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Author
Weber, M.J.

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M.J. Weber

May 1995
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The Role of Lanthanides in Optical Materials

Marvin J. Weber

Life Sciences Division
Lawrence Berkeley National Laboratory
University of California
Berkeley, California 94720

May 1995

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THE ROLE OF LANTHANIDES IN OPTICAL MATERIALS

Marvin J. Weber
Lawrence Berkeley National Laboratory
Berkeley, CA 94720

ABSTRACT

A survey is presented of the use of the lanthanides as chemical components in transmitting optical materials and as activators in materials for luminescent, electro-optic, magneto-optic, and various photosensitive applications.

INTRODUCTION

Lanthanide series elements are used in a multitude of applications—chemical, metallurgical, ceramic, optical, magnetic, and high temperature superconductivity—but their role in optics is one of the most extensive, varied, and significant. Optical applications of the lanthanides span the spectral range from the ultraviolet through the infrared. Their role may be as a constituent of transmitting glasses and crystals, as a colorant, decolorant, or antisolarant, as a luminescent ion in spectroscopy and in laser, phosphor, and scintillator applications, as a magneto-optic ion for optical rotators and isolators, and as an essential element in various photosensitive and photorefractive materials. In applications such as lasers and phosphors, the use of lanthanides is overwhelming compared to most other transition group elements; in other applications the lanthanides play only a minor or negligible role. Lanthanide materials for optics also encompass an impressive range in sizes: from diameters measured in microns for lanthanide-doped optical fibers to dimensions of tens of centimeters for laser amplifier disks and scintillators.

Here we survey the scope and scale of optical applications of materials containing lanthanides. These are principally, but not exclusively, inorganic crystals and glasses. It is not possible to be either inclusive with respect to all applications nor exhaustive with respect to all materials. Instead, a cursory overview of the major uses of lanthanides in optical materials is presented together with a representative range of properties and diversity of chemical compositions. The physical processes involved in their operation are not discussed but are generally well understood.
The discovery and identification of the lanthanides date from 1803 (Ce) to 1945 (Pm). Although the optical spectra of lanthanide ions were used for elemental identification in the late 1800s, the widespread utilization of the lanthanides for optical applications in this century was triggered by and benefited from the concurrence of two developments: (1) an understanding of the optical spectra of the lanthanides derived from many experimental studies and theoretical treatments of crystal fields and of radiative and nonradiative transitions, both conducted primarily in the period from the 1930s through the 1960s, and (2) the availability of high-purity lanthanide materials beginning in the late 1950s-early 1960s.

Lanthanide ions owe their optical properties and extensive utilization to a special combination of spectroscopic features. They are characterized by an electronic structure consisting of an unfilled inner 4f shell and outer filled 5s and 5p shells. When lanthanides are present in a solid, the effects of the crystalline or ligand field are a small perturbation on the 4f states because of the shielding of the outer electron shells. Optical transitions between 4f levels are parity forbidden, hence they are weak and become allowed only by small admixing of states of opposite parity by odd-order terms in the local field or are induced by vibrations. Optical transitions between 4f and 5d states, on the other hand, are electric-dipole allowed and can be intense in solids. Thus the lanthanides exhibit the uncommon (but not unique) feature of having both sharp, weak 4f–4f transitions and broad, intense 4f–5d transitions. The observed optical transitions are predominantly electric-dipole in character (there are, however a few significant magnetic-dipole transitions). Radiative lifetimes range from about $10^{-8} - 10^{-6}$ s for d–f transitions to $10^{-5} - 10^{-2}$ s for f–f transitions. Competing nonradiative decay by multiphonon emission depends on the vibrational properties of the host and is reduced by selecting hosts with low vibrational frequencies.

Today we have a large choice of available glass and crystal compositions from which to tailor optical and other physical properties of the material for a specific application. As we shall see, the lanthanide ions may be present as a dilute impurity ($< 10^{-3}$ in fiber lasers) or as a stoichiometric component of the material (e.g., in magneto-optic and some laser and scintillator applications).

TRANSMITTING OPTICAL MATERIALS

Of the lanthanide ions, trivalent La, Ce, Gd, Yb, and Lu have large regions of optical transparency in the visible. Materials containing these ions can be used for transmitting optical components such as windows, lenses, and substrates. Glasses are more commonly used for these applications because they are optically isotropic and can usually be produced at relatively low cost and in large sizes. Lanthanides
have been incorporated as glass network modifiers into a wide variety of oxide, halide, and chalcogenide glass forming systems (see Ref.1 and the paper by A. J. Bruce and W. H. Grodkiewicz in this volume). These include oxide glasses: silicate, borate, borosilicate, germanate, phosphate, titanate, tellurite, etc.; fluoride glasses: beryllium, aluminum, zirconium, and hafnium fluoride; mixed anion glasses (e.g., fluorosilicates and fluorophosphates); and chalcogenide glasses, such as \( \text{La}_2\text{S}_3-\text{Ga}_2\text{S}_3 \). Most of these glasses are mechanically and chemically robust and can be produced in sizes and of quality sufficient for optical applications. Less common lanthanide-containing glasses are nitrate glasses\(^2\) \( \text{LiGd(NO}_3\text{)}_4 \) and \( \text{MgLa(NO}_3\text{)}_5 \) and \( \text{CH}_3- \) or \( \text{CF}_3- \)-acetate glasses formed using trivalent lanthanides.\(^3\) Refractory lanthanide oxides and \( \text{Ln}_2\text{O}_3-\text{Al}_2\text{O}_3 \) binaries (where \( \text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Ho}, \text{Er}, \text{Yb}, \text{Lu} \)) have been produced by more extreme methods such as splat cooling or from molten droplets spun off a laser-heated ceramic rod and solidified by free-fall cooling.\(^4\)

Lanthanum oxide is introduced into silicate, borate, and borosilicate glasses to increase the refractive index. Several commercial optical glasses contain significant quantities of rare earth oxides. These are the lanthanum flint and crown glasses \( \text{LaF,LaSF and LaK,LaSK} \), the tantalum flint glasses \( \text{TaF and TaSF} \), and the niobium flint glasses \( \text{NbF and NbSF (Schott designations). These glasses are located in the upper right-hand corner of a refractive index–Abbe number plot of optical glasses shown in Fig. 1. The refractive indices of the simple refractory lanthanide oxide glasses noted above are very high, ~1.9–2.1.}\(^4\) Zirconium and hafnium fluoride glasses such as \( \text{ZBL, ZBLA, ZBLAN, HBL, and HBLA contain small quantities of lanthanum, typically <10 mol. %}. \)

Cubic and uniaxial crystals are also used for transmitting optics. Because of the favorable properties and ready availability of many alkali halide and alkaline fluoride crystals, the use of lanthanide crystals for simple transmitting optical components is rare. Crystals are of more interest for their anisotropic optical properties. The properties of many non-centrosymmetric organic and inorganic crystals have been investigated for electro-optic and nonlinear optical applications. Although the second-order optical coefficients of a few lanthanide crystals [e.g., \( \text{K}_2\text{La(NO}_3\text{)}_5, \text{Gd}_2(\text{MoO}_4)_3, \text{Nd}_x\text{Y}_{1-x}\text{Al}_3(\text{BO}_3)_4 \)] and the third-order optical nonlinearities in isotropic materials (e.g., crystalline \( \text{Tb}_3\text{Al}_5\text{O}_{12} \) and \( \text{SF}-7 \) and \( \text{LaSF}-7 \) glasses) have been reported,\(^7\) only the neodymium yttrium borate and \( \text{LaBGeO}_5:\text{Nd} \) have found any significant use arising from their nonlinear optical properties—as self-doubling laser materials. Crystals used for photorefractive, acousto-optic, and birefringent applications have generally been non-lanthanide-containing materials.
Figure 1. Refractive index vs. Abbe number for commercial optical glasses.

Filter Glass

Filter glasses alter the spectrum of the transmitted optical radiation and thereby provide selective filtering for scientific and technological applications, color enhancement in ophthalmic lenses, and contrast enhancement in displays. The transmission characteristics are determined by a combination of the absorption of the base glass and of dopant ions or colloidal colorants. The ultraviolet (UV) and infrared (IR) cutoff wavelengths vary greatly depending on the glass composition, thus the composition can be tailored to achieve transmission with selected cutoff characteristics. All of the trivalent lanthanides from Ce through Yb (with the exception of radioactive Pm) have been introduced into sodium silicate glasses (in concentrations of ∼30 wt. %) for use as filter glasses. Cerium- and gadolinium-containing glasses provide sharp cut-on filters for the near UV; the other lanthanides provide attenuation at a multitude of narrow bands throughout the visible and near-IR regions for special filtering applications.
Colorants and Decolorants

The coloration/decoloration properties of lanthanides in glass have been known and appreciated for many years. When present in large concentrations, lanthanides are colorants in art glass, the most prominent examples being Nd$^{3+}$ for red-violet, Er$^{3+}$ for pink, and Pr$^{3+}$ for green. Lanthanides are also used as decolorants to compensate for coloration due to the presence of unintentional impurities. For example, divalent iron impurities in oxide materials impart a green coloration whereas trivalent iron has only a pale yellow coloration. Cerium oxide, a strong oxidizing agent, is therefore added to glass as a decolorant to keep iron in the Fe$^{3+}$ state.

LUMINESCENCE MATERIALS

Many forms of luminescence occur in optical materials: photoluminescence (excited by optical radiation), electroluminescence (excited by electrons in an applied electric field), radioluminescence (excited by ionizing radiation), cathodoluminescence (excited by an electron beam), and thermoluminescence (thermally-induced from trapping centers). Photoluminescence from lanthanide series ions in insulating solids is exceedingly common and has led to a multitude of useful applications.

Spectroscopy

The 4f-4f optical transitions of lanthanide ions have narrow homogeneous linewidths. When ions are present in many physically different environments, as in a glass, the transition frequency can serve as a sensitive probe of the local field. If monochromatic laser radiation is used to excite luminescence, only those ions in sites resonant with the laser to within the homogeneous linewidth are excited. This is the basic principle of site-selective spectroscopies such as spectral hole burning and fluorescence line narrowing. Using tunable lasers the entire distribution of sites can be probed. Extensive use has been made of laser-excited luminescence from Eu$^{3+}$ to investigate site-to-site variations in the energy levels and transition probabilities of lanthanides in glasses. As another good example of this technique, laser-excited spectra of Er$^{3+}$ were used to identify 20 different charge compensation schemes for lanthanides substituted at divalent calcium site in CaF$_2$.

Lasers

Stimulated emission (laser action) requires an inverted ion population of the excited species. The overwhelming number of reported solid-state lasers have been lanthanide ion lasers. Trivalent and divalent lanthanides provide a plethora of
electronic energy levels and metastable states for optical pumping and low-threshold lasing schemes. Laser action has been reported for all of the lanthanide ions and at wavelengths ranging from the UV to the IR. Host materials have included crystals, glasses, and liquids. Table I lists the many known lasing lanthanide ions, wavelengths, and host materials and is testimony to the widespread use of the lanthanides for solid-state lasers. Neodymium lasers are among the most versatile and widely used solid-state lasers; Er-doped fiber amplifiers are playing an increasingly important role in telecommunications.

Laser action has been demonstrated in hundreds of insulating crystals having many different physical structures and chemical compositions and at wavelengths extending from 0.17 to 7.2 μm. Because the emission lines in crystals are narrower than in glasses, lower lasing thresholds and higher optical gains are possible for crystalline lasers. All trivalent (with the exception of radioactive Pm) and several divalent (Eu, Dy, Tm) lanthanides have been reported to lase in crystals (note: lasing of Gd$^{3+}$ is not well substantiated).

Table I. Lasing Ions, Representative Wavelengths, and Solid-State Laser Hosts.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Wavelength(s) (μm)</th>
<th>Hosts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$^{3+}$</td>
<td>0.28–0.32</td>
<td>fluoride crystals</td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>0.49, 0.53, 0.54, 0.60, 0.64, 0.70, 0.72, 0.86, 0.89, 0.91, 1.04, 1.05, 1.3, 3.6, 5.2, 7.2</td>
<td>oxide and fluoride crystals and glasses</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>0.17, 0.38, 0.93, 1.06, 1.35, 1.8, 5.4</td>
<td>crystals, glasses, liquids</td>
</tr>
<tr>
<td>Pm$^{3+}$</td>
<td>0.93, 1.10</td>
<td>phosphate glass</td>
</tr>
<tr>
<td>Sm$^{2+}$</td>
<td>0.70</td>
<td>fluoride crystals</td>
</tr>
<tr>
<td>Sm$^{3+}$</td>
<td>0.59, 0.65</td>
<td>fluoride crystals</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>0.61</td>
<td>oxide crystal, liquids</td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td>0.31</td>
<td>oxide crystal</td>
</tr>
<tr>
<td>Tb$^{3+}$</td>
<td>0.54</td>
<td>fluoride crystal, liquids</td>
</tr>
<tr>
<td>Dy$^{2+}$</td>
<td>2.36</td>
<td>fluoride crystal</td>
</tr>
<tr>
<td>Dy$^{3+}$</td>
<td>3.0, 4.3</td>
<td>fluoride crystal</td>
</tr>
<tr>
<td>Ho$^{3+}$</td>
<td>0.55, 0.75, 0.98, 1.0, 1.2, 1.4, 1.5, 1.7, 2.1, 2.3, 2.9, 3.4, 3.9</td>
<td>oxide and fluoride crystals and glasses</td>
</tr>
<tr>
<td>Er$^{3+}$</td>
<td>0.47, 0.55, 0.56, 0.67, 0.70, 0.85, 1.0, 1.3, 1.6, 1.7, 2.0, 2.5, 2.8, 4.8</td>
<td>oxide and fluoride crystals and glasses</td>
</tr>
<tr>
<td>Tm$^{2+}$</td>
<td>1.12</td>
<td>fluoride crystal</td>
</tr>
<tr>
<td>Tm$^{3+}$</td>
<td>0.45, 0.48, 1.5, 1.9, 2.3</td>
<td>oxide and fluoride crystals and glasses</td>
</tr>
<tr>
<td>Yb$^{3+}$</td>
<td>1.03</td>
<td>fluoride crystal</td>
</tr>
</tbody>
</table>
An awesome number of lanthanide-containing crystals have been used for lasers. Approximately 175 of the nearly 300 reported crystalline laser hosts contain lanthanide ions are a major cation component. Tables II and III list oxide and halide crystalline hosts (both ordered and disordered) that have been used for lasers. Among the most prominent and commercially available host crystals for trivalent rare earths are Y$_3$Al$_5$O$_{12}$, YAlO$_3$, YVO$_4$, and LiYF$_4$. In so-called stoichiometric lasers, such as PrF$_3$ and NdP$_5$O$_{14}$, the laser ion is a component of the crystal. Of the halide hosts, fluorides have large band gaps and thus are of interest for lasers in the ultraviolet. Examples of UV lasers include the 5d–4f transitions of Nd$^{3+}$ in LaF$_3$ and Ce$^{3+}$ in LiLuF$_4$. The heavier halide hosts have lower vibrational frequencies, hence extended transmission in the infrared and smaller probabilities for nonradiative decay of excited states by multiphonon emission. Such hosts enable longer wavelength emission, e.g., the 5 and 7 μm lasing of Pr$^{3+}$ in LaCl$_3$.

Why the preponderance and massive use of lanthanides crystals as hosts for insulating solid-state lasers? Because by far the largest number of lasing ions have been the lanthanides, one naturally seek hosts having substitutional sites of corresponding size and valence to accommodate the lasing lanthanide. Trivalent La, Gd, and Lu provide these features and had wide regions of optical transparency. The use of lanthanide hosts for other lasing transition group elements is rare, but has included several gadolinium garnets in which transition metal ions are substituted at an Al or Ga site.

As evident from Table I, many different lasing ions (principally trivalent lanthanides) and host glasses (oxides and fluorides) have been used for glass lasers. The materials have been in the form of rods, disks and slabs, fibers, and planar waveguides. The spectral range of glass lasers extends from ~ 0.5 to 3.5 μm. The spectroscopic properties important for laser action vary with the chemical composition of the glass and can be tailored by varying the chemical composition. Although a large number of experimental laser glasses have been reported in the literature, commercial laser glasses are almost exclusively silicates and phosphates. Phosphate glasses generally have narrower linewidths and, for ultraphosphates, have less fluorescence concentration quenching than for silicate glasses. Large quantities of phosphate glasses doped with Nd$^{3+}$ are used in amplifiers for laser systems which provide the versatility of wavelength and pulse duration needed for present-day inertial confinement fusion experiments. Fluoride glasses, such as ZBLAN, due to their lower vibrational frequencies and hence smaller probability for nonradiative decay by multiphonon precesses, are used as hosts to achieve laser action at longer wavelength lasing.
Table II Crystalline Oxide Laser Materials.\textsuperscript{14}

<table>
<thead>
<tr>
<th>Material</th>
<th>Formula</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ln\textsubscript{2}O\textsubscript{3}, Ln = La, Gd, Er</td>
<td>Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12}, Ln = Ho, Er, Tm, Yb, Lu</td>
<td></td>
</tr>
<tr>
<td>La\textsubscript{2}O\textsubscript{3}S</td>
<td>LnAO\textsubscript{3}, A = Al, Ga, Sc; Ln = La, Nd, Gd, Ho, Er, Tm, Yb, Lu</td>
<td></td>
</tr>
<tr>
<td>LuScO\textsubscript{3}</td>
<td>Ln\textsubscript{3}Sc\textsubscript{2}A\textsubscript{3}O\textsubscript{12}, A = Al, Ga;</td>
<td></td>
</tr>
<tr>
<td>Zr\textsubscript{2}O\textsubscript{7}–Er\textsubscript{2}O\textsubscript{3}</td>
<td>Ln\textsubscript{3}(Ln,Ga)\textsubscript{2}Ga\textsubscript{3}O\textsubscript{12}, Ln = La, Lu</td>
<td></td>
</tr>
<tr>
<td>Ln\textsubscript{2}Si\textsubscript{2}O\textsubscript{5}, Ln = Er, Lu</td>
<td>Ln\textsubscript{3}(Ln,Ga)\textsubscript{2}Ga\textsubscript{3}O\textsubscript{12}, Ln = La, Lu</td>
<td></td>
</tr>
<tr>
<td>La\textsubscript{2}Si\textsubscript{2}O\textsubscript{7}</td>
<td>Ln\textsubscript{3}(Ln,Ga)\textsubscript{2}Ga\textsubscript{3}O\textsubscript{12}, Ln = La, Lu</td>
<td></td>
</tr>
<tr>
<td>7La\textsubscript{2}O\textsubscript{3}–9SiO\textsubscript{2}</td>
<td>Ln\textsubscript{3}Ga\textsubscript{3}DO\textsubscript{14}, D = Si, Ge; Ln = La, Nd</td>
<td></td>
</tr>
<tr>
<td>LnVO\textsubscript{4}, Ln = Gd, Er</td>
<td>LnGaGe\textsubscript{2}O\textsubscript{7}, Ln = La, Nd, Gd</td>
<td></td>
</tr>
<tr>
<td>LaNbO\textsubscript{4}</td>
<td>CaLn\textsubscript{4}(SiO\textsubscript{4})\textsubscript{3}O, Ln = La, Gd</td>
<td></td>
</tr>
<tr>
<td>LaBe\textsubscript{2}O\textsubscript{5}</td>
<td>RLn(MoO\textsubscript{4})\textsubscript{2}, R = Na, K, Rb, Cs</td>
<td></td>
</tr>
<tr>
<td>LaBGeO\textsubscript{5}</td>
<td>Ln = La, Nd, Gd</td>
<td></td>
</tr>
<tr>
<td>Ca\textsubscript{4}La(PO\textsubscript{4})\textsubscript{3}O</td>
<td>Ln = La, Nd, Gd</td>
<td></td>
</tr>
<tr>
<td>LaSr\textsubscript{2}Ga\textsubscript{11}O\textsubscript{20}</td>
<td>R\textsubscript{3}Nd(PO\textsubscript{4})\textsubscript{2}, R = Na, K</td>
<td></td>
</tr>
<tr>
<td>LuMgAl\textsubscript{11}O\textsubscript{19}</td>
<td>Na\textsubscript{2}Nd\textsubscript{2}Pb\textsubscript{6}(PO\textsubscript{4})\textsubscript{6}Cl\textsubscript{2}</td>
<td></td>
</tr>
<tr>
<td>La\textsubscript{2}(WO\textsubscript{4})\textsubscript{3}</td>
<td>RLnP\textsubscript{4}O\textsubscript{12}, R = Li, Na, K; Ln = Pr, Nd</td>
<td></td>
</tr>
<tr>
<td>Gd\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3}</td>
<td>LnP\textsubscript{5}O\textsubscript{14}, Ln = La, Ce, Pr, Nd</td>
<td></td>
</tr>
<tr>
<td>R\textsubscript{5}Nd(MoO\textsubscript{4})\textsubscript{4}, R = Na, K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaLnGeO\textsubscript{4}, Ln = Gd, Lu</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg\textsubscript{2}Ga\textsubscript{3}O\textsubscript{7}, M = Sr, Ba</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table III. Crystalline Halide Laser Materials.\textsuperscript{14}

<table>
<thead>
<tr>
<th>Material</th>
<th>Formula</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>LnF\textsubscript{3}, Ln = La, Ce, Pr, Tb, Ho, Er</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LnCl\textsubscript{3}, Ln = La, Ce, Pr, Tb, Ho, Er</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LnBr\textsubscript{3}, Ln = La, Pr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiLnF\textsubscript{4}, Ln = Gd, Ho, Er, Yb, Lu</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiKGdF\textsubscript{5}</td>
<td>α–NaCaLnF\textsubscript{6}, Ln = Ce, Er</td>
<td></td>
</tr>
<tr>
<td>CsGd\textsubscript{2}F\textsubscript{7}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaLn\textsubscript{2}F\textsubscript{8}, Ln = Er, Tm, Yb, Lu</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K\textsubscript{5}NdLi\textsubscript{2}F\textsubscript{10}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MF\textsubscript{2}–LnF\textsubscript{3}, M = Cd, Sr, Ba; Ln = La, Ce, Nd, Gd, Ho, Er, Lu</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaF\textsubscript{2}–LnF\textsubscript{3}–YF\textsubscript{3}, Ln = La, Ce, Nd, Gd, Ho, Er</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaF\textsubscript{2}–ErF\textsubscript{3}–TmF\textsubscript{3}–YbF\textsubscript{3}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaF\textsubscript{2}–SrF\textsubscript{2}–BaF\textsubscript{2}–LaF\textsubscript{3}–YF\textsubscript{3}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
As discussed earlier in connection with Fig. 1, glasses containing large quantities of lanthanides are high-index, high-dispersion glasses. The nonlinear refractive index of these glasses is also large. This, however, is detrimental for high power lasers where intensity-dependent changes in refractive index lower the thresholds for beam distortion and optical damage due to self focusing. Fluorophosphate glasses have been developed for laser applications requiring small nonlinear refractive index coefficients to reduce self focusing.

In contrast to the above lanthanide-containing solid-state lasers, alkali halides have been the principal host materials for color center lasers.

Liquid lasers have incorporated lanthanides as the active ion. These have been of two types: (1) chelate lasers where the lanthanide (Eu$^{3+}$, Tb$^{3+}$, Nd$^{3+}$) is part of a complex in an organic solvent, and (2) aprotic lasers consisting of Nd$^{3+}$ and an inorganic complex of a oxyhalide or halide of heavier elements such as phosphorus, sulfur, selenium, or zirconium.\textsuperscript{17}

The versatility of lanthanide ions is also demonstrated by their use as sensitizer ions for lasers and other luminescent applications. Many sensitization schemes have been reported in which one lanthanide (the donor) absorbs optical radiation and transfers it radiatively or nonradiatively to another ion (the acceptor).\textsuperscript{14} This leads to better utilization of the optical spectrum and an increase in optical pumping efficiency.

The many 4f energy levels of lanthanides also make possible a number of upconversion schemes wherein two or more lower energy photons and transitions are used to populate higher energy levels with resultant emission at energies greater than the pump photons. The development of intense laser diode and laser diode arrays for pumping solid-state lasers in the near infrared has enhanced the prospective use of several upconversion schemes.

Impressive as is the number of demonstrated lanthanide lasers, it is worth noting that for the lanthanide series elements, there are 1639 free-ion energy levels and 192,177 transitions between J states. To date only about 70 transitions have been used for lasing. There is little question that, given an appropriate host and in the absence of excited-state absorption, many more lanthanide lasers are possible.

Phosphors

Many lamp and display phosphor materials are based on the use of lanthanides as the luminescent center. In the past halophosphates activated with luminescent ions
other than the lanthanides have been used for lamp phosphors to convert the 254-
and 185-nm emission from a low-pressure mercury discharge to visible light. 
Now, however, tricolor (red, green, blue) lamps containing a combination of
lanthanide-activated phosphors provide improved efficiency, lifetime, and color
rendering for this application. Examples of these phosphors are included in Table
IV.

Probably the most familiar lanthanide phosphor ion is trivalent Eu used for the red
color in TV and other CRT displays. Although europium is not an abundant rare
earth, its extensive use over the years has resulted in increased availability and an
order of magnitude decrease in price. Other cathode-ray tube phosphors have been
developed to emit at various wavelengths and with either fast decay for flying-spot
scanners or long persistence to avoid or minimize flicker. Commercial lanthanide-
activated phosphors for these applications are listed in Table IV.

Table IV. Common Phosphors Containing Lanthanide Activator Ions.

<table>
<thead>
<tr>
<th>Commercial Phosphors</th>
<th>Lamp and Display Phosphors</th>
</tr>
</thead>
<tbody>
<tr>
<td>P22 YVO₄:Eu³⁺</td>
<td>Red (~610 nm):</td>
</tr>
<tr>
<td>P22 Y₂O₂S:Eu³⁺</td>
<td>Y₂O₃:Eu³⁺</td>
</tr>
<tr>
<td>P43 Gd₂O₂S:Tb³⁺</td>
<td>YVO₄:Eu³⁺</td>
</tr>
<tr>
<td>P44 La₂O₂S:Tb³⁺</td>
<td>Y₂(WO₄)₃:Eu³⁺</td>
</tr>
<tr>
<td>P45 Y₂O₂S:Tb³⁺</td>
<td>Green (~550 nm):</td>
</tr>
<tr>
<td>P45 (red) Y₂O₂S:Tb³⁺, Eu³⁺</td>
<td>CeMgAl₁₁O₁₇:Tb³⁺</td>
</tr>
<tr>
<td>P46 Y₃Al₅O₁₂:Ce³⁺</td>
<td>(Ce,Gd)MgB₅O₁₀:Tb³⁺</td>
</tr>
<tr>
<td>P46 (green) Y₃(Al,Ga)₅O₁₂:Ce³⁺</td>
<td>(Ce,La)PO₄:Tb³⁺</td>
</tr>
<tr>
<td>P47 Y₂SiO₅:Ce³⁺</td>
<td>Blue (~450 nm):</td>
</tr>
<tr>
<td>P48 P46-P47 blend</td>
<td>BaMgAl₄O₁₂:Eu²⁺</td>
</tr>
<tr>
<td>P53 Y₃(Al,Ga)₅O₁₂:Tb³⁺</td>
<td>Sr₃(PO₄)₅Cl:Eu²⁺</td>
</tr>
<tr>
<td>P56 Y₂O₃:Eu³⁺</td>
<td>Sr₂Al₆O₁₁:Eu²⁺</td>
</tr>
<tr>
<td>InBO₃:Eu³⁺</td>
<td>• Electroluminescent Phosphors</td>
</tr>
<tr>
<td>InBO₃:Tb³⁺</td>
<td>Red – ZnS/CaGa₂S₄:Sm²⁺</td>
</tr>
<tr>
<td>• X-ray Storage Phosphors</td>
<td>Green – ZnS:Tb³⁺</td>
</tr>
<tr>
<td>BaFBr:Eu²⁺</td>
<td>Blue – CaGa₂S₂:Ce³⁺</td>
</tr>
<tr>
<td>Ba₅SiO₄Br₆:Eu²⁺</td>
<td></td>
</tr>
</tbody>
</table>
For projection television, saturation of the light output at high excitation intensities is a problem. Red Eu\textsuperscript{3+} phosphors and green Tb\textsuperscript{3+} phosphors are used but no ideal phosphor has been found for the blue. Phosphors containing Eu\textsuperscript{2+}, Ce\textsuperscript{3+}, and Tm\textsuperscript{3+} have been considered to replace ZnS:Ag\textsuperscript{+} for the blue phosphor in projection TV displays.

Lanthanide-containing ceramic phosphors are used in applications where light is integrated, such as in certain radiation detection applications and in computed tomography (CT). Examples of these materials and their properties are given in Table V. An important consideration for CT applications is the afterglow intensity (due to the presence of traps) which should be small (<0.1% at 100 ms) to preserve image contrast. Of the materials in Table V, (Y,Gd)\textsubscript{2}O\textsubscript{3}:Eu,Pr has a relatively long afterglow (3 ms).

<table>
<thead>
<tr>
<th>Property</th>
<th>Reference</th>
<th>(Y,Gd)\textsubscript{2}O\textsubscript{3}:Eu,Pr</th>
<th>Gd\textsubscript{2}O\textsubscript{2}S:Pr,Ce</th>
<th>Gd\textsubscript{3}Ga\textsubscript{5}O\textsubscript{12}:Cr,Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm\textsuperscript{3})</td>
<td>4.52</td>
<td>5.91</td>
<td>7.34</td>
<td>7.09</td>
</tr>
<tr>
<td>Emission max. (nm)</td>
<td>550</td>
<td>610</td>
<td>510</td>
<td>730</td>
</tr>
<tr>
<td>Light output (relative)</td>
<td>100</td>
<td>~67</td>
<td>~75</td>
<td>~60</td>
</tr>
<tr>
<td>Decay time (μs)</td>
<td>0.98</td>
<td>~1000</td>
<td>~3</td>
<td>140</td>
</tr>
</tbody>
</table>

Recent phosphor developments have included the discovery of new and improved lanthanide-activated materials for electroluminescent phosphors in flat panel displays, x-ray intensifier screens, and photostimulable storage screens (see Tables IV and V). Although several models have been advanced to describe the processes active in storage phosphors, details of the storage mechanism is still unclear.\textsuperscript{18}

**Scintillators**

Scintillator crystals are widely used for the detection of ionizing radiation in a variety of applications including high energy and nuclear physics, astrophysics, geophysical exploration, medical imaging, security inspection, and industry. Absorption of ionizing radiation leads the creation of large numbers of electron-hole pairs, subsequent excitation of the activator, and resultant fluorescence which is detected. Major considerations for the selection of scintillator materials include light yield and associated energy resolution, high density and stopping power to minimize the amount of material required, decay time and afterglow, emission wavelength to match photodetectors, and stability with respect to environmental conditions and radiation damage.\textsuperscript{19}
Cerium-activated scintillator materials have been known and used for several decades but have received renewed interest recently because of the favorable spectroscopic properties of Ce$^{3+}$ and the ability to incorporate Ce$^{3+}$ into many different host materials. Among the attractive properties of Ce$^{3+}$ are (1) its luminescence, which occurs in the visible-near ultraviolet region and is well matched to the spectral response of high efficiency photodetectors, (2) the emission involves an allowed transition and thus is fast for good time resolution, (3) the luminescence intensity and decay time are stable and insensitive to temperature for many hosts at room temperature, (4) there are no long-lived radioactive isotopes, and (5) Ce is the least rare of the rare earths. In addition to the 5d-4f transition of Ce$^{3+}$, similar transitions of Pr$^{3+}$ and Nd$^{3+}$ have been explored for use in scintillators.

Silicate glass was used as a host in early scintillator applications of Ce$^{3+}$. Scintillation glasses are available in bulk form for energy calorimetry and in fiber form for particle tracking. Cerium-activated glasses containing $^6$Li, which has a large neutron capture cross section, are also used for detecting neutrons.

The density, dominant decay time, and relative light output of a number of Ce$^{3+}$ activated materials are given in Table VI. All of these materials have emission in the 300 to 500-nm regime which is well matched to the spectral response of photoemissive detector materials. However, there is a large variation in the light yield of Ce$^{3+}$ scintillators; it ranges from values approaching that of the widely used scintillator NaI(Tl) for Lu$_2$SiO$_5$ to values several orders of magnitude smaller for some glasses. The large variation in Ce$^{3+}$ scintillation efficiency is due to differences in the efficiency for excitation transfer from the host to the fluorescing activator. Of the materials listed in Table VI, lutetium compounds are attractive because they combine high density and stopping power with high light yield and are the subject of much current research and development.

For applications requiring large volumes of scintillator materials, such as detectors for medical imaging tomography or high-energy physics experiments (where several thousand crystals and volumes of materials measured in cubic meters are needed), production and cost of the scintillator material become major considerations. Scintillation detectors have been proposed for electromagnetic calorimetry at future high-energy particle colliders where about one hundred thousand crystals several centimeters in width and several tens of centimeters in length are needed. Crystals of CeF$_3$ was seriously considered for this application and would have constituted a massive utilization of a lanthanide, however PbWO$_4$ was selected instead. Although the scintillation properties of PbWO$_4$ crystals were less favorable, their production capabilities were more attractive.
Table VI. Comparison of Properties of Cerium Scintillator Materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm³)</th>
<th>Decay time (ns)</th>
<th>Relative light yield</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Reference</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaI(Tl)</td>
<td>3.7</td>
<td>230</td>
<td>100</td>
</tr>
<tr>
<td><em>Crystals</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lu₂SiO₅ (LSO)</td>
<td>7.4</td>
<td>~40</td>
<td>75</td>
</tr>
<tr>
<td>Gd₂SiO₅ (GSO)</td>
<td>6.7</td>
<td>30–60</td>
<td>20–25</td>
</tr>
<tr>
<td>LuAlO₃ (LuAP)</td>
<td>8.3</td>
<td>20</td>
<td>~20–50</td>
</tr>
<tr>
<td>YAlO₃ (YAP)</td>
<td>5.6</td>
<td>28</td>
<td>40</td>
</tr>
<tr>
<td>LuPO₄</td>
<td>6.5</td>
<td>24</td>
<td>33</td>
</tr>
<tr>
<td>CeF₃</td>
<td>6.2</td>
<td>~5, 30</td>
<td>5–9</td>
</tr>
<tr>
<td><em>Glasses</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>silicate (GS1)</td>
<td>2.5–2.7</td>
<td>~60</td>
<td>~5</td>
</tr>
<tr>
<td>borate</td>
<td>2.4–2.5</td>
<td>~30</td>
<td>~3</td>
</tr>
<tr>
<td>phosphate</td>
<td>~2.6</td>
<td>~30</td>
<td>&lt;1</td>
</tr>
<tr>
<td>fluoride (HfF₄)</td>
<td>~6–7</td>
<td>10–30</td>
<td>≤1</td>
</tr>
</tbody>
</table>

MAGNETO-OPTIC MATERIALS

Optical rotation occurs in a medium when the refractive indices n⁺ and n⁻ for right- and left-circularly polarized light are unequal. The microscopic origin of magnetic optical rotation is the inequality that is created by the splitting of the ground or excited-state energy levels due to an applied magnetic field or magnetization. When the magnetic vector is parallel to the direction of light propagation, the Faraday effect produces a rotation of the plane of polarization given by \( \theta_F = V \ell H \cdot \mathbf{e} \), where \( \ell \) is the pathlength in the material, H is the strength of the applied field, \( \mathbf{e} \) is a unit vector in the direction of light propagation, and the constant of proportionality V is the Verdet constant. In the small-field limit, the Verdet constant is a function of wavelength, temperature, and refractive index and may be of diamagnetic, paramagnetic, or ferromagnetic origin.²⁴

The Faraday effect (which is discussed by J. Kohli elsewhere in this volume) has been utilized in the construction of fast optical switches, modulators, circulators, isolators, and sensors for magnetic fields and electric currents. Diamagnetic and paramagnetic crystals and glasses containing lanthanides have been used in bulk and fiber forms for these applications. The largest diamagnetic Verdet constants are found for high-index, high-dispersion materials such as the oxide glasses located in the upper right-hand corner of the \( n \) vs. \( v_d \) diagram in Fig. 1 and chalcogenide
glasses. The temperature dependence of $V_{\text{dia}}$ is very small which makes diamagnetic materials attractive for high-stability Faraday effect sensors.

Paramagnetic Faraday rotation is dependent on the number of paramagnetic ions present in the material and the frequency of the electronic transitions of the ions contributing to the rotation. The magnitude and the wavelength and temperature dependencies of the paramagnetic Verdet constant vary depending upon the choice of the paramagnetic ion. All transparent materials exhibit diamagnetic Faraday rotation, however when paramagnetic ions are present in sufficient quantities, paramagnetic Faraday rotation may dominate. Because the diamagnetic and paramagnetic effects produce opposite rotations, the sign of the net Verdet constant of a material can change with paramagnetic ion content. The best host materials for paramagnetic rotators are those having a small diamagnetic Verdet constant (low refractive index and dispersion) and capable of incorporating large quantities of the paramagnetic ion. Whereas the concentration of lanthanide ions in glasses is limited by glass formation, lanthanide ions may be a stoichiometric component in crystals and hence produce larger rotations per unit length. Of the paramagnetic lanthanide series ions, Ce$^{3+}$, Gd$^{3+}$, Tb$^{3+}$, and Eu$^{2+}$ have large regions of useful transparency in the visible-near infrared region. Verdet constants of several representative diamagnetic and paramagnetic crystals and glasses are given in Table VII. Terbium is one of the most commonly used ions in paramagnetic rotator materials.

### Table VII. Verdet Constants of Selected Lanthanide Materials (633 nm and 300 K)$^{24}$

<table>
<thead>
<tr>
<th>Crystals</th>
<th>$V$(rad/T m)</th>
<th>Glasses</th>
<th>$V$(rad/T m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaF$_3$</td>
<td>2.5</td>
<td>LaSF31</td>
<td>2.6</td>
</tr>
<tr>
<td>CeF$_3$</td>
<td>-114</td>
<td>LaKN12</td>
<td>6.1</td>
</tr>
<tr>
<td>EuF$_2$</td>
<td>-262</td>
<td>ZBLA</td>
<td>3.1</td>
</tr>
<tr>
<td>Dy$_3$Al$<em>5$O$</em>{12}$</td>
<td>-38</td>
<td>cerium phosphate (FR-4)</td>
<td>-31</td>
</tr>
<tr>
<td>Tb$_3$Al$<em>5$O$</em>{12}$</td>
<td>-180</td>
<td>terbium borosilicate (FR-5)</td>
<td>-71</td>
</tr>
</tbody>
</table>

Ferro, antiferro-, and ferrimagnetic materials are characterized by spin ordering even in the absence of an applied field. Non-metallic ferro- and antiferromagnetic lanthanide materials include EuO, EuS, EuSe, EuTe, TmS, and TmSe.$^{24}$ Nonmetallic ferrimagnetic materials are used extensively for optical rotation and isolators at wavelengths $>1$ μm. Of these, yttrium iron garnet (Y$_3$Fe$_5$O$_{12}$ or YIG) has been the most widely studied. To enhance its magneto-optic properties, lanthanide ions are substituted either partially or wholly for yttrium. Bismuth substitution greatly increases the absolute value of the saturation Faraday rotation. Examples of materials illustrating these effects are listed in Table VIII.

---

14
Table VIII. Faraday Rotation $\theta_F$ of Selected Iron Garnets (1064 nm and 300 K)$^{24}$

<table>
<thead>
<tr>
<th>Material</th>
<th>$\theta_F$ (°/cm)</th>
<th>Material</th>
<th>$\theta_F$ (°/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y$_3$Fe$<em>5$O$</em>{12}$</td>
<td>280</td>
<td>Pr$_3$Fe$<em>5$O$</em>{12}$</td>
<td>-1789</td>
</tr>
<tr>
<td>Gd$_3$Fe$<em>5$O$</em>{12}$</td>
<td>65</td>
<td>Nd$_3$Fe$<em>5$O$</em>{12}$</td>
<td>-1130</td>
</tr>
<tr>
<td>Tb$_3$Fe$<em>5$O$</em>{12}$</td>
<td>535</td>
<td>Gd$_2$Pr$_2$Fe$<em>5$O$</em>{12}$</td>
<td>-790</td>
</tr>
<tr>
<td>Dy$_3$Fe$<em>5$O$</em>{12}$</td>
<td>310</td>
<td>Gd$_2$BiFe$<em>5$O$</em>{12}$</td>
<td>-3300</td>
</tr>
<tr>
<td>Tm$_3$Fe$<em>5$O$</em>{12}$</td>
<td>115</td>
<td>Y$_2$CeFe$<em>5$O$</em>{12}$</td>
<td>-22000</td>
</tr>
</tbody>
</table>

Whereas the Faraday effect is a magneto-optic rotation observed in transmission, the Kerr effect is the corresponding effect observed in reflection from metallic materials. Lanthanides are again of interest. CeSb exhibits the largest Kerr effect of any known materials, however because of its a low Curie temperature (16 K) and the large applied fields required to induce the magneto-optic effect, it has not found practical application.

PHOTOSENSITIVE MATERIALS

Photosensitive glasses are a special class of glasses whose optical properties are changed by optical/thermal treatment. Among these are photochromic glasses that change color under ultraviolet or short wavelength light, then revert back to the original state when the light is reduced. The mechanisms involved in photochromism are complex and include treatment of precipitation kinetics and charge carrier diffusion.\textsuperscript{25} Photochromism is observed in strongly reduced alkali silicate and other multicomponent silicate and borosilicate glasses, in glasses containing suspensions of crystallites, and in glasses colored by silver halides. An example of a photosensitive glass is lithium silicate containing CeO$_2$ as an optical sensitizer and silver, gold, or palladium oxide as nucleating agents. This glass photo nucleates when subjected to ultraviolet or ionizing radiation via the process Ce$^{3+}$ + hv $\rightarrow$ Ce$^{4+}$ + e$^-$ followed by heating and diffusion of the electron to a nearly silver ion where Ag$^+$ + e$^- \rightarrow$ Ag$^0$. Upon heat treatment Ag$^0$ atoms agglomerate to form silver colloids. These are dispersed through the glass and act as nucleation sites for crystal growth which proceeds upon heating at higher temperatures. Because crystallization occurs only in areas exposed to ionizing radiation, spatially selective chemical machining, photoengraving, and photographs are possible.

Light-induced changes in the refractive index and attenuation (photodarkening) have important consequences for the operation of optical fibers and waveguides. These effects have been studied in germanium-doped silica and other inorganic glasses.\textsuperscript{24} Glasses containing the lanthanide ions Ce$^{3+}$, Pr$^{3+}$, and Eu$^{2+}$ exhibit irreversible changes over a broad spectral range at UV irradiation when subjected to resonant
excitation of the 5d state at room temperature. Photodarkening is also observed in Tm$^{3+}$-aluminosilicate glass due to a nonlinear, multiphoton excitation process.$^{26}$

Cerium is an additive in some photorefractive materials. In the photorefractive effect, two coherent light beams incident on a solid sample produce an interference pattern in the optical intensity. Photoeffects may occur differentially between the light and dark regions. If mobile photocarriers are generated in the light regions, they can diffuse or hop to the dark region where they are trapped and cause changes in the refractive index. Cerium ions substituted at Ba or Sr sites in Sr$_{1-x}$Ba$_x$Nb$_2$O$_6$ act as donors to facilitate this photorefractive effect.$^{27}$ Cerium is also added to photorefractive BaTiO$_3$ and LiNbO$_3$ crystals.

Most glasses are photosensitive in the negative sense that they become colored (solarize) after exposure to ultraviolet or ionizing radiation. Photodegradation mechanisms are complex and depend on the material composition. To prevent solarization in optically-pumped laser glass and in glass used for UV lamps, small quantities ($< 1\%$) of polyvalent ions such as cerium, antimony, and molybdenum are added to the glass. Radiation resistant glasses depends on the presence of both Ce$^{3+}$ and Ce$^{4+}$ to capture free electrons and holes.

As a final illustration of a photosensitive lanthanide material, lanthanum-containing zirconium and hafnium fluoride glasses have been used as Brillouin materials for optical phase conjugation.$^{28}$

CONCLUDING REMARKS

As evident from the brief survey above, the role of lanthanide in materials for photonics and opto-electronics has been enormous. These fields remain vigorous areas of research and development. Although the use of the lanthanides have been well exploited, it is not exhausted. One may therefore anticipate further utilization of the special properties of these ions in optical materials.

ACKNOWLEDGMENTS

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6. See, for example, an early report by N. J. Kreidl, J. Am. Ceram. Soc. 25, 141-143 (1942).
23. P. Lecoq, J. Lumin. 60 & 61, 948-955 (1994).


