Recent Developments in Display Phosphors

Ravi P Rao
Authentix, Inc.
Douglassville, PA 19518, USA
ravi.rao@authentix.com

The electronic display has become a part of day-to-day life of modern world. It is considered as an important component of the human-electronic interface.

Displays are broadly divided into emissive and non-emissive displays; both require phosphors to generate visible light. The phosphors employed in displays optimally satisfy the following requirements: high quantum efficiency, high reflectivity to visible light, longevity, required after glow decay or persistence, and proper color coordinates or color gamut and temperature required by NTSC/PAL standards. The morphology (phosphor particle size and shape), particle size distribution (PSD), Zeta potential and surface charge, body color and rheology are the important physical requirements to be considered in the manufacture of displays.

In addition to solid state reaction various other processes are described in the literature to prepare display phosphors viz., sol-gel method, co-precipitation method, hydrothermal technique, spray pyrolysis, combustion synthesis and combinatorial chemistry method. Most phosphors are characterized by physical as well as optical means to determine their practical behavior. Thermal analysis (TA), X-ray powder diffraction (XRD), Photon induced X-ray emission (PXIE) are some commonly used techniques to characterize phosphor materials. Scanning or transmission electron microscopy (SEM) is used to study the morphology of phosphor particle. The particle size distribution is determined with the help the Coulter counter analyzer or by laser scattering. Excitation, emission, persistence and thermoluminescence studies are all used to characterize display phosphor materials. Some of the phosphor synthesis and characterization procedures are presented in this presentation.

Displays with cathode ray tube are very well established as a medium of entrainment with ZnS:Ag, ZnS;Au,Al and Y_2 O_2S:Eu phosphors as blue, green and red phosphors. Various phosphor materials excitable by low voltage electrons are suggested for field emission displays (FEDs). Thin CRTs designed from FED technology are currently using CRT phosphors. Development of ZnS based phosphors is being carried out for Electroluminescence displays (ELDs). Present-day display development activity is fascinating with much of this direction towards plasma display panels (PDPs) as a medium of large format (75+") television (TV) particularly high definition TVs. Since the picture quality of PDP TV depends mainly on the type of phosphors employed in a display, the selection of typical phosphors is utmost important [1]. Currently there are different combinations of phosphors used by most of PDP manufacturers viz., three different green phosphors ($ZnSiO_4$:Mn, $ZnSiO_4$:Mn + Y,$GdBO_3$:Tb blend and $BaAl_{12}O_{19}$:Mn + Y.$GdBO_3$:Tb blend), along with standard blue ($BaMgAl_{10}O_{17}$:Eu^{2+}) and standard red (Y,$GdBO_3$:Eu^{3+}) phosphors.

Divalent europium activated barium magnesium aluminate: $BaMgAl_{10}O_{17}$:Eu^{2+} (BAM) phosphor as a blue emitting component is being used in PDPs due to its high quantum efficiency, color purity (ideal CIE chromaticity color coordinates) and availability. Due to its wide band gap (6.4eV), host-lattice absorption occurs at wavelength shorter than 190 nm. BAM exhibits poor stability or low life with VUV flux. The degradation of BAM starts during the baking cycles, part of manufacturing process and continues during PDP operation. The peak maximum also shifts towards the green during various stages of panel fabrication, known as green shift. The mechanism involved in degradation and green shift in BAM phosphor is very well studied but no one concluded with real causes for degradation but the efforts are being paid off to get less degradable BAM phosphor. One of the alternatives to BAM is high stable Tm^{3+} activated lanthanum phosphate phosphor ($LaPO_4$:Tm^{3+}:LPTM). LPTM has a few drawbacks, viz. low brightness, complicated energy levels, concentration quenching at low concentrations and cross relaxation process [2]. $CaMgSi_2O_6$:Eu [3], $Sr_3Al_{10}SiO_{20}$Eu [4] and (Ba,Mg)$Al_2Si_2O_8$:Eu [5] are few different phosphors suggested as alternatives to replace BAM. Though these phosphors show less degradation, their luminescence efficiency is much lower under VUV excitation than that of BAM phosphor. It is also found that Gd^{3+} activated yttrium-aluminum borate phosphor (YAB:Gd) has a high UV emission at 313 nm under VUV excitation with lesser degradation [YAB]. Yttrium phosphate activated with both Zr and Mn shows UV emission (291nm) and a blue peak at 477nm under VUV excitation.

Manganese activated zinc silicate phosphor (P1) is conventionally used in PDPs as the green emitting component due to its ready commercial availability and its high quantum efficiency. However, compared with red and blue emitting phosphors, zinc silicate exhibits a wide spectrum of emission with low color purity, long persistence and fast saturation with VUV flux. In addition to long decay, P1 also has negative surface charge which reduces the wall discharge and addressing margin of green cell in a PDP. This causes not only non uniformity but also reduces the efficiency and requires higher discharge voltage. By surface coating with metal oxides such as MgO, the negative discharge is slightly improved.

Mn^{2+} activated barium aluminate is being suggested in place P1 as the green emitting PDP phosphors due it its high efficiency and color purity. Because of its poor stability, it is not a potential phosphor for PDP applications. Mn activated lithium zinc germanate, $Li_2ZnGe_3O_8$:Mn (LZG:Mn), has a stronger absorption band in the 100 to 200nm wavelength range. Due to its poor thermal stability, it could not be a good candidate as a PDP phosphor.

Due to their quantum efficiency and thermal stability, Tb activated green emitting lanthanum phosphate and borate phosphors have been well studied and are widely used in PDPs along with P1. The morphology of borate and phosphate phosphors is significantly superior to zinc silicate and aluminate phosphors. It has been shown that the borate based Tb activated green phosphor improved the uniformity of the discharge characteristics in AC PDPs [6]. Due to its sizable contribution in the blue region, only borate or phosphate is not considered to be a viable candidate to replace zinc silicate green phosphor. A little emission peak in the blue region makes these phosphors yellowish. To overcome the blue peak and to take advantage of the superior morphology and longer life, a blend of zinc silicate and yttrium borate phosphor is being used in the manufacture of large area PDPs. The ratio of silicate, aluminate, borate or phosphate can be varied depending upon the required optical and electrical characteristics of a phosphor blend [6]. The phosphor blends not only improve the optical properties but also improve the morphology.

Europium activated yttrium, gadolinium borate [$(Y,Gd)BO_3:Eu^{3+}$] is an efficient red emitting phosphor that is currently used in PDP's due to its high quantum efficiency, persistence characteristics and reduced saturation. But in the case of displays, specifically for television (TV) applications, it is preferable to have more of the red. Different Eu^{3+} activated phosphors to replace RE borates are briefly described in the following.

Gadolinium aluminum borate crystallizes in hexagonal form where the Gd^{3+} ions are separated from each other by BO_3 groups without Gd^{3+} ions sharing the same oxygen ion. The color coordinates of this emission is close to that required by the NTSC color standard. In case of $(Y,Gd)Al_3(BO_3)_4$:Eu, the emission spectrum is dominated by 617nm peak more favorable as a TV phosphor. Eu^{3+} activated yttrium lithium borate, $Li_6(BO)_3$ and lithium lanthanum borate, $Li_3La_2(BO_3)_3$ and similar oxyborate phosphors are being considered for PDP applications due their color point in the deep red. It has been reported that in lanthanum based phosphor Gd^{3+} plays an important role in acting as a sensitizer. The CTS excitation band of Eu^{3+} is enhanced by codoping Al^{3+} into the $BaZr(BO_3)_2$ lattice. The stability has been improved by replacing a small portion of Y_2O_3 with Gd_2O_3. The complex of $(Y,Gd)_2O_3$ phosphor exhibits the same level of brightness and persistence with better stability. By blending $(Y,Gd)BO_3$ with $(Y,Gd)_2O_3$, color purity of the phosphor can be improved with a little loss in brightness [7]. It is reported that the brightness of these oxides can also be improved by codoping with L^+. Li^+ substitution in the lattice leads to a decrease in interstitial oxygen an increase in the quantum yield. Currently, PDP manufacturers are not willing to replace $(Y,Gd)BO_3:Eu^{3+}$ as a red emitting phosphor.

Another interesting area of phosphor development is fluorescent and solid state lighting as back light for non-emissive displays. Trichromatic compact lamp phosphors such as BAM (blue), $LaPO_4$:Ce,Tb (green) and Y_2O_3:Eu (red) are being used in LCD back light panels. Improvements to boost the efficiency, longer life and stability with high temperature are in progress. Efforts are being made to design LCD back light with solid state lighting (SSL) modules. Presently Ce activated YAG based phosphor is used to convert a part of blue light from LED to yellow. The combination of yellow and blue gives required white light. SSL modules with UV LED and RGB phosphors will be an efficient back light for large area LCD monitors. Physical and optical characteristics of various phosphors for SSL applications will be discussed. A new flat panel display technology called surface-conduction electron emitter display (SED) developed by Canon and Toshiba is in the final stage of manufacturing of large area TVs. Phosphor materials employed SED TVs will be presented in this paper. Anti-Stokes or up-conversion phosphors, such as rare earth activated rare earth compounds of oxysulfides or fluorides as blue, green and red emitters after excitation with laser beam are being explored for display applications. Recent developments in the preparation and properties of phosphors for various display applications are presented and discussed in this presentation.

1. Rao, R. P., Phosphors for Plasma Display Panels (PDPs) in *Phosphor Handbook* (Second Edition) Edited by W. Yen and H. Yamamoto, CRC Press (USA) 2006.
2. Rao, R. P., Tm^{3+} activated lanthanum phosphate: a blue PDP phosphor, *J. Luminescence*, 113, 271, 2005.
3. Kunimoto, T., et. al., Luminescent and aging characteristics of test-PDP panel using Gd-codoped $CaMgSi_2O_6$:Eu phosphors, *IDW'04*, 1081, 2004.
4. Kubota, S. and Shimada, M., $Sr_3Al_{10}SiO_{20}$Eu as a blue luminescent material for plasma displays, *Applied Phys. Let*. 81, 2749, 2002.
5. Im, W.B., et. al., Luminescent and aging characteristics of blue emitting $(Ca,Mg)Al_2Si_2O_8$:Eu (M=Ca,Ba) phosphor for PDP applications, *Solid State Communications*, 134, 717, 2005.
6. Rao, R. P., Tb^{3+} activated green phosphors for plasma display panel applications, *J. Electrochem. Soc.* 150, H165, 2003.
7. Bechtel, H., Justel, T., Glaser, H. and Wiechert, D.U., Phosphors for plasma-display panels: demands and achieved performance, *J. SID*, 10, 63, 2002.