Chapter

Rare Earth Elements in New Advanced Engineering Applications

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Abstract

From an engineering approach, rare earth elements (REE) have the extra potential to modify modern engineering in an extraordinary way. Their peculiar optical, mechanical, electronic, and magnetic properties have been used for years and even open up wider possibilities for using rare earth elements. With advances in all fields of engineering, it is predictable that the rare earth elements will play a crucial role. The use of the rare earth elements permits many new advances, including digital and magnetic technologies operating at reduced energy consumption, higher efficiency, miniaturization, speed, and durability. The REEs are particularly crucial components in clean energy applications, which is especially important in the fight against global warming. For these reasons, the rare earth elements will become essential components in the technological revolution in the second quarter of the twenty-first century.

Keywords: REE engineering, permanent magnets, clean energy, phosphors, bioimaging

1. Introduction

Rare earth elements (REE) are extremely important components in high technology, which is why they are sometimes referred to as "vitamins" of the modern economy or industry [1, 2] With the development of high technology, the demand for rare earth elements increases year on year. It is especially visible in the case of searching for clean energy sources or in the development of various types of electronic devices. Rare earth elements are important components in advanced technologies such as smartphones, computers, TVs, LEDs, hard drives, or elements used for the production of clean energy, such as magnets in wind turbines. Therefore, an increase in REE production is observed worldwide (**Figure 1**). In 2021, the extraction of rare earth elements in the world reached 280,000 tons, which was a significant increase compared to 2018, when 110,000 tons less were extracted. China is the largest producer of REE [3]. In 2021, they have produced 168,000 tones of these elements, while the United States came second in this ranking with a much lower production of 43,000 tones [4].

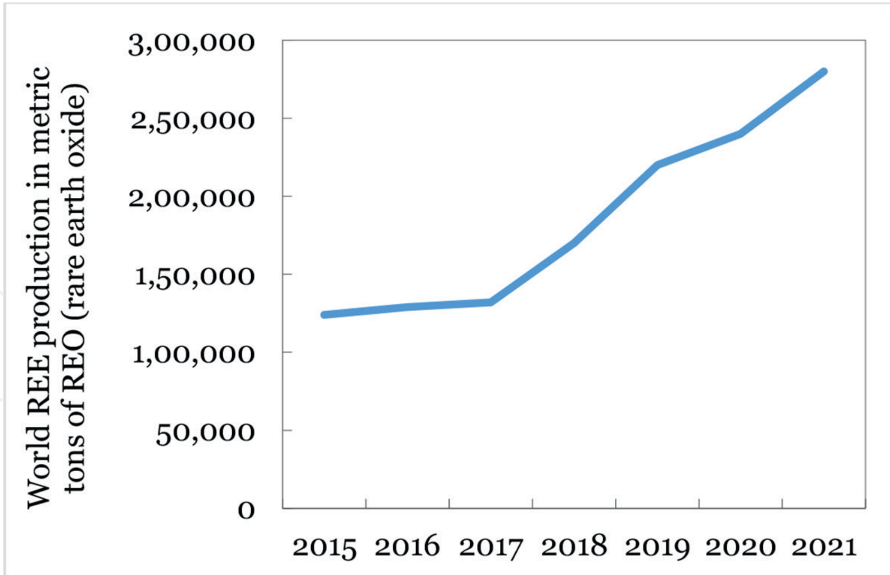

Figure 1.
World mine production of REE (after Ref. [3]).

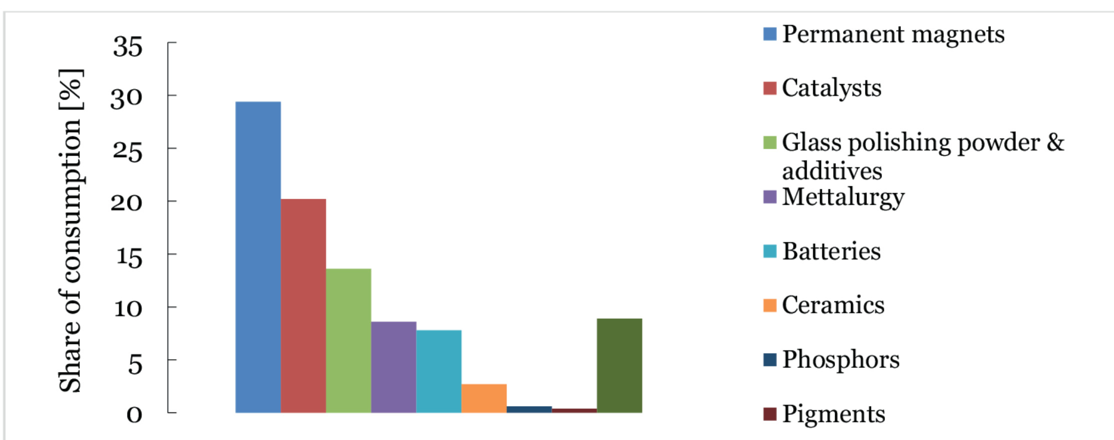

Figure 2.
Distribution of REE consumption worldwide in 2020, by end-use applications (after Ref. [5, 6]).

In the natural environment, REEs do not occur as single native metals, such as gold or silver, they occur together in many ores or minerals as secondary or major constituents [1]. The most economically viable methods of extracting these elements from the ores, as well as separating them from the rest of the components, are being sought. The separation of REEs is difficult and costly due to the similar chemical properties of these elements. In addition to searching for new, more economical methods of their separation, the issue of their reuse - recycling is also very important. Each of the rare earth elements has unique chemical, optical, mechanical, electronic, or magnetic properties and can therefore be used in advanced engineering applications such as permanent magnets, luminescent materials, metallurgy, batteries, catalysts, ceramics, pigments, phosphors, nuclear industry, medicine, and nanotechnology.

The growing importance of these elements in the development of new technologies has made them sought-after raw materials worldwide. It is very important to maintain a proper supply chain for highly developed economies that want to participate in the development of highly advanced technologies. The distribution of the use of these elements in the world, in particular, advanced applications in 2020 is presented in **Figure 2**.

2. Applications of REE

Rare earth elements are applied in many different fields (**Figure 2**). They are used in mature industries such as catalysts, glass production, and metallurgy. However, they play an increasingly important role in the applications of high technology, which include batteries, ceramics, and permanent magnets. In the case of mature markets, elements such as lanthanum and cerium are most often used, in contrast to high-technologies, where dysprosium, neodymium, and praseodymium are used [7]. Permanent magnets production is the largest and most important end use of REE, accounting for over 29% of the total consumption of these elements in 2020 [5]. The main uses of rare earth elements are presented in **Table 1**. Above mentioned applications, there are still areas that use rare earth elements in new ways, such as nanotechnology, which can be employed e.g. in medicine. This chapter focuses primarily on the advanced applications of these elements in nanotechnologies as well as in the most important application in the world today, which are permanent magnets.

REE	Symbol	Applications
Scandium	Sc	High-strength Al-Sc alloys, electron beam tubes
Yttrium	Y	Phosphors for fluorescent lighting and liquid crystal displays (LCDs), capacitors, radars, lasers, superconductors, glasses
Lanthanum	La	Battery alloys, phosphors, glasses, ceramics, car catalysts, lasers, pigments, accumulators
Cerium	Ce	Catalysts, phosphors, ceramics, glasses, pigments
Praseodymium	Pr	Permanent magnets, photographic filters, ceramics, glasses, pigments
Neodymium	Nd	Permanent magnets, catalysts, lasers, pigment for glass and ceramic
Promethium	Pm	Miniature nuclear batteries, phosphors
Samarium	Sm	Permanent magnets, reactor control rods
Europium	Eu	Fluorescent lighting and LCDs
Terbium	Tb	Lighting and displays phosphors, permanent magnets
Dysprosium	Dy	Permanent magnets, lasers, lighting, nuclear industry
Holmium	Ho	Magnets, lasers, nuclear industry
Erbium	Er	Lasers, optical fibers, glass colorant, the nuclear industry
Ytterbium	Yb	Solar panels, fiber optics, lasers, metallurgy, nuclear medicine
Lutetium	Lu	X-ray phosphors
Thulium	Tm	Magnets, electron beam tubes
Gadolinium	Gd	Nuclear fuel bundles, medical imaging, electronics

Table 1.
Applications of REEs (after Refs. [7–10]).

3. Permanent magnets

Rare earth metals are key elements of permanent magnets, which are used as components in clean energy applications such as wind turbines or motors in electric vehicles. Permanent magnets convert electrical energy into mechanical energy (motors) or inversely (generators) by generating a magnetic field [11, 12]. In recent years, the development of wind energy technology has been observed, which is related to the desire to increase the percentage share of renewable energy sources in energy production in the world and, thus reduce carbon dioxide emissions. **Figure 3** shows the periodic table of elements with highlighted rare earth metals used for permanent magnets. As can be seen from the figure, among rare earth metals, lanthanides are used to produce permanent magnets. These elements are characterized by good magnetic properties. The properties of lanthanides are greatly influenced by the *f* orbital, which is also a factor that distinguishes them from transition metals. This orbital is located in the atomic core and therefore does not participate in chemical bonding. Since there are 7 orbitals of the 4*f* type, the number of unpaired electrons can be as high as 7. This results in the formation of large magnetic moments in lanthanide compounds [14]. Lanthanides are paramagnetic except for La^{3+} ($4f^0 5d^0 6s^0$), Ce^{4+} ($4f^0 5d^0 6s^0$), Lu^{3+} ($4f^{14} 5d^0 6s^0$) and Yb^{2+} ($4f^{14} 5d^0 6s^0$), they are diamagnetic – they have no unpaired electrons [15]. Examples of electron configurations of paramagnetic lanthanides are presented in **Figure 4**.

Magnets containing rare earth metals were discovered in the 1960s in the United States. They were based on samarium and the transition metal cobalt (SmCo). The first type of this kind of magnet was SmCo5 which had properties suitable for permanent magnets including large uniaxial magnetocrystalline anisotropy, comparatively high saturation magnetization, high Curie temperature, and maximum energy

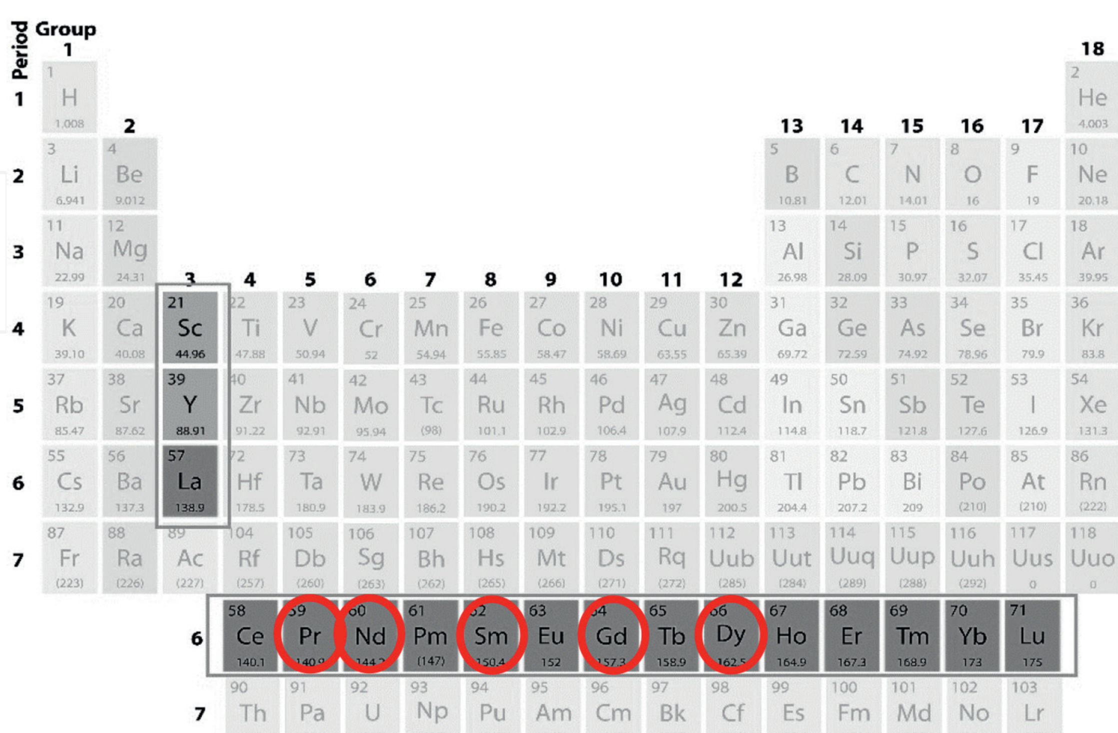

Figure 3.
Location of rare earth metals on the periodic table, elements used in permanent magnets are marked in red [13].

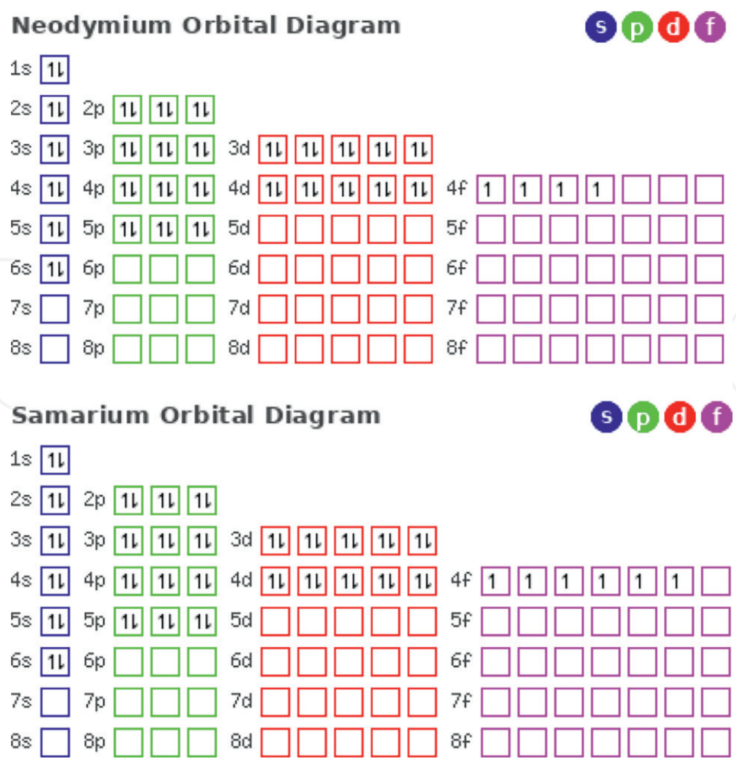

Figure 4.
Electron configuration on orbital diagrams for rare earth elements neodymium and samarium [16].

product [$(BH)_{max}$] with the value of 160 kJ/m^3 [17]. Next, to obtain higher magnetizations, a compound with a stoichiometry of Sm_2Co_{17} was designed. Nevertheless, despite obtaining a higher saturation magnetization and Curie temperature compared to SmCo5, the field anisotropy in the case of Sm_5Co_{17} was smaller [17]. The major disadvantage of these magnets was the relatively high cost of Sm and Co, which resulted that in the 1980s, researchers in Japan and the United States designed a new type of magnet containing the rare earth metal neodymium as well as iron and boron ($Nd_2Fe_{14}B$) [2, 17]. It was cheaper and at the same time stronger compared to the SmCo magnet. The development of permanent magnets in the world is shown in **Figure 5**.

Rare earth magnets are distinguished by excellent magnetic properties determined by high induction and coercive force. They are much more powerful per unit mass and volume than other types of magnets [19]. This is related primarily to the high magnetocrystalline anisotropy. The resistance of the crystal lattice to a change in the direction of magnetization gives these materials a very high magnetic coercivity (resistance to demagnetization), which may be attributed to a strong demagnetizing field in the finished magnet than does not reduce the magnetization of the material [2].

The development of permanent magnet technology has been achieved through the use of alloys containing rare earth elements such as Nd, Sm, Gd, and Pr. The introduction of additives in the form of these elements made it possible to produce magnets characterized by a lower mass, smaller dimensions, and high strength at the same time [20]. As a consequence, it made it possible to significantly reduce the size of various types of electronic devices and their components. Compared to other permanent magnets, rare earth magnets can significantly reduce the size and weight of generators used for the production of clean energy in wind turbines. Such magnets can increase efficiency above 20%, which is also very important from an economic point of view [8].

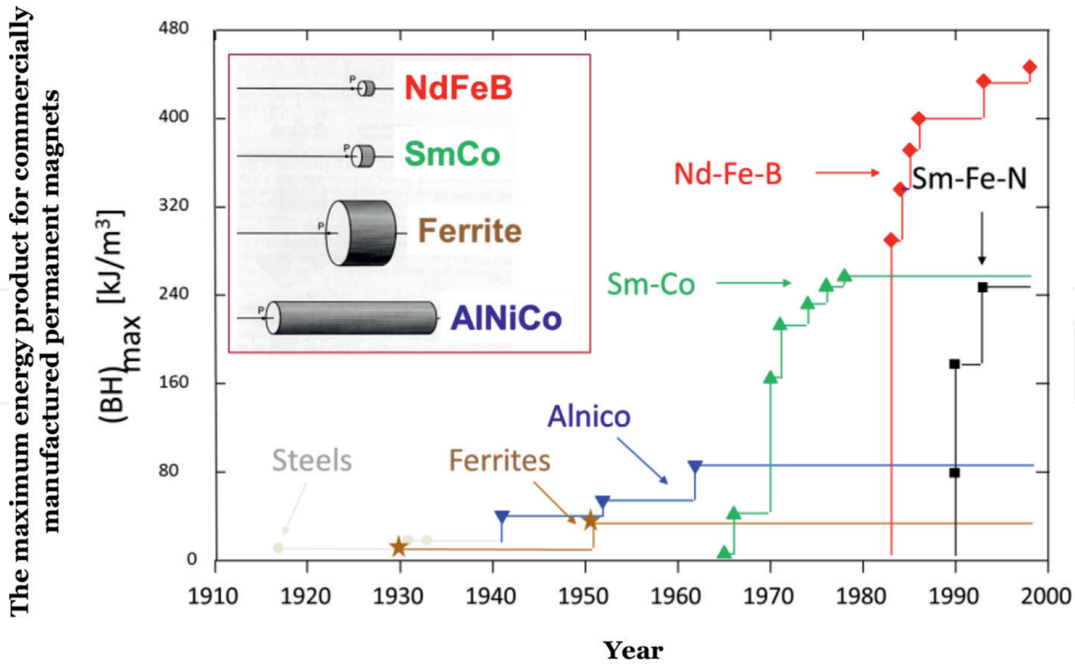

Figure 5.
Development of permanent magnets [18].

Rare earth magnets are employed in applications that require a high magnetic field in difficult operating conditions such as high temperature and high demagnetization forces. In SmCo magnets, samarium is the dominant rare earth metal and cobalt is the primary transition metal, often used with iron, zircon, and copper. The quantity of rare earth elements in such magnets ranges from 25 to 35% by weight. Samarium cobalt magnets are used at high temperatures [2]. However, some disadvantages, include their brittleness which limited the size of the magnet and thus seriously restricts the possibility of their use in certain applications, e.g. in car motors [8]. Another rare earth element, gadolinium, is used to achieve a near-zero change in the residual induction over a wide temperature range. The difference between the SmCo and GdCo magnets is that with increasing temperature, the residual induction decreases in the first case and increases in the second, although from a significantly lower initial value. The combination of SmCo and GdCo allows to obtain magnets with high stability. Magnets based on samarium and cobalt have been used, among others e.g. in generators, actuators, or medical devices [2].

NdFeB magnets (also known as Neo or NIB magnets) [21] are now largely replacing SmCo magnets [22]. NdFeB magnets are more powerful than those of SmCo, and offer the strongest magnetic flux density, therefore are widely used in clean energy technologies such as wind turbines and electric vehicle motors [23]. The neodymium content in these materials is about one-third. The typical chemical composition of NIB magnets is 26.7% Nd, 72.3% Fe and 1.0% B. Although the content of Nd and Fe elements may differ somewhat in commercially used magnets [21]. Frequently other rare earth element praseodymium (Pr) replaced neodymium in these compounds [2, 24]. This is related, among others to the reduction of their production costs.

Previously mentioned use of such magnets are wind turbine generators. Wind turbines require the use of generators with greater power, therefore magnets such as NdFeB are widely used in this type of application. Thus it is possible to substitute the mechanical gears in wind turbines with permanent magnet generators. The advantages of using permanent magnets in wind turbine generators are a reduction in the total weight of the turbine as well as a reduction in the number of moving parts, which results in an increase in the efficiency and reliability of these turbines. The benefits of using permanent magnet generators are especially important for offshore installations, where reliability is a priority. Which is associated with the high cost of repair and maintenance of such turbines [8]. The magnet in a large wind turbine contains as much as 260 kg (or more) of neodymium [25]. Due to their properties, these magnets have also found application in other technologies used to produce renewable energy under the ocean floor and by waves [8].

In addition to wind turbines, where magnets play a key role, they also dominate the market for the production of motors for electric cars. In this case, the size and weight of these components are also important, and they must be adapted to the previously designed engine parameters [8, 22]. As a consequence of the high magnetic strength of NdFeB magnets, they can produce a lot of energy in relation to their weight and size. This makes them ideal for applications that need a high energy-to-weight ratio, such as electric vehicle motors.

It is possible to introduce small amounts of additional ingredients in the form of heavy rare earth metals or other metals, which may improve the properties of the Neo magnets. A very important addition is dysprosium, which increases intrinsic coercivity and resistance to demagnetization of these magnets and in consequence enables the use of them at higher temperatures [22, 26]. The addition of dysprosium is usually from 2 to 5% [2, 8]. As mentioned before NdFeB magnets are requested for applications of small or large motors and generators. Small motors are used e.g. in power disc drivers in computers, while large in electric vehicles. In electric car motors, up to 200 g of neodymium and 30 g of dysprosium are used whereas wind turbine generators can contain 1 ton of neodymium per megawatt of electrical power generated [23, 27].

Another common application of this type of magnets is electronics as well as in lasers and telecommunications, there are 12 times stronger than standard iron magnets [*28*].

4. Using optical properties in new technologies

The optical properties of lanthanides are still number one in rare earth (RE) ions applications since the late nineteenth century. In 1964 two scientists discovered possibilities for this elements group so-called red phosphors. The red phosphors were used mainly in the TV screens production process. That technology used a mixture of two metal elements from the sub-shell „*d*" group of the periodic table as europium and yttrium ions. As a result, it became possible to obtain a TV color [29]. These excellent optical properties of RE are still used in several of new technologies such as modern lighting displays, photodynamic therapy, and biodetection. These technologies give an opportunity to develop numerous industry sectors.

The reason of the great array optical properties is an unusual electronic structure on the sub-shell "*d.*" This characteristic electronic structure is related to the existence of an important phenomenon called luminescence. That phenomena depend on three mechanisms of electron transfer: 4f-4f or 5d-4f and charge transfer (CT).

Moreover in the CT mechanism, the easily oxidizing or reducing ions like Ce^{3+}, Pr^{3+}, Tb^{3+}, and Eu, Tm, Yb entail depending the transitions intensity broad bands produces from the symmetry of the surroundings of the RE ion.

RE ions due to base on their 4f-4f or 5d-4f energy transfer and thus the emission of powerful light sources in a wide range [29]. The 5d-4f energy transfer largely depends on the ligands surrounding the RE ions. Hence it becomes more reactive unluckily. However, the 4f-4f transitions are the most commonly used in the range of visible light the lifetime of the luminescence range from tens of microseconds to single milliseconds. In addition, there is the shielding effect of the filled $5s^2$ and $5p^6$ shells which contributes to the environment protection. Thus external factors have no influence on them. This makes them much better candidates suited to applications in the field of optics than organic compounds.

In the last years, a large development of nanotechnology in optics is observed. Among the interesting new materials, there are also nanomaterials containing RE ions. Those modern nanomaterials are called witching others: fluorescent nanoparticles, quantum dots, or nanocolloidal metallic nanoparticles. The nanoluminophores and nanoplatforms demonstrated desirable properties and were devised functionally in the last years [30]. The most commonly used RE elements in nanotechnology are: Eu^{3+}, Tb^{3+}, and co-doped phosphors Yb^{3+}-Tm^{3+}, Yb^{3+}-Er^{3+}, or Yb^{3+}-Ho^{3+}.The emission of RE ions covers the entire range from UV (Gd^{3+}) by visible light (Tb^{3+}, Tm^{3+}, Sm^{3+},) to the NIR range (Yb^{3+}, Er^{3+}, Pr^{3+} Nd^{3+}). However, two RE ions: La^{3+} and Lu^{3+} are unable to give 4f-4f transfer and do not emit light. A lifetime of emission light depends on the size of the crystallites. It was noted that the light emission in phosphors is growing with the reduction increasing of the phosphors crystalline [31]. This could apply e.g. nanomarkers doped with RE. These nanomaterials can actively influence on the cells. The environment of cells can be heating locally and formation of free-radicals at once. That phenomena have a significant role in photodynamic therapy (PDT) and hyperthermia. The most important is using NIR range light to excite the phosphors which allows to less invasive and deep penetrations of cancer cells.

Currently, however, trials are underway to extend the therapeutic indications for extracorporeal analysis as screening test genetic diseases, detection of infections caused by different microorganisms, and the presence of impurities of bacteria in water and food products [32]. Therefore, nanophosphors becoming increasingly fashionable in various ranges of applications. Their unique physical and chemical properties allow for quick and easy applications in a new range of applications notably in medicine range.

Nevertheless, one of the most developed directions is biological applications such as biodetection and bioimaging [33]. The extraordinary spectroscopic properties of RE as stable luminescence, up-conversion ability, and a narrow band of light emission resulted in an increased interest in them. Recent decades have seen the development of research and an increased interest in RE in nanoform in various biological applications. A pie chart **Figure 6** shows all characteristic biological application RE ions which are the most popular in the last years.

Among the widespread type of biodetection and bioimaging are phosphorus markers. These makers give opportunities for a wide range of applications in medicine as drags transfers, photodynamic therapy, in vivo imaging of biochemical reactions in real-time, cancer therapy, or imaging DNA mutations. From a medical viewpoint, these opportunities give wide and new perspectives.

The use of RE in multiplexing also plays an important role. The multiplexing with RE being capable to for the analysis of multiple analytes in one sample. This possibility allows to apply RE in genetic tests or new studies on cancer drugs.

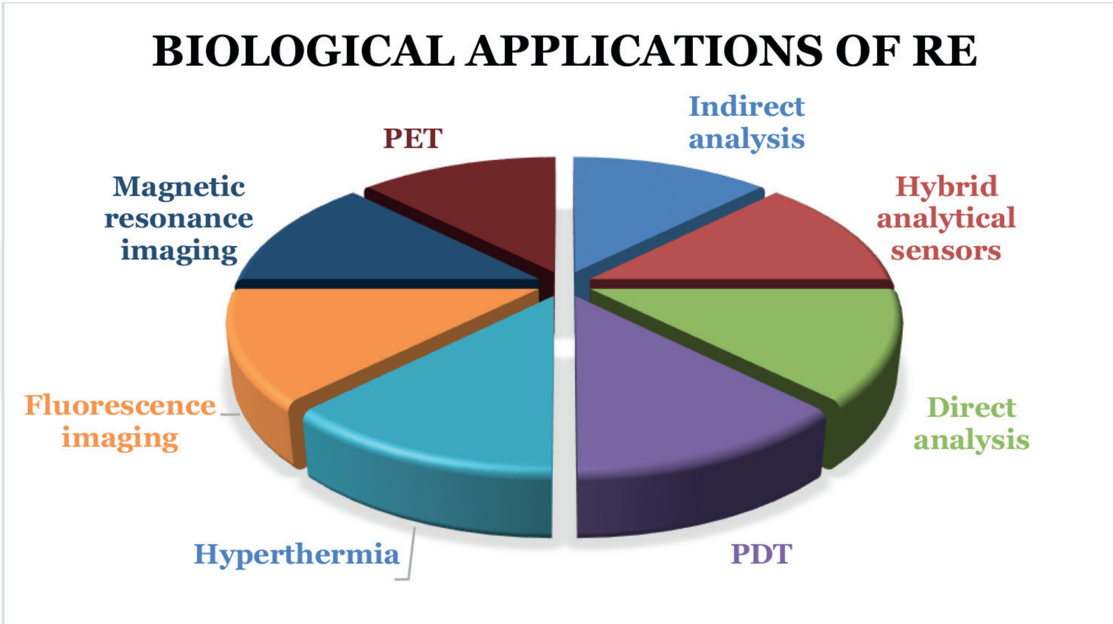

Figure 6.
*New way of biological applications of RE elements. *PET, positron emission tomography; *PDT, photodynamic therapy.*

Interesting results are silica-based or polymeric-based hybrid phosphors. The silica in SiO form and polymeric in PEG form plays a role of ligands. The matrix where RE ions are embedded can be various. The type of matrix usually used in phosphors for biological applications were shown in **Table 2**. As can be observed, all of these list medical applications are based on phosphors or nanophosphors.

Diagnostics and photodynamic therapy in the use of lanthanides are one of the most modern methods of imaging and cancer therapy of PDT. The PDT method is based on the up-convergence mechanism. This process generally depends on the absorption of successive photons (**Figure 7**). For example, the β-NaYF4 matrix doped with Er^{3+} and Yb^{3+} is characterized by about 10^5 times greater efficiency than organic compounds, e.g. rhodamine 6G [39].

Matrics	RE ions	Ligands	Applications
$NaYF_4$	Yb-Tm, Yb-Ho Yb-Ho-Ce	—	In vivo imaging
$NaYF_4$	Yb^{3+}, Er^{3+}	$NaYF_4$/SiO2	Photodynamic therapy
Y_2O_3	Er^{3+}	PEG	Cancer cells detection
$NaYF_4$	Nd^{3+}	—	Hiperthermic
LaF_3	Ce^{3+}, Tb^{3+}	PSS, PAH	Glucose marking
$NaYF_4$	Yb^{3+}, Er^{3+}, Gd^{3+},	^{18}F, citric / oleic acid	Magnetic resonance Emission tomography
Gd_2O_3, Fe_3O_4	Eu^{3+}	DNA	Detection of DNA mutations
LaF_3	Yb^{3+}, Er^{3+}	SiO	Transportation of drugs

Table 2.
A selected list of the luminescence materials with the most popular RE ions used in biological experiments [34–38].

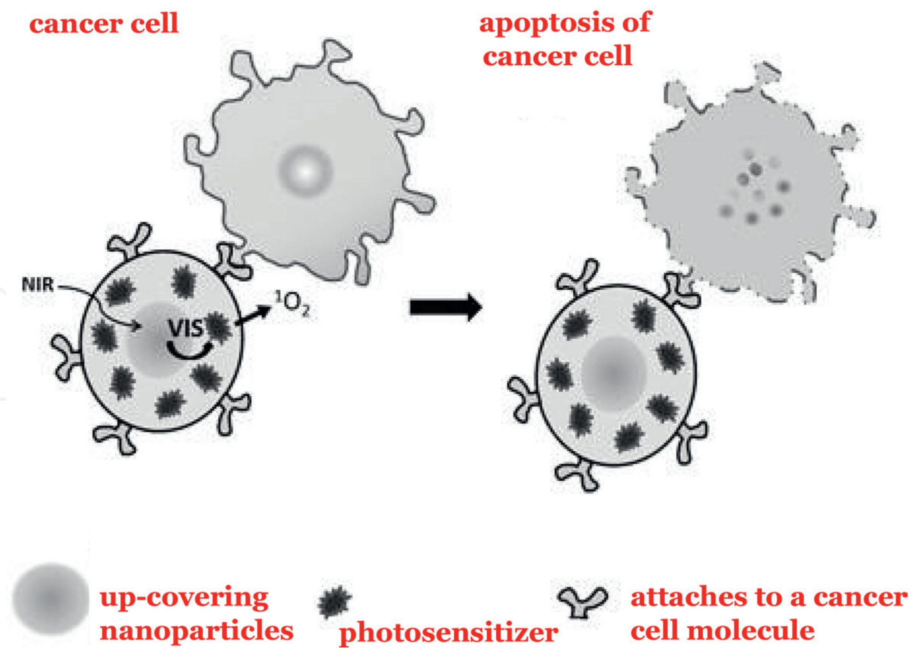

Figure 7.
Scheme of PDT mechanism based on nanoluminophores doped with RE–the matrix with nanoparticles doped RE ions is excited by infrared light NIR and the core is emitting visible light VIS. The VIS light exciting photosensitizers molecules and generate reactive oxygen form $^1O_2$. The cancer cells undergo apoptosis [30].

On the other hand, biological imaging is one of the most important applications of RE elements in a science experiments, various electronic devices, and medicine. NaYF4:Er^{3+}, Tm^{3+}, Ho^{3+} nanocrystallite was used for cancer cells imaging [40]. The up-conversion mechanism of RE ions in special matrix was also used. The deep penetration excitation infrared light of cells and absence of photobleaching problem of nanoparticles especially. In this case doping of several RE ions of matrix NaYbF4 gives the opportunity to obtain wavelength ranges with different colors.

However, biological or medical applications are not the only ones where RE phosphors are used. The up-conversion is using also to various sensors production with nanoluminophores doped with RE ions as pH sensors, oxygen sensors, ammonia sensors, or carbon dioxide sensors [41–43]. The most frequently the ytterbium, thulium, or europium ions are used for this purpose. The first designed oxygen sensors NIR light excited was NaYF4:Yb^{3+}, Tm^{3+}.

Silicate phosphor KBaScSi2O7:Ce^{3+} (KBSS:Ce^{3+}) can emit cyan light with an emission peak at 509 nm under n-UV light excitation (300–400 nm). Those optical properties indicate that KBSS:Ce^{3+} phosphor is favorable in LED and field emission display applications [44].

5. Conclusions

Due to the unique magnetic, luminescent, chemical, and physical properties of rare earth elements, are essential ingredients for many high-technology applications, and there still will be observed demand for them in the future. Especially since their significant use is related to the production of clean energy, which nowadays is a very important issue. The development of wind energy will continue to drive demand for REE used in wind turbine generators. Converting combustion engine cars w to electric vehicles will also increase the need for magnets and rare earth batteries. Of course, the search is ongoing and materials that could replace or reduce the amount of REE in individual applications are considered. However, due to their superior properties, we are currently unable to replace them in some usage because it would involve a deterioration of the quality and efficiency of the components in which they are used. There are still applications where the potential of rare earth elements has not been fully exploited and we will certainly observe their further development.

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