

An ECS Centennial Series Article

Developments in Luminescence and Display Materials Over the Last 100 Years as Reflected in Electrochemical Society Publications

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A brief review of the history of luminescence and display materials is given in conjunction with a summary of the activities of the Luminescence and Display Materials Division in the luminescence field over the first 100 years of the Society together with a compendium of luminescence related papers published in the *Journal* on luminescence. © 2002 The Electrochemical Society. [DOI: 10.1149/1.1502258] All rights reserved.

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Luminescence and Display Materials Division History and Interests^c

Luminescence, the emission of light by a material after it has been exposed to ultraviolet-infraredradiation, electron bombardment, X-rays, or some other method of excitation, has fascinated people since ancient times. Even as late as the early 1900s, Thomas Edison and E. L. Nichols concluded that "unless someone discovers a means of making luminescent bodies that are vastly brighter than the best known now, luminescence may be excluded altogether as a factor in artificial lighting." However, in the mid-1930s a small group of innovative engineers at the General Electric Company (GE) coated linear incandescent lamp tubes with a ground-up mineral phosphor, willemite, evacuted the tubes, dosed them with a small amount of mercury, filled them with a few Torr of argon, and sealed the ends with electrodes. In 1933 GE introduced the first commercial mercury fluorescent lamps. Today fluorescent lamps use synthetically made phosphors; due to their high efficiency, fluorescent lamps produce more light by far than all other lamp types.

In the 1930s a section of the new ECS Electronics Division was formed for those interested in luminescence. This was about the time when the systematic search for and development of synthetic phosphors began, spurred by the invention of the fluorescent lamp and the need for new phosphors for radar screens. Not surprisingly, in the 1930s and 1940s, luminescence was perhaps the most active section in the new Electronics Division, although it was still small compared to the more traditional Divisions of the Society.

From 1948 on, a steady stream of luminescence papers appeared in the *Journal of the Elecrochemical Society*. In a single year, 1949 for example, there appeared in the *Journal*

1. A paper by Butler, which characterized zinc berylium silicate phosphors that made white fluorescent lamps possible;

2. Kroeger and Hellingman described the zinc sulfide phosphors activated with silver and copper, which are the phosphors still used today in color television and display tubes;

3. Jenkins, McKeag, and Ranby presented a definitive characterization of the halophosphate phosphors, which they discovered and which became the standard white emitting phosphors for fluorescent lamps, thankfully replacing the toxic berylium containing phosphors; and

4. A paper by Lowry presented mechanisms of phosphor degradation

in lamps and how to fit the lumen maintenance over time, which is still often used.

The list of authors contributing to the luminescence section of the *Journal* also included Klasens, Hoekstra, Cox, Fonda, Froelich, Lehman, and many others, a veritable who's who of the early fathers of modern luminescence and synthetic phosphor development.

These papers also set the scope of the Luminescence Section; announcing new phosphors, presenting their synthesis and characterization, how they were excited, the wavelengths they emitted with certain activators, and the efficiency of the phosphors. Other papers dealt with applications of these phosphors. The physics and chemistry of luminescent materials and their applications became and still is the core area covered by Luminescence symposia.

The first Electrochemical Society symposium dedicated to luminescence was organized by M. E. Fogel and was held in 1945 at a regional meeting of the Metropolitan New York Section. (There were no general Society meetings that year, because of World War II.) Eight papers were presented by some of the most prominent names in the history of luminescence. Fluorescent lighting was the big topic in those days, with five of the papers dealing directly with that subject. The fact that companies such as RCA, GE, Sylvania, and Westinghouse contributed significant papers established the Society as a forum in which established scientists in luminescence found it valuable to present their results to their peers in other companies. Moreover, the presentations were accompanied by the valuable constructive criticism of the audience.

The second symposium on luminescence was held at the 1947 Spring Meeting held in Louisville, Kentucky. The contributing authors were A. E. Hardy, H. C. Froelich, Keith H. Butler, and Arthur Bramley. Bramley's paper was the first published discussion of aluminized phosphor screens. The first participation by a university professor was in 1948, when Roland Ward of the Polytechnic Institute of Brooklyn gave a paper entitled, "Infrared Sensitive Phosphors of the Alkaline Earth Sulfides and Selenides." This was the first paper in the *Journal* on energy storage and retrieval by infrared radiation, although the subject itself dates from the 1890s with Gudden and Pohl.

In the 1950s and 1960s, with the invention of the transistor and the silicon chip, the Electronics Division grew rapidly while the Luminescence Section remained roughly constant, with many of its papers dealing with improvements in phosphors, such as the halophosphates and television phosphors and their manufacture. In 1982 the Luminescence Section became the Luminescence and Display Materials Group. The Group consisted mostly of people working in luminescence in the industries and plants that had sprung up to produce phosphors for lamps, displays, and X-ray equipment. It was a close group of people, some of whom had worked in luminescence or related areas throughout their careers, and they had a strong loy-

^c Much of this material was obtained from previous histories of the Luminescence and Display Materials Division prepared by W. M. Yen (*Interface*, 1994), T. F. Soules (*Interface*, 1998), and C. W. Struck (*A Centennial History*, 2002).



Figure 1. Charles W. Struck.

alty to the Luminescence and Display Materials Group.

In the 1970s, when it was generally believed that phosphors were as efficient as possible, Verstegen et al. announced a new set of rare-earth activated aluminate compounds, which improved both the color rendition and efficiency of fluorescent lamps and made compact fluorescent lamps possible. Also, greatly improved X-ray phosphors, X-ray storage devices, and scintillation counters for computer-aided tomography became a reality. At the same time, the Journal of Luminescence was formed and it attracted many of the more academic papers in the area of luminescence. Similarly the Society for Information Displays attracted those more interested in the application of phosphors in displays. Finally, several physics journals published most of the papers in the burgeoning field of lasers. The Luminescence Group of The Electrochemical Society continued to attract papers dealing with the physics and chemistry of phosphors and the Group leaders including C. Struck (Fig. 1), R. Peterson (Fig. 2), M. Royce, T. Soules (Fig. 3), W. Yen, and others began to expand the scope of interest of the Group to other areas including sensors, imaging, nonlinear optics, photonics, and excitonics. The most successful of these expansions were co-organized symposia on luminescent related topics with other Society Divisions.

In 1991 the Luminescence Group applied for full Division status in the Society, which was granted and resulted in the formation of the Luminescence and Display Materials Division in 1993. At this time the Division was holding successful symposia both in the area of the physics and chemistry of luminescence and in various luminescence applications. Luminescence was undergoing another renaissance, with renewed interest in colored electroluminescent displays, other types of flat panel displays, X-ray phosphors, high definition and projection display phosphors, and the rare-earth fluorescent lamp phosphors.

Currently, the Division is in a healthy state and serves the international community well as a forum for papers in luminescence and related fields. The field of luminescence is very active both in industry and in universities and it is on the verge of still another major revolution with the invention of high efficiency blue and ultraviolet (UV) gallium nitride light emitting diodes (LEDs) by Nichia. These LEDs, which directly convert electrical energy into light, can surpass the efficiency of fluorescent lamps and can be used to make displays or lamps lasting much longer than current devices. The Division now serves as a forum for papers not only on these and other LEDs and laser diodes but also on cold cathode displays and the luminescent properties of structures exhibiting quantum confinement effects (*e.g.*, semiconductor nanostructures). It has become more international in scope in recent years, as a good deal of work in luminescence is now being done in Japan and Europe. The Society has shown a unique strength right from its beginnings 100 years ago as a meeting place for industry, government, and academia, where physicists and chemists interested in both the fundamentals and applications of electrochemical and solid state science can exchange views and information. All these important attributes of our Society are contained within the operations of the Luminescence and Display Materials Division.

Survey of Luminescence Papers Published in the Journal in the Last 100 Years

The Journal of The Electrochemical Society [and in its former names Transactions of the American Electrochemical Society, Vols. 1-58 (1902-1930) and Transactions of The Electrochemical Society, Vols. 59-92 (1931-1947)] has been a leading journal in reporting major discoveries over the last 100 years in the field of luminescence. In addition, a series of proceedings volumes published by the Electrochemical Society from symposia sponsored by the Luminescence and Display Materials Division, as it is known today, have provided "snapshots" of the then current developments in this field. Here we provide an overview of these developments as portrayed in articles published in the Journal.

When the Society was celebrating its 50th anniversary in 1952, Nagy¹ published a comprehensive review paper entitled "Growth of the Luminescence Section" summing up the development of the study of luminescence as reflected in the *Journal* up to that time. The main points in this review will be repeated here. It should be mentioned that Nagy included in his discussion on the field of "lighting" papers on incandescence, which is no longer considered to be included in the subject of luminescence and will therefore only be very briefly mentioned here.

As early as 1903, Hammer² described a number of methods of producing light. He mentioned an early Edison "X-ray Lamp" which was an early version of the present cathode ray tube. Different phosphors such as CaWO₄, ZnS, and ZnSiO₃ were bombarded by an electron beam and produced light. Various organic and inorganic luminescent materials were shown to emit light of different colors. Papers dealing with mercury and other metallic vapor arcs emitting luminescence were presented in the *Journal* in its early days. In 1905, Weintraub³ discussed the conductivity of metallic vapors and the resulting luminescence. Thirty years later, Meister *et al.*⁴ described high intensity mercury arcs operating up to one thousand atmospheres and with high efficiency. Baskerville⁵ reported in 1906 on the use of UV excitation in studying the fluorescence of 13,000 minerals and compounds.

In 1939, Marden⁶ reported on the fluorescent lamp which had been invented a year before, and discussed the properties of various fluorescent materials. In a meeting of The Electrochemical Society in 1939, a Luminescence subsection of the Electronics Division was established. In the first Society Luminescence Symposium held in 1945, Thayer⁷ presented a paper on the quantum efficiency of fluorescent lamps. He showed that with zinc beryllium phosphor, the fluorescent lamp has a quantum efficiency of 90%.

At the next luminescence meeting, in 1946, Froelich⁸ presented a paper on UV phosphors, which made it possible for the first time to make an efficient fluorescent lamp. Butler⁹ reported on luminescence in barium silicate phosphors, some of which proved to be useful as "black light" (namely light in the near UV range of 320-380 nm) phosphors. Bramley¹⁰ reported on aluminum backed phosphor screens in cathode ray tubes and showed the advantages of having higher output and the reduction of the tendency to phosphor deterioration.





Figure 3. Thomas F. Soules.

Figure 2. Ralph Peterson.

In 1948, Froelich¹¹ had reported on a new calcium silicate phosphor, which was later used in many color corrected fluorescence lamps. Smith¹² showed the importance of the atmosphere of firing of ZnS phosphors. Ward¹³ discussed the doubly activated alkaline earth sulfides. The energy stored by the phosphor as a result of UV excitation is released upon infrared stimulation. The emission spectrum is governed by one of the activators while the infrared excitation spectrum is governed by the other impurity. The effect is termed nowadays photo stimulated luminescence (PSL) or optically stimulated luminescence (OSL).

The number of papers published in the *Journal*, dealing with different aspects of luminescence increased to 26 in 1949. Fonda¹⁴ summed them up, along with papers on luminescence published in other journals, in a review article published in 1950. This included an important paper by Jenkins *et al.*¹⁵ on alkaline earth halofosphates, materials which completely replaced the zinc beryllium silicates previously used in fluorescent lamps. A number of papers on the mechanism of luminescence were presented. These included the works by Kroeger and Hellingman¹⁶ and by Smith¹⁷ who reported on the properties of sulphide phosphors. Garlick and Mason¹⁸ who worked on thermoluminescence (TL) of phosphors discussed the correlation between the impurities in zinc sulphide phosphors and the trap depths.

Fonda¹⁹ gave in 1951 a review on luminescence papers published in the *Journal* and elsewhere in 1950. Of interest is a paper by Smith²⁰ who reported on luminescence in the phosphor CaO·MgO·2SiO₂:Ti, which had high efficiency under cathode ray bombardment. Nagy *et al.*²¹ reported on the luminescence of calcium zinc phosphate activated with thallium. They found that adding ZnO lowered the emission peak from 3280 to 3115 Å. In a meeting in 1951, some more interesting phosphors were discussed. Henderson and Ranby²² described the luminescent properties of barium titanate phosphate, which was found to have an emission spectrum similar to that of magnesium tungstate. Prener²³ showed that an efficient ZnS phosphor could be made using arsenic impurity as an activator. Froelich and Margolis²⁴ reported on red emitting calcium phosphate activated with cerium and manganese. Another red emitting phosphor, namely zinc phosphate activated with manganese was reported by Smith.²⁵ Payne and Mayer²⁶ reported in a paper published in 1951 on the direct excitation of phosphors by electric fields, which was the first in many papers on electroluminescence published in the *Journal* in later years.

Wollentin *et al.*²⁷ reported in 1952 on cadmium chlorophosphate phosphor as a potential material for fluorescent lamp, emitting a yellowish pink light with a peak at 5900 Å. Pfeiffer and Fonda²⁸ described the fluorescence of zinc orthosilicates emitting in the yellow or red, depending on their method of preparation.

A number of papers on luminescence in ZnS induced by UV, cathode rays, X-rays, and electroluminescent excitation were published in 1953. Froelich²⁹ reported yellow and red emissions from ZnS:Cu phosphors. Klasens³⁰ discussed the nature of fluorescent centers and traps in ZnS with S^{2-} impurity. Hoogenstraaten and Klasens³¹ presented the luminescence of ZnS:Cu,Co phosphors and described the role of "killer" centers, namely, additional impurities responsible for the drop of the fluorescence efficiency. In a series of three papers, Ewles and Lee³² discussed the role of large activation centers in crystal phosphors, and reported the luminescence properties of CaO crystals with different impurities. Fonda³³ published a review of articles on luminescence, which had appeared in the literature in 1951-1952.

The pursuit of more phosphors emitting different visible wavelength light continued in 1954, motivated by, among other things, the search for optimal phosphors to be used in color television. Smith³⁴ reported on the properties of several manganese-activated fluoride phosphors. Swindelles³⁵ described the cathode rays excited fluorescence of lanthanum oxychloride. Bismuth, antimony, and samarium impurities were found to result in blue, greenish white, and reddish emissions, respectively. Ginther³⁶ gave results of luminescence of CaF₂:(Ce + Mn) where the Mn impurity acts as an activator and the Ce as a sensitizer.



Figure 4. Henry F. Ivey.

In 1955, Ranby and Henderson³⁷ reported on the preparation of magnesium fluorosilicate phosphors, doped with Ti and Mn, and concluded that the mechanism of luminescence includes sensitization by Ti. Destriau *et al.*³⁸ described the effect of phosphor output enhancement by the application of electric field in materials such as ZnS:Mn and ZnS·CdS:Mn. Fonda³⁹ gave the biannual review report, which included 83 papers on luminescence published in 1953-1954.

In 1956, Butler⁴⁰ discussed the fluorescence of Tl activated halide phosphors such as KCl:Tl and NH₄Br:Tl with different concentrations of thalium, and explained the role of the Tl ions in the excitation and emission. Johnson *et al.*⁴¹ reported on the effect of electron traps on electroluminescence in ZnS powders doped with Cu and Al, and in ZnS single crystals doped with Cu. They showed that a decrease of electroluminescent brightness occurs in the high temperature range where traps are thermally emptied. Wollentin⁴² described the results of luminescence of lead and manganese activated cadmium fluorophosphates.

In 1957, Ginther and Kirk⁴³ had reported on the thermoluminescence of CaF₂:Mn, a material that was very broadly used in subsequent years as a TL dosimeter. McKeag and Steward⁴⁴ described the effect of crystal disorder on the electroluminescence. They showed that many powdered crystal phosphors that are normally nonelectroluminescent, become electroluminescent if they are mixed with suitable powdered metals or with some nonmetals of good electrical conductivity. Lehmann⁴⁵ described the effect of contact electroluminescence in which nonelectroluminescent phosphors become electroluminescent by mechanically mixing them with suitable powdered metals. H. F. Ivey⁴⁶ (Fig. 4) gave a review of electroluminescence and field effects in phosphors and Fonda⁴⁷ compiled the biannual review of luminescence in 1955-1956 with 156 references.

In 1958, Harrison and Hummel⁴⁸ described the luminescent properties of the efficient phosphor prepared by co-crystallization of β -CaSiO₃:Mn,Pb and CaWO₄:Pb. The fluorescence could be excited by either 2537 Å UV light or by cathode rays. Aven and

Potter⁴⁹ reported changes in the emission spectrum of ZnS:Cu by addition of Al, Ag, and CdS. Morehead Jr.⁵⁰ described the effects of temperature and voltage on the electroluminescence brightness of ZnS:Cu. Tregellas-Williams⁵¹ gave a review on the measurement of the quantum efficiency of inorganic phosphors and reported a non-linear dependence of quantum efficiency on the intensity of excitation in sulfide phosphors with nickel impurity.

In 1959, more papers were published on different aspects of luminescence in ZnS. Goldberg⁵² described the action of Ni and Co in electroluminescent ZnS. Goldstein and Dropkin⁵³ reported on the role of shallow traps in the thermoluminescence of ZnS:Cu, Co. Van Gool and Cleiren⁵⁴ discussed the influence of hydrogen on the red fluorescence in ZnS:Cu. Jaffe⁵⁵ reported on the field enhancement of cathodoluminescence in ZnS and ZnCdS with different doping. Apple and Williams⁵⁶ gave a comprehensive study of ZnS:x(Cu or Ag),y(Ga or In) and suggested that the light emission results from donor-acceptor pairs. Allen and Bachman⁵⁷ discussed the reduction of luminescence in ZnS:Ag by Ar⁺, H₂⁺ and O₂⁺ ion bombardment. In 1960, Lempicki⁵⁸ and Birman⁵⁹ found that the fluorescent

In 1960, Lempicki⁵⁸ and Birman⁵⁹ found that the fluorescent emission from hexagonal ZnS and CdS single crystals is polarized perpendicular to the c axis for both polarized and unpolarized excitation. Avinor⁶⁰ discussed the role of gold impurities in ZnS and CdS samples. Wachtel⁶¹ reported on the electroluminescent properties of CaS:Cu,Eu. Two general papers on electroluminescence in ZnS were also published in 1960. Ballentyne⁶² showed that in ZnS powders, electroluminecence only occurs in material containing sphalerite and wurtzite and suggested that electroluminescence is a disorder phenomenon associated with stacking faults in the crystals. Thornton⁶³ discussed the maintenance of electroluminescenct phosphors and showed its dependence on phosphor properties such as Cu and Cl additions (in ZnS:Cu, Cl), on conditions of operation and on the lamp construction.

In a 1961 paper, Thornton⁶⁴ reported that electroluminescence in ZnS-type phosphors is due to minority carrier injection. Wachtel⁶⁵ talked about thermoluminecence and infrared-stimulated emission of different color light with differently doped ZnS samples. Haake⁶⁶ discussed the significance of the temperature dependence of fluorescence intensity. He explained the behavior of an increase up to a maximum and a decrease at higher temperatures as a result of competition of an increasing absorption of the exciting radiation and thermal quenching of the emitted radiation. Ivey, who had compiled a bibliography with 720 articles and patents on electroluminescence and related topics in 1959, made in 1961⁶⁷ several corrections and additions, extending the list to 1307 entries.

Luminescence in materials other than ZnS was discussed in 1962. Ullman⁶⁸ reported on carrier injection electroluminescence in GaP. Adams *et al.*⁶⁹ described some luminescent properties in the system Al₂O₃-AlN. Palilla and Baird⁷⁰ talked about the red emission electroluminescence from the $Zn_{1-x}Cd_xS_{1-y}Se_y$ system and Mooney⁷¹ about the luminescence of Mg₅Li₆Sb₂O₁₃ doped with Mn, U, Ti, Nb, and W.

The extensive study of ZnS with different dopings continued in 1963. Kramer and Turner⁷² described the quenching effect of infrared light on the luminescence of UV excited ZnS. Fischer⁷³ discussed the electroluminescent lines in ZnS powder particles and compared the impact ionization model explaining electroluminescence in ZnS. Lehmann⁷⁴ reported on the emission spectra of ZnS and (Zn,Cd)S phosphors doped with Cu and Ag. Jaffe⁷⁵ communicated on the electroluminescence of (Zn,Mg)S:Cu with and without iodine co-activator. Other luminescent materials were studied as well. Ranby and Hobbs⁷⁶ described some thorium phosphate phosphors and their potential use in lamps. Palilla and Rinkevics⁷⁷ reported on the luminescence induced by ac and dc fields in different powdered phosphors. These included rare earth tungstates, Al₂O₃ and ZnO, self-activated or with rare earth elements impurities. Addamiano *et al.*⁷⁸ studied the photoluminescence of α -SiC and found its efficiency to be $\sim 1\%$. Sarver and Hummel⁷⁹ investigated the luminescence of the systems MgO·GeO2·SiO2·TiO2 and found

Mg₄GeO₆ to be the only efficient red emitter with UV excitation.

In 1964, some more papers on the luminescence of ZnS were published, *e.g.*, a publication by Jaffe and Banks⁸⁰ on iron activated ZnS phosphors. Some researchers reported on the luminescence of rare earths, in particular Europium in different hosts. Wickersheim and Lefever⁸¹ presented the excitation and emission spectra of Y_2O_3 :Eu and emphasized its high efficiency and unusual performance at elevated temperatures. Bril and Wanmaker⁸² reported on the fluorescent properties of different Eu-activated phosphors, which show an emission characteristic of the Europium. It is deduced that, for example in gadolinium oxide or gadolinium borate, the energy absorbed by the gadolinium ions can be transferred to the Eu ions. In other materials, Ropp⁸³ reported on the Cu activated alkaline-earth phosphate phosphors such as Ca₂P₂O₇ and Ba₂P₂O₇ as well as Sr₅(P₃O₁₀)₂:Cu.

In 1965, Ropp⁸⁴ communicated on the luminescence of Eu in the ternary system $La_2O_3 \cdot Gd_2O_3 \cdot Y_2O_3$ and explained the field perturbation of the excited Eu^{3+} state by an exciton mechanism. Brixner⁸⁵ studied the luminescent properties of some rare earth ions in ZnB_2O_4 . Sm³⁺, Eu³⁺, Tb³⁺, Dy³⁺, and Tm³⁺ were introduced into the zinc borate and the emission spectra were determined. Halsted *et al.*⁸⁶ reported the emission spectra of II-VI compounds such as CdTe, ZnTe, CdSe, and ZnSe. The results were compared to the previously known spectra of CdS and ZnS. The existence of analogous defects throughout the II-VI family of compounds was demonstrated.

The emission spectra of the same II-VI compounds, impurityactivated, were given by Lehmann⁸⁷ in 1966. The results of luminescence in various other materials were also reported in the *Journal*. Sarver⁸⁸ presented the results of luminescence in Ti activated zirconia (ZrO₂). He found a broad excitation spectrum in the range of 2100 to 2600 Å, and a slow decay such that the visually detectable emission lasts several minutes. Reade⁸⁹ described some aspects of sensitized fluorescence in Ca(PO₃):Sn,Mn glass phosphors. This occurs via a direct transfer of excitation energy from tin to manganese centers. Addamiano⁹⁰ communicated on the photoluminescence of SiC doped with group IIIa elements (*e.g.*, boron) and with nitrogen. McAllister⁹¹ reported on luminescence in magnesium orthosilicate (Mg₂SiO₄) doped with Tb and Li. The good brightness at high Tb³⁺ levels suggests a very good coupling of the emitting rare earth to the UV absorbing host.

More work on Europium doped materials, was published in the Journal in 1967. Blasse and $Bril^{92}$ reported on Eu^{3+} in $NaCa_2Mg_2V_3O_{12}$ where some Ca^{2+} and Mg^{2+} ions are substituted by $Eu^{3+} + Li^+$. The energy transfer from the vanadate group to the Eu⁺³ ion was found not to be very efficient. Brixner⁹³ measured efficient fluorescence of Eu⁺³ in alkali yitrate and gadolinate hosts of the type ABO₂ where A is Li or Na and B is Y or Gd. The optimum Eu³⁺ concentration was determined for each host. Datta⁹⁴ reported on the luminescent behavior of R2O3:Bi,Eu where R = Y, Gd or La. Energy absorbed by bismuth-oxygen component is transferred by a radiationless process to Eu³⁺ resulting in the final emission from excited Eu³⁺. Luminescence in several other materials was also discussed. Potter and Cusano⁹⁵ reported a luminescence quantum efficiency of $\sim 10\%$ in α -SiC doped with boron and nitrogen. Aia⁹⁶ presented the results of luminescence in phosphate vanadates of Y, Gd, Lu, and La. Compositions containing 25-50 mole % GdVO₄, YO₄ and LuVO₄ exhibited intense blue photo-emission arising from absorption and fluorescence within the vanadate group. Also, Toma et al.⁹⁷ described the energy transfer and fluorescence process in Bi^{3+} and Eu^{3+} activated YVO_4 .

More papers on divalent and trivalent Eu activators in different materials were published in 1968. Palilla *et al.*⁹⁸ reported on the luminescence of alkaline earth aluminates activated by Eu^{2+} , in particular SrAl₂O₄:Eu. The excitation and emission mechanisms are discussed as well as the performance details of these phosphors in fluorescence lamps. Blasse *et al.*⁹⁹ presented the results of fluores-

cence of Eu²⁺-activated Barium Octaborate, namely, Me₃B₂O₃; Me₂B₂O₅; MeB₂O₄; MeB₄O₇ where Me stands for Ca, Sr, and Ba, and of BaB_8O_{13} . Only BaB_8O_{13} : Eu²⁺ was found to be an efficient phosphor under short wavelength UV excitation, showing deep-blue emission. Barry¹⁰⁰ studied the fluorescence of Eu²⁺ activated phases in binary alkaline earth orthosilicate systems such as Ca₂SiO₄-Sr₂SiO₄, concentrating on compositional variations. Burrus and Paulusz¹⁰¹ communicated on the luminescence of Eu³⁺ activated thorium-alkali-metal vanadates and discussed their excitation and emission spectra. Haynes and Brown¹⁰² presented some results of Eu³⁺ activated rare-earth-oxygen-sulfur compounds. Among numerous other papers on luminescence in different materials published in 1968, Bouchard¹⁰³ investigated the emission spectra of individual phosphor particles and found substantial differences in the brightness from particle to particle. Hirayama and Camp¹⁰⁴ reported on the fluorescence of Fe, Co, and Ni in reduced germanate glass. Blasse and Bril¹⁰⁵ presented a theoretical work on the photoluminescent efficiency of phosphors with electronic transitions in localized centers. Mazelsky *et al.*¹⁰⁶ joined the race of searching for laser materials, which took place in the 1960s, and reported on the growth and properties of neodymium-doped calcium pluorophosphate, which is an efficient laser crystal.

The search for different luminescent materials continued in 1969. Peters¹⁰⁷ studied the luminescence properties of $Ly_y(SiO_2)_x$:Tb phosphors. He pointed out the applicability of Tb³⁺ phosphors in tricolor cathode ray tubes. Among the numerous papers on Eu doped materials, the work by Kano and Otomo¹⁰⁸ is mentioned. These authors reported on the effects of impurities of Zr, Th, Mo, and W on the luminescence properties of YVO₄:Eu. Also, Jaffe and Konitzer¹⁰⁹ discussed the properties of YVO₄:Eu which could be considered as the red component in color TV screens. A theoretical work on the general-order kinetics of thermoluminescence was given by Chen.¹¹⁰ He studied TL glow peaks that are neither of first nor of second order kinetics, and developed a method for evaluating the activation energy, the pre-exponential factor and the effective order of kinetics.

With the development of optical and electronic instrumentation, faster luminescence decay could be measured in the early 1970s. Bril *et al.*¹¹¹ reported in 1970 on Ce³⁺-activated phosphors with decay times as short as 25-30 ns. These authors suggested applications in flying-spot cathode-ray tubes and for TV "index tubes," a special type of color TV receiving tube where a UV emitting phosphor is required in order to obtain the index signal. Toma and Palumbo¹¹² studied the excitation and emission in Y₂O₃ and YVO₄ and found in Tl doped sample a decay time of less than 20 ns. The cathode ray efficiency of a variety of phosphors was reported by Ludwig and Kingsley.^{113,114} A theoretical account was given and cathode-ray efficiency was estimated based on the photoexcitation efficiency in the UV.

In 1971, further work on laser materials was reported in the *Journal*. Craford *et al.*¹¹⁵ described the GaAs-GaAsP heterostructure injection lasers and compared their results to the previously known GaAs-GaAlAs lasers. Hopkins *et al.*¹¹⁶ communicated on silicate oxyapatites, high-energy hosts for Nd³⁺ of the form MeLn₄(SiO₄)₃O where Me is a divalent alkaline earth ion and Ln is a trivalent rare earth ion. Among other luminescence properties discussed, Lehmann and Ryan¹¹⁷ reported on green emitting CaS:Ce³⁺, red-emitting CaS:Eu²⁺ and doubly activated CaS:Eu²⁺, Ce³⁺ phosphors, and compared the results to those of ZnS-type phosphors. The optical and electrical properties of another Eu²⁺ doped material, namely SrAl₂O₄:Eu²⁺ was reported by Abbruscato.¹¹⁸ Evidence was given that holes are trapped at defects and the Eu²⁺ emission is associated with thermal deactivation of these traps.

In 1972, Black *et al.*¹¹⁹ studied the suitability of GaAsP wafers for red LEDs, by using a focused laser beam as an excitation source. Parker and Johnson¹²⁰ described the preparation of



Figure 5. Allen J. Bard.

 $(Y, Yb, Er)F_3$ phosphors which can be used for conversion of infrared to visible light. The phosphor converted up to 3% of the infrared radiation of GaAs:Si diodes to green light at 5400Å. Munasinghe¹²¹ reported on the luminescence properties of Ba₂MgGe₂O₇ crystal and glass matrices doped with rare earths, Eu³⁺, Tb³⁺, and Nd³⁺. In 1973, Nuese *et al.*¹²² described the vapor growth of

In 1973, Nuese *et al.*¹²² described the vapor growth of $In_{1-x}Ga_xP$ for P-N junction electroluminescence. From such junctions, laser diodes have been fabricated which emit orange coherent radiation between 6105 and 6150 Å. Saitoh and Minagawa¹²³ communicated on the epitaxial growth and characterization of $GaAs_{1-x}P_x$ and its use for electroluminescent diodes fabricated by diffusing zinc into $GaAs_{0.4}P_{0.6}$ layers. Keszthelyi and A. J. Bard¹²⁴ (Fig. 5) reported on triboluminescence by the motion of mercury over glass coated with scintillator dyes. Twelve scintillator compounds were investigated and the luminescence was found to be characteristic of the coating material.

Verstegen *et al.*¹²⁵ reported in 1974 on a new generation of "deluxe" fluorescent lamps with high efficiency resulting from a blend of blue, green and orange-red emitting phosphors. Hess Jr. *et al.*¹²⁶ described the candoluminescence (flame-excited luminescence) in transition-ion-activated oxide phosphors such as Zn_2SiO_4 :Mn. They found that for all the phosphors studied, a temperature of several hundred degrees is required for most efficient emission. Waite and Vecht¹²⁷ communicated on green dc electroluminescence (DCEL) from ZnS:Mn, Cu powder phosphor. They concluded that DCEL emission at 500 nm is from divalent lead adjacent to substitutional oxygen in the ZnS lattice.

Reisfeld *et al.*¹²⁸ investigated in 1975 the fluorescence of Eu³⁺ in sodium phosphotungstate glasses with various ratios of P_2O_5/WO_3 . They showed that these materials could substitute Eu³⁺ doped tungstate crystals for fluorescence purposes. Bril *et al.*¹²⁹ reported on the efficiency of Yb³⁺-Er³⁺ activated up-conversion phosphors. For one of the best up-conversion phosphors

known at the time, namely α -NaYF₄-0.2, Yb-0.03: Er, the infrared-to-visible (green) efficiency was found to be ~6%.

Shintani and Minagawa¹³⁰ described in 1976 the optical properties of GaN LEDs. By controlling the Zn impurity concentration, the emission could be changed from blue to yellow or green. Kramer¹³¹ described a new technique for excitation of inorganic phosphors by low kinetic energy ions and low kinetic energy electrons. For example, the efficiency of light production in Y₂O₃-Eu is ~1 photon per $40N_2^+$ ions. Wachtel¹³² reported on the fluorescence of YVO₄:Eu³⁺ with SiO₂. The fluorescence intensity was found to be higher than predicted on the basis of phosphor concentration. It was concluded that phosphor particles are encapsulated by vitreous SiO₂, which increased the optical efficiency of excitation.

Suzuki *et al.*¹³³ reported in 1977 on photoluminescence due to Al, Ga, and B acceptors in 4H-, 6H-, and 3C-SiC. All the luminescence at low temperatures is thought to be due to pair recombination between N donor and the mentioned acceptors. Seuter and van den Boom¹³⁴ studied the luminescence in ThOF₂ and found a quantum efficiency of up to 70% for an emission peaking at 313 nm under 254 nm excitation. Deluca and Ham¹³⁵ discussed the luminescent energy transfer from Mn^{2+} to Yb³⁺ in CaF₂: Mn, Yb. They found that the mechanism of energy transfer involves a direct ion-to-ion transfer.

In 1978, Coïsson *et al.*¹³⁶ communicated on electroluminescence in an epoxy resin. The behavior of luminescence bands with increasing applied voltage suggests that charge injection takes place and that the electroluminescence mechanism is that of impact ionization. Neurgaonkar *et al.*¹³⁷ investigated the luminescence of rare-earthactivated tellurate perovskites. Out of several materials studied, only Ca_2MgTeO_6 was found to be an effective host for Tb^{3+} , Dy^{3+} , and Er^{3+} -activated luminescence. Todd Jr.¹³⁸ reported on a new class of cathodochromic material, namely Ge-doped sodalite. He showed that the formation of thermally erasable F centers quenches luminescent centers whereas the formation of optically erasable F centers does not.

In 1979, Takahashi and Yamada¹³⁹ reported on the luminescence of Tb-activated alkali rare earth metaphosphate glasses. The effects of Tb concentration on the intensity of Tb³⁺ emission were measured. Robbins¹⁴⁰ described the effects of crystal field and temperature on the photoluminescence excitation efficiency in YAG:Ce³⁺. The significance of the crystal field effects for the use of YAG:Ce as a high temperature lamp phosphor was discussed.

Todd Jr. and Tranjan^[41] continued in 1980 their study of Gedoped sodalite and reported a bright green luminescence with an emission band peak at 5250 Å and an excitation peak at 3465 Å. Takeda *et al.*¹⁴² discussed the very fast decay (~30 ns) in YAIO₃:Ce (YAP:Ce), a UV emitting phosphor. YAP:Ce with added Ba compound was found to have a radiant efficiency of ~7%. In the search for better neodymium laser materials (other than YAG: Nd), Parent *et al.*¹⁴³ investigated the optical properties of Na₃La_{1-x}Nd_x(PO₄)₂ and Na₃La_{1-x}Nd_x(VO₄)₂. The vanadate was found to have strong luminescence intensity at low concentrations.

In 1981, Hartmann¹⁴⁴ reported on high-resolution real-time X-ray fluorescent screen used in topography. The best conversion efficiency was found in Gd_2O_2S :Tb which showed the highest spatial resolution with grain size <1 nm. Flaherty¹⁴⁵ gave a review of the role played by color centers in the deterioration of light output of lamp phosphors. Ozawa¹⁴⁶ communicated on an experimental proof of radiative recombination mechanisms of electron-hole pairs at activator ions in inorganic crystals. In 1982, Schaper *et al.*¹⁴⁷ described a novel type of electro-

In 1982, Schaper *et al.*¹⁴⁷ described a novel type of electrochemiluminescence (ECL) cell. The luminescence efficiency was $\sim 1\%$ and the lifetimes much longer than those in conventional electrolytic cell. Ozawa¹⁴⁸ reported on the motion of electrons and holes in Y₂O₂S crystal as revealed by cathodoluminescence. Kitahara *et al.*¹⁴⁹ discussed the one-dimensional photoluminescence distribution in semi-insulating GaAs grown by the horizontal Bridgman and circular Czochralski methods.

Hess *et al.*¹⁵⁰ studied in 1983 the photoluminescence of sintered Zn_2SiO_4 doped with Al and Ti. The quantum efficiency for the UVblue emission was measured as well as the decay time, which varied from 10^{-3} s for Ti to 10 s for Al doping. Decker *et al.*¹⁵¹ reported on hole injection and electroluminescence of n-GaAs in the presence of aqueous redox electrolytes. A luminescence signal was observed as a consequence of electron-hole recombination following the hole injection. Okamoto and Kato¹⁵² described the preparation and cathodoluminescence of CaS:Ce and Ca_{1-x}Sr_xS:Ce phosphors. Good crystallinity, large particle size, and high luminescence efficiency were reported.

In 1984, Reisfeld¹⁵³ gave a review on the fluorescence and nonradiative relaxations of rare earths in amorphous media such as oxide, chalcogenide, and fluroride glasses. Also was discussed the spectral behavior of rare earth ions absorbed or incorporated into high surface porous materials. Robbins *et al.*¹⁵⁴ reported on pairing effects in the luminescence spectrum of Zn_2SiO_4 :Mn. Some emission lines are assigned to Mn pair centers involving substitution on nearest neighbor Zn sites. Gilbert Kaufman and Hawkins¹⁵⁵ described the defect luminescence of thin films of Cu₂O on copper. Apparent quenching of luminescence by interaction between vacancies was observed for sufficiently high copper vacancy concentrations.

In 1985, Mo *et al.*¹⁵⁶ gave a comparative study of sensitization of luminescence of trivalent rare earth ions by Ce³⁺ in LaOBr. Takahashi *et al.*¹⁵⁷ communicated on the photostimulated luminescence (PSL) and color centers in BaFX:Eu²⁺ (X = Cl, Br, I) phosphors. They concluded that the PSL was caused by the liberation of electron traps at F centers created by X-ray exposure. Dexpert-Ghys *et al.*¹⁵⁸ reported on the transient properties of the luminescence of Eu³⁺ and Tb³⁺ in oxysulfide matrices. In 1986, Huo and Hou¹⁵⁹ described a chemical etching process

In 1986, Huo and Hou¹⁵⁹ described a chemical etching process developed for the fabrication of a YAG screen. They reported on improvement in phosphor efficiency by a factor of three. Scholl and Trimmier¹⁶⁰ also studied the properties of the YAG host, which, with Tm and Tb impurities yielded a blue phosphor. They reported a resonant energy transfer from the ¹D₂ Tm³⁺ state to the ⁵D₄ Tb³⁺ state. Jorgensen *et al.*¹⁶¹ found high yield luminescence of lanthanide J-levels in fluoride glasses with weak multiphonon relaxation.

Yamashita *et al.*¹⁶² reported in 1987 on the photoluminescence spectra and vibrational structures of the SrS:Ce³⁺ and SrSe:Ce³⁺ phosphors. The vibrational structures of the emission and excitation bands were analyzed, and the coupling constant of the spin-orbit interaction as well as the crystal field parameters were determined. Kiliaan *et al.*¹⁶³ described the luminescence properties of hexagonal Na(Y,Gd)F₄:Ce, Tb. They showed that the excitation energy migrates from the Ce³⁺ ion over the Gd³⁺ sublattice to the Tb³⁺ traps.

In 1988, Matsuoka *et al.*¹⁶⁴ communicated on a Pr-Mn oxide black dielectric developed for a high contrast electroluminescent display panel. The structure used was of a light-absorbing layer in direct contact with a phosphor layer, so as to reduce the light scattering. Gilbert Kaufman and Dickinson¹⁶⁵ showed that luminescence at 4 K of cuprous oxide films on copper metal provide a good insight into the polycrystaline films. The appearance of two lines near 637 nm are attributed to the stress induced at the strongly bonded metal interface.

The number of papers on different aspects of luminescence in the *Journal* increased dramatically in 1989, and the high rate of appearance remained high in subsequent years; only few of these will be mentioned here. Scheps¹⁶⁶ reported on the UV-to-visible luminescence conversion in $CaF_2:Eu^{3+}$ and $SrF_2:Eu^{2+}$ crystals. These materials were found to have potentially wide applications due to their high power conversion efficiency factor, which, for the former material is 0.51. Neumark¹⁶⁷ discussed the donor-acceptor pair (DAP) luminescence, a powerful technique for impurity characterization. A



Figure 6. David J. Lockwood.

systematic review was given of the technique, as well as of its application to ZnSe. Rowell and Lockwood¹⁶⁸ (Fig. 6) described the infrared luminescence spectrum of the vibronic laser material $KZn_{1-x}Co_xF_3$. A detailed understanding of the low-lying electronic properties indicates the optimum condition for laser operation. Zhu *et al.*¹⁶⁹ developed a fiber-optic fluorescence sensor for quantification of atmospheric humidity. The sensor utilizes a fluorescent dye entrapped with a perfluorinated inomer matrix.

The role of Japanese scientists in the search for luminescent materials, as reflected in publications in the *Journal*, was very important in the 1980s and 1990s. In 1990, Amano *et al.*¹⁷⁰ described the growth and luminescence properties of Mg-doped GaN prepared by metalorganic vapor phase epitaxy (MOVPE). The authors stated that by using GaN:Mg/GaN, an efficient near-UV and blue LED can be fabricated. Tajima *et al.*¹⁷¹ discussed the calibration of the photoluminescence method for determining As and Al concentrations in Si. Pappalardo¹⁷² reported on pulsed, combined voltage/UV excitation of the thin-film electroluminescent (TFEL) display panels. The combined photoelectric excitation technique is a valuable diagnostic tool in characterizing the performance of actual TFEL display devices.

in characterizing the performance of actual TFEL display devices. In 1991, Onisawa *et al.*¹⁷³ communicated on the effects of oxygen in SrS phospor powder on the performance of thin film electroluminescent devices. Liu *et al.*¹⁷⁴ described the effect of the energy level separation on the luminescence decay of Cr^{3+} doped mullite-glass ceramics. The luminescence lifetime was found to be a function of the degree of mixing of the ²E and ⁴T₂ states, due to spin-orbit interaction. Collins *et al.*¹⁷⁵ reported on the preparation and photoluminescence of ZnS:Tm films deposited on glass, sapphire and silicon.

In 1992, the first of a long series of papers on luminescence in porous silicon was published in the *Journal*. Gomyou and Morisaki¹⁷⁶ reported on their study of the effect of electrochemical treatments on the photoluminescence from porous silicon, which enabled a better understanding of the mechanisms that limit the quantum efficiency of visible light emission. Another paper on photoluminescence in porous silicon was published by Jung *et al.*,¹⁷⁷ who found broad emission centered between ~620 and 720 nm with

strong intensities measured from 500 to 860 nm. Nogami *et al.*¹⁷⁸ discussed the role of surface states, surface complexes, and donor states in electroluminescence of Nb-doped and defect-doped polycrystalline TiO_2 . Oxygen defects were found to play a decisive role in the luminescence characteristics.

In 1993, Glasbeek *et al.*¹⁷⁹ described the polarization properties of the phosphorescence of 2.818 eV center in diamond. Also, optically detected spin coherent transients were studied for the photoexcited state of this center at 1.4 K. Van Schaik *et al.*¹⁸⁰ reported on the influence of impurities on the luminescence quantum efficiency of (La, Ce, Tb)PO₄. They showed that low concentrations of rareearth ions have only a small effect on the Tb³⁺ quantum efficiency. Jung *et al.*¹⁸¹ gave a review on the developments in luminescent porous Si. The basic models for luminescence mechanisms at that time were described, namely, quantum-sized crystalline Si, surface passivation, Si-H_x alloys, and molecular electronics. In 1994, Alshawa and Lozykowski¹⁸² reported on ac electrolu-

In 1994, Alshawa and Lozykowski¹⁸² reported on ac electroluminescence of ZnS:Tm. The emission intensities (*I*) of different peaks were recorded as a function of the applied voltage (*V*). *ln* (*I*) *vs.* $V^{-1/2}$ showed a straight line over several orders of magnitude, indicating that direct excitation takes place. Steckl *et al.*, ¹⁸³ discussed the PL in stain-etched porous Si. They showed that a certain degree of crystallinity was a necessary condition for the occurrence of PL. Falcony *et al.*¹⁸⁴ described the blue PL from CeCl₂ doped Al₂O₃ films. PL excited by 300 nm consisted of two overlapping peaks at 365 and 395 nm.

Mohler and White¹⁸⁵ considered in 1995 the influence of structural order on the luminescence of Cr^{3+} -activated spinel compounds. They found that such disorder broadens and smears out the phonon fine structure of the Cr^{3+} emission. Ogasawara *et al.*¹⁸⁶ discussed the enhancement of electroluminescence from n-type porous silicon. The enhanced EL properties were studied for two types of porous Si produced in different ways. One consisted of a single layer of fine pores and the other of a double layer of fine and rough pores. Brown *et al.*¹⁸⁷ reported on the positron lifetime spectroscopy and cathodoluminescence of polycrystalline Tb-doped yttria. The correlation between the results demonstrates the utility of positron lifetime measurements for investigating microstructural properties of materials and the importance of these properties to the luminescence.

Many papers on the luminescence of porous silicon were published in 1996 in the *Journal*. Billat¹⁸⁸ reported on the electroluminescence of heavily doped p-type porous silicon under electrochemical oxidation. The authors suggested that crystallites of quantum sizes are responsible for the light emission. Zhang *et al.*¹⁸⁹ described the fabrication of a porous silicon diode with distinct red and orange electroluminescence regions. Maruyama and Ohtani¹⁹⁰ communicated on the high intensity photoluminescence in as-prepared porous silicon, produced by anodization in high concentrations of ethanol. With air exposure, the surface of the porous silicon was oxidized which caused a blue shift in the emission.

More papers on this interesting material were published in 1997. Lim *et al.*¹⁹¹ described the spectral shift of electroluminescence from porous n-Si under cathodic bias. Electropolymerization of aniline on the porous Si surface enhanced the stability of the EL. Further assessment of the conditions influencing porous silicon EL was given by Sen *et al.*¹⁹² Two types of EL instabilities were observed; fast, with time constant of milliseconds, and slow, with time constant of hours. Chang and Gleason¹⁹³ reported on the relationship of processing parameters of photoluminescence intensity and mechanical failure in thick porous silicon layers. An inverse correlation was found and explained between mechanical stability and photoluminescence intensity.

In 1998, Kooij *et al.*¹⁹⁴⁵ suggested a mechanism for chemiluminescence from porous silicon, namely, a hole injection at the silicon/ aqueous electrolyte interface. As for luminescence from other materials, Uchida *et al.*¹⁹⁵ described the photoluminescence of semiinsulating InP wafers. A sharp line at 1.3618 eV was ascribed to vacancy-related defects. Lau *et al.*¹⁹⁶ discussed the role of cerium in the atomic layer epitaxy (ALE) of SrS thin films in TFEL display application.

Further work on luminescence in porous silicon was published in the *Journal* in 1999. This included a paper by Noguchi *et al.*,¹⁹⁷ which described the visible EL from n-type porous silicon in an electrolyte solution. Time-resolved EL spectra measurements showed that the EL spectrum was blue-shifted with time. Green light-emitting porous GaAs was produced for the first time by Schmuki *et al.*¹⁹⁸ using a focused ion-beam patterning procedure. As for other luminescent materials, Sohn *et al.*¹⁹⁹ discussed the effect of co-doping by Mg and/or Cr on the PL behavior of Zn₂SiO₄:Mn phosphors. Both Mg and Cr have a favorable influence on the photoluminescent properties; Mg enhances the intensity of the green emission and Cr shortens the decay time. Djazovski *et al.*²⁰⁰ studied the excitation and emission spectra of nominally pure and Ce³⁺-activated SrGa₂S₄ thin films. They reported preliminary results of a thin-film electroluminescent device with SrGa₂S₄: Ce, Li phosphor layer.

In 2000, van Pieterson *et al.*²⁰¹ communicated on the nature of the efficient blue-white luminescence of Sr_2CeO_4 . The quantum efficiency measured was found to be about 40%. Matsui *et al.*²⁰² investigated the phosphorescence of Eu^{2+} -doped β -alumina. Two strong phosphorescent peaks at 482 and 502 nm were found, which differed from the peak of fluorescence at 465 nm. The authors explained their results by a model in which three different sites could be occupied by Eu^{2+} ions in SrMgAl₁₀O₁₇ whereas only one site could be occupied in BaMgAl₁₀O₁₇. Cho *et al.*²⁰³ reported on the cathodoluminescence characteristics of a spherical Y_2O_3 :Eu phosphor screen for field emission display application. The charging effects of the spherical Y_2O_3 :Eu screen on the luminance under low voltage operation were examined, and the methodology for enhancing the picture quality was discussed.

In 2001, Suh *et al.*²⁰⁴ communicated on the ambient full-color PL from porous silicon produced by electrochemical etching with the aid of an oxidizing metal such as Zn. The emission can be tuned to any wavelength in the visible by changing the anodizing current density from 20 to 100 mA/cm². Lee et al.²⁰⁵ described the structural and luminescent properties of the ZnS:Cu, Al phosphor under low voltage excitation. The material structure was analyzed and found to be composed of cubic and hexagonal phases, the latter having high brightness and low voltage operation. Flynn and Kitai²⁰⁶ reported on ZnGa₂O₄:Mn phosphor and its application as thin film electroluminescent display exhibiting high brightness. A single emission band at 504 nm was observed following a T \geq 750°C annealing. Using a thermal process, Boukherroub *et al.*²⁰⁷ fully passivated the surface of freshly prepared porous silicon with organic molecules such as alkenes and nonconjugated dienes. These molecules protect the surface from oxidation and preserve the original photoluminescence to an unprecedented degree, which is critically important for light emitting device applications in display and sensor technologies.

In the first half of 2002, Kim *et al.*²⁰⁸ described a stable blue photoluminescence from porous silicon. This is clearly visible to the naked eye even after 2 months exposure to air. Using a direct reaction of undecylenic acid with hydrogen-terminated porous silicon, Boukherroub *et al.*²⁰⁹ showed that an organic monolayer is covalently attached to the surface through Si-C bonds. This monolayer protects the surface against hydrolysis and thus preserves the porous silicon photoluminescence. The attached acid is readily transformed to an ester, which allows the addition of biological molecules of interest for sensor applications. Ihara *et al.*²¹⁰ reported on the production of nanocrystals of Tb- and Eu-doped ZnS, which yielded a high luminescent efficiency, about three times larger than in bulk samples. The nanocrystals were coated with glass, which further increased the cathodoluminescent intensities and protected the surface from oxidation.

In summary, the Journal has been a leading vehicle for publications on luminescence and display materials. Well over 1000 papers on different aspects of luminescence in a wide variety of materials have been published in the 100 years of existence of the Journal. In addition, practically every important aspect of the science of luminescence has been covered in the Journal, reported by literally thousands of scientists from all over the world.

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