Phosphors

by A. M. Srivastava and C. R. Ronda

This article reviews the uses of phosphors that continue to be the central component of an increasing number of functional devices such as fluorescent lamps, flat panel displays, and electroluminescent display panels. There are a number of many useful references one might consult for general background on phosphors and on the existing commercial functional devices incorporating luminescent materials. A few suggestions are the following. Readers interested in comprehensive information specific to the subject presented in this article are encouraged to consult Ref. 1. Strongly recommended are the monographs by Butler,[2] Blasse and Grabmaier,[3] and those edited by Kitai[4] and Vij.[5]

Fluorescent Lamp Phosphors

Fluorescent lamp phosphors convert the ultraviolet (UV) emission of rare-gas/mercury discharge plasma into visible (white) light. Typical fluorescent lamp discharge emits UV radiation predominately at 254 nm, but also emit radiation at 185 nm (depending upon conditions, 10-20% of the UV radiation is emitted at 185 nm). The discharge conversion efficiency of electric power to 254 nm UV line is high (65%). The phosphor is responsible for nearly all the visible light produced by the lamp with the visible mercury lines contributing only a few percent to the total lamp light output. The phosphors have been optimized for efficient operation under excitation by 254 nm UV light. In this article we will focus on phosphors for general-purpose illumination, *i.e.*, fluorescent lighting systems used in homes, offices, factories, and shops.

Halophosphate Phosphors

A significant breakthrough in fluorescent lighting occurred in the 1940s with the development of the calcium halophosphate phosphor (Sb^{3+}, Mn^{2+} activated $Ca_5(PO_4)_3(Cl,F)$). As shown in Fig. 1, the complementary blue (Sb^{3+}; emission at 480 nm) and yellow (Mn^{2+}; emission at 580 nm) emission bands of this phosphor offer a resultant white emission in fluorescent lamps. The ratio of the blue to orange emission can be adjusted; increasing Mn^{2+} content, for example, suppresses the blue emission and enhances the orange emission. A range of whitish color from near blue to orange can therefore be attained from a single material. A further variation in color can be achieved by changing the F:Cl ratio.

The color of the halophosophate lamp, although acceptable in many applications, is not sufficiently pleasing for many people to install such lamps in the living areas of their home; hence they tend to be relegated to the basement or the garage. Color rendering index (CRI) values of "cool white" fluorescent lamps are in the upper 50s or lower 60s). Much-improved light is possible through the use of modern rare-earth phosphors where white light is made by mixing red-, green- and blue-emitting phosphors. The rare-earth phosphors and their impact on general lighting applications are discussed below.

Rare-Earth Phosphors in Fluorescent Lamps

The 1970s saw the development of a new generation of low-pressure mercury fluorescent lamps where one could simultaneously combine markedly high color rendering (CRI ~ 80) with high efficacy. Theoretical modeling had already predicted that a spectrum composed of emission in narrow bands near 450 nm (blue), 550 nm (green) and 610 nm (red) contributes to high CRI and efficacy.[6] In the mid-1970s such fluorescent lamps were commercially available and contained the blend of three rare-earth activated phosphors (the

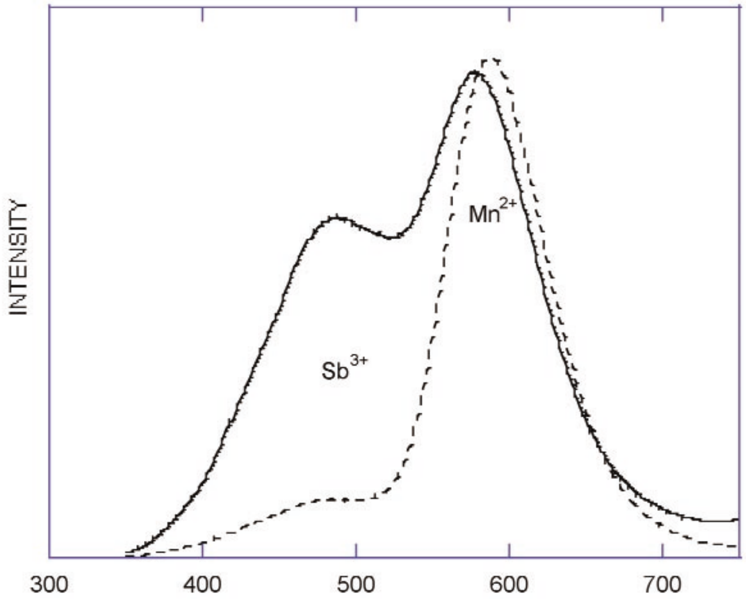

Fig. 1. Room temperature emission spectrum of the halophosphate phosphor.

blends are popularly known as tricolor or triphosphor blends: Eu^{3+} activated Y_2O_3 (red emitting), Tb^{3+} activated $CeMgAl_{11}O_{19}$ (green emitting), and Eu^{2+} activated $BaMgAl_{10}O_{17}$ (blue emitting).[6] (*Editors's Note:* See the first article in this issue.)

We now proceed to briefly discuss the individual rare-earth based phosphors that have played a vital role in the development of tricolor lamps.

Red emitting phosphor (Y_2O_3: Eu^{3+}; YEO)—The YEO phosphor absorbs the 254 nm Hg discharge emission through a charge transfer transition involving the Eu^{3+} ion and the neighboring O_2-ions. This charge transfer transition peaks at about 230 nm. The quantum efficiency of YEO that is the highest of all lighting phosphors is close to unity and constant in the range of europium concentrations from 1 to 15 mole percent. The lumen maintenance of this phosphor is exceptional and exceeds that of the other lighting phosphors. The phosphor has been applied in fluorescent lamps for more than two decades due to its high quantum efficiency, near perfect red emission, and exceptional lumen maintenance.

Green emitting phosphors—The three phosphors that are used as the green photon generators are based on trivalent cerium ion acting as the sensitizer and the trivalent terbium ion as the activator. Incident UV photons are absorbed by the Ce^{3+} ion, which then transfer their excitation energy to the Tb^{3+} ion, which in turn efficiently emits green photons according to the energy level and the transition rates of the Tb^{3+} ion. A typical emission spectrum of the green emitting phosphor is shown in Fig. 2.

$CeMgAl_{11}O_{19}$:Tb^{3+} (CAT)—The phosphor $CeMgAl_{11}O_{19}$ is an efficient ultraviolet emitter when excited by 254 nm radiation. The emission arises from allowed transitions between the ground and excited states of the Ce^{3+} ion, which are derived from the $4f^1$ and $5d^1$ electronic configurations, respectively. The introduction of Tb^{3+} in $CeMgAl_{11}O_{19}$ quenches the Ce^{3+} emission and generates the green Tb^{3+} luminescence as a result of the Ce^{3+}-to-Tb^{3+} energy transfer. The Ce^{3+}-to-Tb^{3+} energy transfer is limited to the six nearest neighbors at 5.6 Å and this requires rather high Tb^{3+} concentration (33 mole percent) for the complete quenching of the Ce^{3+} emission. The optimum phosphor composition $(Ce_{0.67}Tb_{0.33})MgAl_{11}O_{19}$ exhibits high quantum efficiency and excellent lumen output and maintenance during lamp operation.

$LaPO_4$: Ce^{3+},Tb^{3+} (LAP)—The efficient green luminescence of $LaPO_4$:Ce^{3+},Tb^{3+} (monoclinic monazite-type structure) has been known since the 1970s but only recently has the material gained importance as a fluorescent lamp phosphor. The advantages of this phosphor over CAT are the manufacturing ease due to the lower synthesis temperatures (about 1000°C) and the lower Tb concentrations required for optimum performance. Due to considerable energy migration occurring over the Ce^{3+} ions prior to the Ce^{3+} to Tb^{3+} transfer, the amount of Tb^{3+} required for optimum performance is considerably reduced; the commercial formulation contains 27% Ce and 13% Tb ($La_{0.60}Ce_{0.27}Tb_{0.13}PO_4$). The phosphor displays excellent lumen output and maintenance during lamp operation.

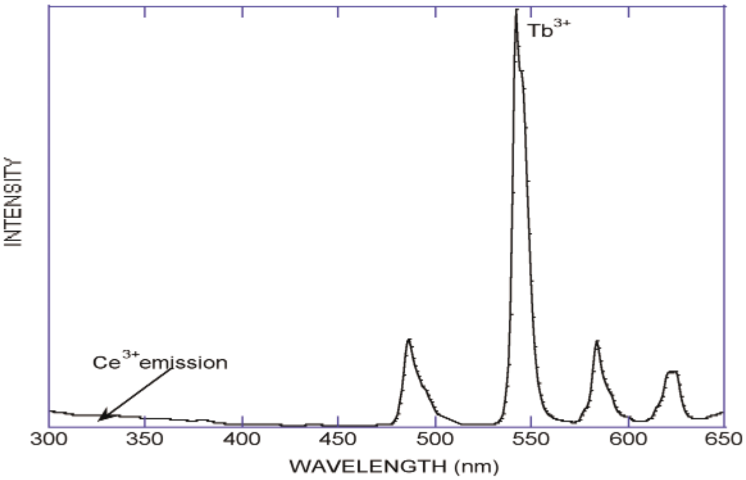

Fig. 2. Typical emission spectrum of a green emitting phosphor based on the Ce^{3+}-Tb^{3+} couple.

$GdMgB_5O10$: Ce^{3+},Tb^{3+} (CBT)—In CBT, the Gd^{3+} ions assist in the transport of energy from the sensitizer (Ce^{3+}) to the activator (Tb^{3+}) ions. The Ce^{3+} emitting levels are resonant with the lowest Gd^{3+} excited levels (6PJ). Energy transfer from Ce^{3+} to Gd^{3+} energy transfer is an efficient process. Efficient green luminescence is generated when the activator (Tb^{3+}) ion intercepts the excitation energy that is percolating over the Gd^{3+} ions. The quantum efficiency is high and the phosphor displays excellent stability in fluorescent lamps.

Blue Emitting phosphors—Two blue emitting phosphors are commonly used in tricolor fluorescent lamps. One is Eu^{2+} activated $BaMgAl_{10}O_{17}$, a material with the beta-alumina structure. Efficient Eu^{2+} luminescence with emission maximum at 450 nm supplies the required narrow band blue emission in the triphosphor blend. The strong absorption in the UV region is due to the allowed $4f^7 5d^{\circ} \rightarrow 4f^6 5d^1$ transitions.

The second commonly used blue phosphor is Eu^{2+} activated $(Sr,Ba,Ca)_5(PO_4)_3Cl$, a material with the apatite structure. The phosphor displays strong ultraviolet absorption with a narrow band emission peaking at 450 nm.

The great interest in phosphors based on rare earth ions is largely due to the success in recent years in turning the luminescence of these ions into commercially important phosphors. Specifically, fluorescent lamps with high-efficacy and high-color-rendering would not have been realized without the use of rare earth phosphors. Further, compact fluorescent lamps (CFLs) would not have been possible without the development of rare-earth phosphors, because their higher wall temperature and higher ultraviolet flux quickly degrades halophosphate materials. The chief drawback of rare-earth phosphors is their high cost that has more than doubled the cost of some fluorescent lamps.

Quantum Splitting Phosphors

Phosphors, which, on average, produce more than one visible photon for each incident ultraviolet photon, are referred to as quantum splitting phosphors (QSPs). For example, the phosphor YF_3:Pr^{3+} yields a room temperature quantum efficiency of 1.40 ± 0.15 under excitation by 185 nm radiation.[6] One can immediately recognize the benefits of the $YF_3:Pr^{3+}$ phosphor in devices that employ VUV emission of rare gas discharge as the primary exciting source.

The process of quantum splitting in Pr^{3+} activated phosphors is shown in Fig. 3a. Incident VUV photons are absorbed via an allowed Pr^{3+} 4f→5d optical transition. The excitation decays to the $^1S_0$ level. The transition probability is then such that the $^1S_0$ level decays radiatively to the $^1I_6$ level resulting in the generation of the first photon. A second transition that connects the upper ^3P level with several of the ground state levels yields the second photon. Quantum splitting has also been demonstrated in oxide materials such as $SrAl_{12}O_{19}$, $LaMgB_5O_{10}$ and LaB_3O_6.[6]

Recently, an effort in quantum-splitting phosphors centered on the trivalent gadolinium ion has been described in the literature.[7] Incident VUV photons are absorbed via the Gd^{3+} $^8S_{7/2} \rightarrow {}^6G_J$ optical transition (Fig. 3b). A cross-relaxation process excites the emission of the intentionally added activator, Eu^{3+} (Step P1 in Fig. 3b). During this cross-relaxation process the Gd^{3+} ion relaxes to the lower ^6P_J state. Energy migrating over the ^6P_J levels is trapped by a second Eu^{3+} ion (Step P2 in Fig. 3b). Hence, two red photons may be produced per incident VUV photon. Indeed, internal quantum efficiencies approaching nearly two in the $Li(Y,Gd)F_4:Eu^{3+}$ has been estimated.

We note that no multi-photon emitting phosphors have been turned into commercially viable products although significant efforts continue in their development.

Phosphors for Plasma Display Panels

A color plasma flat-panel display consists of an intermittent atmosphere-pressure xenon discharge, which excites red, green, and blue phosphors to form color images. In a plasma display panel (PDP), phosphors convert the vacuum ultraviolet (VUV) emission of xenon discharge plasma (emission at 147 nm and 173 nm, respectively) into visible light.

In connection with the quantum efficiency of plasma display phosphors, it is notable that there is very little reliable determination of phosphor quantum efficiency for primary-photons energies greater than about 5 eV. Recently, Justel *et al.*[8] have determined the quantum efficiency of PDP phosphors as a function of the energy of the primary photon.

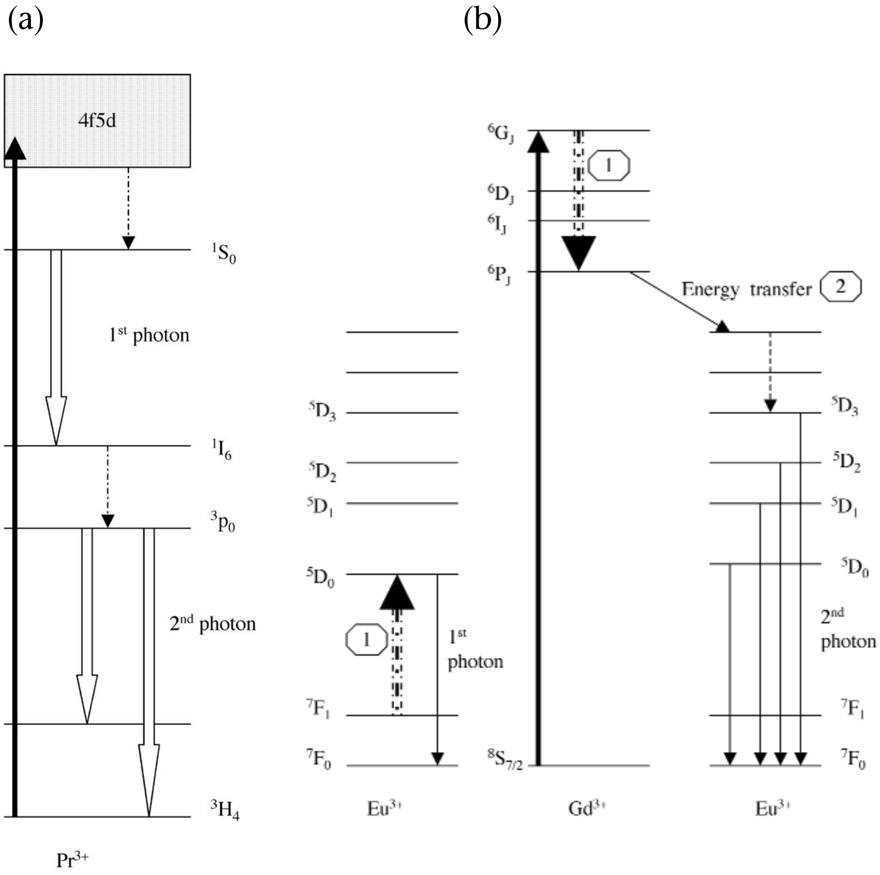

Fig. 3. Schematic representation of multiphoton emission via the Pr^{3+} ion and the Gd^{3+}-Eu^{3+} couple.

Divalent europium activated $BaMgAl_{10}O_{17}$, which supplies the required narrow blue emission in fluorescent lamps, can also be applied in PDPs since the phosphor is efficiently excited to a blue emission by VUV irradiation. According to Justel *et al.*[8] the quantum efficiency of the BAM phosphor for 147 nm and 172 nm excitation is close to unity and hence any effort to replace this phosphor with other alternatives has not met with success.

Three phosphors have been proposed for supplying the primary red color in PDP: Eu^{3+} activated $Y(P,V)O_4$, Y_2O_3 and $(Y,Gd)BO_3$. The quantum efficiency of the red emitting $(Y,Gd)BO_3:Eu^{3+}$ phosphor for excitation wavelengths of 147 nm and 172 nm are 84 percent and 82 percent, respectively.[8] Consequently, the luminescence efficiency of this phosphor is the highest of all the red emitting phosphors that have been proposed for application in PDPs. From the experimental data that has been presented on the variation in the emission characteristics of Eu^{3+} within the $(Y_{1-x}Gd_x)BO_3$ system of phosphors, the composition $(Y_{0.65}Gd_{0.35})BO_3$: Eu^{3+} has been chosen to supply the primary red color in PDPs. This phosphor yields a very orange color point in the CIE colorimetric system due to the presence of the rather intense $^5D_0 \rightarrow {}^7F_1$ emission line at 591 nm (Fig. 4). To enlarge the color gamut, one can alternatively use the $Y_2O_3:Eu^{3+}$ phosphor. In this case lower light output of the display panel is anticipated as a result of the lower luminescence efficiency of $Y_2O_3:Eu^{3+}$ phosphor under VUV excitation.

The Mn^{2+} activated Zn_2SiO_4 (mineral willemite) and $BaAl_{12}O_{19}$ phosphors are efficiently excited to a saturated green luminescence by VUV photons and are currently the best available phosphors for this application. The room temperature emission spectrum of Zn_2SiO_4: Mn^{2+} is shown in Fig. 4. The quantum efficiency of willemite phosphor for excitation wavelengths of 147 nm and 172 nm are 77 percent and 82 percent, respectively.[8] To reduce tailing in moving images, phosphors with short decay times are desirable. The spin forbidden $^4T_1 \rightarrow {}^6A$ optical transition on the Mn^{2+} ion, responsible for the green emission in these materials, exhibits a rather long decay time (tens of milliseconds). This limit the use of Mn^{2+} activated phospho-

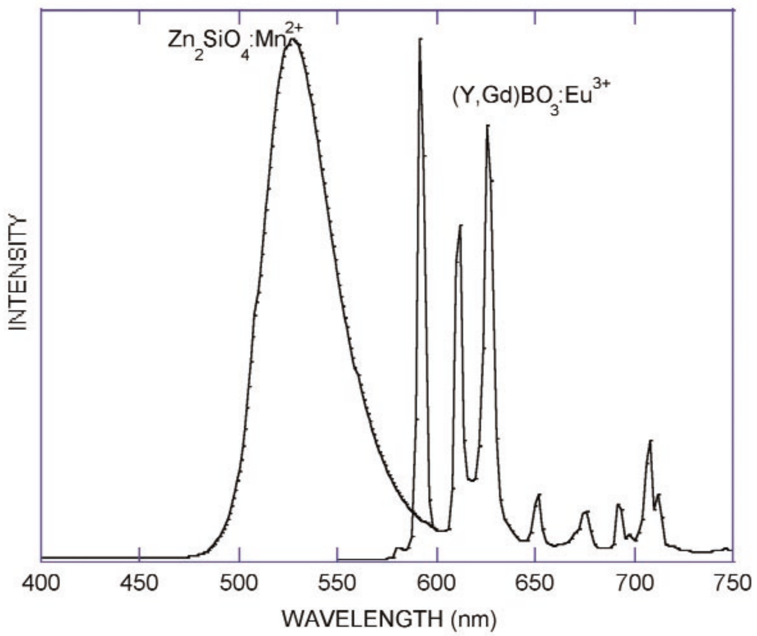

FIG. 4. The room temperature emission spectra of green [Zn2SiO4:Mn2+] and red [(Y,Gd)BO3:Eu3+] emitting plasma display phosphors.

rs in displays where the image changes rapidly. Interestingly enough, a steady decrease in the emission decay time with no deleterious effect on the quantum efficiency is observed when an increasing proportion (up to 10%) of Mn^{2+} is substituted for Zn^{2+} in the host crystal, Zn_2SiO_4.[9] This remarkable result has been explained in terms of the alteration in the transition probability as a consequence of magnetic interaction between pairs of Mn^{2+} ion in the host crystal.[9] The decay time of a 10 to 12 percent Mn^{2+} substituted phosphor is 10 ms making it suitable for PDP application.

The Tb^{3+} based fluorescent lamp phosphors (LAP, CAT and CBT) are also efficiently excited by VUV radiation and their quantum efficiencies are generally competitive with the standard Zn_2SiO_4:Mn^{2+} phosphor.[8] However, the chromaticity of these phosphors (the emission essentially consists of a sharp line near 545 nm) is generally not suitable for use in PDPs. Consequently, the willemite phosphor with saturated green emission color and high luminescence efficiency is preferred as the green color generator in PDP applications.

It is also clear that the energy efficiency of conversion of primary VUV photons to visible light may also be improved with the use of multi-photon emitting phosphors (see above), which produce more than one visible photon per incident VUV photon.

Electroluminescence

In electroluminescent (EL) devices, electrical energy is used to generate light. Technologically, electroluminescent devices are of interest because they are very rugged. Two different principles are in use. The first is high voltage EL, based on an electrical breakdown in the electroluminescent material, observed for the first time in 1936. However, the energy efficiency of such devices is not likely to be very high, mainly due to a very small efficiency of the process with which energy is transferred from lattice states to activator states. The best known example is the orange emitting ZnS:Mn phosphor for which an energy efficiency of 1-2%, corresponding to a lumen efficiency of 5-10 lm/W has been obtained. Other materials have been found as well, although less efficient. All colors can be generated, using this principle.

In the second principle, low voltages are applied, typically less than 10 V. The subsequent recombination of the electrons and holes injected into a material results in the emission of light. The latter process is also known as direct electroluminescence. In view of the direct conversion at low voltage, the energy efficiency is very high. Note that conventional LEDs are also part of this category, however here we will only briefly discuss organic LEDs. Both LEDs and OLEDs are discussed in detail elsewhere in this issue.

At present, rapid developments are especially seen in the field of direct electroluminescence, based on organic materials. Both polymeric substances and small molecules (which can be evaporated) are investigated. Very soon it was realized that in many cases the attainment of high efficiencies is hampered by the fact that a significant part of the excitation energy is stored as triplet excitons, which usually do not emit, thus limiting the efficiency of the final device. Interestingly, triplet excitons can be used by the rare-earth or transition metal dopants.

Since the first reports on OLEDs, great improvements have been realized. Early devices showed green emission only. In the mean time all colours can be generated, with maximum energy efficiency of about 20%.

Other Uses of Phosphors

Luminescent materials find extensive uses in technological areas such as solid-state lasers, phosphorescent paints (persistent phosphors), infrared detectors (upconversion phosphors), scintillators (detectors of X-rays and ionizing radiation), and cathode ray tubes (television phosphors). Readers are encouraged to consult Ref. 1. ■

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