characteristics have been studied to determine the usefulness of oxide thin-film phosphors in field emission displays.

1. Introduction

Field emission display (FED) has several advantages over the current technologies used for flat panel displays. For example, FED require no back light, and have a wide viewing angle, short response time, very high contrast ratio, and excellent color properties. The FED functions on principles similar to the cathode ray tube (CRT) as a beam of electrons is utilized to excite the phosphors, which then emit light. Compared with a conventional CRT screen, an FED operates at lower energy but with higher current density beams impinging on the phosphors. This requires more luminously efficient and thermally stable materials. Advances in FED technology have placed a requirement on the development of a corresponding screen technology [1]. The most efficient phosphors currently available are metal sulfides. However, the lifetime of FED is limited by the degradation of these sulfide phosphors during operation. Oxide thin-film phosphors may emerge as an alternate choice for the blue phosphor, due to their superior chemical and thermal stability in high vacuum, and absence of corrosive gas emission under electron bombardment.

Here I will review our recent work on phosphors based on oxide thin-films. A variety of oxide-based phosphors have been prepared at temperatures suitable for glass substrates in FED using both physical and chemical deposition methods. The

effects of synthesis process and measurements on the cathodoluminescence (CL) are discussed.

2. Oxide thin-film phosphors

The phosphors used currently for CRT and television (TV) are shown in Table 1 [2]. Those commonly used phosphors for red, green and blue (P22R, P22G, and P22B, respectively) have good efficiencies at higher voltages and nearly saturated colors. However, at low voltage the phosphors rapidly lose efficiency. Table 1 also lists some phosphors in FED. Unfortunately, sulfide-based phosphors used in the traditional CRT are known to be rapidly degraded at the high current density needed for FED. Sulfur-containing phosphors have strong changes in surface chemistry by interaction of the ambient vacuum gases and the primary electron beam, leading to the degradation of CL brightness. Furthermore, this outgassing from the highly efficient sulfide-based phosphors has been shown to degrade the cathode tip of the field emitter array and cause irreversible damage.

Table 1 Phosphors for full color CRT and FED

	Blue	Green	Red
CRT	ZnS:Ag:Cl (P22B)	ZnS:Cu:Au:Al (P22G)	Y ₂ O ₂ S:Eu (P22R)
FED	ZnS:Ag:Cl Zn ₂ SiO ₄ :Ti Y ₂ SiO ₅ :Ce	ZnO: Zn ZnS:Cu:Au:Cl Zn ₂ SiO ₄ :Mn Y ₂ SiO ₅ :Tb	Y ₂ O ₂ S:Eu Y ₂ O ₃ :Eu

The study of non-sulfur-containing phosphors which are stable at the high current density has been progressed in many fields. One of solutions to the

problem based on sulfides is searching and developing rare-earth doped oxide phosphors with efficient luminescence. Oxide phosphors are more chemically and thermally stable and absence of corrosive gas emission under electron bombardment in comparison with sulfide compounds. There is, therefore, a need to develop oxide-based phosphors that display a higher efficiency than the materials conventionally used in CRT screens under low to medium electron accelerating voltages. However, the use of stable oxide compounds is limited by their high crystallization temperature. For example, commonly used rare-earth doped oxide blue phosphors such as $Y_2SiO_5:Ce$ listed in Table 1 are generally activated at relative high temperatures for hours and, therefore, are not suitable for the direct use of glass substrates in some types of flat panel displays like thin film electroluminescent (TFEL) devices and field emission displays (FEDs). For this reason, our recent work [3] has been directed to the developing low-temperature technology of rare-earth doped oxide phosphors for TFEL and FED. The goal of our work is the preparation of phosphors which may be compatible with display industry technologies.

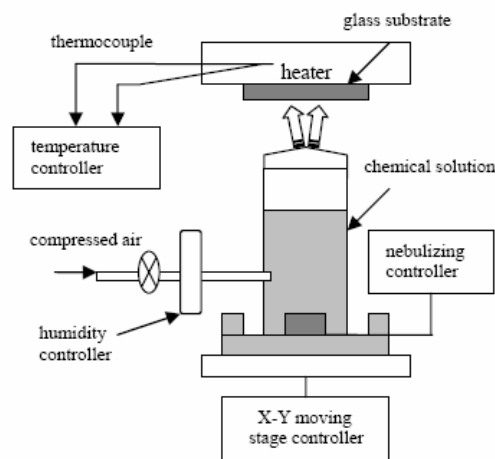
In addition, there are advantages to using thin-film phosphors compared to powder phosphor layers. The thin-film structure makes it possible to use smaller pixel spot sizes to achieve higher resolution. Due to the low excitation voltage in FED, electron penetration into the luminescent particles is very shallow. This means that the effective luminescent region may be confined near the surface of thin-films and that the low voltage excitation favors large specific surface area. For those thin films consisted of nanoparticles, the small size of nanoparticles allows complete penetration by low-voltage electrons for efficient material utilization. For FED, additional advantages would be lower outgassing, facilitated patterning and good adhesion from the thin-films.

3. Experimental

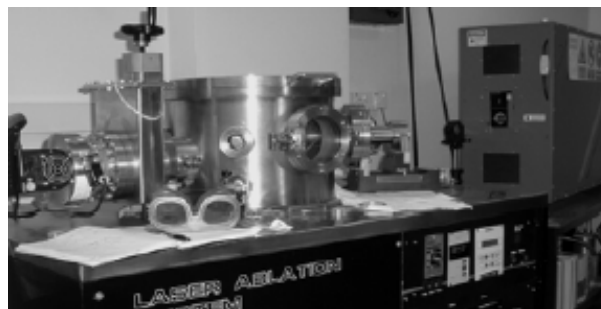
3.1 Synthesis of oxide thin-films

Thin-films of undoped and rare-earth-doped oxides were deposited by both chemical methods such as spray pyrolysis deposition (SPD) and physical methods such as pulsed laser deposition (PLD) on Corning 7059 glass plates. Figure 1 shows schematic systems for SPD (Figure 1a) and PLD (Figure 1b). In brief, the spray pyrolysis solution mostly contained nitrates or chlorides. The spray was developed by an

ultrasonic nebulizer and was directed towards the substrate by a carrier gas of humid air.



(a)



(b)

Figure 1 Deposition system for oxide thin-films. (a) Spray pyrolysis deposition. (b) Pulsed laser deposition.

After deposition, some samples were annealed in a variety of ambients, including air, nitrogen, argon, and forming gas ($H_2: N_2 = 5: 95$). Various annealing temperatures up to 900 °C were provided by a tubular oven using a ramp rate of 30 °C/min. Also, some thin films were rapid annealed at 800 °C for a few minutes.

3.2 Characterization of oxide thin-films

The crystal structure and phase were analyzed by using X-ray diffractometer (XRD) technique. The morphology of the films was determined by using techniques such as scanning electron microscope (SEM) and optical microscope. The composition of

the samples was analyzed by energy-dispersive spectroscopy (EDS).

Optical absorption spectra of the films on quartz were recorded at room temperature using a UV spectrometer with a blank piece of quartz glass in the reference beam. A mercury arc lamp along with a monochromator was used as the excitation source for photoluminescence (PL) measurement. The CL emission was obtained using a home-made system based on a CL luminoscope with a cold cathode electron gun. The CL spectra were measured using a CCD spectrometer with a 400 μm diameter single-strand UV/VIS optical fiber. Spectral resolution of the spectrometer was 1.5 nm. Loading several samples on the sample holder, which was controlled by an x-y positioner, facilitated measuring the emission of the samples in sequence under the same conditions. A metal mask with a hole was placed on each sample to define the emitting spot. Typical conditions consisted of a 5 kV of beam voltage and a beam current of 0.5 mA in a vacuum chamber (20-60 mTorr). Due to the beam scattering in the chamber, the effective current density on the sample was measured to be 62 $\mu\text{A}/\text{cm}^2$ under the typical condition. An illuminance meter was used to measure the luminance of the films.

4. Results and Discussion

4.1 Full color phosphors based on Y_2O_3

One of the promising candidates based on oxides is rare-earth doped yttrium oxide (Y_2O_3). In fact, Eu-doped Y_2O_3 , discovered decades ago, is still considered to be one of the best red oxide phosphors, mainly because of its excellent luminescence efficiency, color purity, and stability. To our knowledge, there are only a few reports on blue luminescence properties of rare-earth doped Y_2O_3 thin films [4, 5], which were prepared by a variety of vacuum techniques. For industrial applications, the spray pyrolysis method may be more attractive from the point of view of large-scale and large-area production of these phosphor films. Figure 2 shows the CL spectra measured at room temperature and 5 kV for Y_2O_3 films doped with 1% Eu-, Tb- and Tm [6]. These films were deposited at 400 $^\circ\text{C}$ and annealed in air at 600 $^\circ\text{C}$. The chromaticity coordinates, dominant wavelength and color purity compared to CIE Standard Source C for each phosphor may be determined from these spectra. For the Tm-doped film, the coordinates are not as good as

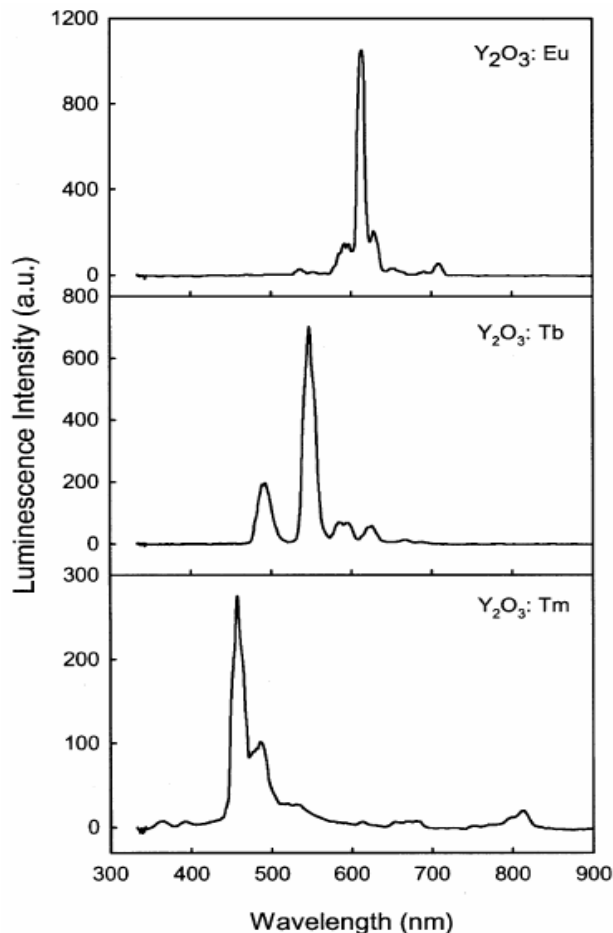


Figure 2 CL spectra for Eu-, Tb- and Tm doped Y_2O_3 films with a 1% concentration of the dopant in the spraying solutions. These films were annealed in air at 600 $^\circ\text{C}$ (from J. H. Hao *et al.*, [6]).

those obtained for the film prepared by electron beam evaporation onto quartz [7]. On the other hand, the color coordinates for our green $\text{Y}_2\text{O}_3:\text{Tb}$ are better than those for powders of yttrium aluminum garnet (YAG) doped with Tb ($x \approx 0.36$ and $y \approx 0.47$) [8] prepared at 1600 $^\circ\text{C}$. Furthermore, our green phosphor has coordinates ($x = 0.319$ and $y = 0.597$) comparable to those for the standard green phosphor. The coordinates of our red $\text{Y}_2\text{O}_3:\text{Eu}$ phosphor are close to those of $\text{Y}_2\text{O}_3:\text{Eu}$ powders prepared and annealed at high temperatures [9].

Similar results in other oxide hosts such as Ga_2O_3 were reported in our previous work [10]. Our results indicate that the color properties of the oxide thin-film phosphors prepared by SPD are approaching those required for FED.

4.2 Blue phosphors based on borates

Selection of blue phosphors for the anode is becoming more critical since FED is now being produced. It is well known that Eu^{3+} is very chemically stable in a variety of host materials and emits a characteristic red emission. On the contrary, Eu^{2+} is instable in an oxidizing atmosphere, and it can be oxidized to Eu^{3+} easily via $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+} + e$. Since Eu^{2+} -doped phosphor is a promising blue phosphor, many researchers have attempted to find host materials that stabilize Eu^{2+} , such as fluoroaluminate glasses, $\text{BaMgAl}_{10}\text{O}_{17}$ (BAM) and ZnS nanoparticles [11-13]. Annealing those phosphors at relative high temperatures for hours in a reducing atmosphere is required for both crystallization of compounds and reduction of Eu^{3+} to Eu^{2+} . Unfortunately, those processes are not suitable for the use of glass substrates in flat panel applications. Also, it is not a convenient method to use reducing atmosphere in large-scale production because of the added safety requirements. Thus, it is imperative to search for novel host materials for Eu^{2+} as a suitable blue phosphor.

Borates, which consist of a rigid three-dimensional network of tetrahedral BO_4 groups, are believed to play an important role in preventing the oxidation of the divalent metal ions. The abnormal reduction of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ was found in borate bulks activated in non-reducing atmospheres [14]. The abnormal reduction of $\text{Eu}^{3+} + e \rightarrow \text{Eu}^{2+}$ could be related to the rigid three-dimensional network of BO_4 tetrahedra, which is necessary to stabilize the divalent rare-earth ions in an oxidizing atmosphere.

As shown in Figure 3 [15], the abnormal reduction of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ in thin films grown on glass substrates may be done at much lower annealing temperatures compared with bulk samples. For the as-grown films of $\text{M}_2\text{B}_5\text{O}_9\text{Cl:Eu}$ ($\text{M} = \text{Ba, Sr, Ca}$) deposited at 450 °C, Figure 3(a) shows the CL spectra at room temperature using a 5 kV excitation voltage. The coexistence of CL spectra corresponding to transitions for both Eu^{3+} and Eu^{2+} was observed for all compounds. The amount of emission due to the $4f^7 \rightarrow 4f^65d^1$ transition of Eu^{2+} followed the sequence of $\text{Ba} > \text{Sr} > \text{Ca}$. These results exhibit that the amount of Eu^{3+} reduced to Eu^{2+} increased when the ionic radius of the alkaline earth in the host was increased, indicating that the cation structures of borates have an influence on the electron transfer. Figure 3(b) shows the CL spectra of the compounds deposited at 450 °C, and then annealed at 800 °C for 2 min in air. Similar

CL spectra were obtained for the films annealed at 630 °C for 1 h. These spectra had an intense single sharp peak in the blue region along with weak peaks due to Eu^{3+} for each compound. The location of the color coordinates of each film on the CIE chromaticity diagram is presented in inset of Figure 3 (b).

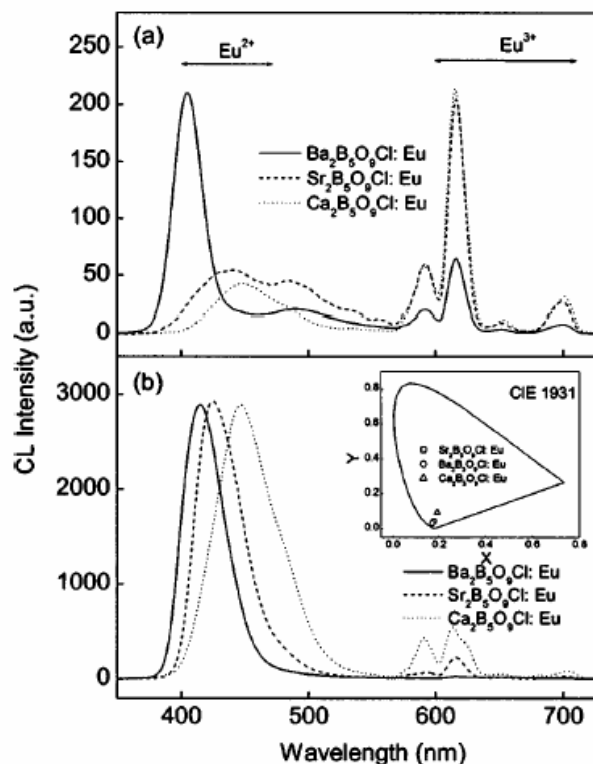


Figure 3 CL for thin films of $\text{M}_2\text{B}_5\text{O}_9\text{Cl:Eu}$ ($\text{M} = \text{Ca, Sr, Ba}$) doped with 2% Eu: (a) as-grown at 450 °C; and (b) deposited at 450 °C and annealed at 800 °C for 2 min in air. A CIE chromaticity diagram showing the chromaticity points of each film is presented in inset. (from J. H. Hao *et al.*, [15])

It is noteworthy that our films of $\text{M}_2\text{B}_5\text{O}_9\text{Cl:Eu}$ had blue emission when the films were annealed in air at temperatures suitable for the use of glass substrates. As a result, a negative M^{2+} vacancy was formed when three M^{2+} ions were replaced by only two Eu^{3+} ions [16]. For this reason, the abnormal reduction was attributed to thermal stimulation of electron transfer from this defect to Eu^{3+} . The results shown in Figure 3 also provide further evidence that the cation of $\text{M}_2\text{B}_5\text{O}_9\text{Cl:Eu}$ could affect the effectiveness of the reduction process.

To verify the usefulness of our developed blue phosphors of thin-films, we have compared the borate phosphors with standard blue phosphor, ZnS: Ag powder, and commonly used oxide blue phosphors, such as Sr_2CeO_4 powders and Y_2SiO_4 [17, 18]. Figure 4 illustrates the location of the colour coordinates of $\text{M}_2\text{B}_5\text{O}_9\text{Cl: Eu}$ thin-films on the CIE chromaticity diagram.

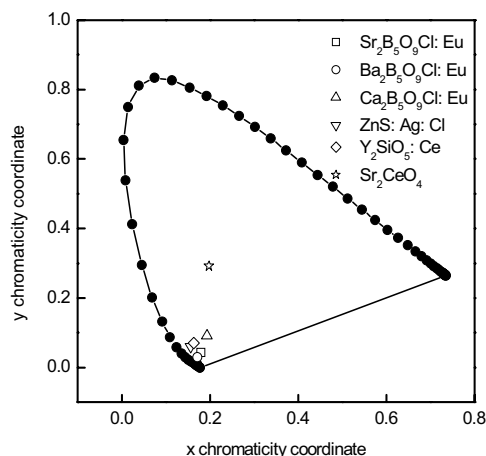


Figure 4 A CIE chromaticity diagram showing the chromaticity points of $\text{M}_2\text{B}_5\text{O}_9\text{Cl: Eu}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$.) thin-films and commonly used blue phosphors.

It turns out that our thin-film phosphors clearly have excellent chromaticity coordinates for the standard blue phosphors. Furthermore, a change in type of alkaline cation in compounds may alter the dominant wavelength from 435 to 465 nm. This observation opens up a possibility of tuning blue emission of other alkaline earth oxide-based hosts by combining different alkaline earth elements.

5. Conclusion

Oxide thin-film may emerge as an alternate choice for the full color phosphors used in flat panel displays. The blue phosphors in this work were activated in air at temperatures suitable for glass substrates, which is used in FED applications. Our thin-film phosphors clearly have excellent chromaticity coordinates for the standard blue phosphors. For industrial applications,

one of deposition techniques named SPD may be more attractive from the point of view of large-scale and large-area production of these phosphor films. For the future work, improving luminous efficiency of oxide thin-film phosphors is much needed.

6. Acknowledgements

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7. References

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