Fluorescent Lamp Phosphors

Energy saving, long life, high efficiency fluorescent lamp products

by Alok M. Srivastava and Timothy J. Sommerer

FIG. 1: Anatomy of a conventional fluorescent lamp.

Fluorescent lamp phosphors convert the ultraviolet emission of a rare-gas/mercury discharge plasma into visible (white) light. 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. This article reviews fluorescent lamp phosphors that are used in general purpose illumination. Readers interested in applications of phosphor in specialized fluorescent lamp products such as skin-tanning lamps, germicidal lamps, lamps used in photocopiers, to name a few, are encouraged to consult References 1 and 2. The article begins with an overview of fluorescent lamp use, construction, and operation, and proceeds with an overview of fluorescent lamp phosphors. Finally, comments on the energy and environmental issues associated with the use of fluorescent lamp products in residential and commercial markets are made.

General-purpose lighting consumes about one-quarter of all electricity produced in the United States. The incandescent lamp, where a filament of material is resistively heated to incandescence by the passage of electrical current, is known for its pleasing appearance to the human eye and its low purchase price. It is also known for its drawbacks, particularly a relatively short operating life (usually 1000 h) and low luminous efficacy (15 lumens/watt, lm/W). The incandescent lamp is thus a very inefficient lamp source, converting only 3–5 percent of the electric energy into visible light. Fluorescent lamps (linear and compact) are known for their high efficacy (80–100 lm/W), long life (10,000–20,000 h or 1–2.5 yr of continuous operation), and pleasing color.

Compact fluorescent lamps (CFLs) usually are integrated with suitable electrical controls and are designed to fit into a conventional incandescent lamp socket. A typical 20 W CFL is rated at 1200 initial lm and 10,000 h life as compared to a 75 W incandescent lamps which is rated at 1170 lm and 750 h life. The replacement of incandescent lamps with CFLs in most industrial, commercial and residential applications could thus yield substantial savings in energy and overall lamp life cost with concurrent reduction in energy use and greenhouse gas emission from fossil-fuel power plants. However, the CFLs are presently used in less than 2 percent of the approximately 2.5 billion incandescent sockets available in residential application in the United States.

In the residential market the low CFL penetration is mainly due to their high purchase price. Residential customers are extraordinarily sensitive to the initial purchase price. For example, a 40 watt fluorescent lamp may consume $70 in electricity over its life, yet consumer purchasing decisions may be swayed by a few cents on its $1 retail cost. Commercial buyers, on the other hand, are more conscious of the total operating cost of a lamp, the so-called "cost of light."

Fluorescent Lamp Construction

The conventional fluorescent lamp (FIG. 1) consists of a soda-lime glass tube filled with a few torr of rare gas (typically argon) and a drop of mercury. Metal electrodes sealed into the tube ends conduct electric current from the external circuit to the interior gas. During operation a small fraction of the mercury atoms are ionized and a positive column discharge forms 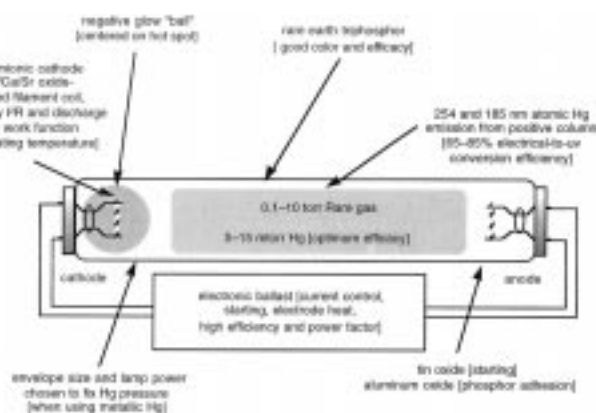which carries 200–400 mA of electric current. The liquid mercury condenses at the coolest location in the tube (usually 40–45°C) and comes into equilibrium with saturated mercury vapor; the mercury vapor pressure is typically 5–10 mtorr and is chosen to maximize luminous efficacy. Because the lowest-lying atomic mercury energy levels are much lower than those of argon, the argon atoms remain in their ground state and emit negligible radiation. The discharge converts about two-thirds of the input electric power into atomic mercury line emission at 254 nm, corresponding to the $^3P_1 \rightarrow {}^1S_0$ intercombination line. An additional 10–20 percent of the input power is converted to 185 nm radiation corresponding to the "true" mercury atom resonance transition $^1P_1 \rightarrow {}^1S_0$. Details of discharge lamp science and technology can be found in the book by Waymouth (3).

The electrodes are coiled tungsten filaments coated with a material (typically a mixture of BaO-SrO-CaO) which emit electrons by thermionic emission at relatively low temperatures. The average arc current is regulated by an external ballast to a value of typically 200–400 mA. The ballast is required because the fluorescent lamp has a negative differential electrical impedance, and if it would be powered directly from the wall socket it would draw a rapidly increasing current until limited by a fuse, circuit breaker or some catastrophic failure.

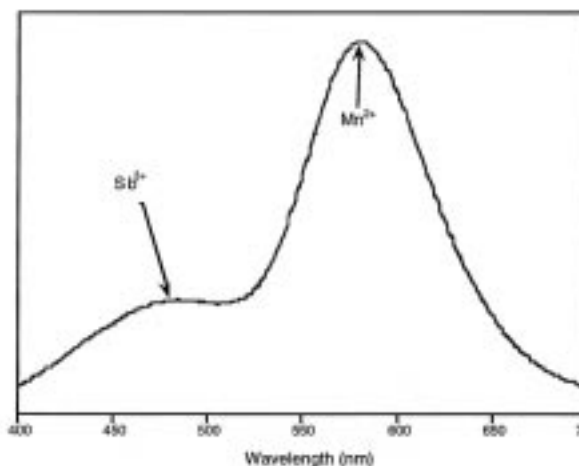Phosphor is coated on the inside of the tube; the coating is conveniently

characterized by the phosphor mass per unit area of the tube commonly denoted as "coating weight." The optimum coating weight occurs where the phosphor layer is sufficiently thick to absorb the incident ultraviolet radiation, but not so thick to cause unnecessary reflection and absorption of the generated visible radiation. The optimum thickness is about four phosphor particles.

FIG. 2: Emission spectrum of a typical cool white halophosphate phosphor showing the Sb^{3+} emission around 480 nm and the Mn^{2+} emission around 580 nm.

Conventional Lamp Phosphors

The early fluorescent lamps used various combinations of naturally fluorescing minerals such as willimite (Mn^{2+}-activated Zn_2SiO_4) to generate white light. A significant breakthrough in fluorescent lighting occurred in the 1940s with the development of the calcium halophosphate phosphor (Sb^{3+},Mn^{2+}-activated $Ca_5(PO_4)_3(Cl,F)$). This phosphor has two emission bands, one in the blue and the other in the orange-red (FIG. 2). The blue band is due to the activator Sb^{3+} ions which absorb the 254 nm radiation of the discharge and emit a part of this energy in a band peaking near 480 nm. The excitation energy is also transferred from Sb^{3+} to Mn^{2+} resulting in the orange-red Mn^{2+} emission peaking at about 580 nm. 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. Generally, the increase in Cl levels results in the peak position of the Mn^{2+} emission band shifting toward the orange. The synthesis of the halophosphate phosphor is complex and is not discussed in this article. Interested readers are encouraged to consult a monograph by Butler (2).

The visible output of an F40T12 (these lamps consume 40 W of electric power and have a tube diameter of 12/8ths inch) halophosphate (cool-white) fluorescent lamp is typically 3050 lumens (efficacy of 76 lm/W). The color rendition index (CRI) is a measure of the accuracy with which white light renders various colors. By definition, a blackbody source has a CRI of 100. The CRI of "cool white" fluorescent lamp are in the upper 50s or lower 60s. The rather low CRI follows from the emission spectrum which shows that the two complementary emission bands do not fill the visible region of the spectrum and in particular are deficient in the red spectral region. Hence, colors are distorted under these lamps compared to their appearance under blackbody radiation sources or sunlight. Improved CRI is obtained by blending halophosphate phosphor with a red emitting phosphor (typically Sn^{2+}-activated strontium orthophosphate). These "deluxe" lamps display higher CRI (85) due to the continuous emission across the visible region from the phosphor blend. The improvement in CRI is, however, accompanied by a marked drop in the lamp brightness (efficacy of 50 lm/W).

Rare-Earth Triphosphors

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. 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 is the focus of the rest of our article.

During the 1970s a new generation of low pressure mercury fluorescent lamps were developed where one could simultaneously combine markedly high color rendering (CRI ~ 80) with high efficacy (3400 lumens in an F40T12 fluorescent lamp). Theoretical modeling had already predicted high CRI and efficacy in a spectrum having three emission bands: red at 610 nm, green at 550 nm and blue at 450 nm (4). These wavelengths are near peaks in the CIE tristimulus functions which are used to define colors. In the mid-1970s such fluorescent lamps were commercially available and contained the revolutionary blend of three rare-earth-activated phosphors (the 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) (5). The individual rare-earth based phosphors which have played an important role in the development of tricolor lamps, will be discussed.

Red emitting phosphor (Eu^{3+}-activated Y_2O_3).—The emission spectrum of this phosphor is ideal for red color generation (FIG. 3a). It consists of a dominant peak at 611 nm which corresponds to the electric dipole transition $^5D_0 \rightarrow {}^7F_2$. The commercial formulation contains relatively high Eu concentrations (3–5 mole percent). At lower Eu^{3+} concentrations emission in the green-yellow, which originate from the higher energy states ($^5D_1$, $^5D_2$), are enhanced at the expense of the red $^5D_0 \rightarrow {}^7F_2$ emission.

The Y_2O_3:Eu^{3+} phosphor absorbs the 254 nm mercury 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. Hence, the absorption of 254 nm radiation is not very high with plaques of the commercial formulation reflecting about 25 percent of this radiation. The reflectivity can be decreased with an increase in the Eu concentration, but the high cost of Eu-based phosphors prohibits such compositions for practical applications. The high reflectivity and the fact that the green and blue phosphors are stronger absorbers of the 254 nm radiation requires the Y_2O_3:Eu^{3+} phosphor to be the dominant component (by weight) of the triphosphor blend.

The quantum efficiency of this phosphor is close to unity and constant in the

range of Eu concentrations from 1 to 15 mole percent. The quantum efficiency is the highest of all lighting phosphors. The lumen maintenance (defined as the change in the lamp brightness with time) of this phosphor is exceptional and exceeds that of the other lighting phosphors. It should be remarked that only a few years ago the Y_2O_3:Eu^{3+} phosphor was the most expensive component of the triphosphor blend. This is no longer the case as less costly sources of this phosphor have appeared in the market. (Reference 6 provides an interesting outlook of the rare-earth industry and market.) Research aimed at replacing this phosphor with less-expensive alternatives have not met with success. The high quantum efficiency, near perfect red emission and exceptional lumen maintenance are the reasons for the application of the Y_2O_3:Eu^{3+} phosphor in fluorescent lamps for more than two decades.

Green emitting phosphors.— *(a)* $CeMgAl_{11}O_{19}$:Tb^{3+}.—This phosphor crystallizes in the magnetoplumbite structure ($PbAl_{12}O_{19}$) in which aluminum (magnesium)-oxygen spinel blocks are separated by mirror planes containing the larger divalent (rare-earth) ions. The large cation sites are ten-coordinated. The composition $CeMgAl_{11}O_{19}$ is derived from $PbAl_{12}O_{19}$ by replacing Pb^{2+} by Ce^{3+} and substituting one of the Al^{3+} by Mg^{2+}.

The compound $CeMgAl_{11}O_{19}$ 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 high efficiency of the Ce^{3+} luminescence in $CeMgAl_{11}O_{19}$ suggests the absence of significant energy migration among the Ce^{3+} ions in this lattice. The spectral overlap between the excitation and emission bands is small due to the relatively large Stokes shift (about 9400 cm^{-1}) of the Ce^{3+} luminescence. 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 (7). 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.

Phosphor synthesis requires high temperatures (1500°C) to promote reaction between rather refractory starting materials. A reducing condition during synthesis is required to maintain the trivalent states of Ce and Tb species.

(b) $LaPO_4$:Ce,Tb—This phosphor is rapidly gaining popularity as an alternative to the $CeMgAl_{11}O_{19}$:Tb^{3+} phosphor. The advantages are the manufacturing ease due to the lower synthesis temperatures (about 1000°C) and the lower Tb concentrations required for optimum performance. The emission spectrum shown in FIG. 3b is dominated by the transition at 543 nm ($^5D_4 \rightarrow \, ^7F_5$).

The first half of the lanthanide series (Ln = La to Gd) crystallizes in the monoclinic monazite-type structure while the later half (Ln = Tb to Lu, Y, Sc) exists as the zircon type structure. In the monazite structure the lanthanide ions are nine-coordinated. The efficient green luminescence of $LaPO_4$:Ce^{3+},Tb^{3+} has been known since the 1970s, but only recently has the material gained importance as a fluorescent lamp phosphor (8).

The role of Ce^{3+} in this phosphor is that of the sensitizer. The allowed Ce^{3+} $4f \rightarrow 5d$ transitions are in resonance with the mercury discharge. In contrast to $CeMgAl_{11}O_{19}$:Tb^{3+}, however, considerable energy migration occurs over the Ce^{3+} ions prior to the Ce^{3+} to Tb^{3+} transfer. This reduces the amount of Tb^{3+} required for optimum performance with the commercial formulation containing 27 percent Ce and 13 percent Tb ($La_{0.60}Ce_{0.27}Tb_{0.13}PO_4$). Energy migration among the Ce^{3+} ions results from the large spectral overlap between the excitation and emission bands due to the relatively small Stokes shift (about 4700 cm^{-1}) of the Ce^{3+}

luminescence in $LaPO_4$.

The phosphor is manufactured at relatively low temperatures (1000°C) with the aid of a suitable flux and under a reducing atmosphere. The phosphor displays excellent lumen output and maintenance during lamp operation.

(c) $GdMgB_5O_{10}$:Ce, Tb—A new class of $Ln(Mg,Zn)B_5O_{10}$ pentaborate materials (derived from $SmCoB_5O_{10}$) have been synthesized and characterized (9). The Ln ions are ten-coordinated with the Mg/Zn ions in a distorted octahedral coordination. The rare-earth polyhedra share edges to form isolated zig-zag chains. The shortest intra- and inter-Ln-Ln distances are about 4 Å and 6 Å, respectively. The structure thus contains one dimensional Ln-Ln chains which has lead to interesting energy migration studies in this material (10).

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 states (^6P_J). Energy transfer from Ce^{3+} to Gd^{3+} energy transfer is an efficient process. Efficient green luminescence is generated when the activator (Tb^{3+}) ions trap 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.

A red-emitting phosphor can be developed by substituting a part of Mg^{2+}/Zn^{2+} with Mn^{2+} ions. The Mn^{2+} ions efficiently trap the migrating Gd^{3+} excitation energy and display a broad band emission peaking at 620 nm. The phosphor is used in high-color-rendering fluorescent lamps (CRI ~ 95), the so called five-band lamps (these lamps have four or five phosphors instead of
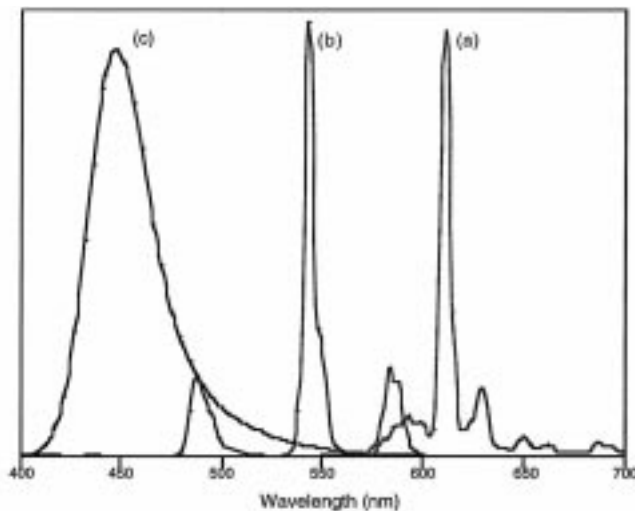

FIG. 3: The emission spectra of rare earth phosphors used in triphosphor blend; (a) red emitting Y_2O_3:Eu^{3+}, (b) green emitting $LaPO_4$:Ce^{3+}, Tb^{3+}, and (c) blue emitting $(Sr, Ca, Ba)_5(PO_4)_3Cl$:Eu^{2+}.

the three of the triphosphor lamp). Such fluorescent lamps with CRI close to an incandescent lamp find application in color critical applications such as display lighting. The increase in CRI occurs at the expense of the lamp efficacy.

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 a 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 $4f^7 5d \rightarrow 4f^6 5d^1$ transitions. The synthesis is generally accomplished under a reducing atmosphere with BaF_2 or MgF_2 as fluxing agents. The second commonly used blue phosphor is Eu^{2+}-activated $(Sr,Ba,Ca)_5(PO_4)_3Cl$, a material with an apatite (halophosphate) structure (FIG. 3c). The phosphor displays strong ultraviolet absorption with a narrow band emission peaking at 450 nm. The blue phosphors represent only a minor weight fraction of the triphosphor blend (about 10 percent for color temperature of 4100 K). However, blends designed for higher color temperatures, say 6500 K, require higher amounts of the blue emitting component.

Cost Issues

The development of high-efficacy and high-color-rendering fluorescent lamps would not have been possible without the application of rare-earth phosphors. Compact fluorescent lamps would not have been possible without the development of rare-earth phosphors, as their higher wall temperature and higher ultraviolet flux quickly degrades halophosphate materials. The main disadvantage of the rare-earth phosphors is their high cost which has more than doubled the cost of some fluorescent lamps. As a compromise between phosphor cost and performance a double coating scheme is widely used in the fluorescent lamp industry. In this scheme a relatively light coat of the high performance rare-earth phosphor blend is coated over a base layer of inexpensive halophosphate phosphor. The rugged rare-earth phosphor coating is directly exposed to the discharge, generating white light with high efficacy and good CRI while protecting the more-easily-damaged halophosphate phosphor.

Cost may also be reduced by decreasing the phosphor particle size. A covering of four layers of phosphor particles requires proportionally less material with decreasing particle size. The reduction in particle size is limited by the ultraviolet absorption strength of the individual particles. As an example, the General Electric Company introduced in 1993 a halophosphate phosphor with a median particle size of 8–9 microns whereas the typical particle size is in the 11–13 micron range.

The concentration of rare-earth ions in a matrix may be affected by a change in the host lattice system. Cost may be reduced by a decrease in the required rare-earth ion concentration, or in some cases, by completely eliminating rare-earth ions. Consider the green emitting phosphors that are based on the narrow line emission of the expensive Tb^{3+} ion. Although narrow spectral emission in the green spectral region is important, it is certainly not the dominant concern for red-emitting phosphor. Hence, efficient broad band green luminescence of Mn^{2+} ion can in principle be used in triphosphor lamps. An interesting example is the broad band green emission (peak at 550 nm) of Mn^{2+} in $Sr_3Gd_2Si_6O_{18}$:Pb^{2+},Mn^{2+}(11). As in $GdMgB_5O_{10}$:Ce^{3+},Tb^{3+}, the Pb^{2+} transfer the energy to the Gd^{3+} ions with the Mn^{2+} ions acting as acceptors of the percolating Gd^{3+} excitation energy. To account for the unusually long wavelength green emission, it is assumed that the Mn^{2+} ions occupy the Gd^{3+} sites of the host. The quantum efficiency of 87 percent is comparable to the quantum efficiency of Tb^{3+} luminescence of rare-earth phosphors. Unfortunately, the phosphor exhibits a efficiency loss of 25 percent when exposed to the full mercury spectrum, thereby eliminating the phosphor as a practical material.

Energy and Environmental Issues

Periodic energy crises can lead to the introduction of new lighting technology. For example, during the energy turmoil of 1970s the General Electric Company introduced the Wattmiser lamps (Wattmiser is a GE trademark; other lighting companies offer similar lamps under their own trademark). This modified fluorescent lamp, when operated on an existing installed base of an electromagnetic ballast designed to produce lamps at 40 W, induced the ballast to operate the lamp at 34 W. This resulted in every fixture consuming about 15 percent less power while also producing 15 percent less light. The government can also legislate changes. Recent energy legislation has effectively outlawed the manufacturing of the 40 W "cool white" fluorescent lamps which has strongly encouraged a move towards accepted alternatives such as 34 W "Wattmiser."

There is an increasing concern that mercury, which is central to the operation of fluorescent lamps, could leach into groundwater supplies when the spent lamps are discarded in solid landfills. Although only about 0.1 mg of mercury is required to generate the desired 5–10 mtorr of mercury vapor pressure, chemical binding of mercury by glass, phosphors and electrodes during lamp operation requires dosing of the fluorescent lamps with several milligrams of mercury to ensure the availability of sufficient free mercury to sustain the desired vapor pressure.

There is thus a significant effort to reduce the amount of mercury in fluorescent lamps. Note that incandescent lamps are mercury-free lighting devices. We may argue that the environmental concerns associated with mercury-based fluorescent lamps can be eliminated by replacing them with energy-hungry and short-lived incandescent lamps. In the global view, however, such a replacement would actually result in more mercury entering the biosphere. This is because fossil fuels, expected to provide the major portion of world's electric energy in the foreseeable future, contain mercury. ∎

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References

1. K. H. Butler, *Fluorescent Lamp Phosphors*, The Pennsylvania State University Press (1980).
2. G. Blasse and B. C. Grabmaier, *Luminescent Materials*, Springer-Verlag (1994).
3. J. F. Waymouth, *Electrical Discharge Lamps*, MIT Press, Cambridge, MA (1978)
4. M. Koedam and J. J. Opstelten, *Lighting Res. Tech.*, **3**, 205 (1971).
5. A. L. N. Stevels, *J. Lumin.,* 12/13, 97 (1976) and references cited therein.
6. Marie Angeles Major-Sosias, *Elements,* March/April (1997), p. 10.
7. J. L. Sommerdijk and J. M. P. J. Verstegen, *J. Luminescence*, **9**, 415 (1974); J. M. P. J. Verstegen, *J. Electrochem. Soc.*, **121**, 1623 (1974).
8. R. C. Ropp, *J. Electrochem. Soc.*, **115**, 531 (1968); J. C. Bourcet and F. K. Fong, *J. Chem. Phys.*, **60**, 34 (1974).
9. B. Saubat, M. Vlasse and C. Foussier, *J. Solid St. Chem.*, **34**, 271 (1980).
10. C. Foussier, B. Saubat and P. Hagenmuller, *J. Lumin.*, **23**, 405 (1981); W. van Schaik and G. Blasse, *J. Lumin.,* 62, 203 (1994).
11. H. C. G. Verhaar and W. M. P. van Kemenade, *Mat. Chem. Phys.*, **31**, 213 (1992).