



Nano phosphors for light emitting diodes (LEDs) Syntheses and Characterization

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Abstract

Syntheses of phosphors for Light Emitting Diodes (LEDs) of various host matrices by different preparative methods are very important and need of the day for the phosphor industry. Role of preparative variables in synthesis of nano phosphors and display phosphors along with basic requirements are discussed in the present paper. Nano phosphors are preferred over micron size phosphors in a number of applications not only due to their particle size but also better optical properties. Some of the techniques such as solid state diffusion, flame and laser pyrolysis and sol-gel process are being employed to manufacture. The main advantages of nanophosphors in potential applications such as solid state lighting, medical, security, displays, remote thermometry and thermoluminescence radiation dosimetry. The present paper discusses the synthesis of display phosphors applicable in Color Picture Tube (CPT) and Plasma Display Panels (PDP) and Phosphor coated LEDs (PLED) for lighting applications.

Keywords: Light Emitting Diodes, Phosphor industry, Plasma Display Panels

INTRODUCTION

Rare-earth-doped phosphors are known to emit at distinct and different wavelengths in the electromagnetic spectrum and have been widely used in color cathode ray tubes (CRT), tri-phosphor fluorescent lamps, X-ray intensifying screens and newly developed vacuum mercury-free lamps, as well as various types of displays such as plasma display panels, field emission displays and projection TVs. Recently, breakthroughs in inorganic light emitting diodes (LEDs) technology are significantly catalyzing the development of energy-efficient solid-state lighting (SSL) with long lifetime. Solid-state lighting technology has now already penetrated in a variety of specialty applications, in effect, LEDs have completely changed the "world of luminance", for example automobile brake lights, traffic signals, liquid crystal displays and mobile backlights, flashlights and all manner of architectural spotlights.

Laser detection phosphors [LDP] are used to detect the presence of lasers in the infra-red region by converting the energy to visible. Storage phosphors react to a broad spectrum of infra-red but require daylight or UV to charge up the phosphor first. Exposure to infra-red will cause the energy to be released resulting in a gradual drop in output. "Anti-Stokes" phosphors directly convert the energy from infra-red to visible with a continuous output. They do not exhibit the same broad response to infra-red though.

Nanophosphors are being extensively investigated due to potential applications during last few years along with nano technology development. Medieval artisans unknowingly became first nanotechnologists when they made red stained glass by mixing gold chloride (nano) into molten glass. Selection of host lattice and suitable activators/ coactivators, doping process and physics of nanophosphors such as quantum confinement, quantum size, surface area, surface morphology, band gap variation, shift in excitation are some of the parameters one has to study before selecting and synthesizing nanophosphors. With so many fascinating scientific and technological developments feeding in to a multi billion dollar phosphor industry it is high time to assess the availability of scientific know-how and technological competence in India in this

area to help evolve goal oriented collaborative research. In what follows a brief account of optimization of conditions for synthesis of nano phosphors. In this paper, display phosphor requirements including, physical, optical and electrical, preparation of phosphors by various methods, effect of preparative conditions, and characterization are described. Operation of various emissive and non emissive displays and the role of number of industrial phosphors are discussed.

DISPLAY PHOSPHORS

Phosphor in a display is considered as equivalent of an eye in a human body. Phosphors employed in various displays for specific application must satisfy above mentioned NTSC/PAL standards. Great effort is being made to develop new phosphors as well as improve the existing phosphors world wide. Synthesis, characterization and manufacturing of most of commercial phosphors are documented in the literature (1-8). Till today, very few phosphors are suitable for display applications. Phosphor materials being used in display manufacturing as well as potential candidates for future displays are reviewed in this chapter. The following briefly describes the phosphor requirements.

Physical Requirements

The morphology (phosphor particle size and shape), particle size distribution (PSD), body color and rheology are the important physical requirements as display phosphors. The rheology of a paste or slurry depends on size and shape of particles, binders and vehicles used in past formulations. Currently, most the displays are manufactured by depositing phosphor particles by settling, slurry, dusting, screen printing or ink jet process. The morphology, PSD and phosphor thickness not only affect the display manufacturing process but also influence the performance of the display. Preparing phosphor in presence of various flux materials, for example, can modify its morphology and improve the luminescent characteristics.

The spherical shape of the phosphor particles helps to minimize the quantity of binder as well as vehicles required in coating process. It is also known that screens with smaller size phosphor particles have higher packing density and better performance.

Optical Requirements

The following optical properties of phosphors need to be optimized in various display applications:

Excitation

For example, PDP phosphors should have a high conversion coefficient under VUV excitation. The photon energy from the plasma discharge is essentially absorbed by the phosphor matrices and then transferred to luminescent centers. Since the emission from plasma discharge (Xe/Xe^*) is limited to two dominant spectral lines at 147 and 172nm, most of the common luminescent materials do not have absorb at these wavelengths (8). Depending on the ratio of gas mixture, the intensity of the two lines varies. Same principles apply to UV (254nm from Hg vapor) excited lamp phosphors being used in LCD backlight applications.

Emission and Brightness

Brightness from a phosphor is a key of its performance in a display. Ideally, phosphor materials should have high quantum efficiency (QE), high reflectivity for visible light. Phosphors with higher QE not only minimize the power consumption but also reduce the cost of electronics required to operate the display. Phosphors in current use have achieved QE up to 95%. The emission of individual phosphors (R,G,B) should satisfy the NTSC requirements.

After Glow Decay or Persistence

For display applications, one has to consider short as well as long time persistence behavior of phosphors. Short time persistence value, defined as the time for the decay to reach 10% of the initial brightness, should be between 6 and 9 ms. The long time persistence component should contribute less than 0.25% to the initial brightness after 2 to 10s after the termination of excitation. The origin of the long persistence is similar to that of fluorescence, but the metastable state to ground state transition is forbidden. Emission occurs when thermal energy raises the electron to a state from which it can de-excite; therefore, this process or phosphorescence is temperature-dependent. MECH

Color Coordinates/ Gamut and Color Temperature

The color purity of a phosphor depends on the spectral energy distribution of the emission. Generally the color purity can be determined by measuring its x,y coordinates on a standard CIE color chart. The color gamut of a phosphor is represented as an area in the CIE 1931 chromaticity diagram with the curved edge representing the monochromatic colors.

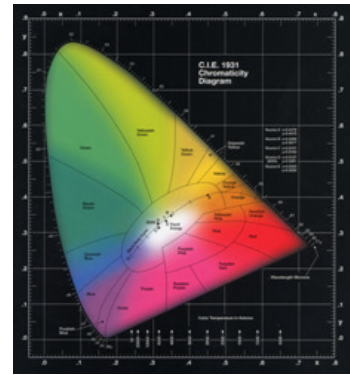


Fig 1. CIE 1931 Chromaticity Diagram.

Gamut areas typically have triangular shapes because most color reproduction is done with three primaries. Color temperature is a simplified way to characterize the spectral properties of emissions from phosphors. In reality the color of spectral energy distribution is determined by how much each point on the spectral curve contributes to the total output; the color temperature of most color TVs is in the 6,500 to 9,500 K range. Higher color temperatures are due to higher brightness and color saturation.

Saturation

Every phosphor saturates with an increasing excitation energy such as VUV flux (PDP) or electron density (FED); for example red ($\text{Y,GdBO}_3:\text{Eu}$) and blue ($\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$) phosphors show luminescence saturation with strong VUV excitation. On the other hand, green ($\text{Zn}_2\text{SiO}_4:\text{Mn}$) phosphors exhibits high saturation. Phosphor saturation leads to image sticking in a display and must be minimized or eliminated.

Degradation

The degradation is related not only to optical exposure or solarization or surface damage but also to thermal or heating processes. The degradation of phosphor starts during the manufacturing process and continues during display operation. The degradation mechanisms involved in specific phosphors are not fully understood. Various factors responsible for the degradation are morphology of phosphor particles, crystal structure, surface defects, stability of activators, location in the lattice and oxidation state of activators, and manufacturing processes.

Phosphor Parameters Purity of raw materials

Even a small amount of impurities, sometimes change phosphor characteristic drastically, therefore the raw materials used must be of high purity. One must exercise all cautions to choose pure raw materials to form the phosphor and prevent further contamination from occurring during the preparation processing to form the phosphor. For example in case of Y_2O_3 the most frequently used rare earth compound, the rare earth other than 'Yttrium' should be kept below 10 ppm and the total amount of heavy metals below 10 ppm. In the present work the rare earth oxides used are procured from Indian Rare Earth's Limited and were of 99.9% purity and other chemicals from Chemical Center and Du Cat chemicals.

Raw materials blend ratio

The completeness of the solid state reaction depends on the relative diffusion rate of the reacting species. The rate of reaction between the two solids is an exponential one, rapid in the beginning but slowing as the components are used up. An asymptote is gradually approached but the reaction never becomes 100 % complete. Thus we always end up with a un reacted components. Any such impurity affects the efficiency of the so-produced phosphor. Therefore in formulating a phosphor composition, one always employs a small excess of the anion reactant so as to avoid the presence of strongly absorbing cationic species in the end product. The excess components either vaporize during the firing or are consumed to create bi-product. They can sometimes be washed away after the reaction and we get the resulting phosphors very close to the stoichiometric composition.

Synthesis

Most of the rare earth activated phosphors are synthesized by solid state diffusion reaction between the raw materials at high temperature. Although the basics of the industrial scale phosphor synthesis were well established a decade ago, the process of optimization is still continuing because of the importance of phosphor efficiency, required for different applications, the production cost and hence market share. The synthesis of a phosphor with reproducible efficiency and chromaticity requires careful control on the purity, stoichiometry and particle size of the starting raw materials [1-4]. The following flow chart gives the general concept of phosphor synthesis process. First the high purity materials of the host crystal, activators, and the fluxes are blended, mixed and then fired in a container. Bellow is the general flow chart of phosphor synthesis process

Refinement of Raw Materials (Matrix, Activator, Flux) → Blending, Ball mill (large scale) Mortar and pestle (Laboratory l scale) → Synthesis (firing [1200°C for 3-4 hours]) → Coarse Crushing → Final Product → Milling and Sieving → Characterization → Applications

As the product obtained by firing is more or less sintered, it is crushed, milled and then sorted to remove coarse and excessively crushed particles. In some cases the product undergoes surface treatment.

Crucibles and atmospheres

In the phosphor industry, quartz and silicon carbide are the most frequently used container materials for firing phosphors. For phosphors requiring higher firing temperatures, (e.g., aluminate phosphors), alumina crucibles are employed. Box-type furnaces are common for small-scale production. For large quantity production, tunnel-type, continuous furnaces are indispensable. Firing is carried out either in air or in a controlled atmosphere. Phosphors activated with Tl^+ , Pb^{2+} , Sb^{2+} , Mn^{2+} , Mn^{4+} , or Eu^{3+} ions can be fired in air, whereas phosphors activated with Sn^{2+} , Eu^{2+} , Ce^{3+} , or Tb^{3+} ions are fired in a reducing atmosphere. As the reducing gas, nitrogen containing several percent hydrogen is most frequently used. The zinc sulfide phosphor is fired in a crucible that contains a small amount of sulfur, as ZnS is oxidized if directly exposed to air. Firing temperatures range varies from 900 to 1200°C for phosphate

phosphors, 1000 to 1300°C for silicates, and 1200 to 1500°C for aluminates.

Fluxes

The purpose of firing is not only to cause solid-state reactions but also to form well crystallized particles with an appropriate average diameter. The substance added to the raw material mixture to help crystal growth is called a flux. Fluxes are usually compounds of alkali- or alkaline earth metals having low melting points. The halides are most frequently used. Concerning the crystal growth of zinc sulfide phosphors during firing, it is known that the growth rate of the particle volume is constant for a constant firing temperature.

Impurities and additives

The presence of some impurity ions reduces luminescence efficiency, sometimes to a very great extent. On the contrary, there are some additives that influence phosphor characteristics in a positive way; they improve efficiency or decrease deterioration. The kind and quantity of the ions that change phosphor characteristics differ from phosphor to phosphor. Some examples are presented in the following. It is well known that the iron group ions drastically reduce the luminescence efficiency of ZnS phosphors, and hence are called killers. In case of the ZnS:Cu,Al phosphor, Ni^{2+} has a stronger effect than Fe^{2+} and Co^{2+} .

Particle size control

Practical phosphors must be prepared so that they can form a dense, pinhole-free coating on a substrate. This property is determined mainly by particle size distribution and surface treatment. In case of a fluorescent lamp phosphor, the optimum coating thickness is roughly proportional to its mean particle size; that is, the smaller the particle size, the thinner the coating can be. When a mixture of phosphors is used, as is the case with three-band fluorescent lamps, the proportion of a component can be made smaller for the same emission color when its particle size can be made smaller. Therefore, a small particle size is advantageous for expensive phosphors. Fine-particle phosphors also yield denser coatings. When a phosphor is prepared in a condition that yields fine particles, on the other hand, luminescence efficiency tends to become lower. Phosphors having a small particle size and high efficiency would be most useful. The flux used plays a determining role in the particle growth process. Each flux influences the particle size and the shape in a different way. Therefore, a combination of fluxes is sometimes used to obtain products with desired morphology.

Firing conditions

Higher firing temperatures and longer firing times result in larger particles. Particle growth is rapid in the initial stage of firing, and slows down after a certain period of time .

Milling

Normally, the fired phosphor is obtained as a sintered cake. This is broken into smaller pieces and then milled into particles. Weak milling (i.e., separation of coagulated particles into primary ones) changes the efficiency little. However, primary particle

destruction lowers efficiency. The possible reasons are that lattice defects created by phosphor crystal destruction act as nonradiative recombination centers, or that a nonluminescent, amorphous layer is formed on the surface of the particles. It is most important to select raw materials, fluxes, and firing conditions so as to avoid strong milling after firing.

Particle classification

Even by careful adjustment of materials, fluxes, and firing conditions, the phosphors obtained usually have a broad particle-size distribution. A process is necessary, therefore, to remove both very fine and coarse particles from the phosphor lots; this is done by means of sedimentation, elutriation, or sieving.

Nano phosphors Synthesis

A Physicist's approach: Top down : 1. Laser ablation , 2. Vacuum evaporation, 3. High energy ball milling, 3. Inert gas condensation, 4. Sputtering

A Chemist's approach: Bottom up: 1. Combustion, 2. Hydrothermal, 3. Sol-gel, 4. Precipitation, 5. Sono-chemical route

Solid State Diffusion Process

The chemical reactions in solidstate can be initiated and accelerated by intimately mixing the reactants in fine powder form and by heating the mixture. Thus, the degree of dispersion and mixing of one reacting solid with another are important to the overall mechanism of solid-state reaction. Thus the overall solid state reaction is dependent upon the rate of diffusion of the two species. These two rates may or may not be the same. The rate of solid state reaction depends on the number of nuclei produced per unit volume. A nucleus is a point where the atoms or ions have reacted and begun formation of the product structure.

Sol-gel Process

The phosphors materials for any application can be synthesized by sol-gel process which includes oxides, sulfides, oxysulfides, halides, silicates, borates, phosphates, tungstates and molybdates can be synthesized by sol-gel process. The main advantages of sol-gel process are dispersions of colloidal particles in a liquid. The gravitational forces on the particles are negligible. Synthesis of nanophosphors by sol-gel process can be described in the following steps: a) reacting dilute solution comprising source of organic or inorganic metal salts, and an organic precursor providing source of boron, silicate, phosphate, sulfide, etc., b) refluxing the solution in required composition in an acid or alkaline medium to form a gel. From a sol, a gel is formed with an interconnected, rigid network, having nanometer pores and a polymeric chain whose average length is of the order of sub-microns, c) converting gel into xerogel, aerogel by drying in air at low temperatures (40 to 60°C) for submicron or in vacuum for nano size particles or gel powder by spray drying and d) thermally decomposing the xerogel or aerogel powders at temperatures below solid state reaction temperatures. Particle size ranging from nano to submicron depends on calcination temperature.

Other techniques employed for nano display phosphors are

1. Laser pyrolysis, is an excellent way of efficiently producing oxide based nanophosphors particles. 2. Flame spray pyrolysis is a promising method in synthesizing nanophosphors. It is more versatile method as a number of precursors including inorganic (acetates or nitrates) and organic (isopropoxide or butoxide) can be employed.

Spray Pyrolysis

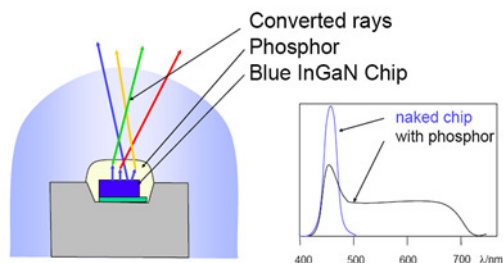
In recent years, spray pyrolysis has become another method to prepare sub-micron and spherical shape phosphors. Here, an ultrasonic spray generator is used to generate fine droplets of suitable precursors to the phosphor to be prepared. Every phosphor particle is of high phase purity as each particle arises from one droplet in which constituents are mixed homogeneously. The preparative conditions, concentration of precursors, nature of additives and flow rate controls the size and morphology of phosphor particles. When the droplets are dried, decomposed and crystallized in dispersed phase when passing through a reactor at high temperature for a short time (seconds).

Requirements of LED Phosphors

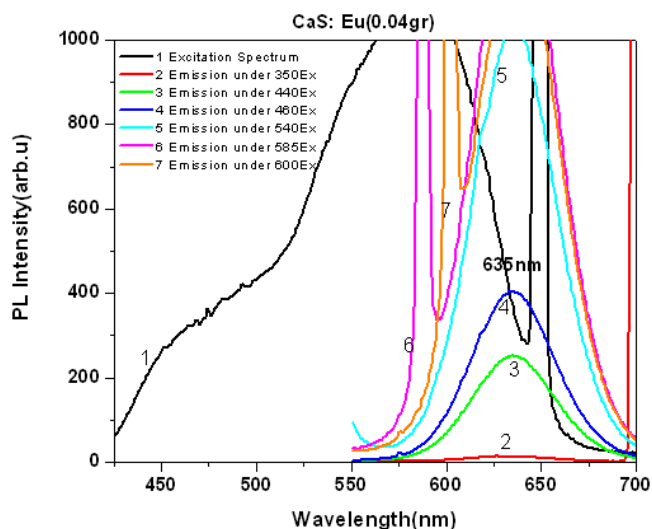
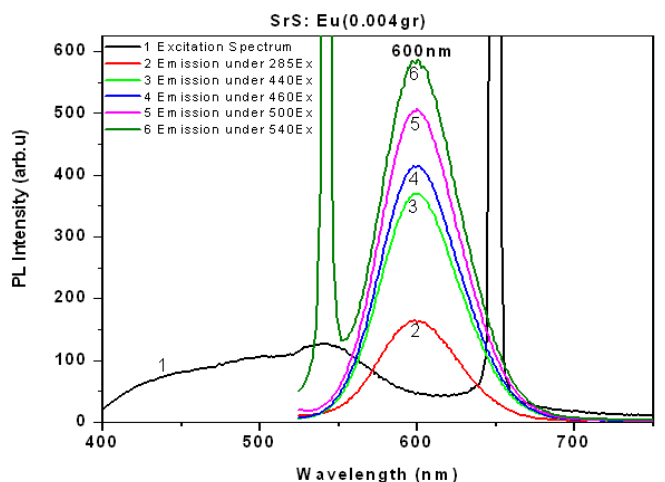
The basic requirements of LED phosphors are as follows: 1) their excitation spectra should overlap well with emission spectra of LED (420-490 nm blue LED) or (360-400 nm near UV LED), 2) their emission spectra should lie in the green and red (500-650 nm) region for blue LED and RGB region for near UV LED, 3) they should not absorb the visible light emission from blue LED or those from other phosphors, 4) they should exhibit high quantum efficiency, 5) light emission should not saturate at very high excitation density of LED chips (200 W cm⁻² which is 3 times higher than FL), 6) LED phosphors must withstand temperatures up to 150°C without significant reduction in luminescence efficiency. So phosphors with very high thermal quenching temperature are desired, 7) their color rendering index (CRI) should be > 80, and finally 8) their chemical and physical stabilities during LED manufacturing are important.

Commercial LED Phosphors

Conventional phosphors used in fluorescent lamps are not ideal for solid-state lighting because they have poor absorption for the LED light (near UV or blue). So researchers worldwide have been investigating other chemical compounds for their suitability as phosphors for solid-state lighting. Band-to-band transitions in direct gap semiconductors such as ZnS, ZnSe, ZnO and CdS offer the strongest absorption to LED light. But the main difficulty of their real value in phosphor convertor LED arises from strong temperature dependencies. Strong absorption can also be expected from dipole-allowed electron transitions in dopant ions, the best examples being Ce³⁺ and Eu²⁺, which can be crystal field shifted in the spectral location of their absorption and emission lines. One essential difference between Ce³⁺ and Eu²⁺ is the width of their emission band: While Eu²⁺ shows typical half widths of 30 to 60 nm, depending on the host material, Ce³⁺ has the widest emission of any RE ions – 80 to 100 nm – because of a spin-orbit ground state. In most hosts, the two transitions are so much broadened that they overlap completely into a broad asymmetric band.



Light from the LED prepared from the materials developed in the laboratory.



Photoluminescence of SrS:Eu and CaS:Eu LED phosphors

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