Kirk-Othmer Encyclopedia of Chemical Technology.

PHOSPHORS

Luminescence is the process of producing light in excess of thermal radiation following an excitation. A solid material exhibiting luminescence is called a phosphor. Phosphors are usually fine inorganic compound powders of a high degree of purity and a median particle size of 3–15 micrometers but may be large single crystals, used as scintillators, or glasses or thin films. Phosphors may be excited by high energy invisible uv radiation (photoluminescence), x-rays (radioluminescence), high energy electrons (cathodoluminescence), a strong electric field (electroluminescence), or in some cases infrared radiation (up-conversion), chemical reactions (chemiluminescence), or even stress (triboluminescence). Figure 1 shows the electromagnetic energy spectrum indicating some of the common energy forms that excite phosphors. Because phosphors convert the exciting energy to visible radiation, they have many everyday applications; phosphors are responsible for the light generated by fluorescent lamps, televisions, computer terminals, etc.

Phosphors usually contain activator ions in addition to the host material. These ions are deliberately added in the proper proportion during the synthesis. The activators and their surrounding ions form the active optical centers. Table 1 lists some commonly used activator ions. Some solids, made up of complexes such as calcium tungstate [7790-75-2], $CaWO_4$, are self-activated. Also in many photoluminescence phosphors, the primary activator does not efficiently absorb the exciting radiation and a second impurity ion is introduced known as the sensitizer. The sensitizer, which is an activator ion itself, absorbs the exciting radiation and transfers this energy to the primary activator.

The optical properties of a phosphor are measured on relatively thick plaques of the phosphor powder. An important optical property for the application of the phosphor is its emission spectrum, the variation in the intensity of the emitted light versus wavelength. Fluorescent lamps must have phosphors which produce white light of high luminous efficiency and with good color rendering properties. Because individual activator centers generally emit in a relatively narrow region of the spectrum producing a colored light, more than one activator or phosphor must be used. Similarly colored televisions employ three phosphors in separate closely spaced dots; one dot contains a phosphor which emits in the blue, one in the green, and one in the red region of the spectrum. Saturated colors are needed in order for the screen to be able to reproduce nearly all colors using these emissions in different relative proportions. In other applications, such as x-ray screens, it is desirable to have an emission spectrum concentrated near the peak in the sensitivity of the receptor, such as the x-ray photographic film. The reflectance spectrum is a graph of the percentage of radiation reflected and absorbed by the powder plaque versus wavelength. The excitation spectrum gives the variation of the light output from the phosphor as a function of the changes in the wavelength of the exciting radiation. When normalized by the reflectance spectrum, the excitation spectrum measures the relative quantum efficiency of a photoluminescent phosphor as a function of the exciting radiation wavelength. The quantum efficiency of the phosphor is the number of quanta emitted by the phosphor divided by the number of quanta absorbed. The methods and precautions needed in measuring these spectra have been discussed (1).

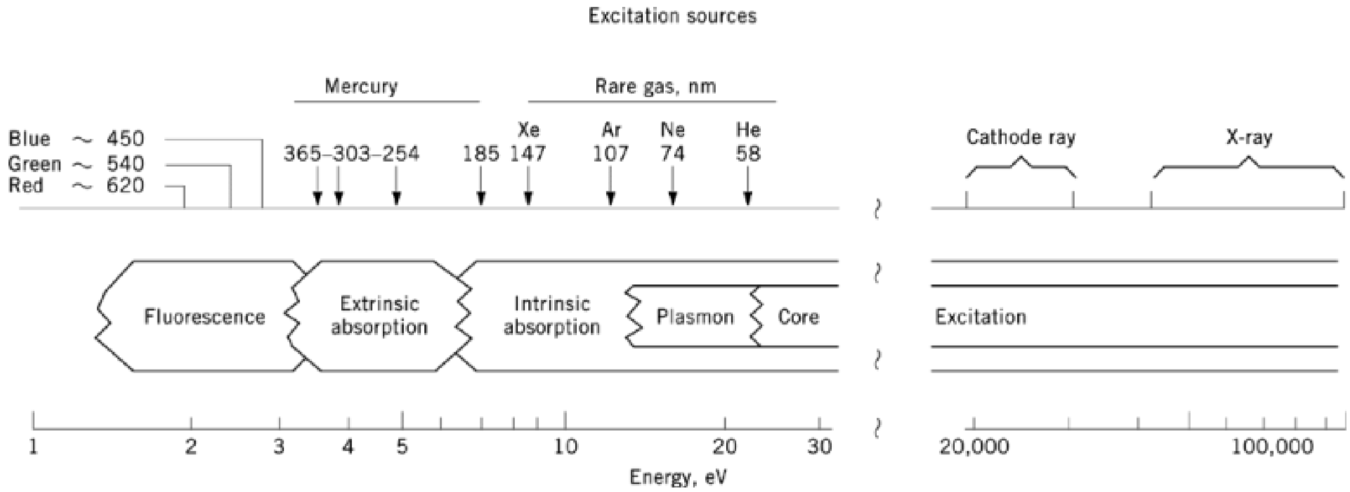

Fig. 1. Common phosphor excitation sources, energies, and the type of solid-state excitation caused by these sources. Following the initial excitation, high energy excitons may create many hole-electron pairs.

Table 1. Common Activator Ions

Type	Important examples	Color range	Others
$s^2 \longrightarrow sp$	Sb^{3+}	blue-green	Tl^+, Ga^+
broad band	Sn^{2+}	visible	Bi^{3+}, In^+
$d \longrightarrow f$	Eu^{2+}	blue-green	
broad (50 nm)	Ce^{3+}	uv-green	
$O \longrightarrow M$	WO_4^{2-}	460–520 nm	$MoO^{2-}4$
very broad (100 nm)	VO_4^{3-}	480–580 nm	NbO_4^{3-}
$d_t \longrightarrow d_e$	Mn^{2+}	510–580 nm	Mn^{4+}, Fe^{3+}
broad and narrow		green-orange	Crr^{3+}, Ni^{2+}
$f \longrightarrow f$	Eu^{3+}	red	Pr^{3+}, Nd^{3+}
narrow	Tb^{3+}	green	Tm^{3+}, Dy^{3+}
			Er^{3+}, Ho^{3+}

1. Theory of Luminescence

1.1. The Configuration Coordinate Model

To illustrate how the luminescent center in a phosphor works, a configurational coordinate diagram is used (2) in which the potential energy of the luminescent or activator center is plotted on the vertical axis and the value of a single parameter describing an effective displacement of the ions surrounding the activator, Q, is plotted on the horizontal axis (Fig. 2). At low temperatures, near room temperature and below, the activator is in the lowest vibrational level of the ground electronic state. Absorption of energy results in transition to an upper electronic state and since electronic transitions occur rapidly the lattice ions cannot rearrange during the transition according to the Frank-Condon principle, and the transition is seen as a vertical line on the configuration coordinate diagram. Following excitation the activator ion is in an excited nonequilibrium vibrational level of the excited state. The center then undergoes severe anharmonic vibrational motion and relaxes to a new equilibrium shape or size. The weak electromagnetic radiation that occurs during this relaxation is called hot luminescence. Relaxation generally occurs within less than one hundred vibrations or tens of picoseconds

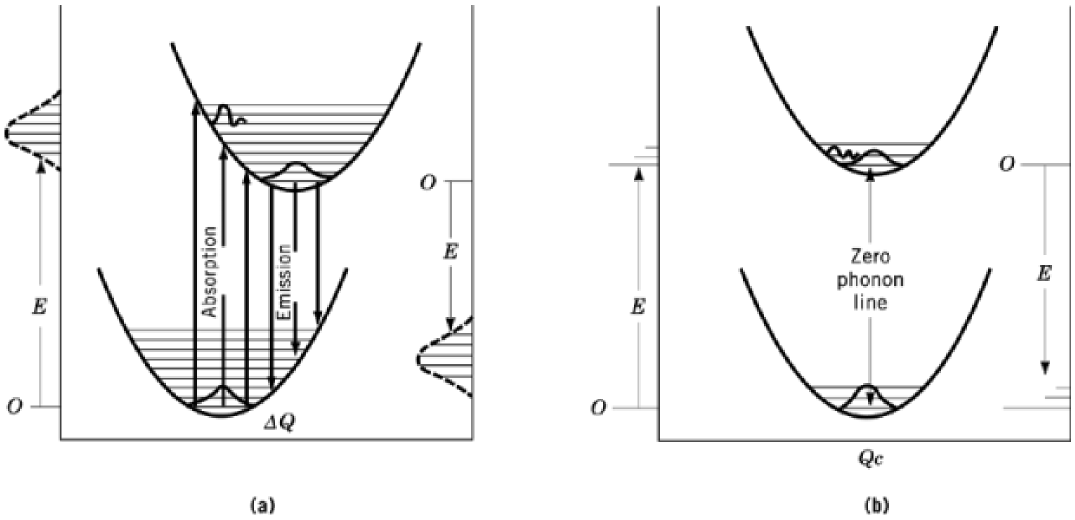

Fig. 2. General configurational–coordinate diagrams for (**a**) broad-band absorbers and emitters, and (**b**) narrow-band or line emitters. The ordinate represents the total energy of the activator center and the abscissa is a generalized coordinate representing the configuration of ions surrounding the activator.

with the result that hot luminescence can only be detected by measuring radiation emitted within picoseconds after excitation. Ordinary luminescence takes place after the luminescent center has relaxed to the lowest vibrational level of the excited state.

Activator ions that are very strongly coupled to the lattice exhibit a large Stokes' shift. The Stoke's shift is the decrease in energy and increase in wavelength of the emitted radiation compared to the exciting radiation. This is shown on the *y*-axis of Figure 2**a**. The energy difference goes into heating the lattice. In such cases both the absorption and emission bands are broad and approximately Gaussian in shape when intensity is plotted against radiation energy. On the other hand, sharp spectral emission lines are indicative of activator ions which do not change shape or size significantly between the ground and excited states (see Fig. 2**b**, Table 1). In addition to the Stoke's shift and the general shape of absorption and emission bands, configurational coordinate models explain a number of other experimental observations associated with phosphor spectra. The diagrams themselves can be constructed from careful measurements of optical properties of the phosphor. Approximate configurational coordinate diagrams can be calculated using a molecular-orbital theory, assuming a molecular cluster consisting of the activator and its surroundings.

1.2. Nonradiative Decay

To have technical importance, a luminescent material should have a high efficiency for conversion of the excitation to visible light. Photoluminescent phosphors for use in fluorescent lamps usually have a quantum efficiency of greater than 0.75. All the exciting quanta would be reemitted as visible light if there were no nonradiative losses.

The occurrence of nonradiative losses is classically illustrated in Figure 3. At sufficiently high temperature the emitting state relaxes to the ground state by the crossover at B of the two curves. In fact, for many broad-band emitting phosphors the temperature dependence of the nonradiative decay rate P_{nr} is given by equation 1:

$$P_{nr} = A\exp\left(-E^{*}/\kappa T\right)$$

where E^* is the activation energy as shown in Figure 3. However, the occurrence of nonradiative processes is better explained by including quantum mechanical tunneling to the ground state as shown by the dashed arrows C (3). The nonradiative decay rate by C can be orders of magnitude greater than the radiative decay rate and occurs even at moderate temperatures, when only the lowest vibrational levels of the excited state are significantly populated. This rate has been shown to depend exponentially on the energy separation between two electronic levels (4).

$$P_{nr} = A\exp(-\Delta E)$$

If the magnitude of ΔE is less than a few vibrational frequencies, radiationless relaxation always occurs. Hence exciting energy cascades down from one electronic level to another, heating the lattice, until it reaches a state for which E^* is large and ΔE is more than a few vibrational frequencies; then the excitation is trapped. If trapped for times long enough, radiation decay dominates, however, although the temperature dependence of the nonradiative decay rate and its dependence on the energy separation of the two parabolas is in good agreement with theory, the nature of the nonadiabatic interaction between an emitting state and the ground state is often unknown. Because energy transfer to the ground state curve may occur at a very high vibrational level where anharmonicity in the ground state has a large influence, a quantitative understanding of the important phenomenon of radiationless decay, and the ability to predict which host plus activator systems result in efficient phosphors, appears hopeless (5).

1.3. Energy Transfer

In addition to either emitting a photon or decaying nonradiatively to the ground state, an excited sensitizer ion may also transfer energy to another center either radiatively or nonradiatively, as illustrated in Figure 4.

Nonradiative energy transfer is induced by an interaction between the state of the system, in which the sensitizer is in the excited state and the activator in the ground state, and the state in which the activator is in the excited and the sensitizer in the ground state. In the presence of radiative decay, nonradiative decay, and energy transfer the emission of radiation from a single sensitizer ion decays exponentially with time, t.

$$I(t) = I(0)\exp(-P_{\mathrm{rad}}t - P_{nr}t - P_{et}t)$$

P_{et} can be written as a series of terms which depend on the distance between the sensitizer and activator ions. Contributions include a leading term, called the dipole–dipole interaction, which is proportional to R^{-6}; a term called electric dipole–electric quadrupole interaction, proportional to R^{-8}; the electric quadrupole–quadrupole, proportional to R^{-10}; an exchange interaction caused by the overlap of the wave functions of the sensitizer and activator ions that varies as $\exp(-cR)$; and an electric dipole–magnetic dipole interaction due to the presence of a magnetic field at the activator ion caused by the motion of the sensitizer electrons. Because different sensitizer ions have different distributions of activators around them, the statistical average of equation 3 gives an observed radiation decay which is nonexponential and when carefully measured can be analyzed to determine the mechanism of energy transfer. Because of the importance of nonradiative energy transfer in many commonly used phosphors, these mechanisms have been extensively studied. In addition to its dependence on the distance between the sensitizer and activator ions, P_{et} is proportional to the overlap of the emission band of the sensitizer with absorption bands of the activator so that energy is conserved in the transfer (6).

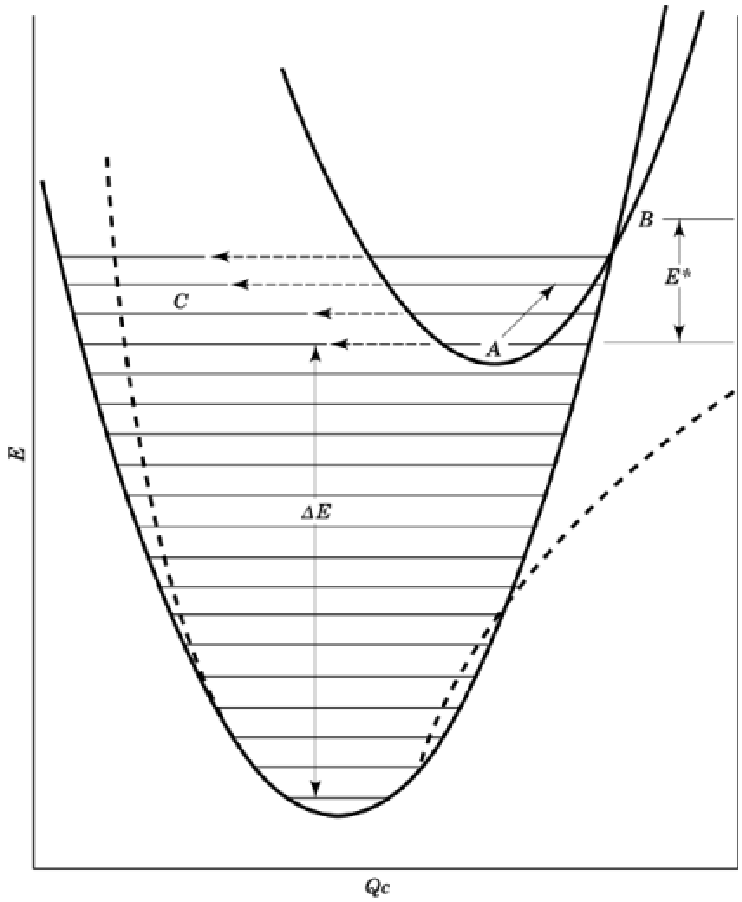

Fig. 3. A configurational–coordinate diagram showing mechanisms of radiationless decay to the ground state. Nonradiative decay to the ground-state vibrational manifold can occur by the semiclassical path $A \longrightarrow B$ or by quantum mechanical tunneling $A \longrightarrow C$ (3). (– – –) represents a more realistic Morse potential for the ground state.

2. Lamp Phosphors

In fluorescent lamps, phosphors are coated on the inside of the lamp tube using a slurry containing the powder and a liquid which is either poured down through the tube, up-flushed, or in some cases the tubes are filled and then drained. Because of concerns over having volatile organic solvents in the air, the liquid medium containing the powder is usually water with an added agent, a thickener, to increase the viscosity of the suspension, such as poly(methacrylic acid) or poly(propylene oxide). Other additives are included, such as dispersants, in order to improve the dispersion of the powder, defoamers (qv), and sometimes powder adherence additives, such as fumed alumina, Alon, or boric oxide.

It is important to dry the coating quickly; usually hot air flowing in and around the bulb is used in order to prevent the powder from flowing off the bulb. This creates a layer of powder of relatively uniform thickness on the tube, although generally the coating is thinner at the top and thicker at the bottom. Phosphor coatings for fluorescent lamps in the center region of the lamp are about four particles thick. Such a thickness is sufficient to cover the glass tube so that statistically there is little area, not more than 1 or 2% of which is uncovered. The

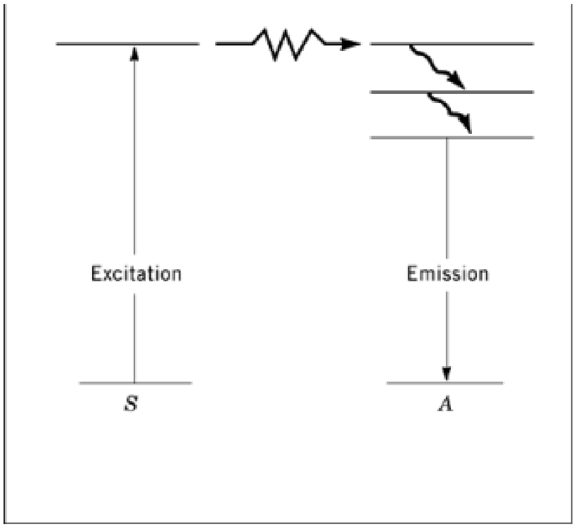

Fig. 4. A schematic diagram showing energy transfer from sensitizer *S* to activator *A* followed by relaxation from one electronic level to another and then emission.

visible reflectance of such a coating is around 55–65%. A still thicker coating would waste phosphor material, and by further increasing the visible reflectance of the coating would make it more difficult for visible light generated near the inner surface of the phosphor layer to get out of the lamp.

During lamp operation mercury atoms are ionized and excited, and after being excited emit their characteristic resonance uv radiation predominately at 254 and 185 nm. The conversion of electrical energy in this way into invisible uv radiation is quite efficient, about 70%. A phosphor for fluorescent lamps must be capable of absorbing the uv and converting it through relaxation between energy levels and the Stoke's shift to visible light of a suitable white color with high luminous efficiency and good color rendering ability. It must also be capable of withstanding the environment of mercury discharge.

2.1. The Calcium Halophosphate Phosphors

Early fluorescent lamps used various combinations of naturally occurring fluorescent minerals. The development of the calcium halophosphate phosphor, $Ca_5(PO_4)_3(Cl, F){:}Sb^{3+}, Mn^{2+}$, in the 1940s was a significant breakthrough in fluorescent lighting (7). As is often the case in new phosphor discoveries, this phosphor was found accidentally while searching for phosphors for radar screens.

In the halophosphate phosphor Sb^{3+} sensitizer ions absorb the uv radiation from the discharge thereby undergoing a transition from the ^1S ground state to the excited singlet ^1P and triplet ^3P state of the $5s5p$ configuration. Relaxation occurs to the lower lying triplet ^3P state. Antimony ions emit part of this energy in a band peaking near 480 nm. Energy is also transferred to Mn^{2+} ions which emit near 580 nm (Fig. 5). By increasing the concentration of the Mn^{2+} activator, more and more of the emission is in the orange Mn^{2+} band allowing attainment of a range of whitish colors from near blue to orange. The energy transfer from Sb^{3+} to Mn^{2+} is key to application of this phosphor. By careful measurement of the decay of the sensitizer Sb^{3+} ion, and a comparison with theory, a comprehensive study of this energy transfer was made which indicates that the energy transfer occurs by an exchange mechanism rather than longer range dipole–dipole or dipole–quadrupole mechanisms (8). A further variation in color can be achieved by changing the F:Cl ratio. As the concentration of F increases, the Mn^{2+} band shifts toward the green. The total range of colors possible with

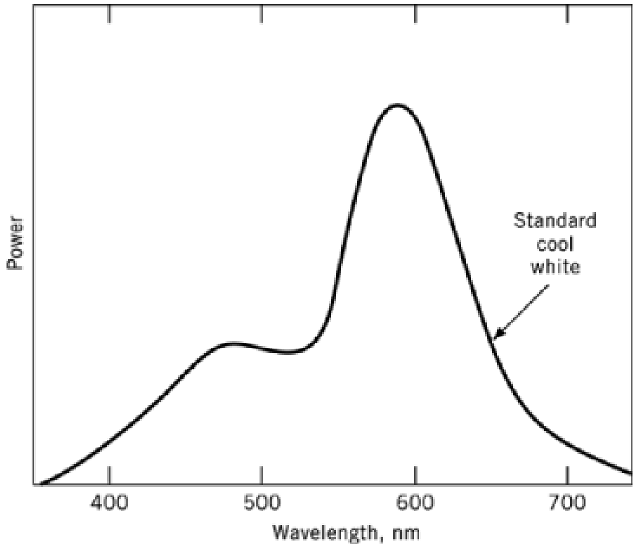

Fig. 5. The emission spectrum of a typical cool white halophosphate phosphor showing the Sb^{3+} emission band around 480 nm and the Mn^{2+} emission band around 580 nm.

halophosphate phosphors in typical fluorescent lamps, which include visible mercury line radiation, is shown on the CIE (Commission de L'Eclairage) color diagram in Figure 6.

The crystal structure of the calcium fluoroapatite has two different crystallographic sites for the Ca^{2+} ion. The Ca(I) site has a threefold axis of symmetry and is coordinated to six oxygen ions at the vertices of a distorted trigonal prism. The Ca(II) ions are located at the corners of equilateral triangles centered around a fluoride ion. The site symmetry for the Ca(II) site is C_{1h}. Epr data suggest that the Mn^{2+} ions occupy both the Ca(I) and Ca(II) sites in the lattice with a preference for the Ca(I) site at low Mn^{2+} concentrations (9). Optical measurements support the epr data. The Mn^{2+} ions on the Ca(I) sites have been shown to be responsible for most of the observed luminescence, whereas emission from the Mn^{2+} ions on the Ca(II) sites occur only for higher Mn^{2+} concentrations. Neutron diffraction studies have also confirmed these results (10).

Because Sb^{3+} does not have any unpaired electrons, its site preference is ambiguous and much more difficult to determine. It has been speculated that the Sb^{3+} ions would occupy the Ca(II) sites with charge compensation achieved by an oxygen replacing an adjacent halogen ion. This model was further supported by comparing predictions of molecular orbital calculations with the excitation spectra for the Sb^{3+} ion in the fluoroapatite (11). A marked change in the excitation spectrum, which occurs when oxygen is excluded from providing charge compensation, is also in agreement with the calculations. X-ray data (12) support the location of the Sb^{3+} ions on the Ca(II) sites and the mentioned nature of charge compensation. Nevertheless an opposing view and some experimental measurements suggest that Sb^{3+} ions may occupy *P* sites in the structure (13).

The halophosphate phosphors are synthesized by first thoroughly blending $CaHPO_4$, $CaCO_3$, CaF_2, NH_4Cl, $MnCO_3$, and Sb_2O_3 powders. The calcium-containing intermediates are generally prepared and purified by the phosphor manufacturer. In particular, the $CaHPO_4$ is often recrystallized after dissolving the initially precipitated $CaHPO_4 \cdot 2(H_2O)$ in an acid solution heated to around 80–90°C. The recrystallized $CaHPO_4$ is of a high degree of purity and consists of clear well-formed plates the size of which determines the size of the final phosphor.

The intermediates are blended in large blenders. Surprisingly, it is important to avoid formulations of the blend which have the stoichiometric cation:phosphate ratio and halide:phosphate ratio for two reasons.

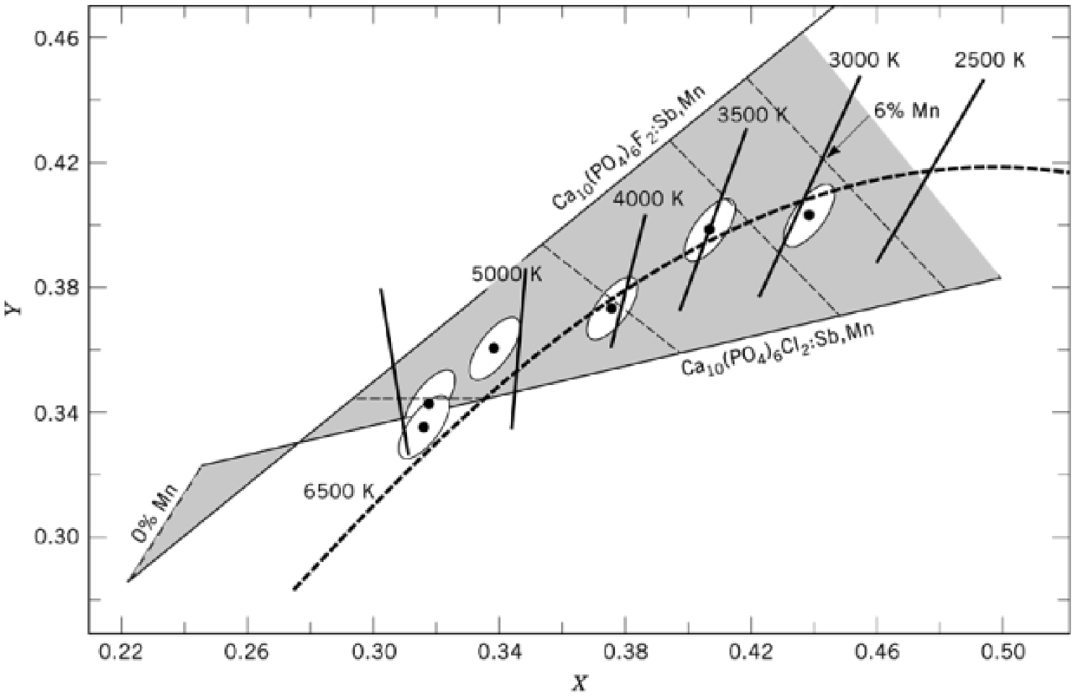

Fig. 6. A portion of the CIE color diagram where *X* and *Y* define the color. The shaded area shows the range of color of fluorescent lamps using calcium halophosphate phosphors. Also shown are standard white lamp colors. The locus of colors of Planckian radiators (– – –) and the correlated color temperatures in Kelvin (—) are indicated.

First, the NH_4Cl and Sb_2O_3 powders react to form volatile antimony oxychloride compounds, hence an excess of these species is required. If the chloride drops below the stoichiometry due to this volatilization then some calcium orthophosphate is formed and the Mn^{2+} activator ions enter this undesired phase giving the cake a pink color. On the other hand a large excess of the chloride results in greater losses due to volatilization and some additional sintering. The losses due to volatilization depend on the amount of excess chloride, the final temperature of synthesis, cake depth, etc. A loosely fitting cover for the crucible in which the blend is fired must be used to prevent variation in the stoichiometry due to volatilization. The second important consideration in the blend formulation is the use of slightly less $CaCO_3$ than is required to meet the stoichiometry of the material. The phase diagram indicates that for such a blend composition a small amount of the calcium pyrophosphate phase is formed. The activator Mn^{2+} ions do not enter this relatively inert second phase; however, a large excess of this phase generally results in excessive sintering and shrinkage resulting in a hard cake which is difficult to process further. If on the other hand the amount of the pyrophosphate phase formed is too little or does not exist at all then the cake is very soft and there is a risk of forming CaF_2 and CaO as undesired second phases due to normal weighing errors in manufacturing. Typically the blend is formulated to give 1–3 wt % of the calcium pyrophosphate phase.

After thorough blending the powder is placed in a suitable crucible and heated in a furnace at temperatures between 1075 and 1150°C. During the heating, H_2O and CO_2 are given off at 450 and 850°C, respectively. The halophosphate phosphor starts to form around 1000°C. At this stage some manufacturers lightly mill the material and second fire it in a nitrogen atmosphere to ensure the full incorporation of the manganese ions in the divalent state.

After firing, the powder is washed in water typically with a small amount of complexing agent such as ethylenediaminetetraacetic acid (EDTA), sodium EDTA, or a weak acid such as citric acid to remove the excess chloride, volatile antimony oxychlorides which have recondensed on the phosphor during cooling, and manganese compounds which are not incorporated in the halophosphate lattice. The powder is then ready for suspension.

The morphology of the resulting halophosphate phosphor closely resembles the plate-like morphology of the starting $CaHPO_4$ but with an important difference: very small submicrometer grains of the calcium halophosphate can be seen. These grains are fused together and oriented but not epitaxial. There are also holes in the particles apparently where water and carbon dioxide have escaped. At least one manufacturer (Nichia, Japan) appears to have been able to make single-crystal particles.

Because it is still by far the most commonly used phosphor in fluorescent lamps, calcium halophosphate total production far exceeds that of all other phosphors put together, in excess of 1000 metric tons per year.

2.2. Deluxe Phosphors

Because the two complementary emission bands from the calcium halophosphate phosphor do not fill the visible region of the spectrum and in particular are deficient in the red region of the spectrum, colors are distorted under these lamps compared to their appearance under blackbody radiator sources or sunlight. This distortion is measured by color rendition indexes for different colors and by the average color rendition index Ra. To improve color rendition, blends of other broad-band emitting phosphors are used in some fluorescent lamps. In particular, strontium or strontium:calcium:barium orthophosphate activated with tin is commonly used to provide a broad-band red emission peaking near 620–630 nm. This phosphor is blended with strontium halophosphates. The strontium halophosphates are completely analogous to the calcium halophosphates but with the Mn^{2+} band shifted toward 560 nm and the Sb^{3+} band shifted toward the green. Using a blend of the broad-band green strontium halophosphate phosphors together with the broad red emission of the orthophosphate there is continuous emission of radiation across the visible region of the spectrum and good color rendering Delux-type lamps can be made. However, because the broad-band emissions extend outside of the range of the eye sensitivity function and because of rather low quantum efficiencies of these phosphors, the lamps only have about two-thirds of the light output of standard halophosphate lamps.

2.3. Triphosphors

The lighting industry underwent a revolution in the 1970s following theoretical work (14, 15) which demonstrated that improved efficiency and a much improved color rendering ability was possible with a spectrum having three emission bands: red at 610 nm, green at 545 nm, and blue at 450 nm. These wavelengths are near peaks in the CIE tristimulus functions which are used to define colors. Further work has shown that it is particularly important to have a narrow emission in the red near 610 nm. If the red emission is moved to longer wavelengths or broadened, color rendition improves but luminous efficiency decreases. If it is moved to shorter wavelengths the color rendering ability of the lamp drops sharply. On the other hand there is more flexibility in choice of green and blue emission bands.

The optimum spectra were made a reality by the discovery in the mid-1970s of a class of rare-earth phosphors which provided these emissions. Activator ions chosen from the rare-earth elements are ideal for providing narrow emission bands in selected wavelength regions due to their many $4f$–$4f$ optical transitions. These levels are weakly coupled to host material and so the ground and excited state curves illustrated in Figure 2 are almost directly above each other. This also explains the good thermal characteristics of these phosphors because thermally induced nonradiative relaxation occurs at a much higher energy. Typically the rare-earth ions relax from one electronic state to another and then emit from a level well separated in energy from any level directly below. In suitable hosts Eu^{3+} emits red-orange radiation from the $5D_0 \longrightarrow F_2$ transition,

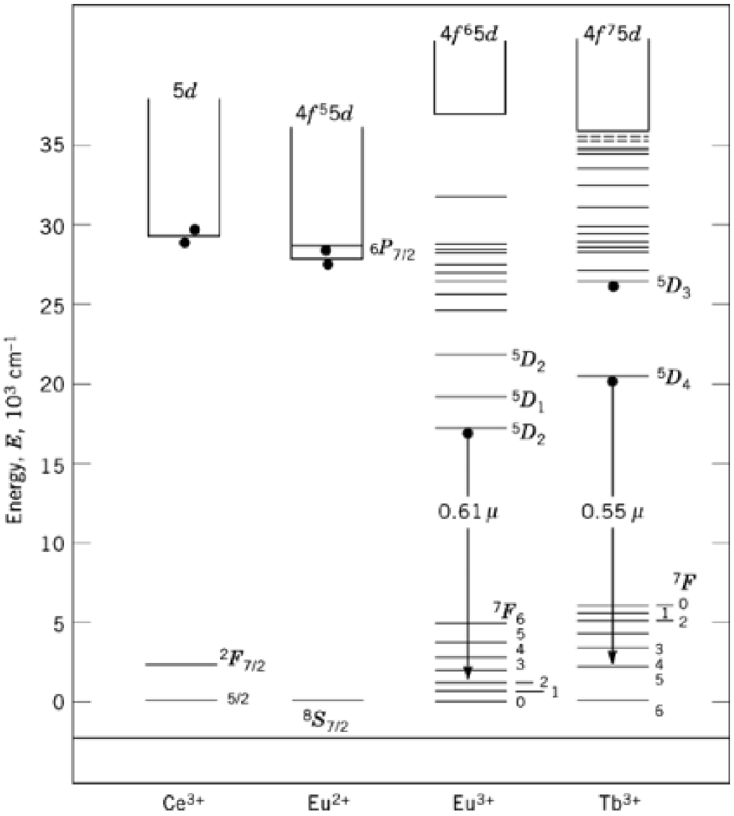

Fig. 7. Energy levels of the most commonly used rare-earth activators.

which is used for the red emission; the Tb^{3+} $^5D_4 \longrightarrow F_4$ transition is used for the green; and divalent europium, Eu$_{2+}$, $d \longrightarrow f$, for the blue band (Fig. 7). The emission spectrum of a plaque of a typical triphosphor blend is shown in Figure 8.

The use of rare-earth phosphors in fluorescent lamps has also resulted in improved maintenance as compared to the halophosphate phosphor throughout the life of a lamp. Phosphor lumen maintenance is determined by the resistance of the material to higher energy 185-nm radiation from the mercury discharge and resistance to mercury ion bombardment. The compact fluorescent lamps which have gained popularity in the 1990s owe their existence to the ability of these phosphors to resist degradation even under high loading over the life of the lamp.

The principal disadvantage of the rare-earth activated phosphors is their high cost. Ores containing the rare-earth elements are found principally in China, where they are particularly plentiful, Australia, and the United States. However, the high cost of rare-earth elements for phosphors is primarily due to the extensive number of liquid separation steps required to isolate individual rare-earth elements from the ore which generally contains many or most of the lanthanides (qv). As a result of the demand for these phosphors for television, x-ray screens, and fluorescent lamps, this technology has been greatly improved and automated thereby providing a ready source of the individual rare-earth elements with only a few to around 10 parts per million or less of the other individual rare-earth elements. Prices have dropped dramatically from, for example, over \$500/kg for Y_2O_3:Eu^{3+} precursor rare-earth oxide precipitate in the mid 1970s to well under \$100/kg in

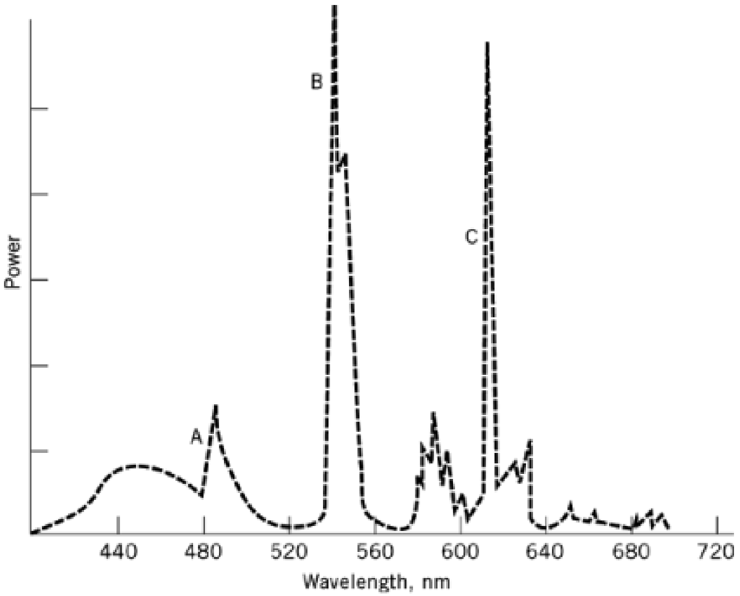

Fig. 8. The emission spectrum of a triphosphor blend where A is $BaMg_2Al_{16}O_{27}$: Eu^{2+}; B, $CeMgAl_{11}O_{19}$: T^{3+}; and C, Y_2O_3: Eu^{3+}.

1994. The principal companies involved in separating rare-earth elements for phosphors include several plants in China, Shin-Etsu in Japan, Rhône-Poulenc in France, and Molycorp in the United States.

The cost of rare-earth phosphors in fluorescent lamps is often reduced by double coating the lamps. The rare-earth phosphor blend is coated over a base layer of the inexpensive halophosphate phosphor (Fig. 9). In this configuration it absorbs a disproportionate amount of the uv discharge. For example, about 70% of the uv is absorbed in the inner coating with only one layer of triphosphor particles on the inside.

Further cost reduction can be achieved by decreasing the particle size of the phosphors. A covering of four layers of phosphor powder requires proportionately less material with decreasing particle size. A decrease in particle size can continue as long as the individual particles remain good absorbers of the ultraviolet radiation. Typically halophosphate phosphors have a particle size distribution which is log normal with a median around 11 micrometers, although at least one manufacturer (General Electric Lighting) has reduced its standard product median size to 8–9 μm.

2.3.1. The Red-Emitting Triphosphor

Eu^{3+}-activated Y_2O_3 phosphor is the universally used red-emitting triphosphor for lamps. The emission spectrum of this phosphor is almost ideal being dominated by one strong line at 611 nm. This $5D_0 \longrightarrow F_2$ transition is called hypersensitive because if, for example, europium occupies a site with a strict center of symmetry then only the magnetic dipole transition $5D_0 \longrightarrow F_1$ is expected, which is in the orange and is not useful. On the other hand, if the site symmetry deviates greatly from inversion symmetry, a significant amount of radiation will come from the $5D_0 \longrightarrow F_{4,6}$ transitions which are in the far red and infrared.

The crystal structure of Y_2O_3 is of the rare-earth sequisoxide *C*-type in which each of the cations are coordinated to six oxygen ions at the corners of the cube. Two of the corners of the cube have anion vacancies, and these vacancies can either be located along the body diagonal or along the face diagonal of the cube, S_6 and C_2, respectively. The S_6 site has inversion symmetry, and since the desired $5D_0 \longrightarrow F_2$ transition dominates in the optical spectra of Eu^3 ion only if the crystallographic site for the rare-earth ion lacks a center of symmetry,

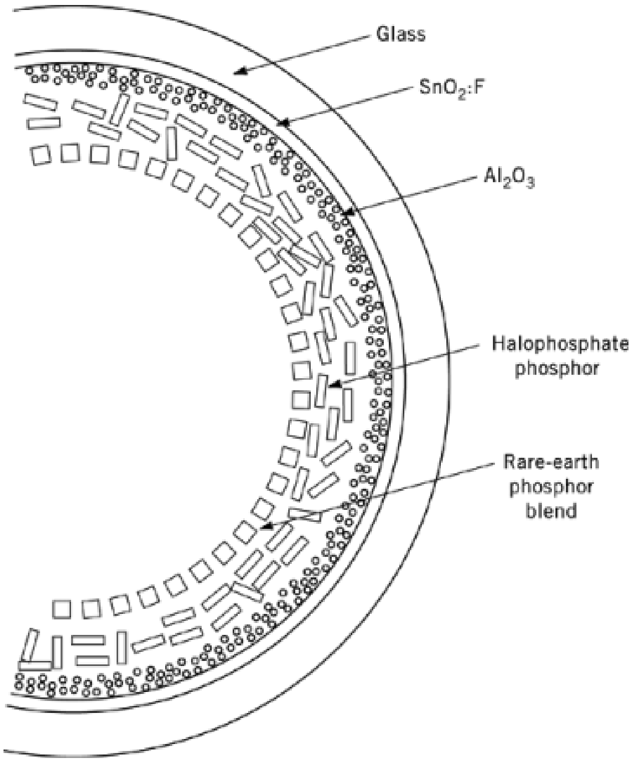

Fig. 9. A modern fluorescent lamp coating including a conductive layer of SnO_2:F, then a protective coating of finely divided alumina, followed by the inexpensive halophosphate phosphor, and finally a thin layer of the triphosphor rare-earth blend.

the bulk of Eu^{3+} emission in Y_2O_3 originates from the C_2 site. It is not easy to distinguish the emission from the two sites. The concentration of the S_6 site is only one-third that of the C_2 site and the rare-earth transitions on this site exhibit low oscillator strength due to the presence of the inversion symmetry. Complex energy-transfer pathways have been determined between the two centers at liquid helium temperatures when exciting within the $4f^6$ levels of the Eu^{3+} ion in Y_2O_3 (16).

In the yttrium oxide europium phosphor, a uv photon is absorbed at the Eu^{3+} activator center and emission comes directly from this same center after relaxation. This fact contributes to the high quantum efficiency, in excess of 90%, of this phosphor. The excitation band is due to a ligand (O^{2-}) to metal (Eu^{3+}) charge-transfer transition and has a maximum at roughly 230 nm. As a result, the absorption of 254 nm uv radiation is not high with plaques reflecting 25–35% of this radiation, depending on the europium concentration. Because the green and blue phosphor components of the blend are generally good absorbers of 254-nm radiation and because a lot of red emission, the amount depending on the desired color of the lamp, is required in triphosphor blends to achieve white light, the yttrium oxide phosphor is the most expensive component of the blend.

In order to make an efficient Y_2O_3:Eu^{3+}, it is necessary to start with well-purified yttrium and europium oxides or a well-purified coprecipitated oxide. Very small amounts of impurity ions, particularly other rare-earth ions, decrease the efficiency of this phosphor. Ce^{3+} is one of the most troublesome ions because it competes for the uv absorption and should be present at no more than about one part per million. Once purified, if not already coprecipitated, the oxides are dissolved in hydrochloric or nitric acid and then precipitated with oxalic acid. This precipitate is then calcined, and fired at around 800°C to decompose the oxalate and form the oxide. Finally the oxide is fired usually in air at temperatures of 1500–1550°C in order to produce a good crystal structure and an efficient phosphor. This phosphor does not need to be further processed but may be milled for particle size control and/or screened to remove agglomerates which later show up as dark specks in the coating.

2.3.2. The Green-Emitting Phosphor

The usual green-emitting phosphors for triphosphor blends contain Ce^{3+} as a sensitizer to absorb the uv from the discharge, and the green-emitting Tb^{3+} ion for the activator. The Ce^{3+} ion both absorbs the uv and emits some broad-band radiation in this phosphor at around 350 nm in the uv, and the Ce^{3+}-only phosphor is sometimes used for suntanning lamps.

2.3.3. $CeMgAl_{11}O_{19}$: Tb^{3+}

The first triphosphor lamps were made possible with the discovery of this phosphor and the class of aluminate-based hosts, the crystal structures of which are the magnetoplumbite ($PbFe_{12}O_{19}$) and β-alumina types. These closely resemble alumina and consist of spinel blocks separated, in the case of magnetoplumbite, by layers of cations including the Ce^{3+} and Tb^{3+} ions, and in the case of β-alumina by large cation–oxygen pairs. A variety of ionic substitutions are possible in the layers between the spinel blocks, and the thickness of the spinel layers also can be varied (17, 18).

The absence of concentration quenching of the Ce^{3+} luminescence up to the stoichiometric composition suggests that there is no energy migration over Ce^{3+} ions in $CeMgAl_{11}O_{19}$. With increasing terbium the emission of Ce^{3+} decreases. However, the energy transfer is not particularly efficient so that the Ce^{3+} emission is effectively quenched and the Tb^{3+} reaches its maximum at about $Ce_{0.65}Tb_{0.35}MgAl_{11}O_{19}$.

The synthesis of this phosphor requires both a strongly reducing atmosphere and a high temperature. The starting materials are the rare-earth oxides CeO_2 and Tb_4O_7, and $Al(OH)_3$ and MgO or basic magnesium carbonate. The firing temperature must be higher than 1400°C and for the stabilization of the trivalent state of the rare-earth ions a strongly reducing atmosphere containing a high concentration of hydrogen is required. Any residual tetravalent oxidation state of the rare-earth ions is detrimental to phosphor performance. A remarkable property of the luminescence in this structure is the maintenance of high quantum efficiency of luminescence at temperatures as high as 500°C.

2.3.4. $LaPO_4$: Ce^{3+}, Tb^{3+}

The green luminescence of a $LaPO_4$ lattice activated with Ce^{3+} and Tb^{3+} has been known since the 1970s, but only in the 1990s has the material gained importance as a green-emitting fluorescent lamp phosphor (19). The crystal structure of mineral monazite $LaPO_4$ is monoclinic where the site symmetry of the rare-earth ions is C_1.

The energy-transfer process between the Ce^{3+} and Tb^{3+} ions in a typical commercial composition, $La_{0.60}Ce_{0.27}Tb_{0.13}PO_4$, is different from that in the aluminate material previously described. At the 27 mol % Ce^{3+} doping in $LaPO_4$ there is considerable migration of the absorbed energy within the Ce^{3+} ions. The activator Tb^{3+} ions capture the migrating excitation energy and then give their characteristic green luminescence.

When properly manufactured the efficiency of this phosphor is 5–6% higher than the aluminate phosphor in most lamp applications. However, perhaps because of the energy transfer between cerium ions and the ease with which cerium can be oxidized, the preparation of this phosphor with good efficiency in a lamp has been elusive. One problem is that after being coated on a lamp and dried, the lamp passes through a lehring oven which heats it to $\sim 600^\circ$C in air. This is necessary to decompose all traces of the organic agents used in the suspension. This lehring, perhaps by oxidizing some of the Ce ions, often has an adverse effect on the efficiency of this phosphor.

The lanthanum phosphate phosphor is usually prepared by starting with a highly purified coprecipitated oxide of lanthanum, cerium, and terbium blended with a slight excess of the stoichiometric amount of di-ammonium acid phosphate. Unlike the case of the aluminate phosphor, firing is carried out in an only slightly reducing or a neutral atmosphere of nitrogen at a temperature $\sim 1000^{\circ}\mathrm{C}$. Also this phosphor is typically made with the addition of a flux, which provides a molten salt medium that dissolves the rare-earth oxides and allows small well-formed crystals of the phosphate phosphor to grow from the melt as it cools. After firing, the flux must be removed by thorough washing in hot water.

2.3.5. $GdMgB_5O_{10}$: Ce^{3+}, Tb^{3+}

A new class of ternary monoclinic pentaborate compounds with the general composition $LnMgB_5O_{10}$ has been synthesized and characterized (20). The crystal structure of the compounds contains the rare-earth ions coordinated by 10 oxygen ions. Asymmetric rare-earth–oxygen polyhedra share edges to form isolated zig-zag chains. The shortest intra-Ln–Ln distances are ~ 0.4 nm, whereas the shortest interchain distance is ~ 0.64 nm. The structure thus displays one dimensionality of the Ln–Ln chains which lead to interesting energy migration studies in this material (21). The visible quantum efficiency of the borate phosphor is high and the phosphor displays excellent stability in fluorescent lamps.

Energy transfer first occurs from Ce^{3+} to Gd^{3+} ions. The energy then migrates along the one-dimensional Gd chains until it reaches a Tb^{3+} ion. This intermediate role of the Gd^{3+} ions in transporting energy from the sensitizer to the activator was first demonstrated in a number of stoichiometric Gd^{3+} compounds (22).

The $GdMgB_5O_{10}$:Ce^{3+}, Tb^{3+} is synthesized by a solid-state firing of the rare-earth coprecipitated oxide plus boric acid and $MgCO_3$ at $\sim 900^{\circ}\mathrm{C}$ in a slightly reducing atmosphere. As in the case of the lanthanum phosphate phosphor, a flux is usually used. The synthesis of this phosphor is further complicated, however, by the fact that it is a ternary system and secondary phases such as gadolinium borate form and must then react to give the final phosphor.

2.3.6. *Blue-Emitting Triphosphor Components*

Two blue-emitting phosphors are commonly used in triphosphor systems. One is the phosphor $BaMg_2Al_{16}O_{27}$:Eu^{2+} which has the β-alumina structure previously discussed. This phosphor composition can be written $(Ba_xEu_yMg_{1-x-y}O)(Al_2O_3)_z$, which shows the alumina spinel blocks and the layers containing the divalent cations and oxygen atoms and illustrates the variability in composition which is possible. Activation with Eu^{2+}, which occupies the Ba^{2+} sites of the host lattice, yields a highly efficient phosphor with emission maximum near 450 nm. The full width at half maximum is ~ 50 nm so that the emission is useful in supplying narrow-band blue emission in the phosphor blend. This host can also be activated with Mn^{2+} and the incorporation of manganese at the magnesium sites results in efficient energy transfer from europium to manganese with the emission from manganese providing a very saturated green peaking around 515 nm.

The synthesis of this phosphor is similar to that described for the green-emitting aluminate phosphor. $Al(OH)_3$, $BaCO_3$, $MgCO_3$, and Eu_2O_3 are blended and typically fired at $\sim 1400^{\circ}\mathrm{C}$ in a mildly reducing atmosphere to maintain the divalent state of the europium ion. Somewhat lower temperatures are possible if BaF_2 and MgF_2 are used as sources of some of the cations to provide fluxing action. Some manufacturers also use zinc oxide and fluoride. The zinc is then incorporated in the phosphor in magnesium locations.

$Sr_{5-x-y}Ba_xCa_y(PO_4)_3Cl$:$Eu^{2+}$ is the second commercially important blue-emitting phosphor. This phosphor is a halophosphate activated with europium which goes into the alkaline-earth sites. The pure strontium halophosphate phosphor gives a narrow blue emission peaking near 450 nm. However, the color rendition of the lamp can be slightly improved by adding barium which results in a second band peaking at somewhat longer wavelengths. Some calcium appears to help the stability of this phosphor but the amount of calcium used should not exceed $y = 1$.

Since there are no volatile components this halophosphate phosphor is prepared with close to the stoichiometric amounts of $SrHPO_4$, $SrCO_3$, $CaCO_3$, $BaCO_3$, $SrCl_2$, or NH_4Cl and Eu_2O_3. The blend is fired under an atmosphere containing 1–2% hydrogen at 1100°C. A small excess of chloride provides some fluxing action and gives well-formed crystals of apatite. The chlorapatites are dimorphous: one modification is hexagonal and the other monoclinic.

2.4. Other Lamp Phosphors

There are a number of other phosphors used in lighting for special applications. For example, there are several uv-emitting phosphors employed in industrial photochemical applications such as polymer curing, skin-tanning lamps used in tanning salons, so-called black lights used to cause dyes in fabrics to fluoresce, and in insect traps; insects can see the ultraviolet emission and are attracted to it. $BaSi_2O_5$:Pb^{2+} has been used as an all purpose uv emitter in the past but because of poor maintenance it is largely supplanted. $Sr_4B_4O_7$:Eu^{2+} emits in a narrow band centered at 368 nm. This phosphor is made by mixing $SrCO_3$ and Eu_2O_3 with an excess of H_3BO_3. The material is fired at around 400°C to dehydrate the H_3BO_3 to B_2O_3 and then fired again at 900°C to form the phosphor. The excess B_2O_3 serves as a fluxing agent and must be removed from the final product by washing. Another uv emitter as mentioned above is the green aluminate phosphor without Tb^{3+}.

Fluorescent lamps used in photocopiers are configured so that part of the lamp acts as a reflector. The lamp is first coated with a high visibly reflecting material, such as finely divided titania used in paints or alumina. It is then coated with phosphor and a window is scraped off to allow the light to escape through the aperture giving the lamp a highly directional output. The phosphor emission is chosen to match the action spectrum of the photosensitive element on the copier drum. Typically a blue-green emission around 490 nm is desired. A commonly used but expensive phosphor for this purpose is magnesium gallate activated with manganese.

Fluorescent lamps for showing plants use a blue-white phosphor blended with a deep red-emitting phosphor. This more closely corresponds to the action spectrum for plant growth; because there is little green in the spectrum, African violets, for example, have leaves which appear more purple in color. The deep red emitter which is commonly used is magnesium fluorogermanate activated by Mn^{4+}.

There are still other fluorescent lamps having improved color rendering ability compared to the triphosphor lamps. These are sometimes called four- and five-band lamps since they use four and five emission bands or phosphors compared to the three of triphosphor lamps. To improve color rendering slightly without losing efficiency, some Japanese lamps include a blue-green phosphor added to their triphosphor blends. The phosphors $SrAl_{14}O_{25}$:Eu^{2+}, $Sr_6P_5BO_{20}$:Eu^{2+}, and $BaAl_8O_{13}$:Eu^{2+} emit near 490 nm and have high quantum efficiencies making them good candidates for the blue-green emission (23). To get very high color rendering close to an incandescent or blackbody radiator, the color rendition index $(Ra) \sim 95$, which is useful for color critical applications such as display lighting, it is necessary to use a deeper red-emitting phosphor than Y_2O_3:Eu^{3+}. European versions of these very high *Ra* lamps use the pentaborate phosphor discussed above activated with Mn**2+** giving a broad red emission peaking at ~ 620 nm. This deeper red emitter is combined with a blue-green phosphor, halophosphate, and triphosphor green and blue phosphors. For lower color temperatures, it is necessary to remove some of the visible blue mercury line emission which can be done either with the magnesium germanate phosphor or with a Ce^{3+} activated aluminate phosphor, yttrium aluminum garnet (YAG). In YAG, Ce^{3+} absorbs both blue and near-uv radiation and emits in the green region of the spectrum.

Finally, phosphors are also used for applications in high pressure mercury discharge lamps. The most commonly used phosphor for this application is yttrium vanadate and yttrium vanadate phosphate activated with Eu^{3+}. In this phosphor the near-uv from the lamp is absorbed by vanadate groups near the surface of the phosphor particle and then the excitation undergoes a random walk migrating from one vanadate group to an adjacent group until transfer occurs to a nearby Eu^{3+} ion. The addition of phosphate groups to the lattice impedes this migration and the vanadate emission increases. The Eu^{3+} ion emits in the red region of the spectrum and provides color correction for the mercury lamp. These lamps sometimes also employ other phosphors including the near-uv absorbing blue and green phosphors, $BaMg_2Al_{16}O_{27}$:Eu^{2+} and $BaMg_2Al_{16}O_{27}$:eu^{2+}, Mn^{2+}, respectively, and may use the filtering action of the Ce^{3+}-activated garnet.

3. X-Ray Excited Phosphors

X-ray intensifying screens make use of phosphors that convert the high energy x-ray photons to visible radiation which sensitizes a photographic film. In order to be useful as an x-ray phosphor the material must have high x-ray absorption, high density, and the activator must emit efficiently in the blue or green spectral region to match the sensitivity of the film. Conventional screens have used $CaWO_4$ as a broad-band emitter in the uv–blue region of the spectrum.

Divalent europium-activated BaFCl was the first rare-earth-activated x-ray phosphor (24). The advantage of $BaFCl:Eu^{2+}$ over the conventional $CaWO_4$ material is in the higher x-ray absorption and better x-ray-to-visible light conversion. The problem with BaFCl for x-ray application is in the lower density ($4.56\ g/cm^3$vs $\sim 6\ g/cm^3$ for $CaWO_4$) and plate-like morphology.

Another x-ray phosphor is LaOBr activated with Tm^{3+}. The density of the host lattice is high ($6.13\ g/cm^3$) and the emission of the Tm^{3+} is in the blue spectral region which matches the sensitivity of the blue photographic film. This phosphor is widely used but is being replaced in some applications by yttrium tantalate–niobate which emits in a very broad band in the blue region of the spectrum. The green-emitting $Gd_2O_2S:Tb_{3+}$ phosphor with a physical density of $7.34\ g/cm^3$ has been described (25). This phosphor exhibits excellent x-ray-to-visible light conversion and is able to efficiently sensitize a green-sensitive film.

Scintillators are phosphor materials made in the form of single crystals or optically transparent polycrystalline ceramic or glass rods. These serve as detectors in computer-aided tomography (CAT) and other applications. The ceramic rod is excited close to the surface on one side or end of the rod. The light generated is detected on the other side by means of a photoconductor, such as a silicon detector. An optically clear dense ceramic of $(Y, Gd)_2O_3:Eu^{3+}$ is used for this application. Because the detector must be repeatedly excited, an important consideration is the elimination of afterglow caused by the recombination of electrons and holes which are created by the x-ray beam. The afterglow is minimized by adding other ions to the structure which remove shallow traps. Other rare-earth phosphors, such as $Gd_2O_2S:Pr^{3+}$, have also been used in CAT applications.

Fuji Corp. commercialized an x-ray photostimulable storage phosphor screen around 1985. In this device the bombardment of the phosphor screen by high energy x-rays generates free electrons and holes which are subsequently trapped. The stored energy can later be released by either thermal or optical stimulation. The stimulation releases the trapped charge carriers which then combine, transferring the recombination energy to a luminescent center, typically Eu^{2+}, which decays radiatively. The intensity of luminescence is proportional to the x-ray dosage. The luminescence can be measured by a photomultiplier tube and the information can be stored in a computer. At present the x-ray storage phosphor used in nearly all commercial systems is $BaFBr:Eu^{2+}$. Other Eu^{2+}-activated materials have been proposed as x-ray storage phosphors including $Ba_2B_5O_9Br:Eu^{2+}$ (26) and $Ba_4OBr_6:Eu^{2+}$ (27).

4. Phosphors for Cathode Ray Tubes

In colored cathode ray tubes (CRTs), such as those used in televisions and computer terminals, three electron gun beams are focused on three different sets of phosphor dots on the front face of the tube. The dots are produced by using a complicated photolithography process. The phosphor dots are produced by settling the three different phosphors, each of which emits one of the primary saturated colors, red, green, or blue. Each phosphor is deposited separately and the three dots in each set are closely spaced so that the three primary colors are not resolved at normal viewing distances. Instead the viewer has the impression that there is only one color, the color achieved when the three primary colors are added together.

The first red-emitting phosphor used in color televisions was Mn^{2+}-activated $Zn_3(PO_4)_2$. The Mn^{2+} emission is a broad band peaking at ~ 630 nm. In 1960 RCA introduced the all sulfide screen which utilized (Zn, Cd)S:Ag^+ as the red-emitting component. Because they have a low band gap energy and accompanying high cathode ray excitation efficiency, sulfides have enjoyed predominance as cathode ray phosphors. Some of these phosphors have energy conversion efficiencies of 20% or more which implies that one electron with thousands of volts of energy must excite hundreds of thousands of elementary excitations in the solids which in turn excite activator ions. In the case of the red phosphor, the sulfide is roughly three times as efficient as the earlier phosphate. The main problem, however, with both of these materials is that the broad Mn^{2+} emission does not provide a saturated red and is of low luminous efficiency. In 1964 Sylvania introduced Eu^{3+}-activated YVO_4 as the red-emitting component of the color television CRT. The emission spectrum of this phosphor is dominated by strong lines at 620 nm and its brightness exceeds that of the sulfide. However, the vanadate phosphor has been largely superseded in the United States for color television application by two other Eu^{3+}-activated phosphors: $Y_2O_3{:}Eu^{3+}$ and more recently $Y_2O_2S{:}Eu^{3+}$ which has a high efficiency and a nearly ideal spectrum. Most of its emission is concentrated in lines around 620–630 nm which is saturated enough to look red and not orange and yet is of relatively high luminous efficiency.

For the green-emitting component, the U.S. green phosphor (Zn,Cd)S:Cu,Al is used. One drawback of this sulfide-based green phosphor is that it saturates under a high electron current which prevents achievement of a very high brightness screen. This is particularly important, for example, in projection television screens. There are several rare-earth activated phosphors that could be used instead of the sulfide including $Y_4(SiO_4)_3{:}Tb^{3+}$, $La_2O_2S{:}Tb^{3+}$ (27), $CaS{:}Ce^{3+}$ (28), and $SrGa_2S_4{:}Eu^{2+}$ (29). Terbium-activated cathodoluminescent phosphors, such as $La_2O_2S{:}Tb^{3+}$ and yttrium silicate, do not provide a saturated enough green color. Two approaches have been taken to improve this. One is to use a filter or interference coating to absorb or reflect some of the orange emission from Tb^{3+}. Alternatively the Tb^{3+}-activated phosphor may be blended with a more saturated green, such as the Mn^{2+}-coactivated barium–magnesium–aluminate.

The blue-emitting component of most television screens and computer terminals is another sulfide, ZnS:Ag,Al. Although rare-earth activated blue-emitting phosphors $ZnS{:}Tm^{3+}$ and $Sr_5(PO_4)_3Cl{:}Eu^{2+}$ (30) have also been evaluated for this application, the search for a good blue phosphor that does not saturate at high current densities and maintains well continues.

5. Light-Emitting Diodes and Electroluminescence

A phosphor which generates light directly when an applied electric field is impressed across it is most desirable for flat panel displays. There are two ways this can be done with present materials. The first is to use a light-emitting diode (LED). These are single crystals usually of GaP doped with trace amounts of nitrogen. GaP is a wide band gap semiconductor. It is coated on alternate sides with metallic and transparent electrodes. When an applied d-c voltage of only a couple of volts is placed across the semiconductor, electrons tunnel into it and radiatively recombine with holes in the valence band near the surface. Energy efficiencies are currently on the order of a few percent but significant improvements have been reported. The emission is in the red. Unfortunately efficient green and blue LEDs remain elusive (see Light generation, light-emitting diodes).

The second way to directly convert electric energy into light is with an electroluminescent phosphor. By far the best electroluminescent phosphor is $ZnS{:}Mn^{2+}$. Electroluminescent (EL) devices using this phosphor can have very high surface brightness and generate about 6 lumens per watt of input power. By comparison fluorescent lamps with triphosphors have efficiencies about 90 lumens per watt. Modern EL panels were developed originally by Sharp Corp. in the mid-1970s. These employ thin films. The $ZnS{:}Mn^{2+}$ phosphor is deposited between two layers of dielectrics, such as Y_2O_3. The dielectric layers in turn are in contact with the top and bottom electrodes, one of which is transparent.

In contrast to the LEDs, electroluminescent phosphors operate under high voltage and very high electric fields. The Sharp devices are ac and purely capacitively coupled to the external circuit. As the applied voltage is increased, carriers tunnel out of interface states and are accelerated into the phosphor until some reach energies sufficient to excite the luminescent centers and generate light. The field polarizes the device and light output ceases until the field polarity reverses and carriers are reaccelerated back across the cell in the opposite direction. The Mn^{2+} emission in ZnS is in the yellow region of the spectrum so that the first displays using this technology were always yellow. A concerted effort has been going on to develop other colors. Planar has displayed a colored electroluminescent screen using a filtered $ZnS:Mn^{2+}$ phosphor for the red, $ZnS:Tb^{3+}$ for the green, and $CaGa_2S_4$:Ce for the blue. As electroluminescent phosphors improve they will become more and more important in the search for a true flat panel display that directly converts electricity to light.

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