Luminescence Science and Display Materials

by Cees Ronda and Alok Srivastava

Luminescence is defined broadly as the generation of light in excess of that radiated thermally. Man's fascination with luminescence stems from when an otherwise invisible power is converted into visible light. The commercial importance of luminescence is ubiquitous, being manifest in lamps, displays, X-ray machines, etc. In ECS, the Luminescence and Display Materials (LDM) Division provides a forum for work on the physics and chemistry of light generation from electrical energy and the technology of the various light producing devices. Aspects of these areas are briefly described in the following sections.

Luminescence Science and Technology

Materials that generate luminescence are called phosphors. Commercial phosphors are mostly inorganic compounds prepared as powders (with grain sizes usually in the order of 2-20 µm) or thin films. The phosphor materials contain one or more impurity ions or activators (A), typically present in 0.01-100 mol % concentrations. The actual emission is generated on these activator ions. Typical activators are rare earth- or transition-metal ions, ions undergoing s-p transitions (like Bi^{3+}), and molecular anions like the tungstate or vanadate groups. Sensitizers (S) are useful if the activator ions cannot be excited, *e.g.*, because of forbidden transitions. In such cases, the exciting energy is absorbed by the sensitizers and subsequently transferred to the activator ions. Common to all these moieties is the not completely filled electron shell in at least one state (ground state, excited state) involved.

Activators or sensitizers may be excited by high-energy photons, such as X-rays or ultraviolet radiation from mercury discharge (photoluminescence) or electron bombardment (cathodoluminescence). In addition, luminescence may be generated directly from an electric field (electroluminescence) or from infrared radiation (up-converting luminescence) or even mechanically (triboluminescence).

To have any technical importance, a luminescent material must be easily excited by the appropriate excitation and must have high quantum efficiency, the ratio of the number of quanta absorbed to the number emitted. Nonradiative losses are commonly caused by interactions with lattice vibrations and what are known as killer impurities. Further, the activator must convert the energy absorbed to a useful frequency of visible light. A suitable phosphor must maintain well under the excitation mode and must be easily manufactured. The synthesis of efficient phosphors not only requires the best in high temperature chemistry, but also in precursor preparation and handling and purity of starting materials. Device manufacturing involves still other sciences, such as thin film technology and suspension chemistry.

Lighting and Imaging Devices

Photoluminescence. In the fluorescent lamp, the cathode at one end of the lamp emits electrons and the anode collects electrons at its other end. (In ac operated devices, the electrodes act both as anode and cathode, depending on the phase of the current.) The electrons excite and ionize mercury atoms in the vapor phase. UV radiation from the excited mercury atoms is absorbed by impurity ions in the powder phosphor coating on the lamp wall. The activator impurities in turn relax and may transfer energy to other ions, which then re-emit radiation at a lower energy in the visible region of the spectrum or emit themselves.

The development of the Sb^{3+} and Mn^{2+} activated halophosphate phosphor [$Ca_5(PO_4)_3(F,Cl)$:Sb,Mn] in the 1940s was a significant breakthrough in fluorescent lighting. The lighting industry underwent a revolution in the 1970s when a blend of three rare-earth ion containing phosphors [activators: Eu^{2+} (blue), Tb^{3+} (green), and Eu^{3+} (red)] was proposed for good color rendering, higher efficiency, and better maintenance in fluorescent lamps. Prior to their discovery, three-band spectra were predicted to provide good color rendition and maximum luminous efficiency. These and newer rare-earth phosphors have revolutionized fluorescent lamps, making high current density compact lamps possible and providing the best efficiency, even more than 100 lumens per watt, and good color rendition (mid-1980s) in 36 W fluorescent lamps. In recent years, research on new luminescent compositions for fluorescent lamps has come to a standstill. Important issues nowadays are Hg consumption by fluorescent lamps and reduction of the price of the phosphor layer.

Fluorescent lamps are used not only for interior lighting. Liquid crystal display (LCD) screens have boosted the demand for fluorescent lamps with a small diameter. Generally, the color temperature of the light emitted by such lamps is high, some 9000 K.

The advent of efficient near UV and blue light-emitting diodes (LEDs) has revived research on photoluminescent materials. The requirement of absorption in the near UV/blue region and emission in the visible part of the spectrum, coupled to the necessity of strong (optically allowed) absorption of the LED radiation by the phosphors has induced a world-wide research activity for Eu^{2+} and Ce^{3+} doped inorganic phosphors. To tune the optical properties of these activator ions as to their suitability in LEDs, apart from well-known yttrium-

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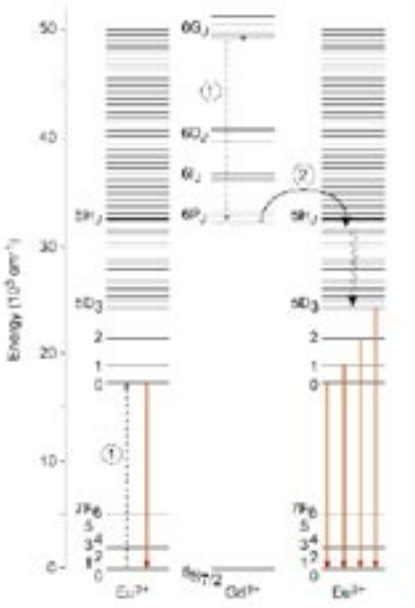

Fig. 1. *Energy level scheme and quantum cutting in the Gd^{3+}-Eu^{3+} ion pair. In step 1, energy is transferred from Gd^{3+} to Eu^{3+} by cross relaxation, leaving a still excited Gd^{3+} ion behind, which transfers the remaining energy to a second Eu^{3+} ion in step 2.*

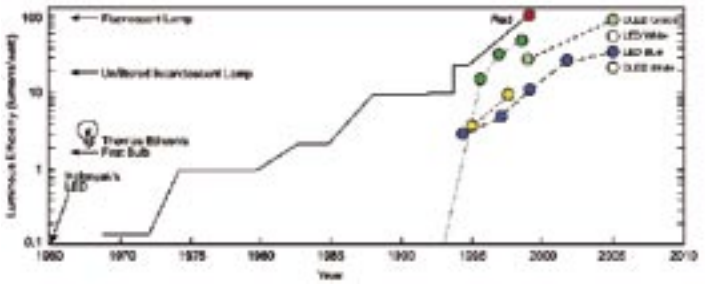

Fig. 2. *Evolution of light sources.*

aluminum-garnet (YAG):Ce, many new compositions based on or containing N^{3-} ions have been developed. This race is still going on. In the meantime, efficacies have reached those of fluorescent lamps, albeit at lower light levels. At this time, LEDs are used for backlighting in (small) displays, in automotive applications, and for decorative and signing purposes. General lighting is a next target. In addition, solid-state light sources can be solar powered, enabling light generation at virtually all places in the world.

Vacuum UV phosphors. Vacuum UV excited phosphors lead to the possibility of developing a mercury-free fluorescent lamp. Quantum efficiencies in excess of unity (up to 140%) have been reported by GE and Philips research groups in Pr^{3+} activated fluorides. In addition, GE also reported quantum cutting of Pr^{3+} in oxides. Such multiphoton emission may be used to generate good overall conversion efficiency in fluorescent lamps or in plasma display panels where the ultraviolet radiation is provided by a xenon discharge (emitting between 147 and 200 nm) instead of the conventional mercury-based discharge (254 nm).

Quantum cutting based on energy transfer in ion pairs (like Gd^{3+} -Eu^{3+}, see Fig. 1) has been studied in detail after pioneering work at Utrecht University in The Netherlands. In principle, the quantum efficiency can be high, but is hampered by the weak absorption of the Gd^{3+} ion. No suitable sensitization schemes have been identified thus far. Until now, no systems suitable for practical applications have been found.

A third mechanism in which quantum cutting proceeds via host lattice states (multiplication over the bandgap) has also been investigated. In this mechanism, although quantum cutting occurs, the overall efficiency is too low for application in light sources.

X-ray Phosphors and Imaging. Exciting developments in X-ray excited phosphors include materials with much greater X-ray stopping power and better conversion efficiency. This greatly reduces the patient exposure needed for a good quality picture. The luminescent materials applied are X-ray stimulated phosphors in the form of a single crystal, a sintered ceramic, or a glass, which converts the X-ray radiation to a wavelength detectable by a light detector that is placed on one side of the rod. These rods form the detectors for the computed tomography (CT) unit. The X-ray scintillation counters must be efficient in converting X-ray radiation into visible or near IR radiation, must be able to be fabricated so as not to scatter light, and must have little or no afterglow. The scintillators CsI:Tl and $CdWO_4$ are currently used as single crystal detectors in commercial CT scanners. Examples of commercial ceramic scintillator materials are $(Y,Gd)_2O_3:Eu^{3+}$ and $Gd_2O_2S:Pr^{3+}$.

Scintillators are also used in high-energy particle detection, such as γ-rays. A total of 12,000 crystals of $Bi_4Ge_3O_{12}$ (BGO) are used at CERN (Geneva) for this purpose. In addition, the medical imaging modality positron emission tomography (PET) also relies on high-energy particle detection. For this application, very fast scintillators with a high density (in view of the high energy of the particles) are required. Examples are BGO, Gd_2SiO_5:Ce, and Lu_2SiO_5:Ce. A material which is less dense but extremely fast and bright is $LaBr_3$:Ce.

Developments in ceramic crystals are also driven by the laser industry. Ceramic crystals have distinct advantages over single crystal rods in terms of ease of production and costs.

Electroluminescence

Apart from inorganic LEDs (see above), there is strong interest in electroluminescence originating from organic or polymeric molecules (OLED). Work on organic luminescence started in the late 1980s, after exploring work by Tang and van Slyke. Electrons and holes recombine in organic layers, leading to the emission of (visible) light. Issues here are charge transport (toward the emitting layer) and device stability. Emission can be due to band-to-band like transitions but also to optical transitions on rare earth- (like Eu^{3+}) or transition-metal ions (like Ir^{3+}). Apart from the search for efficiently emitting compositions, stability of these compositions and their machinability are issues. The efficacies reached are lagging behind those achieved in inorganic LEDs, see Fig. 2. Organic electroluminescence has placed organic materials on the map of the Luminescence Science and Display Materials Division activities.

Infrared Light Sources and Detectors

Strictly, infrared (IR) radiation is not light. However, sources and detectors are often phosphors, some of which convert IR to visible light, the so-called up-converting phosphors. Semiconductors used to detect IR are the reverse of LEDs, converting light to current by exciting an electron to a conduction band. Complex imaging systems, including ones involving quantum-well devices are currently receiving much attention. Up-converting glasses (mainly fluorides) have gained interest for application in fiber lasers and even for displays. Glasses have the advantage of the ease of fiber fabrication. Some fiber lasers have been realized with the up-converting glasses that are not possible with crystals.

Up-conversion can also be used in biolabeling. There it has the specific advantage that excitation with IR light does not result in autofluorescence of biological tissue.

Luminescent Quantum Dots

Luminescence in quantum dots (size 1-10 nm) has contributed greatly to our understanding of the electronic properties of quantum dots. Optical absorption and emission of quantum dots is governed by the size of the dots, in this way acting as artificial atoms in which the atomic properties are determined by the size (in contrast to normal atoms, where the properties are determined by the atomic number). Quantum dots enable tunable line emission, in contrast to the energies of the emission lines of rare-earth ions, which are energetically almost fixed. One successful demonstration of emitting quantum dots was, *e.g.*, their use in LEDs in which they partially converted the light emitted by the LEDs to result in white light emitting LEDs.

Outlook

Luminescence science is very much alive. New devices like LEDs or new application areas in the medical arena have fueled research on luminescent compositions and form factors. In addition, luminescence science integrates chemistry, materials science, and physics. In this field of overlapping disciplines, many exciting challenges are still in front of us. ■

Additional Reading

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About the Authors

Cees Ronda *joined Philips Research in Eindhoven, The Netherlands in 1986 and moved to Philips Research in Aachen, Germany in 1989. Currently, he is a research fellow, one of the highest technical ranks within the Philips Research organization. Cees Ronda has worked on luminescent materials for a number of applications; his current interest is in luminescent materials for medical applications and for application in Light Emitting Diodes (LEDs). Apart from working at Philips, he is a professor at Utrecht University, The Netherlands (condensed matter and interfaces), and at Zhejiang University, China (optical and electromagnetic research). He may be reached at cees.ronda@philips.com.*

Alok M. Srivastava *is a senior materials scientist at the GE Global Research in Niskayuna, New York. Dr. Srivastava's research describes the relationship between the synthesis, crystal structure, and optical properties of rare earth and transition metal ions in solids. For his pioneering research to achieve the first demonstration of quantum splitting in oxide phosphors, he was awarded the First Centennial Outstanding Achievement Award of the ECS Luminescence and Display Materials (LDM) Division. His work has resulted in the discovery of new phosphors, phosphor quality improvements, and phosphor compositional modifications for superior performance in linear and compact fluorescent lamps and white light emitting LEDs. He is the former chair of the ECS LDM Division. He serves on the editorial board of* Optical Materials. *He may be reached at srivastava@crd.ge.com.*