The Research Dialogue

An Online Quarterly Multi-Disciplinary
Peer-Reviewed / Refereed Research Journal
ISSN: 2583-438X
Volume-04, Issue-02, July-2025
www.theresearchdialogue.com

"Basic Mechanisms of Photoluminescence"

Dr. P. P. Zala
Assistant Professor, Physics
Shri Natvarsinhji Arts and Science College and Shri S. G.
Patel Commerce College,
Chhotaudepur - 391165 (Gujarat)

Abstract:-

Photoluminescence (PL) is light emission from matter after energy absorption, primarily linked to semiconductors and insulators but also found in metals, phosphors, and biomolecules. It has spurred research in optics, condensed matter physics, spectroscopy, and biophysics. Despite extensive studies, a fundamental understanding of its mechanisms is lacking. This work investigates the basic mechanisms of the photoluminescence effect, providing a foundation for researchers. Key mechanisms are summarized in the figure. It introduces the two main types of PL—fluorescence and phosphorescence. Next, the excitation mechanisms are detailed, differentiating direct and indirect processes. The emission mechanism highlights transitions from excited to ground states, resulting in photon emission. The impact of defects and temperature on PL properties is examined. It identifies various materials displaying PL and their relevance to discussed mechanisms. The chapter surveys applications in technology and science, showing the practical significance of these principles. It also addresses current challenges in research and highlights recent advances, outlining future directions. A comprehensive conclusion synthesizes insights into the mechanisms of photoluminescence.

Keywords: Photoluminescence, Mechanisms, Energy, fluorescence, etc.

1. Introduction to Photoluminescence

Photoluminescence encompasses all processes in which a material—whether a molecule, atom, or solid surface—is illuminated by photons and subsequently emits light (Bozsoki et al., 2005). Photoluminescence measurements are among the most versatile analytical probes available for the study of semiconductors (Varkentina et al., 2022). Photoluminescence is distinguished from thermal luminescence, where light emission is caused by high temperature, as well as from electroluminescence, where light emission is caused by an electric current. It can be further classified into fluorescence and phosphorescence, between which a distinction is made on the basis of the time scale of decay of the luminescence following the removal of the exciting radiation. Fluorescence comprises those photoluminescence phenomena that cease within nanoseconds or less, whereas phosphorescence comprises those that persist for much longer.

Until the end of the 1850s, the word fluorescence was used for all phenomena of luminescence; subsequently, discoveries of various materials that emitted light after removal of the excitation source—that is phosphorescence, will be described—showed the need for a distinction.

2. Historical Background

The study of photoluminescence traces back to the observation of “luminous vapour” over heated substances by H. G. Ford, which was later understood as photoluminescence. More recently, electron bombardment of solids in rarefied gases provided a means to examine photoluminescence when the vapour phase was unavailable or unsuitable. Early theoretical treatments focused on describing the spectral distribution and intensity of photoluminescence, laying the groundwork for quantitative experiments and practical applications. Photoluminescence was discovered in solids shortly after its contact with vapour was understood and gained renewed interest following the invention of the transistor. Quantum mechanics stimulated further progress, leading to models such as the Quantum Theory of Photoluminescence (Varkentina et al., 2022). An empirical correlation with energy-band theory soon followed, known as the Fundamental Principles of Photoluminescence.

3. Fundamental Principles

Photoluminescence (PL) involves materials absorbing and re-emitting photons at longer wavelengths, useful for analyzing properties in materials like MoS2 flakes. It consists of fluorescence (nanosecond lifetimes) and phosphorescence (microseconds to hours). Light emission theories in microstructures derive from quantized electromagnetic fields. In weak-coupling, the emission decays exponentially, influenced by atom-cavity coupling and decay rates. For layered structures, PL follows a generalized Kirchhoff's law, reaching local thermodynamic equilibrium (LTE) when relaxation times exceed those needed for Planck's law and energy redistribution. Under LTE, the emission spectrum mirrors absorption and temperature similar to Planck's law and the van Roosbroeck–Shockley relation, with efficient radiative energy exchange between emitters and their environment. A Langevin approach to spontaneous emission aligns mathematically with generalized Kirchhoff's law. Analytical PL spectra expressions for multilayered quasi-one-dimensional systems, like doped photonic crystals, provide a robust framework, simplifying calculations relative to direct methods, especially for low quantum efficiency materials. Emission analysis in a two-layer photonic crystal reveals emission peak asymmetry near photonic band gaps and their variation with period numbers. (M. Voronov, 2016)

3.1. Quantum Theory of Photoluminescence

Photoluminescence is the emission of light from a substance that has absorbed electromagnetic radiation without chemical changes. This process begins when a material moves from its ground state to an excited state upon light absorption, then returns to the ground state, emitting photons. Emissions typically occur at longer wavelengths than the absorbed radiation due to energy loss to nonradiative processes. This phenomenon is observed in various substances, especially phosphorescent materials, and has broad applications in low-energy lighting and high-efficiency phosphorescent lamps. The Quantum Theory of Photoluminescence explains the interaction between electromagnetic radiation and matter. Central to this theory are electromagnetic fields and atomic electrons, with classical descriptions relying on Maxwell–Lorentz equations and quantum mechanical explanations using Quantum Electrodynamics. Since the early 20th century, PL has been studied extensively, remaining a significant research topic due to its applications and role in understanding light–matter interactions. Albert Einstein's work in 1917 elucidated key characteristics of PL, building on Bohr's atomic emission theory to reveal how PL results from incoherent radiation's interaction with matter, highlighting the emitted light's temporal incoherence. (Khosla et al., 2018)(Bozsoki et al., 2005)

3.2. Energy Band Theory

The energy-band structure of an ideal crystal is fundamental to the theory of photoluminescence (PL). This model utilizes translational symmetry and unit cells to explain PL mechanisms in insulators and semiconductors. Quantum theory employs potential periodicity, indicating that electronic states resemble Bloch waves. Due to the Pauli principle, electrons with wave vectors in filled bands cannot be excited, while those in unfilled bands can be. The energy-band structure consists of two main groups: the valence-band group, fully occupied by electrons, and the conduction-band group, devoid of electrons. The bandgap refers to the energy difference between these groups, defined as the smallest nonzero difference within the entire Brillouin zone. (Bozsoki et al., 2005)

4. Types of Photoluminescence

The ultimate emission of a phosphor depends on excitation processes. Direct excitation into emitting states via Bremsstrahlung, electron bombardment, or high-energy bands results in fluorescence with short lifetimes, ranging from nanoseconds to microseconds. In contrast, direct excitation into triplet levels of Eu2+ and Mn2+ leads to longer emissions, lasting from microseconds to seconds. If excitation first occurs in the host material followed by energy transfer to emitting levels, the emission is fluorescence-type with a longer lifetime due to the longer pulsed host excitation. For instance, silicon shows indirect excitation processes due to forbidden transitions, resulting in high emission lifetimes. Thin films of Bi2SiO5 exhibit a short emission peak (17 ns) through an indirect band gap process. Typically, host excitation lasts in the nanosecond range, while microsecond pulsed excitation, such as from flash lamps, is distinct. Continuous electron bombardment also leads to indirect emission, as seen in most electroluminescent devices which operate in acidic conditions. The excitation mechanism is defined by the type of excitation and emission within the phosphor's space charge area. Mn2+ ions are excited by holes through direct excitation yet retain phosphor-like emitting characteristics. Additionally, tiny amounts of Cu2+, Fe3+, or Co2+ can provide strong luminescence, excitable through various means, including electron bombardment and infrared radiation.

4.1. Fluorescence

Fluorescence is a photoluminescence phenomenon with nanosecond lifetimes. When a material absorbs photons, it emits light instantaneously while being excited. This emission lasts nanoseconds beyond the excitation pulse, ending afterward due to the transition mechanisms. The process starts with absorbing radiation, exciting electrons from valence to higher bands in an indirect path. This involves radiation-free transformations, with carriers moving through energy states before radiative recombination. The excitation wavelength differs from the produced luminescence. Direct excitation promotes electrons from a valence state to an excited state, leading to internal non-radiative conversion until the emitting transition occurs. (E. Ogluzdin, 2012)(I. Deych et al., 2006)

4.2. Phosphorescence

Phosphorescence is a photoluminescence process characterized by lifetimes that span microseconds to minutes, distinctly longer than the nanosecond-scale lifetimes typical of fluorescence (Patrick Zobel et al., 2023). The mechanism involves photoexcitation to a singlet excited state, followed by intersystem crossing to an energetically proximate triplet state; the system subsequently fluoresces from this triplet state (Kurtulik et al., 2021). At low temperatures, phosphorescence decay manifests as a monoexponential function, while at ambient conditions a power-law decay with an exponent of approximately 1.0 emerges, suggesting a universal decay pattern in inorganic, organic, and biological phosphors.

5. Excitation Mechanisms

Photoluminescence involves a multistep process including excitation, scattering, energy transfer among lattice vibrations, ions, electron–hole pairs, and, finally, emission (Varkentina et al., 2022). Optical excitation mechanisms can be divided into direct and indirect ones. Direct excitation creates an electron–hole pair in or near the emitting center through absorption of a photon or an electron–hole pair. Indirect excitation includes energy transfer from other lattice vibrations, ions, electron–hole pairs, or the host to the emitting center (Zalogina et al., 2022).

5.1. Direct Excitation

The direct excitation mechanism is essential in photoluminescence (PL), where charge carriers like electrons and holes are excited into higher-energy states without using intermediate levels. This differs from indirect excitation, where carriers first move to higher energy states before settling at a luminescent center. In direct excitation, the incident electromagnetic radiation has photon energy just above the material's bandgap or resonant with impurity states. Key factors are the intensity and photon energy of the light, which work independently of the material's previous photoexcitation. When irradiated, electrons absorb photons, getting excited into higher energy states or the conduction band, depending on the photon energy and electronic transitions. This forms electron-hole pairs, and their relaxation and recombination lead to photoluminescence emission. (Zalogina et al., 2022)(Lu et al., 2014)

5.2. Indirect Excitation

Indirect excitation selectively brings atoms or molecules from a ground state to an emissive state. Initially, a non-emitter entity, such as an atom or molecule, is excited. This energy does not remain localized and transfers to other atoms or molecules, which then emit. An analogy can be drawn with groups of people: exciting one person leads to collective excitation within their group, which then influences subsequent groups until the final group emits. Most indirect excitation methods involve energy or charge transfer, where the excited state moves to a molecule favoring radiative relaxation. Typically, two conditions must be met: the emitted wavelength must match what the separating material absorbed, and the acceptor must have a lower energy gap than the initially excited atoms. The acceptor's excited electron can then relax into the lower energy state. These mechanisms can be non-radiative or “non-resonant” and radiative or “resonant,” with the resonant process involving two steps. (Matsuda et al., 2015)

6. Emission Processes

The emission process in photoluminescence occurs when an excited state returns to the ground state, releasing light. This return typically happens via the same radiative transition that excited the state. For instance, if the quantum system is excited through an allowed optical transition from the ground state to the excited state, it can only return via an allowed optical transition since the excited electron cannot instantly thermalize to other states. When excitation occurs via an indirect transition, additional states may be populated during thermalization. This can lead to more complex emission properties, often resulting in multiple emissions peaks being observed. (Bozsoki et al., 2005)(Merino et al., 2018)

7. Role of Defects in Photoluminescence

The intrinsic photoluminescence in defect-free wide-bandgap materials is due to transmission electrons in valence-band states. Point defects introduce additional electronic states within the bandgap, often near the band extrema, arising from impurity atoms or lattice atoms struggling with periodicity. These defects disrupt the ideal lattice symmetry, allowing new optical transitions. While these transitions generally exhibit smaller optical matrix elements than those between free carriers, the localization of defect-bandgap wavefunctions can increase these matrix elements, making defect-related photoluminescence notable. However, defects primarily reduce photoluminescence efficiency by acting as nonradiative recombination centers that shorten the effective lifetime of luminescent electrons. Hence, photoluminescence measurements are valuable for evaluating crystal purity. Additionally, defect levels may trap free carriers or facilitate electron-hole recombination, generating extra bands in the spectrum that align with defect-level positions relative to the conduction or valence bands. The spectral profiles of these defect bands and their phonon replicas are significantly influenced by atomic configuration changes during optical ionization, which excite lattice vibrations linked to the defect. (Meindert Feenstra, 1982)

8. Temperature Dependence

Photoluminescence offers valuable insights into material temperature phenomena and enables optical-control setups. Recent experiments show that PL at low temperatures maintains photon emission rates, while at higher temperatures, it shifts to thermal emission. Thermally stimulated luminescence methods utilize defect filling efficiency's temperature evolution, revealing the thermal history of materials and analyzing processes such as gas emission, dislocation, stress, and radiation damage from high-energy excitation. The 1960s and 1970s studies recognized temperature dependence trends. Direct excitation involves photon absorption by neutral donors or acceptors, described by the Braun model, predicting recombination intensity changes with temperature. More frequently, excitation occurs through a charge-transfer state with transition-metal ions, influencing photoluminescent and kinetic properties significantly. Temperature dependence is evident in luminescence spectral shape, band intensity, and shifts, with luminescence lifetime typically decreasing as temperature increases. A Maxwell distribution model predicts fluorescence lifetime reduction with higher temperatures, explaining longer delay times exceeding 10^(-6) s, occurring in bursts. The temperature effect on fluorescence lifetime is less notable than in phosphorescence. (Kurtulik et al., 2021)(Xia et al., 2021)(Chimczak, 2006)

9. Materials Exhibiting Photoluminescence

Materials showing photoluminescence include alkaline earth fluorides doped with rare-earth ions, diamond containing nitrogen vacancies, rare-earth-doped garnets, and direct bandgap semiconductors such as gallium arsenide. Alkaline earth fluorides like CaF2 and SrF2 doped with rare-earth ions combine the large bandgap of the host with the strong emission of the dopant. Diamond hosts nitrogen vacancies that produce photoluminescence at several wavelengths. Rare-earth-doped garnets provide efficient emission from the rare-earth ions and allow tuning of the excitation spectrum. While gallium arsenide's emission at 860 nm limits its applications, other direct bandgap semiconductors can overcome this constraint (Varkentina et al., 2022) (Garshasbi et al., 2021) (Xu et al., 2015).

11. Applications of Photoluminescence

Photoluminescence properties of various materials are essential for numerous technological and scientific applications, such as luminescent labels, displays, information storage, photonic devices, and solar cells. Analyzing the luminescence spectrum and its lifetime offers valuable insights into the electronic structure and susceptibility of materials, aiding in phase matching and device engineering. Evaluating luminescence under different conditions, like activator concentration, temperature, and environment, helps address nonradiative quenching issues. Understanding the lifecycle of optical excitation, from creation to photon decay, is crucial for studying optical properties. Photoluminescence excitation spectroscopy reveals unique information on material photophysics, which has significant implications in quantum optics and photovoltaics. However, excitation and emission pathways are influenced by nanometer-scale variations, affecting device performance. Analyzing energy loss during excitation alongside visible-UV photon emission uncovers decay pathways from initial excitation to light emission. This analysis applies to both phase-locked and non-phase-locked interactions, such as localized surface plasmons and point defects in semiconductors. Additionally, cathodoluminescence excitation spectroscopy provides imaging of energy transfer pathways at the nanoscale, complementing tools for exploring nanoscale materials. (Khosla et al., 2018)

12. Challenges and Limitations

Despite recent progress, challenges remain in quantifying excitation-emission pathways in materials, with no dominant mechanism. Light diffraction limits photoluminescence excitation spectroscopy to hundreds of nanometers, hindering nanoscale materials research. The mechanisms transitioning from non-luminescent to luminescent states in indirect bandgap semiconductors, and from forbidden to permitted transitions in direct bandgap semiconductors, are debated. Nanocrystalline systems like silicon nanocrystals and double perovskite Cs2AgBiX_6 nanocrystals show efficient luminescence and high quantum yields. The Localized State-Induced Enhanced Emission (LIEE) model explains silicon nanocrystals' luminescence, yet its universality is unconfirmed, and the fluorescence mechanism in Cs2AgBiX_6 nanocrystals is unclear. Understanding these luminescence mechanisms and enhancing luminous performance remain key research challenges in developing luminescent nanocrystalline materials. (Varkentina et al., 2022)(Wang et al., 2024)

13. Recent Advances in Photoluminescence Research

The ongoing development of novel nanomaterials and surface modification methods has yielded various luminescent metal-based nanomaterials, including metal-polymer composites, metal-organic frameworks, cluster-assembled materials, and self-assembled nanostructures. Understanding the origin of photoluminescence is crucial for designing materials with controlled performance. In metal nanoclusters, localized metal-centered quantum-confined states govern the photoemission process, which can be modulated through charge transfer to the ligand shell. Photoluminescence properties are sensitive to experimental conditions such as medium, temperature, and surface ligands. Factors like the metal core structure, packing mode, ligand topology, and assembly directly influence these properties and applications. Recent studies on perovskite have shown that a significant excitation and emission channel can circumvent slow indirect bandgap transitions. Size limitations or partial doping have been proposed to explain the anomalous luminescence found in various perovskite nanocrystals. These insights aid in designing efficient lead-free perovskite nanocrystals and enhancing optical transitions. Achieving effective luminescence with high quantum yields in challenging nanocrystalline systems, such as silicon nanocrystals and lead-free double perovskites, remains an area of active research. (Yang et al., 2020)(Wang et al., 2024)

14. Future Directions

Recent developments are leading to novel strategies for improving photoluminescence study efficiency. Enhanced excitation pathways through resonant effects in subwavelength nanoresonators show promise. Mie-resonance-induced enhancement of five-photon photoluminescence in a single AlGaAs nanoantenna has resulted in a significant efficiency increase, validating the concept and encouraging exploration of alternative excitation channels. Cathodoluminescence excitation spectroscopy provides quantitative insights into decay regimes by examining energy lost by monochromated electrons alongside photon emission. This technique has been applied to localized surface plasmons, where excitation and emission are phase-locked, and to single point defects in hexagonal boron nitride, exhibiting non-phase-locked behavior. These advances offer nanometer-scale imaging of energy-transfer pathways, directly probing excitation mechanisms and illuminating new materials and spatial regimes, suggesting ongoing progress in understanding photoluminescence. (Zalogina et al., 2022)(Varkentina et al., 2022)

15. Conclusion

Photoluminescence (PL) is a common process in which an incident electromagnetic wave produces an excited state in a substance; the excited substance relaxes to the ground state with emission of an electromagnetic wave. The overall properties of the EM propagation and luminescence of a substance are closely related to the basic structure of the material. The nature of luminescence depends greatly on the basic structure and state of a substance. In an atomic system, luminescence would be closely correlated with the excited states of the atoms involved. Another important issue on the basic mechanisms of PL is the role of the defects in the materials. In relation to the emission intensity of a light source, it is also important to investigate the temperature dependence of PL intensity. Various materials exhibit photoluminescence ranging widely and applications of the products are also important at the present time. Some representative applications of PL are also introduced to understand the importance of the study of its basic mechanism. Because of insufficient or poor information of basic mechanism, some critical issues still exist on the PL field, for instance, lack of critical information on excitation processes still remains for the universal application of PL phenomenon.

References:

* Bozsoki, P., Kira, M., Hoyer, W., Meier, T., Varga, I., Thomas, P., & W. Koch, S. (2005). Microscopic modeling of photoluminescence of strongly disordered semiconductors.

- Varkentina, N., Auad, Y., Y. Woo, S., Zobelli, A., Blazit, J. D., Li, X., Tencé, M., Watanabe, K., Taniguchi, T., Stéphan, O., Kociak, M., & H. G. Tizei, L. (2022). Cathodoluminescence excitation spectroscopy: nanoscale imaging of excitation pathways.
- M. Voronov, M. (2016). Application of the generalized Kirchhoff's law to calculation of photoluminescence spectra of one-dimensional photonic crystals.
- Khosla, M., Rao, S., & Gupta, S. (2018). Polarons Explain Luminescence Behavior of Colloidal Quantum Dots at Low Temperature. ncbi.nlm.nih.gov
- E. Ogluzdin, V. (2012). Photoluminescence, amplification and generation of optical media in without inversion and of induced radiation.
- Deych, L., V. Erementchouk, M., A. Lisyansky, A., L. Ivchenko, E., & M. Voronov, M. (2006). Exciton luminescence in resonant photonic crystals.
- Patrick Zobel, J., Radatz, H., & González, L. (2023). Photodynamics of the Molecular Ruby. ncbi.nlm.nih.gov
- Kurtulik, M., Weill, R., Manor, A., & Rotschild, C. (2021). High-temperature photoluminescence reveals the inherent relations between quantum efficiency and emissivity.
- Varkentina, N., Auad, Y., Y. Woo, S., Zobelli, A., Bocher, L., Blazit, J. D., Li, X., Tence, M., Watanabe, K., Taniguchi, T., Stéphan, O., Kociak, M., & H. G. Tizei, L. (2022). Cathodoluminescence excitation spectroscopy: Nanoscale imaging of excitation pathways. ncbi.nlm.nih.gov
- Zalogina, A., Tonkaev, P., Tripathi, A., Lee, H. C., Carletti, L., Park, H. G., S. Kruk, S., & Kivshar, Y. (2022). Enhanced five-photon photoluminescence in subwavelength AlGaAs resonators.
- Lu, T., Ma, Z., Du, C., Fang, Y., Wu, H., Jiang, Y., Wang, L., Dai, L., Jia, H., Liu, W., & Chen, H. (2014). Temperature-dependent photoluminescence in light-emitting diodes. ncbi.nlm.nih.gov
- Matsuda, T., Yokoshi, N., & Ishihara, H. (2015). Up-converted photoluminescence induced by radiative coupling between excitons.
- Merino, P., Rosławska, A., Große, C., C. Leon, C., Kuhnke, K., & Kern, K. (2018). Bimodal exciton-plasmon light sources controlled by local charge carrier injection. ncbi.nlm.nih.gov
- Meindert Feenstra, R. (1982). Electronic and Vibrational States of Point Defects in Semiconductors.

- Xia, Y., Du, S., Huang, P., Wu, L., Yan, S., Wang, W., & Zhong, G. (2021). Temperature-Dependent Photoluminescence of Manganese Halide with Tetrahedron Structure in Anti-Perovskites. ncbi.nlm.nih.gov
- Chimczak, E. (2006). Model of photon emission from luminescent center.
- Garshasbi, S., Huang, S., Valenta, J., & Santamouris, M. (2021). Enhancing the cooling potential of photoluminescent materials through evaluation of thermal and transmission loss mechanisms. ncbi.nlm.nih.gov
- Xu, B., He, J., Mu, Y., Zhu, Q., Wu, S., Wang, Y., Zhang, Y., Jin, C., Lo, C., Chi, Z., Lien, A., Liu, S., & Xu, J. (2015). Very bright mechanoluminescence and remarkable mechanochromism using a tetraphenylethene derivative with aggregation-induced emission. ncbi.nlm.nih.gov
- Wang, F., Ou, Q., & Zhang, S. (2024). Localized State-Induced Enhanced Emission in Perovskite Nanocrystals.
- Yang, T. Q., Peng, B., Shan, B. Q., Zong, Y. X., Jiang, J. G., Wu, P., & Zhang, K. (2020). Origin of the Photoluminescence of Metal Nanoclusters: From Metal-Centered Emission to Ligand-Centered Emission. ncbi.nlm.nih.gov

Cite this Article:

Dr. P. P. Zala “Basic Mechanisms of Photoluminescence” *The Research Dialogue,* An Online Quarterly Multi-Disciplinary Peer-Reviewed & Refereed National Research Journal, *ISSN: 2583-438X (Online), Volume 4, Issue 2, pp-232-242, July 2025. Journal URL: https://theresearchdialogue.com/*

THE RESEARCH DIALOGUE

An Online Quarterly Multi-Disciplinary
Peer-Reviewed & Refereed National Research Journal
ISSN: 2583-438X
Volume-04, Issue-02, July-2025
www.theresearchdialogue.com
Certificate Number July-2025/23
Impact Factor (RPRI-4.73)

Certificate Of Publication

This Certificate is proudly presented to

Dr. P. P. Zala

for publication of research paper title

“Basic Mechanisms of Photoluminescence”

Published in ‘The Research Dialogue’ Peer-Reviewed / Refereed Research Journal and E-ISSN: 2583-438X, Volume-04, Issue-02, Month July, Year-2025.

Dr. Neeraj Yadav
Executive Chief Editor

Dr. Lohans Kumar Kalyani
Editor-in-chief

Note: This E-Certificate is valid with published paper and the paper must be available online at www.theresearchdialogue.com

INDEXED BY