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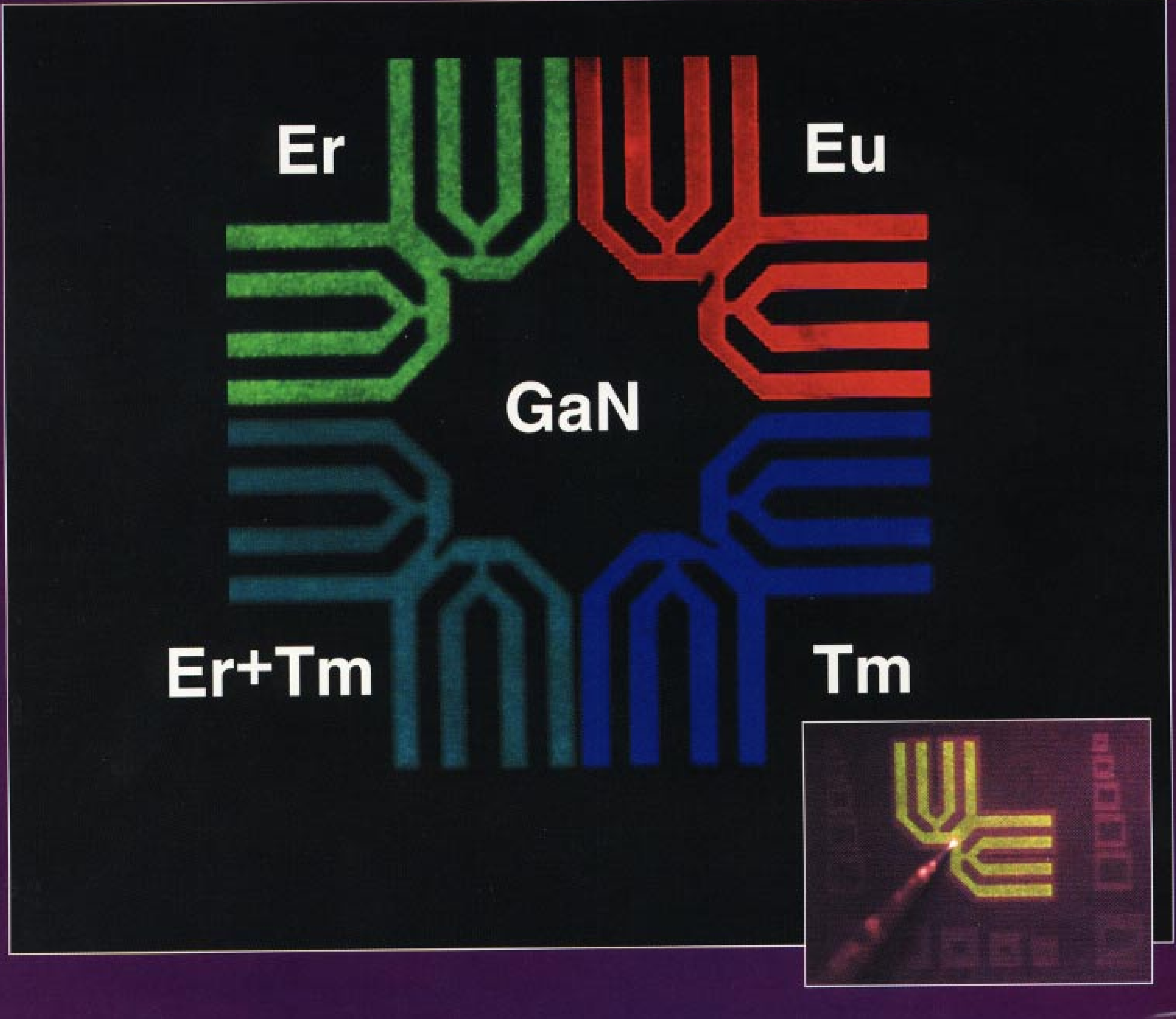
Photonic Applications of Rare-Earth-Doped Materials



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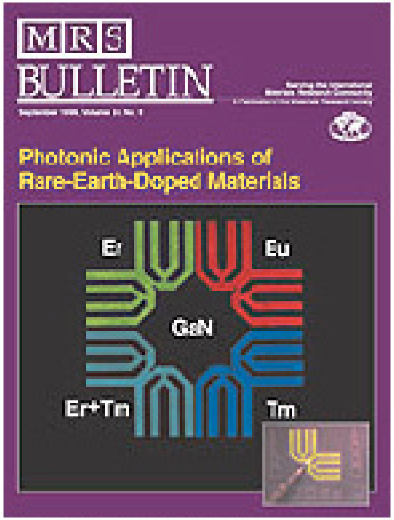

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Photonic Applications of Rare-Earth-Doped Materials

Andrew J. Steckl and John M. Zavada, Guest Editors

The elements of the lanthanide series, from Ce (atomic number 58) to Yb (atomic number 70), form a group of chemically similar elements that have in common a partially filled 4*f* shell. These so-called "rare earth" (RE) elements usually take on a 3+ ionic state (RE^{3+}). Because the 4*f* electronic-energy levels of each lanthanide ion are shielded from external fields by $5s^2$ and $5p^6$ outer-shell electrons, RE^{3+} energy levels are predominantly independent of their surroundings.

The characteristic energy levels of 4*f* electrons of the trivalent RE elements have been investigated in detail by Gerhard Heinrich Dieke and co-workers and were reported[1] approximately 30 years ago. The Dieke diagram showing RE^{3+} energy levels is a familiar tool of scientists and engineers working with RE elements. However, the history of RE elements goes back to the year 1787 in the small Swedish town of Ytterby near Stockholm and to the gifted amateur mineralogist and military man Lt. Carl Axel Arrhenius. Arrhenius discovered an unusual black mineral in Ytterby (perceived initially as much rarer in occurrence and in concentration than the common ores or earths of aluminum, calcium, etc.). Many new elements were discovered by various chemists upon analysis of this black stone and others like it. The names given to these elements are variations of the location where the first discovery was made: yttrium, ytterbium, terbium, and erbium. The history of RE elements is fascinating[2] and involves many other famous names in science: Berzelius, Gadolin, Bunsen.

The properties of these elements and their multifaceted applications to science and industry are equally fascinating and have remained important to this day. Commercial applications of RE elements began after World War II, when their available quantity and purity were greatly enhanced by improved separation techniques developed as a part of the Manhattan Project. Until fairly recently, the main industrial application of RE elements has been in permanent magnets. The unpaired 4*f* electrons result in some RE elements having the highest magnetic moments of any element. The development and applications of RE magnets are reviewed in a very interesting article by Livingston[3] in a previous *MRS Bulletin* issue. In this issue of *MRS Bulletin*, we have taken as our aim to review some of the properties and applications of RE elements relevant to photonics.

A simple but useful definition of photonics is the technology of generating and harnessing light and other forms of radiant energy whose quantum unit is the photon. The range of photonics applications extends from energy generation and detection to communications and information-storage processing. The basic mechanisms through which RE elements play a role in photonics involve excitation and luminescence between the energy levels of RE^{3+} ions with partially filled 4*f* shells from Ce^{3+} to Yb^{3+}.

Photonic applications of RE elements discussed in this issue include solid-state lasers for ultraviolet (UV) and visible wavelengths, the prospects for lasers in semiconducting materials (primarily Si), visible and infrared (IR) light-emitting devices in the wide-bandgap semiconductor GaN, RE-doped glass fibers for telecommunications, optical data storage using RE-doped crystals, and the incorporation of RE elements into a variety of host materials for achieving visible displays.

As Moncorgé, Merkle, and Zandi state in the introduction to their article: "An issue on novel applications of materials doped with rare-earth ions can scarcely fail to address lasers. . . ." Their article concentrates on the possibilities for RE-based solid-state lasers for UV and visible wavelengths rather than the near-IR region where significant successes have already been established with Nd^{3+} as well as Er and Tm lasers. They discuss a variety of approaches that are being explored: up-conversion or frequency-multiplication (doubling, tripling, etc.) phenomena, optical parametric oscillator tuning, or a combination of these mechanisms. They also discuss related applications, such as environmental monitoring of pollutants, that would greatly benefit from UV lasers at very specific wavelengths.

The extension from RE-based solid-state lasers to semiconductor-based lasers is treated by Gregorkiewicz and Langer. They review the issues and conditions relevant to efficient light emission in semiconductors in general and then apply them to the Si:Er material system. They also discuss the use of a free-electron laser at mid-IR wavelengths to probe the energy-transfer mechanisms limiting the excitation process. This is a critical issue, in that the energy "back transfer" results in luminescence quenching at higher temperatures. As a result, the authors state in their concluding paragraph, ". . . lasing in these systems still remains to be demonstrated. Several directions are still largely unexplored. One is host bandgap manipulation."

The utility of increasing the bandgap of the semiconductor host is seen in the article by Steckl and Zavada. They discuss the recent development in the RE doping of the wide-bandgap semiconductor GaN for RE-activated light emission at visible and near-IR wavelengths. They show that in GaN, unlike in narrower-bandgap semiconductors, no significant thermal quenching of the luminescence activity is observed up to temperatures as high as 275°C. Furthermore, high levels (up to a few atomic percent) of RE incorporation are possible without precipitation- or concentration-induced quenching of the optical activity. Doping of GaN with a variety of RE elements has been utilized to fabricate light-emitting devices with red (Pr, Eu), green (Er), and blue (Tm) emissions. Simultaneous codoping with two RE species has also produced mixed hues between the primary colors, leading to the possibility of covering a multitude of light-emitting applications with this technique.

An extremely successful and widely utilized photonic application of RE elements is in the area of optical-fiber-based telecommunications. As Dejneka and Samson state in their article, "...fiber optics have revolutionized the telecommunications industry." The critical component in this application is the Er-doped fiber amplifier, which provides optical gain in the 1530–1560-nm low-loss window of glass fibers. While the most common implementation uses Er-doped silica glass fiber, the use of other glasses to increase the optical gain and wavelength window is discussed. These include heavy-metal fluoride glasses, tellurite and borate glasses, and even two-phase glass-ceramics that contain Er^{3+} in both the glassy phase and crystal phase. The use of other RE elements for optical-fiber communications is also reviewed: Pr^{3+}, Nd^{3+}, and Dy^{3+} for operation at the glass fiber dispersion minimum at a wavelength of 1310 nm; and Tm^{3+} for operation in the 1450–1510-nm window. Finally, fiber lasers doped with Yb^{3+} or Nd^{3+} or codoped with Yb^{3+}-Er^{3+} are discussed. Note that many developments in RE elements linked to Si technology are not included in this issue, as they were reviewed in an earlier issue of *MRS Bulletin* ("Light Emission from Er-Doped Si" by Coffa et al.,[4] "Silicon-Based Microphotonics and Integrated Optoelectronics" by Fitzgerald and Kimerling,[5] and "Erbium-Doped Optical-Waveguide Amplifiers on Silicon" by Kik and Polman[6]).

The unusual optical properties of RE elements are being explored for optical data storage. As discussed in the article by Maniloff, Johnson, and Mossberg, significant increases in storage density can be achieved when multiple data bits are stored at the same location but multiplexed spectrally. This so-called spectral-hole-burning technique utilizes excitation of ground-state RE ions to produce a dip (or spectral hole) in the absorption spectrum. Spectral hole-burning is reported for a variety of RE/host material combinations at temperatures ranging from 1.4 K to 6 K for trivalent ions (Pr^{3+}, Eu^{3+}, Tm^{3+}) and from 2 K to 77 K for divalent ions (Sm^{2+}). In Eu-doped Y_2SiO_5, the potential to access 10^7 individual spectral bits per spatial location is discussed. Methods for increasing the data bandwidth are also discussed, along with designs for using this technique to implement optical dynamic random-access memory, or ODRAM.

The last article in this issue deals with the applications and device implementations of RE-based displays. Ballato, Lewis, and Holloway review the properties required for displays for both RE ions (such as matching of transition energy to desired emission wavelength, long excited-state lifetime, and narrow spectral linewidth) and host materials (such as low phonon energy, high refractive index, and suitable bandgap). Visible emission from several RE ions is discussed for each primary color: red (Pr^{3+} and Eu^{3+}), green (Tb^{3+} and Er^{3+}), and blue (Ce^{3+} and Tm^{3+}). The use of RE elements in several types of display devices is reviewed by the authors: plasma displays, thin-film electroluminescent displays, field-emission displays, and volumetric (three-dimensional) displays. Novel RE host materials are also addressed: glass-ceramics, polymers, and polymer composites.

We hope, in this issue, to introduce the reader to the still exciting science and new photonic applications of rare-earth-doped materials, a subject that had its birth more than 200 years ago. To paraphrase a statement by Ballato and his colleagues in this issue, *the future is bright for applications of rare-earth-doped materials.*

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From 1976 to 1988, Steckl was a faculty member in the Electrical, Computer, and Systems Engineering Department at Rensselaer Polytechnic Institute, where he carried out research activities in the fields of semiconductor devices and microfabrication. He founded the multidisciplinary Center for Integrated Electronics in 1981 and served as director of the Center for its first five years.

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