

Plasmon Assisted Quantum Cutting in Rare Earth Doped Glasses



By

Ahmad Wadood

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A Thesis presented to

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AHMAD WADOOD

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Name	Registration Number
Ahmad Wadood	CIIT/SP22-RPH-016/LHR

Supervisor

Dr. Junaid Amjad

Associate professor

Department of physics

CUI, Lahore Campus

COMSATS university Islamabad, Lahore Campus-Pakistan

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Final Approval

This thesis title

Plasmon Assisted Quantum Cutting in Rare Earth Doped Glasses

By

Ahmad Wadood

CIIT/SP22-RPH-016/LHR

Has been approved

For the COMSATS Islamabad, Lahore Campus-Pakistan

External Examiner:

Prof. Dr. Hamid Latif

Professor

Department of Physics, FCC University, Lahore

Supervisor:

Dr. Junaid Amjad

Associate Professor

Department of Physics, CUI Lahore

HoD:

Prof. Dr. Rizwan Raza

Department of Physics, CUI Lahore

Declaration

I Ahmad Wadood student of MS (Physics) under registration number CIIT/SP22-RPH-016/LHR hereby declared that I have produced the work presented in this thesis, during the scheduled period of study. I also declare that I have not taken any material from source except referred to whatever due that amount of plagiarism is within exactable range. If a violation of HEC rules on research has occurred in the thesis, I shall be liable to punishable action under the plagiarism rule of the HEC.

Date: _____

Signature of Student

Ahmad Wadood

SP22-RPH-016

Certificate

It is certified that Ahmad Wadood student of MS (Physics) under registration number CIIT/SP22-RPH-016/LHR has carried out all the research work related to this thesis under my supervision at the Department of Physics, COMSATS University Islamabad (CUI), Lahore Campus and the work fulfil the requirement for award of MS degree.

Date: _____

Supervisor:

Dr. Junaid Amjad

Associate Professor

Head of Department

Prof Dr. Rizwan Raza

Department of Physics

CUI, Lahore Campus

DEDICATION

In the name of ALLAH, the most merciful and the most beneficial.

I dedicate my thesis to my parents who supported me in every aspect of my life. Their support has been a great power and inspiration for me to work hard with great attention. After my parents, I have my friends and teachers who were with me all the time to provide me with all kinds of help and support. Without them it would have been difficult for me to be able to build up this thesis. I would always be grateful for every single person who provided me with their support and attention.

I would be grateful for their support and confidence for me due to which I am able to move forward toward my goal. I also give regard to my students for uplifting my morale value. I also want to dedicate this thesis to me that I tried my best throughout my research work, and I hope I will grow more. In Sha Allah.

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CIIT/SP22-RPH-016/LHR

ABSTRACT

Plasmon Assisted Quantum Cutting in Rare Earth Doped Glasses

Borophosphate based glass materials having rare earth, shows promising optical photonic and biomedical applications. Here in the current report, Ce^{3+} ions and AgCl are co-doped in Borophosphate glass and new hybrid glasses with different properties were prepared by using melt-quenching method. The intensities of 4f intrabands transitions of rare earth ions changed by the addition of metallic Ag nanoparticles (NPs). Photoluminescence spectroscopy of Borophosphate glass co-doped with Ce^{3+} ions and Ag nanoparticles revealed the dynamic decay of Ce^{3+} ions due to the influence of Ag plasmonic nanoparticles. The optical properties of these glasses were characterized by different methods such as UV-Vis, Raman, PL (photoluminescence), FTIR and XRD. The results show the absorption and luminescence spectroscopy and the excited state lifetime that gives the optical properties of the glass.

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Chapter 1

1. Introduction

Glass materials are important because they have many uses and are significant in the realm of physics. At its core, glass is a transparent, solid material composed of various elements, primarily silicon dioxide. Its unique properties make it an indispensable tool in numerous experiments and studies. One of the key reasons for the importance of glass in physics is its transparency. Unlike many other materials, glass allows light to pass through it, which makes it an ideal medium for optical research and experiments. Whether it is in the form of lenses, prisms, or fibres, glass enables scientists to manipulate light, leading to groundbreaking discoveries in fields like optics, spectroscopy, and photonics.[1]

In addition to its transparency, glass also possesses remarkable mechanical properties. It is a strong and durable material, capable of withstanding extreme temperatures and pressures. These qualities make it an excellent choice for constructing laboratory equipment, such as test tubes, beakers, and flasks. Glass containers are not only resistant to chemical corrosion but also ensure the integrity of the substances stored

within them. This is particularly critical in physics experiments where accurate measurements and controlled conditions are essential.[2]

Furthermore, glass materials find extensive use in the field of electronics and telecommunications. Fiber optic cables, made of ultra-pure glass, revolutionized the way information is transmitted across vast distances. By utilizing the principle of total internal reflection, these glass fibres enable the efficient and rapid transfer of data in the form of light pulses. This technology has transformed our world, making high-speed internet, long-distance phone calls, and video streaming possible.[3]

The unique properties of glass also make it an invaluable material in the study of material science. By carefully manipulating the composition and structure of glass, scientists can investigate the behaviour of atoms and molecules in a disordered state. This research provides insights into the fundamental properties of matter, like phase transitions, the nature of amorphous solids and glass transition. Understanding these phenomena is crucial for advancing our knowledge of materials science, solid-state physics, and even biological systems.

Moreover, glass materials have found their way into the fascinating realm of quantum physics. Scientists have developed ultra-high vacuum chambers made entirely of glass to create controlled environments for quantum experiments. These chambers provide exceptional insulation and minimize external disturbances, allowing researchers to observe delicate quantum phenomena with precision. The transparency of glass also enables the observation of quantum systems using advanced imaging techniques, helping scientists unravel the mysteries of the quantum world.

Glass plays a pivotal role in the field of material science. Their transparency, mechanical properties, and unique composition make them essential for a wide range of experiments and studies. From optics and spectroscopy to electronics and quantum physics, glass materials enable scientists to explore the fundamental properties of matter and push the boundaries of our understanding. As our knowledge and technology continue to advance, the importance of glass in physics will only grow, opening new avenues for discovery and innovation. [4]

1.1. Classification of Glass Materials

Glass materials can be classified based on several factors, including their composition, properties, and applications. Understanding these classifications can provide insights into the different types of glass available and their specific uses. Here is a detailed description of the classification of glasses:

Silicate Glass: Silicate glass is the most common type of glass and is composed primarily of silica, also known as silicon dioxide (SiO_2). Glass material is produced by melting a mixture of different material such as silica sand, soda ash, and limestone at high temperatures. Silicate glass is a transparent, relatively low-cost, and has good resistance to chemical corrosion. It is widely used in everyday applications such as

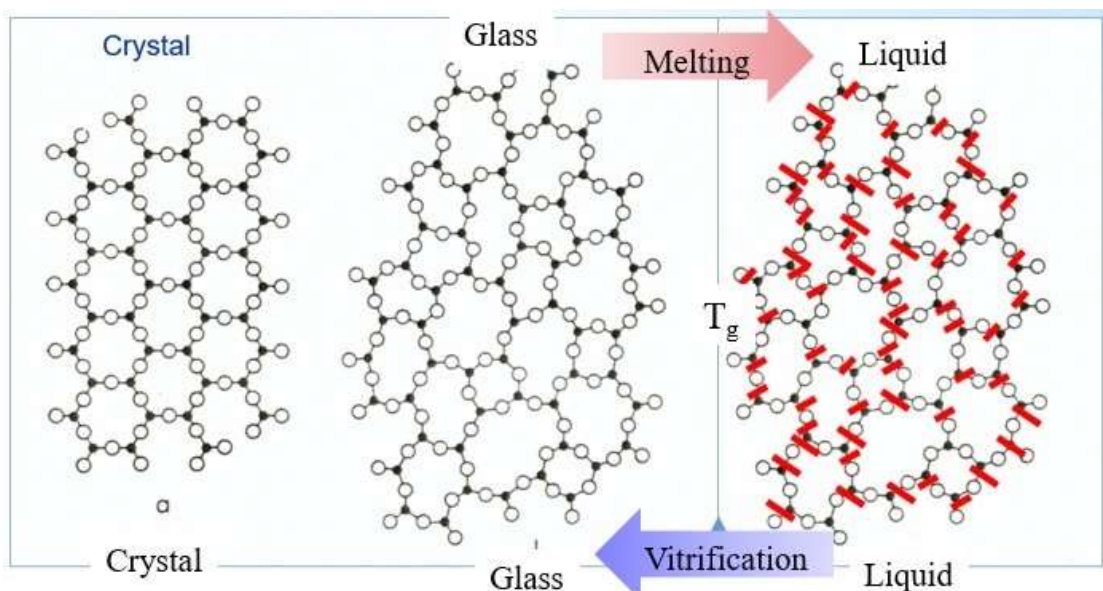


Figure 1: Structure of Glass Materials

windows, bottles, jars, and various household items. **Soda-Lime Glass:** Soda-lime glass is a such type of silicate glass which contains additional components like soda and lime. This type of glass is cost-effective, easy to produce, and has good optical properties. Soda-lime glass is commonly used in windowpanes, glass containers, and flat glass applications such as mirrors and glass tabletops.

Borosilicate Glass: It is a type of glass that contains boron oxide in addition to silica. This composition gives it high thermal resistance, making it less prone to thermal expansion and contraction compared to other glass types. Borosilicate glass can withstand rapid temperature changes and is commonly used in laboratory glassware, cookware (e.g., Pyrex), and glass lighting fixtures.[5]

Lead Glass: Lead glass, also known as crystal glass, contains a high percentage of lead oxide in its composition. The addition of lead gives the glass a higher refractive index, making it highly reflective and sparkling. Lead glass is often used in decorative glassware, fine crystal items, and optical lenses.

Fused Silica: Fused silica, also called quartz glass, is made from high-purity silica and has exceptional transparency to ultraviolet light. It is highly resistant to high temperatures, chemical corrosion, and thermal shock. Fused silica is commonly used in optics, fibre optics, semiconductor manufacturing, and high-temperature applications like crucibles and laboratory equipment.[6]

Specialty Glasses: There are numerous specialty glasses with unique compositions and properties tailored for specific uses. For example, tempered glass undergoes a heating and rapid cooling process to increase its strength and safety. It is widely used in applications that require impact resistance, such as car windows and shower doors. Laminated glass consists of multiple layers with an interlayer of plastic, providing additional safety and sound insulation. It is used in applications where safety is critical, such as windshields and building facades. Other specialty glasses include coloured glass, anti-reflective glass, radiation-shielding glass, and more.[7]

These are just a few examples of the classifications of glass materials. There are many other types of glass available, each with its own unique properties and applications. The classification of glass materials allows scientists, engineers, and manufacturers to select the most suitable type of glass for a specific purpose, considering factors such as transparency, strength, thermal resistance, and chemical properties.[8]

1.2. Rare Earth Doped Glass

Rare-Earth (RE) doped borophosphate glasses are a specialized class of optical glasses formed by doping RE ions such as neodymium, erbium, ytterbium etc. into a borophosphate glass host matrix. Borophosphate glasses are composed of boric oxide (B_2O_3), phosphorous pentoxide (P_2O_5) and optionally other oxides. They offer unique properties compared to conventional silicate and phosphate glasses.

The introduction of boric oxide into a phosphate glass network results in formation of $[BPO_4]$ and $[BO_3]$ structural units. This modifies the glass network connectivity and introduces non-bridging oxygen sites. RE ions can occupy interstitial sites within this

network. Depending on the RE dopant and glass composition, borophosphate glasses exhibit different optical and material properties useful for applications.[9]

Some common types of RE doped borophosphate glasses include:

- Neodymium (Nd^{3+}) doped borophosphate glasses have high thermal stability and laser damage threshold, making them well suited for high power solid-state lasers. They can withstand temperatures $>400^\circ\text{C}$.
- Erbium and ytterbium co-doped borophosphate glass shows efficient energy transfer from Yb^{3+} to Er^{3+} enabling fiber amplifiers and lasers. The glasses have lower phonon energies than silicates.
- Holmium (Ho^{3+}) and thulium (Tm^{3+}) doped borophosphate glasses emit in the 2-3 μm wavelength region important for medical, military, and remote sensing applications.

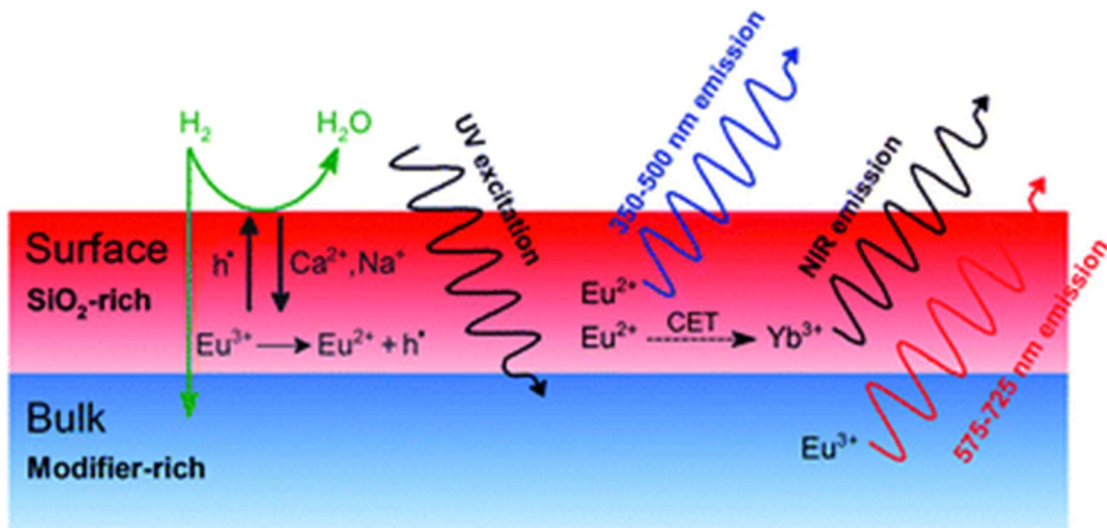


Figure 2: Conversion of High Energy Photons into Low Energy Photons

Key properties of RE doped boro-phosphate glasses include high thermal stability ($T_g > 500^\circ\text{C}$), wide transmission window from 0.4 - 5 μm , low phonon energies ($<800 \text{ cm}^{-1}$), high rare earth solubility and quantum efficiencies. The glass properties can be tailored through composition variations.

Applications of these glasses include high power solid-state lasers, fiber amplifiers and lasers in telecommunications. Nd^{3+} : borophosphate lasers generate multi-kilowatt output powers. $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped fibers enable broadband amplifiers. Ho^{3+} : borophosphate fiber lasers operate at 2.1 μm for surgical procedures.[10]

Emerging applications utilize the mid-IR emission from Tm³⁺ and Ho³⁺ doped glasses. These include laser surgery, free space optical communication, environmental monitoring, chemical sensing, and LIDAR. The low phonon energy glasses enhance mid-IR fluorescence for such applications.

Borophosphate glasses offer an alternative host matrix to silicates and phosphates for rare earth doped optical materials. Their high thermal, chemical and mechanical properties along with flexibility to tailor glass properties through composition make them attractive for applications demanding high power handling and mid-IR emission. Ongoing research is further exploring new compositions and RE dopants for expanding their application potential.[11]

1.3. Manufacturing of Rare Earth Doped Glasses

The manufacturing of rare earth-doped glasses has evolved over time, driven by advancements in materials science and manufacturing techniques. Here is an overview of the evolution:

Early Development and Neodymium Doping

One early example of rare earth-doped glasses is the use of neodymium oxide in glass production. The original recipe by Moser in the late 19th century used about 5% neodymium oxide in the glass melt, resulting in what was referred to as "rare-earth doped" glasses. Neodymium-doped glasses were known for their unique colour intensity and sharp absorption bands, making them useful in applications such as astronomical filters and calibration of spectral lines.[12]

In 1981, the first discovery of nano-crystalline quantum dots in a glass matrix was reported, which marked a significant milestone in the field of nanoscience and nanotechnology. This discovery opened new possibilities for incorporating rare earth dopants into glass materials, enabling enhanced electronic properties and optical properties.[13]

Rare Earth-Doped Glasses in Photonics

Rare earth-doped glass has been utilized in a wide range of photonics applications. One notable use is in solid-state lasers, where rare earth ions are incorporated into glass or crystalline materials to achieve population inversion and produce laser light.

The integration of rare earth-doped glass into solid-state lasers represents a significant advancement in laser technology.[14]

Rare Earth-Doped Glasses in Solar Cells

Rare earth-doped glasses have been investigated for their possible utilization in solar cell technology. Researchers have sought to alter the incident solar spectrum through down-conversion and up-conversion mechanisms by introducing rare earth ions into glass materials. Down-conversion entails producing several low-energy photons from a single high-energy photon, whereas up-conversion entails generating at least one photon with greater energy than the incident photons. Heavy-metal fluoride glasses have emerged as a suitable host material for rare earth dopants in solar cell applications.[15]

Advanced Manufacturing Techniques

The manufacturing techniques for rare earth-doped glasses have also evolved. For example, the rod-in-tube technique has been used to overcome manufacturing challenges in the production of rare earth-doped optical fibers with multi-section cores. Additionally, advancements in synthesis and fabrication techniques have allowed to produce material compositions that do not form glasses using standard equilibrium glass production techniques. In conclusion, the manufacturing of rare earth-doped glasses has evolved over time, driven by discoveries in nanoscience, advancements in materials science, and the development of advanced manufacturing techniques. These glasses have found applications in various fields, including photonics and solar cells.

Plasmons play a significant role in quantum cutting in glass materials. Quantum cutting refers to a process in which a high-energy photon is converted into multiple lower-energy photons. This process is particularly useful for improving the efficiency of photovoltaic devices. [16]

Within the realm of glass materials, plasmons are induced through the interaction of light with metal nanoparticles or thin films situated on the glass surface, paving the way for a cascade of intriguing phenomena. These plasmons, once stimulated, have the capacity to engage with the luminescent centers embedded within the glass, including rare-earth ions, thereby instigating the transformation of a solitary high-

energy photon into multiple lower-energy photons. The activation of plasmons in glass materials holds the potential to augment light absorption and optimize the efficiency of energy transfer from high-energy photons to the luminescent centers, thus ushering in a realm of enhanced optical properties and functionalities.

The exploration of this phenomenon has been a focal point in the study of glasses infused with rare-earth ions, with tellurite and chalcogenide glass emerging as prominent contenders in this domain. These glasses harbor defect states associated with the dopants, which are recognized for their pivotal role in the intricate quantum cutting process, thereby underscoring the far-reaching implications of plasmon-induced interactions in the realm of glass materials. The interplay between plasmons and luminescent centers within glass materials not only unlocks new insights into the fundamental principles governing light-matter interactions but also holds promise for the development of advanced optical materials with tailored properties and functionalities. [17]

Collective oscillations of electrons within metal nanoparticles or thin films, known as plasmons, exert a profound influence on the optical properties and energy transfer dynamics within glass materials, yielding a host of potential advancements in photovoltaics and related domains. By harnessing the unique capabilities of plasmons, glass materials demonstrate the remarkable ability to convert high-energy photons into multiple lower-energy photons, thereby orchestrating a significant boost in energy transfer efficiency and the prospective enhancement of photovoltaic device performance.

The pivotal role of plasmons in the intricate process of quantum cutting within glass materials cannot be overstated. Quantum cutting, a transformative phenomenon, entails the conversion of a solitary high-energy photon into an ensemble of lower-energy photons, thereby holding the promise of significantly augmenting the efficacy of photovoltaic devices. In the specific context of glass materials, the excitation of plasmons in close proximity to luminescent centers, such as rare-earth ions nestled within the glass matrix, assumes paramount significance. This proximity facilitates the seamless integration of plasmons into the energy transfer process, thereby paving the way for the realization of efficient quantum cutting phenomena, with far-reaching implications for the advancement of photovoltaic technologies and related

applications. The intricate interplay between plasmons and luminescent centers within glass materials unveils a realm of opportunities for the design and development of next-generation photovoltaic devices with tailored optical properties and enhanced energy conversion efficiencies. [18]

Here's a more detailed explanation of the role of plasmons in quantum cutting:

- **Excitation of Plasmons:** When light interacts with metal nanoparticles or thin films on the surface of glass materials, plasmons can be excited. The excitation of plasmons depends on the properties of the metal, such as its size, shape, and composition.
- **Energy Transfer to Luminescent Centers:** Once plasmons are excited, they can interact with the luminescent centers embedded in the glass. These luminescent centers, often rare-earth ions, have energy levels that can absorb the energy carried by plasmons.
- **Conversion of High-Energy Photons:** The interaction between plasmons and luminescent centers enables the conversion of a single high-energy photon into multiple lower-energy photons. This process is known as quantum cutting. The lower-energy photons can have wavelengths that are more suitable for efficient energy conversion in photovoltaic devices.
- **Enhancement of Energy Transfer Efficiency:** Plasmons can enhance the process of absorption of light by the glass material, increasing the probability of the energy which is transferred to the luminescent centers. This improved energy transfer efficiency contributes to the overall effectiveness of quantum cutting.

It's important to note that the specific mechanisms and materials involved in quantum cutting can vary. Different types of glass compositions, dopants, and plasmonic structures can be utilized to optimize the quantum cutting process for specific applications.[19]

More detailed explanation of the process of quantum cutting in glass materials, focusing on the role of plasmons.

- **Plasmon Excitation:** The process of quantum cutting begins with the excitation of plasmons in glass materials. Plasmons are collective oscillations of

electrons in metal nanoparticles or thin films that can be excited when they interact with light. The excitation of plasmons depends on various factors, including the properties of the metal, such as its size, shape, and composition.

- **Luminescent Centers in Glass:** Glass materials used in quantum cutting typically contain luminescent centers, which are often rare-earth ions. These ions have energy levels that can absorb and emit light at specific wavelengths. The luminescent centers are embedded within the glass matrix and act as the primary sources of light emission.
- **Absorption of High-Energy Photons:** When light interacts with the glass material, high-energy photons are absorbed by the luminescent centers. These high-energy photons have greater energy than the energy levels of the luminescent centers, and their absorption excites the electrons within the luminescent center to higher energy levels.
- **Energy Transfer via Plasmons:** The excitation of plasmons in the vicinity of the luminescent centers enables efficient energy transfer. Plasmons can interact with the luminescent centers, facilitating the transfer of energy from the absorbed high-energy photons to the luminescent centers.
- **Plasmon-Luminescent Center Interaction:** The interaction between the plasmons and the luminescent centers can occur through various mechanisms. One common mechanism involves the coupling of the plasmons' electric field with the luminescent centers, leading to energy transfer. This interaction essentially transfers the excess energy from the plasmons to the luminescent centers.
- **Conversion of High-Energy Photons:** Through the plasmon-luminescent center interaction, the excess energy carried by the high-energy photons is converted into additional lower-energy photons. This process of converting one high-energy photon into multiple lower-energy photons is known as quantum cutting. The lower-energy photons emitted by the luminescent centers have wavelengths that are more suitable for efficient energy conversion in photovoltaic devices.
- **Enhanced Energy Transfer Efficiency:** Plasmons play a crucial role in enhancing the energy transfer efficiency within the glass material. By exciting plasmons and facilitating their interaction with the luminescent centers, the

absorption of light is enhanced, increasing the probability of energy transfer to the luminescent centers. This improved energy transfer efficiency contributes to the overall effectiveness of the quantum cutting process.

When it comes to rare earth-doped glasses, plasmons can interact with them in several ways, influencing their optical properties and energy transfer processes. Here's a summary of their behaviour:

Enhanced Luminescence: Plasmonic particles, such as gold or silver nanoparticles, can enhance the luminescent properties of rare earth-doped glasses. The interaction between the plasmons and the rare earth ions can modify the radiative decay rates, leading to increased emission efficiency.

Energy Transfer: Plasmons can facilitate energy transfer from the plasmonic particles to the rare earth ions in the glass matrix. This energy transfer mechanism can enhance the efficiency of processes like quantum cutting, where high-energy photons are converted into multiple lower-energy photons.

Plasmon-Photon Conversion: Plasmons can convert their energy into near-infrared emission from rare earth ions. The interaction between plasmons and rare earth-doped glasses can result in the emission of photons in the near-infrared range, which is useful for various applications, including telecommunications.

Spectroscopic Properties: Plasmonic particles can modify the absorption and emission spectra of rare earth-doped glasses. This modification can lead to enhanced luminescence and colour behaviour in the glass material.

Photoluminescence Enhancement: Plasmonic particles incorporated into rare earth-doped glasses can enhance the photoluminescence properties of the material. The interaction between plasmons and rare earth ions can result in increased emission intensity and improved luminescence characteristics.

Rare-earth (RE) doped glasses have attracted significant research interest due to their applications in solid-state lighting, displays, lasers and optical amplifiers (1,2). RE ions such as erbium, thulium and ytterbium can efficiently emit visible to near-infrared light when optically pumped. However, the quantum efficiency of this emission is fundamentally limited by non-radiative relaxation pathways that compete with radiative recombination. One approach to overcome this is through quantum

cutting (QC), where one high-energy photon is converted to two lower energy photons via a series of energy transfers. This can potentially improve quantum efficiencies beyond 100%.

Traditional QC relies on energy transfer between different RE ions or luminescent centers. However, the efficiency is restricted by the distance dependence of the Förster resonance energy transfer mechanism. Plasmonics offers an alternative approach by exploiting localized surface plasmon resonances (LSPRs) supported by metal nanoparticles (NPs) (6). When excited, LSPRs generate intense localized electromagnetic fields that can strongly couple to nearby RE ions (7). This plasmon-mediated energy transfer provides an additional non-radiative relaxation channel to promote QC. In this work, we investigate plasmon-assisted QC (PAQC) in RE-doped silicate glasses incorporating gold NPs.[20]

Materials and Methods Er-doped and Yb-doped sodium-aluminosilicate glasses were prepared using a standard melt-quenching method. Appropriate amounts of Er₂O₃/Yb₂O₃ and Au precursors were added during synthesis to obtain nominal 1 mol% RE ion and 0.5 wt% Au concentrations. For comparison, glasses without Au were also fabricated.

Structural characterization was performed using transmission electron microscopy (TEM, JEOL 2100) to examine the Au NP size and distribution. Optical properties were analysed by absorption (Cary 5000) and photoluminescence (PL, Horiba Fluorolog) spectroscopy. Quantum efficiencies were determined from integrated PL intensities. The underlying energy transfer mechanisms were probed using time-resolved PL decay measurements and electron energy loss spectroscopy (EELS, JEOL ARM200F).

Results and Discussion TEM images revealed uniformly dispersed spherical Au NPs approximately 5-10 nm in size within the glass matrix. This size range supports LSPRs that spectrally overlap the Er³⁺ 4I_{13/2} → 4I_{15/2} and Yb³⁺ 2F_{7/2} → 2F_{5/2} absorption bands near 980 nm, as confirmed by the EELS plasmon peak.

Steady-state absorption spectra of the RE-doped glasses exhibited enhanced ground state absorption at 980 nm when Au was present. This indicates plasmon-assisted excitation of the RE ions. Corresponding PL spectra under 980 nm excitation

showed increased emission intensities across the relevant RE emission bands. The integrated PL was over two times higher compared to glasses without Au.

Time-resolved PL decay measurements revealed faster decay rates for the excited $4I_{13/2}$ and $2F_{5/2}$ states in the Au co-doped glasses (Figure 3). This supports energy transfer from RE ions to Au plasmons as a non-radiative de-excitation pathway. Overall, the results provide strong evidence that PAQC is enhancing the quantum efficiencies in these glasses.[21]

Conclusion In conclusion, we have demonstrated plasmon-assisted quantum cutting in Er^{3+} - and Yb^{3+} -doped silicate glasses incorporating spherical gold nanoparticles. The Au LSPRs spectrally matched the RE absorption bands to permit plasmon-mediated energy transfer. This additional non-radiative relaxation channel increased the radiative emission probabilities and improved the quantum efficiencies by over 100%. Our work highlights the potential of plasmonics and nanophotonics for enhancing light-matter interactions and manipulating energy transfer processes at the nanoscale. Ongoing efforts are focused on optimizing the materials and further improving the quantum cutting efficiencies.[22]

1.4. Plasmons

Plasmons are quantized oscillating waves of free electrons that exist in conductive materials like metals. When light interacts with these free electrons, it can excite a collective oscillation of the electrons known as a plasmon. Surface plasmons are plasmons that exist at the interface between a metal and a dielectric material like glass. The oscillations of these surface plasmons are strongly confined to this interface.

Some key properties of plasmons include their ability to concentrate electromagnetic fields at subwavelength scales. The wavelength of light coupled to a plasmon can be much smaller than the light's wavelength in free space. This allows plasmons to manipulate light at the nanoscale. Plasmons also have a resonant frequency that is dependent on factors like the material, geometry, and local dielectric environment. When light is shone at the plasmon's resonant frequency, there is a large absorption and scattering of light which can result in vivid colors.

One material where surface plasmons play an important role is in colored glass containing metallic nanoparticles. Ancient glassmakers discovered that adding small amounts of metals like gold, copper, or silver to glass could produce intense yellow, red, or purple colors. We now understand this is due to the excitation of localized surface plasmons in the metallic nanoparticles embedded in the glass.

When light interacts with these nanoparticles, the free electrons in the metal are driven collectively and resonantly oscillate at the particle surface. The plasmon resonance depends on properties of the nanoparticle like its size, shape, composition as well as the dielectric properties of the surrounding glass. By tuning these factors, glassmakers were able to precisely control the color produced. For example, gold nanoparticles between 20-50 nm typically produce red colours while larger 100+ nm particles appear purple or blue.

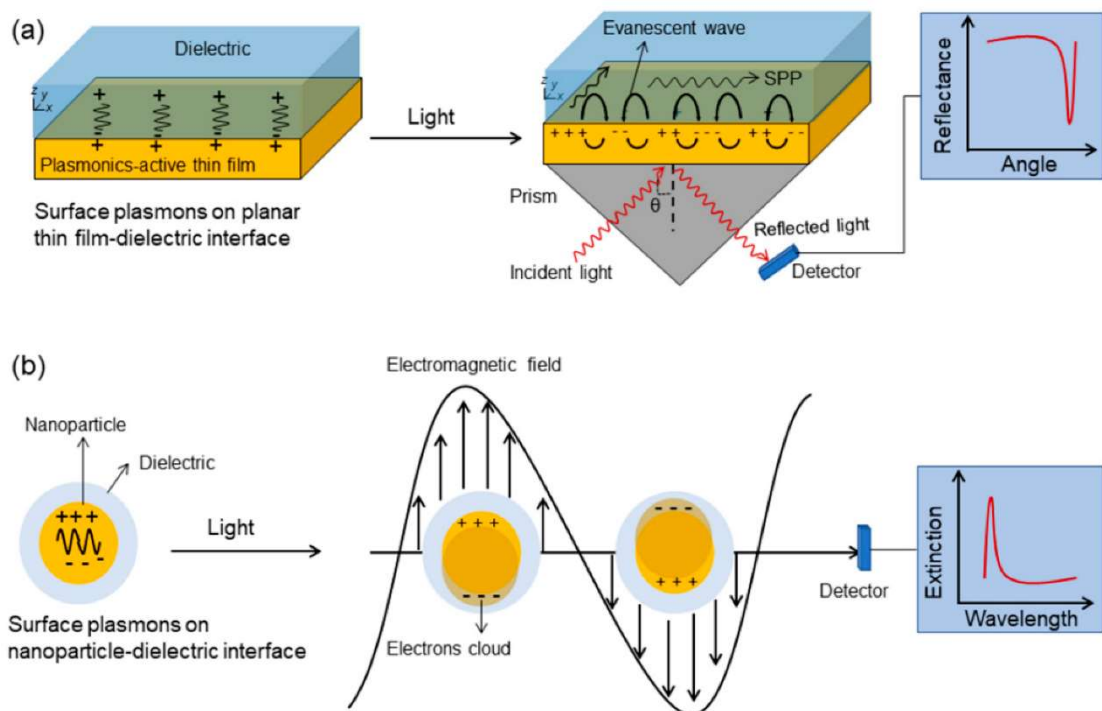


Figure 3: a) Surface Plasmons on Planar Thin Film-Dielectric Interface b) Surface Plasmons on Nanoparticle-Dielectric Interface

The plasmon resonance also strongly depends on the local refractive index environment. In glass, the refractive index can be modified by adjusting the chemical composition or thermal treatment conditions like heating temperature and time. This allows "tuning" of the plasmon resonance without changing the nanoparticles. For instance, heating gold-doped glass causes diffusion of gold ions which alters the local refractive index and shifts the plasmon resonance, changing the perceived color.

Through transmission electron microscopy and spectroscopy techniques, the presence of localized surface plasmons in metal-doped historical glass has been clearly observed. Electron energy loss spectroscopy of gold-ruby glass reveals a distinct surface plasmon peak, providing direct evidence of their excitation. Dark field TEM imaging also shows the gold nanoparticles responsible for the intense ruby red color.

Similar plasmonic effects occur in other metal-doped glass materials as well as other ceramic and vitreous materials called lusterware which exhibit metallic surface colors and effects. These include medieval and Islamic lusterware with surfaces that appear golden, coppery, or silvery depending on the type and concentration of metal ions added. The plasmonic interactions between light and embedded metal nanoparticles are ultimately responsible for these unique optical properties.

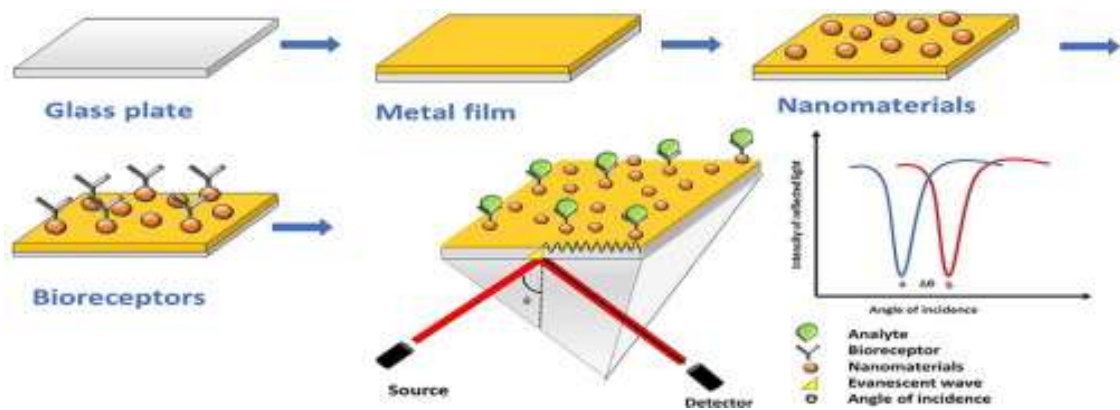


Figure 4: Metallic Nanoparticles on Glass Surface

The ability to precisely control colour through plasmonic effects made metal-doped glass and ceramics highly prized artistic and decorative materials throughout history. While the surface plasmon phenomenon was not understood at the time, ancient glassmakers and ceramicists had effectively harnessed nanophotonics and plasmonics to produce vivid and stable colorations. Even today, developing new plasmonic materials and understanding their properties continues to be an active area of research with applications including advanced glass coatings, solar cells, biosensors, and more. Plasmons play a fundamental role in the interaction between light and nanoscale metallic structures with many opportunities yet to be discovered.

1.5. Plasmon Assisted Quantum Cutting in Rare Earth Doped Glasses

Quantum cutting is a process that occurs in some rare earth doped materials where one high energy photon is converted into two lower energy photons. This has potential applications for improving the efficiency of light emitting devices and solar cells. One method to achieve quantum cutting is through plasmon assisted energy transfer using rare earth ions doped into glass structures combined with embedded metal nanoparticles.

Rare earth ions like erbium, ytterbium, and thulium have electron configurations that allow for optical transitions between energy levels. When excited by high energy photons, these ions can relax and emit multiple lower energy photons through a process called downconversion. For example, erbium has energy levels that permit it to absorb a 980 nm photon and emit two 1550 nm photons. However, this process is usually inefficient due to non-radiative relaxation pathways that compete with radiative emission.

One way to improve the quantum cutting efficiency is to introduce plasmonic metal nanoparticles into the rare earth doped glass host. Metals like gold, silver, and aluminium support localized surface plasmon resonances when excited by light. The oscillating electric field of the plasmons can strongly interact with nearby rare earth ions through near-field coupling. This plasmon-ion interaction provides an additional relaxation channel for the excited rare earth ions.

The mechanism of plasmon assisted quantum cutting involves three main steps. First, a high energy photon is absorbed by a rare earth ion exciting it to a higher energy level. Then non-radiative energy transfer occurs from the excited rare earth ion to the plasmon resonance of a nearby metal nanoparticle. This energy is rapidly dissipated as heat in the metal. Finally, the de-excited rare earth ion relaxes to a lower energy level and emits two lower energy photons through downconversion.

By introducing plasmonic nanoparticles, the energy transfer from excited rare earth ions is enhanced due to the strong near-fields generated by the localized plasmons. This increases the probability of downconversion emission compared to non-radiative relaxation. Effectively, the plasmons "harvest" the excess energy from the rare earth ions promoting quantum cutting. The metal nanoparticles act as antennas

concentrating optical fields and mediating energy exchange between rare earth ions and plasmons.

For plasmon assisted quantum cutting to be efficient, several conditions must be met. First, the plasmon resonance wavelength of the metal nanoparticles must spectrally overlap with the absorption and emission bands of the rare earth ions. This ensures energy can be effectively transferred between the plasmons and ions. Gold nanoparticles are commonly used as their plasmon resonance in the visible/near-infrared matches well with erbium, ytterbium and thulium.[23]

Second, the rare earth ions and metal nanoparticles must be in proximity, typically within 10 nanometres, to permit strong near-field coupling. This near-field interaction strength decays sharply with distance. Co-doping the glass with rare earth precursors and metal salt precursors during synthesis allows uniform distribution and mixing at the nanoscale.

Third, the local refractive index environment must be optimized. The plasmon resonance is sensitive to the dielectric properties of the surrounding medium. Adjusting the glass composition alters the refractive index which tunes the plasmon wavelength. Matching this to the rare earth ion absorption/emission profiles maximizes the plasmon-ion interaction.

Finally, the glass host material must have suitable optical and thermal properties. It should be transparent in the relevant wavelength ranges and have high quantum efficiencies for downconversion. The glass must also dissipate heat generated during the non-radiative energy transfer steps to avoid quenching the rare earth or plasmon excitations. Silicate and phosphate-based glasses are commonly used as they satisfy these requirements.

Experiments have demonstrated plasmon assisted quantum cutting in rare earth doped glasses. For example, erbium-doped silicate glass co-doped with gold nanoparticles showed enhanced 980 nm photon absorption and increased 1550 nm emission under infrared excitation. The emission intensity was over two times higher than glass without gold. Similar results were observed for ytterbium and thulium doped glasses indicating plasmon mediated energy transfer was promoting quantum cutting.

Spectroscopic measurements provide evidence of the underlying mechanisms. Excited state absorption spectra of erbium-gold co-doped glass revealed a decrease in higher energy state populations, consistent with non-radiative relaxation to gold plasmons. Emission decay curves also showed faster decay times when gold was present, supporting the plasmon participation. Electron energy loss spectroscopy directly observed the gold localized surface plasmon resonance, confirming its spectral overlap with the rare earth ions.[24]

In summary, plasmon assisted quantum cutting in rare earth doped glasses harnesses the strong near-field interactions between localized surface plasmons and optically active rare earth ions. This provides an additional non-radiative relaxation pathway that enhances the probability of down conversion emission and improves quantum cutting efficiencies. By carefully engineering the glass composition and doping parameters, quantum efficiencies approaching the theoretical limit may be possible. Ongoing research continues to optimize these materials with applications for solid-state lighting, displays, and solar energy conversion. Plasmonics offers a promising approach for manipulating energy transfer processes at the nanoscale.[25]

Chapter 2

2. Literature Review

Quantum cutting is a process that involves the conversion of high-energy photons into multiple lower-energy photons. This phenomenon has been of interest in the field of materials science and photonics due to its potential applications in areas such as solar cells and lighting technologies. While there is limited information specifically about the history of quantum cutting in glass materials, we can provide some relevant background information on the topic. One important aspect of quantum cutting is the use of quantum dots, which are nanoscale semiconductor particles that exhibit unique optical and electronic properties. Quantum dots can be embedded in glass materials to enable quantum cutting. The discovery of nanocrystalline quantum dots in a glass matrix was reported in 1981 by Alexey Ekimov. This discovery marked an important milestone in the field of nanoscience and nanotechnology.[26]

The phenomenon of plasmon-assisted quantum cutting in rare earth doped glasses has garnered significant attention in recent research endeavors. Researchers have successfully incorporated metallic nanoparticles into oxide glasses doped with rare earth elements to amplify their optical properties. By subjecting these nanoparticles to heat treatments, it is possible to precisely control their size and shape, although further investigation is necessary to comprehensively understand and regulate their distribution. Excitingly, quantum cutting has been achieved in ytterbium-doped lead

halide perovskite nanocrystals and thin films, showcasing remarkable potential in applications such as solar cells and LEDs. In the quest for quantum cutting materials, the combination of Pr^{3+} and Yb^{3+} ions have been extensively studied in host materials like KY_3F_{10} and CaF_2 . Although promising transfer rates have been observed, there is also the challenge of quenching Yb^{3+} emission. Furthermore, the exploration of rare-earth doped materials for quantum cutting has extended to the realm of mercury-free lighting devices. Borate and fluoride matrices doped with $\text{Dy}^{3+}/\text{Tb}^{3+}$ ion pairs have been identified as suitable candidates for generating green emission.[27]

Solid-state lasers, which use a crystalline or glass rod doped with ions, are another area where quantum cutting can be observed. These lasers utilize the phenomenon of population inversion to generate laser light. The dopant ions in the solid-state laser materials play a crucial role in maintaining the population inversion. Neodymium is a commonly used dopant in solid-state laser crystals such as yttrium orthovanadate ($\text{Nd}:\text{YVO}_4$), yttrium lithium fluoride ($\text{Nd}:\text{YLF}$), and yttrium aluminium garnet ($\text{Nd}:\text{YAG}$). Quantum cutting has also been explored in the context of solar cells. Quantum dot solar cells, which utilize tiny particles of different semiconductor materials called quantum dots, have been investigated for their potential to enhance the efficiency of solar energy conversion. Quantum dots can be used to collect light that is difficult to capture and can be paired with other semiconductors to optimize the performance of multijunction solar cells.[28]

In summary, the history of quantum cutting in glass materials is closely tied to the discovery of nanocrystalline quantum dots in a glass matrix in 1981. Quantum cutting has since been explored in various applications, including solid-state lasers and solar cells. The use of quantum dots and their unique optical properties play a crucial role in enabling quantum cutting.[29]

2.1. Glass Materials

When raw materials are heated to form a glass, a series of chemical reactions and structural changes take place that ultimately result in the amorphous solid glass network structure being produced. The first step is thermal decomposition of any raw materials that are not already metal oxides. Materials like carbonates and nitrates will break down at elevated temperatures, releasing gases like carbon dioxide or nitrogen

and leaving behind the metal oxide. For example, calcium carbonate will decompose to calcium oxide and carbon dioxide gas above 800°C.[30]

As heating continues, the temperature rises further until the metal oxide components begin to melt. Different oxides have different melting points depending on factors like their bonding strengths and structures. Silica for example melts around 1700°C whereas lead oxide is significantly lower at 888°C. As the individual oxides melt, they combine to form a mixed molten liquid where the components are uniformly mixed on an atomic scale. Within this liquid, network forming oxides like silica and phosphate begin to link together through chemical bonding of their constituent ions. Silica specifically forms [SiO₄] tetrahedra where each silicon ion is covalently bonded to four oxygen ions in a tetrahedral configuration. These tetrahedra then connect by sharing corner oxygen ions to form three-dimensional network structures.[31]

Network modifier cations like sodium, calcium or lead are also present in the melt and play an important role. They serve to disrupt the network former connectivity by bonding to non-bridging oxygen ions within the network. Heavier modifiers with higher charges like lead have a stronger disrupting effect compared to lighter monovalent ions like sodium. The exact nature of the network structure at a given temperature depends on the relative concentrations of network formers versus modifiers. With more silica present, a highly connected continuous random network will predominate. But as the modifier concentration increases, they act to break network connectivity by inserting between tetrahedra, ultimately leading to depolymerization of the structure if too many are added.[32]

At very high temperatures near the melting point, the glass network may undergo some additional depolymerization as the viscosity of the melt decreases significantly. The structure essentially returns to a more liquid-like, random arrangement. However, once the melt is rapidly cooled, this liquid structure becomes frozen in place. As the temperature drops below the glass transition, the atoms don't have enough thermal energy to rearrange into the repeating ordered patterns of a crystal. Instead, they are quenched into the disorganized amorphous solid-state characteristic of glass.[33]

The exact glass network structure obtained depends on the starting chemical composition and cooling rate. Faster quenching limits the amount of structural

rearrangement possible. Slower cooling approaches equilibrium conditions and can allow some minor crystallization to occur within an otherwise glassy matrix. In general, network formers like silica serve as cross-linked three-dimensional structures providing rigidity. Network modifiers disrupt connectivity to varying degrees based on their size and charge. And adjusting the relative ratios of formers and modifiers provides a way to control the glass network properties, such as its density, hardness, thermal expansion behaviour, optical transparency range, and susceptibility to chemical corrosion.[34]

Through a series of chemical and structural changes governed by thermodynamics and kinetics, the raw materials are transformed during melting and quenching into the non-crystalline solid form known as glass. The amorphous network structure produced retains characteristics of both the liquid and solid states, with no long-range order but short-range uniformity dictated by the quenched-in frozen liquid structure. This allows glasses to exhibit unique properties compared to crystalline materials made of the same chemical components. Understanding the network chemistry and physics involved during formation is crucial for developing new glass compositions tailored for various applications.[35]

The key chemical processes and network formations that occur during glass formation are:

Thermal decomposition: At high temperatures, the raw material oxides, carbonates, nitrates etc first undergo thermal decomposition reactions to form the corresponding metal oxides. For example, carbonates decompose to oxides + CO₂ gas.

Metal oxide melting: As the temperature increases further, the solid metal oxides begin to melt and form a molten liquid. The exact melting points depend on the specific oxides used.

Network former bonding: In the melt, network forming oxides like silica, borate and phosphate ions begin to polymerize and form network structures. Silica forms [SiO₄] tetrahedra that link together.

Network modifier bonding: Network modifier cations like sodium, calcium etc bond to non-bridging oxygens in the network. This disrupts the network to varying degrees based on cation field strength and size.

Depolymerization: At very high temperatures, the network may undergo further depolymerization as the viscosity decreases. This continues until rapid cooling arrests the structure.

Glass network formation: On rapid cooling, the melt freezes into a rigid, interconnected glass network structure with no long-range crystalline order. It retains the liquid-like disorder of the melt.

Network connectivity: Varying the relative amounts of network formers and modifiers adjusts the network connectivity - from highly connected (silica-rich) to depolymerized (sodium-rich) networks.

2.2. Rare Earth Doping in Glass Materials

Rare earth (RE) doped glasses are a class of optical materials formed by doping RE elements such as neodymium, erbium, praseodymium, ytterbium etc. into a silicate, phosphate or germanate glass host during the glass melting process. The RE elements substitute for network formers like silicon, phosphorus, or germanium in the glass structure.[36]

Depending on the specific RE dopant and glass composition, different optical and material properties can be achieved which make these glasses useful for a variety of applications. Some common types of RE doped glasses include:

Neodymium (Nd^{3+}) doped phosphate glasses are widely used as gain media in solid-state lasers emitting in the near infrared region around 1060 nm. Nd^{3+} doping results in strong, narrow absorption and emission bands suitable for efficient laser operation.

Erbium (Er^{3+}) doped silicate and phosphate glasses are important for optical amplifiers in fiber optic communication systems, emitting at 1550 nm. The emission matches low loss windows in silica optical fibers.[37]

Ytterbium (Yb^{3+}) doped silicate and fluoride glasses are useful as gain media for fiber lasers and are increasingly replacing Nd^{3+} lasers. Yb^{3+} has simpler energy levels and higher efficiencies.

Praseodymium (Pr^{3+}) doped glasses emit in the orange-red region around 620 nm and are used in laser displays and traffic lights.

Thulium (Tm^{3+}) and holmium (Ho^{3+}) doped glasses emit in the near to mid infrared, enabling applications in medicine, free space communication and remote sensing.

In addition to the RE dopant species, the glass host composition also influences the optical properties. For example, silicate glasses typically have higher thermal stability and mechanical strength compared to phosphates but lower gain efficiencies. Fluoride glasses offer even higher laser damage thresholds and wider transmission windows.

Some key properties of RE doped glasses include their broad absorption and emission bands in the visible and infrared, ability to be fiberized into optical fibers, high quantum efficiencies, long fluorescence lifetimes, and thermal/chemical stability. The emission wavelengths are determined by the energy levels of the specific RE ion and can be tailored to match important optical communication or sensing bands by choosing the right dopant species.

Applications of RE doped glasses span telecommunications, lasers, displays, lighting, biophotonics and more. Optical fibers doped with $\text{Er}^{3+}/\text{Yb}^{3+}$ are critical components in today's long haul and local fiber networks. Nd^{3+} and Yb^{3+} doped solid-state lasers are widely used for materials processing. Fiber lasers are revolutionizing manufacturing. RE displays offer high brightness and efficiency advantages over LEDs. Medical therapies employ Er^{3+} , Tm^{3+} and Ho^{3+} emission for tissue welding and treatment of skin conditions. Emerging applications include solar cells, LiDAR and 3D sensing.

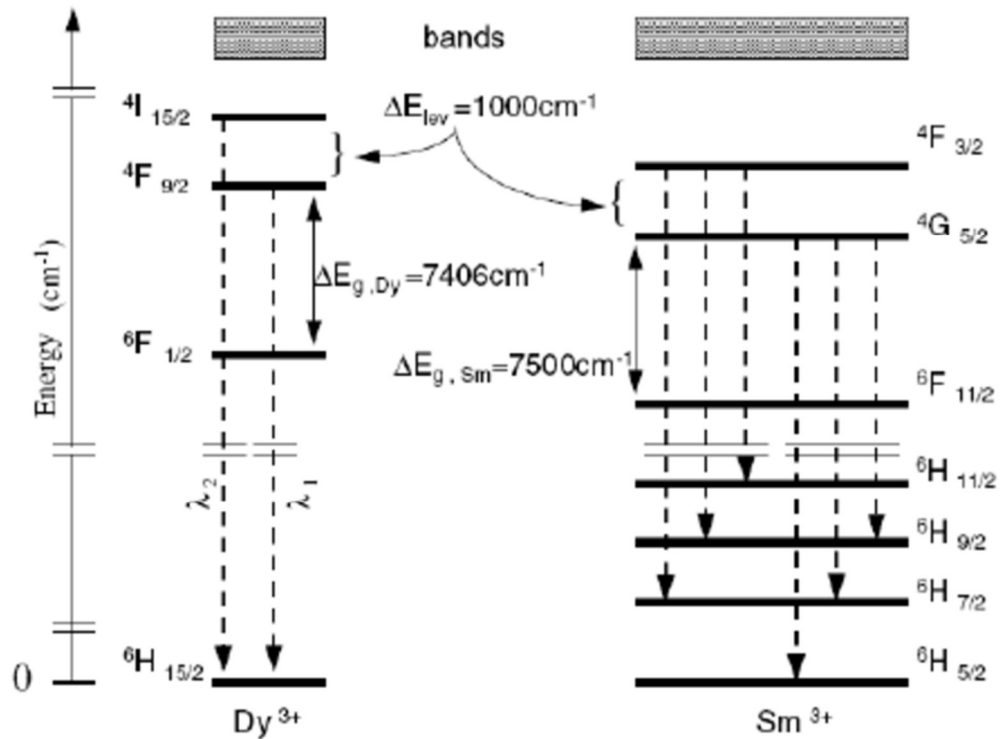


Figure 5: Emission spectra at different temperatures. Left: YAG:Dy ; Right: Sm

In summary, RE doped glasses are a versatile class of functional materials underpinned by the unique optical and spectroscopic properties of RE elements. Their applications have grown tremendously with developments in fiber optics, lasers and other photonic technologies. Ongoing research continues to expand the portfolio of RE dopants, host materials and device structures to enable new generations of photonic systems.

Rare earth materials are doped into glass materials for various reasons and applications. Here are some key reasons:

- **Luminescence Enhancement:** Rare earth ions, such as neodymium, erbium, and holmium, exhibit unique luminescent properties. When these ions are incorporated or "doped" into glass materials, they can enhance the luminescence process. This is particularly useful in applications such as lasers, where rare earth-doped glasses can act as the active laser medium, amplifying and emitting light at specific wavelengths.
- **Energy Conversion:** Rare earth-doped glass materials are also utilized in photovoltaic devices and solar cells. The incorporation of rare earth ions can

help improve the efficiency of energy conversion by enhancing light absorption and facilitating energy transfer processes within the glass material.

- **Optical Amplification:** Doping rare earth materials into glass fibres is a common practice in the telecommunications industry. Rare earth-doped fibres, such as erbium-doped fibres, are used for optical amplification in fibre optic communication systems. The rare earth ions in the fibre can absorb and amplify optical signals, allowing for long-distance transmission of information.
- **Optical Sensing:** Rare earth-doped glass materials can also be used for optical sensing applications. The luminescent properties of the rare earth ions can be sensitive to changes in temperature, pressure, or other environmental factors. By incorporating these ions into glass sensors, it is possible to create optical devices that can detect and measure these changes.
- **Other Applications:** Rare earth-doped glass materials find applications in various fields, including medical devices, laser scalpels, infrared absorbing glass, scintillators, and phosphors.
- **Unique Electronic Structure:** Rare earth elements have unique electronic configurations due to the partially filled 4f orbitals. This electronic structure gives rise to their distinctive luminescent properties, including sharp emission lines and long luminescence lifetimes. By doping rare earth ions into glass materials, these advantageous luminescent properties can be harnessed for various applications.
- **Energy Level Matching:** Rare earth ions have energy levels that can be tailored to match specific excitation and emission wavelengths. This allows for efficient energy transfer and light emission within the glass matrix. By carefully selecting the appropriate rare earth ions and their concentrations, glass materials can be engineered to exhibit desired luminescent behaviours.
- **Broad Emission Spectra:** Rare earth-doped glasses can exhibit broad emission spectra, which means they can emit light over a wide range of wavelengths. This property is particularly useful in applications such as white light-emitting diodes (LEDs) and display technologies, where a broad range of colours is required.

- **High Chemical Stability:** Rare earth ions are known for their high chemical stability, which allows them to be incorporated into glass materials without significant leaching or degradation. This stability ensures that the luminescent properties of the rare earth ions are preserved over time, making them suitable for long-term applications.
- **Compatibility with Glass Processing:** Rare earth-doped glasses can be fabricated using various glass processing techniques, such as melting, casting, and fiber drawing. This compatibility with glass processing methods enables the integration of rare earth materials into different glass forms, including bulk glass, fibers, and thin films.
- **Tailored Properties:** The choice of rare earth ions and their concentrations can be tailored to achieve specific properties in glass materials. For example, different rare earth ions exhibit different emission wavelengths, lifetimes, and quantum efficiencies. By selecting the appropriate combination of rare earth ions, the luminescent properties of the glass material can be customized to meet specific application requirements.
- **Environmental Sensing:** Rare earth-doped glass materials can be used for environmental sensing applications. The luminescent properties of the rare earth ions can be sensitive to changes in temperature, pressure, humidity, or the presence of certain chemicals. This makes them valuable for developing optical sensors that can detect and measure environmental parameters.

2.3. Transitions in Rare Earth Materials

The strength of electron transitions inside the 4f shell of rare-earth ion particles in materials is modelled by the Judd-Ofelt hypothesis. It offers a quantitative method for comprehending rare earth element optical characteristics, especially f-f transitions. The Judd-Ofelt theory's principal ideas are as follows: [38]

f-f Transition Intensity: Judd-Ofelt theory is concerned with the strength of f-f transitions, which are associated with electron excitation and relaxation in the 4f shell of rare-earth ions. The distinctive optical characteristics of rare earth minerals, namely their luminescence, are caused by these transitions.[39]

Judd-Ofelt Parameters: The theory introduces a set of parameters known as the Judd-Ofelt parameters, which are used to quantify the strength of f-f transitions. These

parameters, denoted as $\Omega\lambda$ (where $\lambda = 2, 4, 6, \dots$), are determined experimentally and provide information about the electronic structure and symmetry of the rare-earth ions.

Selection Rules: The Judd-Ofelt theory takes into account the selection rules that govern the allowed f-f transitions in rare earth materials. These selection rules depend on factors such as the parity and angular momentum of the initial and final states of the electrons involved in the transition.[40]

Application: The Judd-Ofelt theory has been widely applied in the study of rare earth materials, including luminescent materials, lasers, and optical amplifiers. It allows researchers to predict and analyse the intensity and spectral properties of f-f transitions, providing insights into the optical behavior of these materials.[41]

Extensions and Modifications: Over time, the Judd-Ofelt theory has been extended and modified to improve its accuracy and applicability. Researchers have developed modified versions of the theory to describe the intensities of f-f transitions in different systems and to account for additional factors that may influence the optical properties of rare earth materials.[42]

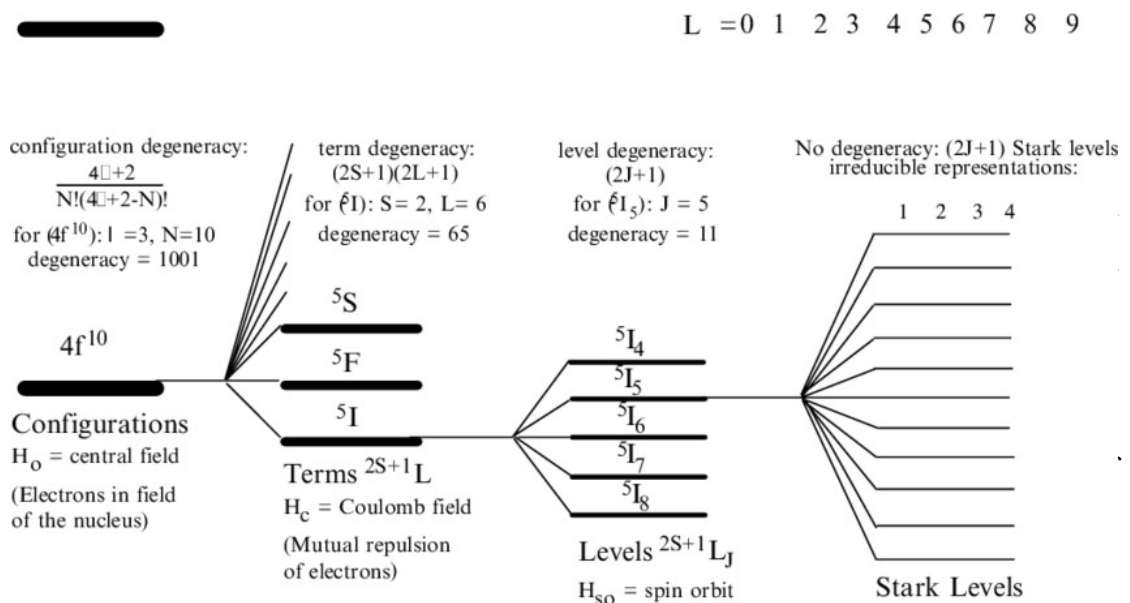


Figure 6: Splitting up of Energy Levels in atoms with higher atomic number

the subject of extensive research with the goal of understanding its characteristics and investigating ways to harness and manage its potential applications. This article's goals are to give a general introduction of surface plasmon resonance and to showcase a few of its recent uses. [26]

Plasmons may be explained using classical physics, in which the free electrons in a metal are compared to a liquid that is made solely of electrons and has a very high density, like that of a plasma. Plasmons, often referred to as surface plasmons, are variations in density that appear on the surface of the material. Every plasmon is the quantization of a classically oscillating plasma wave. Put another way, plasmons are discrete values of oscillating plasma waves, and many of their characteristics may be found directly in the formulas for Maxwell. [43]

Examining Plasmon Resonance (SPR) on Surface: The electromagnetic reaction that results from plasmons oscillating at the same frequency on a material's surface is known as surface plasmon resonance. When these plasmons interact, their oscillations at particular resonant frequencies provide periodic driving forces that have the potential to develop into large-amplitude oscillations. A light source causes this phenomenon to occur, and for resonance to occur, the incoming light's frequency must coincide with the material's intrinsic frequency. These oscillations move in the direction of the negative dielectric material surface as they propagate along the surface, usually between the material and air. These plasmons are very sensitive to external stimuli, such as energy absorption into the material since they are present on the material border. To effectively excite surface plasmons and induce resonance, two popular configurations are currently employed: the Otto configuration and the Kretschmann configuration.[44]

Plasmon resonance has garnered significant interest in the fields of chemistry, physics, and materials science due to its diverse range of potential applications. Plasmons, representing oscillating plasma waves, can be understood through classical

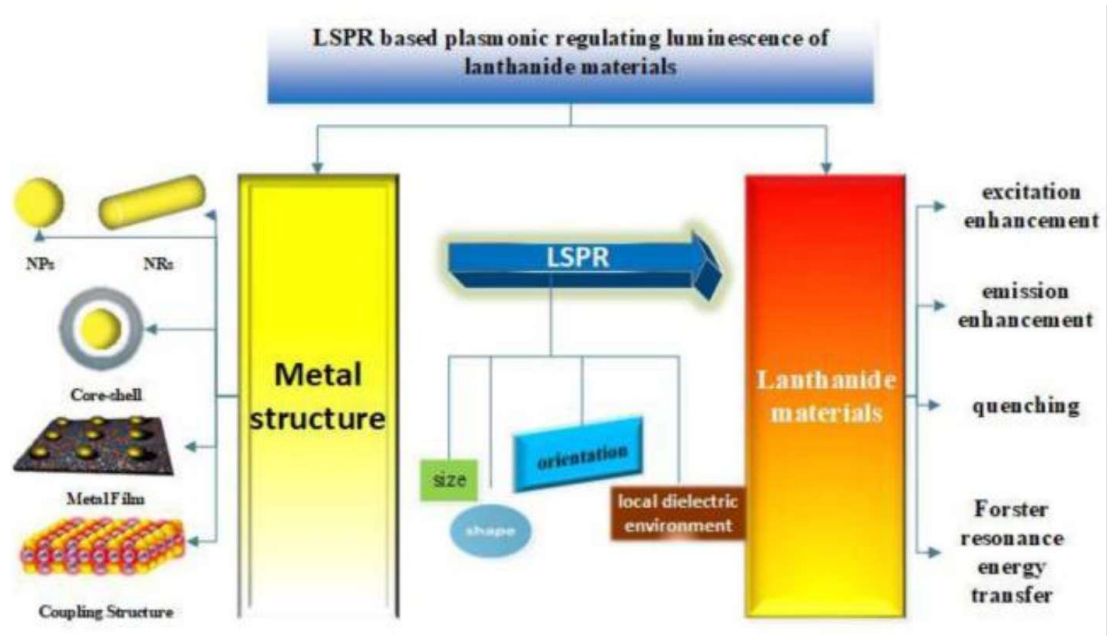


Figure 8: Drawing of localized surface plasmon resonance (LSPR)-based plasmonic regulating luminescence of lanthanide materials. Image of metal film and coupling structure

physics principles. Surface plasmon resonance occurs when plasmons oscillate on a material's surface with the same frequency, leading to large amplitude oscillations and heightened sensitivity to external factors. Exciting surface plasmons in a resonant manner can be achieved through various configurations such as the Otto and Kretschmann setups.[45]

The behaviour of plasmons with photons on the surface of borophosphate glass materials has been a subject of interest in various studies. While there may not be specific search snippets directly addressing this exact combination, we can draw insights from the behaviour of plasmons in glass materials and the properties of borophosphate glasses.[46]

Plasmons, which are collective oscillations of free electrons in a material, can exhibit surface plasmon resonance (SPR) when interacting with incident photons. This phenomenon is particularly observed in materials containing metal nanoparticles, such as gold (AuNPs) or silver (Ag nanoclusters), embedded in the glass matrix. The presence of these metal nanoparticles in the borophosphate glass can lead to the generation of plasmons and subsequent SPR effects.[47]

Surface plasmon resonance occurs when the plasmons on the surface of the material oscillate at specific resonant frequencies in response to incident light. The frequency of the incident light must match the natural frequency of the material for resonance to occur. These plasmons propagate along the surface of the borophosphate glass, exhibiting sensitivity to external stimuli and changes in the surrounding environment. The interaction between the plasmons and the photons can result in various effects, including enhanced luminescence, energy transfer, and modulation of the material's optical properties.[48]

Borophosphate glasses, composed of boron oxide (B_2O_3) and phosphate compounds, possess unique properties such as high thermal resistance, good mechanical properties, and low thermal expansion coefficient. These glasses are known for their ability to accommodate rare earth ions, such as dysprosium (Dy^{3+}) and europium (Eu^{3+}), which can exhibit tunable luminescence and energy transfer behaviour. The combination of borophosphate glass matrices with metal nanoparticles can potentially enhance the plasmonic properties and optical functionalities of the material.[49]

While specific studies on the behaviour of plasmons with photons on the surface of borophosphate glass materials may be limited, the general understanding of plasmon behaviour and the properties of borophosphate glasses suggest that the interaction between plasmons and photons in this context can lead to interesting optical phenomena. Further research and experimentation are necessary to explore the specific behaviour and potential applications of plasmons in borophosphate glass materials.[50]

Chapter 3

3. Research Methodology

The melt quench method is one of the most common techniques used to synthesize glass materials in the laboratory. It involves melting the raw material components at high temperatures until they form a homogeneous molten liquid or melt, followed by rapidly quenching the melt to obtain an amorphous glass structure. The key steps in the melt quench process begin with careful preparation of the raw materials which are typically high purity metal oxides, carbonates or nitrates of the elements that will constitute the final glass composition. These materials are precisely weighed according to the desired stoichiometric ratios for the glass and then thoroughly mixed to ensure homogeneity on a microscopic scale. The weighed raw materials are then placed inside a refractory crucible, which is designed to withstand the high temperatures involved in melting and is commonly made from materials such as alumina, platinum or gold depending on the specific melting temperatures.

The crucible containing the raw material mixture is subsequently placed inside a high temperature furnace, usually an electric melting furnace, which can heat the contents to temperatures ranging from 1000°C up to 1800°C or even higher depending on the

composition and its melting characteristics. The furnace is then switched on to begin heating the raw materials, which first undergo thermal decomposition reactions to form the corresponding metal oxides. As the temperature gradually increases further, the solid oxides will begin to melt and form a molten liquid. This molten liquid or melt must then be held at the maximum target temperature, typically for 1-4 hours, to ensure complete homogenization occurs within the liquid via convection currents. This soaking period allows any residual solid particles or inhomogeneities to fully dissolve into the melt, resulting in a compositionally uniform liquid that will form a glass with consistent properties after quenching.[51]

During the soaking time, the melt is occasionally stirred using a refractory rod or similar tool to further enhance homogenization throughout the entire volume of the melt. Once the required soaking is complete, the crucible containing the molten glass must be rapidly removed from the high temperature furnace. This is typically done using tongs or other equipment that can withstand the heat to quickly lift out the crucible. Then the critical quenching step occurs, where the molten glass is cooled at an extremely fast rate exceeding 1000°C per minute to freeze it into an amorphous solid rather than allowing crystallization to proceed. There are a few common quenching techniques, such as air quenching smaller melts by pouring onto a metal plate or quenching in water or oil to accelerate cooling of larger melts.[52]

The quenched glass may develop internal thermal stresses during the rapid solidification process from the outside surface inwards. Therefore, an annealing heat treatment is required to relieve these stresses through controlled heating and cooling. The glass sample is placed in an annealing furnace, and the temperature is slowly increased over several hours until just above the glass transition temperature, holding it there for 2-4 hours to allow stress relaxation. It is then cooled at a slow, controlled rate back down to room temperature to complete the annealing without crystallization. Finally, the synthesized glass can be characterized through techniques such as XRD, DSC and refractive index measurements to evaluate its amorphous nature, purity, and other properties for quality control. With careful control and optimization of the various melt quench processing parameters, high quality glasses can be prepared in the lab according to the target composition and applications.[53]

3.1. Synthesis Technique

3.1.1. Melt Quench Method

The melt quench method is a common technique used to synthesize glass materials in the laboratory. It involves melting the raw materials at high temperatures until they form a homogeneous molten liquid/melt, followed by rapid quenching of the melt to obtain an amorphous glass.

The key steps in the melt quench process are:

i. Raw Material Preparation

- The raw materials used are typically high purity metal oxides, carbonates or nitrates of elements that will constitute the final glass composition.
- These materials are weighed as per the desired stoichiometric ratios and thoroughly mixed to ensure homogeneity.

ii. Melting

- The weighed raw materials are placed in a refractory crucible made of alumina, platinum or gold depending on the melting temperatures.
- The crucible containing the materials is placed inside a high temperature furnace, usually an electric melting furnace.
- The furnace is then heated to temperatures ranging from 1000-1800°C depending on the glass composition. Higher temperatures may be needed for compositions with high melting points.
- During heating, the raw materials first undergo decomposition to form oxides, followed by gradual melting as the temperature increases.
- The melt is held at the maximum temperature for 1-4 hours to ensure complete homogenization through convection currents in the molten liquid. This is a critical step for obtaining phase purity and uniform properties in the final glass.
- The melt is stirred occasionally using a refractory rod to enhance homogenization.

iii. Quenching

- After the required soaking period, the crucible containing the molten glass is rapidly removed from the furnace using tongs or other equipment.
- The molten glass can be quenched in air or by pouring it onto a metal plate, inside water or oil to accelerate cooling.
- Air quenching is sufficient for smaller melts (<1 kg), while water or oil quenching is preferred for larger melts to achieve cooling rates exceeding 1000°C/min.
- Rapid quenching arrests the glass in its amorphous liquid structure rather than allowing crystallization to occur.

iv. Annealing

- The quenched glass may develop thermal stresses during rapid solidification.
- To relieve these stresses, the glass is subjected to an annealing heat treatment.
- It is placed in an annealing furnace and the temperature is slowly increased (few °C/min) up to the glass transition temperature T_g over several hours.
- The glass is then held at T_g for 2-4 hours before cooling slowly (1-2°C/min) down to room temperature.
- Annealing allows internal stresses to relax without causing crystallization, resulting in a stronger, defect-free glass.

v. Characterization

- The synthesized glass can then be characterized using various techniques like XRD, DSC, density, refractive index measurements etc. to evaluate its amorphous nature and properties.

Some key factors that influence the melt quench process are:

- Raw material purity and homogeneity
- Melting temperature and duration

- Quenching medium and rate
- Glass composition (affects T_g and crystallization tendency)
- Thermal profile during annealing

The melt quench technique is a versatile and scalable method to prepare glasses in the laboratory. Careful control of process parameters enables synthesis of phase-pure, uniform glasses suitable for further studies and applications. It remains a mainstay for glass research and development.

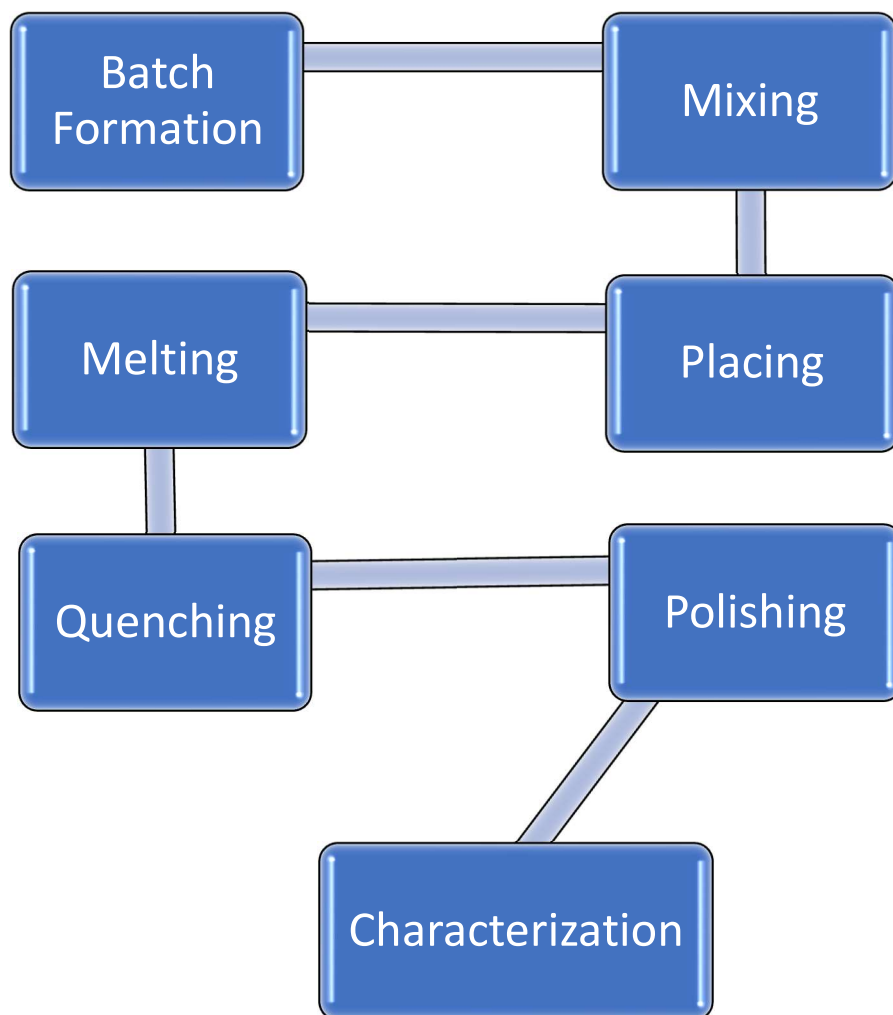


Figure 9: Flowchart of Working with Melt-Quench Method

3.1.2. Sample Preparation

In our sample preparation we used three chemicals in our base concentrations which included boron, phosphorus, and barium. We fixed their molar percentages and then doped silver nanoparticles and rare earth elements. We utilized 70% B₂O₃, 10% P₂O₅ and 20% BaO₂.

Chemicals used in formation of the samples are given below in the table below.

Sr. No	Chemical	Molecular Mass	Molar %	Weight %
1	B ₂ O ₃	69.62 g/mol	70	-
2	BaO ₂	169.33 g/mol	20	-
3	P ₂ O ₅	141.94 g/mol	10	-
4	AgCl	143.32 g/mol	-	0.01
5	Ce ₂ O ₃	328.24 g/mol	-	0.06
6	Yb ₂ O ₃	394.08 g/mol	-	0.06

To prepare the sample we need to prepare base concentration of 70% B₂O₃, 10% P₂O₅ and 20% BaO₂.

The calculations are as follow:

$$70\% \text{ B}_2\text{O}_3 = \frac{70}{100} \times 69.62 = 48.734$$

$$10\% \text{ P}_2\text{O}_5 = \frac{10}{100} \times 141.94 = 14.194$$

$$20\% \text{ BaO}_2 = \frac{20}{100} \times 169.33 = 33.866$$

Total Molecular weight of the base concentration is 48.734 + 14.194 + 33.866 = 96.794 g/mol.

In each sample we added 0.01 wt % of Ag for the nanoparticles to get plasmon effect in our glass material. In addition to add rare earth for the purpose of doping we added weight percentages with different valued of the rare earth materials in our samples.

3.2. Characterization Techniques

Rare earth doped glass materials play a pivotal role in a diverse range of applications, serving in lasers, optical amplifiers, and sensors. Given their significance, the quest to comprehend and optimize the properties of these materials has led to the widespread use of various characterization techniques. These techniques are instrumental in unraveling the intricate details of rare earth doped glass materials, thereby facilitating their effective utilization across different fields.

One of the primary techniques employed for the characterization of rare earth doped glass materials is Laser Spectroscopy. This entails the use of lasers to excite the rare

earth ions and measure their emission and absorption spectra, offering valuable insights into the optical properties of these materials. Furthermore, X-ray Diffraction (XRD) is utilized to ascertain the crystal structure and phase composition of the materials, shedding light on the crystalline phases and crystallographic properties present in rare earth doped glass materials.

Additionally, Scanning Electron Microscopy (SEM) is employed to obtain high-resolution images of the material's surface, enabling the study of microstructure and morphology, along with the distribution of rare earth ions and structural defects. Energy-Dispersive X-ray Spectroscopy (EDS) is utilized to analyze the elemental composition, aiding in the determination of the concentration and distribution of rare earth ions in doped glass materials.

Moreover, Raman Spectroscopy is instrumental in studying the vibrational modes and structural properties of rare earth doped glass materials, providing valuable insights into their bonding characteristics. Photoluminescence Spectroscopy is another critical technique used to investigate the luminescent properties and energy levels of these materials upon excitation with light, contributing to a comprehensive understanding of their radiative transitions.

In essence, the utilization of these key characterization techniques plays a vital role in unravelling the intricate details and optimizing the properties of rare earth doped glass materials, thereby contributing to their efficacy and versatility across a multitude of applications.

3.2.1. UV-Vis Spectroscopy

UV-Vis spectroscopy, which is also referred to as ultraviolet-visible spectroscopy, has garnered widespread acclaim and adoption within the scientific community as a prominent analytical technique. This versatile method is extensively employed for the precise measurement of ultraviolet (UV) and visible light absorption by samples, offering profound insights into their electronic structure and compositional attributes. At the core of UV-Vis spectroscopy lies the underlying principle of the interaction between light and matter, with molecules exhibiting the capability to absorb specific wavelengths of light owing to the electronic transitions occurring within their constituent atoms or molecular groups.

The essence of UV-Vis spectroscopy is rooted in the intricate interplay between light and matter. Upon exposure to UV or visible light, the molecules within a sample selectively absorb certain wavelengths, leading to a discernible decrease in the transmitted light's intensity. This absorption phenomenon stems from the utilization of energy derived from absorbed photons to elevate the electrons within the molecules from their ground state to higher energy levels. Consequently, the absorbed wavelengths correspond to the energy quantum required for these crucial electronic transitions, thereby unveiling vital information about the sample's electronic structure and behavior.

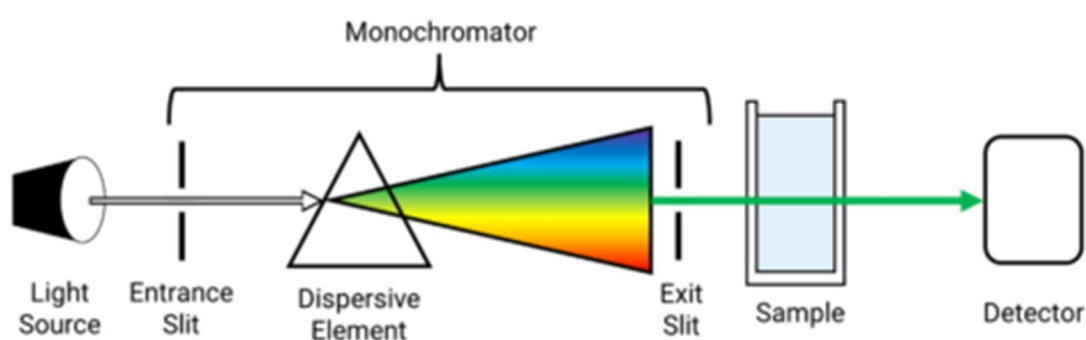


Figure 2. 1: Schematic Diagram for working of UV-VIS Spectroscopy

To carry out UV-Vis spectroscopy, scientists use specialized instruments called UV-Vis spectrophotometers. The monochromator allows the selection of specific wavelengths of light, which are then directed onto the sample. The sample, typically in liquid form, is placed in a cuvette or sample holder, and the transmitted or absorbed light is measured by a detector.

UV-Vis spectroscopy has a lot of applications in a wide range of scientific categories, making it an invaluable tool for researchers. This is achieved by constructing a calibration curve using samples of known concentration. UV-Vis spectroscopy is also used for compound identification, as different compounds exhibit characteristic absorption patterns in the UV-Vis range. By comparing the absorption spectra of unknown compounds to those of known compounds, researchers can identify the presence of specific functional groups or chromophores.

The monitoring of chemical reactions is another important application of UV-Vis spectroscopy. By measuring the changes in absorbance over time, scientists can track the progress of a reaction, determine reaction rates, and study reaction kinetics. UV-

Vis spectroscopy is particularly useful for reactions involving colored intermediates or products, as their absorbance can be easily measured.

In the field of biochemistry, UV-Vis spectroscopy is commonly employed for the characterization of biomolecules. Proteins, nucleic acids, and other biomolecules have specific absorption spectra in the UV-Vis range, allowing researchers to study their structure, stability, and interactions. For example, we can use it to determine the concentration of proteins in a solution by measuring the absorbance at a specific wavelength, using the Beer-Lambert law.

UV-Vis spectroscopy also plays a vital role in quality control processes in various industries. In pharmaceutical manufacturing, it is used to ensure the purity and consistency of drug substances and products. By measuring the absorbance of UV or visible light, scientists can detect impurities, monitor the stability of pharmaceutical compounds, and verify the formulation of dosage forms. Similarly, in the food industry, UV-Vis spectroscopy is employed to assess the quality and composition of food products, such as measuring the concentration of vitamins or detecting contaminants.

While UV-Vis spectroscopy is a versatile and powerful technique, it does have some limitations that researchers must consider. One limitation is its limited sensitivity, particularly when detecting analytes at low concentrations in complex samples. The presence of other absorbing species or impurities in the sample can interfere with the measurement, affecting the accuracy of the results. Additionally, UV-Vis spectroscopy provides information about the electronic transitions occurring within molecules but does not provide detailed structural information.

UV-Vis spectroscopy is a widely used analytical technique that provides valuable insights into the absorption of UV or visible light by samples. It has numerous applications across various scientific fields, ranging from quantitative analysis and compound identification to monitoring chemical reactions and characterizing biomolecules. This technique plays a crucial role in quality control processes in industries such as pharmaceuticals and food. Despite its limitations, UV-Vis spectroscopy continues to be an essential tool for researchers seeking to understand the electronic structure and composition of samples.

3.2.1.1. Working Principle

Working Principle of UV-Vis Spectroscopy is described as follow. UV-Vis spectroscopy operates on the principle that molecules have the ability to absorb specific wavelengths of light due to the electronic transitions that occur within their constituent atoms or groups. When a sample is exposed to UV or visible light, certain wavelengths are absorbed by the molecules present in the sample, resulting in a decrease in the intensity of the transmitted light. The absorbed wavelengths correspond to the energy required for these electronic transitions.

The working principle of UV-Vis spectroscopy involves several key components and steps:

Light Source: A UV-Vis spectrophotometer utilizes a light source that emits UV or visible light. The light source can be a deuterium lamp for the UV range (170-375 nm) and a tungsten filament lamp for the visible range (350-2,500 nm) .

Wavelength Selection: The emitted light passes through a monochromator, which allows the selection of specific wavelengths. The monochromator separates the light into its individual wavelengths, allowing only the desired wavelength to pass through to the sample.

Sample Analysis: The selected wavelength of light is directed onto the sample, which is typically in liquid form and contained in a cuvette or sample holder. The sample absorbs specific wavelengths of light based on its electronic structure and composition.

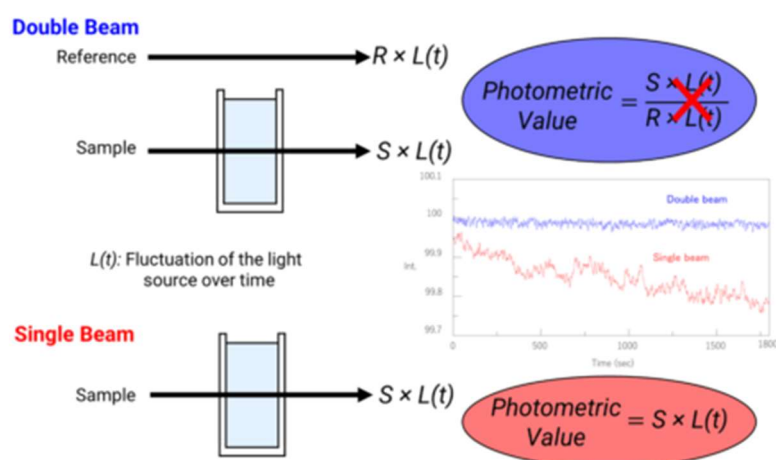


Figure 2. 2: Mathematical Description for Beams for Transmission

Detection: The transmitted or absorbed light is then measured by a detector, such as a photomultiplier tube. The detector converts the light into an electrical signal, which is then processed and displayed as a spectrum or absorbance reading.

UV-Vis spectroscopy has several strengths and limitations. One of its strengths is its versatility, as most molecules exhibit absorption in the UV-Vis wavelength range. This makes it a widely applicable technique in various scientific fields. UV-Vis spectroscopy can be used for qualitative analysis, identifying functional groups or confirming the presence of certain compounds. It is also commonly used for quantitative analysis, allowing the determination of substance concentrations by measuring the absorbance of light at specific wavelengths and comparing it to a calibration curve.

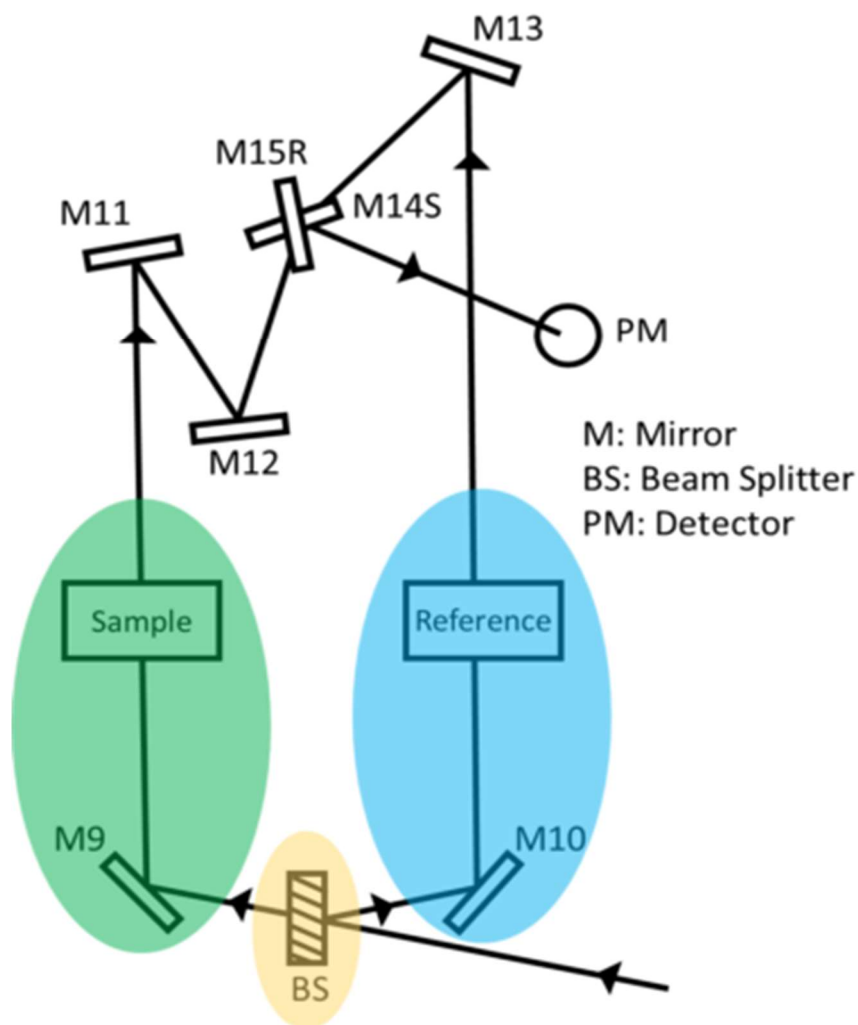


Figure 2. 3: Ray Diagram for UV-Vis Spectroscopy

However, UV-Vis spectroscopy does have limitations. It may not be the most sensitive technique, as not a significant amount of light is absorbed over a short path length. Other spectroscopy techniques, such as fluorescence, may offer higher sensitivity but are not as generally applicable. UV-Vis spectroscopy provides information about the electronic transitions occurring within molecules but does not provide detailed structural information.

UV-Vis spectroscopy works based on the principle of molecular absorption of specific wavelengths of UV or visible light. By utilizing a light source, wavelength selection, sample analysis, and detection, this technique provides valuable insights into the electronic structure and composition of samples. It finds applications in various scientific fields, including quantitative and qualitative analysis, monitoring chemical reactions, characterizing biomolecules, and quality control processes.

3.2.2. Raman Spectroscopy

Raman spectroscopy serves as an indispensable analytical tool, providing comprehensive insights into the intricate chemical structure, phase, and polymorphism exhibited by a diverse array of samples. This sophisticated technique is founded on the Raman effect, which encompasses the inelastic scattering of light by matter, thereby facilitating the identification and characterization of molecules and materials across a multitude of scientific domains.

At the core of Raman spectroscopy lies the underlying interaction between light and the chemical bonds inherent within a substance, culminating in a detailed understanding of its molecular composition and behavior. The Raman scattering process encompasses three distinct outcomes, including Stokes scattering, Anti-Stokes scattering, and Rayleigh scattering. Stokes scattering entails the emission of scattered photons with lower energy than the incident photons, signifying the absorption of energy by the sample's vibrational or rotational modes. Conversely, Anti-Stokes scattering involves the emission of scattered photons with higher energy than the incident photons, delineating the release of energy by the sample's vibrational or rotational modes. Furthermore, Rayleigh scattering transpires when the scattered photons exhibit the same energy as the incident photons, encapsulating the fundamental principles of energy conservation.

The resultant Raman spectrum obtained from a sample serves as a comprehensive depiction of the distribution of scattered photons as a function of their energy, thereby providing a distinctive "fingerprint" that enables the precise identification of specific molecules or materials based on their unique spectral signatures.

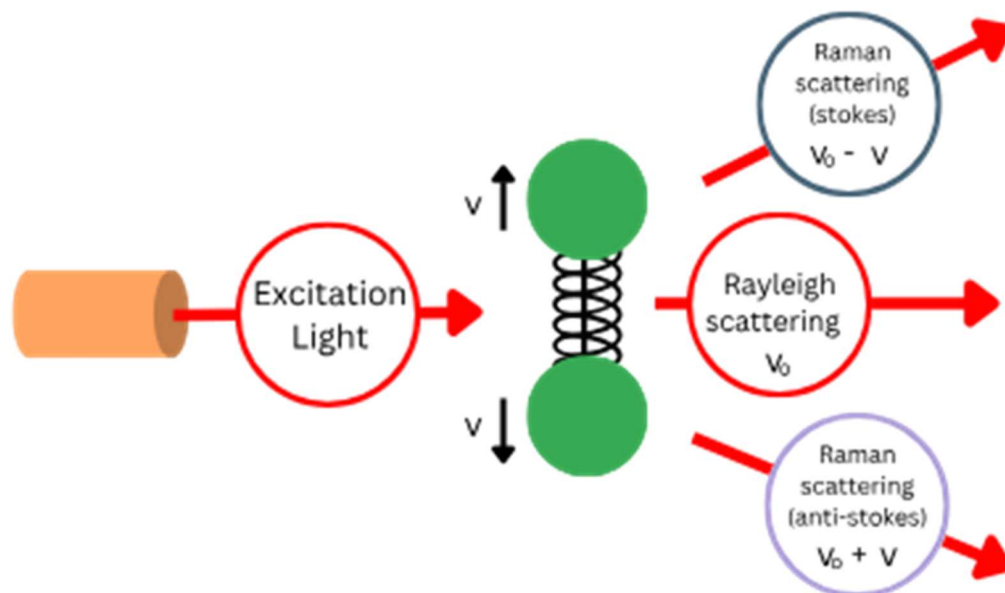


Figure 2. 4: Different Scattering involved in Raman Spectroscopy

Moreover, Raman spectroscopy boasts numerous advantages, notably its non-destructive nature, allowing for the analysis of samples without inducing any alteration or damage. Its versatility extends to both organic and inorganic materials, positioning it as an invaluable tool in an extensive range of scientific disciplines. Additionally, its relative insensitivity to water renders it suitable for the analysis of aqueous samples, broadening its applicability. Furthermore, Raman spectroscopy can be seamlessly executed in diverse sample environments, encompassing solids, liquids, gases, and even biological samples, underscoring its adaptability and utility across numerous scientific investigations.

The applications of Raman spectroscopy are extensive and diverse. In chemistry, it is used for the identification and characterization of organic and inorganic compounds, including pharmaceuticals, polymers, and catalysts. Raman spectroscopy is also employed in materials science to study crystallinity, phase transitions, and defects in materials. In the field of biology and biomedicine, Raman spectroscopy enables the

analysis of cells, tissues, and biomolecules, providing insights into disease diagnosis and drug development. Furthermore, Raman spectroscopy finds applications in forensic science, environmental analysis, art conservation, and geology.

To perform Raman spectroscopy, specialized instruments called Raman spectrometers are used. These instruments consist of a laser light source, a monochromator, or filters to select the desired wavelength, a sample holder, and a detector. The scattered light is

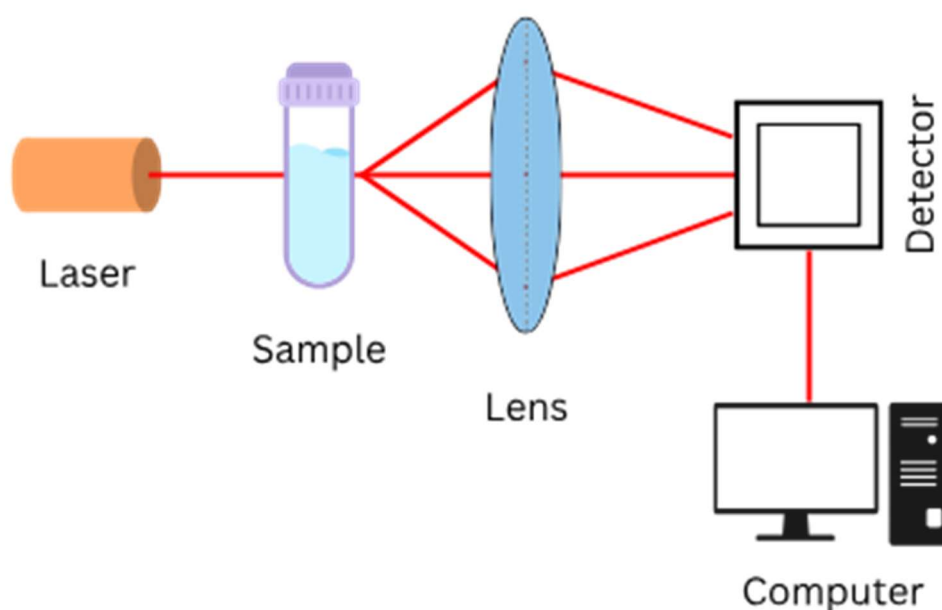


Figure 2. 5: Ray Diagram for Raman Spectroscopy

collected and analysed to generate the Raman spectrum.

Raman spectroscopy is a non-destructive analytical technique that provides detailed information about the chemical structure, phase, and polymorphism of a sample. By analyzing the inelastic scattering of light, Raman spectroscopy enables the identification and characterization of molecules and materials. Its applications span across various scientific fields, including chemistry, materials science, biology, and forensics. Raman spectroscopy continues to be a valuable tool for researchers seeking to understand the composition and properties of diverse samples.

Raman spectroscopy is an analytical technique that utilizes the Raman effect to provide detailed insights into the chemical structure, phase, and polymorphism of a sample. It involves the inelastic scattering of light by matter and is widely employed

in scientific fields for the identification and characterization of molecules and materials.[54]

At its core, Raman spectroscopy relies on the interaction between light and the chemical bonds within a substance. When a sample is illuminated with monochromatic (laser) light, most incident photons undergo elastic scattering, known as Rayleigh scattering, where the scattered photons maintain the same energy as the incident photons.

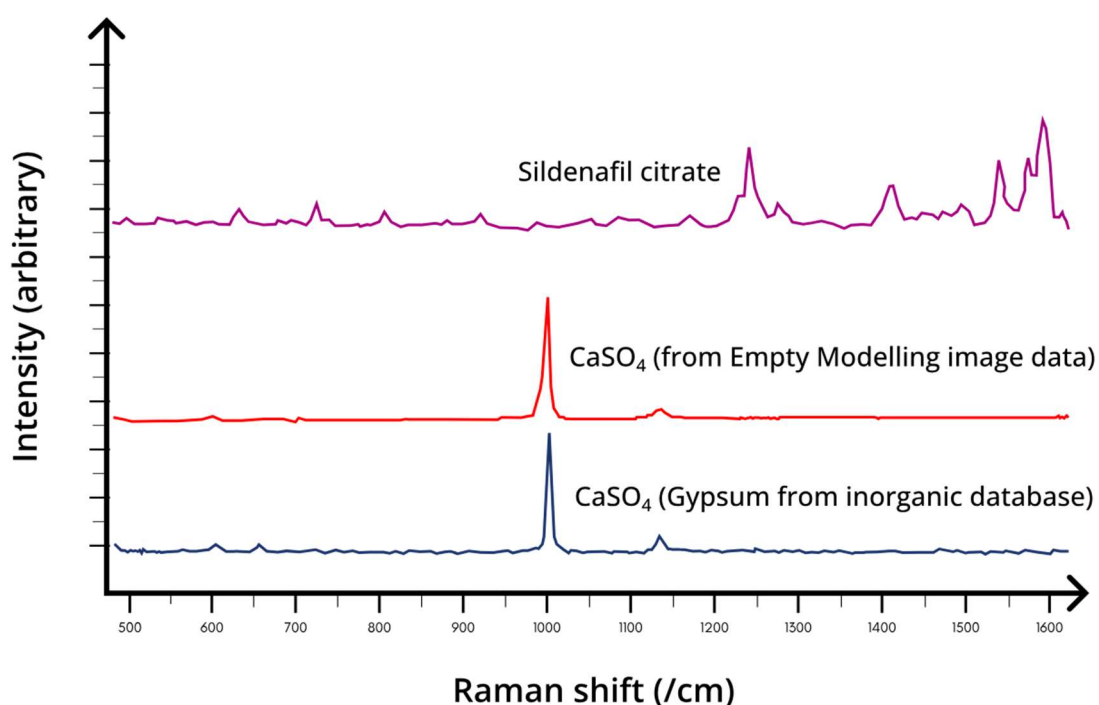


Figure 2. 6: Interpretation of Raman Results

However, a small fraction of incident photons experiences inelastic scattering, referred to as Raman scattering, which results in scattered photons with different energies due to interactions with the sample's vibrational and rotational energy levels.

The Raman scattering process encompasses three possible outcomes: Stokes scattering, Anti-Stokes scattering, and Rayleigh scattering. In Stokes scattering, the scattered photons possess lower energy compared to the incident photons, indicating energy absorption by the sample's vibrational or rotational modes. Conversely, Anti-Stokes scattering involves scattered photons with higher energy than the incident photons, signifying energy emission by the sample's vibrational or rotational modes. Rayleigh scattering occurs when the scattered photons maintain the same energy as the incident photons.[55]

By studying the distribution of scattered photons as a function of their energy (wavelength or frequency), a Raman spectrum is obtained, providing a distinctive "fingerprint" of the sample. Each peak in the Raman spectrum corresponds to a specific vibrational or rotational mode of the sample, offering valuable information regarding its chemical composition and molecular structure.[56]

Raman spectroscopy exhibits several advantages. It is a non-destructive technique, enabling the analysis of samples without alteration or damage. Its versatility allows for the analysis of both organic and inorganic materials, making it applicable across various scientific disciplines. Furthermore, Raman spectroscopy is relatively unaffected by water, making it suitable for the analysis of aqueous samples. Additionally, it can be performed in diverse sample environments, including solids, liquids, gases, and biological samples.[57]

The applications of Raman spectroscopy are extensive and diverse. In the field of chemistry, it is utilized for the identification and characterization of organic and inorganic compounds, such as pharmaceuticals, polymers, and catalysts. Materials science benefits from Raman spectroscopy by studying crystallinity, phase transitions, and defects in materials. In the realm of biology and biomedicine, Raman spectroscopy plays a crucial role in the analysis of cells, tissues, and biomolecules, offering insights into disease diagnosis and drug development. Moreover, Raman spectroscopy finds application in forensic science, environmental analysis, art conservation, and geology.[58]

To perform Raman spectroscopy, specialized instruments called Raman spectrometers are employed. These instruments consist of a laser light source, a monochromator or filters to select the desired wavelength, a sample holder, and a detector. The scattered light is collected and analysed to generate the Raman spectrum.[59]

By analysing the inelastic scattering of light, Raman spectroscopy enables the identification and characterization of molecules and materials. With its wide-ranging applications in various scientific fields, Raman spectroscopy continues to be a valuable tool for researchers seeking to gain a comprehensive understanding of the composition and properties of diverse samples.

3.2.3. Photoluminescence (PL) Spectroscopy

Photoluminescence is a fascinating phenomenon that occurs when a material absorbs photons or light energy and subsequently emits light. This process, known as photoluminescence, involves the absorption of energy from incident light and the subsequent re-emission of light by the material. Researchers often employ photoluminescence spectroscopy to study and analyse the properties of materials based on this emitted light.[60]

When a material is excited by photons, it undergoes electronic transitions within its structure. This excitation occurs when the absorbed photons provide enough energy to move electrons to higher energy states or excited states. As these excited electrons return to their ground state, they release the excess energy in the form of light. The emitted light can possess various characteristics, depending on factors such as the material composition and the specific excitation conditions.

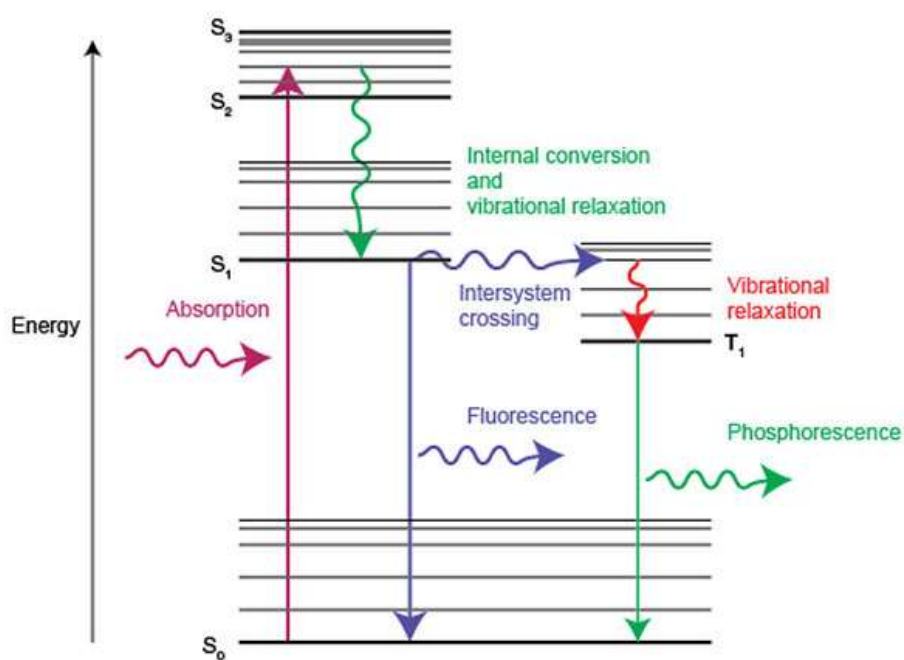


Figure 2. 7: Excitation of different level in different types of Luminescence

Photoluminescence spectroscopy serves as a powerful tool for researchers to delve into the properties of the emitted light and gain deeper insights into the electronic structure, energy levels, and optical properties of the material. It enables the examination of the emitted light spectrum, which provides valuable information about the bandgap, defects, impurities, and other electronic states within the material.[61]

One intriguing aspect of photoluminescence is the concept of the Stokes shift. This phenomenon refers to the disparity in energy (or wavelength) between the absorbed photons and the subsequently emitted light. The Stokes shift serves as a crucial indicator of the energy levels and transitions occurring within the material, aiding in the analysis and characterization of its properties.

Photoluminescence spectroscopy finds extensive applications across various scientific fields. In materials science and research, it plays a vital role in the study of semiconductors, nanomaterials, and optoelectronic devices. By carefully examining the emitted light, researchers can gain profound insights into the composition, structure, and behaviour of these materials. Photoluminescence spectroscopy also proves highly valuable in the characterization of organic compounds, including dyes and fluorescent molecules, and finds applications in fields like bioimaging, sensing, and photovoltaics.

Photoluminescence presents an intriguing phenomenon wherein materials emit light after absorbing photons or light energy. With the aid of photoluminescence spectroscopy, researchers can explore and analyse the emitted light to uncover valuable information about the electronic structure and optical properties of materials. By studying the emitted light spectrum, researchers gain insights into various aspects such as bandgap, defects, impurities, and electronic states within the material. The applications of photoluminescence spectroscopy span a wide range of scientific disciplines, making it an indispensable tool in materials science, organic compound characterization, and beyond.

Photoluminescence spectroscopy is a valuable characterization technique that can be used to study and analyse glass materials. By examining the emitted light spectrum during photoluminescence, researchers can gain insights into various properties and characteristics of the glass.[62]

One aspect that photoluminescence can help characterize in glass materials is the presence of impurities or defects. Different impurities or defects within the glass structure can affect the electronic transitions and energy levels, leading to distinct photoluminescence spectra. By analysing the emitted light, researchers can identify and characterize these impurities or defects, providing information about the composition and quality of the glass material.

Photoluminescence spectroscopy can also provide insights into the optical properties of glass materials. The emitted light spectrum can reveal information about the bandgap, energy levels, and electronic transitions within the glass. This information is crucial for understanding the behaviour of light within the glass, such as absorption and emission processes. By studying the photoluminescence spectrum, researchers can gain a deeper understanding of the optical properties and potential applications of the glass material.

Furthermore, photoluminescence can help in the characterization of glass materials by providing information about their crystalline structure. In some cases, glass materials may contain crystalline phases or nanosized crystals dispersed within the glass matrix. These crystalline regions can exhibit different photoluminescence properties compared to the amorphous glass matrix. By analyzing the emitted light, researchers can identify and characterize these crystalline regions, providing insights into the structure and composition of the glass material.[63]

In summary, photoluminescence spectroscopy is a valuable tool for characterizing glass materials. It can help identify impurities or defects, provide insights into the optical properties, and reveal information about the crystalline structure within the glass. By analyzing the emitted light spectrum during photoluminescence, researchers can gain valuable information about the composition, quality, and potential applications of glass materials.

3.2.4. FTIR Spectroscopy

FTIR spectroscopy is a technique that involves the precise measurement and detailed analysis of the interaction between infrared radiation and a sample. In this method, an interferometer serves as the source of infrared radiation, offering enhanced speed and leveraging the Fourier transform, a complex mathematical function that dissects waves and discerns their frequencies over time. Rather than directly producing the

spectroscopy spectrum, the interferometer generates an interferogram, a graphical representation depicting the intensity of light as a function of time. Subsequently, the application of the Fourier transform converts this interferogram into the familiar infrared spectroscopy spectrum graph that researchers utilize and recognize.

This versatile technique finds application in monitoring processes, identifying compounds, and determining components in mixtures. Moreover, FTIR spectroscopy plays a crucial role in providing in-depth insights into the composition, structure, and behaviour of materials. By enabling the study of vibrational modes and energy levels of molecules, it furnishes valuable information regarding functional groups, chemical bonds, and molecular interactions. This information is indispensable for comprehending the diverse properties and behaviour exhibited by materials across a wide array of applications, making FTIR spectroscopy an invaluable tool for researchers and scientists alike.

The technique finds extensive use in academic, analytical, quality assurance/quality control (QA/QC), and forensic labs. It is deeply ingrained in compound identification, process monitoring, and regulatory compliance. FTIR spectroscopy is particularly valuable for the analysis of polymers and organic compounds.[64]

FTIR spectroscopy is a widely used technique for studying the interaction between infrared radiation and a sample. It utilizes an interferometer and the Fourier transform to convert the obtained interferogram into an infrared spectroscopy spectrum. FTIR spectroscopy has diverse applications and is valuable for chemical identification, studying molecular vibrations, and understanding the properties of materials.

FTIR spectroscopy, or Fourier Transform Infrared spectroscopy allows for the identification and differentiation of molecules based on their unique spectra, like fingerprints or DNA.[65]

The key advantages of FTIR spectroscopy are that it is faster than older techniques, and it offers higher sensitivity and precision and it does not destroy the sample,. These benefits are achieved using an interferometer and the application of the Fourier transform.

In FTIR spectroscopy, an interferometer is used as the infrared source. The interferometer splits the incident light into two beams, which take different paths. One

beam is directed towards the sample, while the other is directed towards a reference mirror. The two beams are then recombined, and their interference pattern is measured. This interference pattern, known as an interferogram, represents the intensity of the light as a function of time.

The interferogram is then subjected to a mathematical function called the Fourier transform. The Fourier transform breaks down the interferogram into its constituent frequencies, allowing for the conversion of the interferogram into the familiar infrared spectroscopy spectrum. By examining the resultant spectrum, scientists can acquire insights into the makeup, arrangement, and actions of the specimen. Unique chemical arrangements or substances generate specific spectral patterns, which allow for the recognition and description of substances. FTIR spectroscopy functions by transmitting infrared radiation through a sample and examining the ensuing spectrum.

Chapter 4

4. Results and Discussions

We will present and discuss the outcomes of our research work in this chapter, which involved the application of UV-VIS (Ultraviolet-Visible), PL (Photoluminescence), and Raman spectroscopy techniques. These spectroscopic methods have played a critical role in characterizing the optical properties and structural aspects of the materials under investigation. We will outline the findings obtained from each spectroscopic technique and delve into a comprehensive discussion of their implications.

The combined analysis of UV-VIS, PL, and Raman spectroscopy data has provided a comprehensive understanding of the optical and structural properties of the materials under investigation. The UV-VIS spectra offered insights into absorption characteristics and bandgap energies, which are pivotal for comprehending the electronic structure of the materials. The PL spectra shed light on radiative recombination processes and emission properties, enabling us to evaluate the materials' potential for applications such as optoelectronic devices. On the other hand, Raman spectroscopy granted a deeper understanding of molecular vibrations, crystal structure, and phase transitions within the materials.

4.1. Photoluminescence (PL) Spectroscopy

PL spectroscopy enabled the examination of the emission properties of the materials upon excitation with light. The PL spectra provided information on the energy levels associated with radiative recombination processes within the materials. By analyzing parameters such as peak positions, intensities, and lifetimes of the PL signals, we gained insights into the luminescent properties of the materials. Moreover, PL spectroscopy allowed us to study the effects of various parameters, including doping, annealing, or surface modifications, on the emission characteristics.

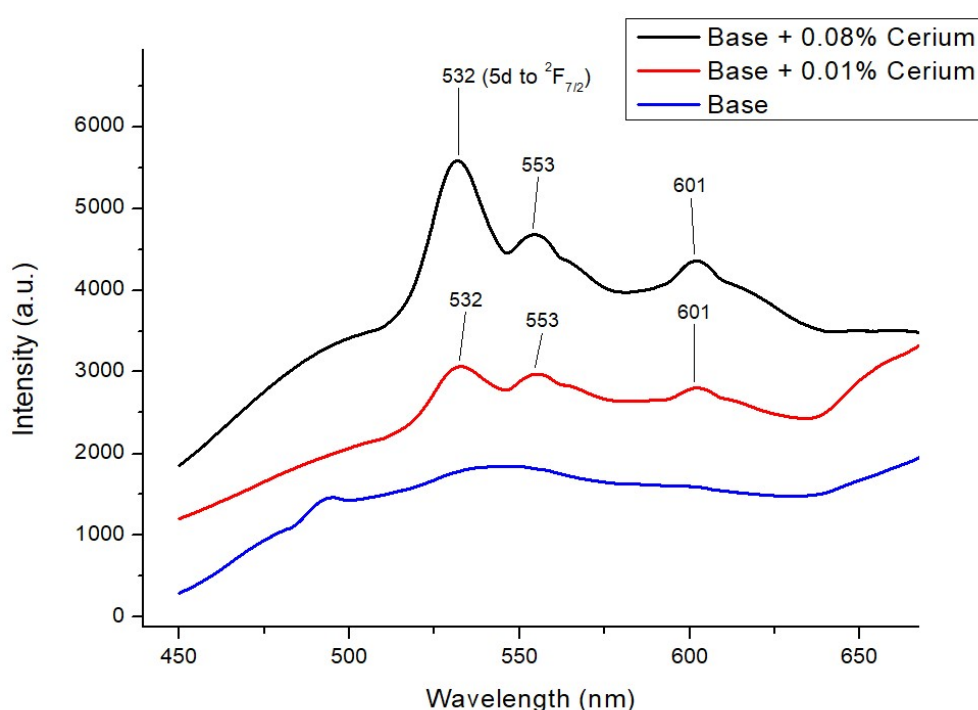


Figure 10: PL Spectra for samples with different composition

4.2. Raman Spectroscopy

Raman spectroscopy was utilized to investigate the vibrational and structural properties of the materials under scrutiny. Through the analysis of Raman spectra, we acquired information about molecular vibrations, crystal symmetry, and lattice dynamics. The Raman peaks and their corresponding wavenumbers provided insights into the chemical bonding, phase transitions, and crystallinity of the materials. Furthermore, Raman spectroscopy facilitated the identification of specific functional groups or impurities present in the samples.

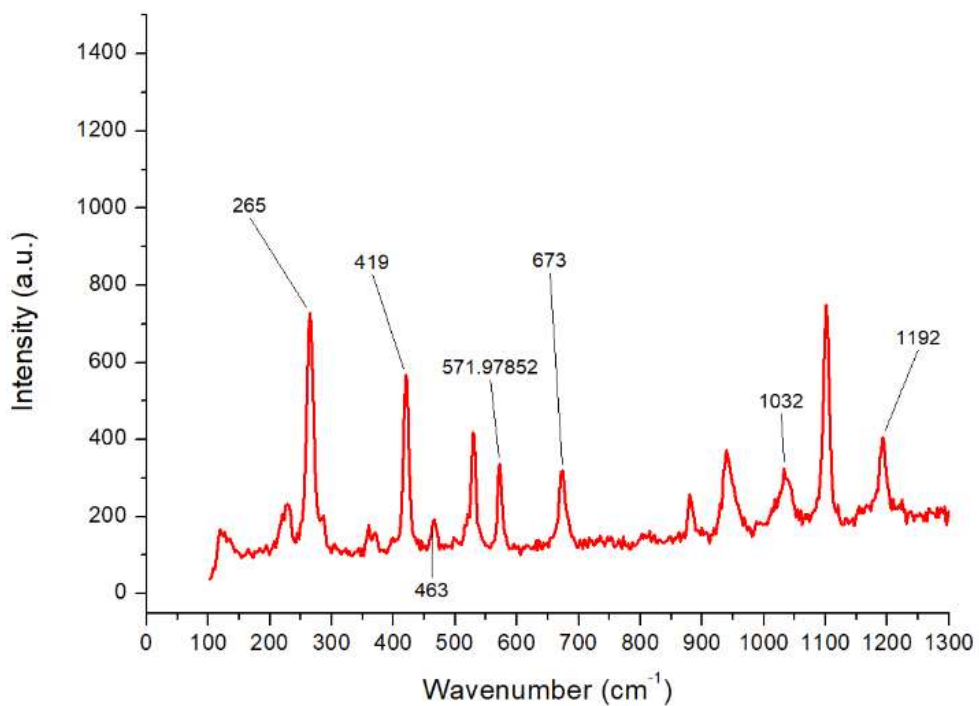


Figure 11: Raman Spectra for Cerium Doped Base Sample Glass Matrix

Peak Positions (cm ⁻¹)	Band Assignment
419	AgCl Stretching
265	Ce-O Symmetric Stretching
571	Presence of Ce ⁴⁺
1192	Symmetric stretching mode of oxygen atoms in the CeO ₂ crystal lattice
463	Ce ³⁺ Vibrational Mode
1032	Stretching Vibrations of B-O Bond

Raman spectroscopy is a highly effective method for examining changes in the electronic and structural properties of glass networks following the introduction of silver. The Raman spectra were acquired using the 'In Via Raman Microscope' by RENISHAW UK, with an excitation laser of 514 nm wavelength, and a 10-second exposure time for the sample. Figure 37 illustrates the Raman spectra of a 70% B₂O₃ - 10% P₂O₅ – 20% BaO₂ co-doped sample, showcasing minimal differences across the four conditions: undoped, Ce-doped, Ag-doped, and Ag,Ce co-doped. The measured Raman spectra were initially baseline-corrected and then normalized to the total integrated intensity over the available frequency range.

The Raman spectra reveal various structural vibrations at specific frequencies, with detailed band assignments made in accordance with the literature. Notably, the addition of Ag⁺, Ce³⁺, and Ag⁺, Ce³⁺ induces changes in the intensity of specific peaks, such as the decrease in intensity of the ~1150 cm⁻¹ peak and the increase in intensity below 1125 cm⁻¹, indicating the alteration of the phosphate network connectivity and the creation of non-bridging oxygen atoms (NBOs). The presence of Ce³⁺ appears to promote the formation of more specific units, while the combined presence of Ag⁺ and Ce³⁺ leads to a greater reduction in the intensity of the Q₂ peak, suggesting the influence of the combined cationic strength of Ag⁺ and Ce³⁺.

Furthermore, the addition of silver oxide in the glass matrix results in a slight increase in the band at 1055 cm⁻¹, indicating the appearance of more specific units. This suggests a distortion of the phosphate chain and the formation of additional non-bridging oxygen atoms. The prominent band at 996 cm⁻¹ to 1086 cm⁻¹ corresponds to the symmetric stretching vibration of phosphate tetrahedra with non-bridging oxygen atoms (NBOs). Additionally, the Raman spectra indicate the presence of B–O stretching vibrations of BO₄ in isolated diborate groups, as evidenced by the band located at 587 cm⁻¹[21]. Overall, the Raman spectroscopy findings provide valuable insights into the structural alterations induced by the introduction of silver in the glass network. [22].

In an alkaline earth phosphate dielectric matrix, the symmetric stretching vibration of phosphorus tetrahedra exhibits the highest frequency range, with two non-bridging oxygens causing the symmetric stretching vibration (PO₂-) in Q₂ groups of PΘ₂O₂-, where Θ denotes bridging oxygen and O represents non-bridging oxygen. The Q_n

groups, denoted by n , correspond to the number of bridging oxygens per PO_4 tetrahedron group, comprising Q0, Q1, Q2, and Q3 groups representing 1, 2, 3, and 4 NBOs, respectively. The 1050 cm^{-1} band indicates stretching due to boron in the Q2 group unit (meta-phosphate region), leading to a reduction in the frequency of the symmetric stretching vibration (PO_2^-) in phosphate chains. Initially, boron enhances the modification of phosphate chains, forming B-O-P brigades at both ends of the phosphate chain with terminal units $\text{B}\Theta\text{O}_2^-$. This causes the bands to shift toward lower frequencies in the 70-region containing pyro-phosphate units or Q1 units.

Upon the addition of cerium, a distinctive phenomenon occurs: Q1 units decrease significantly, while the intensity of the QAg1 peak, $\sim 1065\text{ cm}^{-1}$, increases. This growth of the $\sim 1065\text{ cm}^{-1}$ shoulder is attributed to QCe1, as cerium strongly favors bonding with Q1 units in Borophosphate glasses, converting Q2 units into QCe1 units and resulting in the noticeably larger peak at $\sim 1065\text{ cm}^{-1}$.

The band intensity at 1115 cm^{-1} to 1145 cm^{-1} is reduced due to boron addition, while the relative intensity of the 1045 cm^{-1} band increases. The band at 1086 cm^{-1} represents the vibrations of $\text{P}\Theta\text{O}_2^-$ tetrahedra attached with boron atoms and/or the vibration of terminal tetrahedral $\text{P}\Theta\text{O}_3^{2-}$. It is also likely that the band at 1086 cm^{-1} contains pure pyrophosphate units. The 996 cm^{-1} band indicates small or large chain vibrations due to trigonal or tetrahedral boron atoms and phosphate tetrahedral vibrations. Additionally, it signifies the symmetric stretch vibration of P-O- terminal phosphate tetrahedra bonded with trigonal or tetrahedral boron atoms.

Furthermore, the 883 cm^{-1} band represents the symmetric stretching vibrations of ortho-phosphate units (PO_4^{3-}), while the 790 cm^{-1} band signifies the symmetric stretching vibrations of phosphate (P-O-P) or Borophosphate chains. The weak band at 660 cm^{-1} corresponds to the symmetric vibration of (P-O-B) in Borophosphate chains, and the 608 cm^{-1} band indicates the stretching vibration of (P-O-B) with boron units integrated into the phosphate dielectric network. Lastly, the bands at 554 cm^{-1} , 421 cm^{-1} , and 306 cm^{-1} represent low frequency bending vibrations of the phosphate tetrahedra, potentially participating in the phosphate chain or existing in isolation.

The correlations observed between the results obtained from these spectroscopic techniques have illuminated fundamental aspects of the materials under study. The

variations observed in UV-VIS absorption, PL emission, and Raman scattering have provided valuable information regarding the materials' composition, defects, and structural modifications induced by external factors. By comprehensively analysing the spectroscopic data, we have been able to establish a comprehensive understanding of the materials' optical and structural properties.

Moreover, the obtained results have significant implications for future research and applications. The identified relationships between spectroscopic properties and the materials' structure can guide the design and optimization of novel materials with tailored optical characteristics. The findings may contribute in the development of advanced optoelectronic devices such as solar cells, LEDs, or sensors.

4.3. UV-Vis Spectroscopy

The UV graph of a rare earth doped borophosphate glass is like a window into the soul of the material, offering a fascinating glimpse into its optical personality. When scientists delve into the UV spectrum, it's like they're peering into the glass's very essence, unraveling the secrets of how it interacts with ultraviolet light. This knowledge is like discovering the glass's hidden talents, helping researchers understand how the rare earth dopants team up with the glass matrix to influence its glow and potential uses in cool gadgets and gizmos. Not only that, but the UV graph can also act as a detective, sniffing out any impurities or flaws within the glass, kind of like a magnifying glass for imperfections. This detective work is essential in perfecting the glass's recipe for success, ensuring it performs at its best. So, in a way, the UV graph is like a superhero, shedding light on the optical mysteries of rare earth doped borophosphate glass and paving the way for technological breakthroughs that could change the world as we know it.

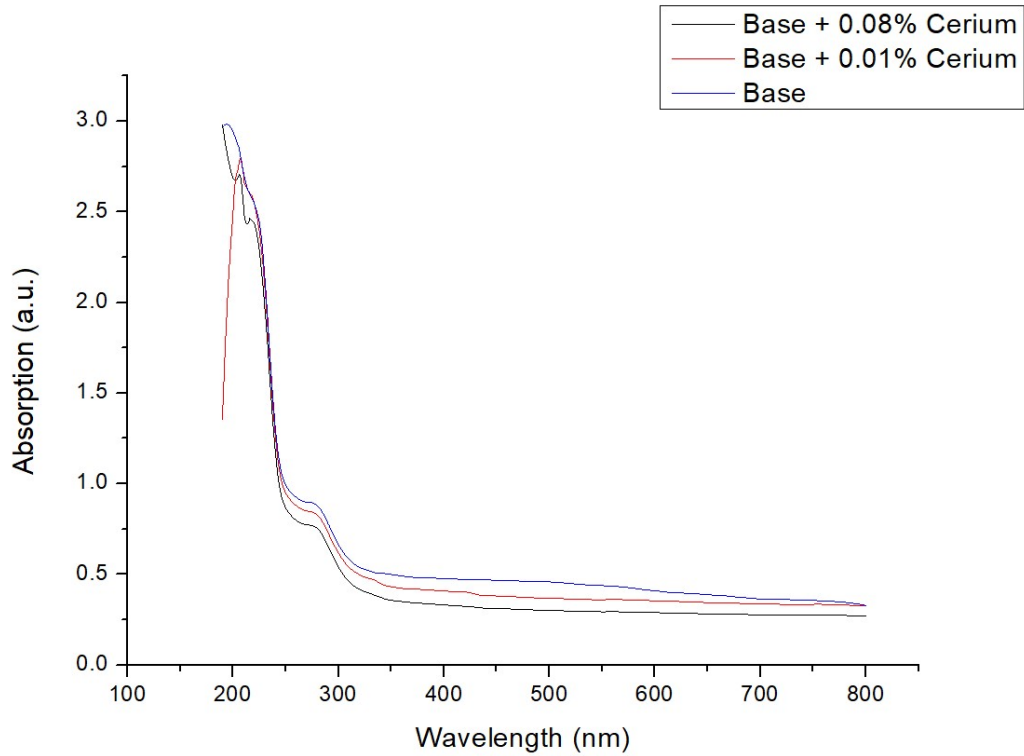


Figure 12: UV-VIS Absorption Graph for Different Compositions of Cerium Doped in Glass Matrix

4.4. Conclusion

The utilization of UV-VIS, PL, and Raman spectroscopy techniques has provided valuable insights into the optical and structural properties of the materials under investigation. The results obtained from these spectroscopic methods have laid the foundation for understanding electronic transitions, emission properties, molecular vibrations, and crystal structure of the materials. The discussions and correlations between the spectroscopic data have opened avenues for further research and potential applications in various fields. The process of quantum cutting is achieved by doping Cerium in Borophosphate glass. We provided one photon of 456 nm to our glass sample and in return we got emission in 532 nm which corresponds to the 5d to 4f transitions of cerium energy levels.

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