Advances in rare earth spectroscopy and applications

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Advances in Rare Earth Spectroscopy and Applications

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Rare earth (RE) elements are prime constituents in a large amount of innovative materials and several technological advances would not be possible without their contribution. In this review, recent progress in the field of rare earth spectroscopy is highlighted, with a special emphasis on clean energy, sensors and telecommunications, providing a broad view on past and recent developments.

**Keywords:** Rare Earth, Spectroscopy, Lanthanides, Solar Cell, Telecommunication, Clean Energy, Light Emitting Diode.

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**1. INTRODUCTION**

The study of \( f \)-shell electrons is of paramount importance due to their unique optical and magnetic properties, often related to potential applications in a variety of fields. Spectroscopy of lanthanide (Ln) elements is a hot topic of research as they not only cover vast commercial applications but also help to understand basic mechanisms of several peculiar emission dynamics. Ln elements present several interesting luminescent properties such as sharp emission lines, meta-stable states and high quantum efficiency (QE) which make them suitable for the manufacture of numerous optical devices.\(^1\) Their use permits technological applications of a number of materials like superconductors, miniaturized magnets, catalysts, lamp, display devices, lasers, biomedical, memory devices, sensors, optical amplifiers, and so on. In particular, regarding the issue of energy generation and its related harmful environmental impact, RE doped materials are alternative sources of clean energy through their applications in nuclear reactors, solar cells, wind turbines, light emitting diodes (LEDs) and others. RE ions exhibit the ability of converting long-wavelength near infrared radiation to shorter visible wavelengths, through a process known as frequency upconversion (UC). Several exclusive optical UC phenomena using RE elements were invented, such as APTE [Addition de Photon par Transfert d’Energie], cooperative emission, multi-photon absorption, photon avalanche, and so on. With the advent of nanotechnology, it is worth it to re-investigate these processes for RE ions confined in nano-structures. Despite the countless potential applications of RE doped materials, several puzzling problems are yet to be solved, suggesting the need of further research effort. Some of the technological challenges in RE spectroscopy is to understand opto-magnetic interactions, optimizing black body radiation (heat generation) and finding single phase multifunctional luminescent material compatible with biomedical purposes.

It is interesting to note that even though these elements are quite important for the development of new technological products, this area is under threat after the announcement made by the largest supplier, China, to limit exports to 40% (especially, of heavy Ln ions) from 2010 to 2015. This announcement immediately impacted the global market and the prices of a few elements faced unexpected increase.

The economical aspect raised questions on future research using RE materials and encouraged the governments to formulate regulation policies to assure sustainable production of these metals. Another issue of growing interest is the ecological and biological impacts of Ln, as their true toxicity level is not well known, especially when used as dopants in nano-dimension structures. It is interesting...

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to note that the worldwide annual consumption of RE elements in 2010 was about 136 million tons, in prime sectors like electric vehicles, wind turbines, rechargeable batteries, night vision, weapons guidance systems, security inks, polishing, lens making, Ni battery coating, magnets, petroleum products, catalytic applications, cell phone power sources, flat screen TVs, solid state lasers, LEDs, optical telecommunications, biological imaging, radiation sensors, lighting and displays, lasers, homeland security, agricultural fertilizer and many other products. Some of the prime sectors of RE consumption are highlighted in Figure 1. High intake and/or chronic exposure of these elements lead to bioaccumulation, a supposed threat to the neural system and liver, in addition to damage to cell membranes of aquatic animal species with negative effects on the reproduction and the nervous system.

The present article reviews one of the most discussed fields of spectroscopy, namely rare earth spectroscopy, and some of its applications in frontline research. It is appropriate to consider RE spectroscopy as a different branch of spectroscopy, as experimentations, optical processes and analysis are different from conventional spectroscopy. Since it is practically impossible to cover all the aspects of RE spectroscopy in a brief review, here we emphasize three technological frontiers of RE spectroscopy, namely, clean energy, sensors and telecommunications, by giving a brief account on the current status of each subject.

2. UNIQUENESS OF RE SPECTROSCOPY

The discovery of rare earth elements probably occurred in the summer of 1787, at the island of Roslaga, near Stockholm, when an exceptionally heavy piece of black rock, found in the dumps of the Ytterby quarry, called the attention of Lieutenant Carl Axel Arrhenius (1757–1824). Further analysis of the stone revealed a new element, later named Yttrium (atomic number 39). Thereafter, a whole range of elements was discovered, which are now known as Ln elements, with atomic numbers ranging from 57 to 71. Though Ln and Yttrium elements occupy different positions in the periodic table, they are collectively referred to as rare earths because of their similar chemical properties. Occasionally, Scandium (Sc) and Thorium (Th) are also referred as rare earths elements. As a matter

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of fact, the name of this unique family is misleading as these materials are quite abundant in the Earth crust. Tm for example, which is estimated to be less abundant among the Ln, has an abundance in the Earth crust comparable to Silver and Cadmium (Cd), while Ce is more common than Tm. However, as most of the rare earths are found in ores, ultrapure Lns are still difficult to obtain.

Ln elements possess electronic configuration [Xe] 4f\(^n\) 6s\(^2\) or [Xe] 4f\(^{n-1}\) 5d \(\geq\) 5 f\(^2\), where [Xe] stands for the Xenon electronic structure. When Ln elements are dispersed in a host matrix, they may attain either +2, +3 or +4 oxidation states, with +3 oxidation state being the most common. When a trivalent ion is formed, the atom gives up its outermost 6s electron, besides losing its 5d electron, if it has one. If it doesn't, it loses one of the 4f electrons, leaving a partially filled 4f shell, shielded by the outer 5s and 5p shells. In appropriate conditions, Ln ions also show +2 and +4 oxidation states, such as Sm\(^{3+}\), Eu\(^{3+}\), Yb\(^{3+}\) (stability order Eu\(^{3+}\) \(\gg\) Yb\(^{3+}\) \(\gg\) Sm\(^{3+}\)), and Ce\(^{4+}\), Pr\(^{4+}\) and Tb\(^{4+}\). Similar to Ln ions, Y also shows a +3 ionic state but it has no optical transitions. Among Ln ions, La\(^{3+}\) and Lu\(^{3+}\) have a completely empty and a completely filled 4f shell, respectively, and therefore they have no optical transitions. Ce\(^{3+}\) has one electron and a single 4f level just above the ground state. Due to the small energy difference between the inner 4f levels and the outer or valence electrons, it takes only a minimal amount of energy to change the relative occupancy of the electronic levels. Hence, Ce possesses dual valence states: Ce\(^{4+}\) (ceric) (4f\(^0\)) and Ce\(^{3+}\) (cerois) (4f\(^1\)).\(^6\) Ce\(^{4+}\) ion has a higher stability as a consequence of the unfilled orbital. For this reason, it is reasonable to assume that the Ce\(^{4+}\) ion has a lower ionization potential and would be a good hole trap. The tetravalent oxidation state of cerium ions does not contain any electron in the 4f orbital and so, no emission from Ce\(^{4+}\) ions is observed. Trivalent Yb ion also possesses one excited state in the 4f configuration, at ~10,000 cm\(^{-1}\). Another Ln ion, Pm, is a non-natural occurring radioactive material and exists only as a temporary intermediate product in the ongoing radioactive decay of other elements.

The 4f orbitals in the RE\(^{3+}\) ion is shielded by 5s\(^2\) and 5p\(^6\) orbitals and thus, their spectroscopic and magnetic properties are nearly unaffected by the host. In Ln ions, different types of transitions may take place, namely 4f \(\rightarrow\) 4f, 4f5d \(\rightarrow\) 4f, and change transfer band \(\rightarrow\) 4f sub-shell. Among them, the intrashell 4f \(\rightarrow\) 4f transition is parity forbidden due to Laporte's rule which states that electric dipole transitions can only occur between levels of opposite parity. These transitions appear as low intensity lines because odd-order terms in the crystal Stark field mixes the 4f\(^n\) states to higher lying opposite parity states, such as 4f\(^{n-2}\) 5d, partially relaxing the Laporte’s selection rule.\(^7-\)\(^8\) Besides providing a split of the energy levels by removing the 2J + 1 degeneracy. A weaker mechanism that can also contribute to the mixing of states is the interaction of electronic states with lattice vibrations. This mechanism becomes dominant when the ions occupy sites with inversion symmetry, as the crystal field contribution vanishes in this case. Since the electric dipole transitions are weakly allowed, they present low absorption coefficients and relatively long lifetimes (up to several milliseconds). 4f electrons do not take part in the bond making with the host and are well shielded by the s and p shells, resulting in narrow line transitions in absorption and emission spectra. Though the shielding of the 4f electrons makes them almost insensitive to the near field, a few transitions exaggerate the small changes in the lattice coordination sphere. These transitions are termed hypersensitive transitions. Their intensity is significantly enhanced as the symmetry of the Ln complex lowers or the polarizability of the ligands increases. Jørgenson and Judd\(^+\) noted that hypersensitive transitions obey the selection rules \(\Delta J \geq 2, \Delta L \geq 2,\) and \(\Delta S \geq 0\). In contrast to electric dipole, magnetic dipole transitions do not violate the parity selection rule once they can occur between states of the same parity. However, the strengths of these transitions are much weaker than the allowed electric dipole transitions. Magnetic dipole contributes to the intra-4f electronic transitions of Ln ions such as Eu\(^{3+}\), Eu\(^{4+}\) and Tb\(^{3+}\). A detailed discussion on RE spectroscopy, including energy level calculation, strength and other spectroscopic characterization techniques, can be found in Refs. [10–15].

As 4f \(\rightarrow\) 4f transition probabilities are very weak to yield efficient light, an option to improve emission is to enhance the electric field by means of metal nanoparticles (NPs), core–shell structures, sensitization via host, organic, or RE ions.\(^16-\)\(^20\) Ln ions belong to the hard acid class\(^21\) and so, they have the tendency of binding with hard bases, primarily those that contain oxygen and nitrogen as donor atoms, resulting in RE tri-cations of a hydrophilic nature. Dense energy levels and splitting produce several exclusive optical phenomena in Ln ions, such as excited state absorption (ESA), APTE, cooperative emission, multiphoton absorption, photon avalanche and crossrelaxation. These processes produce photons of higher energy upon excitation with lower energy photons, a phenomenon that is known as upconversion.\(^22-\)\(^25\) It may also occur through energy transfer via host, hetero RE ions, organics, etc., phonon assisted energy transfer and cooperative processes.\(^26-\)\(^29\) UC processes can be induced by a low power (1–10\(^3\) W cm\(^{-2}\)) continuous wave laser. In contrast to a costly high-intensity (10\(^8\)-10\(^9\) W cm\(^{-2}\)) pulsed laser source for the generation of a two-photon process.

3. CLEAN ENERGY APPLICATIONS

The growing global concerns on the predicted reduction in fossil energy and environmental pollution foster great enthusiasm for clean energy alternatives. In addition, the ever increasing demand for electricity aggravates the situation. Usually, two approaches are considered to handle this situation. First, to search alternative clean (low carbon)
or renewable energy sources for individual purposes and second, to improve the efficiency of existing equipment in order to reduce energy consumption. In recent years, at least three different technologies, namely wind turbines, nuclear reactors and solar cells, boosted up the clean energy sector, suggesting that they may be the future energy sources. According to the report of the Nuclear Energy Institute, the contribution of nuclear energy in 2012 was 64%, solar/wind 13.5% and hydro energy 22.6%.30

Energy sources that release carbon intensities lower than 0.82 metric tons per megawatt-hour are considered clean energy sources.31 Existing natural renewable energy sources based on water, wind, biomass and sunlight are considered clean energy sources. Nuclear energy is also an alternative, despite the debate whether it may be considered renewable or clean sources since its byproducts may bring serious threat to the environment. Moreover, the security of large nuclear plants is a concern of local inhabitants as any leak may contaminate the water and soil, and may worsen their life. Nuclear power plants do not emit toxic gases like CO₂ or SO₂. Despite the various concerns about nuclear energy production, it is regarded as a clean energy source and is being used by almost every major country around the world. By May 2013, 30 countries worldwide were operating 436 nuclear reactors for electricity generation and 70 new nuclear plants are under construction in 14 countries.30 It is also noted that nuclear power plants provided 12.3% of the world’s electricity production in 2011.

The major contribution of Ln elements for clean energy production is multifaceted. It includes preparing neutron absorbers for nuclear reactors, high efficiency magnets for wind turbines, quantum cutting and IR absorbing materials for solar cell application, coating materials for LEDs, phosphor for lamps, and others. The use of Ln in a nuclear reactor, especially Samarium, Gadolinium, and Europium, is to control the fusion, as the Lns have large neutron cross-sections and are highly efficient for capturing neutrons. One of the Samarium isotopes, Sm,49 is frequently used in nuclear control rods.

In addition to nuclear energy, another widely used source takes advantage of the kinetic energy of the wind to produce mechanical energy. The mechanical power can be used for specific tasks (such as grains grinding or water pumping) or a generator can convert it to electricity. Wind energy can be transform to electrical energy through giant wind turbines which essentially need high performance Ln supermagnets. Wind turbines can produce energies in the range from a few kilowatts to several megawatts. Small single turbines, below 100 kilowatts, are used for homes, telecommunications dishes or water pumping. China has the largest wind resources in the world and researchers from Harvard University and Tsinghua University have found that the China could meet all of its electricity demands from wind power by 2030.32

Wind turbines use Ln-flecked supermagnets inside the turbines, such as Neodymium–Iron–Boron and Samarium–Cobalt magnets, which are powerful, lightweight, strong and relatively cheap. The world production of Neodymium is about 7,000 tons per year and Nd magnets are used in a variety of other products like cars, engines and head phone sets. Ln improves the efficiency of iron alloys, especially through the use of terbium and dysprosium elements. These blends expand and contract efficiently in the presence of a magnetic field, helping sensors, actuators and injectors to perform better. Car batteries used in electric-powered vehicles also rely heavily on RE elements. As this work relates only to spectroscopy, we will not discuss other applications of Lns such as magnets and neutron absorbing rods. Details on the use of Lns in these two sectors can be found in Ref. [33].

Important applications still seeking some breakthrough from Ln elements are solar cells and LEDs. Similar to wind energy, solar energy is also a clean and renewable energy as it directly converts sunlight into electrical energy, while the use of efficient LEDs could reduce the worldwide electricity consumptions up to 20%.

3.1. Solar Cells

A solar or photovoltaic cell is a device that converts energy radiated from the sun into heat or electricity. When a photon hits a photovoltaic cell an electron–hole pair is created and if collected properly, these carriers lead to an electric current. The process of converting solar power to electricity is called photovoltaics (PV). The PV process includes light absorption followed by the generation of electron–hole pairs or excitons, the separation of charge carriers of opposite types and the extraction of those carriers to an external circuit. Though the theoretical efficiency limit of a solar cell (ratio of the electrical output to the incident energy in the form of sunlight) is estimated to be ~33.7% (in single p–n junctions of crystalline silicon),34 the maximum efficiency so far reported in practice is ~24% at the cell level and 20% at the module level, as reported by SunPower company35 http://us.sunpowercorp.com/, while a recent report from the University of New South Wales indicates an efficiency achievement of ~25%. Details on efficiency comparisons can be found in Ref. [36]. The efficiency of solar cells further increase up to ~40.7% and 42.8% in multiple-junctions solar cell with dies assembled into a hybrid package.37 The efficiency of a solar cell is a function of several factors that include reflectance efficiency, thermodynamic efficiency, charge carrier separation efficiency and conductive efficiency. The overall efficiency is the product of these individual efficiencies. The efficiency of solar cells largely depends on the deposition of nanomaterials on a conductive electrode. Various techniques of extremely thin semiconductor quantum dots deposition has been discuss in a review by Yin et al.38 Solution-based electrochemical deposition of ZnO
nanowire arrays for large area deposition, and large scale production were discussed by Zeng et al.\(^{39}\) Singh et al.\(^{40}\) reviewed various techniques to synthesize TiO\(_2\) and CuO nanotubes and nanowires.

The sun is regarded as a black-body radiator, with a temperature around 6000 K, and the solar spectrum covers a broad spectral region ranging from 300 to 2200 nm, with a peak around 500 nm (2.4 eV). However, silicon can absorb only a part of this spectrum, as shown in Figure 2(D). The main hurdle to improve efficiency in semiconductors is that low energy photon (sub-bandgap energy) cannot excite the electrons from the valence to the conduction band and simply pass through the cell. In contrast, high energy photons (above-bandgap energy) produce a pair of \(e^-\)-hole but lose their energy as heat, limiting the cell performance. Approximately, 47% of the solar energy is converted into heat and 18% of the photons pass through the solar cell.

Due to the Si-based solar cell limited absorption, UV and IR radiations are considered as unwanted. Ln elements can help to absorb these unwanted wavelengths and convert them into photons that can absorbed by silicon, improving the overall efficiency. They do it by the processes of downconversion (DC), especially quantum cutting, where the UV photon is absorbed to produce two IR photons,\(^{41}\) and by upconversion (UC), where infrared radiation is converted into visible wavelengths.\(^{42}\) Through the processes of DC and UC, 32% (149 W m\(^{-2}\)) and 35% (164 W m\(^{-2}\)) of the sunlight intensity can be respectively accessed,\(^{43}\) improving significantly the solar cell efficiency. In a typical DC/UC-Si bifacial solar cell, a DC or UC layer is coated on the back side of the cell (Fig. 2(A)) and a reflector returns all emitted photons back into the solar cell.

A theoretical study on realistically modeled UCs reveals that the cell efficiency can be enhanced up to 44%.\(^{44}\) Older studies show that the upper limit of the PV conversion efficiency of a single junction solar cell coupled to an ideal UC device is 47.6%, when the sun is modeled as a 6000 K blackbody, and 50.7% under the standard air-mass (AM1.5) terrestrial spectrum.\(^{42,45}\) Briggs et al.\(^{46}\) investigated the effect of narrow-band UC on the efficiency of a solar cell and determined that the addition of an ideal upconverter with absorption bandwidth between 0.1 eV and 0.5 eV should boost the efficiency of a 1.7 eV bandgap cell from 28.2% to between 33.5% and 43.6%.

Among Ln elements, Er and Yb ions are promising candidates for UC solar cells. However, other elements like Tm, Ce and Ho were also reported to be suitable for solar cell applications.\(^{47}\) Er\(^{3+}\) is a favorable ion to

\[\text{Figure 2. (A) Schematic layer arrangement for UC or DC phosphor solar cell, (B) green and red upconversion emission in Er:Yb doped Y\(_2\)V\(_2\)O\(_7\) nanophosphor under 976 nm excitation, (C) red downconversion emission in Eu(DBM)\(_3\)Phen upon excitation with LED (~395 nm), (D) solar and Silicon absorption spectra. Reprinted with permission from [41], B. S. Richards, \textit{Sol. Energy Mater. Sol. Cells} 90, 2329 (2006). © 2006, Elsevier.}\]
study the UC process with NIR and IR lasers (796, 976 and 1550 nm) as it has metastable levels ($^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ near $\sim 12,000$, $\sim 10,000$ and $\sim 6450$ cm$^{-1}$) and so, it offers interesting possibilities of excited-state absorption and cross-relaxation processes. One inherent problem of Lns is the weak absorption, which can be solved by using a sensitizer (with broad emission) or through plasmonic coupling. The absorption cross-section of trivalent erbium ion at 980 nm is of the order of $10^{21}$, while for the $^2F_{5/2} \leftrightarrow ^2F_{7/2}$ transition of Yb is roughly 10 times higher, suggesting that it can act as an effective sensitizer for Er ions and improve absorption at 980. However, the addition of Yb may induce a possible loss mechanism as Si and Yb both absorb around 1000 nm. Several efforts have been made to improve the efficiency by using a more efficient UC material, namely NaYF$_4$ doped with Er and Yb ions. Shalav et al. showed UC under lower excitation density crystalline silicon solar cell with NaYF$_4$ doped with Er and Yb both absorb around 1000 nm. Several efforts have been made to improve the efficiency by using a more efficient UC material, namely NaYF$_4$ doped with Er and Yb ions. Shalav et al. showed UC under lower excitation density crystalline silicon solar cell with NaYF$_4$ doped with Er and Yb both absorb around 1000 nm. Several efforts have been made to improve the efficiency by using a more efficient UC material, namely NaYF$_4$ doped with Er and Yb ions. Shalav et al. showed UC under lower excitation density crystalline silicon solar cell with NaYF$_4$ doped with Er and Yb.

Henke et al. reported improvement in the external quantum efficiency by using Er:Yb codoped ZBLAN glasses subjected to 1540 nm excitation. de Wild et al. investigated $\beta$-NaYF$_4$:Yb$^{3+}$ (18%), Er$^{3+}$ (2%) coated solar cell excited with 980 nm diode (28 mW) and observed a maximum current enhancement of 6.2 $\mu$A, which corresponds to a solar cell external quantum efficiency of 0.03%. It was also verified that broad-band excitation may be more effective because different wavelengths can be simultaneously absorbed and converted. The response of the solar cell due to the upconverted emission of Gd$_3$O$_5$:Er:Yb under broad-band excitation was compared to that of a monochromatic laser light and the responses were about the same, despite the fact that the power density of the laser was three times higher.

Similar to the Er$^{3+}$ ion, Ho$^{3+}$ ion also yields beneficial Vis-NIR emission on excitation with infrared ($\sim 1 \mu$m) radiation. Lin et al. observed the enhancement of NIR emission of Ho:Yb combination in a BaGdF$_4$ host, mainly through second- and first-order energy transfer (ET) processes: $\text{Ho}^3(\text{F}_{5/2}) \rightarrow 2\text{Yb}(\text{F}_{5/2}) + h\nu$, $\text{Ho}(\text{S}_2) + \text{Yb}(\text{F}_{5/2}) \rightarrow \text{Ho} (\text{I}_0) + \text{Yb} (\text{F}_{5/2}) + h\nu$ and the corresponding QE were calculated to be 192%.

Pillai et al. carried out an investigation on the effect of silver nanoparticles on the absorption character of Si and reported that surface plasmons can increase the spectral response of thin-film cells over almost the entire solar spectrum. At wavelengths close to the Si band gap, a significant enhancement of the absorption was observed for both thin-film and wafer-based structures. A seven-fold enhancement was reported for wafer-based cells at $\lambda = 1200$ nm and up to 16-fold enhancement at $\lambda = 1050$ nm for 1.25 $\mu$m thick silicon-on-insulator cells, and the results were compared with a theoretical dipole-waveguide model. An effort to harvest solar radiation using an upconverted plasmonic nanocrystal was made by Atre et al. Numerical calculations revealed a $> 10$-fold absorption enhancement in a broad range of sub-bandgap wavelengths throughout the entire upconverting core and nanocrescent, enabling a 100-fold increase in the above-bandgap power emission.

In contrast to the UC process, where successive absorption of infrared photons results in UV-Vis photons, the DC process converts a UV-blue photon to lower energy photons (down shift) or in two photons by the quantum cutting (QC) process. The latter is a very important process as emission of two visible photons from a single UV photon increases the efficiency of light-emitting devices up to 200%. The mechanism for QC or cascaded emission includes mainly two different processes: simultaneous energy transfer from a donor to two acceptors that equally shares the energy and sequential emission of two photons after the absorption of a UV photon as in the Ln ion. Examples of the first type of QC are Tb:Yb, Bi:Yb, Ce:Yb, Eu$^{2+}$:Yb, VO$_2$ group:Yb$^{3+}$. While for the second type of QC is YF$_3$:Pr$^{3+}$. Another type of QC that includes a two-step energy transfer process was reported in the Gd:Eu system. In this case, a 202 nm photon is absorbed in $^6G_4$ levels of Gd ion and the energy is transferred to Eu ions in two steps, resulting in a bright visible emission. Low energy photons can also be obtained through the process of phonon-assisted energy transfer, as reported for the Eu:Yb codoped system.

For Pr$^{3+}$ ions, the QC occurs from the $^1S_0$ ($\sim 47,000$ cm$^{-1}$) state only when it does not overlap with the $4f5d$ band. The excited Pr ion relaxes to the ground-state through a two-step process: (1) $^1S_0 \rightarrow ^3I_0$, $^3P_J$ ($\sim 400$ nm) and (2) $^3P_0 \rightarrow ^3F_J$, $^3H_J$ (480–700 nm). The QC process is observed in various Pr doped fluoride hosts YF$_3$ (excitation at 185 nm), oxide hosts SrAl$_2$O$_4$:Pr$^{3+}$, LaMgB$_2$O$_4$:Pr$^{3+}$, LaB$_3$O$_6$:Pr$^{3+}$, Kuck et al. investigated different Pr-doped fluoride hosts YF$_3$, LuF$_3$, PrF$_3$, BaMgF$_4$, LiCaAlF$_6$, LiSrAlF$_6$ and KMgF$_3$ which exhibit QC under vacuum ultraviolet synchrotron excitation at $\sim 200$ nm, with a theoretical internal QE higher than 100. However, the application of these materials for lamps is inadequate because the emission occurs at $\sim 405$ nm, where the human eye is not sensitive.

Ikeda et al. investigated the QC in SrAl$_2$O$_4$:Pr for 172 nm excitation and observed two visible photons, one at 401.8 nm and the other at either 486.3, 526.3, 623.7 or 644.6 nm via $^1S_0$ state. Photoluminescence measurements showed that the relative QE of SrAl$_2$O$_4$:Pr to BaMgAl$_2$O$_4$:Eu$^{2+}$ is 38.4%. Lee et al. observed Pr-sensitized QC in K$_2$GdF$_5$:Eu$^{2+}$, Pr$^{3+}$ phosphor through cross-relaxation and direct energy transfer process. It was suggested that due to the increased absorption in the UV and UVC spectral regions, the theoretical QE of K$_2$GdF$_5$:Eu$^{2+}$, Pr$^{3+}$ increases to 138%. Loef et al. discussed a case of visible QC in LiGdF$_4$:Er and Tb. Upon UVC excitation to the $4f^{10}5d$ levels of Er, part of the excitation energy can be transferred to Gd by cross-relaxation, resulting in both Er and Gd in excited-states. This is followed...
by the emission of two visible photons: one from Er and the other from Tb, after the energy transfer from Gd to Tb. Yim et al.\textsuperscript{71} introduced green emitting \( \text{Y}_2\text{SiO}_5\text{:Tb}^{3+} \) nanophosphors into a TiO\textsubscript{2} based dye sensitized solar cell and monitored its performance. \( \text{Y}_2\text{SiO}_5\text{:Tb}^{3+} \) absorbs UV light from 220 to 300 nm which is then downconverted into visible-light at \( \sim 545 \) nm. Recently, Chen et al.\textsuperscript{72} reported QC in Pr/Yb:YF\textsubscript{3} nanocrystals under excitation with 482 nm, which yielded 976 nm through an efficient cooperative energy transfer from Pr to Yb. The optimal QE was found to be around 200%. Dwivedi et al.\textsuperscript{73} observed bright red emission following 266 nm excitation in Pr:Y\textsubscript{2}O\textsubscript{3} nanocrystals with QE greater than 80%.

Recently, Han et al.\textsuperscript{74} observed QC in \( \text{Na}_x\text{Gd}_{1-\text{x}}\text{Y}_2\text{SiO}_5\text{:Tb}^{3+} \) phosphor for 274 nm excitation. QC in Nd:Yb system was also observed by Sun et al.\textsuperscript{75} and Meijer et al.\textsuperscript{76} in CaWO\textsubscript{4}, and YF\textsubscript{3} hosts, respectively. Wegh et al.\textsuperscript{77} studied the visible QC in LiGdF\textsubscript{3}:Eu\textsuperscript{3+} and LiGdF\textsubscript{3}:Er,Tb, whose QC efficiency has found to be 190% and 130%, respectively, when the absorption from other centers than Gd or Er is neglected. Liu et al.\textsuperscript{78} reported a two-step energy transfer QC in BaF\textsubscript{2}:Gd,Eu with visible QE up to 194%. QC process in Tm–Yb doped LaF\textsubscript{3} nanocrystals were observed with 468 nm excitation in Tm\textsuperscript{1G\textsubscript{4}} energy level which results in emission between 950 and 1100 nm from Yb ions. The maximum QE reported was 162% in 0.5Tm–8Yb composition. Deng et al.\textsuperscript{79} demonstrated QC in NaYF\textsubscript{4}:Ho,Yb synthesized by the hydrothermal method. With 359 nm excitation, near-infrared QC could occur through cross-relaxation in a two-step resonance energy transfer from Ho to Yb, with a maximum QE of 155.2%. Yu et al.\textsuperscript{80} observed QC in hexagonal beta-NaYF\textsubscript{4} doped with Ho:Yb by exciting with 300–550 nm, yielding two NIR photons. It was found that NIR-QC can occur via two energy transfer mechanisms: through the simultaneous excitation of two Yb ions via cooperative energy transfer and via resonant energy transfer followed by a sequential \( \text{l}_6 \rightarrow \text{l}_4 \rightarrow \text{l}_6 \) transition in Ho ion. Zhou et al.\textsuperscript{81} observed a three-photon cutting in CaAl\textsubscript{2}O\textsubscript{4} phosphor doped with Yb ions via the energy transfer from Yb\textsuperscript{3+} to Yb\textsuperscript{3+} ions. Chen et al.\textsuperscript{82} reported two-photon QC in Ce\textsuperscript{3+/Yb\textsuperscript{3+}} co-doped borate glasses on 330 nm excitation via energy transfer from Ce\textsuperscript{3+/5d} to Yb\textsuperscript{3+/2F\textsubscript{5/2}} ions. The maximum ET and the corresponding DC efficiencies were estimated to be 74% and 174%, respectively. Near infrared (\( \sim 1000 \) nm) QC was observed in Yb:NaY(WO\textsubscript{4})\textsubscript{2} phosphor by Deng et al.\textsuperscript{83} through cooperative energy transfer in high Yb concentrations (up to 40%). QC in chalcolohide glasses was also reported, occurring from Eu\textsuperscript{2+} to Yb\textsuperscript{3+}.\textsuperscript{84} Detailed information on various upconversion and downconversion materials that can be used for solar cell can be found in Ref. [85].

### 3.2. Light Emitting Diodes

As stated earlier, there may be several possible ways to tackle the interconnected problems of pollution and clean energy production. One is to use efficient renewable energy sources and the other is to make devices more efficient, especially for illumination purposes, where around 20% of the electricity consumed worldwide is used. The global electricity consumption has increased faster than the overall energy consumption because of the versatility nature of its production. The worldwide electricity consumption in 2006 was 16378 TWh, which was 11.8% of the total primary energy consumption. According to the 2009 International Energy Outlook, the world’s total net electricity production in 2030 is expected to increase by 77% compared to the 2006 level.\textsuperscript{86}

Another concern is the bulky, expensive and less efficient conventional illumination sources (lamp, bulb, tube light, etc.) that is also one of the primary domestic pollutant sources as it contains or emits toxic materials like mercury (Hg), sulphur, carbon dioxide (CO\textsubscript{2}) and uranium. The need for efficient, economical and eco-friendly sources brought a surge of research works and the most suitable replacement suggested for conventional illumination sources is the light emitting diode (LED), which is supposed to reduce the consumption up to 70–80% when compared to conventional lamps. According to the researchers of Strategies Unlimited LED Lighting, sales increased from $2.7 billion in 2008 to $9.4 billion last year and the growth is expected to be at a breathtaking annual rate of 20% through 2016. The research group noted that LED lighting products are becoming mainstream in various markets. Frost and Sullivan, a market trends research group, anticipates revenues in the efficient lighting market in Europe to hit just under $2bn by 2018, double the last year’s figure, driven largely by the legislation of the European Commission to rule out various traditional light bulbs.\textsuperscript{87}

The concept of a LED\textsuperscript{88} for general illumination is attractive due to the reliability of solid-state devices, the potential for delivering very high luminous efficiency compared to conventional incandescent and fluorescent sources, long lifetime, vivid color emission, possibility of variable and multihued devices, its compact, environment friendly (mercury free) and designable features. LEDs are subcategorized in three types, inorganic, organic and hybrid LEDs. Recently, Reineke et al.\textsuperscript{89} reported excellent white organic LED, more efficient than fluorescent tube light. However, the performance of organic LEDs is deleteriously affected at high temperature and additionally the materials in an organic LED are sensitive to air and moisture, which leads to their degradation as well as to the quenching of excited-states within the molecule.\textsuperscript{90} As most of the highly fluorescent materials yields poor electroluminescence compared to optical excitation, a concept of hybrid LED coated with yellow organic/inorganic phosphor materials are also mostly acceptable.\textsuperscript{91}
Figure 3. Schematics of layers configuration of an EL cell.

great interest because of their possible applications as low voltage operating large-area light-emitting displays. In general, a thin layer of Ln-complex (amorphous or crystalline) is sandwiched between a hole transport layer and electron transport layer. When an electric field is apply, the generation of light results from the recombination of holes and electrons injected from the electrodes. Such recombination in the emitter layer excites the emitter material. The efficiency can be further improved by blocking electrons and holes from moving into the electrode without recombination.

The problems related to organic LEDs could be overcome up to some extent by using Ln-doped inorganic phosphors, which provide narrower and efficient emission. For single color LEDs, Eu$^{3+}$ (red), Eu$^{2+}$ (blue, yellow), Tb (green), Tm (blue), Dy (yellow), and Ce (blue, yellow) ions complexes are used. Organic molecules that can act as sensitizer for Ln ions are beta-diketone functional groups such as acetylacetone, dibenzoylmethane (DBM), 2-thienyltrifluoroacetone, carboxylic groups such as acetylacetone, dibenzoylmethane (DBM), 2-thienyltrifluoroacetone, carboxylic groups such as o-benzoyl benzoic acid, salicylic acid, o-phthalic acid, organic compounds which have ketone or aldehyde groups adjacent to hydroxy groups, such as salicylaldehyde, o-hydroxycetonephenone or o-hydroxybenzophenone, oxime analogues such as 5-hydroxyquinoline or 5,7-dibromo oxime; pyridine analogues such as 2,2'-dipyridine, 2,2' 2'-tripyridine, 1,10-phenanthroline and cryptates and crown ethers. These ligands can also be combined, using more than one ligand in the same device. Additionally, various semiconductor hosts and inorganic nanophosphors are also considered for LED applications. Recently, gallium nitride based devices, co-doped with Eu and Mg, showed luminescence efficiency as high as 77%. Mg doping selectively enhances a specific emission site and increases emission intensity at least by one order, suggesting that Eu and Mg doped GaN may be used for new devices. However, for general household lighting purposes mostly white light is desired.

In practice, a blue emitting GaInN LED chip was coated with Yttrium Aluminum Garnet (YAG) doped with Cerium, absorbing blue emission from the LED and yielding yellow emission, which apparently looks white to the eye. However, the concept of yellow and blue mixing may not be so good because it has a few disadvantages, such as poor color rendering index (CRI) property, blue/yellow color separation and lacking of red component in the spectrum of this kind of LED. This problem can be solved to some extent by co-doping with Gd ion along with Ce, which causes a shift in yellow–orange range.

Divalent Eu ion usually yields blue emission but it can also be tuned in a wide range of green, yellow and red regions, as well. Park et al. reported bright green emission in (Ba$_3$Cu$_{3-x}$Eu$_x$)$_2$SiO$_4$ phosphor. Xiea et al. found a bright yellow emission in Eu doped oxynitride phosphor $a$-SiAlON. Due to the formation of Eu$^{2+}$ ions, light is efficiently absorbed in the UV-visible spectral region and results in a single intense broadband emission at 583–603 nm, which is used to create white light with 450 nm LED excitation. Kuo et al. reported a red phosphor, CaZnOS:Eu$^{2+}$, which has a broad absorption band in the 450–550 nm region and emits ~600–700 nm. This phosphor was combined with green ((Ba,Sr)$_2$SiO$_4$:Eu$^{2+}$) and yellow (YAG:Ce) emitting phosphors to produce white light. Similarly, broad red emission was also observed in Sr$_2$Si$_3$N$_8$:Eu$^{2+}$, CaAlSiN$_3$:Eu$^{2+}$, while white light emission was reported for single crystalline Ca$_3$Ga$_5$(PO$_4$)$_3$:Eu$^{2+}$, Mn$^{2+}$ phosphor, which exhibits a broad blue–green emission band at 490 nm and a red emission band at 645 nm, originating from the Eu$^{2+}$ and Mn$^{2+}$ ions, respectively. When Sr$_3$SiO$_5$:Ce$^{3+}$, Li$^+$ and high quality TOP/TOPO/HDA-capped CdSe quantum dots (QDs) were coated on a blue LED chip, white LEDs with an excellent color rendering property were obtained. The white LEDs exhibited a luminous efficiency of 14.0 L mW$^{-1}$, $R_g$ ~ 90.1, and $T_r$ ~ 8864 K, which is acceptable for general lighting, indicating that the combination of phosphor and QDs in LEDs can be a good solution to produce white light sources with high color rendering properties. Kim et al fabricated a GaN-LED using a mixture of Ba$_3$Mg$_2$O$_{12}$:Eu$^{2+}$ and Sr$_3$SiO$_4$:Eu$^{2+}$ phosphors which yielded a broadband spectrum, higher color rendering index and higher color stability against forward bias currents than Y$_2$Al$_3$O$_ {12}$:Ce$^{3+}$-based white LEDs. Li et al. synthesized a new material, MSi$_2$O$_{2-x}$N$_ {2/3+3/4}$:Eu$^{2+}$ (M = Ca, Sr, Ba), which yielded blue–green emission at 490–500 nm for BaSi$_2$O$_ {2-x}$N$_ {2/3+3/4}$:Eu$^{2+}$, yellow emission at 560 nm for CaSi$_2$O$_ {2-x}$N$_ {2/3+3/4}$:Eu$^{2+}$ (x ~ 0) and a green-yellow emission peaking from 530 to 570 nm for Sr$_3$SiO$_ {2-x}$N$_ {2/3+3/4}$:Eu$^{2+}$ (x ~ 1), being the maximum dependent on the exact value of x. BaSi$_2$O$_ {2-x}$N$_ {2/3+3/4}$:Eu$^{2+}$ is the most promising conversion phosphor for white-light LEDs due to its high conversion efficiency for blue light from InGaN-based LEDs related to its very small Stokes shift. White light was also reported from the combination of complementary colors in Dy doped SrSiO$_3$ long-lasting phosphor which yielded two emissions at 480 nm and 590 nm.

Figure 3. Schematics of layers configuration of an EL cell.
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572 nm. White light was also simulated by RGB color mixing in TmErYb, TmHoYb, PrErYb (Fig. 4). However, the suitability of these materials still needs to be tested in real devices.

4. SENSORS
It has been previously recognized that since Ln complexes exhibit characteristically narrow excitation and emission bands, intense fluorescence and long excited-state lifetimes, they are suitable to be used as chemical sensors. Ln exhibits intra-configuration optical transitions and just a few of them, known as hypersensitive, are susceptible enough for environment sensing. However, in addition to them, paramagnetic Ln elements have a large number of degenerate energy levels and are sensitive to a variety of metal ions, anions, humidity, hydrogen peroxide, magnetic field, pH and various gases like NH₃ and O₂. Readers are referred to Ref. [111] for more detailed information.

4.1. Gas Sensor
As mentioned earlier, Ln elements possess a small absorption cross-section and to improve their sensitivities, sensitizer ligand molecules are usually employed. It is interesting to note that the coordination number of Ln is > 6, providing enough sites to accommodate both the sensitizer ligand and the analyte in their inner coordination sphere. Two types of coordination ligand are in practices: (1) saturated (Caged complex, cyclohexane complex, helicate etc.) and (2) unsaturated ligands (Beta-Diketonate complex, triprode complex, porphyrinate complex, oligopyridinedicarboxylate complex, dendrimer complex etc.). The saturated sensitizer ligand provides an additional advantage for shielding Ln ions from ambient hydroxyl-like solvent molecules that would otherwise quench the Ln luminescence and are used for the labeling of biological proteins and DNA molecules. However, for sensing purposes, the ligand should be sufficiently nearby to the emissive site to permit efficient energy transfer, besides containing vacant sites for the guest ion. The complexes of Eu³⁺ and Tb³⁺ exhibit red and green luminescence, while Nd³⁺ and Yb³⁺ complexes provide NIR emission. They are highly luminescent and desirable for in vitro and in vivo analyses. The long-lived energy levels of Ln also offer an advantage over shorter lived background emission (auto-fluorescence) and light scattering from biological environments.

Ln ions probe some of the toxic gases as soman, which was reported to be used in wars. It should be noted that one of the serious threats of chemical warfare is the use of nerve agents that causes rapid and severe effects on humans. Basically, these nerve agents are made of organophosphates that stops the function of the acetylcholinesterase enzyme, leading to various organ failures. Ln has the property of linking to organophosphate and helps to detect the nerve agent. Detection of nerve agents are based on variations of the fluorescence intensity upon complexation to Ln (Eu and Tb) ions (Fig. 5). Comparing the fluorescence intensity of free ligand and complex, the chemical agent can be detected. By tailoring the nature of the metal-ligand interactions, it is possible to enhance the sensitivity of such systems and improve their selectivity towards different analytes. Another advantage of Ln sensors is its exceptional selectivity to other chemical compounds like ester, ketones, etc.

Knapton et al. reported Mebip-functionalized ethynylene derivatives for the detection of organophosphate and demonstrated the ability of readily controlling the extent to which the fluorescence of the Mebip ligands changes upon metal binding. It was observed that upon binding with La³⁺, the emission spectrum of the ligand experiences a significant bathochromic shift (Δmax = 73 nm, emission color change from blue to green and the fluorescence intensity is significantly decreased).

Tremblay et al. proposed a general strategy for the rational design of ratiometric, luminescent probes based on a heterometallic bislanthanide (Eu³⁺ and Tb³⁺ or Dy³⁺) platform. The relative emission intensities can be tuned by adjusting the stoichiometry and since the luminescence is sensitized by a single antenna, changes in its electronic structure can manifest themselves as changes in the relative ratio of luminescence from each metal. Jenkins et al. reported a fluorescence based fiber optic probe for organophosphates, using a supramolecular complex up to
the detection limit of 660 ppq. They used a molecularly imprinted polymer sensor of \([\text{Eu-}(\text{dvmb})_3(pmp)(\text{NO}_3)_2]\), a Eu\(^{3+}\) complex with three different ligands. Although the response of this sensor is limited by analyte diffusion, the sensitivity is high enough for precise detection even in the presence of chemically similar organophosphates.

Eu complex coated tiny silica particle shows instantaneous and significant color change, from pink to blue, on exposure to liquid and vapor (for 2 h at 60 °C) triethyl phosphate. Another approach for detection is by using an enzyme as the binding motif in presence of Au-NPs. This concept is based on the variation of the fluorescence intensity of Ln ions with the relative distance to the metal NPs owing to changes of the field near the Ln ion. Detachment of NPs from Ln complex occurs in the presence of a weakly bound phosphate derivative, fluorophore, to the enzyme which is, by its turn, covalently attached to gold nanoparticles. Separation of the metal NP from the complex reduces the emission intensity of the Ln complex. This displacement occurs through the competitive binding with an analyte that has a higher binding affinity to the enzyme than the phosphate derivative. Simonian et al.\(^{119}\) reported organophosphorus hydrolase as the receptor for organophosphorus analytes.

Koshizaki and Oyama\(^{120}\) investigated the selective enhancement of NO\(_3\) against NO sensing by rare earth element doping. Er-doped ZnO film exhibited good sensitivity in the sub-ppm concentration range, good selectivity and fast response time to NO above 200 °C.

An amount of H\(_2\)S gas over > 250 ppm is known to be a potentially hazardous gas for the health. Hence, it is necessary to determine H\(_2\)S quantitatively, especially at the coal oil or natural gas manufacturing site or laboratories. Zhong et al.\(^{121}\) reported a novel Ln (Eu, Gd, Ho)\(_{1-x}\)In\(_x\)O\(_3\) gas sensor and found that 5 wt.% Ho\(^{3+}\)–In\(_x\)O\(_3\) sensor exhibited the highest response value, excellent selectivity and quick responsive for H\(_2\)S gas in the range from 1–100 ppm. Li et al.\(^{122}\) studied a simple and effective solvent swelling method to prepare PMMA/Eu complex hybrid nano-spheres (100–200 nm). These luminescent nano-spheres show high sensitivity in the luminescence sensing of hydrogen peroxide in a broad linear concentration range.

Tsang and Bulppt\(^{123}\) reported superior performance of rare earth oxides over tin oxide-based ethanol sensors. They proposed that adsorbed oxygen of strong basicity can facilitate the oxidative dehydrogenation of ethanol, with the intermediate acetaldehyde giving a high molecular response. They further investigated a different sensing mechanism in the case of Pr oxide-based sensor, where their labile lattice oxygen is active for ethanol oxidation even at low temperatures (≥ 150 °C). The electron hopping sites associated to the mixed valence cations are partially destroyed in a stream of ethanol vapor, causing an increase in the electrical resistance. Upon removal of ethanol, molecular oxygen in air replenishes the vacant oxygen sites, reverting sensor to its initial resistance value. The lattice oxygen can be tuned to react only with ethanol but not with n-butane at or below 300 °C, achieving 100% selectivity. This mechanism can selectively transduce the ethanol concentration into an electrical signal. Niu et al.\(^{124}\) reported nanometer materials of REFeO\(_3\) (RE = Eu, Gd) which were sensitive to C\(_2\)H\(_5\)OH, H\(_2\)S, gasoline and H\(_2\). The studies of gas-sensing characteristics show the sensitivities of EuFeO\(_3\) (20 nm) and GdFeO\(_3\) (21 nm) nanometer materials to gasoline are 39 and 45 ppm at 340 °C, respectively, and both have the appropriate selectivity. Aono et al.\(^{125}\) accounted for NO\(_2\) sensing using SmFeO\(_3\) and REFeO\(_3\) (Re = La, Nd, Sm, Gd, and Dy) materials.

### 4.2. Ion, pH and Hydrocarbon Sensors

Ln based sensors were studied for the detection of metal cations, organic and inorganic anions, small neutral molecules in solution and various volatile organic chemicals detection. The use of encapsulated Ln as sensitized photoactive centers capable of analyte binding has emerged as a compelling strategy for luminescent supramolecular sensor development.\(^{126}\) They utilize the large absorption cross-sections of selected organic molecules and the long lifetime and sharp emission characteristics of Ln ions to generate very efficient molecular...
devices. One of the major constituents of our environmental system, Nitrogen, is generally not considered toxic for living bodies though its metabolites may be carcinogens. However, the use in large scale of nitrogen- and phosphorus-based fertilizers in the agriculture sector may pollute the soil, wastewater and ultimately food, via plants. The detection of excess amounts of nitrates generally is based on the ion exchange principle. It is known that counter ions can coordinate to Ln ions in unsaturated ligands to fulfill the coordination requirements for Ln ions. Generally, there are two ways of modulating the emission property of Ln complexes by anions. First, water molecules bound to the Ln center should be displace by anions, leading to an enhanced luminescence intensity and second is the displacement of ligands by anions resulting in the increase or decrease of the luminescent intensity. Ln based anions detection can be possible by the careful design of antenna ligands that leave some coordinate vacancy for anion binding to Ln. In general three design strategies are considered to sense anions (1) supramolecular recognition, such as hydrogen bonding interactions, (2) Lewis acid–base interactions, and (3) anion ion-induced chemical reactions.

Yang et al. reported an efficient long fluorescence lifetime polymer-based sensor based on Eu(TTA), vinylphen complex [TTA := thiophenylfluoracetone; Phen = phenanthroline] as chromophore for the specific detection of F-, CH₃COO⁻, and H₂PO₄⁻ in DMSO solution. On binding to F-, CH₃COO⁻, and H₂PO₄⁻ fluorescence of Eu-polymer quenched by an approximately 95% due to strong hydrogen bonding interaction and deprotonation interaction at high concentration for F-, due to which Eu-polymer sensor selectively sense F⁻ even in the presence of CH₃COO⁻ and H₂PO₄⁻.

Douce et al. synthesized the Eu complex of bis-bipyridinephosphine oxide and reported an increase in luminescence yield and lifetime due to the anion binding. The authors concluded that this new system is applicable to other molecules because it allows detection of traces of halides and nitrates by luminescence monitoring of the Eu center, whose long excited-state lifetime allows the enhancement of the signal-to-noise ratio with the use of time-resolved spectroscopy. Santos et al. investigated interesting anion-sensing with cyclen Ln complexes which recognize CH₃COO⁻ and H₂PO₄⁻ through hydrogen bonding interactions and potential metal ion coordination to Tb³⁺ ion. Zhang et al. synthesized Eu(DBM),DPPZ (DBM = dibenzoylmethane, DPPZ = dipirido[3,2-x:2,3′-c]phenazine), which was found to be efficient to recognize AcO⁻ ions over other anions due to the replacement of DPPZ by AcO⁻. The output of a sharp characteristic Eu³⁺ emission is read as “0” only in the absence of AcO⁻ ion under oxygen atmosphere. Optical sensing of Cl⁻ and NO₃⁻ anions were reported in Eu and Tb complexes with tetradentate tripodes. Parker et al. reported the emission intensity variation of Eu ions as a function of halide ions (Cl, Br, I) in aqueous solution of Eu-octadentate monoamindetriphosphinate or chiral tetraamid complex, which was attributed to the competition between the excited-state quenching rate of the chromophore and the rate of intersystem crossing from triplet state of the chromophore to the 4f level of Eu ion. Faulkner et al. showed the selective stabilization of a more luminescent bound form to give an intense near-infrared Yb³⁺ luminescence on addition of SCN⁻ ion in a dendrimer complex. Wang et al. found that the phenanthroline-based imidazolate Eu or Tb-complexes can efficiently detect different anions (F⁻, CH₃COO⁻, and H₂PO₄⁻) through hydrogen bonding interaction. Parker et al. reported on heptadentate cyclen ligands for Ln ions that selectively bind bidentates such as HCO₃⁻ and carboxylate anions and found greater dynamic displacement of the coordinated water molecules by the guest anions than octadentate cyclen complexes. Distinctive anion-selective (NO₃⁻ and Cl⁻) luminescence enhancement was demonstrated by Kataoka et al. in different Eu-tripodes complexes bearing quinoline chromophores.

Ln ions, Eu:Tb ions dispersed in a polymer hybrid and doped with a proton-sensitive amide-type beta-diketonated photosensitizer, N-(2-pyridinyl)benzoylacetamide was shown to be highly luminescence sensitive to OH⁻ concentrations, thus representing a new paradigm for full color displays.

Various cations sensors were developed for selective detection of alkaline and alkaline earth metals (Li, Na, K, Zn, Ca, Mg) that are necessary to monitor and regulate a number of cellular functions and heavy metal cations (Pb, Cu, Hg) for biomedical purposes. It is interesting to know that bound Cu²⁺ plays a vital role in many enzymatic processes, while free Cu²⁺ can disrupt and damage various biological processes, causing several conditions such as Wilson and Menkes diseases. Similarly, Hg²⁺ is toxic to humans and can accumulate in the blood-brain barrier, resulting in severe neurological disorders. Lead is also a cumulative poison, with fetuses, infants, and pregnant women being the most susceptible to adverse health effects, especially in the central nervous system. Evident signs of acute intoxication include dullness, restlessness, irritability, poor attention, headaches, muscle tremor, hallucinations and loss of memory. In addition, there are several other environmental concerns regarding cations. The emission intensity of Eu ions is enhanced after the addition of alkali metal ions (Na⁺, K⁺) by at least one order of magnitude in Ln ion azacrown molecular complex due to the suppression of electron transfer from the nitrogen atom of azacrown to excited Eu ion. Nevertheless, this result was analogous to the case of Tb-complex, which is thought to be due to the existence of additional relaxation nonradiative pathways for Tb³⁺.

A Tb³⁺-cycloexdextrin-based sensor was proposed for the pH independent, selective detection of Cu²⁺ and Hg²⁺ ions in water. The changes in the Tb³⁺ emission were monitored...
by carrying out metal titrations which quenches Tb emission by ca. 65% (Cu) and 40% (Hg).145 Plush and Gunnlaugsson146 designed and synthesized a novel stable dinuclear Eu conjugate by tethering a mono-aza-18-crown-6-ether moiety to a cyclen macrocycle. The analysis of this conjugate showed that anions such as acetate and L-aspartate give rise to quenching of the Eu\(^{3+}\) emission, while malonate give rise to large luminescent enhancements, where the largest changes were seen in the hyper-sensitive transition.

Hanaoka et al.147 reported the design and synthesis of a novel Ln sensor molecule, using the quinolyl ligand, to detect Zn\(^{2+}\) ions. Upon the addition of Zn\(^{2+}\) to a solution of Eu complex, the luminescence of Eu\(^{3+}\) is strongly enhanced, with high selectivity for Zn\(^{2+}\) over other biologically relevant metal cations. One of the important advantages of this complex is that it can be excited with longer excitation wavelengths (~340 nm) as compared with previously reported Zn\(^{2+}\)-sensitive luminescent Ln sensors, whose excitation wavelength is at too high an energy level for biological applications. This complex was claimed as the first Zn\(^{2+}\) sensitive Ln chemosensor that can be used for studies of the biological functions of Zn\(^{2+}\) and the design strategy should yield a range of long-lived Ln probes for sensing Zn\(^{2+}\) or, after appropriate modification of the acceptor moiety, other molecules of interest in biological applications.

Charbonniere et al.148 observed the increase of the Eu complex luminescence lifetime (combining a hard donor with two soft pyridine donors) upon the addition of ATP, whereas ADP and AMP did not induce significant changes. Ln ions in liquid chromatography149 can also serve the purpose of detection of single stranded nucleic acids,150 hormones,151 amino compounds152 and labeled thiols.153

Determining the fluorescence pH probe molecules for imaging purposes in living cells is one of the very important aspects as minor variations of intracellular pH may induce cellular dysfunction, desirable pH fluorescent probes should be able to respond sensitively to a minor change of pH, and to avoid interference from native cellular species. Liu et al.154 discuss time-resolved luminescence bioassay technique using highly stable Europium and terbium (4-hydroxy-2,2′:6′,2″-terpyridine-6,6″-diyl) bis(methyleneiminililo) tetrakis(acetic acid) (HTTA) complexes as luminescent probes/sensors. It was reported that the HTTA–Eu\(^{3+}\) is strongly dependent on the pH values in weakly acidic to neutral media (\(pK_a = 5.8, \ pH \ 4.8–7.5\)), while that of HTTA–Tb\(^{3+}\) is pH-independent. Using the intensity ratio of Tb\(^{3+}\) emission at 540 nm to its Eu\(^{3+}\) emission at 610 nm in HTTA–Eu\(^{3+}\)/Tb\(^{3+}\) mixture the UV absorption spectrum changes at different pHs (pH 4.0–7.0) also display a ratiometric response to the pH changes with the ratio of absorbance at 290 nm to that at 325 nm. Zhag et al.155 synthesized new complexes Eu(TTA)\(_3\)/DSQ and Eu(TTA)\(_3\)/DR1 (HDSQ = 5-(dimethylamino)-N-(4-(2-((8-hydroxyquinolin-2-yl)methylene)hydrazinecarbonyl)phenyl)naphthalene-1-sulfonamide, DR1 = N\(^3\)-(4-(dimethylamino)-benzylidene)-N\(^3\)-(rhodamine-6G) lactamethylene-diamine). These pH-sensitive emitter components have \(pK_a\) values of 5.0 and 7.2 respectively. Eu(TTA)\(_3\)/DR1 was able to detect pH values at both near neutral pH and acidic pH ranges, and was also able to detect pH in both cultured cells and in vivo.

Ln ions are also used for protein labeling, specifically metalloproteins which are reported to form stable Ln complexes. Two of the natural occurring proteins, transferrin and lactoferrin, contain a Fe\(^{3+}\) metal center. It is interesting to note that two bound Fe\(^{3+}\) cations are released from lactoferrin at pH 2.5–4.0 while transferrin loses Fe\(^{3+}\) cations at pH 4.0–6.0, which are substituted by Ln ions, thus forming an emissive complex.156 Another protein, apoferritin, is reported to form complex with Tb ions157 and make the Tb luminescence longer. Kataoka et al.158 reported pH-dependent Tb luminescence in proteins apolactoferrin and apotransferrin.

Since hydrocarbons do not coordinate to Ln ions, a rather different technique is needed to detect them. In this case, two different ligands are used, one for the Ln ion (aza crown) and the other for the hydrocarbon (functionalized cyclodextrin).159 Mortekkari et al.160 introduced a tri-ionic diethylentriaminepentaaacetate to the Tb-cyclodextrin complex to improve the strength of aromatic hydrocarbon binding and reported effective sensitivity of such complex towards hydrocarbon. The detection of protease inhibitors is very important due to its application in curing different diseases (cancer, AIDS, inflammatory disorders, etc.). Karvinen et al.161,162 reported a protease assay based on a complicated time-resolved fluorescence resonance energy transfer (TR-FRET). Mizukami et al.163 developed a novel luminogenic Tb probe for detecting protease activities.

4.3. Magnetic Field Sensor

Magnetic field sensing is one of the requirements in the fields of navigation, vehicle detection, current sensing, and spatial and geophysical research. Optical magnetic field sensors are desirable because of their immunity to electromagnetic interference, low weight, small size and long-distance signal transmission for remote operation. The well-known Faraday effect rotates the plane of polarization of an optical wave in the presence of an external magnetic field and hence it can be used for magnetic sensing.164 Optical current/magnetic-field sensors based on the Faraday effect offer the advantages of simplicity and high electrical insulation. Optical magnetic-field sensors based on rare earth iron garnets, such as Y\(_3\)Fe\(_5\)O\(_{12}\) and Gd\(_2\)BiFe\(_3\)O\(_{12}\), have an extremely large Verdet constant, which characterizes the Faraday effect, yielding higher sensitivity, frequency response, temperature characteristics and domain effects than sensors based on diamagnetic and paramagnetic materials.165
The Faraday effect of rare-earth-containing oxide, fluoride and oxyfluoride glasses has been well discussed. It is known that trivalent Ce, Pr, Tb, Dy and divalent Eu result in large Verdet constants in the visible range. Tanaka et al. measured the Faraday effect and optical absorption of Pr-containing lithium borate glasses and reported large magneto-optical figures of merit in the visible range. In particular, 25Pr₂O₃–75B₂O₃ and 20Pr₂O₃–5Li₂O–75B₂O₃ glasses exhibit figures of merit larger than 250 °/μm at 400 nm under an external magnetic field of 15 kOe. Therefore, these glasses are promising materials for use as an optical isolator for the (Ga,In)N laser diode with the emission wavelength of 400 nm. Itoh et al. developed a 5 mm wide optical magnetic-field sensor based on the novel Bi₅o.89Ga₆o.11Laₐ,o3Y₁,o7Fe₄.72Ga₉o.₂₈O₃₂ garnet, that demonstrated high accuracy with ±1.0% error and shows high temperature stability for sensitivity of less than 2.0% from 20 to +80 °C. Potter and Sinclair review two inorganic materials classes used for optical sensors: photosensitive glasses and rare-earth doped materials. The discussion on rare-earth doped optical sensor materials emphasizes the important contribution of the host material to the observed optical behavior of rare-earth ions. The use of rare-earth doped materials in applications ranging from temperature sensing to fiber-optic gyroscopes is also described. Sun et al. accounted for a 2 cm long of 56 wt% terbium doped silicate fiber as a Faraday rotator, with a Verdet constant of −24.5 rad/Tm at 1053 nm. The sensor had a sensitivity of 0.49 rad/T and can measure magnetic fields from 0.02 to 3.2 T. The highest Faraday rotation in the visible spectral regimes was obtained in the composite film (BiDy)₃(FeGa)₅O₁₂:Bi₂O₃ with values 10°/μm, 2.6°/μm, and 1.9°/μm for wavelengths 532, 635 and 670 nm, respectively. In this composite film, it was demonstrated that as the wavelength of the incident light increases, the Faraday rotation decreases. Similarly, at the telecommunication wavelength of 1.55 μm, the Faraday rotation measured in CeYIG:Co-doped CeO₂₈ films, CeFeO₃ films, YbIG, Sc doped EuIG, scandium substituted EuIG films were found to be 0.44, 0.60, 0.60−0.0420, −0.0450 and −0.0500 deg/μm, respectively. Sekhar et al. measured the Faraday rotation in Bi₅Ce₁₋ₓFe₅O₁₂ films prepared by pulsed laser deposition and found 1.6 and 50 times larger than that of CeYIG and YIG, respectively.

5. TELECOMMUNICATIONS

Nowadays, probably the most important commercial products are television, internet and communication systems. In these systems, the signal transmission is carried out through an optical fiber. Long-distance data transport was a challenge and witnessed a series of developments starting from optical fiber transmission at low attenuation to the now fourth generation data transmission of 14 tera bit per second at 160 km. The future of fiber optics relies on transmitting signals over a larger bandwidth, with minimum attenuation. Optical fibers work in the condition of total internal reflection, where the electromagnetic wave is reflected when passing from a higher index materials to a lower refractive index material above the critical angle. Fibers can be made of glasses or polymers (PMMA, polystyrene, etc.), but for long distance data transmission, silica fibers are used because they are more transparent in the NIR region. The signal amplitude at the receiver depends on several factors, but the two most important factors are attenuation and dispersion. The signal attenuation is due to absorption and scattering. Optical fiber for communications typically operates in several electromagnetic spectral windows, as given in Table I. Evidently, the transparency at long wavelengths is limited by the infrared vibrational or multiphonon absorption edge, which is determined by the frequency of the fundamental lattice vibration, as shown in Figure 6.

The dispersion, which produces a pulse spreading, accounts for the fact that different wavelengths travel with different speeds in a dispersive medium, being inversely proportional to the bandwidth. Several fibers were studied with this respect: polymer fibers, quantum dot dispersed fiber and micro-structured fibers.

Among oxide glasses, silica offers the advantages of the smallest amount of absorption at ~1550 nm (losses ~0.2 dB/km) and highest bandwidth and as a result, it is the choice for long distance communications purpose, while still, polymer fibers can be used for short distance (~≤500 m) applications. To improve the signal quality at the receiver, repeaters can be used to convert the optical into electronic signal, amplify it and re-transmit in the form of an optical signal at higher intensity. However, the use of repeaters decreases the transmission rate and is expensive.

<table>
<thead>
<tr>
<th>Window</th>
<th>Range (nm)</th>
<th>Transmission</th>
<th>Ln element</th>
</tr>
</thead>
<tbody>
<tr>
<td>First window</td>
<td>~800–900</td>
<td>Due to high losses use for short distance communication only.</td>
<td>Tm, Er</td>
</tr>
<tr>
<td>Original (O) band</td>
<td>~1260–1360</td>
<td>Region of almost zero dispersion.</td>
<td>Pr, Nd, Dy</td>
</tr>
<tr>
<td>Extended (E) band</td>
<td>~1360–1460</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Short (S) band</td>
<td>~1460–1530</td>
<td>Lower silica absorption, some dispersion, long range communication</td>
<td>Tm</td>
</tr>
<tr>
<td>Conventional (C) band</td>
<td>~1530–1565</td>
<td></td>
<td>Er</td>
</tr>
<tr>
<td>Longer (L) band</td>
<td>~1565–1625</td>
<td></td>
<td>Pr, Pr:Er, Er:Yb</td>
</tr>
<tr>
<td>Ultra (U) band</td>
<td>~1625–1675</td>
<td></td>
<td>Ho</td>
</tr>
</tbody>
</table>
The preferable solution to this problem is to use an optical amplifier (OPAM) that is much faster as it directly amplifies the signal via stimulated emission. Up to now, several optical amplifiers are used, including Raman, semiconductor, optical parametric, Ln based amplifiers and so on. The performance of optical amplifiers is affected by many factors such as optical amplifying gain and noise figure, that are related to the gain medium parameters (geometry, compositions of gain materials, etc.), working conditions, pumping method wavelength and power of the input signal. In general, Ln:OPAM possesses some advantages over other OPAM because it is transparent to bit rates and transmission formats, and allows simultaneous amplification of a large number of channel wavelengths. The gain of RE doped fiber amplifiers is insensitive to polarization because the active dipoles are randomly oriented in the glass matrix and are stable over a 100 °C temperature range due to the homogeneous line broadening. Owing to the relatively long upper level lifetime, the gain is nearly immune to the interference between light channels and noise figures close to the theoretical limit of 3 dB can be achieved. Ln fiber amplifiers are compatible with transmission fibers and other fiber components and when compared to Raman amplifiers it requires less laser power. In Ln, optical amplification is achieved by the process of stimulated emission after a high power pump excites the Ln ion to an excited energy level. Energy levels of different telecommunication important Ln ions are given in Figure 7.

The excited ions are distributed in diverse levels possessing long and different lifetimes. When the energy of a given frequency signal matches the energy of an excited level, the ions get depopulated by emitting an additional photon of same phase, direction and frequency of the signal. In this way, the signal in the fiber is strongly amplified in the propagation direction. Other options of amplifying media are disperse Ln ions encapsulated by sensitizer ligands (in a polymer matrix) and quantum dots of Ln elements in fibers. The use of sensitizer ligands presents three important advantages that include the increased solubility of Ln ions (to avoid aggregation) in polymer matrix, the sensitization for Ln ions and the shielding from vibrations of the host matrix. Several Ln ions are considered as potential candidates for optical amplifier, but just a few are in use. Currently, OPAM are mainly based on Er³⁺ (~1550 nm) and Pr³⁺ (~1330 nm). There is, however, great interest in developing efficient OPAMs with other Ln ions in order to achieve amplification in all windows. An inherent problem with Ln:OPAM is the concentration quenching (>5 ppm) occurring because of clustering that deleteriously affects the gain. To circumvent this problem, Ln:OPAM fibers are usually made longer and with lower concentrations. Other drawbacks are the noise induced by the amplified spontaneous emission (ASE) and gain saturation. Readers are suggested to read Ref. [179] for more details.

The first communication window (800–900 nm) is used for short distance signal distribution and local area network. Among the Lns, only Er³⁺ and Tm³⁺ ions provide efficient amplification in this band through their °S_{1/2} to °S_{1/2} and °F_{j} to °H_{k} transitions, respectively. However, only a few reports are available for this band.
ion not only provides amplification at 800 nm but also at 1470 and 1900 nm.\textsuperscript{180} Dye et al.\textsuperscript{181} reported the first engineered 800 nm Tm:OPAM using two pump lasers of a single wavelength (780 nm), which was further modified by Akasaka et al.\textsuperscript{182} They demonstrated a Tm-doped optical amplifier with 30 dB gain at the 850 nm window using a special fiber subjected to excitation with 690 and 1400 nm. Watekar et al.\textsuperscript{183} reported a simulation model and the experimental realization of a novel single-mode Tm-doped silica glass optical fiber amplifier optimized for the 800 nm window and a gain of about 11 dB at 840 nm was obtained upon pumping with a 1064 nm Nd-YAG laser source. Whitley et al.\textsuperscript{184} demonstrated an Er-doped fluorozirconate fiber amplifier providing over 20 dB of small signal gain at 850 nm by pumping with 801 nm. Gonzalez et al.\textsuperscript{185} reported optical gains of 1.33 cm\(^{-1}\) (5.7 dB/cm) and 0.63 cm\(^{-1}\) (2.73 dB/cm) for the 0.25 and 0.5 mol% Er-doped fluorindate glass samples at 840 nm.

The second and third windows (O and E band) lie in range from 1260 to 1460 nm, where at least three Ln ions, Nd, Dy and Pr, can be used. The Nd-doped OPAM was first discussed by Koestner and Snitzer.\textsuperscript{186} It works over the range 1310–1360 nm and 1360–1400 nm in ZBLAN and silica glass, respectively, on excitation with 795 and 810 nm radiations.\textsuperscript{187} Nevertheless, the quantum efficiency is very low, leading to a small gain that makes Nd:OPAM inappropriate as an amplifier. The low efficiency of Nd:OPAM is due to losses by excited-state absorption and amplified spontaneous emission that reduce the overall gain. ASE arises due to the low branching ratio of the 1.3 \(\mu\)m transition, with two competing transitions, at 0.9 \(\mu\)m and 1.06 \(\mu\)m, both having much higher branching ratios. Similar to Nd ions, the Dy ion also suffers from nonradiative decay processes and hence, the quantum efficiency at the 1300 nm transition of \(^{2}H_{9/2} \rightarrow ^{6}F_{3/2}\) to \(^{2}H_{15/2}\) varies from 1.5% in oxide\textsuperscript{188} to 19% in sulphide\textsuperscript{189} and 90% in selenide glass.\textsuperscript{190}

Pr is the preferred dopant choice as it provides efficient amplification at 1300 nm due to the radiative transition from the metastable \(^{3}G_{4}\) to the \(^{3}H_{5}\) state. However, the gain in Pr:OPAM is deleteriously affected by the small energy separation (\(\sim 3000\) cm\(^{-1}\)) between \(^{3}G_{4}\) and \(^{3}F_{3}\) levels. This promotes a non-radiative relaxation that leads to the reduction of the radiative lifetime of the \(^{3}H_{5}\) state, ultimately affecting both gain and efficiency of the OPAM. In the presence of high frequency vibrational groups in the host, such as B–O (\(\sim 1400\) cm\(^{-1}\)), P–O (\(\sim 1200\) cm\(^{-1}\)), Si–O (\(\sim 1100\) cm\(^{-1}\)), –OH (\(\sim 3600\) cm\(^{-1}\)), –CO (\(\sim 1100\) cm\(^{-1}\)), C–H (\(\sim 3000\) cm\(^{-1}\)) and N–H (\(\sim 3300\) cm\(^{-1}\)), the probability of nonradiative relaxation increases due to the emission of phonons and thus, efforts were made to select lower phonon vibration hosts. This is the big hurdle in the development of OPAMs for O and E band. In silica glass (1200 cm\(^{-1}\)), the QE at 1300 nm is <1% while in fluorozirconate ZBLAN glass (580 cm\(^{-1}\)) it is \(\sim 4\%\).

6. CONCLUDING REMARKS
Rare earth (or Ln) elements have unique optical and chemical properties which make them most appropriate non-isotopic alternative to organics. The exploitation of
their multifunctional properties brings new energy efficient devices. In this review article we tried to give insights of Ln spectroscopy applications in at least three frontline research topics, namely clean energy, sensors and telecommunications. These fields are supposed to be frontline topics as they not only cover huge commercial aspect but also make human life easier and comfortable. We have tried to give a glimpse of these developments in the context of optical techniques.

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