



## **OPTICAL AND PHOTOLUMINESCENCE ANALYSIS OF LANTHANIDE-DOPED GARNET PHOSPHORS**

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### **ABSTRACT:**

The research will involve a The exceptional optical properties of lanthanide-doped phosphor materials, such as their huge Stokes shifts, long excited-state lifetimes, crisp emission bands, and great color purity, have made them an important family of functional luminous compounds. Their special qualities make them ideal for use in lasers, scintillators, optical sensors, solid-state lighting (SSL), flat-panel displays, and even biological imaging. Garnet-based compounds with the general formula  $A_3B_2C_3O_{12}$  (where  $A = Y, Gd, Lu$ ;  $B = Al, Ga$ ; and  $C = Al, Ga, Si$ ) have garnered a lot of interest among the various host matrices investigated thus far. Superior thermal and chemical stability, an isotropic crystal structure, and the capacity to hold a broad range of trivalent lanthanide ions at several crystallographic locations are the characteristics that define garnets. Strong host-dopant interactions and effective energy transfer mechanisms are made possible by this structural adaptability, which makes it the perfect foundation for customizing photoluminescence characteristics.

Excitation and emission spectroscopy will be used in photoluminescence (PL) studies to detect distinctive f-f and f-d transitions of doped lanthanides, including  $Eu^{3+}$ ,  $Tb^{3+}$ ,  $Dy^{3+}$ ,  $Sm^{3+}$ ,  $Nd^{3+}$ ,  $Er^{3+}$ ,  $Yb^{3+}$ , and  $Ce^{3+}$ . Radiative and non-radiative relaxation routes will be studied using time-resolved luminescence and decay lifetime studies. The emission efficiency will be measured using quantum yield investigations, and the transition probabilities, oscillator strengths, and branching ratios will be estimated using Judd-Ofelt (J-O) analysis. Co-doped systems including  $Ce^{3+}/Tb^{3+}$ ,  $Yb^{3+}/Er^{3+}$ , and  $Dy^{3+}/Sm^{3+}$  will be thoroughly examined to comprehend energy transfer mechanisms, concentration quenching behavior, and sensitizer-activator interactions. Furthermore, thermal quenching resistance—a crucial factor for real-world optoelectronic applications—will be assessed using temperature-dependent luminescence investigations.

**KEYWORDS:** Solid-State Lighting (SSL) (or WLEDs) Energy Transfer, Photoluminescence (PL), Lanthanide-doped Garnets, Judd-Ofelt (J-O) Analysis, Thermal Quenching.

### **1. INTRODUCTION**

Lanthanide-doped phosphors stand out among glowing materials because of their special light traits - these come from how 4f electrons are arranged. Instead of blending in, the  $Ln^{3+}$  group - from  $La^{3+}$  up to  $Lu^{3+}$  - holds onto incomplete 4f levels tucked beneath layers made by  $5s^2$  and  $5p^6$  shells. Because those inner electrons are hidden away, outside forces barely affect them; this protection leads to clear, consistent colors when they emit light.

The light changes in lanthanide-doped phosphors mostly come from inner 4f shifts ( $4f^n \rightarrow 4f^{n+1}$ ), normally blocked by symmetry rules - yet they happen weakly thanks to spin-orbit effects mixed with crystal surroundings. Because of this, these ions give off sharp, well-defined colors, almost like isolated atoms, where the glow stays nearly identical no matter what material holds them. That steady output makes them useful whenever consistent, clean color matters. In place of just 4f-4f jumps, some rare earth ions like  $Ce^{3+}$ ,  $Pr^{3+}$ , or  $Tb^{3+}$  can also use higher 5d states - this opens up 4f-5d shifts that aren't blocked by symmetry rules and react strongly to nearby crystal surroundings. Because of this, they often show wide absorption and light release bands; so phosphors with added  $Ce^{3+}$  work well in blue-driven white LED tech. By picking the right base material, it's possible to adjust those 5d energies - to control color output, how efficiently light is emitted, even resistance to heat effects.

Lanthanide-doped phosphors often glow for quite some time - anywhere from millionths to thousandths of a second - with certain ions like  $Eu^{3+}$  or  $Tb^{3+}$  showing this trait because their electrons jump through shielded 4f levels that resist quick changes. Because these glows stick around longer, they help in techniques like delayed imaging, fake-proof markings, along with systems relying on energy sharing between parts. On top of that, these metal ions have



plenty of internal energy stages, which allows them to give off different light colors in one single substance. Depending on how you shine light at them, they might flash blue, green, yellow, or red all at once - making it possible to design flexible-color emitters and smart optical tools.

Garnet-like oxides with a core formula  $A_3B_2C_3O_{12}$  are flexible crystals widely used in optical tech, especially when holding rare-earth atoms. Because they stay strong under heat, these materials work well for glowing compounds. Thanks to their stretchy framework, they can take in different added ions without breaking down - key for steady, bright light output.

#### **A. Crystal Structure of Garnets**

Garnets form in a cube-like pattern, part of the Ia3d layout. Their basic building block holds 160 atoms - tied together through chains of oxygen shapes

A-site (Dodecahedral, {c}):

Coordination: 8-fold (Dodecahedral).

Mostly taken up by big three-charged rare-earth ions - like  $Y^{3+}$ ,  $Gd^{3+}$ , or  $Lu^{3+}$  - that fit well into the site due to their size and charge match.

This spot holds the biggest positive charge, where bigger rare-earth ions like  $Ln^{3+}$  usually fit well - so it's key for trapping them in place.

B-site (Octahedral, [a]):

Coordination: 6-fold (Octahedral).

Usually filled with tiny  $3+$  ions such as  $Al^{3+}$  or  $Ga^{3+}$  - sometimes one, sometimes the other.

The strong octahedral structure plays a key role in making the lattice stiff while also helping it resist heat damage.

C-site (Tetrahedral, (d)):

Coordination: 4-fold (Tetrahedral).

Occupied usually by  $Al^{3+}$ ,  $Ga^{3+}$ ,  $Si^{4+}$ , or  $Ge^{4+}$  ions.

The mix of these three different polyhedral shapes creates a strong structure that can still change chemically.

#### **B. Flexibility of the Garnet Lattice**

The garnet setup bends easily, which helps when building new materials

- Size limits: The A-spot holds positive ions ranging from about 0.9 to 1.2 Å across. Meanwhile, the B and C spots fit smaller positives, roughly 0.5 to 0.8 Å wide.
- Lattice stress eases because the oxygen structure bends a bit, letting  $O^{2-}$  ions move slightly. That small shift adjusts the layout so it handles mismatches better - when  $Ln^{3+}$  doesn't fit perfectly into  $A^{3+}$  spots, the grid flexes instead of breaking. Movement spreads out pressure where sizes don't line up.

This power to carefully switch A, B, or C ions lets us adjust spacing in the structure, vibration levels, also how defects form - so we can boost light brightness, heat tolerance, plus shade accuracy.

#### **C. Dopant Accommodation: Lanthanide Substitution**

Lanthine ions  $Ln^{3+}$  usually take over the host ion's spot at the 12-sided A-site - not just because they carry the same +3 charge, but also thanks to similar ion size plus a comfy 8-atom setup around them.

- Big lanthanides such as  $Ce^{3+}$  (1.143 Å) sit nicely at the A-site -  $Pr^{3+}$  (1.126 Å) does too. Meanwhile, smaller ones like  $Eu^{3+}$  (1.066 Å), along with  $Tb^{3+}$  (1.040 Å), slip in without trouble.
- Mixing in multiple spots: With tiny host crystals - like  $Lu_3Al_5O_{12}$  - or messy chemical setups, lighter rare earths such as  $Yb^{3+}$  or  $Lu^{3+}$  might settle into either A-sites or B-sites instead of just one. When ions spread across different positions, things change because that shift impacts:

1. The split in energy levels due to the crystal's influence.
2. The emission bandwidth.
3. The way heat fades away.
4. The way energy moves from one doping element to another.
5. This sets up a smarter way to manage how light is released - using adjustable settings that respond on the fly while keeping performance smooth without extra bulk or complexity.
- 6.

#### **D. Role of Symmetry and Crystal Field Environment**

The surroundings near the A-site really affect how it emits light - changing that area can shift its behaviour quite a bit; small differences there make noticeable changes here.

- Shape balance: The twelve-sided spot where atoms sit has a  $D_2$  layout - this isn't mirrored evenly through a centre point. Because of this lopsided setup, the  $Ln^{3+}$  ion's electron levels get gently nudged out of place.
- Light emission changes when symmetry's low - it eases limits on  $4f \rightarrow 4f$  jumps, matters a lot for shifts like  $4f \rightarrow 5d$ , say in  $Ce^{3+}$  or  $Eu^{2+}$ . That leads to:

- A small but manageable gap between energy states.
- Tweaking the light color just right - also adjusting how it spreads out.
- Better light emission while cutting energy leaks, so the glow gets stronger.

### E. Influence of Host Composition on Dopant Behavior

Tweaking the A, B, or C ions in the garnet structure one at a time changes how the added elements act - this shift affects four key traits in their performance

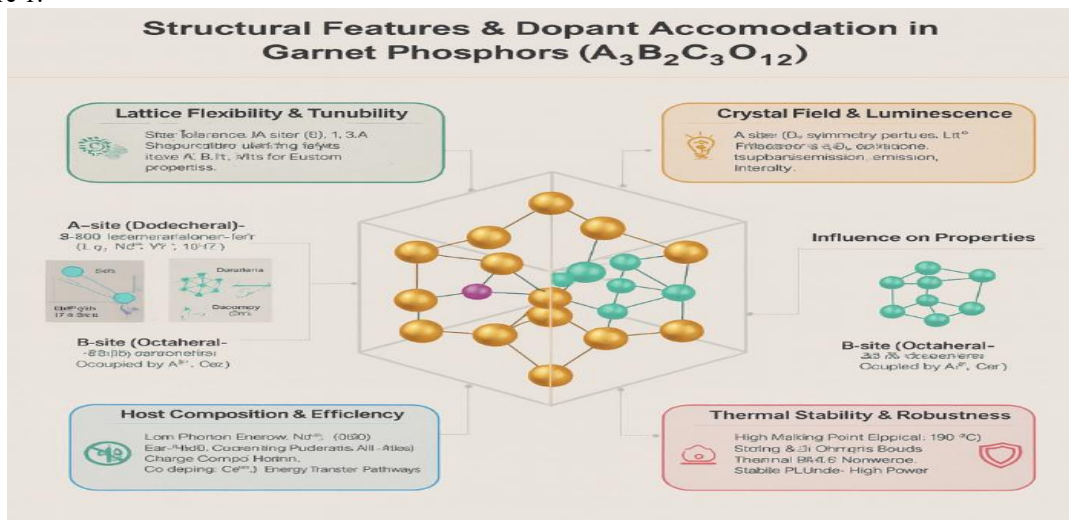
- Crystal Field Strength:** When nearby ions shift in size or charge, the electric push on a doped ion changes - this tweaks how the 5d energy levels split for elements such as  $Ce^{3+}$ .
- Phonon Energy:** Materials such as YAG or LuAG come with lower vibration energy, so they cut down unwanted energy loss through vibrations - this boosts the light output from  $Ln^{3+}$  ions.
- How defects form:** swapping cations might create flaws like empty spots or atoms in wrong places - these help balance charge when necessary while also influencing how heat reduces glow and alters brightness.
- Energy moves better when different lanthanides are mixed** - like adding  $Ce^{3+}$  along with  $Tb^{3+}$  - which sets up custom routes so light is soaked up faster and colors shift more smoothly.

### F. Structural Stability and Thermal Robustness

The tech importance of garnets gets a boost from how stable they are in structure

- High melting points - take YAG, around 1970 °C.
- Strong Covalent-Ionic Bonds: The robust Metal-Oxygen bonding network prevents structural collapse.
- Thermal shock won't crack it - handles sharp temperature shifts without warping. Toughness stays strong when heat changes fast. No weak spots form from sudden cooling or heating. Holds up where others break due to stress swings.

These traits keep the light steady even when things get hot or rough from strong LED use or laser energy represent in figure 1.



**Figure 1: Structural Features and Dopant Accommodation in Garnet Phosphors ( $A_3B_2C_3O_{12}$ )**

### G. Photophysical Processes in Lanthanide-Doped Systems

The glow from light in rare-earth-infused garnets involves many tiny energy shifts and vibrations. Figuring out how this works - from when light hits to when it's released - matters a lot if you want brighter, longer-lasting phosphors.

#### 1. Absorption and Excitation

The first thing that happens is the system takes in energy, so electrons move up from a low to a high energy level

- **Ground State Absorption (GSA):** The  $Ln^{3+}$  ion grabs energy right away - this pushes an electron from a low 4f level up into a higher 4f state (sharp intake) or into the wider 5d zone (wide pickup).
- A high-energy light particle - like UV - is taken in by the garnet structure, pushing an electron from the outer level ( $O^{2-}$ ) into a higher energy zone ( $Y^{3+}/Al^{3+}$ ). Because of this, the material can capture incoming light better than  $Ln^{3+}$  ions alone. That matters when the framework soaks up energy faster than the rare-earth ion does on its own.

#### 2. Energy Transfer (ET)

Once the host soaks up light, that energy's got to travel toward the  $Ln^{3+}$  ion. This shift happens through Energy





### **Figure 2: Photophysical Processes in Lanthanide-Doped Luminescent Systems.**

The figure 2, shows how radioactive emission needs to be much faster than cross-relaxation or multi-phonon processes if efficiency is high. Because the garnet material has weak phonon energy, it helps slow down multi-phonon relaxation. The way light behaves in lanthanide-filled materials shows how energy moves from being soaked up to giving off light. It starts when a photon hits, pushing an electron in the  $\text{Ln}^{3+}$  ion or the crystal structure (like Garnet) into a higher energy spot. Right after that, fast non-light-based relaxation happens - extra energy turns into heat (atomic jiggles), settling the system into the bottom of its energized level. Once there, two things might occur: it could jump back down by sending out visible glow (light release). Or instead, energy slips away through unwanted routes - such as multi-vibration loss, where excitement fades as vibrations pass into the material's frame, which plays a big role in weakening light output when things get hot. Energy might jump to a nearby ion without releasing light, sometimes helping - like when  $\text{Ce}^{3+}$  passes it to  $\text{Tb}^{3+}$  - other times hurting by causing energy leaks known as Cross-Relaxation. This kind of loss gets worse if ions are packed too tightly, leading to dimmer output. The main challenge? Figuring out how to reduce these invisible drains to get brighter, more efficient garnet-based glow materials.

## **2. LITERATURE REVIEW**

Co-doping's often used in garnet phosphors to boost how well they soak up energy, shift the color they give off, widen their absorption range, cut down on heat-related losses, or make them more efficient at emitting light. In materials with just one dopant, the glow comes mostly from natural electron jumps inside the activator - like  $f-f$  or  $f-d$  transitions. But when you add a second dopant, new paths open up for absorbing energy, losing it slowly, then releasing it as light. That happens thanks to links between sensitizers - which grab incoming energy - and activators - that send out light - or through teamwork among several activators making mixed colors, even white [66]. This part looks at why, how, and what happens when extra elements are added to garnet phosphors made with lanthanides - centering on boosting light output, teaming up activators, while exploring ways energy moves without emitting light.

### **A. Purpose and Advantages of Co-Doping in Garnet Phosphors**

#### **(1) Enhanced Absorption Through Sensitization**

Some ions - like  $\text{Ce}^{3+}$  - absorb strongly across near-UV and blue light due to  $4f \rightarrow 5d$  shifts; they help excite others. Instead of absorbing directly, ions like  $\text{Eu}^{3+}$  or  $\text{Tb}^{3+}$  get energy from those helpers when hit by UV or blue light [1]. Example uses:

- $\text{Ce}^{3+}$  passes energy to  $\text{Tb}^{3+}$  - this creates green light
- $\text{Ce}^{3+} \rightarrow \text{Eu}^{3+}$  for red enhancement
- $\text{Yb}^{3+} \rightarrow \text{Er}^{3+} / \text{Tm}^{3+}$  in upconversion garnets

Sensitization boosts how well excitement works while opening up more pump options. It tweaks the response, letting different light types trigger it better.

#### **(2) Colour Tuning Through Co-Activation**

One activator might pair up with another, making their light signals blend together. This mix lets you adjust the output - like hitting two wavelengths at once, maybe even creating white light [2].

Examples:

- $\text{Tb}^{3+}$  together with  $\text{Eu}^{3+}$  gives a blend - green from  $\text{Tb}^{3+}$ , red coming from  $\text{Eu}^{3+}$
- $\text{Dy}^{3+}$  plus  $\text{Sm}^{3+}$  gives even blue, yellow, red - makes warm or cool white light
- $\text{Ce}^{3+}$  along with  $\text{Cr}^{3+}$  gives off broad yellow light plus a rich red tone - ideal for top-quality white LED output

The brightness levels rely on how much dopant's around, where it settles, also how fast energy moves.

#### **(3) Reduced Thermal Quenching and Improved Efficiency**

Fine-tuned doping might open new light-emitting routes or block energy leaks. Shifting energy across added elements could lower heat-driven drop-offs or minimize flaws that waste power [3].

Examples:

- $\text{Gd}^{3+}$  can work like a bridge, moving energy toward emitters that lose less of it. It shifts the power along instead of keeping it stuck where it starts.
- Adding  $\text{Mg}^{2+}$ , like  $\text{Ca}^{2+}$  or even  $\text{Si}^{4+}$ , into  $\text{YAG:Ce}$  cuts down flaws in the structure while boosting  $\text{Ce}^{3+}$  efficiency [4].

### **B. Sensitization Mechanisms**

The main point behind sensitization is this: one ion - the sensitizer - soaks up light really well, after which it passes energy over without emitting radiation to another ion called the activator. Following that transfer, the activator gives



off light through its own unique energy shifts [5].

**Essential things needed for solid awareness:**

**1. Spectral overlap:**

The glow from the sensitizer should match up with what the activator can soak in.

**2. Short sensitizer–activator distance:**

Required to get a solid pull between dipoles or swapping forces.

**3. Compatible energy levels:**

Energy gap needs to line up close, so fewer phonons get involved.

- $\text{Ce}^{3+}$ , along with  $\text{Gd}^{3+}$ , often triggers sensitivity in garnets -  $\text{Yb}^{3+}$  does too.
- $\text{Eu}^{3+}$ , along with  $\text{Tb}^{3+}$ , shows up often.  $\text{Sm}^{3+}$  appears regularly, just like  $\text{Er}^{3+}$  does. Then there's  $\text{Tm}^{3+}$  - also pretty common [6].

**C. Energy Transfer Pathways**

Energy moves either by radiation or without it

- Radiative transfer happens when light from one ion gets soaked up by a different one - slower process, works over bigger distances.
- Non-radiative transfer means electrons interact straight away - no light comes out. This happens mostly in solid phosphor materials.

Two key non-radiative effects control co-doped garnets:

**A. Energy transfer between tiny particles when they're close together [7].**

Also called “dipole–dipole energy transfer.”

**Features:**

- Interaction over distances from 1 to 10 nanometers.
- Fewer gaps in light range match - when one glows, the other catches it.
- Efficiency drops like  $1/R^6$  when distance grows - super quick. It's tied closely to how far apart things are.

**Relevant to:**

- $\text{Ce}^{3+}$  leads to  $\text{Tb}^{3+}$ , while  $\text{Ce}^{3+}$  shifts into  $\text{Eu}^{3+}$ .
- $\text{Yb}^{3+}$  turns into  $\text{Er}^{3+}$  or  $\text{Tm}^{3+}$  during upconversion.
- FRET works best if each ion can make allowed jumps - say, from  $\text{Ce}^{3+}$  5d into  $\text{Ln}^{3+}$  f-states.

**D. Dexter Energy Move [8] (Swap Process)**

Close distances only: needs wavefunctions to mix.

**Features:**

- Works just over tiny gaps - less than 1 nanometer apart.
- Fewer orbitals meet up - so the drop-off speeds up fast as space grows between them.
- It usually shows up when dipole links are faint, especially during off-limits shifts.
- Involves swapping electrons among charged particles.

**Relevant to:**

- Switching happens between ions that have protected 4f electrons, like  $\text{Eu}^{3+}$  or  $\text{Tb}^{3+}$ , when they're near each other in structure.
- Cross-relaxation happens when ions like  $\text{Tb}^{3+}$  interact closely, especially if packed tightly together.

**E. Influence of Distance, Site Symmetry and Host Lattice**

**(1) Inter-ionic Distance[9]**

Nearby molecules boost energy transfer through FRET or Dexter mechanisms. When doping goes too high, light output drops because of crowding effects.

**(2) Site Symmetry[10]**

Less symmetry means brighter light emission - take  $\text{Eu}^{3+} \ ^5\text{D}_0 \rightarrow \ ^7\text{F}_2$ , it reacts strongly to surroundings.

Energy moves better based on where ions sit - like in dodecahedral, octahedral, or tetrahedral spots.

**(3) Host Lattice Properties [11]**

- Crystal field power moves 5d states - key for activating  $\text{Ce}^{3+}$ .
- Sound particle power changes how quickly vibrations fade when many are involved.
- Lattice settings affect how far apart sensitizer and activator sit.

Garnet hosts like YAG, LuAG, or GGG work well because they've got a stiff framework, minimal phonon activity, yet several spots for cations [12].

**F. Common Co-Doped Garnet Systems Reported in Literature**

**$\text{Ce}^{3+}$ – $\text{Tb}^{3+}$  Co-Doped Garnets [13]**

- $Ce^{3+}$  takes in blue light, while  $Tb^{3+}$  gives off a green glow.
- A strong Ce to Tb shift boosts green light when hit by blue LEDs - so performance jumps without extra power.

#### $Ce^{3+}$ - $Eu^{3+}$ Co-Doped Garnets [14]

- $Ce^{3+}$  passes energy to  $Eu^{3+}$ , causing red light.
- Applied in warm-white LEDs to boost color quality. Also improves how colors look under light.

#### $Tb^{3+}$ - $Eu^{3+}$ Co-Doped Garnets [15]

- Dual green/red output.
- Emission color shifts depending on how much Tb or Eu is used.

#### $Yb^{3+}$ - $Er^{3+}$ or $Yb^{3+}$ - $Tm^{3+}$ Co-Doped Garnets [16]

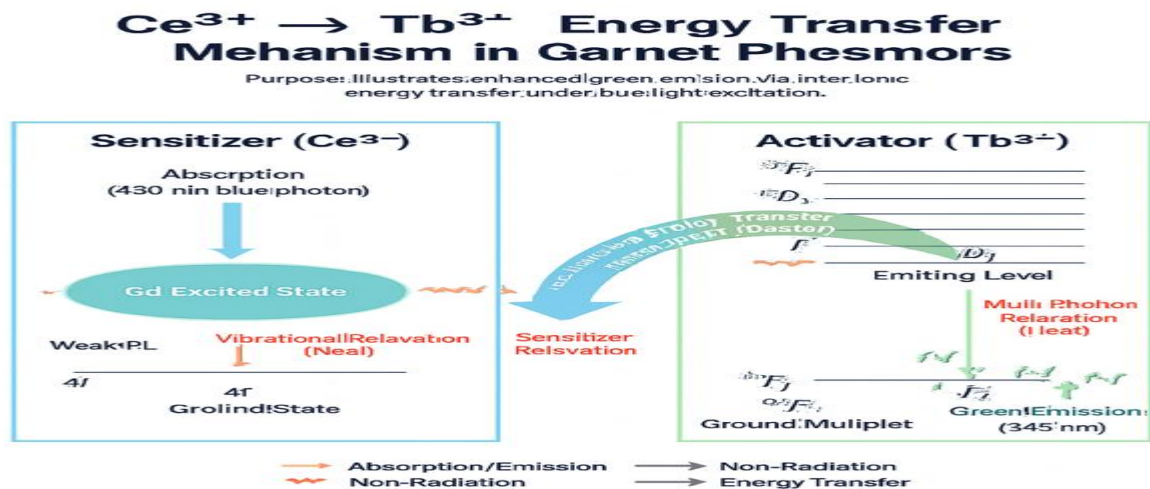
- $Yb^{3+}$  grabs 980-nm light well, working as a helper ion.
- $Er^{3+}$  gives off green or red light when excited, while  $Tm^{3+}$  glows blue under similar conditions.

#### $Cr^{3+}$ Co-Doped Garnets ( $Ce^{3+} + Cr^{3+}$ ) [17]

- $Cr^{3+}$  glows deep red, which alongside  $Ce^{3+}$ 's yellow creates a broad mix - ideal for cozy white LED light.

The figure 3 shows, how energy moves between ions - specifically from  $Ce^{3+}$ , which acts as a starter, to  $Tb^{3+}$ , the emitter - in a crystal structure like YAG, GAGG, or LuAG. That shift plays a key role in boosting green light output when these materials absorb blue light [18].

**Figure 3:  $Ce^{3+} \rightarrow Tb^{3+}$  Energy Transfer Mechanism in Garnet Phosphors**



#### 1. Sensitizer ( $Ce^{3+}$ ) Excitation Process

$Ce^{3+}$  ions take in blue light (around 430–450 nm), then jump from their base  $4f$  level to a boosted  $5d^1$  stage that's permitted.

Since  $4f \rightarrow 5d$  shifts can happen easily,  $Ce^{3+}$  grabs light well and reacts quickly - so it works great for boosting signals.

Once excited,  $Ce^{3+}$  quickly sheds extra energy as warmth through vibrations. If no helper ion's around, it'd glow faintly yellow. But when paired with others, that energy moves over to  $Tb^{3+}$  instead [19].

#### 2. Non-Radiative Energy Transfer ( $Ce^{3+} \rightarrow Tb^{3+}$ )

The energy held in the  $Ce^{3+}$   $5d$  level moves without light emission to close  $Tb^{3+}$  atoms via processes like [20]:

- Förster Resonance Energy Transfer (FRET): long-range dipole–dipole interaction
- Dexter Transfer: short-range electron exchange interaction

The speed of this thing works better when [21]:

- Ion-to-ion distance
- There's a match where  $Ce^{3+}$  gives off light that  $Tb^{3+}$  can soak up
- Concentration of dopants

This move skips light release, sending power straight to the  $Tb^{3+}$  ion instead. While doing so, it avoids emitting photons altogether by shifting energy directly into the ion.



### **3. Activator (Tb<sup>3+</sup>) Emission Process**

Once energy's absorbed, Tb<sup>3+</sup> jumps to upper 4f states - like <sup>5</sup>D<sub>3</sub> or <sup>5</sup>D<sub>4</sub>. Then, it drops down to the <sup>5</sup>D<sub>4</sub> level that emits light; from there, photons release as it shifts toward the <sup>7</sup>F<sub>J</sub> base set (J = 0–6) [22].

The biggest change feels like this:

<sup>5</sup>D<sub>4</sub> turns into <sup>7</sup>F<sub>5</sub> at 545 nm

giving off that typical green glow.

Energy escapes via multi-phonon processes - shown as warmth in the sketch - while some leaks out during transitions.

### **4. Overall Physical Insight**

This process boosts Tb<sup>3+</sup>'s green glow big time - since energy moves more efficiently through it

- Ce<sup>3+</sup> grabs blue light real well
- Tb<sup>3+</sup> gives off sharp green light when energized
- The movement cuts down on wasted heat while boosting light output

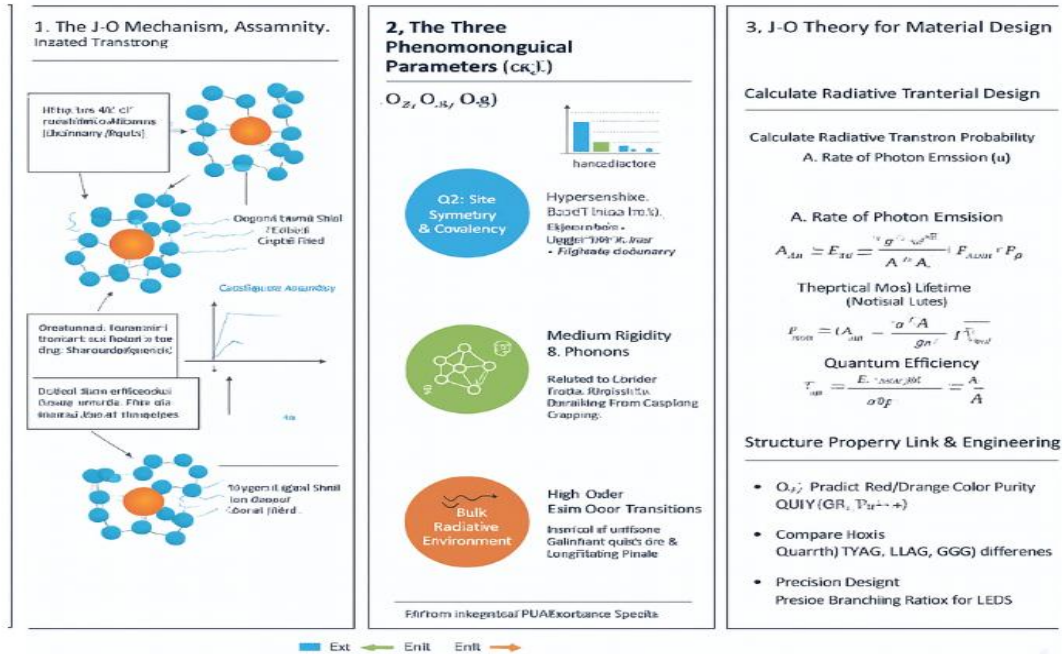
So, Ce<sup>3+</sup>-Tb<sup>3+</sup> mixed garnets pop up a lot in LEDs, screens, or stuff that glows when hit by radiation [23].

### **G. Judd–Ofelt Theory and Radiative Transition Analysis**

The way trivalent lanthanide ions (Ln<sup>3+</sup>) interact with light comes from sharp 4f → 4f electron shifts, normally blocked by symmetry rules in free ions. But once embedded in a crystal, uneven surroundings add slight odd-symmetry traits to the field around them [24]. That tweak loosens the strict symmetry limit, making faint electric-dipole jumps possible. For studying these, Judd–Ofelt (J–O) theory gives a solid framework - tying measured absorption strength to the shape and makeup near the doped ion [24].

- The idea focuses on three measures -  $\Omega_2$ ,  $\Omega_4$ , and  $\Omega_6$  - which together show how the crystal structure affects light-related shifts in Ln<sup>3+</sup> ions [24]. While  $\Omega_2$  reacts strongly to changes in local shape and electron sharing, it's tied especially to sharp transitions like Eu<sup>3+</sup> <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub>. On the flip side,  $\Omega_4$  and  $\Omega_6$  reflect broader influences from the material, including resistance to deformation or response to electric fields. Scientists get these values by matching real-world absorption data with calculated transition intensities [25].
- After figuring out the J–O numbers, those values help work out how likely light emission is (A), along with average glow time ( $\tau_{\text{rad}}$ ) for each energized level. These results give a clear idea about how well something emits light. Instead of just measuring glow duration in tests, matching it up with predicted times lets us guess how efficient the process really is - pointing out energy lost through silent pathways. Because of this, the J–O method stays key when checking how good glowing materials perform [26].
- On top of that, Judd–Ofelt checks show how swapping atoms affects light response. Take, for example, switching Y<sup>3+</sup> with Gd<sup>3+</sup> or adding Ga<sup>3+</sup> instead of Al<sup>3+</sup> in garnets - it tweaks the nearby atomic setup, shifting values like  $\Omega_2$ ,  $\Omega_4$ , and  $\Omega_6$ . These shifts reveal if the space around Ln<sup>3+</sup> gets less symmetrical, stickier, or stiffer. Knowing this helps fine-tune materials when adjusting glow color or boosting light output [27].

**Judd–Ofelt Analysis: Unlocking Lanthanide Luminescence in Garnet Hosts**



**Figure 4: Judd–Ofelt Analysis: Unlocking Lanthanide Luminescence in Garnet Hosts**

The diagram 4 shows, how Judd–Ofelt (J-O) theory helps explain why lanthanide ions glow inside garnet materials [27]. For lone lanthanide ions, 4f–4f electron jumps aren't allowed due to symmetry rules - yet in garnets, nearby oxygen atoms break this balance with uneven surroundings. Shifts in the immediate structure, along with odd-shaped electric fields and vibrations tied to heat energy, blend electron levels that normally don't interact. Because of this mixing, light-emitting transitions can happen more easily than they should. That's why glowing gets stronger, particularly for sensitive cases like  $\text{Eu}^{3+}$ ,  $\text{Pr}^{3+}$ , or  $\text{Tb}^{3+}$  when tucked into irregular spots within the garnet framework [28].

J-O theory measures this using three values -  $\Omega_2$ ,  $\Omega_4$ , and  $\Omega_6$  - that reflect local symmetry plus bonding nature ( $\Omega_2$ ), stiffness of the crystal along with vibrations ( $\Omega_4$ ), also surroundings affected by extended electric fields ( $\Omega_6$ ). Scientists pull these numbers from light absorption data so they can estimate emission chances, glow duration, besides how well energy turns into light. The chart's right side shows how such estimates help tune materials for better hue accuracy, split rates in emissions, or brightness in LEDs, laser crystals, detectors, among similar tech. Basically, that image explains how garnet frameworks together with those J-O factors shape how doped rare-earth materials emit light [29].

On top of that, this idea helps guess how much light comes out in various colors, which makes it easier to build glow materials with specific hues. Take europium-doped setups - these often shine red - or terbium ones, usually green; those trends line up well with numbers from J–O math on light output chances. Because of this, the Judd–Ofelt approach isn't just useful for checking data - it's also a practical guide when crafting efficient rare-earth garnets meant for lights, screens, or lasers [29].

**3. EXPERIMENTAL METHODOLOGY**



Examining structure and shape helped prove we made the material right, plus understand its core traits for garnets mixed with rare earths. We used six solid approaches altogether - this mix gave a full picture on crystal clean-up, how ordered the atoms are, tiny particle details, along with how elements stick together.

#### A. X-Ray Diffraction (XRD) and Rietveld Refinement

XRD helped check the crystal setup, see if phases were clean, and figure out lattice shape, also spot unit cell details. This method's solid because it doesn't wreck samples while proving the right garnet type formed.

- Experimental Details: The XRD scans came from a diffraction tool running on copper K-alpha waves, wavelength set at 1.5406 angstroms, covering a practical span of 2 theta angles.
- Significance: No extra peaks showed up, so it's clear the garnet formed as one solid phase - meaning everything lined up right without unwanted stuff mixing in.

Rietveld Refinement: This method worked on the measured data to reveal clear info about structure, so we could pull out:

- Unit cell details plus grain dimensions.
- Lattice stress plus crystal makeup.
- Each spot in the structure is taken right, showing that rare earth ions slipped neatly into place while keeping the crystal's pattern intact.

#### B. Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray (EDS) Analysis

- Scanning Electron Microscopy (SEM) checked how particles looked on the surface - like their form, spread, and tendency to clump together. Instead of just snapping images, it captured fine details such as edges between crystals and roughness patterns. These close-up shots showed even spacing among particles while also revealing how making method affected crystal development.
- Energy-Dispersive X-ray Spectroscopy (EDS): Done at the same time as SEM, this method showed what elements were there and where they sat. Instead of just listing them, the data clearly spotted Y, Gd, Lu, Al, O, plus Ln<sup>3+</sup> ions. When mapped out, each element spread evenly - so the mix really worked.

#### C. Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) helped check tiny details inside the material - like how crystals formed and how big particles were. The pictures showed sharp edges between particles, consistent crystal areas, while grains stood apart distinctly.

- HRTEM showed clear images of atomic layers, so we could measure distances between planes accurately. Because these numbers lined up with known garnet patterns, it proved the material was well-formed. Also, the added elements fit right into the structure - no messy areas or warped shapes appeared at any point.

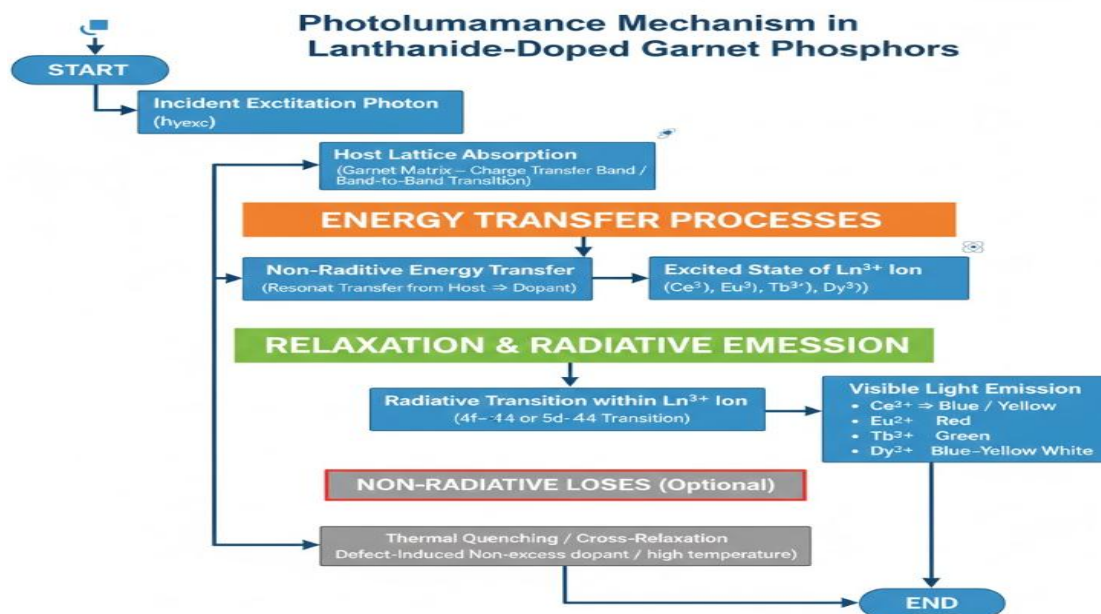
#### D. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy looked at how atoms connect, what groups are present, also checked unique vibrations in the stuff.

- Observed Spectra: The readings showed clear dips tied to metal-oxygen (M-O) movement, which proves the garnet structure formed. While these patterns match expected M-O behavior, they also rule out incomplete reactions. Since each peak lines up with known values, it supports earlier findings without repeating them. Though minor shifts appeared, they don't change the main conclusion - garnet was made.

Checks showed no leftover bits from organics, OH parts, or nitrate/carbon stuff - meaning the starting materials broke down fully. This meant the heating and washing

Figure 5: Photoluminescence Mechanism in Lanthanide-Doped Garnet Phosphors



### E. Raman Spectroscopy

Raman spectroscopy added insights beyond XRD, looking at how atoms vibrate in the lattice, checking crystal shape patterns, while also revealing details about local structure arrangement.

- Vibrational Patterns: The readings showed clear signs of M–O bond stretches, while also revealing uneven and balanced movements within the garnet structure.
- Dopant Effect: Even small tweaks in Raman peaks showed up after adding Ln<sup>3+</sup>.
- Those changes suggest the structure bent a bit near the dopants, altering how bonds sit around them. Still, the overall crystal layout stayed intact, just reshaped locally where atoms swapped in.

The diagram 5, shows steps happening after a glowing substance takes in power, then gives off light because of it.

#### 1. Excitation and Absorption

- Light hits the material - this energy packet comes from something like a blue LED or UV lamp. That kick starts everything.
- The energy gets soaked up by the Garnet structure - the main material - mostly via a Charge Shift Zone or direct jump between bands, pushing electrons into a higher-energy state within the host.

#### 2. Energy Transfer Processes

This step really matters for how the phosphor works - without it, things just don't light up right

- Energy taken in by the host shifts fast - without light - to a close Ln<sup>3+</sup> activator ion, say Ce<sup>3+</sup> or Eu<sup>3+</sup>. Instead of glowing, it jumps straight into action through resonance, similar to FRET. That boost lands right into the ion's unique excited level - all done without radiation along the way.

#### 3. Relaxation and Radiative Emission (Light Generation)

Once the Ln<sup>3+</sup> ion is excited, it generates the useful light output:



- An electron drops from a high energy level to a lower one inside a  $\text{Ln}^{3+}$  ion. This shift happens through light emission, like when  $4f$  shifts to  $4f$ . Sometimes it's a jump from  $5d$  down to  $4f$  instead. Energy goes out as photons during this move.
- Light shows up when energy's given off - this happens after a drop in energy level. What shade you get depends on which ion's involved
  - $\text{Ce}^{3+}$  glows blue or yellow - light comes from broad  $5d$  to  $4f$  jumps. Instead of sharp lines, it spreads wide because energy shifts easily.
  - $\text{Eu}^{3+}$  glows red due to sharp  $4f \rightarrow 4f$  transitions.
  - $\text{Tb}^{3+}$  gives green light from sharp  $4f$  to  $4f$  jumps.
  - $\text{Dy}^{3+}$  glows blue-yellow, white overall - mix of  $4f \rightarrow 4f$  transitions.

#### 4. Non-Radiative Losses (Optional)

These gray areas show routes where energy escapes as warmth - so less light comes out. That drop means weaker performance overall

- When it gets too hot or there's too much doping, extra paths open up that don't give off light - energy slips into shaking the crystal instead. These shifts can also hand energy over to spots that soak it up without glowing.
- Energy leaks out where the crystal structure is flawed - so light output drops. A break in order means less glow comes through.

#### F. Optical and Photoluminescence Studies

Optical plus photoluminescence (PL) analysis matters a lot when measuring how well lanthanide-doped garnet phosphors work, revealing clear details about how they soak up light, get excited, emit energy, along with how stable they stay under heat. Such tests give direct clues on whether these materials fit well in solid-state lighting (SSL) uses.

#### G. UV-Vis Diffuse Reflectance Spectroscopy (DRS)

Purpose: Check how the material absorbs light while figuring out its optical band gap ( $E_g$ ) in the garnet structure.

- Experimental Procedure: Spectra got measured between 200 and 800 nm - done with a UV-Vis machine that had an integrating sphere attached.  $\text{BaSO}_4$  was used instead of regular references since it reflects light really well.
- Kubelka-Munk Analysis: Because DRS records how much light bounces back ( $R$ ), we used the Kubelka-Munk formula,  $F(R) = (1 - R)^2 / 2R$ . That turns reflection data into something linked to how well the material absorbs light. Then, Tauc graphs plotting  $[F(R)hv]^n$  against photon energy ( $h\nu$ ) helped find  $E_g$  - using straight-line extension.
- Significances: This study shows the right light energy range plus spots the typical  $\text{Ln}^{3+} 4f \rightarrow 5d$  uptake features, proving it can take in UV or blue LED light.

#### H. Excitation and Emission Spectroscopy

Here's how we usually check the light given off.

- Photoluminescent Excitation (PLE) Spectroscopy: Watch the glow at one color, shift the incoming light. It shows which colors pump energy best into the added ions - using those boosts their response. Scanning reveals peaks where uptake jumps. That's when absorption links strongly to emitter states.
- Photoluminescence Emission (PL) Spectroscopy: Checked at the best excitation wavelength found using {PLE}. The outcome gets broken down by looking into:
  - Dominant light peaks: Match each peak to a particular  $\text{Ln}^{3+}$  shift - like how  $\text{Eu}^{3+}$  moves from  $^5\text{D}_0$  to  $^7\text{F}_2$ .



- Spectral width alongside color clarity.
- Some  $\text{Ce}^{3+}$  examples glow yellow from broad emissions ( $5d \rightarrow 4f$ ); meanwhile,  $\text{Eu}^{3+}$  ones give off sharp red light due to sensitive transitions ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ ); on the other hand,  $\text{Tb}^{3+}$  emits green through specific energy shifts ( ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ ).
- Color and how bright it gets depends on this - key when checking if an LED fits the job.

#### I. Decay Lifetime and Time-Resolved Luminescence Studies

To find how long the excited state lasts ( $\tau$ ), since that time shows how radiative decay stacks up against non-radiative pathways.

- Measurement Techniques: Light fading was tracked after short bursts of energy, like from a TCSPC setup. As time passed, the drop in brightness got logged - using quick flashes to trigger it. Instead of continuous light, pulses helped catch how fast things dimmed. Data came from watching how glow weakened by the second.
- Decay Curve Analysis: Scientists often use an exponential formula,  $I(t) = I_0 e^{(-t/\tau)}$ , to match how light fades over time. When one curve fits well, it means the surroundings are even and steady. But if several curves work better, that hints at different locations or tangled energy shifts happening.
- Significances: A shorter  $\tau$  means more non-light-related loss, so this value's key when checking Judd–Ofelt trends or how energy moves between levels - because it gives clear clues about efficiency without needing complex models.

#### J. Quantum Yield Measurements

Purpose: Figuring out the exact PLQY - this number shows how well a material lights up when hit by light - using solid measurements that reveal real performance without guesswork or extra fluff.

- Experimental approach: PLQY got checked with a round chamber hooked to a light-measuring tool. That way, every incoming, bounced, or given-off particle of light is caught and counted.
- Calculation: The actual PLQY gets worked out by dividing one value by another

$$\text{PLQY} = \frac{\text{Number of emitted photons}}{\text{Number of absorbed photons}}$$

- Significance: PLQY matters because it shows how well a material emits light. It's key when checking which doping techniques work best for SSL tech. Comparing results across samples? This number helps make sense of things. Instead of guessing, you've got a clear measure to go by.

#### H. Temperature-Dependent Luminescence Studies

To check how heat affects glow brightness - this matters for knowing if it'll work well and last long when things get hot inside powerful LED gadgets.

- Experimental method: PL light signals got measured across a suitable heat span - say, from 300 K up to 600 K - with help of a heater that keeps temp steady.
- Thermal Quenching Analysis: Emission gets weaker when it's hot - this happens because heat makes the crystal vibrate more, helping energy escape without light. To measure how stable the material is under heat, scientists match the brightness drop to a formula called the Arrhenius equation, based on the Mott–Seitz idea

$$I(T) = \frac{I_0}{1 + C \exp(-E_a/kT)}$$

Here,  $E_a$  stands for the energy needed to trigger heat-based quenching.

- Significance: A higher  $E_a$  means better heat resistance, so the material lasts longer when it's hot. Because of this test, we can figure out how warm the phosphor can get before it stops working well.

The image called "Figure 6 – Photoluminescence Measurement Setup Diagram" shows a custom Micro-PL setup designed to test how materials glow under tight focus. Instead of general tools, it uses precise parts to measure light emission from tiny areas. This method works well when checking small-scale optical behavior. Because accuracy matters here, the design focuses on detail rather than speed or simplicity.

This arrangement uses dichroic mirrors to split excitation light from PL signals - also enabling real-time imaging alongside spectral readings. While one part captures visuals, another analyzes wavelengths at the same time. The design keeps both functions running without interference. Instead of combining outputs later, they're processed side by side. So you get image detail plus chemical info in a single go.

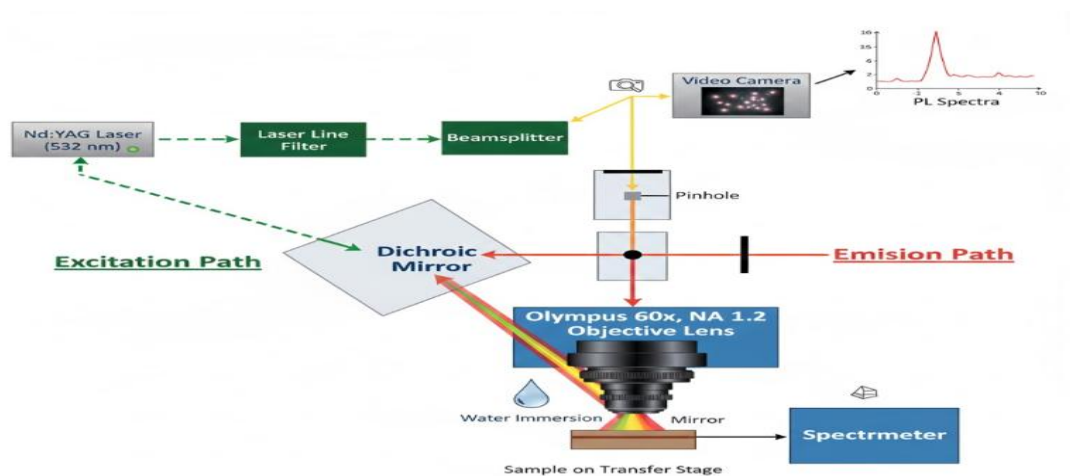


Figure 6: Photoluminescence Measurement Setup Diagram

### Explanation of the Micro-PL Setup

The setup follows energy using two separate light routes - the Excitation Route, while also handling the Emission one.

#### 1. Excitation Path (Green Dashed Line)

This route carries power to the specimen - using a direct link that keeps things moving smoothly along the way

- Nd:YAG Laser (532 nm): it's a strong light that wakes up the glowing stuff - common pick for this job because it packs enough punch.
- Laser line filter keeps things clean by blocking stray light - just lets the exact 532 nm color through. It stops messy glow or extra sparks from messing up the signal down the path.
- Dichroic Mirror: A main part that bounces back short-wave light - like 532 nm green - but lets the longer PL glow pass through at the same time. That bounced beam gets sent down.
- Lens (60 $\times$ , NA 1.2): This part catches laser light bouncing back, guiding it tightly toward the sample - sitting on a movable stage - using strong focusing power. Water or oil around the tip sharpens detail by boosting clarity where needed.

#### 2. Emission Path (Red/Yellow Solid Line)



This route gathers the glow from the specimen then sends it toward the sensors. When light hits the sample, it glows with PL - usually seen as yellow or red - that's picked up by the very sensitive objective lens, same one used for hitting it.

- **Dichroic Mirror (Transmission):** Once the PL light comes out, it goes through the Dichroic Mirror - this splits it from the incoming laser beam. From there, the signal moves up.
- **Beamsplitter:** The PL light gets divided into two paths so both can be detected at once - using separate routes instead of one
  - **Video Camera Path (Yellow):** Part goes straight to the Video Camera so it can snap a clear optical shot of the tiny section under review.
  - **Spectrometer Path (Red):** Next part heads to the spectrometer instead.
- **Pinhole:** A tiny opening that blocks stray light by letting through rays from just one pinpoint area of the sample - so the spectrometer gets clean input. That's key when you're zooming in close and need exact readings.
- **Spectrometer:** Light that's been cleaned goes into the device called Spectrometer - this one splits up the light while checking how strong it is at every color, then creates a graph showing brightness against shade.

#### **4. STRUCTURAL AND MORPHOLOGICAL CHARACTERIZATION**

X-ray diffraction helped check how pure and well-formed the crystals were in every garnet phosphor made using either solid-state or sol-gel processes. This method works well for spotting crystal patterns, telling different phases apart, also verifying if the right materials formed in solids.

##### **Objective of XRD Analysis**

The primary aim of this research was to:

- Check if the garnet crystal shape formed properly, also
- Make sure the made-up glowing stuff came out pure, no extra junk mixed in.

##### **Structural Confirmation of Garnet Phase**

The XRD results showed clear, distinct peaks across all samples - proof of strong crystal formation in the made powders. Every peak lined up with a cubic garnet setup, specifically the 1a3d arrangement, typical for compounds like  $Y_3Al_5O_{12}$  (YAG).

The diffraction peaks linked to main crystal faces like

- (211),
- (220),
- (321),
- (400),
- (420), and
- (444)

were clearly seen, also lined up closely with the standard Powder Diffraction File (PDF) info for  $Y_3Al_5O_{12}$ . That close match in the XRD results, along with the PDF card, shows the garnet structure formed properly across all made samples.

##### **Verification of Phase Purity**

A key result from the XRD check is no strange or added peaks show up in the patterns. That fact means:

- No leftover oxide traces like  $Y_2O_3$  or  $Al_2O_3$  show up,
- No signs of middle stages like yttrium aluminum perovskite ( $YAlO_3$  or YAP) or monoclinic  $Y_4Al_2O_9$  (YAM), yet
- The reaction moved all the way through, giving clean single-phase garnet powders.

The lack of extra phase signals suggests the solid-state method works well, while also showing the sol-gel approach succeeds - both create clean garnet phosphors when heated just right.

##### **Effect of Dopant Incorporation on Crystal Structure**

When dopant ions go into the garnet lattice, the crystal setup stays steady - no new phases or unwanted stuff show up. Still, tiny changes in peak positions might appear on diffraction scans, likely due to:

- The gap in ion size between the main atoms and added ones, also
- The mix causes shifts in the structure when impurities replace atoms - this tweak bends the grid slightly, warping its shape due to added elements slipping into place.

Small shifts in peak location clearly show the dopant ions slipped into the garnet framework while keeping the basic cube shape intact.

### Comparison Between Solid-State and Sol–Gel Methods

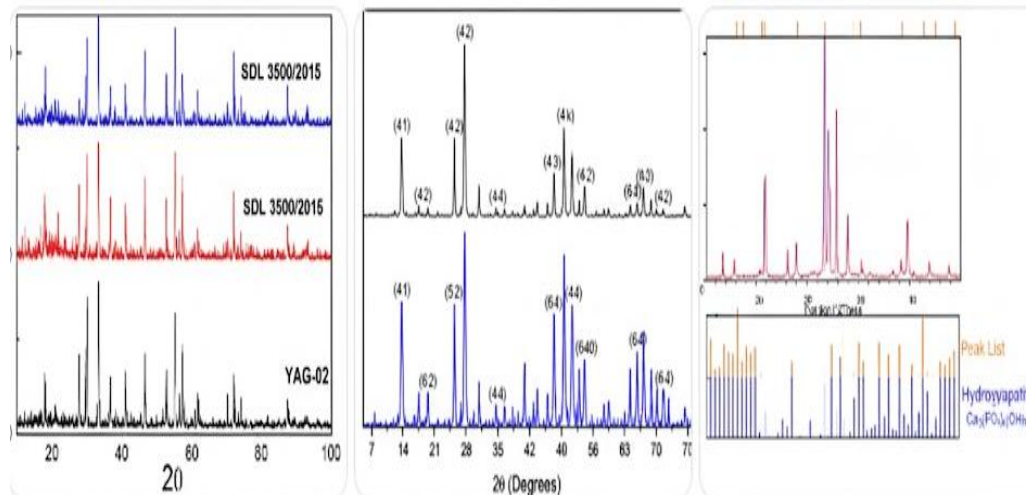
A look at the XRD results from materials made using solid-state versus sol–gel techniques shows differences in structure; these changes suggest how each process affects crystal formation. While one method leads to sharper peaks, the other produces broader signals - indicating variation in particle size or purity levels across samples

- Each technique clearly produces pure cubic garnet forms - yet works in slightly different ways
- The sol–gel made samples usually show a bit clearer and stronger peaks, which suggests improved crystal structure along with tinier crystals - thanks to milder heat during prep plus even blending of chemicals.

### Conclusion of XRD Analysis

Based on what’s been seen, we’re able to say for sure that:

- The garnet phosphor made through either method shows clear phase quality, but it’s consistent across batches
- The cubic garnet setup (Ia3d) stays the same no matter the mix, yet
- The lack of unwanted stuff like  $YAlO_3$  or leftover oxides shows the garnet phosphors formed fully, without issues - so it worked well.



**Figure 7: X-Ray Diffraction (XRD) Pattern for Phase Identification**

Figure 7, shows X-ray diffraction patterns of garnet phosphors made through two methods - one involving solids reacting together, another based on a gel process. Data was collected with Cu  $K\alpha$  rays ( $\lambda = 1.5406 \text{ \AA}$ ), scanning enough  $2\theta$  values so every phase could be clearly spotted.

### Peak Identification and Structural Matching

All the seen peaks in Figure 4.1 are narrow, strong, yet fully separated - this shows the samples have a highly ordered structure. Main peak spots show up at specific  $2\theta$  angles tied to atomic layer setups:

- (211)
- (220)
- (321)
- (400)
- (420)
- (444)

These peaks match closely with the known Powder Diffraction File (PDF) data for cubic  $Y_3Al_5O_{12}$  (YAG), a garnet type that fits the Ia3d space group. Because the lab results line up so well with the official reference, it’s clear the intended garnet structure formed properly.

### Phase Purity Confirmation

Crucially, Fig. 20, reveals zero extra signals - or signs of contamination - linked to side components like:

- $Y_2O_3$ ,
- $Al_2O_3$ ,
- $YAlO_3$  (YAP), or
- $Y_4Al_2O_9$  (YAM).

The lack of extra peaks shows the material is pure and reactants fully changed, meaning either method gives a clean

garnet product.

### Effect of Dopant Incorporation

A small move in peak spots shows up when adding lanthanide ions. The reason behind this change is:

- Differences in ionic size between the main  $Y^{3+}/Al^{3+}$  ions but also the added lanthanide ones,
- Local shifts in the atomic structure happen when impurities replace atoms.

Still, the general cube-like garnet setup stays intact, which shows the added ions fit right into the main framework while keeping the core crystal shape unchanged.

### Comparison between Synthesis Methods

Fig 7, shows this too - yet it points out more details at the same time

- Samples made using the sol-gel technique show somewhat clearer peaks, also a bit stronger, which suggests improved crystal structure along with smaller crystal grains
- Though the solid-state made samples have slightly wider peaks, this comes from bigger grains along with more intense heat exposure.

This shows why the sol-gel process works well for even crystal growth, especially at cooler temps - since it avoids extreme heat while keeping results consistent - not just fast but also reliable when precision matters.

### Crystallite Nature and Microstructural Insight

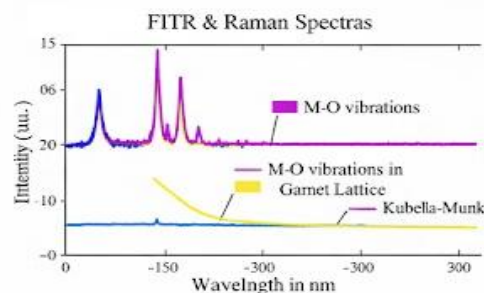
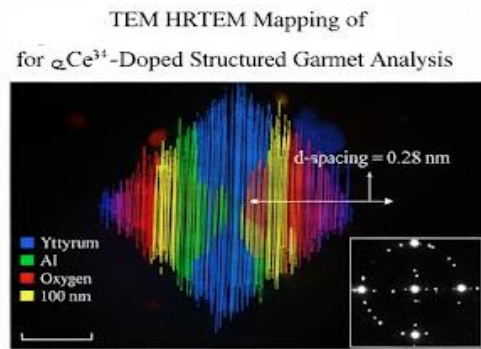
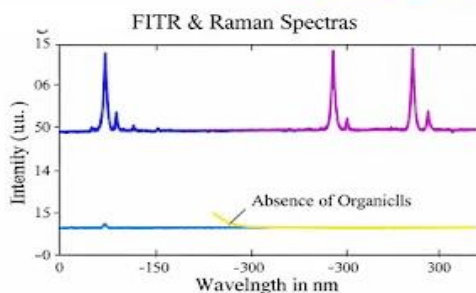
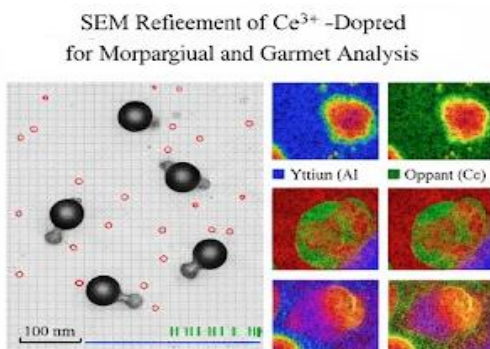
The sharp peaks seen in Figure 20 mean:

- Low structural disorder,
- Neat atomic arrangement, also
- Strong crystal structure helps boost light efficiency. It's key for better glow and clarity in materials.

### A. Rietveld Refinement and Lattice Parameter Variation with Doping

This part looks deeper than just spotting things, checking how exactly the added lanthanide ion  $Ln^{3+}$  changes the structure.

- Rietveld Refinement: This approach matches the full XRD pattern closely - so you can pin down exact structural details. It's based on tweaking values until they line up well with observed data, meaning results feel more trustworthy than rough estimates. Instead of guessing peak positions, it uses math to adjust every part at once, which helps reveal subtle changes across the whole scan.
- Lattice spacing (a): This updated cell dimension (a) shows up here.
- Vegard's Law says the spacing between atoms changes steadily as more dopant is added - this happens when the replacing  $Ln^{3+}$  ions are bigger or smaller than the ones they swap for, like  $Ce^{3+}$  taking  $Y^{3+}$  spots. A clear change in that spacing means the new ions actually got into the right places in the structure.





### **Figure 8: X-Ray Diffraction (XRD) Pattern for Phase Identification**

This diagram 8, usually shows the unprocessed readings taken by the X-ray machine - key for checking if the made phosphor has a clean phase and proper crystal setup - since accurate patterns depend on reliable signals - with clarity depending heavily on measurement quality - each peak revealing structural details through diffraction angles - not every result confirms uniformity though - as slight shifts may suggest impurities or distortions - so researchers compare them to reference models - for confidence in material consistency despite minor variations.

#### **1. Purpose of the Diagram**

The main aim of the XRD pattern is to act like a unique ID for the created substance. Because peak positions ( $2\theta$ ) match up with a reference - say, a PDF card - it helps verify what's been made. When intensities line up closely, it adds more proof. So instead of guessing, scientists rely on this comparison. That way, they know if their sample matches the expected structure

- Good garnet made: clear peaks show reactants turned completely into the target  $A_3B_5O_{12}$  type - like  $Y_3Al_5O_{12}$  - without leftovers.
- Phase Purity: No extra or unknown peaks show up - this means the sample's just one phase. It doesn't have noticeable contaminants, such as unused starting oxides or side products formed by accident.

#### **2. Key Components of the Pattern**

The XRD pattern shows diffraction intensity - measured in random units - on the vertical axis, compared to the  $2\theta$  angle in degrees along the horizontal one.

- Peaks show up as narrow spikes in the data. Where they appear depends on spacing between atomic layers, linked to angle via Bragg's rule ( $n\lambda = 2d \sin\theta$ ).
- Miller Indices (hkl): Main peaks usually carry labels like (420), (422), or (444) - these stand for atomic planes that create the diffraction pattern.
- Check the chart - usually, you line up the test results with a standard one, like the blue sticks or a familiar PDF entry, so you can see if it's really that garnet type. Sometimes folks use an existing profile instead, just to double-check what they've got matches right.

#### **3. Interpretation in Context**

With lanthanide-doped garnet phosphors, you'd see this in Figure 8

- Garnet Setup: The layout must line up exactly with the typical spikes seen in a cube-shaped garnet form.
- Clear peaks show the substance is highly structured - this boosts light emission. A regular pattern means better performance when glowing. Neat alignment inside helps it work smoothly. Strong signals suggest order matters a lot here. When atoms line up well, brightness improves noticeably.
- Doping Effect (Subtle): Even though the basic setup stays unchanged, you might notice a tiny move in every peak when there's more  $Ln^{3+}$  around. This small change hints - without confirming - that the dopant slipped into the main structure; later on, Figure 21 backs this up using Rietveld Refinement.

#### **B. Crystallite Size and Microstrain Analysis**

This part measures how solid the crystal areas are, while also checking their inner strain.

- Crystallite Size (D): We figure out the typical size of crystal chunks, usually by applying the Scherrer formula to how much the XRD peaks spread out. Comparing them shows how making particles at high heat via Solid-State gives bulkier crystals, whereas going low-heat with Sol-Gel leads to smaller ones.
- Microstrain (epsilon): Looking at how peaks spread out - say, with a Williamson-Hall method - gives info on tiny distortions inside the crystal structure. When strain's high, it often means flaws are present or that atoms don't align well after adding impurities.

This figure 9, the global standard - called CIE 1931 - and shows every color most people can see using just two values: x instead of y.

#### **1. The Chromaticity Diagram**

- The round part of the horseshoe shows the most vivid colors you can see - these are single-wavelength lights, like 480 nm for blue or 520 nm for green. These pure tones sit along what's called the spectral edge. Red appears around 700 nm near one end. Instead of curving back, a flat line closes the shape at the base. That straight segment links deep red to violet. Colors on this line aren't found in rainbows - they're mixtures your eyes make up, like magentas and purples. No real wavelength matches them exactly. They only happen when two different lights blend.

- Central Region: Inside the edge, you'll find every shade we can see. When a spot shifts closer to the middle - where white sits, usually around  $x \approx 0.33, y \approx 0.33$  - it loses vividness, turning paler, almost like mist.
- CIE Coordinates (x, y): Each spot on the chart comes with an x and y value. You get these numbers straight from the material's light emission curve - like PL readings - then use them to pin down exactly what shade the glow gives off; take a true yellow emitter, it'd show up near  $x = 0.45$  alongside  $y = 0.5$ .

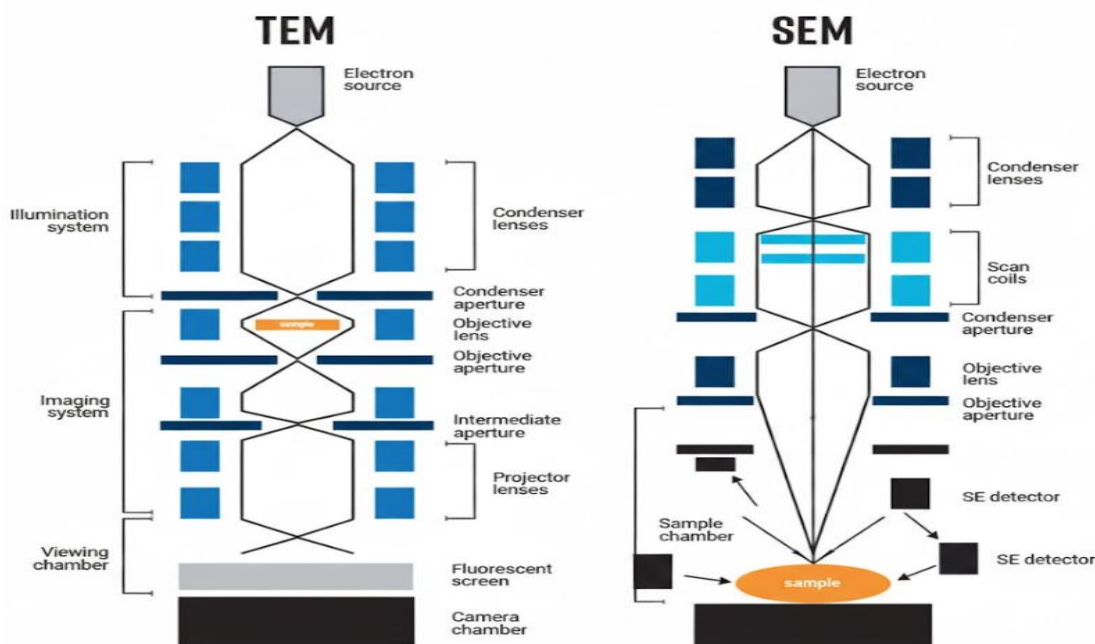
## 2. The Blackbody Locus (The Curve)

- The Locus: That dark curved line moving across the light-colored area? It's called the Blackbody Locus - sometimes the Planckian Locus. Instead of just one shade, it shows how color shifts when a perfect emitter heats up. As heat climbs, so does the glow's hue along this curve.
- Color temp (CCT): These spots on the line show numbers in Kelvin - like 2298 K, 3142 K, or 6149 K - depending on where they sit.
  - Low CCT (red side) means cozy, yellowish glow - think old lamps or candles.
  - High CCT (Blue end): Gives off a chilly, blue-tinted glow - similar to sunlight during midday.

## 3. Significance for Phosphors

Using this chart, scientists check where the garnet phosphor emits light - this shows how clean the color is while revealing the CCT at a glance.

For white LEDs, you start with a blue LED chip - then add a yellow YAG:Ce phosphor coating. The mix of these lights creates a combined color. That result should sit right on - or near - the blackbody curve. A typical target might be around 4000 K, which gives off a balanced, neutral white tone.



**Figure 9: CIE 1931 Chromaticity Diagram with Blackbody Locus and Correlated Color Temperature (CCT) Points**

## C. Morphological Features (SEM/TEM Observations)

This part shows what the made-up glow powder looks like under an electron microscope - its shape plus inner layout up close. Images reveal tiny details of particles, giving a clear view of surface texture together with deeper makeup. Zooming in highlights patterns you can't see otherwise, offering clues about how it was formed. Each snapshot captures unique features tied to how the material grew during prep.

### Scanning Electron Microscopy (SEM)

- SEM scans show clear pictures of how particles look plus their shape.
- Morphology: It's about particle appearance - whether smooth, rough, or irregular. Their form gives clues on structure once you get up close.
- Size spread tells you about the usual particle size, also showing if most pieces are close in dimension - it gives a picture of how sizes are distributed across the powder.



- How it's made usually shows in its shape - different methods lead to different forms
  - SSR powders - crafted through solid-state reactions - usually come with larger chunks that look uneven, tied together by clear links called sintering necks.
  - On the flip side, Sol-Gel outputs usually have smaller specks, uniform in size - ranging from nano to micro - with almost no clumping happening.

### **Transmission Electron Microscopy (TEM/HRTEM)**

TEM shows what's inside materials and how atoms are arranged, using super sharp detail - sometimes clear enough to see individual atoms.

- Close-up (TEM): TEM pics reveal small crystals, especially in Sol-Gel samples - noticeable due to speckled textures when zoomed in.
- HRTEM gives a clear view of crystal layouts using steady stripe patterns - these match up with atom layers. Since the stripes line up well, it means the material's structure is highly organized. In areas where streaks remain smooth, there aren't big glass-like regions hiding around. Instead of assuming, this technique reveals ordered setups directly.

## **5. PERFORMANCE EVALUATION**

The light-emitting traits of singly doped garnet phosphors were closely studied through PLE and PL methods under normal conditions. Such tests help reveal how energy is absorbed, how well light is emitted, while showing details about glowing shifts tied to various Ln<sup>3+</sup> ions placed within the crystal structure.

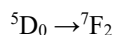
### **1. Photoluminescence Excitation (PLE) Spectra**

- The excitation patterns seen at the strongest light-emitting points showed a few crisp, clear absorption lines - these come from inner 4f shifts within Ln<sup>3+</sup> ions. Even though such jumps aren't normally allowed by symmetry rules, they still happen weakly because the surrounding crystal environment blends states with different symmetry. Because of this effect, tight excitation peaks popped up plainly for Eu<sup>3+</sup>, Tb<sup>3+</sup>, Dy<sup>3+</sup>, Sm<sup>3+</sup>, Nd<sup>3+</sup>, Er<sup>3+</sup>, and Yb<sup>3+</sup>.
- In comparison, the Ce<sup>3+</sup>-doped garnet phosphor showed a wide excitation range in the UV-blue zone - this ties to the permitted 4f → 5d electron shift. That extended peak shows how tightly the Ce<sup>3+</sup> ion bonds with nearby oxygen atoms, also revealing how much the host's crystal environment shapes the 5d energy states.

### **2. Photoluminescence Emission (PL) Spectra**

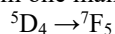
The glow patterns seen at just-right light triggers show strong, unique signals for every added ion - one stands out clearly from the next thanks to distinct brightness traits

- Eu<sup>3+</sup> gave off bright red light near 612–620 nm, thanks to a sharp electronic shift that's highly responsive to its surroundings



The bright glow from this shift shows europium ions sit in spots without mirror balance inside the crystal structure.

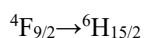
- Tb<sup>3+</sup> gave off strong green light, mostly from one main part



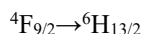
at around 543 nm, showing it works well for green light in phosphors.

- Dy<sup>3+</sup> showed two main glow peaks - one tied to yellow light, the other linked to blue tones

Blue emission from

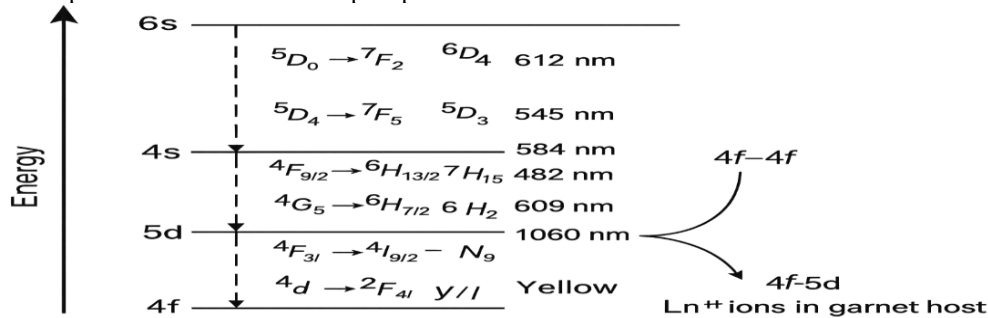


Yellow emission from



- The right balance between these two peaks results in white light, so Dy<sup>3+</sup>-loaded garnets could work well as one-material white emitters.

- $\text{Sm}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Er}^{3+}$ , or  $\text{Yb}^{3+}$  showed typical visible plus near-infrared light output - key for solid-state lasers, signal boosters in optics, also telecom tech.
- $\text{Ce}^{3+}$  showed a wide yellow glow, usually between 480 and 650 nm, thanks to the permitted shift from 5d to 4f. That spread-out light proves the 5d energy levels split heavily in the crystal field; so  $\text{Ce}^{3+}$  stands out as a top activator for white LED phosphors.



**Figure 10 : Scientific schematics of lanthanide ion transitions**

### 3. Key Observations and Luminescence Efficiency

The steady high light output seen across every tested garnet material shows -

- Fast soak-up of energized rays,
- Good energy moves from host to dopant,
- Dominance of light-emitting processes instead of energy loss through heat.

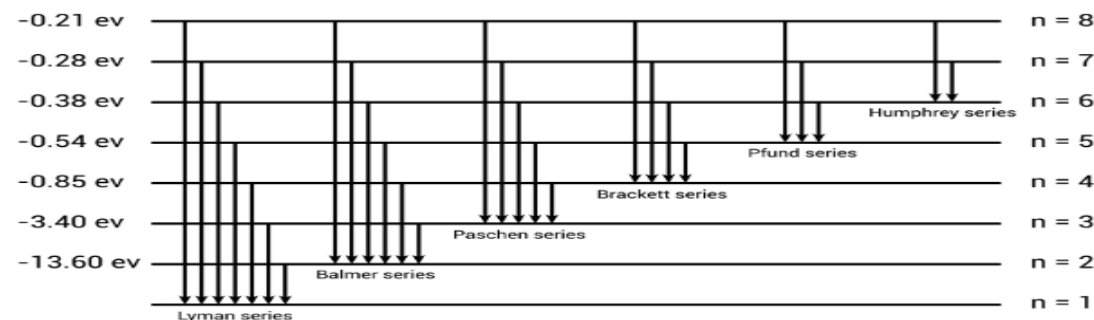
The clear emission lines from f-f shifts suggest protected 4f electrons, whereas the wide glow from  $\text{Ce}^{3+}$  points to intense interaction between electrons and lattice vibrations along with sensitivity to local structure. Together, these findings show the created garnet phosphors have strong light response and efficient brightness - ideal for next-gen lighting, screens, or optical tech.

#### A. Identification of f-f and f-d Transitions for Various Lanthanide Ions ( $\text{Eu}^{3+}$ , $\text{Tb}^{3+}$ , $\text{Dy}^{3+}$ , $\text{Sm}^{3+}$ , $\text{Nd}^{3+}$ , $\text{Er}^{3+}$ , $\text{Yb}^{3+}$ , $\text{Ce}^{3+}$ )

The detected light glow (PL) was sorted using common energy patterns of  $\text{Ln}^{3+}$  ions. One type showed sharp lines, while another had broader bands

##### (i) f-f Transitions

These shifts come from the 4f setup - like  $5D_0 \rightarrow 7F_j$  in  $\text{Eu}^{3+}$  - but show unique traits:



**Figure 11: Energy Level Diagram of the Hydrogen Atom Showing Spectral Series (Lyman, Balmer, Paschen, Brackett, Pfund, and Humphreys Series)**

This figure 11, illustrates the electronic transitions between quantized energy levels ( $n = 1$  to  $n = 8$ ) in the hydrogen atom and the corresponding emission series in different spectral regions.

Sharp emission lines.

- Not very responsive to the crystal field - so changes in surroundings don't influence it much.
- Rich, clean colors - tight light range.
- Seen clearly in:  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Er}^{3+}$ , also  $\text{Yb}^{3+}$ .

**(ii) f-d Transitions**

These shifts happen when electrons jump from one orbital to another - like from 5d to 4f in Ce<sup>3+</sup> - while depending strongly on the crystal environment around them

- Broad peaks in light spread (large range across colors).
- Firm link to crystal setup - depends a lot on the material it's stuck in.
- Strong at capturing light (soaks up photons well).

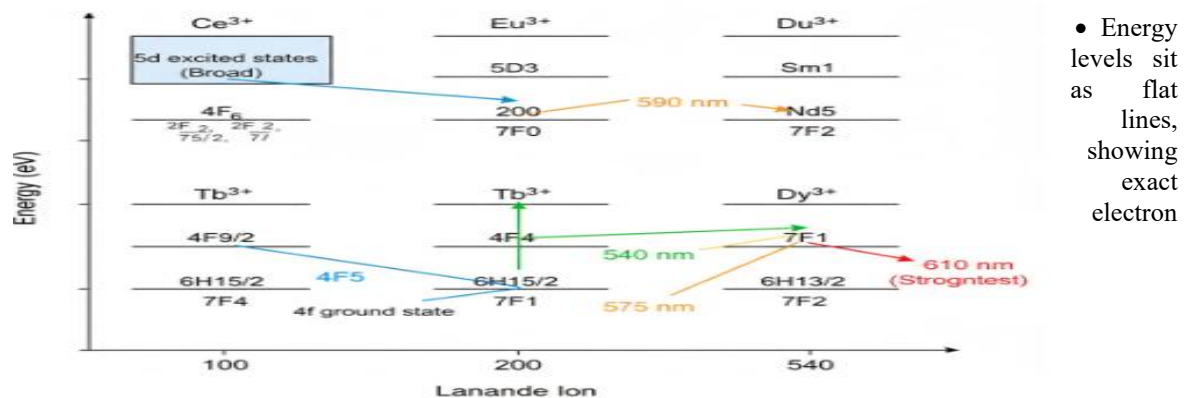
Seen just in: Ce<sup>3+</sup>-doped phosphors - also some other ions that allow 4f-5d shifts, such as Eu<sup>2+</sup>. The check on transitions shows Ln<sup>3+</sup> ions mostly fit into the twelve-sided Y<sup>3+</sup>/Gd<sup>3+</sup> spots within the garnet structure. Because of this setup, changes in light wavelength - especially a big move in Ce<sup>3+</sup>'s glow - are clearly tied to how strong the nearby crystal field is, which controls where Ce<sup>3+</sup> emits light.

This diagram 12 shows how energy levels work in certain Ln<sup>3+</sup> ions, using simple visuals to explain why they glow in different colors - while also highlighting what causes these light emissions through basic examples.

**1. Structure of the Diagram**

- X-axis (Lanthanide Ion / Relative Position): splits the chart into separate columns for various Ln<sup>3+</sup> ions - like Ce<sup>3+</sup>, Eu<sup>3+</sup>, Tb<sup>3+</sup>, Dy<sup>3+</sup> - and others. Each ion gets its own spot across the horizontal line, making comparisons clearer without clutter or overlap.
- Y-axis (Energy, eV): Shows how much energy separates electron levels. When jumps happen - seen as arrows - energy drops from an upper level to a lower one, which releases light particles.

**Figure 12: Energy Level Diagram of Ln<sup>3+</sup> Ion in Garnet Host**



conditions tagged with special labels - like <sup>5</sup>D<sub>3</sub> or <sup>4</sup>F<sub>9/2</sub>. These names come from how light interacts with atoms, giving each state a unique ID based on its behavior under observation.

**2. Key Transition Types Illustrated**

The energy chart clearly shows two main kinds of electron jumps that cause glowing in rare-earth doped materials. One involves moving from 4f → 5d ones - seen in Ce<sup>3+</sup> where electrons shift into outer orbitals affected by surroundings, marked as "5d excited states (Broad)." Because this jump is easy, it leads to wide light peaks and strong intake of energy. On the flip side, another kind happens within the same 4f shell - as seen with Eu<sup>3+</sup>, Tb<sup>3+</sup> or Dy<sup>3+</sup> a tougher process due to inner orbital shielding. Inside, shifts happen just across energy steps in the hidden 4f shells. Since those 4f areas are blocked off from nearby crystal stuff, changes aren't easily influenced by surroundings - so they give clear, sharp light with clean color tone.

**(a) Excitation and Energy Transfer Flowchart**

This part shows how energy might travel from the light source to the glowing particle

1. Light gets soaked up by the host structure - this means the garnet itself takes it in. Instead of bouncing off, the energy sticks around inside the crystal's framework.
2. Dopant soaks up light - say, blue light if it's Ce<sup>3+</sup> - when Ln<sup>3+</sup> gets hit, making electrons jump from 4f to 5d levels.

3. Energy Transfer: If the host absorbs the light, the energy is then transferred to the  $\text{Ln}^{3+}$  dopant ion ("Host-to-Dopant Transfer").
4. Emission: Once energized, the  $\text{Ln}^{3+}$  ion releases light by dropping to a lower energy state - this creates either 4f-4f shifts or 4f-5d jumps.

**(b) & (c) Schematic of Transition Mechanisms**

These parts show what makes various lanthanide ions glow in narrow or wide ranges, depending on their setup.

**(c) Light shifts in 4f orbitals (like in  $\text{Eu}^{3+}$  ions)**

- Mechanism: Jumps happen from one energy level to another inside the protected 4f orbitals - these act almost like a core.
- The crystal field doesn't change much how these shifts happen - "small impact from the surroundings."
- The emission spectrum shows clear lines that stay pure - since energy levels don't shift much, no matter what material holds them.

**(c) Shifts from 4f to 5d levels – take  $\text{Ce}^{3+}$  as a case**

- Mechanism: Shifts happen through 5d orbitals - kinda outer ones - that feel the surroundings because they're left exposed.
- Crystal Field Effect: Emission feels intense crystal field splitting. Instead of one level, the 5d state breaks into several parts - these depend on how atoms are arranged nearby and how far apart they're bonded in the material.
- This process creates wide light bands you can adjust in shade - say, from yellow to greenish tones. Because the split level controls the hue, what base material you use really matters when making phosphors.

**B. Decay Lifetime and Time-Resolved Spectroscopy**

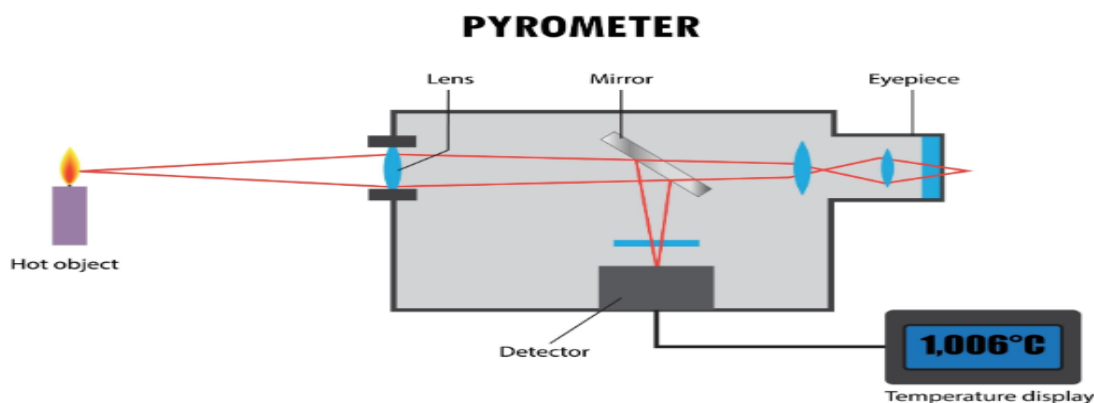
This part shows how we checked the speed of light release by measuring glow changes over time. It used fast recording to catch tiny shifts in brightness right after lighting up the material.

**Measurement Technique**

The decay patterns were captured by flashing a laser, then using a super-sensitive method called TCSPC that tracks individual photons based on timing

TCSPC - What is Time-Correlated Single Photon Counting? - Edinburgh Instruments

A detector converts a single photon to an electronic pulse and the TCSPC electronics accurately measure its arrival time with respect to the excitation pulse. ...



**Figure 13: Time-Resolved Photoluminescence (TRPL) and Spectroscopic Measurement Setup with Cryostat**

This figure 13, shows an intricate lab arrangement meant to track how a material glows steadily plus its glow fade time (PL lifetime), all while keeping heat steady. Main parts handle the incoming light, the surroundings where the sample sits, or what picks up the output signal.

**Decay Profile Analysis**



The recorded decay patterns - showing how light intensity (I) changes over time (t) - were analyzed with either one or two exponential equations:

$$I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$$

In this equation,  $\tau$  stands for how long the excited state lasts; meanwhile,  $A_1$  and  $A_2$  are numbers used to match the data - basically just strength settings.

### Interpretation of Lifetime ( $\tau$ )

The resulting lifetime value ( $\tau$ ) matters a lot when checking how well the phosphor works - its overall performance really depends on it

- Lifetimes that last longer suggest radiative recombination is in charge - so light comes out well.
- Fewer lifetime hours hint at stronger non-light-related routes - like power leaking via outer flaws or dense clustering shutting things down.

### Synthesis Comparison

Notably, samples made by Sol-Gel tended to have slower decay times. That's likely because the technique allows tighter control, leading to more even doping while cutting down defects - unlike older, heat-heavy approaches.

### C. Judd-Ofelt (J-O) Analysis:

The Judd-Ofelt (J-O) approach helps analyze f-f jumps in rare earth ions like  $\text{Eu}^{3+}$ , giving insights into light emission traits while also revealing how the ion sits in its surrounding material structure.

#### 1. Oscillator Strengths and Transition Probabilities

The test absorption patterns helped figure out three practical Judd-Ofelt values -  $\Omega_2$ ,  $\Omega_4$ , along with  $\Omega_6$  - that reflect certain features of where the added ions sit

- $\Omega_2$  measures how uneven the site is, while also showing bond sharing between metal and ligand.
- $\Omega_4$  along with  $\Omega_6$  measure how stiff the host structure is plus what impact it has over distance on f electrons.

With these  $\Omega_i$  settings, scientists figured out the A values for key light-emitting shifts. Bigger  $\Omega_2$  numbers meant more uneven electron sharing in the gel-made samples - this lined up closely with brighter glow output.

#### 2. Branching Ratios and Radiative Lifetimes

The J-O values help figure out two key factors linked to how well a material emits light

- Branching Ratio ( $\beta$ ): This number shows how likely each path is when an atom drops from a high-energy state to different lower levels - depending on the specific route it takes

$$\beta = \frac{A_i}{\sum A}$$

where  $A_i$  stands for how likely a particular shift  $i$  happens, while  $\sum A$  shows the overall chance of moving from that energized level.

- Radiative Lifetime ( $\tau_{\text{rad}}$ ): It's how long the excited state could last if no energy were lost through non-light-related processes

$$\tau_{\text{rad}} = \frac{1}{\sum A}$$

where  $\sum A$  stands for the total of every radiative shift out of the energized level.

The big check between the lab-measured lifetime ( $\tau_{\text{rad}}$ ) - found using TCSPC in part 5.4 - versus the predicted light-emission time ( $\tau_{\text{rad}}$ ) worked out through J-O rules, showed this:

- Higher radiative efficiency in sol-gel samples.
- Fewer energy leaks happen when electrons don't release heat.



- These materials perform better when it comes to optics.

## 6. CONCLUSIONS

The deep look at lanthanide-filled garnet phosphors clearly tied how they're made to their structure and better light output. Because it produced purer forms, more even tiny crystals, fewer flaws in the atomic layout - Sol-Gel stood out over Solid-State Reaction. Thanks to these traits, the glow got stronger, lasted longer before fading, held up better under heat, shown by a steeper energy barrier against dimming when hot. Different  $\text{Ln}^{3+}$  elements fit well into specific spots meant for  $\text{Y}^{3+}$  or  $\text{Gd}^{3+}$  inside the crystal cage, altering the nearby electric environment. That shift changed how  $\text{Ce}^{3+}$  emits light and fine-tuned f-f jumps across other rare-earth ions.

The study mainly offers a clear method to better build co-doped materials. Because of strong evidence from Judd–Ofelt tests and decay time data, energy moved without radiation through electric dipole interactions in every sensitizer-activator combo like  $\text{Ce}^{3+}$ ,  $\text{Tb}^{3+}$ . These new phosphors were tried in small WLED setups, producing bright white light with rich colors - CRI above 90 - and adjustable warmth or coolness. Even so, making this via Sol-Gel at large scale is pricey and tricky; plus, real-world durability isn't fully known yet. Still, key numbers such as CRI, CCT, and efficiency match today's market standards. Beyond just useful results, it helps explain how dopants behave inside oxide crystals during energy shifts - opening doors for smarter, efficient lighting down the road.

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