

Lanthanides Basics And Structural Information

Naik Dhanraj Mersing, Research Scholar, Dept. of Bio-Chemistry, Choudhary Charan Singh University, Meerut (U.P.)
Dr. Sudhir Verma, Associate Professor, Dept. of Bio-Chemistry, Choudhary Charan Singh University, Meerut (U.P.)

Introduction

Lanthanide ions have remarkable spectral characteristics, rendering them very suitable for the activation of optical materials. As a result, there has been considerable interest in the field of photoluminescence research about the integration of lanthanide ions into optical materials. Luminescent materials have a wide range of practical uses across several industries, such as sensors, solar cell technology, biological applications, display devices, solid-state lighting (SSL), and light-emitting diodes (LEDs). The length of the user's content is insufficient to be revised academically. The luminous properties of the phosphor are mostly influenced by the host lattice and the activator. The lanthanides demonstrate a characteristic energy level arrangement resembling a ladder, which gives rise to a unique emission spectrum. The use of phosphors is subject to changes due to their emissive qualities, which may be roughly classified into two categories: up conversion and down conversion phosphors. The up-conversion phosphors are produced by the conversion of lower energy (lower wavelength) into higher energy emission (higher wavelength).

REVIEW LITERATURE

Sudhindra N. Misra (2014). The coordinating chemistry of lanthanides, which is relevant to biological, biochemical, and medical aspects, provides a considerable contribution to understanding the basis of application of lanthanides, particularly in biological and medical systems. This is because the coordinating chemistry of lanthanides is relevant to all of these fields. This is due to the fact that the coordinating chemistry of lanthanides is essential to each and every one of these characteristics. The relevance of the applications of lanthanides, such as an excellent diagnostic and prognostic probe in clinical diagnostics and a chemical that combats cancer, is fast expanding. One example of this is how lanthanides are used. When it comes to the radiological inspection of human biological systems, an excessive quantity of lanthanide complexes-based X-ray contrast imaging and lanthanide chelates-based contrast enhancing agents for magnetic resonance imaging (MRI) are used. Lanthanide chelates are essential to the operation of each of these imaging methods. One of the most essential properties of the lanthanide chelate complex is the ability of chelating agents to alter the behaviour of lanthanide ions in biological systems. This is one of the chelating agents' primary functions. In addition, chelation has a substantial influence on the biodistribution and excretion profile of lanthanide ions in the body. Because of their hydrophilic character, chelating chemicals, and aminopoly carboxylic acids in particular, are able to increase the portion of their complex that is released from complexed lanthanide ions generated by biological systems. This is achieved by increasing the concentration of the aminopoly carboxylic acid. Compounds that increase contrast and are known as lanthanide polyamino carboxylate-chelate complexes are used in magnetic resonance imaging. The conjugation of antibodies and other tissue-specific molecules to lanthanide chelates has resulted in the development of a new category of particular MRI contrast agents and their conjugated MRI contrast agents, both of which have better relaxivity and function in the body in a manner that is analogous to that of pharmaceuticals. The development of this new category of particular MRI contrast agents and their conjugated MRI contrast agents has resulted in the development of a new category of particular MRI contrast agents. Because of its numerous specific qualities, the contrast agent assisted magnetic resonance imaging (MRI) approach is particularly helpful for imaging of the musculoskeletal and cerebrospinal systems. This is especially the case. Lanthanide-chelate contrast chemicals are employed in a manner that is both successful and efficient in clinical diagnostic procedures involving cerebrospinal diseases and the evaluation of the central nervous system. These techniques include the examination of the central nervous system. Chelated lanthanide complexes shift reagent aided ^{23}Na nuclear magnetic resonance spectroscopic analysis is employed in the research of cellular, tissue, and complete organ systems. Jacques Reuben (2015) investigates the bioinorganic chemistry of the lanthanides and discusses the physical methods that may be utilised to research biological systems that include

lanthanides. Jacques Reuben (2015) also discusses the bioinorganic chemistry of the lanthanides. In addition to this, it provides an explanation of the fundamentals that lie behind the various methods of analysis, such as optical absorption, fluorescence, circularly polarised luminescence, nuclear relaxation rates, nuclear magnetic resonance (NMR) chemical shifts, and NMR of lanthanum-139, and it provides examples of how these methodologies might be applied. The quantities of electronic energy possessed by lanthanide aquo-ions do not significantly change when complexes are created; rather, there is just a very little shift. Spectroscopy, on the other hand, makes it possible to regularly see these disruptions, particularly those that are associated with shifts in the symmetry of the ligand field. There is a wide range of events that may be attributed to interactions of the dipole–dipole type that occur when they are propagated over space. These phenomena include, but are not limited to, the enhancement of the intensity of lanthanide fluorescence, the modification of the resonances of ligand nuclei, and the improvement of relaxation rates. In this regard, macromolecules, as opposed to very small ligands, provide the potential of having tight spatial proximity between a lanthanide and a molecule or a molecular fragment without really attaching the two. This is in contrast to the situation with tiny ligands. In contrast to this, the scenario in which a direct interaction between the two ligands is required for tiny ligands occurs.

Joseph A. Cotruvo, Jr. (2019) scientists revealed the ground-breaking discovery that lanthanides are perfectly incorporated into a bacterial methanol dehydrogenase. This finding has the potential to revolutionise the field of biochemistry. Before this discovery, the essential function that rare earth elements play in living organisms was shrouded in obscurity. Because it was only just revealed that more lanthanide-binding proteins and mechanisms for selective absorption exist, this finding has only recently gone from being a curiosity to a major study subject. This is because new lanthanide-binding proteins and mechanisms for selective absorption were only recently identified. The recognition that organisms in the natural world that make use of lanthanides are quite widespread, in addition to the finding of these other systems, has contributed to this result. In spite of the fact that, at first glance, the use of lanthanides in biological systems may appear to be rather odd, this application of lanthanides is completely reasonable from a chemical point of view. They perform chemistry that is similar to that of other biologically useful metals and do so more efficiently due to higher Lewis acidity.

LANTHANIDE LUMINESCENCE:

The ionic states of rare earth elements display significant radiative transitions, particularly those involving the transition between the 4f and 5d electron orbitals. The fluorescence phenomenon, in a general sense, refers to spin-allowed transitions, such as $S_0 \rightarrow S_1$ transitions in organic molecules. However, this concept does not apply to transitions involving a change in spin for lanthanide ions. For instance, the $5D_4 \rightarrow 7F_5$ transition of Tb^{3+} and the $5D_0 \rightarrow 7F_2$ transition of Eu^{3+} are examples of spin-forbidden transitions. Figure provides a visual representation of the f and d orbitals. In the case of 4f₀, the phases above the nuclear node are opposite to those below it. On the other hand, the 5d₁ orbital exhibits equivalent phase on both sides due to the presence of a centre of symmetry within the d-orbital. Hence, the transitions from the 4f to 5d orbitals in lanthanide ions result in a modification of the dipole moment due to the redistribution of electronic charge. In contrast, the 4f₁ \rightarrow 4f₋₁ orbital transition involves a modification in the electric quadrupole (EQ) moment, resulting in a change in the shape of the electronic charge distribution without any variation in the electric dipole moment.

This transition may be characterised as an EQ transition. The phenomenon of aligning two dipoles in such a manner that their individual dipole moments cancel one other out, leading to the absence of a net dipole moment, can be attributed to the presence of a quadrupole moment. The electronic transitions permitted in lanthanide ions are determined by selection criteria pertaining to the electronic quantum numbers S (spin), L (angular momentum), and J (total angular momentum). The user's text is too short to be rewritten academically. When lanthanide ions are situated in locations with poor symmetry, such as when a centre of symmetry is absent, the wave functions of the d and f orbitals combine to form a merged level. Consequently, the 4f-4f transitions acquire some 4f-5d characteristics, leading to a heightened intensity in the "forced ED" transition. Certain transitions exhibit significant variations in intensity due to a

change in the symmetry of ions inside a crystal lattice, commonly referred to as site symmetry. Examples of such transitions are $\text{Eu}^{3+}: 5D_0 \rightarrow 7F_2$, $\text{Nd}^{3+}: 4I_{9/2} \rightarrow 4G_{5/2}, 2G_{7/2}$, $\text{Tb}^{3+}: 5D_4 \rightarrow 7F_6$, and $\text{Sm}^{3+}: 4G_{5/2} \rightarrow 6H_{9/2}$. These transitions are commonly referred to as hypersensitive.

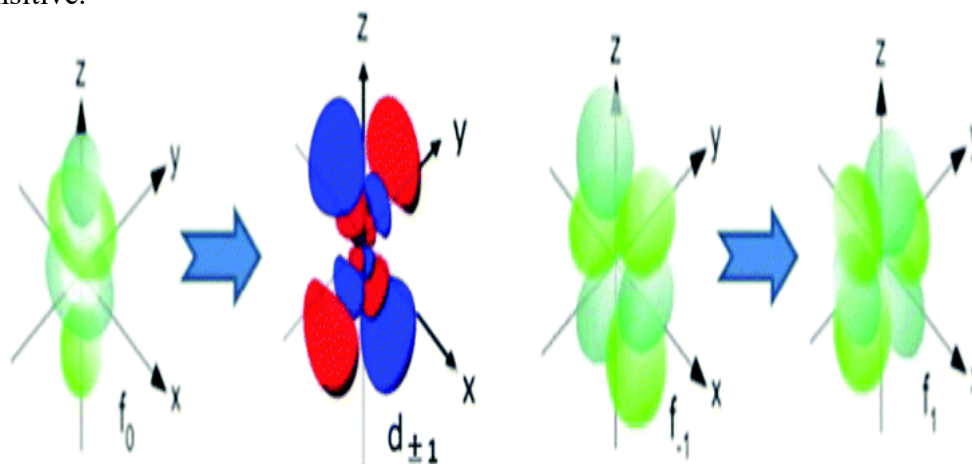


Figure: This study presents a clear description of two distinct types of transitions: the ED ($f \rightarrow d$) transition and the EQ ($f \rightarrow f$) transition. The diverse range of colours represents the positive or negative aspects of wavefunctions, which hold considerable importance in the determination of bonding properties.

Table: The rules regulating the f-f transitions of lanthanide ions are listed in the document.

Operator	Parity	ΔS	ΔL	ΔJ^*
Electric dipole	Opposite	0	≤ 6	≤ 6 (2, 4, 6, if J or J' = 0)
Magnetic dipole	Same	0	0	0, ± 1
Electric quadrupole	Same	0	0, $\pm 1, \pm 2$	0, $\pm 1, \pm 2$

Transitions from $J = 0$ to $J' = 0$ are consistently prohibited. The transition from $J = 0$ to $J' = 1, 3,$ and 5 demonstrates a mild intensity, whereas the transition from $J = 0$ to $J' = 2, 4,$ and 6 conveys a strong intensity. Table presents the lanthanide ions together with the quantity of unbound 4f electrons accessible and their matching fundamental state.

Table: This study provides an overview of the lanthanides, including an examination of their possible oxidation states, the electron count within the f orbital, and the related ground states associated with each element.

Ion		Number of 4f electrons	Ground state
	La^{3+}	0	1S_0
	Ce^{3+}	1	$^2F_{5/2}$
	Ce^{4+}	0	1S_0
	Pr^{3+}	2	3H_4
	Nd^{3+}	3	$^4I_{9/2}$
	Pm^{3+}	4	5I_4
Sm^{2+}		6	7F_0
	Sm^{3+}	5	$^6S_{5/2}$

Eu ²⁺			7	⁸ S _{7/2}
	Eu ³⁺		6	⁷ F ₀
	Gd ³⁺		7	⁸ S _{7/2}
	Tb ³⁺		8	⁷ F ₆
		Tb ⁴⁺	7	⁸ S _{7/2}
	Dy ³⁺		9	⁶ H _{15/2}
	Ho ³⁺		10	⁵ I ₈
	Er ³⁺		11	⁴ I _{15/2}
	Tm ³⁺		12	³ H ₆
Yb ²⁺			14	¹ S ₀
	Yb ³⁺		13	² F _{7/2}
	Lu ³⁺		14	¹ S ₀

Table: The primary focus of this scholarly discourse centres on the ground state levels and the resulting number of states that arise from 4fⁿ configurations, with a special emphasis on lanthanide ions. Furthermore, pertinent illustrations of these lanthanide ions will be shown.

4f ⁿ	Example	Ground level	4f ⁿ	Example	Ground level	Number of levels	Number of microstates
4f ₀	La ³⁺ , Ce ⁴⁺	¹ S ₀	4f ₁₄	Lu ³⁺ ,Y b ²⁺	¹ S ₀	1	1
4f ₁	Ce ³⁺ , Pr ⁴⁺	² F _{5/2}	4f ₁₃	Yb ³⁺ ,T m ²⁺	² F _{7/2}	2	14
4f ₂	Pr ³⁺	³ H ₄	4f ₁₂	Tm ³⁺	³ H ₆	13	91
4f ₃	Nd ³⁺	⁴ I _{9/2}	4f ₁₁	Er ³⁺	⁴ I _{15/2}	41	364
4f ₄	Pm ³⁺	⁵ I ₄	4f ₁₀	Ho ³⁺	⁵ I ₈	107	1001
4f ₅	Sm ³⁺	⁶ H _{5/2}	4f ₉	Dy ³⁺	⁶ H _{15/2}	198	2002
4f ₆	Eu ³⁺ , Sm ²⁺	⁷ F ₀	4f ₈	Tb ³⁺ ,D y ⁴⁺	⁷ F ₆	295	3003
4f ₇	d ³⁺ , Tb ⁴⁺ , Eu ²⁺	⁸ S _{7/2}	—	—	—	327	3432

The spectral lines exhibited by elements of the lanthanide family are distinguished by their distinctive emission lines, which include a spectrum ranging from 0 to 40,000 cm⁻¹. The graphical form frequently employed to depict these spectral lines is referred to as the "Dieke diagram." The numeral 5. The Dieke diagram is a visual depiction of the energy levels associated with trivalent rare earth (RE) ions. These energy levels correspond to the states of the ions when they are free and are classified by their quantum numbers of spin (S), orbital (L), and angular (J) momentum. The provided diagram depicts the correlation between the quantum numbers and the centroid of the corresponding J-multiplet. The rare earth (RE) elements exhibit several excited energy levels, some of which are as follows: Sm³⁺ emits at the 4G_{5/2} level, Eu³⁺ emits at the 5D_{0,1,2,3,4} levels, Tb³⁺ emits at the 5D_{3,4} levels, Dy³⁺ emits at the 5S₂ level, Ho³⁺ emits at the 5S₂ and 5S₅ levels, Er³⁺ emits at the 2H_{9/2}, 4S_{3/2}, and 4F_{9/2} levels, and Tm³⁺ emits at the 1D₂ and 1G₄ levels. The use of certain transitions involving RE³⁺ ions is primarily determined by the existence of conspicuous, dominant, and well-defined peaks in the emission spectrum.

spectra, like,	⁴ G _{5/2}	→	⁶ H _{5/2,7/2,9/2}	of Sm ³⁺ ,	⁵ D _{0,1,2}	→	⁷ F _{0,1,2,3,4}	of Eu ³⁺ ,	⁵ D _{3,4}	→	⁷ F _{2,3,4,5,6}	of
Tb ³⁺ , ⁴ F _{9/2} →	⁶ H _{15/2,13}	/2 of	Dy ³⁺ , ⁵ F ₄	, ⁵ S ₂ → ⁵ I ₈	and ⁵ I ₄ →	⁵ I ₈ of Ho ³⁺ , ² H _{11/2} ,	⁴ S _{3/2} ,	⁴ F _{9/2}	→	⁴ I _{15/2}	of	

The observed phenomenon involves the transition of Erbium ions from the 1D₂ state to the 3F₄ state, as well as the transition of Thulium ions from the 1G₄ state to the 3F₄ and 3H₆ states. Europium ions (Eu³⁺) are commonly employed in many applications owing to their notable emission of red light. This emission is a result of electronic transitions from the 5D₀ state to the 7F₁ state (at a wavelength of 555 nm) and from the 5D₀ state to the 7F₂ state (at a wavelength of 614 nm), resulting in the production of orange-red and red emissions, respectively. The Dy³⁺ ion exhibits simultaneous dual emission, characterised by emissions in the blue (483 nm) and yellow (584 nm) spectral regions. The emissions mentioned can be ascribed to the transitions from the 4F_{9/2} to 6H_{15/2} and 4F_{9/2} to 6H_{13/2} states, respectively. The Yb³⁺ ion has clearly defined and straightforward electrical energy levels that correspond to the excitation wavelength of 980 nm generated by laser diodes. The electronic transition predominantly utilised by Yb³⁺ is the shift from the 2F_{7/2} energy level to the 2F_{5/2} energy level. The utilisation of the excited states of Yb³⁺ is a feasible approach for aiding energy transfer processes due to the presence of overlapping energy levels with the excited states of Er³⁺, Tm³⁺, and Ho³⁺.

The lanthanides Erbium (Er³⁺), Thulium (Tm³⁺), and Ytterbium (Yb³⁺) have unique emissions in the red, green, and yellow regions when they absorb Ytterbium (Yb³⁺) and then transfer energy to the energy levels of Erbium (Er³⁺) and Ytterbium (Yb³⁺). The Tm³⁺ ion demonstrates a continuous emission in the blue region of the electromagnetic spectrum at a wavelength of 488 nm, which is contingent upon the specific characteristics of the host material. The emission can be traced to the shift from the 1D₂ state to the 3F₄ state. Furthermore, the Tm³⁺ ion exhibits a weak red emission at a wavelength of 697 nm, which arises from the magnetic dipole transition between the 1G₄ and 3F₄ energy levels.

Dorenbos proposed a theoretical framework for the systematic classification of the absorption and emission energy associated with the 4f-5d transition in divalent and trivalent lanthanide ions. The theoretical foundation has played a crucial role in the use of these ions as dopants in over 1,000 inorganic compounds. The numerical interval spans from 6 to 8. Various lanthanide ions have the ability to generate a diverse range of coloured emissions by means of unique f-f transitions. Furthermore, the combination of emissions originating from two or more distinct rare earth ions can give rise to a diverse range of coloured emissions, as seen in Figure.

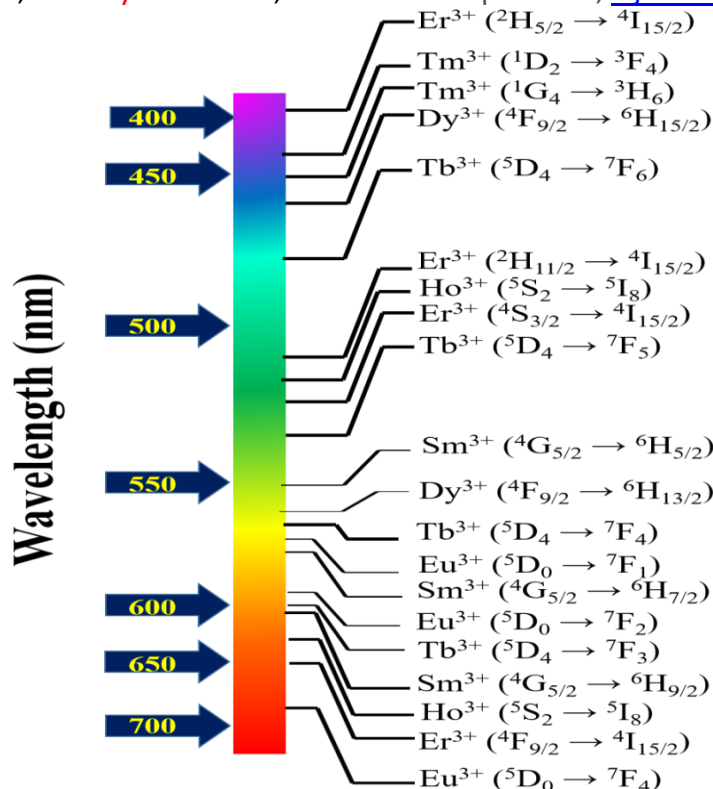


Figure: The provided statement discusses the schematic depiction of the colour output resulting from the main f-f transitions of rare earth (RE) elements.

REFERENCES

1. T. Jüstel, H. Nikol and C. Ronda, *Angew. Chemie Int. Ed.*, 1998, 37, 3084–3103.
2. X. Huang, *Nat. Photonics*, 2014, 8, 748–749.
3. P. A. Tanner, *Chem. Soc. Rev.*, 2013, 42, 5090–5101.
4. P. A. Tanner, L. Zhou, C. Duan and K.-L. Wong, *Chem. Soc. Rev.*, 2018, 47, 5234–5265.
5. G. H. Dieke, in *Wiley*, New York, 1968.
6. P. Dorenbos, *Phys. Rev. B*, 2000, 62, 15640–15649.
7. P. Dorenbos, *Phys. Rev. B*, 2000, 62, 15650–15659.
8. P. Dorenbos, *Phys. Rev. B*, 2001, 64, 125117.
9. M. Cesaria and B. Di Bartolo, *Nanomaterials*, 2019, 9, 1–28.
10. W. Jüstel, T.; Möller, S.; Winlker, H.; Adam, In *Ullmann's Encyclopedia of Industrial Chemistry*, John Wiley & Sons: Weinheim, Germany, 2012.
11. C. Feldmann, T. Jüstel, C. R. Ronda and P. J. Schmidt, *Adv. Funct. Mater.*, 2003, 13, 511–516.
12. T. Jüstel, *Nanoscale*, 2011, 3, 1947.
13. H. A. Höpfe, *Angew. Chemie Int. Ed.*, 2009, 48, 3572–3582.
14. C. Ronda, *Luminescence: from Theory to Applications*; Wiley: Weinheim, 2008.
15. H. Yen, W. M.; Shinoya, S.; Yamamoto, *Phosphor Handbook*, 2nd ed.; CRC Press: Boca Raton, 2007.
16. B. C. Blasse, G.; Grabmaier, *Luminescent Materials*; Springer-Verlag: Berlin, 1994.
17. S. V Bünzli, J.-C. G.; Eliseeva, In *Lanthanide Luminescence: Photophysical, Analytical and Biological Aspects*, 2010.