Chapter 1:

Luminescence properties of

Rare earth elements

1.1 Luminescence:

Light is considered to be a type of energy. A different kind of energy must be supplied to generate light [1]. There are two typical ways for this to occur: incandescence and luminescence. Incandescence is the more common method. Incandescence is light produced by an object when it attains higher temperature. Luminescence can occur at normal and lower temperatures since it is cool light derived from various energy sources. The term luminescence came from Latin and was first introduced as luminescenz by German physicist and science historian Eilhard Wiedemann in 1888. There are several definitions of the term luminescence. One of them that it is a phenomenon of light emission from materials, which are not solely conditioned by the rise in temperature or a spontaneous emission of radiation from an electronically excited species or a vibrationally excited species, not in thermal equilibrium with its surroundings. There are several types of luminescence, each named after what the excitation source of energy is or what causes the luminescence, such as Photoluminescence, when electromagnetic radiation is used as an excitation source Cathodoluminescence, when an energetic electron beam is used as excitation source; Electroluminescence, when electric field is used as excitation source, Radioluminescence, when high energy X-rays or ϒ rays are used as an excitation source, Sonoluminescence, when the ultrasonic waves are used as an excitation source, Triboluminescence, when a material is subjected to mechanical treatment to get light emission, Chemiluminescence, when light is emitted during a chemical reaction, Bioluminescence, when chemiluminescence is from living organisms and Thermoluminescence, which is a type of luminescence that occurs when previously absorbed energy from electromagnetic radiation or other ionizing radiation is re-emitted as light on heating the material [1].

1.2 Photoluminescence:

Photoluminescence occurs when the material absorbs at least one photon and spontaneously emits another with a different energy, the process depending upon the structure of phosphor materials, surrounding environment, and type of activators used. Depending on the time period of the emission, photoluminescence can be subdivided into two different categories [1] [2].

1) Fluorescence: An exponential afterglow with a lifetime of less than 10^{-8} seconds is observed after the excitation has been removed, and it is independent of the excitation intensity and temperature [1].

2) Phosphorescence: After excitation is removed, an afterglow occurs with a lifetime of more than 10^{-8} seconds, which is frequently dependent on the excitation intensity and is strongly temperature-dependent [1].

A Jabłoński diagram typically depicts the process of light absorption and emission. The Jabłoński diagram is frequently used to begin discussions of light absorption and emission. They come in a variety of forms to illustrate the molecular processes that can occur in excited states. These diagrams are named after Professor Alexander Jabłoński, who is widely considered to be the father of fluorescence spectroscopy [3].

Professor Alexander Jabłoński (1898-1980) [www.lumipedia.org]

An illustration of Jablonski diagram showing the two types of down conversion mechanism is given below.

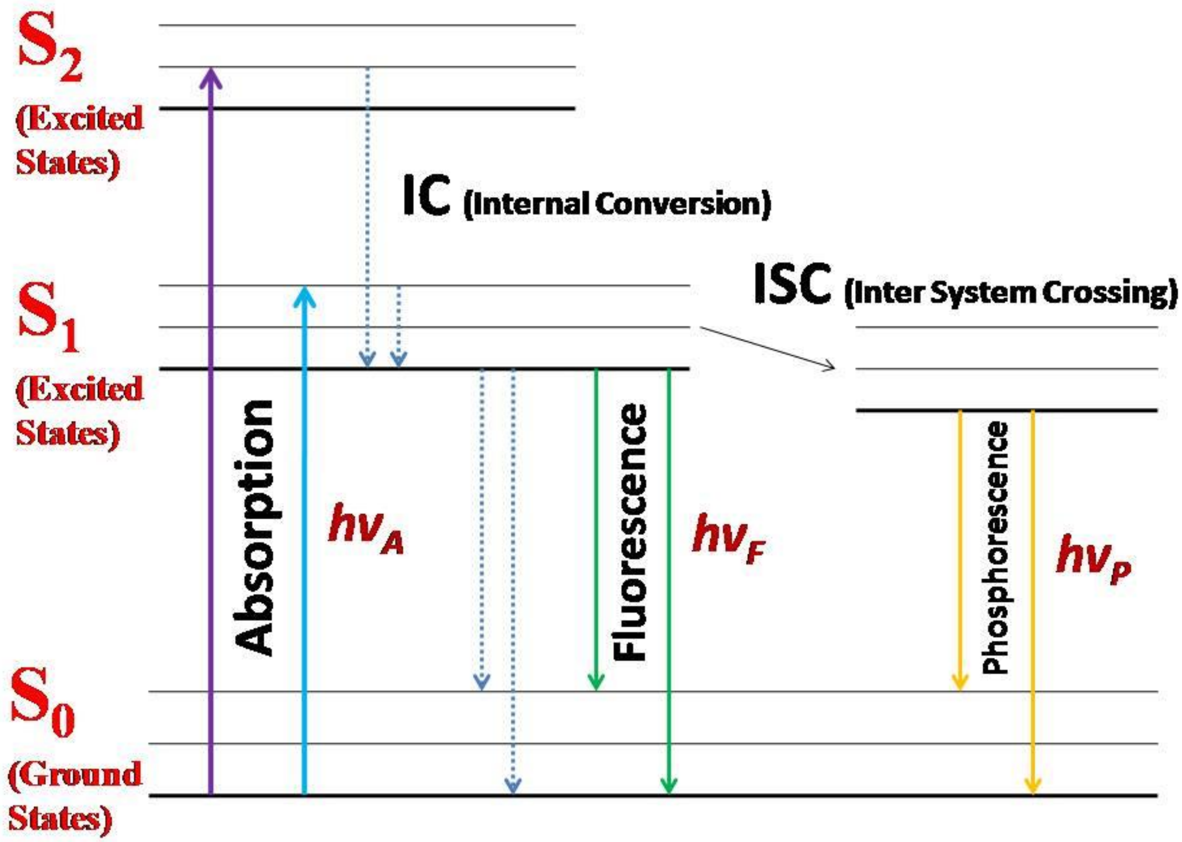


Figure 1.1 One form of a Jabłoński diagram

On absorption of a photon of energy $h\nu_A$, the molecules are propelled to the excited states S_1 and S_2 or any other from the ground state S_0, as shown in figure 1.1. Because the molecules in the excited state are unstable and will eventually return to their stable ground state. However, the return journey is not straightforward. In a series of transitions, also known as Internal Conversions (IC), they transit to lower levels losing vibrational or thermal energy. In the latter case, a photon with energy $h\nu_F$ is emitted, resulting in an overall process with a short decay time of fewer than ten nanoseconds and is termed as fluorescence. Alternatively, a quantum-mechanically less likely process involving electron spin reversal may occur. It is known as an Inter System Crossing (ISC), and it also results in the emission of photons of energy $h\nu_P$. The process, however, has a longer decay time of more than a millisecond and is known as phosphorescence. Figure 1.1 depicts it schematically [3].

1.3 Upconversion Photoluminescence: Mechanism and Applications

Another type of luminescence mechanism, which is one of the focuses of the present work is given below.

A lower energy photon is produced on excitation by a higher energy photon in the general process of luminescence, which is termed as downconversion. In the case of upconversion, however, the process is precisely the opposite. Higher energy photons are produced as a result of the excitation of multiple low-energy photons. In general, two lower-energy electrons in the near-infrared region carry out the excitation process via subsequent absorption. The emission process is a one-step process that results in a photon in the visible region via radiative energy transfer. The process differs from simultaneous multiphoton absorption in that the intermediate level is virtual, whereas it is real in the case of upconversion [4].

This results in increased efficiency during the upconversion process, which leads to a variety of applications, such as improving solar cell efficiency [5]; because the excitation often occurs within the biological transparency windows [6], they have found their way into a variety of biological and medicinal applications [7], provided that the particle size is sufficiently small to cause no unwanted disturbance to the living cells [8].

Upconverting nanoparticles (UCNP) have received a lot of attention in recent years because of their wide range of potential applications in nanothermometers [9], biological labeling [10] and imaging [11], cancer treatment or drug delivery and therapy [12], etc. This is reflected in the increase in the number of studies on UCNP in the last three decades [13]. Only 5 papers contained the term "upconversion nanoparticles" in 1990. The trend gradually increased for another decade, reaching 127 papers in 2000. Since then, interest in UCNP has grown at an unprecedented rate with 951 articles published in 2010 and 8640 expected by 2020.

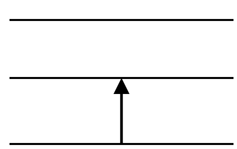
The mechanism of upconversion is a two-step procedure [14],

a. Absorption
b. Energy transfer (non-radiative)

The term "absorption process" can be divided into two categories:

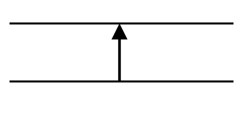
i) Ground State Absorption (GSA)

An ion in the ground state absorbs energy for transition to the excited state.



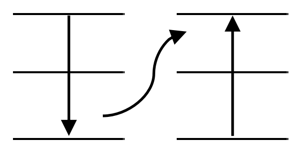
ii) Excited-State Absorption (ESA)

In this case, an ion in the excited state absorbs energy and progresses to a higher excited state.

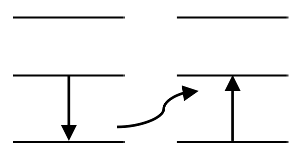


The process of energy transfer can be divided into the following categories [15] [16].

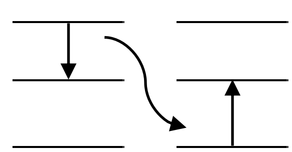
1) Energy transfer between ions of the same type, which is a prevalent type of energy transfer.



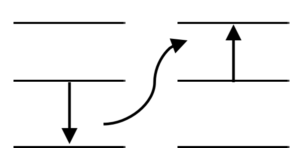
2) “Energy Transfer” between different kinds of ions. One serves as an activator and another sensitizer.



3) When an ion transits from a higher excited state to a lower excited state, the energy released by the first ion is absorbed by the second ion, which then transitions from a ground state to a lower excited state. As a result, both ions are in lower excited state. This is referred to as “Cross Relaxation” (CR)



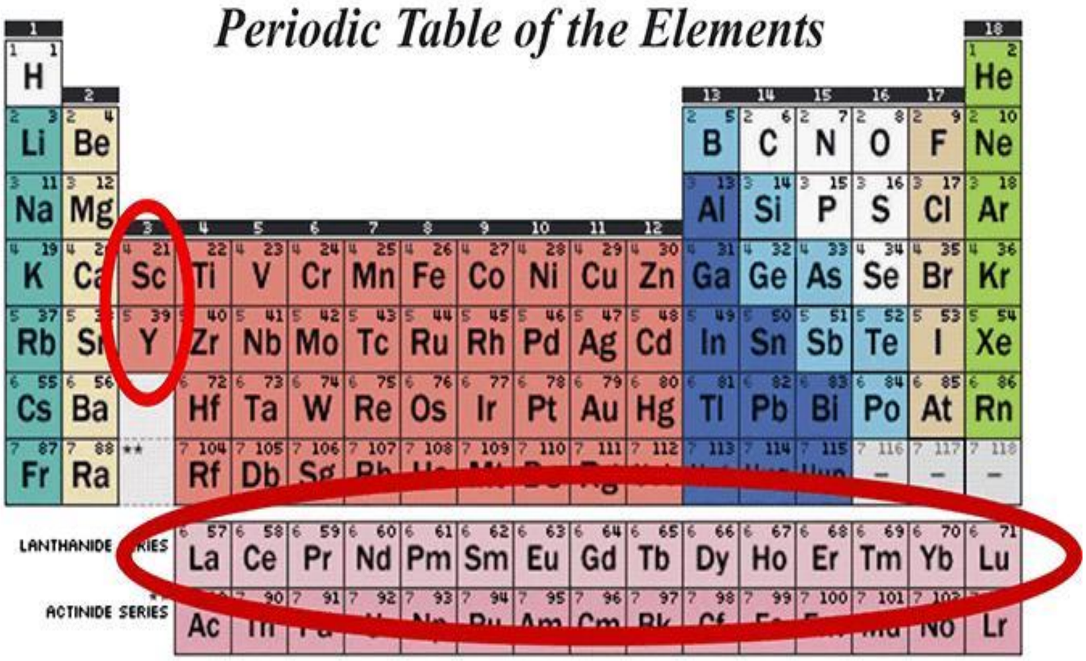
4) An ion in the lower excited state releases energy to come down to the ground state. The energy released is then absorbed by another ion which is in the lower excited state to transit to the higher excited state. This process is referred to as "Energy Transfer Upconversion (ETU)."



A set of processes listed above work together to complete the upconversion process in its entirety.

1.4 Photoluminescence properties of Rare Earth Elements:

Rare earth materials are referred to by various names, including rare earth elements (REEs), rare earth metals (REMs). For the most part, rare earth materials are classified into two categories: light rare earth elements (LREEs), which are also known as the Cerium group, consisting of Lanthanum - Europium and heavy rare earth elements (HREEs), also known as the Yttrium group, which is composed of elements such as Gadolinium - Lutetium - Yttrium. Rare earth elements are made up of a group of 17 chemical elements that are included in the periodic table of elements. Furthermore, 15 lanthanides, Scandium and Yttrium are included among the 17 rare earth minerals. They tend to exist in the same core deposits as lanthanides and have identical properties to those of lanthanides [17].



[Source: http://tnahistoryoftechnology.wikispaces.com/Rare+Earth+Metals]

Element (symbol)	Atomic Weight	Atomic Number	Valance electrons
Scandium (Sc)	45	21	3
Yttrium (Y)	88.9	39	3
Lanthanum (La)	139	57	3
Cerium (Ce)	140	58	3, 4
Praseodymium (Pr)	141	59	3
Neodymium (Nd)	144	60	3
Promethium (Pm)	145	61	3
Samarium (Sm)	150	62	2, 3
Europium (Eu)	152	63	2, 3

Gadolinium (Gd)	157	64	3
Terbium (Tb)	159	65	3
Dysprosium (Dy)	162	66	3
Holmium (Ho)	164.9	67	3
Erbium (Er)	167	68	3
Thulium (Tm)	169	69	3
Ytterbium (Yb)	173	70	2, 3
Lutetium (Lu)	175	71	3

Table 1.1 Seventeen rare earth elements and their properties

Despite their name, rare earth elements are plentiful in the earth's crust.

World Rare earth materials Production and Reserves (2020 Estimates)		
Country	**Production (Metric Tons)**	**Reserves (Metric Tons)**
United States	38,000	1,500,000
Australia	17,000	4,100,000
Brazil	1,000	21,000,000
Burma	30,000	not available
Burundi	500	not available

Canada	--	830,000
China	140,000	44,000,000
Greenland	--	1,500,000
India	**3,000**	**6,900,000**
Madagascar	8,000	not available
Russia	2,700	12,000,000
South Africa	--	790,000
Tanzania	--	890,000
Thailand	2,000	not available
Vietnam	1,000	22,000,000
Other Countries	100	310,000
World total (rounded)	240,000	120,000,000

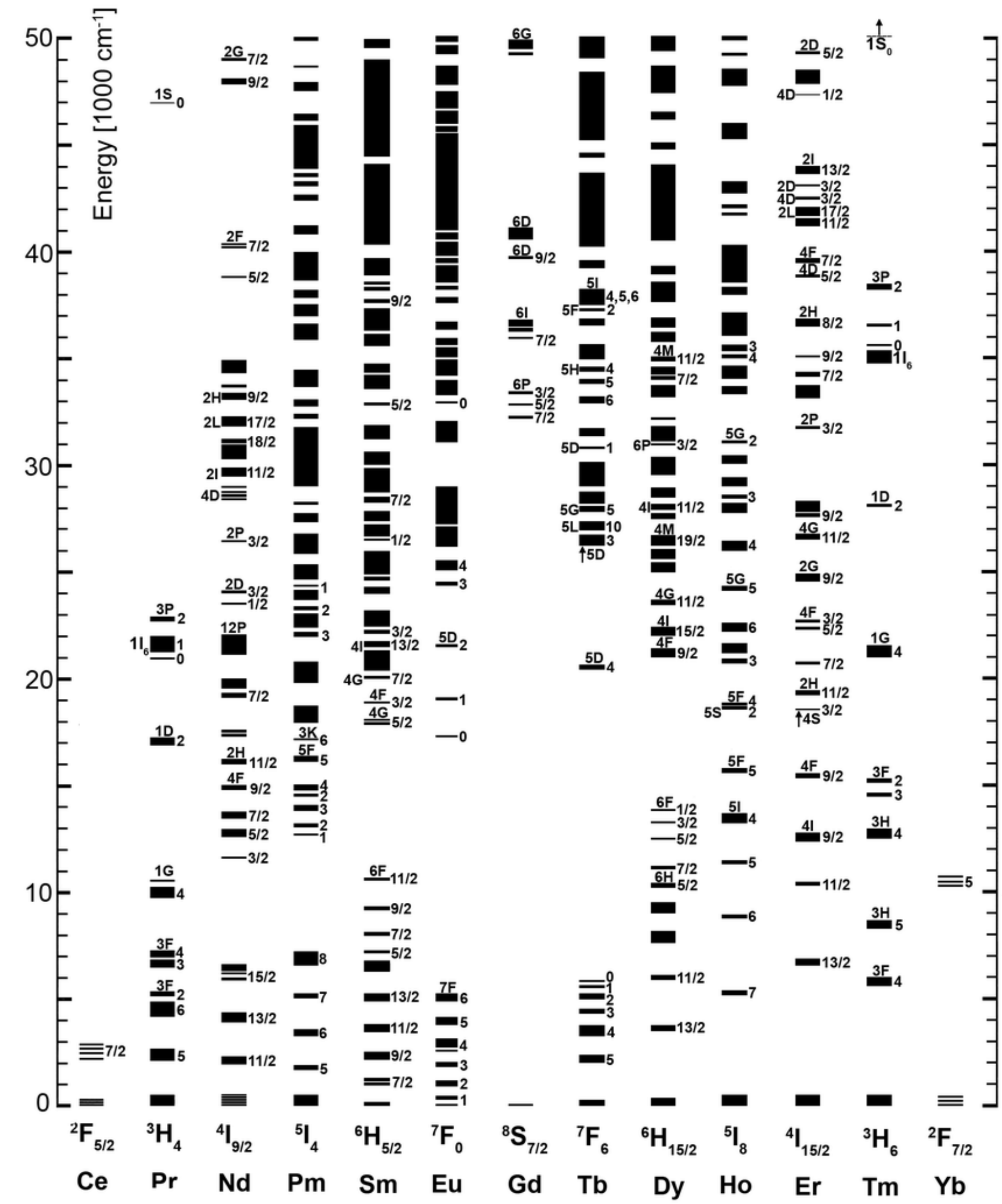
[Source: Hobart M. king (www.geology.com)]

Rare earth materials find wide-ranging use in various commercial, industrial, medical, military, and space applications. Rare-earth materials also play an important role in industries such as optical technology, petrochemicals, ceramics, electronics, agriculture, metallurgy, biotechnology, and pharmaceuticals.

Lanthanide–activated light emitting materials, also known as phosphors have many applications ranging from high–resolution luminescence imaging to next-generation volumetric full-color display, high-performance luminescence, and display devices such as solid-state lighting, field emission diodes, in-vivo fluorescence imaging, MRI imaging, UV-LED, LASER, and biotechnology. Some of these applications are relevant to the properties of materials chosen for this study [17].

All rare-earth elements have similar chemical properties but differ in physical properties due to their electronic structure. There are seventeen rare earth elements and all have unique optical properties, mainly due to two reasons. They possess the same order of magnitude of Coulomb interactions and spin-orbital interactions. Hence, the intermediate coupling scheme (LS coupling) is followed for transitions. Secondly, they have partially filled 4f orbitals surrounded by completely filled 5s and 5p orbitals. This makes the radial wave function of 4f orbitals less extended than 5s and 5p orbitals, which results in sharp inter-configurational transition lines between 4f levels. There is a limited class of solids that emits the sharp line spectra. There is no hesitation in saying that only rare earth salts can produce the sharp line emission. To achieve sharp line spectra, valence electrons are separated from those of their neighbors. In the traditional sense, this indicates that these electrons must be in inner orbits that are shielded by outer electrons. In wave mechanics terms, this means that the wavefunctions of these electrons from surrounding atoms must not overlap significantly. The 4f orbits of rare earth elements lie well inside the electronic shell and are well protected; this enables them to emit sharp lines [18].

These elements are known to emit light (luminescence) under specific excitations when used as activators or co-activators in certain host matrices. Photoluminescence occurs when the material absorbs at least one photon and subsequently emits another with a different energy spontaneously, the process depending upon the structure of phosphor materials, surrounding environment and type of activators used. The rare-earth hosts doped with another lanthanide ion are very efficient luminescent materials due to the high thermal stability, low phonon energy, and high energy transfer rates [18].



Energy level diagram of lanthanide ions
[Source: Marcus True (Hamburg, Univ., Diss, 2004)]

References:

[1] K. V. R. Murthy, J. K. Kapoor, Sachin Shah, Glimpses of 125 years of Lamps and Technology, 2015. ISBN: 978-93-82570-69-1.

[2] K. Shah, A. Ćirić, K.V.R. Murthy, B.S. Chakrabarty, Investigation of a new way of synthesis for Nano crystallites of La2O2S & 1%Ln3+ (Ln = Pr, Eu, Tb, Dy, Er) doped La2O2S and study their structural and optical properties, J. Alloys Compd. 851 (2021) 156725. https://doi.org/10.1016/j.jallcom.2020.156725.

[3] Joseph R. Lakowicz, Principle of Fluorescence Spectroscopy, Springer. ISBN: 0-306-46093-9.

[4] C.D.S. Brites, P.P. Lima, N.J.O. Silva, A. Millán, V.S. Amaral, F. Palacio, L.D. Carlos, Thermometry at the nanoscale, Nanoscale. 4 (2012) 4799. https://doi.org/10.1039/c2nr30663h.

[5] M.D. Dramićanin, Trends in luminescence thermometry, J. Appl. Phys. 128 (2020) 040902. https://doi.org/10.1063/5.0014825.

[6] F. Wang, D. Banerjee, Y. Liu, X. Chen, X. Liu, Upconversion nanoparticles in biological labeling, imaging, and therapy, Analyst. 135 (2010) 1839. https://doi.org/10.1039/c0an00144a.

[7] G. Chen, H. Qiu, P.N. Prasad, X. Chen, Upconversion Nanoparticles: Design, Nanochemistry, and Applications in Theranostics, Chem. Rev. 114 (2014) 5161–5214. https://doi.org/10.1021/cr400425h.

[8] C. Wang, L. Cheng, Z. Liu, Drug delivery with upconversion nanoparticles for multi-functional targeted cancer cell imaging and therapy, Biomaterials. 32 (2011) 1110–1120. https://doi.org/10.1016/j.biomaterials.2010.09.069.

[9] D. Kucharavy, R. De Guio, Application of Logistic Growth Curve, Procedia Eng. 131 (2015), 280–290. https://doi.org/10.1016/j.proeng.2015.12.390.

[10] G. De Tarde, The laws of imitation, H. Holt, 1903.

[11] E.M. Rogers, Diffusion of innovations, Simon and Schuster, 2010.

[12] F. Auzel, Upconversion and Anti-Stokes Processes with f and d Ions in Solids, Chem. Rev. 104 (2004) 139–174. https://doi.org/10.1021/cr020357g.

[13] C. Strohhöfer, A. Polman, Absorption and emission spectroscopy in Er3+–Yb3+ doped aluminum oxide waveguides, Opt. Mater. (Amst). 21 (2003) 705–712. https://doi.org/10.1016/S0925-3467(02)00056-3.

[14] Na Li, Nengqain Pan, Danhong Li, Shwei Li, “International Journal of Photoenergy”,Vol. 2013, Article id- 598753, Hindawi Publication.

[15] Anner Ur Rehman, Farooq Aslam and Haseeb Ahmad Khan, “Analyze the absorption Properties and I-V characterization of DSSC using Ruthenium Dye”, American Journal of Engineering and Applied Sciences, 7 (4), 2014, pp. 387-390.

[16] J. G. Rowley, B. H. Farnum, S. Ardo and G. J. Meyer, “Iodide chemistry in dye-sensitized solar cells: making and breaking I-I bonds for solar energy conversion”, J.Phys. Chem. Lett.,1 (2010), pp. 3132-3140.

[17] A.R. Jha, Rare earth materials: Properties and applications, 2014. doi:10.1201/b17045.

[18] G.H. Dieke, H. Crosswhite, Spectra and Energy Levels of Rare Earth Ions in Crystals, che.13,Intersciencepublishers,968.