



Rare earths in electroluminescent and field emission display phosphors

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Abstract

Monochrome electroluminescent flat panel displays based on ZnS:Mn have commercially been available for several years and now multicolor devices are coming to the market. Colors are usually produced by rare earth activators in ZnS or alkaline earth sulfide matrices. The materials studied include ZnS:Tb, ZnS:Sm, ZnS:Tm, CaS:Eu, CaS:Tb, SrS:Ce and thiogallates (Ca, Sr)Ga₂S₄ doped with Ce or Eu. The most promising approach to full color devices is that with ZnS:Mn (yellow) and SrS:Ce (blue–green) broad band phosphors and color filters. Field emission displays (FED) are based on cathodoluminescence where the electrons used in excitation originate from an addressable array of microtip cathodes. The operation voltage can vary (300 V–8 kV) but green emitting ZnO:Zn is so far the only phosphor which gives applicable luminance efficiency at low voltages. The problems in FED phosphors and the results obtained with rare earth containing phosphors are reviewed. © 1998 Elsevier Science S.A.

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1. Flat panel displays

The term flat panel display unites all the non-cathode ray tube (CRT) direct-view-displays. The flat panel displays can further be divided into liquid crystal displays (LCD) and emissive displays. LCDs hold almost 90% of the market for small flat panel displays (<14") [1]. In demanding applications found in military applications, medical instruments, vehicles and dusty environments the weaknesses of LCDs are severe, viz. small viewing angle, limited operation temperature, relatively low brightness, sensitivity for constant movement. Therefore considerable amount of research has been focused on the development of emissive flat panels. The most important emissive flat panel types are: electroluminescent (EL), field emission (FED) and plasma displays (PD). In FEDs the excitation mechanism is cathodoluminescence and in PDPs photoluminescence. EL devices are solid state analogs to cathodoluminescent vacuum tubes (CRT). Monochrome yellow–black EL displays based on ZnS:Mn have commercially been available for several years. Multicolor EL devices are coming on to the market and EL devices are expected to grow its share in the flat panel display market [2]. PDs have also been commercially available for years but FEDs are still in the development stage.

This paper concentrates on EL and FED devices, their structures and the use of rare earth phosphors in these devices is highlighted.

2. Structures of the devices

2.1. Electroluminescent devices

EL devices can be grouped in different types depending on the form of the phosphors (powder vs. thin film) and of the driving voltage (DC vs. AC). Two of these types, viz. AC driven thin films electroluminescent devices (AC-TFEL) and AC driven powder electroluminescent devices are commercially available. Due to its good performance (brightness, viewing angle, ruggedness) ACTFEL is the most important EL device type and is the longest lasting and most reliable flat panel display technology on the market [3,4]. AC powder EL has found use in lighting applications for example in a back light in LCDs. In addition to this, there is a growing interest in organic EL displays and their performance has recently significantly improved [5].

An ACTFEL device consists of a metal–insulator–semiconductor–insulator–metal structure deposited on a glass substrate (Fig. 1). In other words there is a dielectric–semiconductor–dielectric (DSD) film stack sandwiched between electrodes. The DSD structure is deposited on a transparent patterned electrode (for example ITO) and covered by a metal electrode [6]. Another structure is the so called inverted structure where the placing of the transparent and metal electrode has been changed and which are not viewed through the glass substrate [7]. That

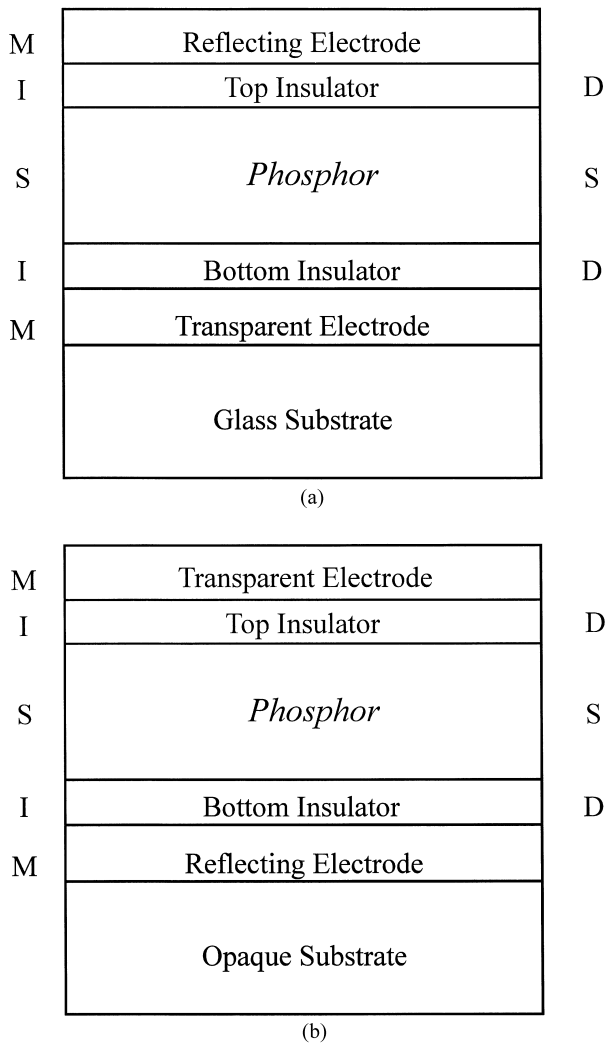


Fig. 1. Cross-sectional view of (a) normal and (b) inverted ACTFEL device structure.

structure allows the use of opaque substrates as is the case in the active matrix EL devices and thick film dielectric hybrid EL devices [8,9].

Three basic device structures have been proposed for multicolor ACTFEL devices. The first one was hybrid multicolor structure based on two substrates [10]. The advantages of this method is the possibility of using higher fill factors which improves the luminance, but the structure is too expensive for commercial production. Tanaka et al. [11] also presented for the first time the so-called color by white structure where no patterning of the phosphors is needed and the colors are filtered from a white phosphor. The lack of an efficient white phosphor kept this structure on the sidelines for almost a decade. The third multicolor EL structure is that where three different phosphors giving the necessary colors are used. The drawback of this structure is the extra processing steps coming from the patterning of the phosphors. The patterned phosphor system can be used both in the conventional and inverted

structures [7,12]. Color by white based on stacked ZnS:Mn/SrS:Ce phosphors is today the most important approach to multicolor EL devices [13]. The improvements achieved in the development of SrS:Ce has made this possible.

2.2. Field emission displays

A FED contains an array of addressable cold cathode field emitters to provide the electron emission (Fig. 2). The cathodes are point or edge emitters (curvature <100 nm) fabricated from metal (molybdenum, tungsten, platinum) or semiconductor (silicon, diamond) by integrated circuit technology [14–17]. The metal tips were those used in first display prototypes [18] but very different tip structures and materials have been proposed [19]. Each pixel has its own electron source which means that the number of emitters can be as high as 10^8 per cm^2 meaning that the intertip spacing is a few micrometers. Emission current and thus the brightness of the device depends on the work function of the emitting material. Cleanness and uniformity of the tips is essential [20]. The tips are separated by dielectric material and gate electrodes are placed above the tips (Fig. 2) [21]. In operation electrons tunnel from the tips and are accelerated towards the phosphor screen placed only a few hundred micrometers apart from the tips.

The FEDs are grouped in two categories depending on the voltage used: low-voltage devices (<1 kV) and high-voltage devices (3–8 kV) each having their own advantages and disadvantages. For safety reasons and lower vacuum requirements low-voltage operation is preferred but, on the other hand, low operation voltage requires higher current densities which may result in fast degradation and outgassing of the phosphor. Phosphors show coulombic aging and typical phosphor lifetimes to half brightness are about 200 C cm^{-2} [22]. Also in low-voltage operation the remarkable charging of the phosphor provides the use of a conductive layer to prevent the charging [1]. In that case the phosphor layer is deposited on ITO covered glass plate. Low-voltage operation requires that the phosphors have low threshold voltages, high thermal conductivity and some electrical conductivity.

In high-voltage operation the charging and degradation

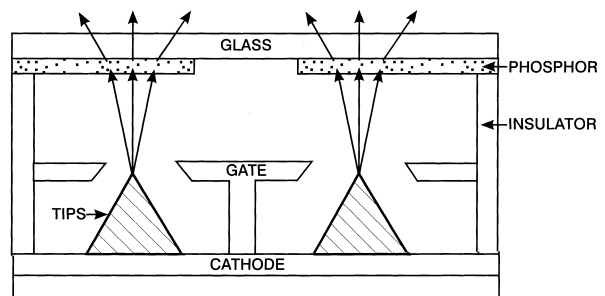


Fig. 2. Cross-sectional view of a field emission display.

problems of the phosphor are not so severe but it has problems of its own: vacuum breakdown problems, electrical leakage problems, aluminization of the phosphor screen and focusing of the electron beam [23]. FEDs are usually evacuated to low pressures to provide a long enough mean free path for the electron. Such low pressures are required in the high-voltage devices, where due to electrical reasons the space between the cathode and phosphor must be only a few millimeters, the use of spacers to hinder the bending of the glass plates must be employed. The shape and the size of the spacers have to be suitable and small so that they stay invisible. The electron stream from the microtip due to the shape of the tip can be wide leading to a poor resolution. The picture resolution can be improved by using a focus grid.

The degradation of phosphors, at least those containing sulfide ions, takes place during the electron bombardment and is due to the sulfur depletion out of the surface which results in the formation of a non-luminescent surface layer. The residual gases, consisting of impurities in phosphors may be activated during the electron beam bombardment and form volatile species which further react with the surface of the sulfide phosphor [24]. The small distance between the tip and gate electrode means high electric fields (10^5 V cm^{-1}) which may result in ionization of residual gases and corona discharge which can defocus the electron beam and sputter the cathode tip [21,22]. The vacuum needed to avoid the problems is in the order of 10^{-7} – 10^{-10} torr. Residual gases are thus a critical issue to the performance and lifetime of a FED. The common sources for the gases are outgassing, vaporization, leaks, and permeation.

3. Electroluminescent phosphors

The present prospect of rare earth containing EL phosphors has recently been reviewed by several authors [2,4,6,13,25–28]. The first approach to color EL displays was that based on patterned red, green and blue phosphors

and accordingly the phosphors for each color were developed. Rare earths are good candidates for dopant ions but the poor size match into the ZnS lattice may cause some troubles. The rare earth ions fit better into the lattice of alkaline earth sulfides but the charge mismatch, except in the case of Eu^{2+} , remains and codoping is maybe needed.

CaS:Eu shows a deep red emission with nice color purity but the brightness and efficiency are far too low for application (Table 1). The electronic transition in Eu^{2+} is an intershell 5d–4f transition which is affected by the environment, and the replacing of 50% of sulfur by selenium shifts the emission towards higher energy and doubles both brightness and efficiency [29]. Samarium is the other rare earth ion used for the red emission. The 4f–4f transitions from the $^4\text{G}_{5/2}$ level give orange–red emission in the ZnS lattice with the same brightness and efficiency as CaS:Eu [30]. Cross-relaxation between the ^6H and ^4G states quenches the red emission and hinders the applications of Sm^{3+} doped materials.

Eu^{3+} doped Y_2O_3 and $\text{Y}_2\text{O}_2\text{S}$ are the well-known red PL and CL phosphors but as they are highly insulating materials, they do not show EL. $\text{Y}_2\text{O}_3:\text{Eu}$ and $\text{Y}_2\text{O}_2\text{S}:\text{Eu}$ when sandwiched between ZnS layers have been reported to show relatively efficient EL [31,32]. The development of rare earth based red EL phosphor has almost vanished since the development of a filter which allows the filtering of red light out of the broad emission band of ZnS:Mn [33]. The filtered ZnS:Mn is currently the brightest (70 cd m^{-2} at 60 Hz) and most efficient (0.8 lm W^{-1}) AC-TFEL red phosphor.

Green-emitting ZnS:Tb thin films show good EL properties which exceed those required in displays. Terbium does not fit well into the ZnS lattice because of its larger size and +3 charge. Fluorine has been introduced as a charge compensator, oxygen has been incorporated more or less unintentionally and centers like TbOF, $\text{Tb}_2\text{O}_2\text{S}$, and TbS_x have been found [34–36]. Fluorine may compensate the charge but also improve the crystallinity of the film. The oxygen containing complex centers may have two

Table 1
Composition, color, luminance, efficiency and color coordinates of rare earth ACTFEL phosphors [2,4,6]

Composition	Color	Luminance L_{40} at 60 HZ (cd m^{-2})	Efficiency (lm W^{-1})	CIE coordinates	
				x	y
CaS:Eu	Red	12	0.05	0.68	0.31
CaS _{0.5} Se _{0.5} :Eu	Red	25	0.25	0.66	0.33
ZnS:Sm,Cl	Red	12	0.08	0.64	0.35
ZnS:TbOF	Green	100	1.3	0.30	0.60
ZnS:Tb	Green	70	0.6	0.30	0.60
CaS:Ce,Cl	Green	10	0.10	0.27	0.53
SrS:Ce	Blue–green	100	0.80	0.30	0.50
SrS:Ce/filter	Blue	10	0.10	0.13	0.18
ZnS:Tm	Blue	0.2	<0.01	0.15	0.15
CaGa ₂ S ₄ :Ce	Blue	10	0.04	0.15	0.19

benefits: they lower the symmetry making the Tb intrashell 4f–4f transitions less forbidden (by relaxing the Laporte selection rule) resulting in the luminescent centers having a larger cross-section for the impact excitation than the pure Tb^{3+} ion.

Cerium emits in the CaS green light but its EL performance is clearly worse than that of ZnS:Tb. On the other hand, Tb emits quite efficiently also in the CaS matrix. Without any optimization a brightness of 20 cd m^{-2} has been measured in an ALE deposited sample [37].

During the 1990s the EL phosphor research has concentrated in developing a blue phosphor and a major part of the work has been focused on SrS:Ce. The brightness and efficiency of the blue–green emission of SrS:Ce are satisfactory (Tables 1 and 2) but after filtering the blue emission is still weak. The EL performance of SrS:Ce including stability has improved continuously along the quality of the SrS host material and control of Ce doping and Ce environment. The keys to obtaining a good SrS:Ce EL phosphor are having as crystalline and stoichiometric an SrS material as possible, suitable codoping, and filling of Sr vacancies [13]. The crystallinity has been improved by annealing, ZnS crystallization layers or codopants. Stoichiometry has been improved by annealing in a sulfur atmosphere which seems to be necessary in sputter and evaporation deposited devices [6]. Recently the incorporation of Zn or Mn at the Sr vacancies in MBE and electron evaporated devices has doubled the luminous efficiency and stabilized significantly the devices [38–40]. Very good results have recently been obtained with silver codoping [65].

The luminescence and structural properties of rare earth doped thiogallates (MGa_2S_4) were initially reported in early 1970s but the EL properties of Ce doped thiogallates were only reported in 1993 by Barrow et al. [41]. $Ca_xSr_{1-x}Ga_2S_4:Ce^{3+}$ shows a pure blue color emission but the efficiency is low. Oxygen doping results in a blue shift (15 nm) and improves both luminance and efficiency [42].

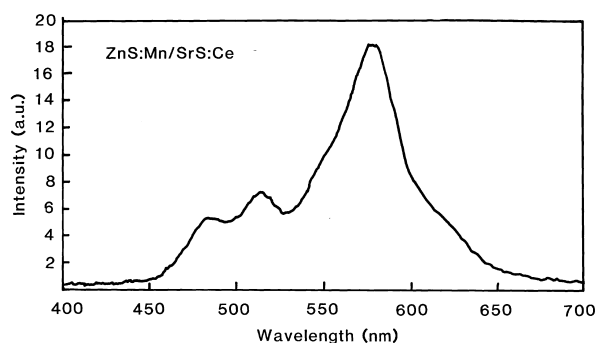


Fig. 3. EL emission spectrum of a SrS:Ce/ZnS:Mn device.

However, to obtain a crystalline, luminescent thiogallate film, a high-temperature treatment has to be carried out, thus setting requirements for the glass substrates which can be used.

White EL emission has been achieved by many materials which are SrS based doubly doped rare earth ions [43] but the best results (36 cd m^{-2} ; 0.2 lm W^{-1}) are those obtained with Ce, Eu doping [44,45]. SrS doped with praseodymium also gives white EL but the intensity is weak. Due to the narrow emission lines SrS:Pr can not be used alone in full color displays, by doping, but codoping with Ce improves the situation [46,47].

The stacked SrS:Ce/ZnS:Mn ‘white’ phosphor is by far the most suitable EL phosphor for a ‘color by white’ full color approach. The broad emission spectrum covers almost the whole visible range, only the wavelengths below 450 nm are missing (Fig. 3). For example in ALE deposited devices luminances of 97, 220 and 11 cd m^{-2} , respectively for red green and blue have been obtained [13,48] but devices prepared by other techniques have also shown good results as well [49,50]. ANSI (American National Standard Institute) requires at the first stage of color displays, a white luminance of 35 cd m^{-2} which corresponds to pixel luminances for red, green and blue of 58, 104 and 10 cd m^{-2} , respectively, if the filling factors

Table 2
The EL performance of SrS:Ce thin films prepared by different methods [13,65]

	Deposition method			
	MBE	ALE	Sputtering	EBE
$U_{\text{thresh}} + 50 \text{ V}$	160 V	170 V	150 V	220 V
$L_{50} (\text{cd m}^{-2})$	140	130	100	55
$\eta_{50} (\text{lm W}^{-1})$	1.2	0.9	0.8	0.8
CIE:				
x	0.26	0.30	0.30	0.21
y	0.48	0.54	0.52	0.40
$L_{50} \text{ blue } (\text{cd m}^{-2})^a$	14	8	7.5	9
$\eta_{50} \text{ blue } (\text{lm W}^{-1})$	0.12	0.06	0.06	0.12
CIE:				
x	0.10	0.08	0.09	0.13
y	0.16	0.20	0.18	0.15
Codopants	Mn, Ag, Cl	–	Ga, F	Zn

^aBlue values have been calculated using a fictitious filter.

are 16, 22 and 28%, respectively [25]. EL devices fulfil these requirements but higher luminances are needed if EL devices are to penetrate the personal computer applications area.

4. Field emission phosphors

The phosphors studied for FED applications have mainly been powders and studies of thin films other than ZnO:Zn are sparse [51]. At low-voltage operation the penetration depth of the electrons into the phosphor is of the order of few nanometers. This puts high demands on the phosphor surface which is often known to be non-stoichiometric or to have coatings which act as dead layers [52]. The perfection of the surface layer is one of the key issues in efficient low-voltage phosphors and, as mentioned above, the residual gases in the device strongly affect the cleanness of the surfaces.

A monochrome FED based on ZnO:Zn powder phosphor shows applicable brightness (300 cd m^{-2}) at 200 V and in the back-reflection mode efficiency even at 500 V 13 lm W^{-1} [53]. The target is a multi or full color display in which the color of ZnO:Zn ($x=0.25$, $y=0.44$) (Fig. 4) has not much use. The known CRT phosphors have been the obvious first choices for FED phosphors in test devices. Unfortunately, in CRT the best known phosphors are based on zinc sulfide and their brightness depends linearly on the voltage in a wide voltage range and at low-voltages their performance is modest. In addition, in FEDs at low-voltage operation, high current densities are needed to maintain constant power and, with sulfide phosphors, this results in fast degradation as presented above.

Rare earth oxysulfides, especially $\text{La}_2\text{O}_2\text{S:Tb}$ and

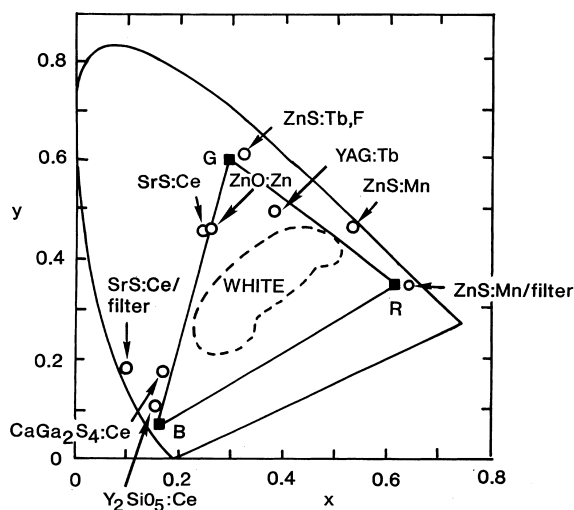


Fig. 4. CIE chromaticity diagram for the common TFEL and FED phosphors. R, G, B denote the coordinates of most common CRT phosphors.

Table 3

Composition, color and efficiency at low-voltage operation of selected FED phosphors

Composition	Color	Efficiency (lm W^{-1})
500 V [1]		
ZnO:Zn	Green	10.7
$\text{Gd}_2\text{O}_2\text{S:Tb}$	Green	7.9
$\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Tb}$	Green	2.0
$\text{Y}_2\text{O}_2\text{S:Eu}$	Red	3.5
$\text{Y}_2\text{O}_3:\text{Eu}$	Red	2.2
$\text{YVO}_4:\text{Eu}$	Red	0.4
300 V, 131 μA [52]		
CaS:Ce	Green	3.10
$\text{SrGa}_2\text{S}_4:\text{Eu}$	Green	3.00
$\text{La}_2\text{O}_2\text{S:Tb}$	Green	5.20
$\text{Gd}_2\text{O}_2\text{S:Tb}$	Green	3.52
$\text{Y}_2\text{O}_2\text{S:Eu}$	Red	2.20
$\text{Y}_2\text{O}_3:\text{Eu}$	Red	1.57
$\text{Y}_2\text{SiO}_5:\text{Ce}$	Blue	0.25
$\text{Y}_2\text{SiO}_5:\text{Tb}$	Green	1.05
LaOBr:Tb	Green	1.95
LaOCl:Tb	Green	0.36
LaOBr:Tb	Blue	0.54
LaOBr:Tm	Blue	0.17

$\text{Gd}_2\text{O}_2\text{S:Tb}$ green phosphors are reasonable efficient and stable materials (Table 3). $\text{Y}_2\text{O}_2\text{S:Eu}$ is also the most efficient red phosphor. The stability of the oxysulfides can be improved by carefully removing the traces of flux used in phosphor synthesis and heat treating in an inert atmosphere. Aging can be decreased by coating but this results in a reduction in efficiency [52]. A comparison between oxysulfide and sulfide phosphors under high coulombic load and an Auger study thereafter clearly shows the better stability of oxysulfide phosphors [54]. On the other hand, thiogallates seem to be efficient and a comparatively stable sulfide based phosphor as exemplified by $\text{SrGa}_2\text{S}_4\text{Eu}$ (Table 3).

Due to the problems in sulfide based phosphors several rare earth doped oxide materials have been studied as possible FED phosphors. Chakhovskoi et al. [55] showed that reasonable colors can be obtained from electrophoretically deposited YAG:Eu red, YAG:Tb green and $\text{Y}_2\text{SiO}_5:\text{Ce}$ blue powders (Fig. 5). At low-voltages ($<2 \text{ kV}$) especially the blue phosphor is dim but on the other hand no saturation was observed in any phosphor up to 8 kV excitation. The level of outgassed carbon oxides from the phosphor remain at a low level.

The FED phosphor development has concentrated in improving and changing the known CL or PL phosphors to better suit FED applications. New techniques have been studied for the synthesis of rare earth doped oxides and garnets and these techniques include low-temperature sol gel methods based on alkoxide precursors and combustion synthesis [56,57]. The particle size affects the efficiency and in the size range of a hundred nanometers efficiency increases with the size [58]. It is not clear what the optimum particle size is and how the optimum changes

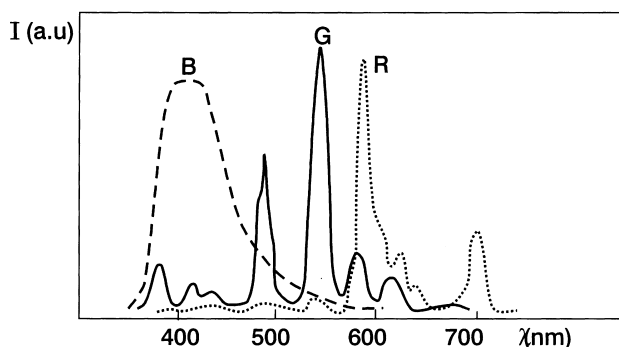


Fig. 5. CL spectra of R-red YAG:Eu (rescaled), G-green YAG:Tb and B-blue $Y_2SiO_5:Ce$ phosphors [55].

with the voltage used. According to Petersen [53] $1 \mu m$ is the optimum size when 5 kV is used and the intrinsic efficiency should be similar to that of today's phosphors which are typically of 3–6 μm size. The shape of the particles may also affect the properties of the phosphor and Matsuda et al. have developed a thermal plasma treatment for rare earth oxide and oxysulfide phosphors which produces spherical particles [59]. A small change in composition may affect the threshold voltage and change the conductivity as was the case when In was added to gallium containing YAG phosphors [60].

There are not many examples of new phosphors which have been designed for FEDs. The group of Vecht has systematically studied refractory oxides doped with rare earth or transition metals. One of their interesting findings is bismuth doped yttrium niobate which is a promising low-voltage blue phosphor [61]. Efficient low-voltage blue phosphor is a decisive factor in the development of full color FEDs.

Only few thin film FEDs have been studied. The films have been prepared by laser ablation, molecular beam epitaxy or spray pyrolysis techniques [61–63]. In general the films have had efficiencies about a factor of five less than the powders with similar composition. But as mentioned in the SrS:Ce EL phosphor case the improvement in film quality substantially improves the luminescent properties. There is much to be done in the development of thin film FED phosphors. Minimum outgassing is one immediate benefit achieved with thin film phosphors [62].

Color FEDs have not yet been commercialized but one close to that is based on $Gd_2O_2S:Tb$ green, $Y_2O_3:Eu$ red and $Y_2SiO_5:Ce$ blue phosphors, the blue component being the biggest problem. In near term applications the high-voltage operation is more probable than the low-voltage one [53]. Low-voltage color FEDs can only be operated in semi-dark room or offices unless the phosphor efficiency is improved. PixTech-LETI, however, reports that with their new inverted structure a low-voltage applicable FED is possible [64].

5. Conclusions

The recent TFEL phosphor research has focused on blue phosphors. Because SrS:Ce has proven to be the best material emitting at the blue region, the majority of the research has concentrated on the improvement of this phosphor. Steady progress has been made in the properties of SrS:Ce thin films and stacked SrS:Ce/ZnS:Mn white phosphor is almost ready for color EL applications. The quality of the SrS:Ce films is, however, far behind that of SrS:Ce powder which indicates that further progress can be expected in brightness, efficiency and stability of SrS:Ce films.

As field emission is a young flat panel display technology, there is much to be studied and many problems to be solved before color FEDs are on the market. There has been considerable progress in microtip fabrication but the phosphor development has been slower. Modification of existing CL phosphors has been the main focus of the research. For further phosphor development many basic aspects including: how different the surface compared to the bulk may be, how conductive the phosphor should be, what is the optimum particle size and why thin films are worse than powders, have to be studied. The efficiency and aging problems in the low-voltage operations are so severe that obviously displays operating with high-voltages are first to come on to the market.

References

- [1] M.T. Anderson, R.J. Walko, M.L.F. Phillips, *Mat. Res. Soc. Symp. Ser.* 345 (1995) 269.
- [2] P.D. Rack, P.H. Holloway, *Mater. Sci. Eng. Repts.* In press.
- [3] R. Törnqvist, *Acta Polytechn. Scand., Ser. Appl. Phys.* 170 (1990) 1.
- [4] C.N. King, *J. SID* 4 (1996) 153.
- [5] S.A. van Slyke, P.S. Bryan, C.W. Tang, in: R.H. Mauch, H.-E. Gumlich (Eds.), *Inorganic and Organic Electroluminescence*, Wissenschaft and Technik Verlag, Berlin, 1996, p. 195.
- [6] M. Godlewski, M. Leskelä, *Crit. Rev. Solid State Mater. Sci.* 19 (1994) 199.
- [7] J. Haaranen, R. Törnqvist, J. Koponen, T. Pitänen, M. Surma-aho, W. Barrow, C. Laakso, *SID 92 Digest* 23 (1992) 348.
- [8] R. Khormanei, S. Tayer, K. Ping, C.N. King, G. Dolney, A. Ipri, F.-L. Hsueh, R. Stewart, T. Keyser, G. Becker, D. Kagey, M. Spitzer, *SID 94 Digest* 25 (1994) 137.
- [9] X. Wu in: R.H. Mauch, H.-E. Gumlich (Eds.), *Inorganic and Organic Electroluminescence*, Wissenschaft and Technik Verlag, Berlin, 1996, p. 285.
- [10] S. Tanaka, Y. Mikami, J. Nishiura, S. Ohshio, H. Yosiyama, H. Kobayashi, *SID 87 Digest* 18 (1987) 234.
- [11] S. Tanaka, H. Yosiyama, J. Nishiura, S. Ohshio, H. Kawakami, H. Kobayashi, *SID 88 Digest* 19 (1988) 293.
- [12] R. Törnqvist, *Electroluminescence*, in: *Proceeding of the 6th International Workshop on Electroluminescence*, Cinco Puntos Press, El-Paso, 1992, p. 329.
- [13] R. Törnqvist, *SID 97 Digest* 28 (1997) 855.
- [14] C.A. Spindt, I. Brodie, L. Humphrey, E.R. Westerberg, *J. Appl. Phys.* 47 (1976) 5248.

- [15] I. Brodie, C.A. Spindt, *Adv. Electron. Electron Phys.* 83 (1991) 1.
- [16] H.H. Busta, J.E. Pogemiller, B.J. Zimmerman, *IEEE Trans. Electron Devices* ED 40 (1993) 1530.
- [17] D. Hong, M. Aslam, *J. Vac. Sci. Technol. B* 13 (1995) 427.
- [18] A. Ghis, R. Meyer, P. Rambaud, F. Levy, T. Leroux, *IEEE Trans. Electron Devices* ED 38 (1991) 2320.
- [19] J. Itoh, *Appl. Surf. Sci.* 111 (1997) 194.
- [20] K. Derbyshire, *Solid State Technol.*, November 1994, p. 55.
- [21] P.H. Holloway, J. Sebastian, T. Trottier, S. Jones, H. Swart, R.O. Petersen, *Mater. Res. Soc. Symp. Proc.* 424 (1996) 425.
- [22] P.H. Holloway, J. Sebastian, T. Trottier, H. Swart, R.O. Petersen, *Solid State Technol.*, Aug. 1995, p. 47.
- [23] A.G. Chakhovskoi, W.D. Kesling, J.T. Trujillo, C.E. Hunt, *J. Vac. Sci. Technol. B* 12 (1994) 785.
- [24] H.C. Swart, J.S. Sebastian, T.A. Trottier, S.L. Jones, P.H. Holloway, *J. Vac. Sci. Technol. B* 14 (1996) 1697.
- [25] Y.A. Ono, *Electroluminescence*, World Scientific, Singapore 1995.
- [26] G. Härkönen, M. Leppänen, E. Soininen, R. Törnqvist, J. Viljanen, *J. Alloys Comp.* 225 (1995) 552.
- [27] C.N. King, *J. Vac. Sci. Technol. A* 14 (1996) 1729.
- [28] H. Kobayashi, S. Tanaka, *J. SID* 3–4 (1996) 157.
- [29] T. Yoshioko, Y. Sano, K. Nakamura, C. Tani, *SID 89 Digest* 20 (1989) 313.
- [30] K. Hirabayashi, H. Kozawaguchi, B. Tsujiyama, *Jpn. J. Appl. Phys.* 26 (1987) 1472.
- [31] T. Suyama, K. Okamoto, Y. Hamakawa, *Appl. Phys. Lett.* 41 (1982) 462.
- [32] K. Ohmi, S. Tanaka, H. Kobayashi, T. Nire, *Jpn. J. Appl. Phys.* 31 (1992) L1366.
- [33] R.T. Tuenge, J. Kane, *SID 91 Digest* 22 (1991) 279.
- [34] K. Okamoto, T. Yoshimi, S. Miura, *Appl. Phys. Lett.* 53 (1988) 1570.
- [35] Y. Charreire, A. Marbeuf, M. Leskelä, L. Niinistö, E. Nykänen, P. Soininen, O. Tolonen, *J. Electrochem. Soc.* 139 (1992) 619.
- [36] G. Härkönen, K. Härkönen, R. Törnqvist, *SID 90 Digest* 21 (1990) 232.
- [37] M. Leskelä, M. Mäkelä, L. Niinistö, E. Nykänen, M. Tammenmaa, *Chemtronics* 3 (1988) 113.
- [38] R. Mauch, K.-O. Velthaus, B. Hüttl, U. Troppenz, R. Herrmann, *SID 95 Digest* 26 (1995) 720.
- [39] B. Hüttl, K.-O. Velthaus, U. Troppenz, R. Herrmann, R.H. Mauch, *J. Cryst. Growth* 159 (1995) 943.
- [40] K. Ohmi, T. Hirose, M. Harada, S. Tanaka, H. Kobayashi, *Jpn. J. Appl. Phys.* 36 (1997) L33.
- [41] W.A. Barrow, R.C. Covert, E. Dickey, C.N. King, C. Laakso, S.S. Sun, R.T. Tuenge, R. Wentross, J. Kane, *SID 93 Digest* 24 (1993) 761.
- [42] P.D. Rack, P.H. Holloway, S.S. Sun, *J. SID* 4 (1996) 281.
- [43] S. Okamoto, E. Nakazawa, Y. Tsuchiya, *Jpn. J. Appl. Phys.* 29 (1990) 1987.
- [44] S. Tanaka, H. Yoshiyama, J. Nishiura, S. Ohshio, H. Kawakami, H. Kobayashi, *Proc. SID* 29 (1988) 305.
- [45] Q.Z. Gao, J. Mita, T. Tsuruoka, M. Kobayashi, K. Kawamura, *J. Cryst. Growth* 117 (1992) 983.
- [46] Y. Abe, K. Onisawa, K. Tamura, T. Nakayama, M. Hanazono, A. Ono, *Jpn. J. Appl. Phys.* 28 (1989) 1373.
- [47] W. Kong, J. Fogarty, R. Solanki, R.T. Tuenge, *Appl. Phys. Lett.* 66 (1995) 419.
- [48] M. Leppänen, G. Härkönen, A. Pakkala, E. Soininen, R. Törnqvist, *Proceedings of the 13th International Display Research Conference, Eurodisplay 93, Strasbourg, 1993*, p. 229.
- [49] R.H. Mauch, K.O. Velthaus, B. Hüttl, H.W. Schock, *SID 93 Digest* 24 (1993) 709.
- [50] A. Mikami, I. Yashima, F. Kajikawa, in: R.H. Mauch, H.-E. Gumlich (Eds.), *Inorganic and Organic Electroluminescence*, Wissenschaft and Technik Verlag, Berlin, 1996, p. 369.
- [51] A. Vecht, D.W. Smith, S.S. Chadha, C.S. Gibbons, J. Koh, D. Morton, *J. Vac. Sci. Technol. B* 12 (1994) 781.
- [52] R.O. Petersen, *First International Conference on the Science and Technology of Display Phosphors, San Diego, Extended Abstracts, 1995*, p. 11.
- [53] R.O. Petersen, *Information Display, March, 1997*, p. 22.
- [54] T. Trottier, H. Swart, S. Jones, J. Sebastian, P.H. Holloway, *First International Conference on the Science and Technology of Display Phosphors, San Diego, Extended Abstracts, 1995*, p. 263.
- [55] A.G. Chakhovskoi, M.E. Malinowski, A.A. Talin, T.E. Felter, J.T. Trujillo, C.E. Hunt, K.D. Stewart, *Mater. Res. Soc. Symp. Proc.* 424 (1996) 415.
- [56] D. Ravivhadran, R. Roy, A.G. Chakhovskoi, W.B. White, C.E. Hunt, *Second International Conference on the Science and Technology of Display Phosphors, San Diego, Extended Abstracts, 1996*, p. 219.
- [57] L.E. Shea, J. McKittrick, L.F. Phillips, *Mater. Res. Soc. Symp. Proc.* 424 (1996) 409.
- [58] L.E. Shea, I.S.R. Sastry, J. McKittrick, L.F. Phillips, *Second International Conference on the Science and Technology of Display Phosphors, San Diego, Extended Abstracts, 1996*, p. 295.
- [59] N. Matsuda, M. Tamani, M. Okumura, A.K. Albessard, Y. Inoue, K. Kawasaki, *Second International Conference on the Science and Technology of Display Phosphors, San Diego, Extended Abstracts, 1996*, p. 307.
- [60] H. Yamamoto, Y. Suda, *Second International Conference on the Science and Technology of Display Phosphors, San Diego, Extended Abstracts, 1996*, p. 253.
- [61] A. Vecht, C.S. Gibbons, D.W. Smith, X. Jing, *Second International Conference on the Science and Technology of Display Phosphors, San Diego, Extended Abstracts, 1996*, p. 277.
- [62] A.G. Chakhovskoi, C.E. Hunt, T. Yang, B. Wagner, C. Summers, M.E. Malinowski, T.E. Felter, *Second International Conference on the Science and Technology of Display Phosphors, San Diego, Extended Abstracts, 1996*, p. 273.
- [63] S.L. Jones, D. Kumar, R.K. Singh, P.H. Holloway, *Second International Conference on the Science and Technology of Display Phosphors, San Diego, Extended Abstracts, 1996*, p. 283.
- [64] R. Meyer, *Second International Conference on the Science and Technology of Display Phosphors, San Diego, Extended Abstracts, 1996*, p. 9.
- [65] K.O. Velthaus, B. Hüttl, U. Troppenz, R. Herrmann, R.H. Mauch, *SID 97 Digest* 28 (1997) 411.