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CHAPTER

Introduction

- ❖ *This chapter provides an in-depth overview for the need for more efficient methods of energy generation and usage are discussed.*
 - ❖ *This chapter presents a thorough exploration of luminescence, covering its core principles and different forms. The main focus is on the process of photoluminescence, with special attention given to downconversion and upconversion photoluminescence.*
 - ❖ *This chapter reviews recent advancements in phosphor lattice doped with rare earth ions. It also examines the role of the host lattice, its characteristics, and the behavior of various rare earth ion dopants.*
-

1.1. LUMINOUS TECHNOLOGY:

Over the last century there has been immense increase in the global energy demand due to growing population, economic development and improved standard of living. This economic advancement and expanded energy consumption has been achieved at the expense of climate change and global warming [1]. The climate crisis issues have pressed upon achieving sustainable development goals by focussing on energy-efficient technologies and clean energy sources that can reduce our dependence on conventional resources while decreasing overall energy consumption [2,3]. Power demand in lighting sector contributes a significant portion towards power consumption. Therefore, development and improvement of solid-state lighting (SSL) devices, particularly white light-emitting diodes (w-LEDs) is need of the hour.

The artificial lighting technology has evolved through three distinct generations driven by technological advancement. The first generation comprises, incandescent sources which emit light upon being heated to high temperatures. Invented by Edison in the nineteenth century, these bulbs are remarkably inefficient, and converts only 5% of their energy into visible light.

The Compact Fluorescent Lamps (CFL), emerged in the mid-20th century belong to second generation and uses electrical discharge in low-pressure gases like mercury or argon to generate ultraviolet light, which is then converted to visible light by phosphor coatings. Though CFLs are more efficient than incandescent bulbs they are unsafe for the environment and human health because of the toxic mercury coming out of the used or broken Fluorescent lamps [4].

The Solid-state lighting (SSL) based inorganic light emitting diodes (LEDs) belonging to the third generation represents a revolutionary breakthrough. This technology has great potential to generate white light with maximum efficiency. The development of efficient solid-state lighting systems has fundamentally relied on the phenomenon of luminescence.

1.2. LUMINESCENCE:

The process of absorption of energy by electrons in a material which is subsequently liberated in form of visible photons with negligible thermal energy output is called Luminescence. This mechanism displays superior efficiency than incandescence because here the light-producing mechanism doesn't involve heating the material, eliminating energy losses through thermal radiation. The material involved in luminescent process are called luminescent materials or

phosphor material. The process of luminescence can be classified in to different categories based on the source of excitation.

1.2.1. Photoluminescence: Photoluminescence as the name suggests requires photons to push electrons to higher energy levels which while relaxing to ground state produce emission. Depending on the duration of emission of light it can be further categorized in to fluorescence and phosphorescence.

Fluorescence: The photoluminescent process exhibits emission of photon instantly that occurs just in 10^{-8} seconds of cessation of excitation as electrons settles back from excited state to a lower ground state.

Phosphorescence: This class of Photoluminescent process also called afterglow is characterized by delayed emission which persists for time ranging from milliseconds to few seconds to even several hours.

1.2.2 Electroluminescence: Luminescence produced by application of electric fields is called electroluminescence. In this process, electrons are injected from an external DC voltage supply across a semiconductor p-n junction and luminescence is produced by the electron-hole recombination in that region. The light emitting diodes (LEDs) work on this mechanism.

1.2.3 Cathodoluminescence: The luminescence that occurs when fast moving electrons or cathode rays strikes the material. The striking electrons imparts their energy to excite electrons to higher levels which while returning to ground state emits electrons. The cathode ray tubes (CRT), field emission display and TV sets are common examples of cathodoluminescence.

1.2.4 Chemiluminescence: During certain exothermic chemical reactions emission of photons take place with a wavelength varying from UV- Visible to IR. This phenomenon called chemiluminescence happens when the exothermic chemical reaction produces an intermediate product in excited state which subsequently releases energy in form of light as it returns to ground state through radiative decay. The specific frequency or energy of the emitted photon can serve as identifier for a particular molecular group involved in reaction. Therefore, this technique enables highly sensitive analytical detections and measurements across diverse sample types and concentrations [5,6].

1.2.5 Bioluminescence: The emission of photons from living organisms when enzymes (luciferase) breakdown organic substances present in them (luciferin) through oxidation and a part of chemical reaction energy is converted in to photon. Fireflies and jellyfish are some of the organisms that exhibits bioluminescence [7].

1.2.6 Radioluminescence: Radioluminescence or scintillation is the phenomenon of emission of light from certain materials when they are exposed to ionising radiation.

1.2.7 Sonoluminescence: The luminescence process where the materials are excited by action of ultrasonic fields. In sonoluminescence emission takes place through acoustic cavitation from the collapsing bubbles inside a liquid when triggered by ultrasound [8].

1.2.8 Thermoluminescence: The Luminescence process in which thermal stimulation causes photon emission by releasing the trapped electrons that were previously generated by irradiating the material with ionising radiations. It has applications in radiation dose monitoring in environment [9].

1.3 HISTORY AND GENERAL FEATURES OF PHOTOLUMINESCENCE:

As discussed in previous section the photoluminescence requires photons as source of stimulation for luminescence process. The mechanism behind the photoluminescence process generally involves two stages. The first one is excitation in which absorption of photonic energy at the activator site takes place thereby taking the electrons to higher energy level. The excited system then loses energy either radiatively by emitting a photon or non-radiatively by releasing a phonon. The photon emission constitutes luminescence process while the phonon emission has no role in luminescence and it leads to loss of energy in form of heat through lattice vibrations in the host material. The latter process needs to be dominant in order to achieve maximum efficiency of the luminescent material [10,11]. Fig. 1.1 depicts the process of luminescence at activator level by energy level diagram. The process labelled E shows the excitation stage; the one labelled R represents radiative emission, while the one labelled N represents non-radiative transition.

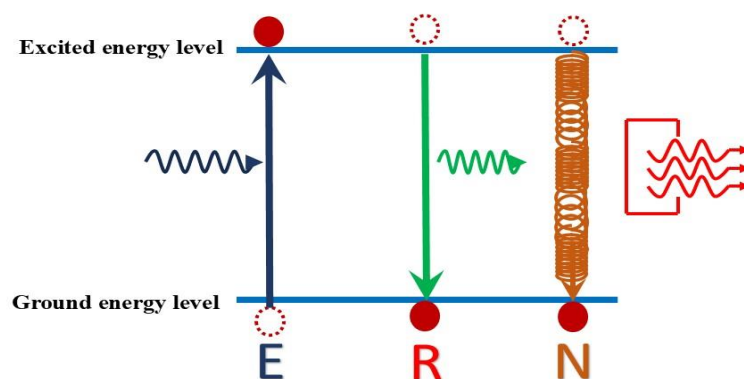


Fig.1.1. Schematic diagram representing various stages of a luminescence process.

Based on whether emission of photon is immediate or delayed after the source of excitation is taken off photoluminescence is further categorized in to fluorescence and phosphorescence. Though both the processes involve excitation of electrons followed by emission of photons they bear significant differences in the underlying mechanisms, emission lifetimes and their applications.

Historically there has been vigorous debate on distinction between the two-phenomenon based on how long the luminescence persisted after termination of excitation and its variation with temperature. The contemporary scientific knowledge articulates that in case of inorganic phosphors the luminous output which occurs simultaneously as the excitation source is applied is fluorescence while the visible afterglow that remains perceptible to human eyes even when the source of excitation is removed is phosphorescence. The origin of delayed emission lies in presence of quasistable excited states and traps in inorganic phosphors.

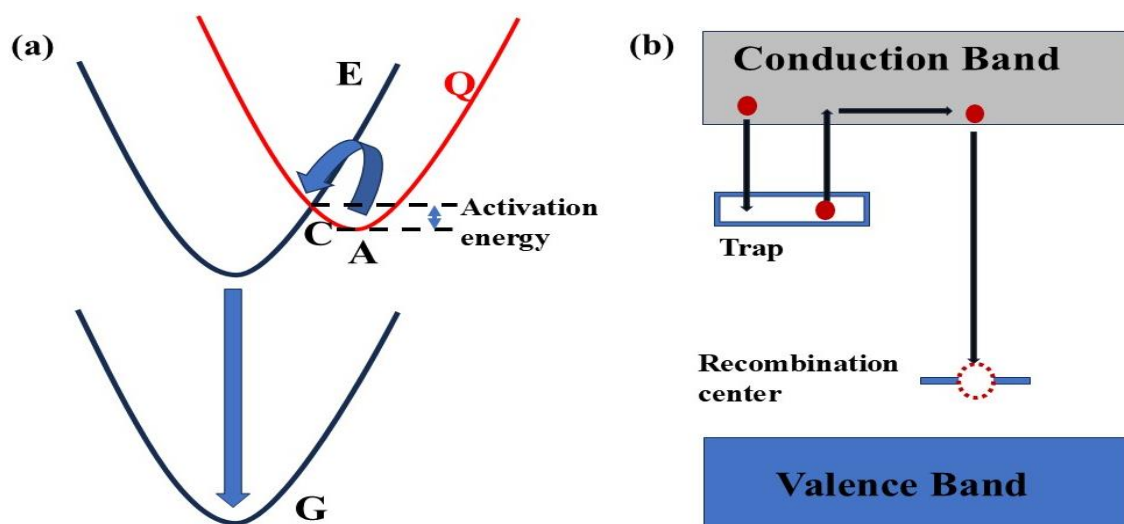


Fig. 1.2. Schematic diagram representing process of phosphorescence due to presence of (a) quasistable states and (b) trap levels of a luminescence process.

The Quasistable states are the excited states with very long lifetime. When after excitation some of the luminescent centres stay in these states which are then brought back to ground state by thermal activation. The mechanism is depicted in Fig. 1.2 (a). The Thermal activation of quasistable state Q causes the luminescent centre settled at A in state Q to excited state E via C. If the radiative transmission probability of state E is greater than probability of thermal activation from Q to E then the emission decay time is equal to the lifetime of the quasistable state which generally is no longer than a second [12]. The defects in the crystal structure due

to foreign impurity or structural irregularities gives rise to discrete energy states within the band gap of the crystal. So, at defect sites the electrons can occupy otherwise forbidden energy levels called Traps. The probability of recombination of trapped electron (or hole) with hole (or electron) or to be re-excited to conduction band (or valence band) is very small. The process of phosphorescence occurs when these trapped charge carriers are reactivated to their respective bands. The simple model explaining phosphorescence with a single trap level is shown in Fig. 1.2(b) [12–14].

For organic phosphors the basic mechanism behind the fluorescence and phosphorescence is shown in Fig. 1.3. depicting a simplified form of Jablonski diagram. In order to comprehend the difference between mechanism involved in both the processes it is imperative to examine the spin multiplicity of the involved electronic states. The singlet states possess paired electrons with opposite spins ($+\frac{1}{2}$, $-\frac{1}{2}$), therefore they have a total spin of zero and a spin multiplicity of unity ($2S + 1 = 1$, where $S = 0$). While triplet states contain unpaired electrons with parallel spins, resulting in a total spin of one and a spin multiplicity of three ($2S + 1 = 3$, where $S = 1$).

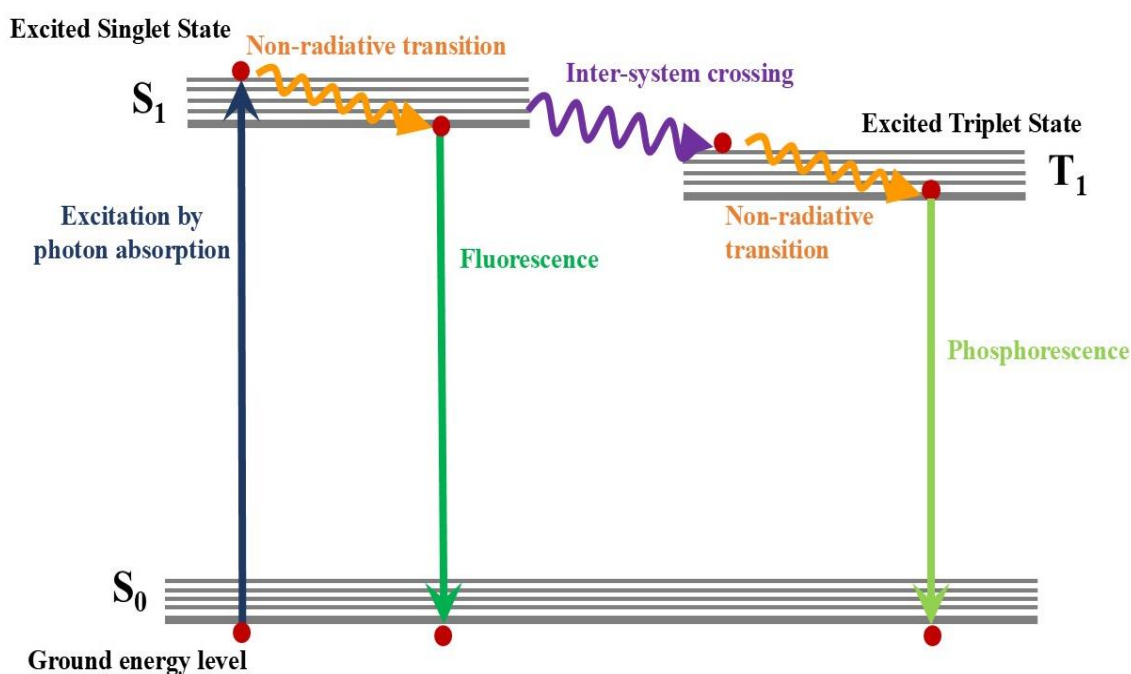


Fig. 1.3. Simplified form of Jablonski diagram

The process of fluorescence is a spin allowed transition with a short lifetime. The incident photons (source of excitation) are absorbed by the electrons in ground state S_g which push them to higher energy singlet states where they occupy various vibrational levels of the excited state. The excited electrons then rapidly transit non- radiatively to lower vibrational levels within the

excited energy state, dissipating excess energy as heat via vibrational relaxation. Finally, electrons return back to ground state (S_0) from the lowest excited singlet state (S_1) resulting in fluorescence. The whole process takes a time of 10^{-9} to 10^{-3} seconds. The Phosphorescence on the other hand is a spin forbidden process which follows a more complex mechanism. Once the electrons are excited to higher energy singlet state (S_1) they can change their spin resulting in a transition from singlet excited state (S_1) to a triplet excited state (T_1) called intersystem crossing. The triplet excited state in general lies lower in energy than singlet excited state and it possess metastability having lifetime values more than 10^{-4} sec. So, when electron under goes the spin forbidden transition from triplet excited state (T_1) to singlet ground state (S_0) the time scale of the transition would be nearly equal to lifetime of metastable triplet state and takes a duration of 10^{-3} to 10 seconds and resulting emission is phosphorescence. The Phosphorescence in comparison to fluorescence typically possess broader emission spectra and longer emission wavelength relative to the excitation wavelength due to energy losses during intersystem crossing [10,15–17]

1.4 PHOSPHORS:

Phosphors are the inorganic materials that displays luminescence upon excitation by an appropriate source. They produce emission around the visible region of electromagnetic spectrum when excited by some external energy source or photons. The phosphor material can be a semiconductor or an insulator. When the band gap of phosphor corresponds to visible photon frequency they emit in visible spectrum and they are called self-luminescent materials. Since the materials having such favourable band gap is few so, the materials with wider band gap can be engineered to produce visible light by introducing defects and impurities in the host lattice structure. When the added impurities known as dopants are incorporated inside the host matrix their energy levels position themselves inside the forbidden energy gap of the host lattice. The luminescence process then takes place through the transitions between the energy levels of dopants. Based on the functionalities of dopant ions they can be classified as activator, co-activator and sensitizer.

Activator: When the dopant ion electron gets excited to higher energy level and emits photon of a lower energy while relaxing back to ground state, they are activators or luminescent centres.

Coactivator: Coactivator ions are added along with activator ions to support the emission from activator. They do not participate in direct emission but supports activators by acting as charge compensators or by creating electron/hole traps [18].

Sensitizer: In some cases, due to weak absorption by the activator a different impurity is added along with activator which enhances the absorption by activator by acting as a bridge for transferring energy from source of excitation to activator ion. So, a part of energy absorbed by sensitizer is transferred to the activator for producing luminescence.

1.4.1 Stokes and anti-Stokes emission:

The process in which the frequency of the emitted photons is smaller than the photons employed for excitation is called stokes emission or down conversion. The non radiative lattice relaxation contributes to stokes shift which is the difference in energy (or wavelength) between the absorbed and emitted photons. In contrast it is also possible that the emitted photons have a greater frequency than the absorbed photons such emission is designated as anti-Stokes emission or up-conversion. The up-conversion process involves sequential absorption of multiple photons from NIR region to emit photon in UV to IR region. The basic process for stokes and anti-Stokes emission is shown in Fig 1.4. [19,20].

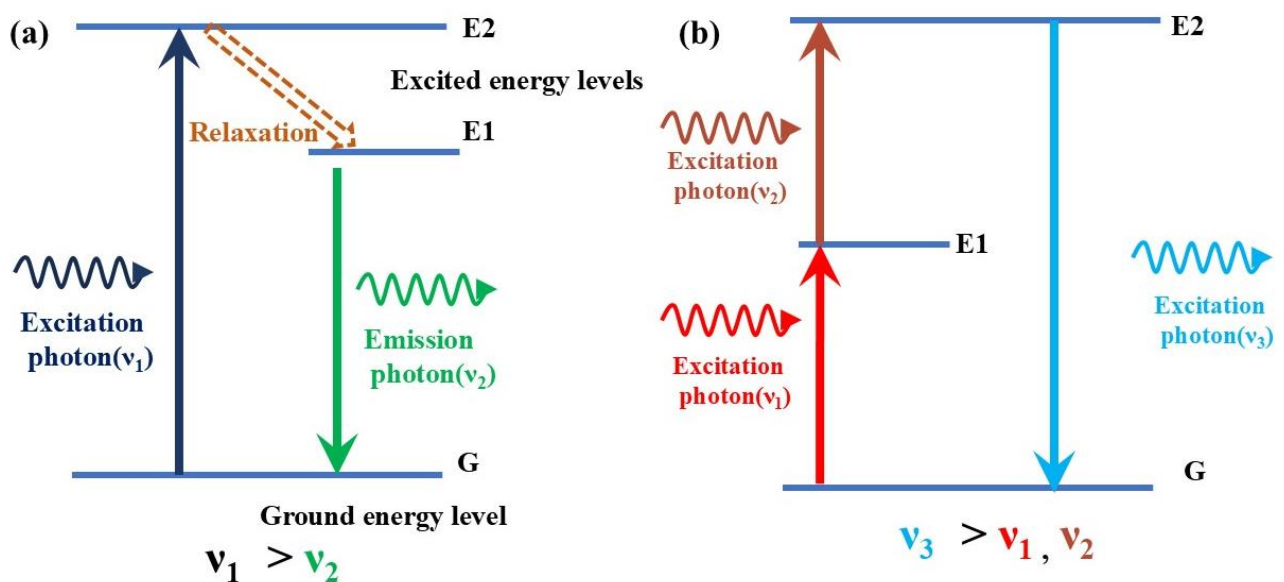


Fig. 1.4. Process of (a) Stokes and (b) anti Stokes emission

1.4.2 Absorption of energy and excitation:

The photon emission occurs when phosphor is excited to higher energy level by absorption of energy from the source of excitation. The excitation process can take place directly by absorption by activator ions to get excited (Fig. 1.5 (a)). However indirect excitation of activator also happens, where energy is first absorbed by host material then it is transferred to the activator ions. When host material absorbs the energy, it may lead to self-luminescence which is usually absorbed in vanadates, tungstates and molybdates Fig. 1.5 (b) [21]. In some cases, host act as sensitizer by transferring the absorbed energy to the activator ion thereby exciting it to higher levels for subsequent emission Fig. 1.5 (c). Host can also lose the absorbed energy non-radiatively by dissipating it in form of heat via lattice vibrations. Additionally, deliberately added sensitizer can also absorb the energy from excitation to transfer it to activator thereby sensitizing it for emission (Fig. 1.5 (d)).

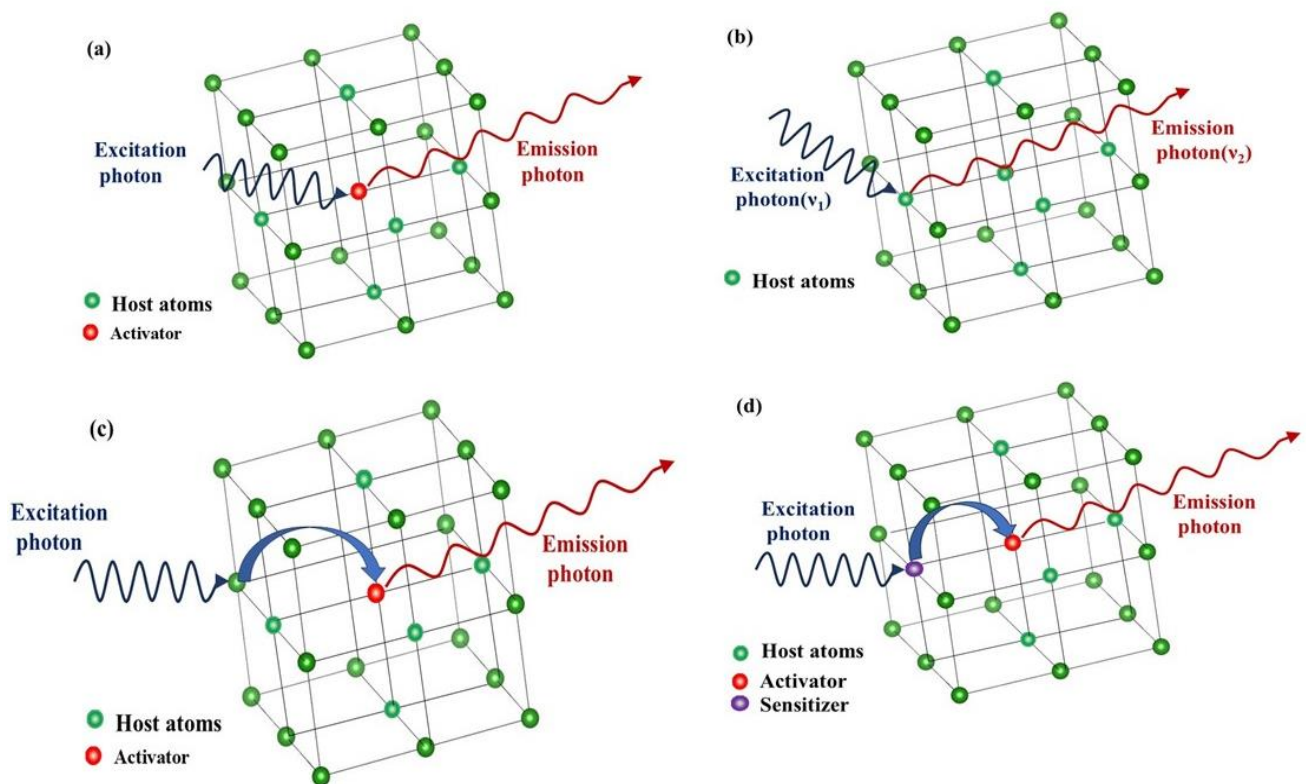


Fig. 1.5. Photon Absorption, excitation and luminescence (a) Activator sensitized luminescence (b) Self luminescence (c) Host sensitized luminescence (d) Sensitizer - activator induced luminescence.

1.4.3 Energy transfer Mechanism.

The energy transfer process involves the absorption of energy in form of light by the host or ions acting as sensitizer which may be referred to as donors (D). These donors after absorbing the energy transfer it to another ions or activators which are referred to as acceptors(A). The acceptors then emit this energy in form of photons. There exist four basic mechanisms responsible for energy transfer from donors to acceptors are:

1. **Radiative Energy transfer:** In this mechanism illustrated in Fig. 1.6 (a) the photon which gets emitted from donor is absorbed by the acceptor or activator ion [22]. The substantial overlap of emission spectrum of acceptor/activator with the absorption spectrum of donor is required for this mechanism. Moreover, the efficacy of radiative transfer is determined by the efficient excitation of acceptor by the donor emission. When the dominant mechanism for energy transfer is radiative ET in that case the decay time for sensitizer emission doesn't vary with the concentration of activator ions [23].
2. **Non radiative resonant energy transfer:** This mechanism relies on quantum mechanical resonance phenomenon for transferring energy from sensitizer to activator ions without involving intermediate photon for emission and absorption processes. As shown in Fig 1.6 (b) this mechanism requires that the difference between energy levels of sensitizer and activator ions should be equal and they should be coupled by some interaction which can be exchange interaction or electrostatic interaction. Exchange interaction requires overlap of electronic wavefunction as depicted in Fig 1.6 (c). The electrostatic multipolar interactions shown in Fig.1.6 (d) can manifest in form of either dipole-dipole (d-d), dipole-quadrupole(d-q) or quadrupole-quadrupole(q-q) interaction depending on the nature of transition of donor and acceptor ion. The probability of energy transfer is given by Dexter's theory for d-d, d-q, and q-q interaction and it is proportional to 6^{th} , 8^{th} and 10^{th} power of distance R between donor and acceptor. When energy transfer takes place by resonant non radiative mechanism, the decay time decreases as the activator ion concentration is increased [11,23–26]
3. **Multiphonon assisted energy transfer:** When there exists some difference between the transition energies of donor and acceptor ion, the resonance condition is not well fulfilled, in such a case phonon assisted energy transfer takes place where the energy gap is filled either by absorption or emission of a phonon as depicted in Fig 1.6 (e). The

Miyakawa and Dexter theory establishes exponential dependence of probability of phonon assisted ET on energy gap [15,27]

4. **Cross relaxation:** The cross-relaxation mechanism involves transfer of energy between same type on ions. As shown in Fig 1.6 (f) this process involves an intermediate state for transfer of energy between identical ions. The ion in excited state is relaxed to the intermediate state thus transferring energy to the other ion in ground state thereby exciting it to the intermediate level. Thus, both the ions undergo simultaneous change of states: the excited ion transfers energy to the ground-state ion, and both ends up in intermediate energy levels [28,29].

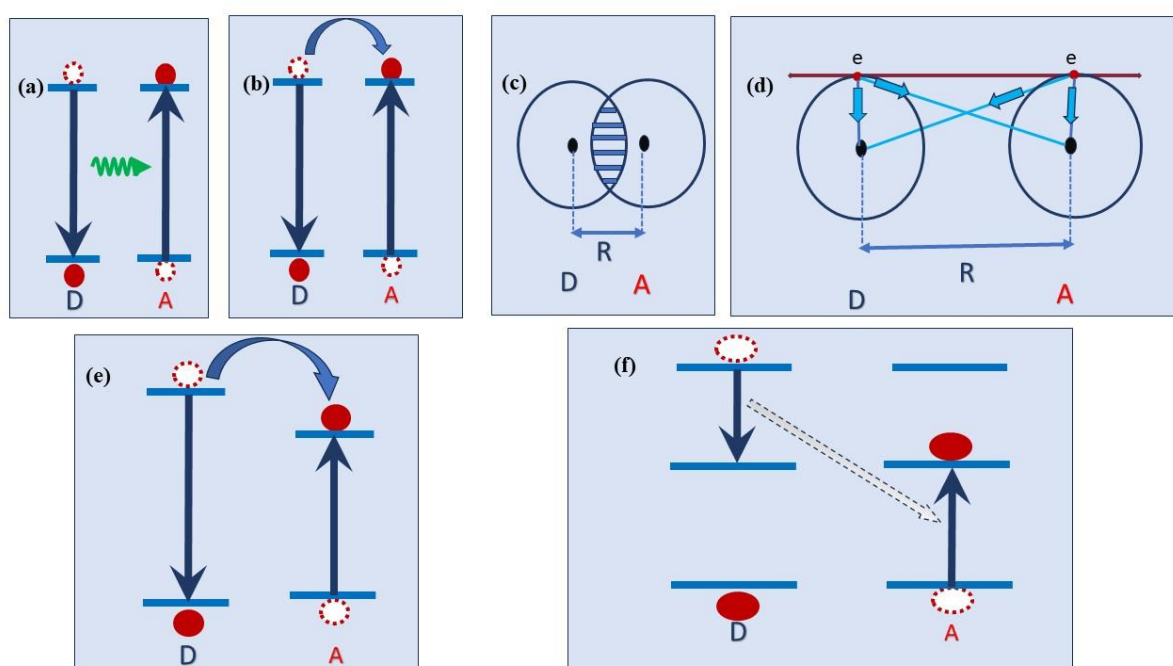


Fig. 1.6. Different energy transfer mechanisms (a) Radiative energy transfer (b) Resonant energy transfer (c) Exchange interaction (d) Electrostatic multipolar interactions (e) Multiphonon assisted energy transfer (f) Cross relaxation

1.4.4 Emission process

The luminescence process can be analysed by understanding the configurational coordinated diagram (CCD) model. This model is helpful in understanding the mechanism of luminescence including excitation, emission, includes the effect of lattice vibrations and takes in to account the crystal relaxation followed by electronic transitions. In this model as depicted in Fig. 1.7 the potential energy curves are plotted against the configurational coordinates or bond distance.

These curves assume parabolic shape representing harmonic behaviour of the electronic levels and it is not necessary that the minima of these curves coincide with the equilibrium internuclear distance. The lowest potential energy curve describes the ground state while the higher curves express the excited states. Within an electronic state exists various quantised vibrational levels that are represented by horizontal lines. The electronic transitions involved in excitation and emission process are governed by Frank-Condon principle. This principle asserts that the electronic transitions are expeditious relative to the vibrational transitions due to the significantly heavier mass of nuclei compared to the electronic mass and nuclei may be considered stationary during the transitions. So, the internuclear distance may be considered unchanged during the transitions which are represented by vertical lines in the configurational coordinate diagram. The energy from the incident photons is absorbed by the bound activator ion thus exciting it vertically from the equilibrium ground state to the excited state keeping the configurational coordinate constant. In excited state the ion occupies higher vibrational level resulting from asymmetrical nature of the curves of two states. The ion then relaxes to lowest vibrational state of the excited electronic state by phono relaxation thus losing some energy in form of vibrational or thermal energy. The ion then returns from the lowest vibrational level of excited electronic state to ground state resulting in emission of photon thus producing luminescence. Thus, as depicted in Fig 1.7 the excitation photon energy is more than the emitted photon thus configurational coordinate diagram also takes in account the Stokes shift.

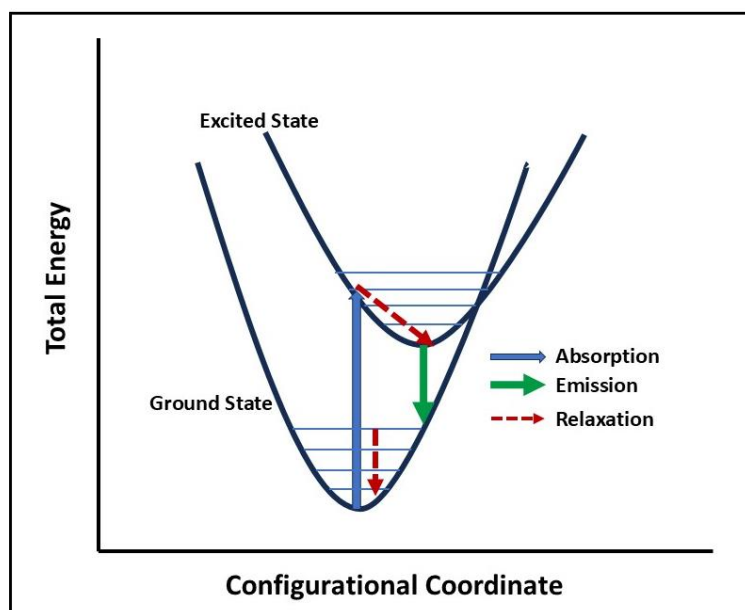


Fig.1.7. Emission and excitation process on a configurational coordinate diagram.

Apart from radiative emission configurational coordinate diagram also attributes different non radiative emission mechanisms contending along with the luminescence process. The multi-phonon relaxation process that transpires at crossover points between ground and excited states is one of them. As shown in Fig. 1.8 (a) when the crossover point is below the initial excitation vibrational level the system may go through a fast non radiative relaxation to arrive at a vibrational level matching the crossover point. At crossover point the electron can cross the intersection to the vibrational states of ground state suppressing the radiative emission and returning to the ground state through non radiative multi-phonon relaxation. On the basis of configurational coordinate diagram, the thermal quenching phenomenon can also be explained where the luminescence intensity decreases at higher temperature. At elevated temperatures the higher vibrational levels are thermally populated in both excited and ground states. So even if the crossover point lies above the initial excitation vibrational level as depicted in Fig 1.8 (b) the probability of reaching the crossover point between electronic states becomes large. This makes non-radiative relaxation more favourable as electron cross the intersection between electronic states, thus diminishing emission intensity through enhanced non-radiative pathways [15,30,31].

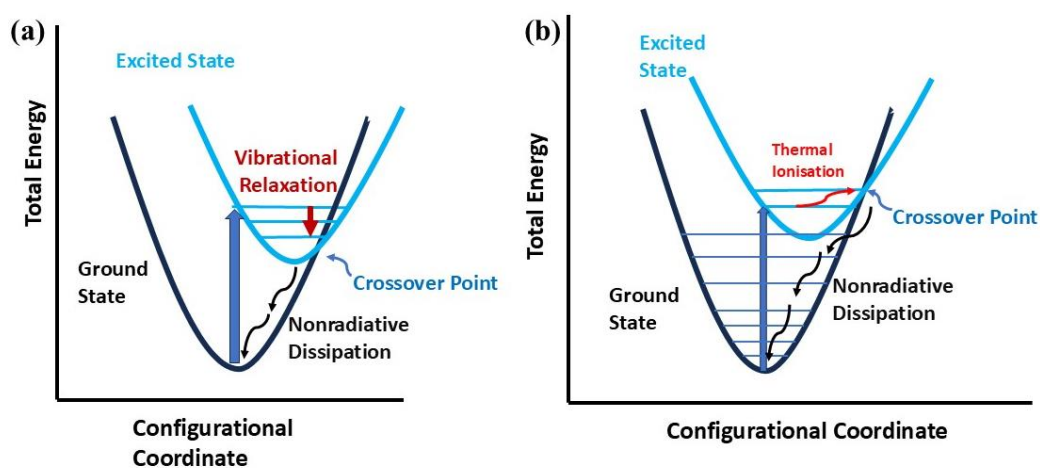


Fig. 1.8. Nonradiative emission mechanism relaxation process via crossover point **(a)** when crossover point is below the excited vibrational state **(b)** when crossover point is above the excited vibrational state

1.4.5 Theoretical frameworks for energy transfer mechanism and concentration quenching

The doped phosphor materials exhibit utmost luminescence for some optimum concentration of activator ion over which with further addition of dopant the emission intensity decreases this

phenomenon is called concentration quenching. Initially the emission intensity increases as absorption efficiency increases with more concentration of activator ions, but after a certain point the distance between the nearest activator ions decreases thus making transfer of energy between neighbouring activator ions having identical excited states more probable leading to quenching of emission intensity. The process of energy transfer requires some conditions to be fulfilled i.e. resonance between energy levels of the ions is there and there exist some interaction between the ions. The interaction involved in energy transfer can either be exchange interaction or multipolar interaction [11,23,25]. For the purpose of assessing the nature of interaction involved Blasse gave formulation for estimating the critical distance (R_c) between the ions at which quenching happens which is related to unit cell volume V of the host lattice, critical concentration x_c and available host cations sites in unit cell N and is given by equation 1.1 [24]:

$$R_c = 2 \sqrt[3]{\frac{3V}{4\pi x_c N}} \quad (1.1)$$

The exchange interactions require overlap of electronic wavefunction and can take place only when this critical distance is below 5 Å. If critical distance is more than 5 Å then multipolar interactions explained by Dexter's theory are involved in energy transfer.

Dexter Theory:

The Dexter theory provides formulation to identify the nature of electrostatic multipolar interaction between the nearest interacting ions which can be dipole-dipole, dipole-quadrupole or quadrupole-quadrupole in nature. The Dexter's Energy transfer equation relates photoluminescent intensity I , with the concentration of activator ions by the relation given by equation 1.2 given by [32,33]:

$$\frac{I}{x} = K \left((1 + \beta(x))^{\frac{Q}{3}} \right)^{-1} \quad (1.2)$$

Where, K and β are constants, characteristic for a host lattice and excitation. The value of Q depends on the nature of electric multipole interaction and is 6 for dipole-dipole, 8 for dipole-quadrupole, and 10 for quadrupole-quadrupole interaction.

In case of co-doped phosphors where along with activator sensitizer is also added the multipolar interaction responsible for energy transfer from sensitizer to activator can be identified from the emission spectra data by applying Dexter and Reisfeld's approximation.

Dexter and Reisfeld's approximation:

Reisfeld's and Dexter theory relates the quantum efficiencies η_0 and η_s to total concentration C of activator and sensitizer ions by relation

$$\frac{\eta_0}{\eta_s} \propto C^{\frac{n}{3}} \quad (1.3)$$

Where, η_0 is emission quantum efficiency of sensitizer emission sans activator and η_s being its value in the presence of activator and n takes different values for dipole-dipole ($n = 6$), dipole-quadrupole ($n = 8$) and quadrupole-quadrupole interactions ($n = 10$). The ratio of quantum efficiencies η_0/η_s can be approximated to the ratio I_{s0}/I_s , where I_{s0} and I_s represents integrated emission intensity of sensitizer transition without and with activator ions. Therefore equation (1.3) can be transformed to equation (1.4)

$$\frac{I_{s0}}{I_s} \propto C^{\frac{n}{3}} \quad (1.4)$$

So, if a plot for I_{s0}/I_s versus $C^{(n/3)}$ for different values of n is obtained and the linear correlation coefficient (R^2) is analysed then the dominant energy transfer mechanism can be identified. The highest R^2 value indicates the most likely interaction type [34].

1.5 ACTIVATORS/DOPANTS

The luminescent centres are incorporated in form of activators in small quantity inside a host material. These activators are generally rare earth ions and transition metal ions.

1.5.1 Rare Earth Ions

The 15 lanthanides of f-block elements from Lanthanum (La) to Lutetium (Lu) plus Scandium (Sc) and Yttrium (Y) from d block together comprises rare earth family of 17 members and is depicted in Fig 1.9. Although their name suggest that they are sparse, but rare earths are relatively abundant in Earth's crust. Since they are not available as dense minerals ore deposits and have remarkably similar chemical properties so it is challenging to mine them as well to separate and obtain in pure form cost effectively. Their distinctive electronic configuration gives them the unique physicochemical characteristics. The ground state configuration for Sc is $[\text{Ar}]3d^14s^2$ and for Y it is $[\text{Kr}]4d^15s^2$. The La, Ce, Gd and Lu have a configuration of $[\text{Xe}]4f^{n-1}5d^16s^2$ while the rest of Rare -Earths bear $[\text{Xe}]4f^n6s^2$ configuration. Such distribution of electrons establishes a shield for partially filled inner orbitals (3d, 4d and 4f) by the outer $5s^2$ and $5p^6$ shells. The relative ease of getting rid of two 6s electrons and 1 electron from 5d or 4f shell drive them to predominantly exhibit trivalent ionic state. In trivalent ionic state these rare earth ions from La^{3+} to Lu^{3+} begets synonymous configuration of $[\text{Xe}]4f^{n-1}$ which gives rise to reduction in ionic radii across the lanthanide series (lanthanide contraction) and is shown in Fig. 1.9. This contraction makes incorporation of different rare earth ions into single phase

materials for development of materials with diverse properties. While they pre-eminently bear trivalent state alternative oxidation states stabilized by empty ($4f^0$), half-filled ($4f^7$), or completely filled ($4f^{14}$) $4f$ orbital configurations also exist. For example, Ce^{4+} ($[Xe]4f^0$), Eu^{2+} ($[Xe]4f^7$), Tb^{4+} ($[Xe]4f^7$), and Yb^{2+} ($[Xe]4f^{14}$). Since the outer electrons shields the $4f$ electrons thus making $4f$ electrons reclusive to chemical bonding thus making their emission remarkably stable to environmental changes due to crystal field. Ordinarily free rare earth and activated ion in host lattice both have energy levels similar to each other. Moreover, the presence of unpaired $4f$ electrons engenders paramagnetic behaviour to most trivalent lanthanides with exceptions being La^{3+} and Lu^{3+} which are diamagnetic. The electronic configuration and other physical properties of rare earth ions is presented in Table.1.1. [23,35–39].

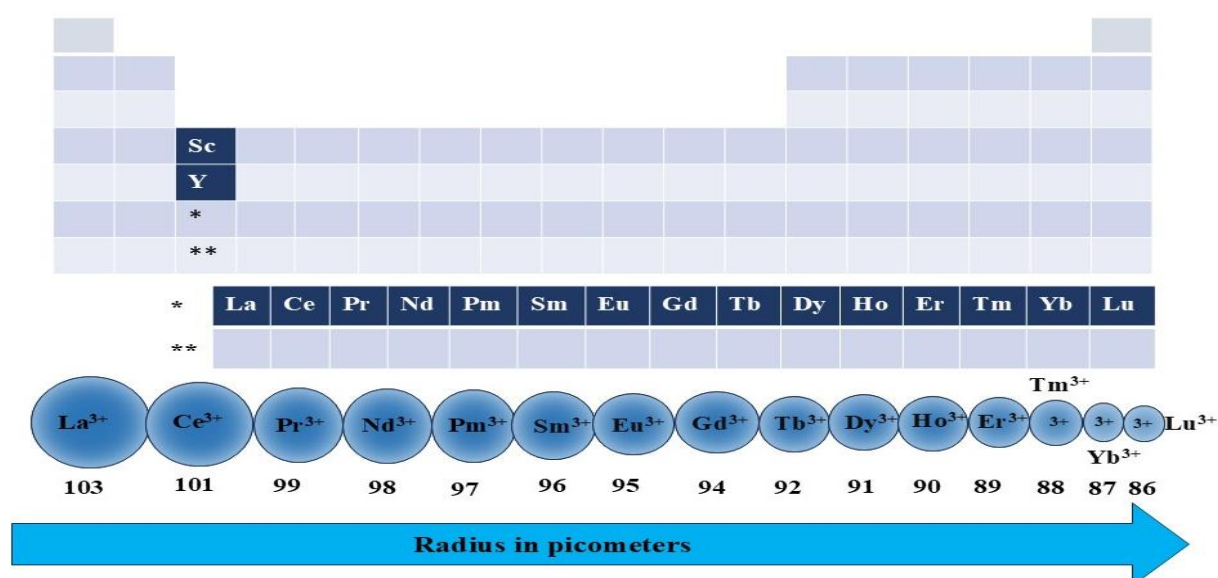


Fig. 1.9. Rare earth elements on periodic table and depiction of lanthanide contraction among rare earth ions

Symbol (Atomic number)	Atomic weight	Ionic radii for 6-fold coordination of ions in +3 oxidation state(pm)	Electronic Configuration (Ln^{3+})	Ground state
La (57)	138.905	103.2	$[Xe]4f^0$	1S_0
Ce (58)	140.115	101	$[Xe]4f^1$	$^2F_{9/2}$
Pr (59)	140.91	99	$[Xe]4f^2$	3H_4
Nd (60)	144.24	98.3	$[Xe]4f^3$	$^4I_{9/2}$
Pm (61)	145	97	$[Xe]4f^4$	5I_4

Sm (62)	150.36	95.8	$[Xe]4f^5$	$^6H_{5/2}$
Eu (63)	151.965	94.7	$[Xe]4f^6$	7F_0
Gd (64)	187.25	93.8	$[Xe]4f^7$	$^8S_{7/2}$
Tb (65)	158.925	92.3	$[Xe]4f^8$	7F_6
Dy (66)	162.5	91.2	$[Xe]4f^9$	$^6H_{15/2}$
Ho (67)	164.93	90.1	$[Xe]4f^{10}$	5I_8
Er (68)	167.26	89	$[Xe]4f^{11}$	$^4I_{15/2}$
Tm (69)	168.934	88	$[Xe]4f^{12}$	3H_6
Yb (70)	173.04	86.8	$[Xe]4f^{13}$	$^2F_{7/2}$
Lu (71)	174.98	86.1	$[Xe]4f^{14}$	1S_0

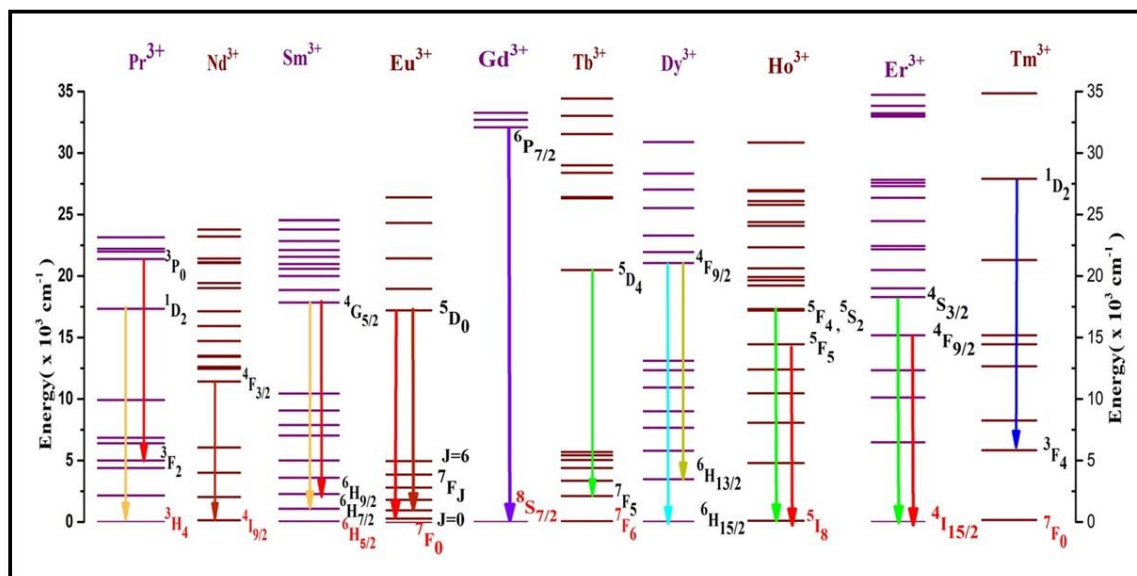


Fig. 1.10. Deike's energy diagram for some rare earth depicting energy levels and selective transitions.

Based on the electronic configuration the energy levels can be designated in form of the spectral term symbol ($^{2S+1}L_J$) defined by H. N. Russell and F. A. Saunders obtained from spin orbit coupling [40]. These energy levels have a definite value and they are represented in Dieke's energy level diagram shown in Fig 1.10. The energy levels of the rare earth ion in host lattice gets accommodated inside the host material optical band gap. The partially filled 4f orbitals of

rare earths in RE activated phosphors are responsible for photoluminescent properties enabled due to intra-configurational $4f^n$ transitions or inter-configurational $4f^n-4f^{n-1}5d^1$ which are explained as follows:

1.5.1.1. 4f-4f transitions:

These transitions take place between excited 4f states to the ground 4f states. The 4f orbitals in rare earths are partially filled inner orbitals which are shielded by completely filled outer $5s^2$ and $5p^6$ shells. This screening effect makes these orbitals minimally influenced by the crystal field of host lattice which limits the crystal field splitting to 100 cm^{-1} only resulting in sharp line shape emission. These transitions can be classified according to three different modes:

(i) Induced Electric Dipole transitions: The optical transitions in rare-earths primarily occur through induced electrical dipole mechanism. In this mechanism the lanthanide ion interacts with the electric field component of light via electric dipole. These transitions have odd parity. So, the electric dipole operator displays odd symmetry properties under inversion operation about an inversion centre. Since there is no change in parity in 4f-4f shell electric dipole 4f-4f transitions are forbidden as per Laporte selection rule. These rules are applicable strictly when the rare earth ion is present in centrosymmetric environment in the gas phase. But when these ions are incorporated in the host matrix the crystal field symmetry around them may influence the parity of 4f wave functions and allows these transitions to gain some intensity. These transitions therefore are called forced or induced electric dipole transitions instead of just electric dipole transitions. Some Electric Dipole transitions having $|\Delta S| = 0$, $|\Delta L| \leq 2$ and $|\Delta J| \leq 2$ are hypersensitive and shows a large variation in oscillator strength from 10^{-5} to 10^{-8} . So even with a small deviation from inversion symmetry around the lanthanide ion their intensity gets enhanced up to 100 folds [27,28,41,42].

(ii) Magnetic Dipole Transitions: If the charge moves along a curved path during transition, then it indicates that the nature of transition is magnetic dipole. As the name suggests these transitions occur when the rare-earth ion interacts with the magnetic component of light via a magnetic dipole. They have an oscillator strength of the order of 10^{-8} . These transitions have even parity so intra configurational 4f-4f magnetic dipole transitions are allowed but they possess weak intensity in comparison to induced electric dipole transitions. Furthermore, these transitions are not affected by site symmetry around the rare earth ion so crystal field wave function is not required and only free ion wave function is sufficient for the calculation of the intensity of the transitions [27,41].

(iii) Electric Quadrupole transitions: A transition occurring due to displacement of a charge having quadrupole nature is an electric quadrupole transition. A quadrupole is formed by arrangements of two dipoles in a manner having net zero dipole moment. The quadrupole nature is possessed by electric fields in inhomogeneous dielectric having oscillating dipoles being distributed asymmetrically. These transitions are the weakest of all the three transitions. Though the existence of such transitions is claimed by some authors but there is no experimental evidence in support of this claim [43]. Since the hypersensitive magnetic dipole transitions follows the same selection rules $|\Delta S| = 0$, $|\Delta L| \leq 2$ and $|\Delta J| \leq 2$ these transitions are occasionally referred to as Pseudo-quadrupole transitions.

1.5.1.2. 4f-5d transitions:

In Contrast to 4f-4f transitions in 4f-5d transitions the electron moves from lower energy 4f shell to high energy 5d shells thus changing the configuration during transition. Since these transitions are not forbidden by Laporte's law so they have high probability of occurrence and have a strength of 10^6 times compared to 4f-4f transitions. Since 5d orbitals are outer orbitals and have large radial expansion so they are highly sensitive to crystal field environment and ligand field strength. These transitions can be altered by varying the crystal field environment around the rare earth ion. The big energy gap between the excited 5d state and ground 4f state is decreased in case of Eu^{2+} and Ce^{3+} ions in certain hosts resulting from crystal field splitting and low shifting of 5d levels centroid due to reduction of interelectronic repulsion resulting from the electron sharing between activator ions and the neighbouring ligand ions. They exhibit broad emission band attributed to Franck-Condon principle and removal of degeneracy of 4f ground state. The Franck Condon principle describes that there exist multiple vibrational states within each electronic state, resulting in transitions spanning a broad energy range. Moreover, the degeneracy of 4f level is broken in to multiple levels due to spin orbit coupling [11,38,42,44,45]

1.5.2. Transition ions

Besides rare earth ions the transition metal ions are extensively used as activators as well as sensitizers. Since rare earths suffer limited natural availability and high-cost transition metal ions have become a contender as activator in phosphors. These metals due to their cost effectiveness and unique electronic configuration act as potent luminescent centre. These ions possess incompletely filled d shells which is responsible for their spectroscopic properties.

Unlike rare earth ions the d shell is outer shell thus exposure of outer electrons makes their emission is significantly impacted by the crystal field environment [11,14,28]. So, when these ions are incorporated in host matrix, they interact with the lattice crystal field influencing their luminescence properties. The Mn^{4+} ion has drawn attention as an activator for red emission due to its cost effectiveness compared to rare earth ions without compromising the optical properties [46]. Similarly transition metal Cr^{3+} has garnered substantial interest as deep/far red emitter due to its tuneable emission in red to near red region [47]. Furthermore, the transition metal ion Bi^{3+} has been the subject of investigation due to its cost effectiveness, abundance and tuneable emission from violet to near infra-red. The emission originating from $^1S_0 \rightarrow ^3P_1$ transition can be tuned by modifications in the composition of host thus adjusting crystal field strength rendering it appropriate for different optical applications [48–52].

1.6 JUDD-OFELT ANALYSIS OF RADIATIVE PROPERTIES FROM EMISSION

The Judd-Ofelt (J-O) theory provides significant insight about the spectroscopic behavior of trivalent rare earth ions in a particular coordination environment. The J-O Intensity parameters Ω_λ ($\lambda=2, 4$, and 6) are evaluated to conclude radiative potential of RE ions in different hosts, and identifying bonding and local structure in vicinity of RE ions. Usually, these intensity parameters are derived from absorption spectrum but in case of Eu^{3+} activated host matrices we can evaluate Ω_2 and Ω_4 using emission spectrum due to special energy level structure of Eu^{3+} ions [53].

The transition 5D_0 to 7F_1 is magnetic dipole transition and is untrammelled from crystal field. As per J-O theory its spontaneous transmission probability (A_{01}) is related to magnetic dipole strength by following relation [53–55].

$$A_{01} = \frac{64\pi^4\nu^3n^3s_{md}}{3h(2J+1)} \quad (1.5)$$

where ν is energy in cm^{-1} corresponding to 5D_0 to 7F_1 transition, h is Planck's constant, $(2J+1)$ is degeneracy of initial state, s_{md} is magnetic dipole strength and n the refractive index of the host matrix which can be obtained using equation (1.6) [56] :

$$\frac{n^2-1}{n^2+1} = 1 - \sqrt{\frac{E_g}{20}} \quad (1.6)$$

where, E_g the optical band gap is obtained from DRS.

The transitions 5D_0 to 7F_J ($J= 2,4$ and 6) corresponds to electric dipole transitions and their corresponding spontaneous transmission probability(A_{0J}) is related to electric dipole strength by following relation

$$A_{0J} = \frac{64\pi^4\nu^3 e^2 n(n^2+2)^2}{3h(2J+1)} \sum_{\lambda=2,4,6} \Omega_{\lambda} \left| \langle 5D_0 || U^{(\lambda)} || 7F_J \rangle \right|^2 \quad (1.7)$$

where ν is energy in cm^{-1} corresponding to 5D_0 to 7F_J transition, n is refractive index, $J = 0$ for 5D_0 state, e is electronic charge (4.8×10^{-10} esu) and $\left| \langle 5D_0 || U^{(\lambda)} || 7F_J \rangle \right|^2$ is the squared reduced matrix elements, which are zero for all electric dipole transition originating from 5D_0 level except for $j'= 2, 4$ and 6 with values 0.0032 , 0.0023 and 0.0002 respectively. The ratio of radiative transition probability can be expressed in terms of ratio of integral intensity of corresponding peaks in emission spectra and hence Ω_{λ} can be obtained as per following equation (1.8) [57]:

$$\Omega_{\lambda} = \frac{8\pi\nu^3}{e^2\nu_{\lambda}^2} \frac{9n^3}{n(n^2+2)^2} \frac{\int I_{\lambda}(\nu)d\nu}{\left| \langle 5D_0 || U^{(\lambda)} || 7F_J \rangle \right|^2 \int I_1(\nu)d\nu} \quad (1.8)$$

The value of transition energy for calculation of JO parameters can be obtained as an average over the selected transition region from emission spectra:

$$\nu_{\lambda} = \frac{\int \nu I(\nu)d\nu}{\int I(\nu)d\nu} \quad (1.9)$$

The Ω_2 parameter which is associated with hypersensitive electric dipole transition 5D_0 to 7F_2 is responsive to crystal field. The parameters Ω_4 and Ω_6 on the other hand are attributed to macroscopic bulk properties such as rigidity and viscosity of the compounds [58].

The fluorescent branching ratio, which gives the ratio of emission of a level with respect to other levels, and is a measure of potential of emission of a level, for 5D_0 to 7F_J transitions can be obtained using the following relation [59]:

$$\beta = \frac{A_{J-J'}}{\sum A_{J-J'}} \quad (1.10)$$

The observed fluorescent lifetime(τ_{obs}) can be related to total transition rate (A_T), radiative transition rate (A_R) and non-radiative transition rate (A_{NR}) as:

$$\frac{1}{\tau_{obs}} = A_T = A_R + A_{NR} \quad (1.11)$$

The radiative transition rate can further be used to evaluate non-radiative transition rate. The quantum efficiency defined as fraction of photons emitted to those of absorbed by Eu^{3+} ion can thus be obtained by following equation (1.12):

$$\eta = A_R / (A_R + A_{NR}) \quad (1.12)$$

1.7 SOLID STATE LIGHTING: THE PHOSPHORS CONVERTED LED

Since the conventional lighting sources namely incandescent lamps and fluorescent lamps both face the drawback of large energy losses the SSL based on LEDs have captured significant attention distinguished by properties of having better efficiencies, improved lifetimes and low power consumption. The white light can be generated using LEDs broadly by three different routes which are displayed in Fig.1.11. The first route involves use of three different LEDs, each emitting a different color—red, green, and blue—so that the mixed emission is white. Though this technique yields good color rendering index but it suffers the drawback of complicated electronic tuning due to different driving currents for each LED. The second method employs integrating Ce^{3+} activated $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG: Ce^{3+}) yellow phosphor with a InGaN LED chip having blue emission. Though this approach gives high photoluminescence (PL) efficiency with blue light excitation, the obtained wLEDs have below par color-rendering indices (CRI) and elevated correlated color temperatures on account of missing emission in red region [60,61]. In the third approach improved CRI and tunable correlated color temperatures are achieved by devising Red, Green and Blue phosphor amalgamated on a LED chip having emission in near UV region [62]. The emission from this approach also possess weak emission in red region and suffers complex blending due to distinct characteristics of LEDs [63]. The first approach belongs to multichip wLEDs category while the second and third approach falls under category of phosphor converted wLEDs. Since phosphors plays a critical role in fabrication of wLEDs considerable research interest have focussed on exploring suitable phosphor material.

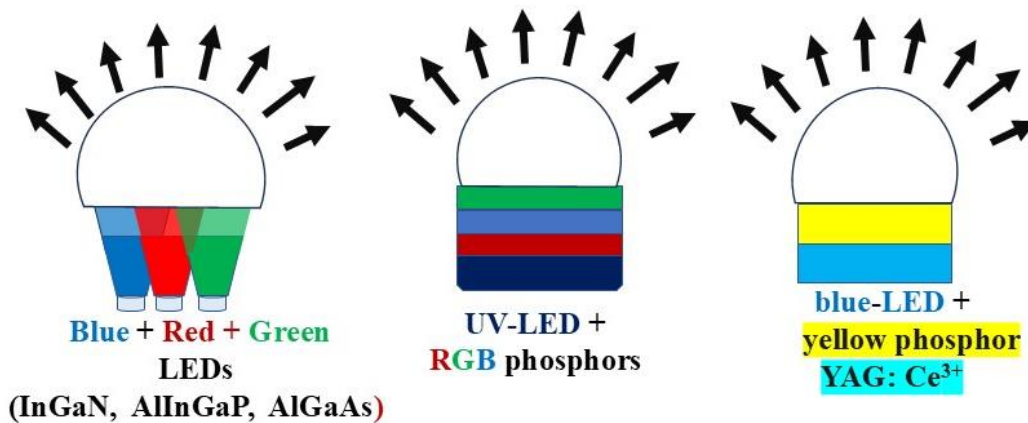


Figure 1.11. Depiction of different routes for generation of wLEDs

1.8 SOME GENERAL ASPECTS OF LED PHOSPHORS

1.8.1 Color rendering index

The color rendering index (CRI) is a dimensionless metric and measures the quality of light in terms of its ability to reproduce the color of the illuminated objects with reference to the natural source like day light or sunlight. The scale ranges from 0 to 100 where higher value indicates superior accuracy of color. So, a CRI of 100 is considered perfect rendition of color which means that the color of illuminated object using the light source is identical to the one observed when illuminated by reference source. On the other hand, lower values of CRI imply poor color representation leading to incorrect perception of color of illuminated object. So, it is essential to have high quality phosphors with elevated CRI in order to maintain consistent color purity and accuracy [18,28,64].

1.8.2. Correlated color temperature (CCT)

It is a fundamental parameter which correlates the value of the temperature of a blackbody on absolute scale when its chromaticity resembles the color appearance of the light source. A black body is a theoretical object which absorb all the radiation incident on it and emits light when heated to a higher temperature. It emits in red, orange, yellowish white and ultimately bluish white as its temperature is raised. So CCT indicates whether the light source is emitting cool or white light. A low value of CCT (<5000 K) indicates warm emission with yellowish red tones while high value (>5000 K) indicates cool light with bluish characteristics resembling to day light. The value of CCT for a light source can be evaluated using McCamy's formula from

CIE coordinates (x,y) of the source and epicentre coordinates ($x_e=0.3320$, $y_e= 0.1858$) given by equation (1.13) [65]:

$$CCT = -437 \left[\frac{x-x_e}{y-y_e} \right]^3 + 3601 \left[\frac{x-x_e}{y-y_e} \right]^2 - 6861 \left[\frac{x-x_e}{y-y_e} \right] + 5514.31 \quad (1.13)$$

1.8.3. CIE chromaticity coordinates

In order to characterize and quantify the color of emission from a luminescent material the Commission Internationale de l'Eclairage (CIE) 1931 chromaticity coordinate system is used. This system describes any color using three primary colors red, green and blue which are represented by tristimulus values X, Y and Z that gives the degree of stimulation required to match the color of specified spectral power density $P(\lambda)$. The emission intensity data are transformed to trichromatic colour space with the help of tristimulus values obtained by using [60,66,67]:

$$X = \int L(\lambda) \bar{x}(\lambda) d\lambda \quad (1.14)$$

$$Y = \int L(\lambda) \bar{y}(\lambda) d\lambda \quad (1.15)$$

$$Z = \int L(\lambda) \bar{z}(\lambda) d\lambda \quad (1.16)$$

Where $L(\lambda)$ denotes spectral radiance and $\bar{x}, \bar{y}, \bar{z}$ are standard CIE observer curves. CIE coordinates (x,y) are then calculated using following equation:

$$x = \frac{X}{X+Y+Z}, \quad y = \frac{Y}{X+Y+Z} \quad (1.17)$$

the obtained values of chromaticity co-ordinates are plotted on CIE 1931 diagram which is depicted in Fig. 1.12. The chromaticity diagram is a curve with horse shoe shape and it bounds which represents all the perceivable colors. The perimeter of the curve represents monochromatic wavelengths while bounded area represents mixed colors. The coordinate points (0.67,0.33), (0.14, 0.08) and (0.21, 0.71) on chromaticity diagram represents the primary colors red, blue and green respectively. The (0.33,0.33) represents the equal energy point or pure white light co-ordinates. The monochromaticity of a light source can be assessed by evaluating its color purity which is calculated by dividing distance between sample co-ordinates and equal energy point by distance between dominant wavelength points and equal energy point on the chromaticity diagram [68]. So, the expression for color purity is given by equation (1.18)

$$\text{Color purity} = \frac{\sqrt{(x-x_i)^2+(y-y_i)^2}}{\sqrt{(x_d-x_i)^2+(y_d-y_i)^2}} \times 100\% \quad (1.18)$$

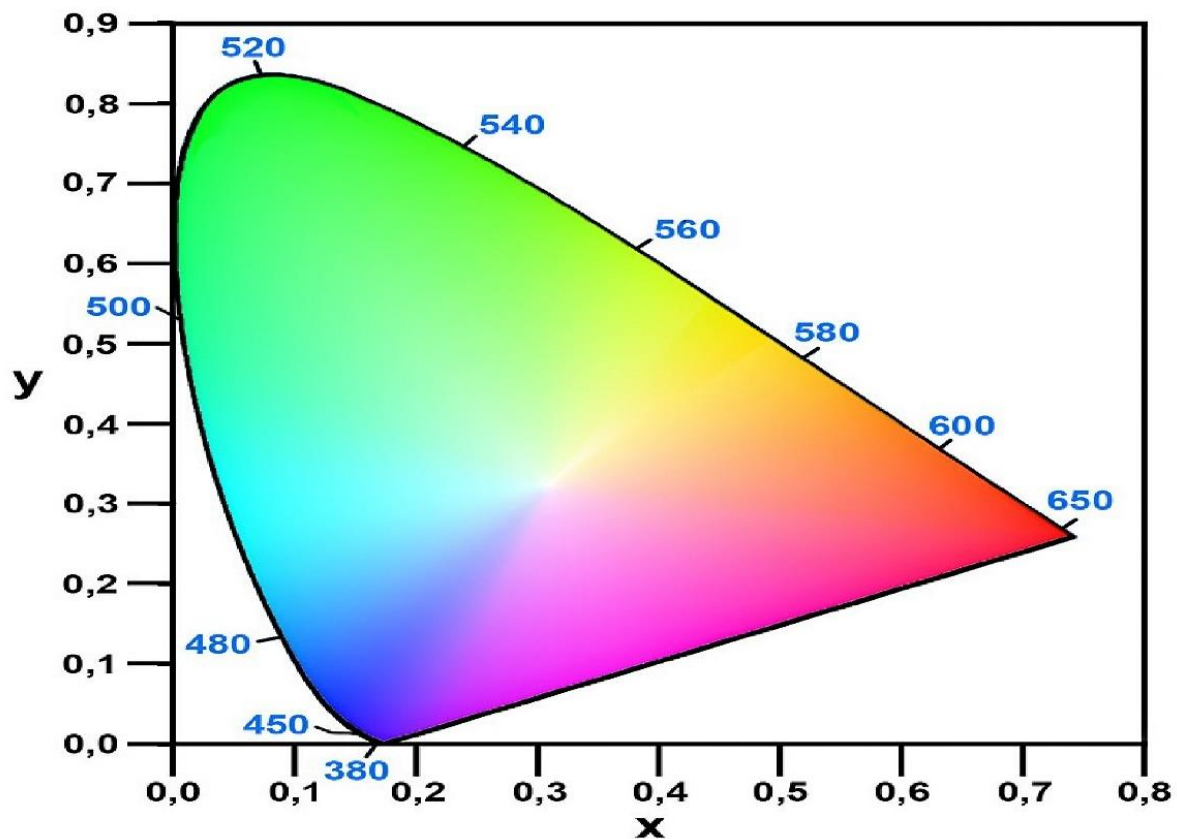


Fig. 1.12. The CIE 1931 chromaticity plot

1.8.4. Decay kinetics

The dynamics of the excited state of the luminescent material can be investigated by analyzing the photoluminescent decay process. It provides an insight in to various processes including radiative relaxation, non-radiative relaxation, inter system crossing and energy transfer mechanism while system returns from excited state to the ground state. The PL decay spectroscopy the emission intensity is measured with respect to time after pulsed excitation. The obtained decay curve can be used to obtain the fluorescent lifetime values of the phosphor which is defined as the average time for which an ion remains in excited state before returning to the ground state. When the concentration of activator is low the interaction between the activator ions is negligible and the decay curve follows single exponential function given by:

$$I_t = I_0 + C_1 e^{\left(\frac{-t}{\tau}\right)} \quad (1.19)$$

Where I_0 is initial fluorescent intensity corresponding to time $t=0$ and τ represents fluorescent lifetime value. The single exponential decay also indicates that the activator is present at single site in crystal lattice. However, for higher concentration activators or for co-doped system having multiple activators or multiple sites occupied by the activator the energy transfer and cross relaxation processes comes in to the picture and decay curve follows biexponential function which relates the luminescence intensity at time t , I_t with that at time $t=0$ as:

$$I_t = I_0 + C_1 e^{\left(\frac{-t}{\tau_1}\right)} + C_2 e^{\left(\frac{-t}{\tau_2}\right)} \quad (1.20)$$

Where C_1 and C_2 are constants, τ_1 and τ_2 are fast and slow lifetimes respectively. The average lifetime τ , for the phosphors was calculated from the fitted parameters using the relation:

$$\tau = \frac{C_1 \tau_1^2 + C_2 \tau_2^2}{C_1 \tau_1 + C_2 \tau_2} \quad (1.21)$$

So, a decay curve fitted to single exponential function reveals insignificant energy transfer among the luminescent centers while biexponential nature of decay curve indicates presence of ion-ion interactions and multiple relaxation channels [69–71].

1.8.5. Thermal Stability

For a phosphor to have application in LEDs where the operating temperatures can reach around 473 K thermal stability of phosphor is a crucial parameter. If a phosphor is thermally stable it is able to maintain its emission at higher temperature which is crucial for the consistent performance of the optoelectronic devices. The thermal stability of a phosphor material can be investigated by carrying out temperature dependent photoluminescent studies. Thermal quenching is described by diminished emission intensity at elevated temperatures which is caused by non-radiative relaxations in phosphor material. These non-radiative relaxations increases exponentially and non-radiative emission rate is related to temperature by equation (1.22)

$$R_n = k \exp\left(\frac{\Delta E_a}{K_b T}\right) \quad (1.22)$$

Where k is some constant, K_b is Boltzmann's constant and ΔE_a is activation energy. The activation energy of the phosphor is a quantitative measure of its thermal stability and it is the energy barrier between the lowest point of excited state parabola and the crossover point with

the ground state. A higher value of activation energy indicates better thermal stability of the phosphor. Moreover, the value of activation energy can be evaluated from the dependence of luminescence on temperature which is governed by the Arrhenius equation given below [72]:

$$I_T = I_0 \left[1 + A \exp \left(-\frac{\Delta E_a}{K_b T} \right) \right]^{-1} \quad (1.23)$$

Where I_T is intensity of emission at temperature T , I_0 represents intensity of emission monitored at ambient temperature, A is arbitrary constant, ΔE_a is activation energy, K_b represents Boltzmann constant (8.629×10^{-5} eV/K). So, if a graph is plotted for $\ln((I_0/I_T)-1)$ against $1/K_b T$, a straight-line curve will be obtained whose slope will give value of activation energy.

1.9 IMPORTANCE OF PRESENT HOST MATRIX

The luminescent properties and performance of a phosphor based solid state lighting device is greatly dependent on the choice of appropriate host material. A suitable chosen host lattice has huge impact on the efficiency and functionality of the single-phase phosphor based LEDs. The host should be chosen based on certain characteristics for effective integration of phosphor in optoelectronic applications. In order to have efficient excitation of the phosphor the host should offer high absorption in blue and near UV range. A chemically and thermally stable host ensures the durability and consistent performance under operating conditions. The host material should support narrow bandwidth emission in visible region in order to achieve superior color purity. Moreover, achieving maximum photon output requires high luminescence energy transfer efficiency and high quantum efficiency [11,15]. The host should be so chosen that manufacturing of phosphor and thus fabrication of device based on it should be economical. The furthermore the ingredients involved in manufacturing of phosphors should be nontoxic and environment friendly. The recent studies have revealed that inorganic oxides stand out as prospective host materials owing to their significant merits which includes facile preparation methods, cost effectiveness, environment friendliness, excellent thermal and chemical stability. The oxide groups that have garnered considerable attention from researchers belong to vanadates, tungstates, niobates, phosphates, aluminates, and silicates. Among the inorganic oxides, the phosphates have been a popular choice as a host material due to their significant attributes such as remarkable physical and chemical stability, excellent thermal and optical stability, low temperature synthesis, cost effectiveness, eco- friendliness and a large

optical band gap [73]. Therefore, oxide-based phosphate host matrix has been chosen to investigate luminescent properties by subsequent addition of dopant ions. The $\text{BaZr}(\text{PO}_4)_2$ (BZP) belongs to orthophosphate family having 3-D rigid framework of polyhedrons of BaO_{10} , ZrO_6 , and PO_4 which possess stability at high temperatures, low thermal conductivity, fast ionic conductivity and low thermal expansion. Their structure provides flexibility to accommodate different cations with in their framework or inter-framework positions without disturbing the basic structure of their lattice[74–76] .

1.10 OBJECTIVES OF PRESENT WORK:

1. To do literature survey rigorously in order to learn about the desired properties of phosphor
2. To synthesize Rare Earth/Transition metal doped phosphate phosphors and to study the structural, morphological, optical and luminescence properties of phosphors for their applications in SSL devices
3. To improve the emission intensity:
 - i. By exciting at different wavelengths
 - ii. By varying dopant ion concentration
 - iii. By co-doping with suitable activator/sensitizer ions
 - iv. By appropriate incorporation of fluxes
4. Preparation of phosphors for multicolor emissions and optimization of RE ions concentration for better luminescence efficiency
5. Finally understanding the usage of as prepared phosphors for solid state lightning applications through down-conversion.

2

CHAPTER

Synthesis and Characterization Techniques

- *This chapter gives a detailed account of the preparation of undoped and doped BaZr(PO₄)₂ phosphors using the solid-state reaction route.*
 - *It explains the experimental procedures followed in the study, along with short descriptions of the working principles and instruments involved.*
 - *The chapter also includes the different analytical methods adopted to study the structural, morphological, vibrational, and luminescent features, together with the related luminescence measurements.*
-

2.1 SYNTHESIS OF PHOSPHOR MATERIALS:

Synthesis involves producing a material by combining selected precursors under controlled conditions. Although many phosphors are commercially available, research continues to focus on reducing costs while improving thermal stability and performance. The properties of phosphors are strongly influenced by the synthesis method, which affects their microstructure, luminescence efficiency, and quantum yield. Various approaches are employed to enhance fluorescence in powder form, including traditional solid-state reactions and alternative methods such as sol-gel, co-precipitation, spray pyrolysis, combustion, hydrothermal, and microwave-assisted techniques. Choosing an appropriate method is crucial for preparing high-performance phosphors.

2.1.1 Solid-State Reaction Technique

The solid-state reaction method is a widely used approach for synthesizing multicomponent oxide phosphors. In this method, solid reactants are mixed and heated at high temperatures, either in air or in a controlled atmosphere, to induce chemical reactions. The process usually involves high-purity starting materials, with repeated sintering and intermediate grinding steps. This technique is preferred over liquid-based methods due to its simplicity, easy access to precursors, and ability to produce large quantities. In this study, the high-temperature solid-state reaction was employed to synthesize the phosphors.

2.1.1.1 Stoichiometric Weighing of Raw Materials

The raw materials were selected based on purity, particle size, reactivity, and chemical composition. The required stoichiometric amounts were calculated according to the chemical formula and weighed accurately to ensure correct composition.

2.1.1.2 Mixing

The weighed powders were thoroughly mixed in acetone using an agate mortar and pestle to form a uniform, fine powder. Proper mixing is essential to achieve homogeneity, minimize agglomeration, and support uniform phase formation.

2.1.1.3 Calcination and Sintering

The mixed powder was calcined at a temperature below its melting point to initiate the solid-state reaction and remove volatile impurities. The powders were placed on silica trays to

prevent contamination. Subsequently, sintering was carried out at 80–90% of the melting temperature, which helped particles bond together and form the desired crystal phase. After sintering, the material was ground into a fine powder to obtain the final phosphor product.

In this work, $\text{BaZr}(\text{PO}_4)_2$ phosphors doped with various concentrations of RE^{3+} ions were prepared using this high-temperature solid-state reaction method, as shown in Fig. 2.1. High-purity oxides served as the starting materials, and this procedure ensured the formation of phosphors with the desired structural and luminescent properties.

In this process, high-purity oxides were used as the starting materials.

Sr. No.	Chemical Name	Chemical Formula	% Purity	Supplier
1.	Barium carbonate	BaCO_3	99.99	Fisher Scientific
2.	Zirconium Dioxide	ZrO_2	99.99	Fisher Scientific
3.	Diammonium Hydrogen Phosphate	$(\text{NH}_4)_2\text{HPO}_4$	99.99	Fisher Scientific
4.	Samarium Oxide	Sm_2O_3	99.99	Sigma-Aldrich
5.	Europium Oxide	Eu_2O_3	99.99	Sigma-Aldrich
6.	Dysprosium Oxide	Dy_2O_3	99.99	CDH
7.	Bismuth Oxide	Bi_2O_3	99.99	Sigma-Aldrich
8.	Terbium Oxide	Tb_2O_3	99.99	Sigma-Aldrich

Table 2.1. List of chemicals used in the present thesis work.

In this preparation, the required oxides were accurately measured according to stoichiometric ratios and finely ground in an agate mortar with acetone to form a homogeneous powder. The mixture was transferred to a silica crucible and subjected to heat treatment in a furnace. The sample was heated at 1373 K. Once cooled to room temperature, the material was ground again into a fine powder to obtain the final phosphor. The stoichiometric reaction is represented as:



The optical properties of the phosphor are dependent on the activator ion concentration. One of the key advantages of the solid-state reaction method is its ability to produce materials with precise structural characteristics, controlled by the sintering temperature. This method has been extensively employed to synthesize a variety of compounds, including silicates, borates,

oxides, tungstates, and phosphates. The powders obtained are highly pure, free from significant contamination, and the process is environmentally safe, making it suitable for large-scale production without generating harmful byproducts.

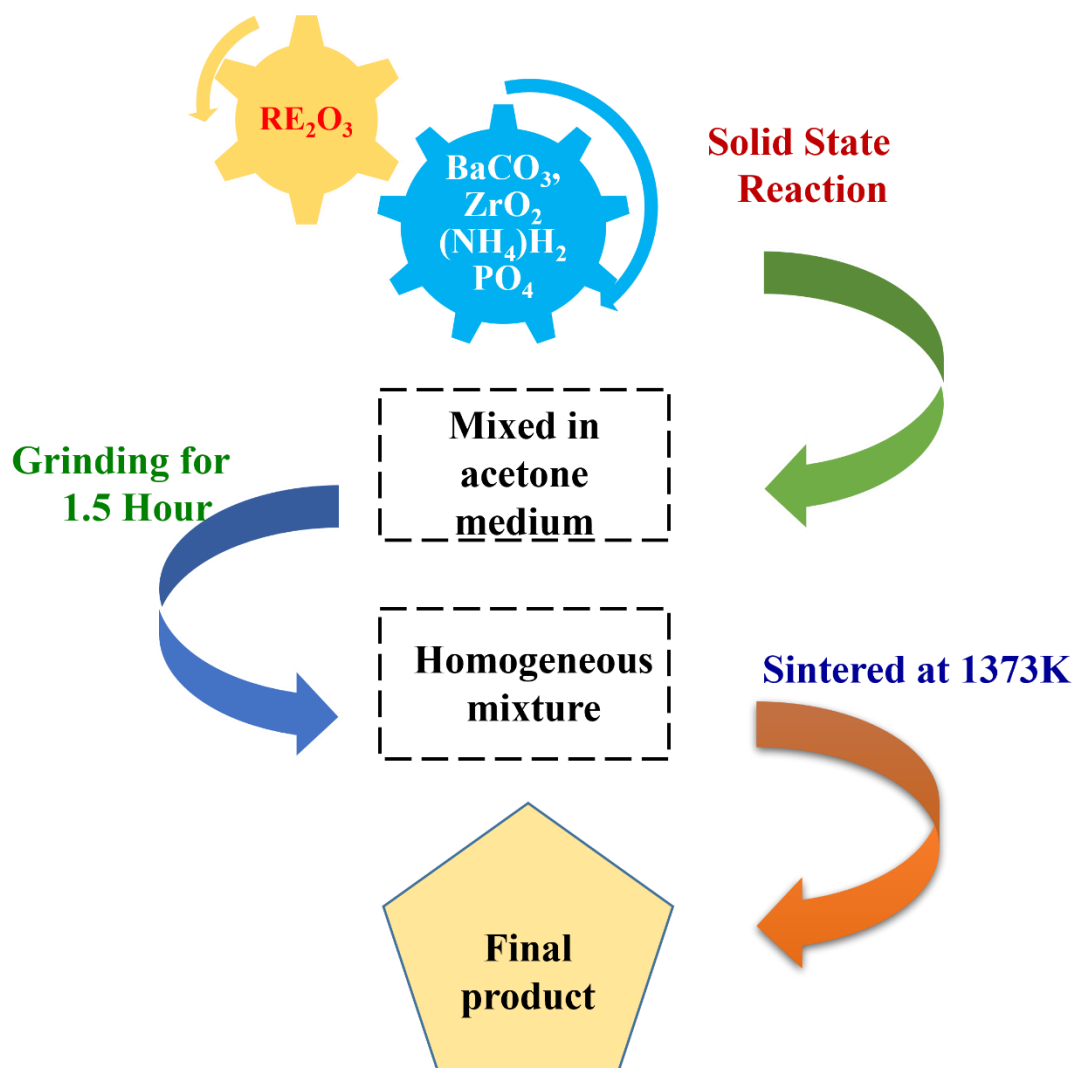


Fig. 2.1. Schematic representation of the sequential steps followed during phosphor synthesis.

2.2 CHARACTERIZATION TECHNIQUES:

Comprehensive characterization is crucial for evaluating the properties of the synthesized phosphors and enhancing their performance as luminous materials in lighting applications. Various standard instruments are employed to study these phosphors, emphasizing their morphology, structural features, and luminescent behavior. The subsequent sections of this

chapter provide detailed explanations of the instruments and analytical techniques utilized for this purpose.

2.2.1 X-ray diffraction (XRD):

The major scientific advancement occurred when researchers observed that X-rays striking a solid substance produced an interference or diffraction pattern. This finding provided clear evidence of the wave nature of X-rays. Expanding upon Laue's earlier work, W. H. Bragg and W. L. Bragg discovered that the wavelength of X-rays is of atomic scale—about a thousand times shorter than visible light. Because of this, X-rays can interact with the atomic layers of solids, enabling the study of their crystal structures.

From this understanding, Bragg derived a mathematical relation known as Bragg's law to describe the conditions for constructive interference. According to this law, diffraction occurs when the path difference between the incident and reflected X-rays is an integer multiple of the wavelength. If this condition is not fulfilled, destructive interference takes place. The resulting diffraction pattern shows peaks that correspond to specific atomic planes within the crystal, providing insights into the arrangement of atoms, as shown in Fig. 2.2.

Bragg's law is expressed as:

$$2d \sin \theta = n\lambda \quad (2.2)$$

where d is the distance between adjacent atomic planes (interplanar spacing), λ is the wavelength of the incident X-rays (commonly $1.54 \text{ \AA}$), θ is the angle of diffraction, and n is the order of reflection.

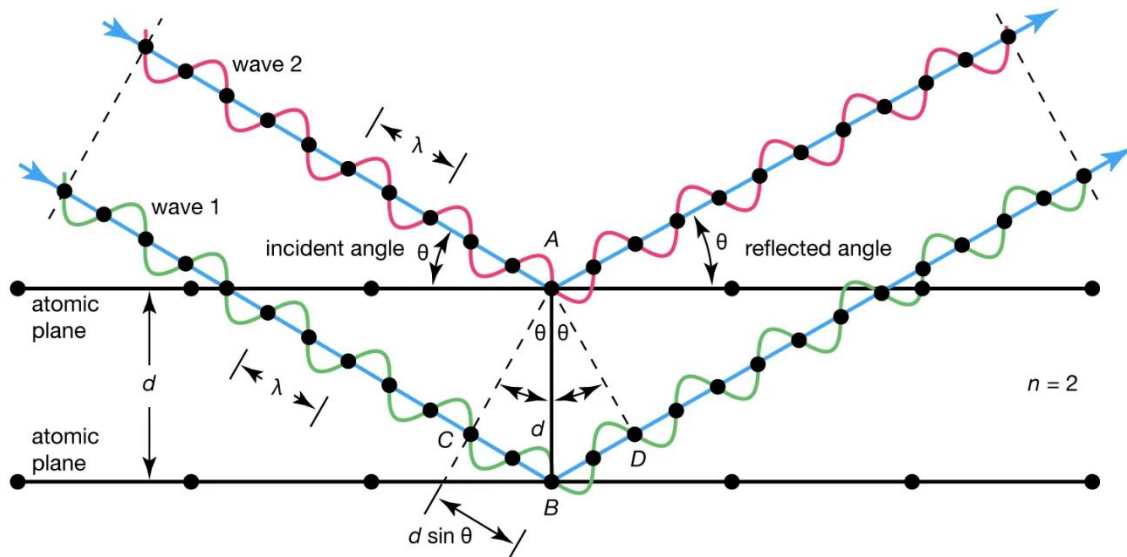


Fig. 2.2. Visual representation of the diffraction of X-rays from atomic planes within a crystal lattice.

Bragg's equation is used to determine the distance between atomic layers (interplanar spacing) when both the wavelength of the incident X-rays and the diffraction angle (θ) are known. By changing the crystal's orientation to satisfy Bragg's condition for different sets of atomic planes, the corresponding d values can be obtained. This generates multiple X-ray diffraction patterns from various orientations, allowing the determination of the crystal structure and unit cell parameters. However, repeatedly repositioning the crystal to record diffraction from different planes is cumbersome and time-consuming. To simplify the analysis, the powder diffraction method is generally adopted.

In this approach, the crystal is finely crushed into a powder composed of numerous microcrystals randomly oriented in all directions. When X-rays are incident on this powdered sample over an angular range (typically 0° – 90°), many crystallites simultaneously meet Bragg's condition, producing a diffraction pattern with peaks at different angles corresponding to specific interplanar spacings. A goniometer rotates the X-ray source and detector throughout this angular range to collect the diffraction data. In the present investigation, XRD measurements were performed using a Bruker D8 Advance diffractometer with a graphite-monochromated Cu-K α radiation source ($\lambda = 1.5406 \text{ \AA}$) operating at 30 kV and 30 mA within the 15° – 60° range, as illustrated in Fig. 2.3.

Currently, X-ray diffraction (XRD) is one of the most effective techniques for studying the structural characteristics of materials. It helps in identifying crystalline phases, detecting

impurities, and calculating lattice parameters (a, b, and c), crystallite size, and unit cell volume. XRD also distinguishes between amorphous and crystalline materials. The broadening of diffraction peaks provides additional information about whether the sample is microcrystalline or nanocrystalline. In this study, crystallite size was evaluated using both the Debye–Scherrer equation and the Williamson–Hall method.

The Debye–Scherrer equation (2.3) is given as:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (2.3)$$

where D is the average crystallite size, λ is the wavelength of the X-rays, k is a shape factor (constant), β is the full width at half maximum (FWHM) of the diffraction peak, and θ is the diffraction angle. This formula provides an estimate of the crystallite size and insight into the material's microstructural features.

The Williamson–Hall (W–H) method was also applied to calculate both the crystallite size and lattice strain using the following relation:

$$\beta \cos\theta = \frac{k\lambda}{D} + 4\epsilon \sin\theta \quad (2.4)$$

Here, ϵ represents the average lattice strain. A graph of $\beta \cos\theta$ versus $4\sin\theta$ was plotted for each dopant concentration, from which the slope provides the strain (ϵ) and the y-intercept gives the value of $K\lambda/D$.

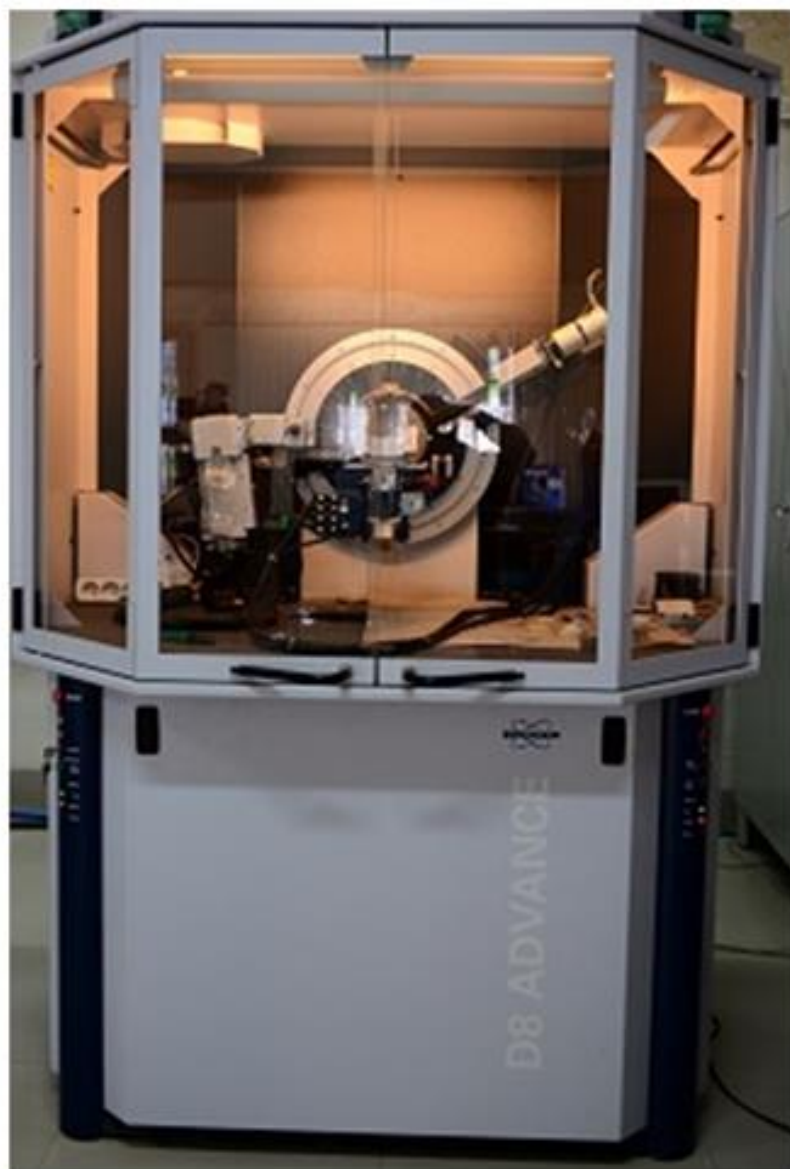


Fig. 2.3. Bruker D8 Advance X-ray diffractometer.

Rietveld refinement is an advanced diffraction analysis technique that utilizes X-ray or neutron data to accurately determine the crystal structure of a material. First developed by Hugo Rietveld, this method systematically refines a theoretical diffraction pattern so that it aligns closely with the experimentally recorded one. It is particularly useful for investigating structural changes caused by factors such as doping, temperature variation, applied pressure, or internal strain. The refinement process applies a least-squares fitting procedure to the entire diffraction profile, continually modifying structural parameters until the best correspondence between the observed and calculated intensities is achieved.

The quality of the refinement is measured by the goodness of fit (χ^2), which is expressed as:

$$\chi^2 = \frac{R_{wp}}{R_{exp}} \quad (2.5)$$

where R_{wp} denotes the weighted profile residual and R_{exp} represents the expected profile residual. A lower value of χ^2 indicates a closer agreement between the calculated and experimental results.

The refinement procedure is typically conducted using specialized software such as FullProf Suite, which requires detailed input information about instrument settings, background intensity, crystal phase models, and peak characteristics. The pseudo-Voigt function is often used to represent the diffraction peak shapes. Throughout the refinement, parameters may either remain fixed or be adjusted iteratively. Each cycle's output serves as the input for the next iteration, and this sequence is repeated until the system converges, providing the most accurate and consistent set of structural parameters for the material.

2.2.2 Fourier transform infrared spectroscopy (FT-IR):

Fourier Transform Infrared (FT-IR) Spectroscopy is a commonly employed analytical method used to identify functional groups and examine the molecular structure of compounds. Although it is widely applied to organic materials, it can also be utilized for inorganic substances containing specific functional groups. The term *FT-IR* is derived from the Fourier transform process, which converts raw interferogram data into an interpretable infrared spectrum.

The technique functions by determining how a material absorbs infrared (IR) radiation, with results displayed as absorbance or transmittance versus wavenumber. Each peak in the resulting spectrum corresponds to the vibrational frequency of a molecular bond. When IR radiation interacts with a molecule, it causes transitions between different vibrational energy levels. Absorption occurs only when the IR energy matches the energy difference between these levels, and the molecule undergoes a change in dipole moment.

Infrared spectroscopy is categorized into three regions:

- Near-Infrared (4000–14,000 cm^{-1})
- Mid-Infrared (400–4000 cm^{-1})
- Far-Infrared (50–400 cm^{-1})

The mid-infrared region is the most extensively used, as it encompasses the characteristic vibrational frequencies of most organic and inorganic materials.

An FT-IR spectrometer provides rapid and high-resolution spectra across a broad range, typically between 400 and 4000 cm^{-1} . The instrument utilizes an interferometer to modulate the infrared radiation emitted from a broadband source, and a detector records the transmitted or reflected intensity. The collected signal is mathematically processed using a Fourier transform to produce the final spectrum, generally plotted as absorbance or transmittance against wavenumber.

FT-IR spectroscopy offers several advantages, such as faster measurements compared to conventional dispersive instruments, high precision, and versatility in analyzing solids, liquids, and gases. It provides detailed insights into molecular bonding and interactions since every chemical bond exhibits its unique vibrational frequency. In the present study, the FT-IR spectrum was recorded using a PerkinElmer Fourier Transform Spectrometer, as presented in Figure 2.4.



Fig. 2.4: Perkin Elmer's Frontier FT-IR spectrometer

2.2.3 Field Emission Scanning Electron Microscopy (FE-SEM):

A Scanning Electron Microscope (SEM) is an analytical instrument used to examine the surface features of materials by scanning them with a focused electron beam. SEM provides detailed information on a sample's topography, morphology, and composition, and is commonly applied to both organic and inorganic materials at the nanoscale and microscale. Standard SEM instruments can achieve magnifications of up to 30,000×, while more advanced systems can reach 1,000,000×.

When the electron beam interacts with the sample, it produces various signals, such as secondary electrons, backscattered electrons, Auger electrons, and characteristic X-rays. Secondary electrons, being highly sensitive to surface details, are mainly used to generate high-resolution images. SEM also allows for the analysis of grain size and surface texture. However, conventional SEM has a resolution limit of roughly 10 nm, making it difficult to observe features smaller than about 50 nm.

The Field Emission Scanning Electron Microscope (FE-SEM) overcomes this limitation by employing a more finely focused electron beam, achieving a resolution of approximately 2 nm and allowing visualization of particles down to 20 nm. In this work, the microstructure and surface morphology of the sintered pellets were studied at room temperature using a JEOL 7610F Plus FE-SEM, as presented in Fig. 2.5.



Fig. 2.5. JEOL 7610F Plus Field- Emission Scanning Electron Microscope.

2.2.4 Energy dispersive X-ray spectroscopy (EDAX):

Energy Dispersive X-ray Analysis (EDAX) is a technique used to determine the elemental makeup of a sample or a selected region. In SEM-based EDAX, a focused electron beam strikes the sample, knocking electrons out of the inner atomic shells. Electrons from outer shells then fill these vacancies, emitting X-rays in the process. The energy of these X-rays depends on the shell-to-shell transition, and since each element produces X-rays with characteristic energies, they can be used to identify the elements present in the material.

The EDAX spectrum shows the number of X-rays detected at different energies. Each peak corresponds to a specific element, with the peak height indicating its relative concentration. Different types of X-ray emissions can also be identified, such as K-alpha (from L-to-K shell transitions) and K-beta (from M-to-K shell transitions). EDAX is similar in principle to electron probe microanalysis, where the X-ray energy is directly linked to the atomic number of the element, enabling both qualitative and quantitative elemental analysis.

2.2.5 Diffuse Reflectance Spectroscopy (DRS):

Fig. 2.6 shows two modes of light reflection from a material: specular and diffuse. In specular reflection, light reflects off the surface at the same angle as it strikes, providing minimal information about the material. In diffuse reflection, light interacts with the internal structure of the material, offering insight into its absorption, transmission, and scattering properties. This makes DRS an effective technique for investigating the optical and structural characteristics of materials.

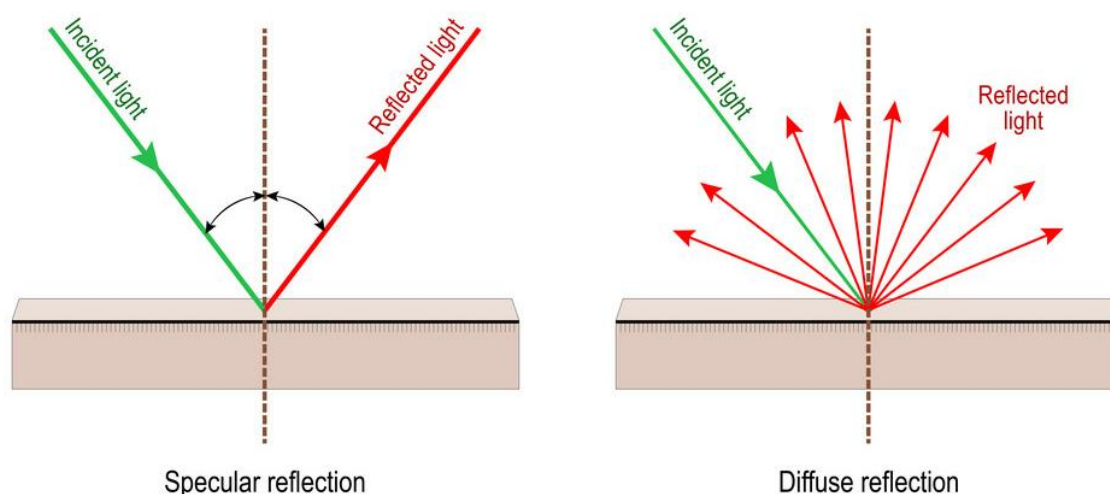


Fig 2.6. Illustration of specular and diffuse reflectance phenomena.

UV-Vis Diffuse Reflectance Spectroscopy (DRS) is a commonly used technique for examining the optical behavior of solid materials. It measures light scattered from a sample in all directions, offering both qualitative and quantitative information about its electronic and vibrational properties. Typically, DRS is performed using visible and near-infrared light. Compared to transmission measurements, it provides a better signal-to-noise ratio and higher sensitivity, although the resulting spectra can be more complex and require careful interpretation.

In this study, DRS analysis was carried out on the as-titled samples using a Jasco UV-770 UV-Vis Spectrophotometer (Fig. 2.7), covering a wavelength range of 190–2700 nm. Barium sulfate (BaSO_4) was used as a reference for baseline correction. The single monochromator system allows higher energy throughput despite a narrow spectral bandwidth, improving the signal-to-noise ratio across the spectral range.

The reflectance data were transformed into absorption coefficients using the Kubelka-Munk (K-M) function:

21

$$F(R) = \frac{(1-R^2)}{2R} = \frac{\alpha}{S} \quad (2.6)$$

where R is the reflectance, α is the absorption coefficient, and F(R) represents the K-M function.

The band gap energy (E_g) of the materials was estimated using Tauc plots, following the equation:

$$F(R)hv = C(hv - E_g)^n \quad (2.7)$$

Here, hv is the photon energy, C is a proportionality constant, and n indicates the type of electronic transition: $n = 1/2$ for direct transitions and $n = 2$ for indirect transitions. The Tauc plot, typically plotted as $(\alpha hv)^2$ versus hv , allows determination of the band gap from the intersection of the extrapolated linear region of the absorption edge with the energy axis.

6



Fig. 2.7. Jasco V-770 Spectrophotometer.

2.2.6 Photoluminescence Spectroscopy (PL):

Photoluminescence (PL) Spectroscopy is an essential analytical technique employed to investigate the optical and electronic characteristics of solid-state materials, particularly those utilized in optoelectronic applications. It offers valuable insights into the electronic structure of a material, including the influence of dopants, by analyzing the spontaneous emission of light that follows photon absorption.

The photoluminescence process generally consists of two stages: **excitation** and **emission**. During excitation, when the material is exposed to light of a specific wavelength, electrons absorb energy and transition from their ground state to an excited energy level—this is referred to as *photoluminescence excitation (PLE)*. As these excited electrons return to their ground state, they emit photons of characteristic wavelengths, which form the PL emission spectrum. To record this spectrum, the excitation wavelength is kept constant while the emitted light is analyzed using an emission monochromator. In contrast, the PLE spectrum is obtained by fixing the emission wavelength and varying the excitation wavelength.

PL analysis is typically carried out using a **spectrofluorometer**, comprising a light source, wavelength selectors, a sample compartment, detectors, and analytical software. A **150 W Xenon arc lamp** is frequently employed as the excitation source. The emitted radiation is directed toward the excitation monochromator slit by a diamond-turned elliptical mirror. A quartz window separates the lamp from the monochromator to provide proper ventilation and prevent overheating during measurement.

The main components of a PL spectrofluorometer include:

1. Monochromators – Two monochromators (excitation and emission) provide high-resolution spectral analysis.
2. Gratings – Disperse light into its component wavelengths; typically, they have 1200 lines/mm and are coated with MgF_2 to prevent oxidation.
3. Slits – Control the bandwidth of light entering and exiting the monochromator.
4. Shutters – Protect samples from photodegradation due to continuous light exposure.

5. Sample compartment – Directs the excitation beam to the sample and channels emitted light to the monochromator through optical fibers.
6. Detectors – A signal detector (R928P PMT) measures emitted light, while a reference detector (UV entrance silicon photodiode) monitors the lamp output.
7. Computer interface – Controls the system and processes the spectral data.

The commonly used instruments include the Horiba Fluorolog spectrofluorometer and the Jasco-8300 fluorescence spectrometer, as shown in Fig. 2.8.



Fig. 2.8. Jasco Spectrophotometer Spectrofluorometer FP-8300.

Up-conversion is a process where a material absorbs low-energy photons and re-emits them as higher-energy photons. This property is important for applications such as solid-state lighting, display technologies, and solar energy conversion. In phosphor materials, excitation with a 980 nm near-infrared laser results in the emission of visible light. The up-conversion emission spectra in this study were measured using a Horiba PTI Quanta Master with a 980 nm laser, as shown in Fig. 2.9.



Fig. 2.9. Upconversion luminescence measurement setup using a Horiba PTI QuantaMaster spectrofluorometer with a 980 nm laser.

Time-Resolved Photoluminescence (TRPL) monitors the decay of emitted light over time after the material is excited by a brief light pulse. This technique provides information about excited-state lifetimes, recombination mechanisms, and energy transfer processes. In this work, TRPL measurements were performed using an Edinburgh FL920 spectrometer along with a 150 MHz digital oscilloscope (HM 1507, Hameg Instruments), as shown in Fig. 2.10.

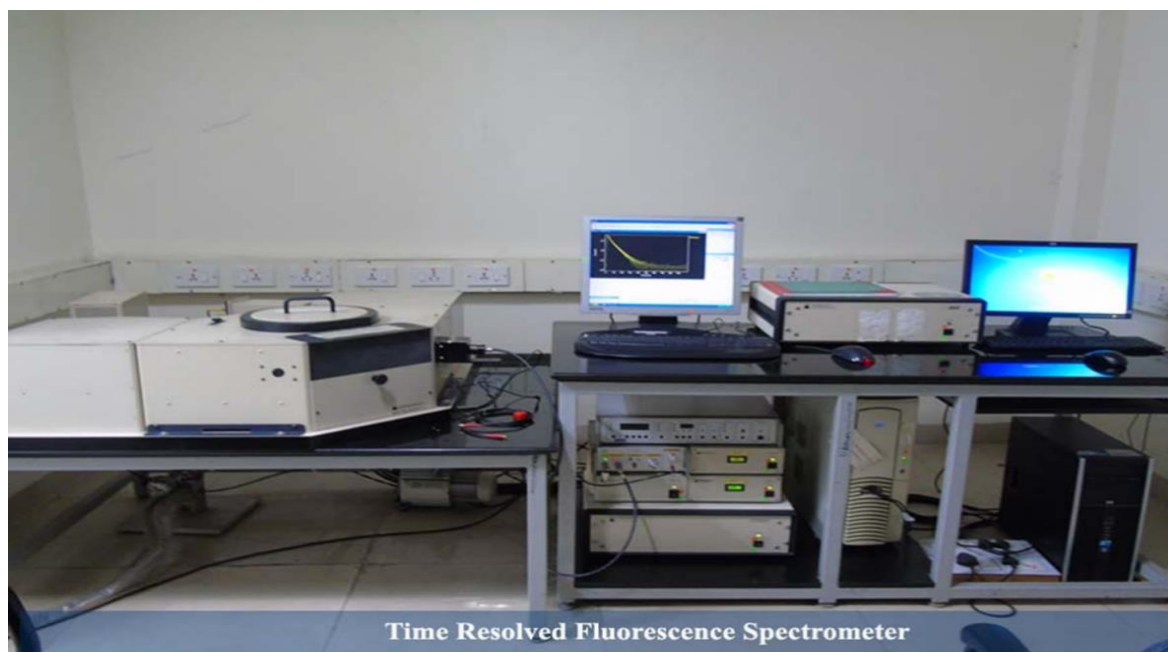


Fig. 2.10. Edinburgh FL920 Fluorescence Spectrometer.

2.2.7 Temperature dependent photoluminescence (TD-PL):

Temperature-Dependent Photoluminescence (TD-PL) is used to study how the light-emission properties of phosphor materials change with temperature. This technique is crucial for evaluating thermal stability, emission efficiency, and color fidelity in optoelectronic devices. In phosphors, light is absorbed—commonly in the UV or blue range—and then re-emitted as visible light after a short delay. TD-PL tracks this emission over different temperatures, providing insight into how luminescence intensity and color output are affected by heat.

TD-PL is especially useful for identifying phosphors that maintain consistent performance under high-temperature conditions. While many phosphors retain their emission profiles at elevated temperatures, thermal quenching can reduce the emitted intensity. Reducing this effect is essential to improve material stability and ensure reliable device operation.

In this study, TD-PL measurements were conducted using an Ocean Optics FLAME-S-XR1-ES spectrometer, as shown in Fig. 2.11.

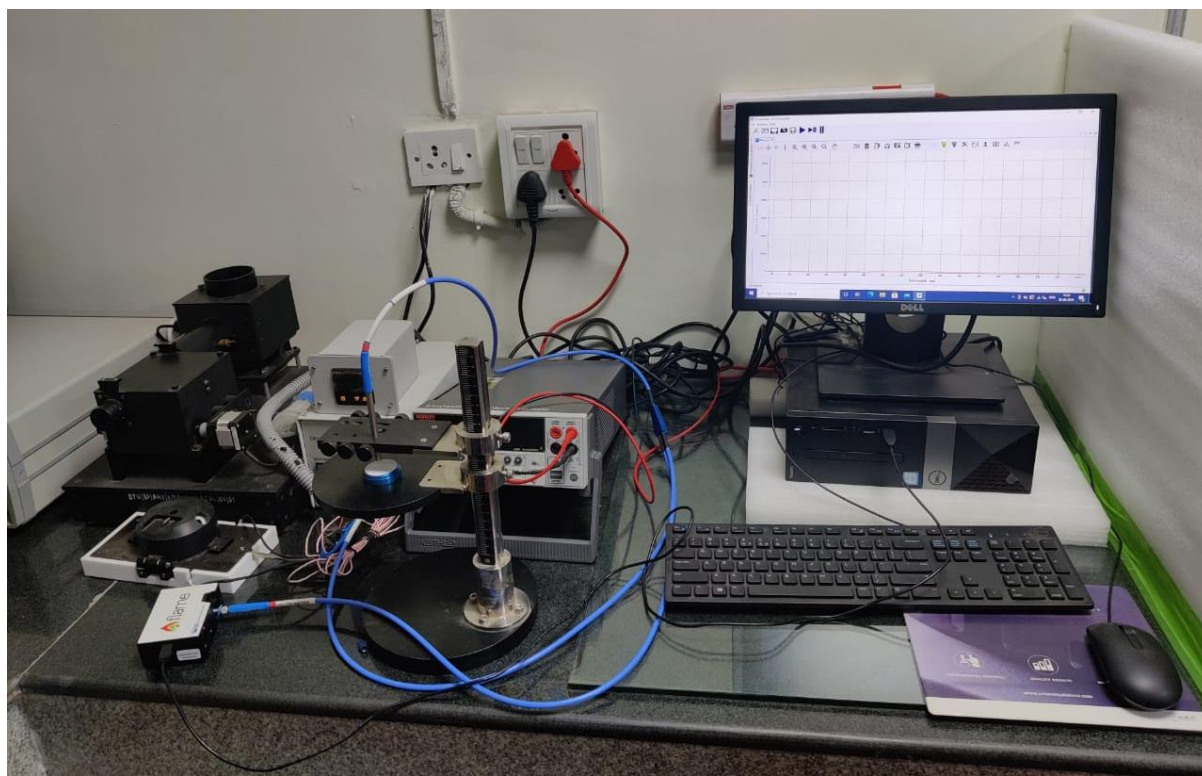


Fig. 2.11. Ocean Optics FLAME-S-XR1-ES Spectrometer

In Temperature-Dependent Photoluminescence (TD-PL), the intensity of light emitted by a phosphor change with temperature under a fixed excitation wavelength. This information is essential for assessing phosphors used in optoelectronic devices and temperature sensors. For applications like LEDs, it is important that the phosphor maintains consistent emission intensity at higher operating temperatures. By analyzing the temperature-dependent emission spectra, the relative intensity at elevated temperatures can be compared with the intensity at room temperature.

1 The change in emission intensity with temperature can be used to calculate the activation energy (ΔE) of the phosphor using the Arrhenius equation:

$$I_T = \frac{I_0}{1 + C \exp\left(-\frac{\Delta E}{k_B T}\right)} \quad (2.8)$$

18 where I_0 is the emission intensity at 293 K, I_T is the intensity at temperature T (in Kelvin), C is a constant, and k_B is the Boltzmann constant (8.629×10^{-5} eV/K). The slope of a plot of $\ln [(I_0/I_T) - 1]$ versus $1/k_B T$ provides the value of ΔE . A larger ΔE indicates higher thermal stability, meaning the phosphor is less susceptible to thermal quenching at elevated temperatures.

3

CHAPTER

Optical characteristics, Judd-Ofelt analysis of enhanced luminescence by flux in thermally stable, novel Eu^{3+} -doped $\text{BaZr}(\text{PO}_4)_2$ phosphor for indoor lighting application

The study focuses on synthesizing the suitable phosphors for reddish-orange components in w-LEDs, display panels, and other photonic devices

- Novel Eu^{3+} -doped $\text{BaZr}(\text{PO}_4)_2$ red phosphor synthesized via solid-state method.
- Pure monoclinic phase confirmed with optimized Eu^{3+} concentration at 3 mol%.
- NH_4Cl flux enhanced luminescence intensity by ~ 1.43 times.
- Strong thermal stability with 75% emission retained at 420 K ($E_a = 0.333$ eV).
- Emission peak at 612 nm with CIE = (0.650, 0.354) indicating pure red light.
- Judd-Ofelt analysis confirmed increased asymmetry and high branching ratio.
- Promising material for red component in wLED and laser applications.

3.1 INTRODUCTION

Historically, economic upsurge has been inextricably linked with elevated energy requirements thereupon raised up carbon emissions (greenhouse gas emissions), causing remarkable impact on environment [1]. So the energy efficient devices and clean energy sources play important role in attaining sustainable development goals [2]. It is widely known that a large portion of power consumption is directly contributed by lighting power demand. With emergence of solid state lighting the traditional filament-based lamps and compact fluorescent lamps were proved incompatible for efficient lighting owing to their demerits of high energy consumption, low efficiency and short lifespan. White light emitting diodes (wLEDs) nevertheless stands tall on all fronts with its relevant merits of low power consumption, extended lifetime, environment friendliness, stable physical and chemical properties high luminous efficiency wide colour gamut, lower operating temperature and robustness [132–135]. Nowadays two common routes are used for fabrication of wLEDs. The first method employ integrating Ce^{3+} activated $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG: Ce^{3+}) yellow phosphor with a InGaN LED chip having blue emission. Though this approach gives high photoluminescence (PL) efficiency with blue light excitation, the obtained wLEDs have below par color-rendering indices (CRI) and elevated correlated color temperatures on account of missing emission in red region [60,61]. In the second approach improved CRI and tunable correlated color temperatures are achieved by devising Red, Green and Blue phosphor amalgamated on a LED chip having emission in near UV region [62]. The emission from this approach also possess weak emission in red region and suffers complex blending due to distinct characteristics of LEDs [63]. So efficient red phosphors need to be investigated for development of wLEDs by either of the approach. Commercially, for red phosphors, sulphides and nitrides-based materials are used. The synthesis of nitride-based phosphors is challenging and expensive due to high temperature and high pressure synthesis requirement [97,135]. The commercially used red emitting $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ phosphor has below par efficiency owing to low absorbance in near UV region. Furthermore, it suffers from poor chemical stability and decomposes into toxic by-products [136]. So, for development of highly efficient, environment friendly red phosphor to achieve high luminous efficiency of wLEDs a novel red emitting phosphor which is chemically and thermally stable is required. Among various activators, Eu^{3+} has significantly good luminescence with narrow emission band in red region, having absorption in near UV/blue region attributed to its 4f transition [61,132,133,135]. Moreover, in the past decades rare earth doped glasses and phosphors have

drawn attention for their applications in solid state lasers, indoor lighting, and wLEDs [137,138].

Recently, many articles have been reported recognizing strong red emitted Eu^{3+} doped molybdates materials for their use in LEDs [134]. Eu^{3+} doped tungstate, Zirconate, tantalate, phosphates etc have also been explored for potential material as efficient red phosphor [136,139–141]. Since the crystal field of host material can manipulate the emission and absorption from the activator ion so choice of host can affect the efficiency of phosphor [92]. In the last decade various works have been reported in which phosphates have emerged as a potential material for phosphors as they possess excellent thermal chemical and hydrolytic stability with low phonon energy [63,92,142,143]. Phosphate material offer favourable parameters like large optical band gap, high index of refraction, lower sintering temperatures and low synthesis cost to be considered as lucrative host material [63,144].

In the present study, we have investigated $\text{BaZr}(\text{PO}_4)_2$ (BZP) as a novel host material for red emission using Eu^{3+} as activator. To the best of our knowledge, the as studied phosphate hasn't been reported for any PL studies. The effect of variation of Eu^{3+} concentration, and role of different chloride fluxes in improving luminescent properties has also been investigated systematically. Judd-Ofelt (JO) theory has been applied to understand various parameters and analysing them for indoor lighting applications.

3.2 PREPARATION AND CHARACTERIZATION:

A batch of $\text{Ba}_{(1-x)}\text{Zr}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($x = 1.0\text{-}5.0$ mol%) powder samples were fabricated via simple solid reaction route. The schema chart depicting the process followed for optimisation of synthesis parameters to obtain pure phase is displayed in Fig.3.1. The precursors Eu_2O_3 (99.9%), BaCO_3 (99.99%), ZrO_2 (99.99%) and $(\text{NH}_4)\text{H}_2\text{PO}_4$ (99.99%) taken were all highly pure and of analytical grade. First the undoped $\text{BaZr}(\text{PO}_4)_2$ was prepared by taking the stoichiometric amount of precursors mixed together in acetone in Agate mortar and grinded thoroughly for 90 minutes. The blend powder was sintered in a programable high temperature furnace at variable temperatures from 1073-1373 K to obtain pure phase $\text{BaZr}(\text{PO}_4)_2$. The specimens were milled into fine powder for subsequent investigations. The optimum temperature for obtaining the pure phase was identified at 1373 K. Under the aforementioned temperature conditions the Eu^{3+} doped $\text{BaZr}(\text{PO}_4)_2$ were synthesized by adding stoichiometric amount of Eu_2O_3 to the other precursors. The chloride flux assisted samples were prepared with different weight % of NH_4Cl (99.99%), KCl (99.99%), LiCl (99.99%) and NaCl (99.99%)

added separately with the precursors. The nomenclature used in this paper for different flux assisted samples is given in Table 3.1.

The phase identification and structural studies were done by using Bruker D8-Advanced X-Ray diffraction which employs Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$). The surface morphology along with qualitative analysis of elemental composition using energy dispersive spectrometer (EDS) was studied using Scanning Electron Microscope (SEM) instrument Zeiss EVO50. The diffuse reflectance spectra were recorded in 200-800 nm range using Jasco UV-Vis-IR spectrometer. Perkin Elmer spectrum 2 equipment was employed for recording the Fourier-transform infrared spectroscopy (FTIR) spectra. The Photoluminescence (PL) spectra and photoluminescence excitation (PLE) spectra were studied using JASCO FP-8300 Spectro-fluorophotometer. For the lifetime measurements decay traces were recorded on HORIBA scientific-Fluorolog-3 instrument equipped with pulsed Xenon lamp.

The FLAME-S-XR1-ES model ocean optics spectrometer was employed for temperature dependent PL characteristics investigated in 300 K to 420 K range with an interval of 30 K.

NAME	BZ P1	BZ P3	AC1	AC2	AC3	AC4	AC5	AC6	NC	L C	K C
Eu³⁺ conc (mol%)	1	3	1	1	1	1	1	3	1	1	1
Flux	--	--	NH ₄ Cl	NH ₄ Cl	NH ₄ Cl	NH ₄ Cl	NH ₄ Cl	NH ₄ Cl	Na Cl	Li Cl	K Cl
Flux dosage (wt %)	--	--	2.5	5	10	15	20	5	5	5	5

Table 3.1. Nomenclature for samples prepared with different weight percent of flux and Eu³⁺ concentration.

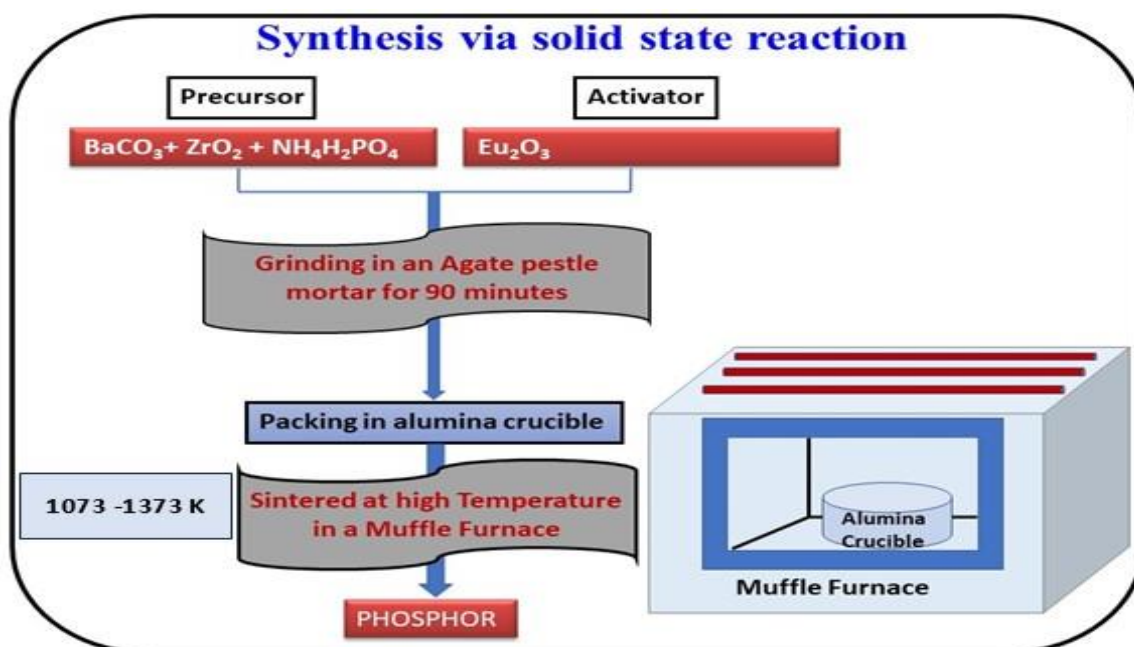


Fig.3.1. Flowchart of solid-state reaction synthesis.

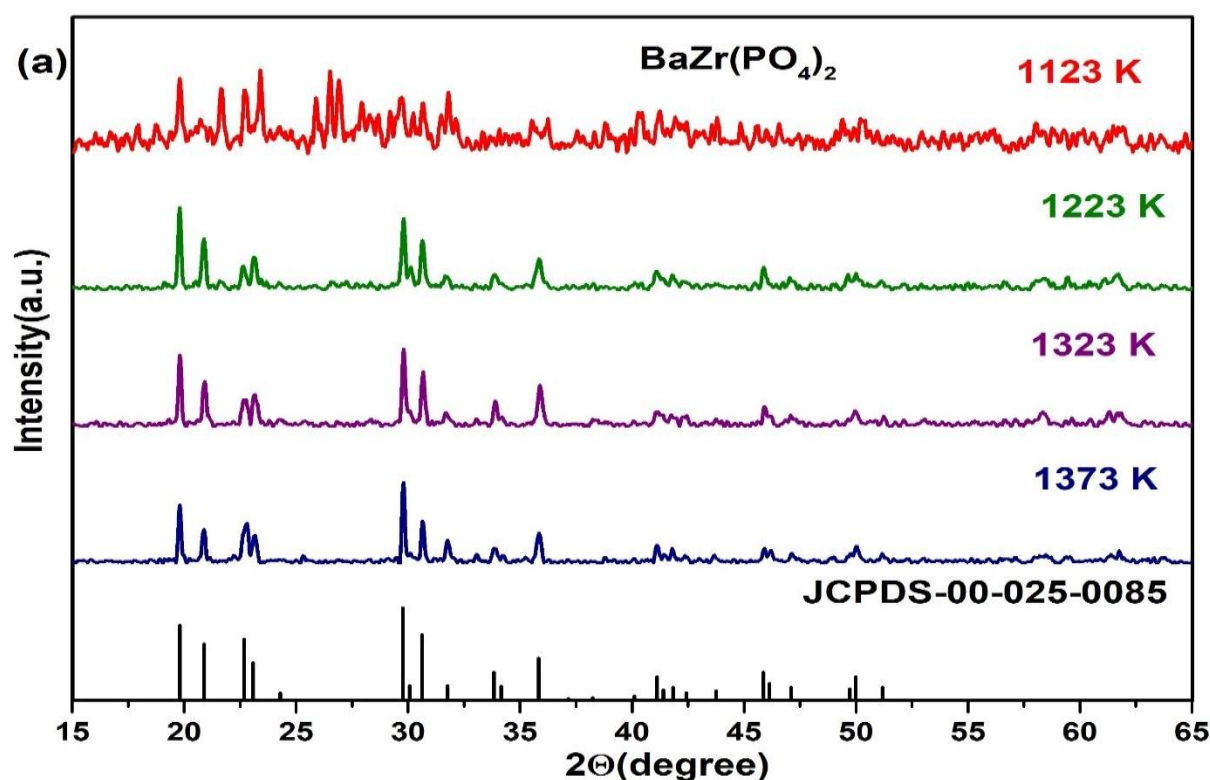
3.3 RESULTS AND DISCUSSION:

3.3.1 XRD analysis:

The powder X-Ray Diffraction (XRD) patterns for undoped $\text{BaZr}(\text{PO}_4)_2$ sintered at different temperatures for obtaining pure phase are shown in Fig.3.2(a). The peaks present due to impurities vanishes as the sintering temperature is raised from 1023 K and pure phase is obtained at a temperature of 1373 K, where the peaks are in agreement with standard data corresponding to JCPDS card no 00-025-0085, and with earlier reports, confirming the presence of pure phase [145]. The prepared compound has monoclinic structure with C2/m space group having lattice parameters of $a = 8.5310 \text{ \AA}$, $b = 5.2930 \text{ \AA}$, $c = 7.8750 \text{ \AA}$ and cell volume of $354.81 \text{ \AA}^3$ with 2 molecules per unit cell. The constituent units of structure include three polyhedrons viz. ZrO_6 , BaO_{10} and PO_4 . The PO_4 tetrahedra and BaO_{10} forms 2-D sheets in a plane parallel to (001) by sharing edges, which are stacked along c directions. The ZrO_6 octahedra is alternatively stacked with BaO_{10} along these sheets in c directions linked with its oxygen atoms O (1) and O (3) [146,147].

The XRD patterns for Eu^{3+} doped $\text{BaZr}(\text{PO}_4)_2$ at optimised temperature for different dopant concentration is displayed in Fig.3.2(b). The diffraction patterns with varied concentrations of dopant (Eu^{3+}) ion shows iso-structural phases, and no new peaks corresponding to any impurity phase emerge after doping with Eu^{3+} ions establishing integration of Eu^{3+} in crystal structure

without altering the monoclinic phase. The enlarged XRD pattern in range 29.5° to 30.0° in Fig.3.2(b) distinctly shows a slight peak shift to higher angles with augmented concentration of Eu^{3+} , which is attributed to substitution of smaller ionic radii Eu^{3+} in place of higher ionic radii Ba^{2+} [148]. Also considering the oxidation state and ionic radii difference Eu^{3+} will favourable occupy larger Ba^{2+} ions site rather than smaller Zr^{4+} ion site. The Scherrer formula given by $d = 0.9\lambda/\beta\cos\theta$ for crystallite size (d), was used to determine average crystallite size for the samples, where λ is wave-length of X-rays used ($\lambda = 1.5406 \text{ \AA}$), β is full width at half maximum corresponding to diffraction angle θ . The calculated mean crystallite size for $\text{Ba}_{(1-x)}\text{Zr}(\text{PO}_4)_2:x\text{Eu}^{3+}$ for $x = 0, 1.0, 3.0$ and 5.0 mol% was obtained as 45.44, 38.79, 37.66 and 35.54 nm respectively. The shrinking crystallite size with increased concentration is attributed to smaller dopant size as compared to substituted ion leading to lattice contraction [77].



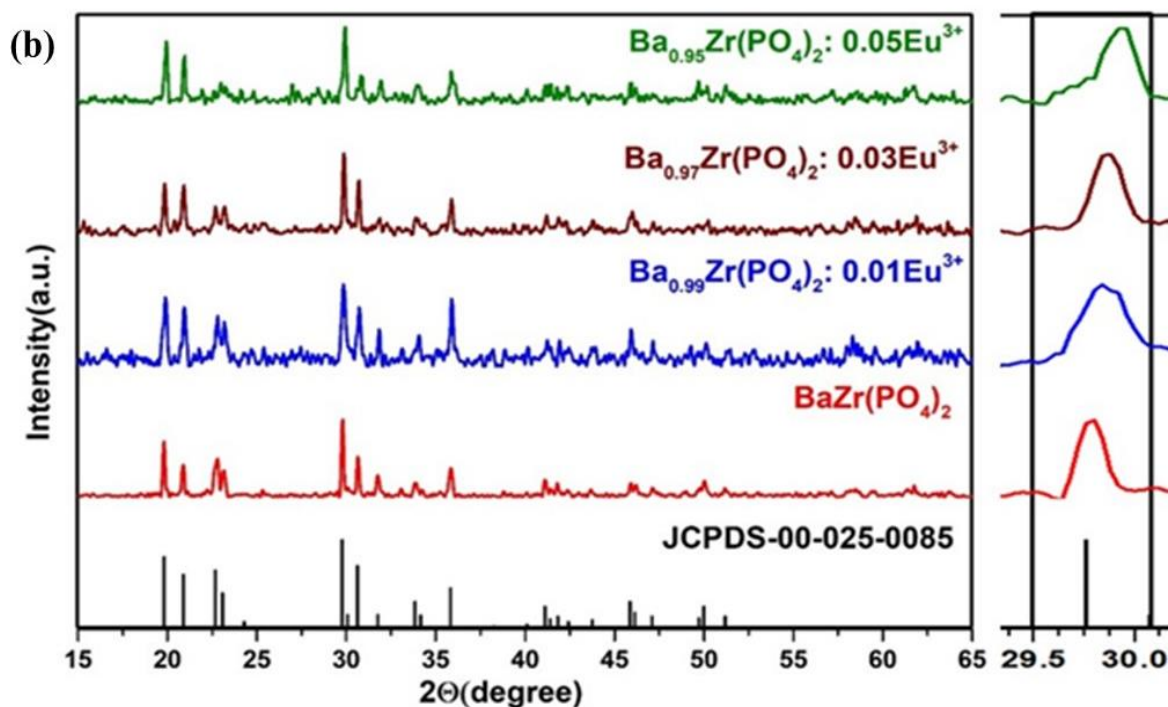


Fig.3.2. (a): XRD pattern for $\text{BaZr}(\text{PO}_4)_2$ with variation of sintering temperature along with standard diffraction pattern. **(b):** XRD pattern for $\text{Ba}_{(1-x)}\text{Zr}(\text{PO}_4)_2 : x\text{Eu}^{3+}$ ($x = 0, 1.0, 3.0$ and 5.0 mol%) along with standard diffraction pattern.

3.3.2 Surface Morphology and elemental analysis

The surface morphology of the $\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$ synthesized with 0 and 5 weight percent of NH_4Cl (AC6) is displayed in Fig. 3.3(a) and (b) respectively. The image 3.3(a) reveal non uniform shape and size of the particle ranges from 3 to 15 μm suggesting that the high temperature sintering lead to agglomeration to bigger particle. In contrast the flux assisted AC6 sample in fig.3.3(b) reveals smaller and nearly uniform shape of particles with size ranging in 1-5 μm range indicating role of flux in improving size distribution and the morphology of the phosphor. In fact, presence of flux at grain boundaries inhibit the steady crystal growth thus reducing the particle size, which also helps in enhancing the luminescence of the phosphor [149]. Also, the texture of the obtained powder phosphor also gets improved with flux. The morphological results suggests that the addition of flux has given favourable results in improving the morphology of the prepared phosphor. The particle size is found to be similar with the mostly available commercial phosphor [109].

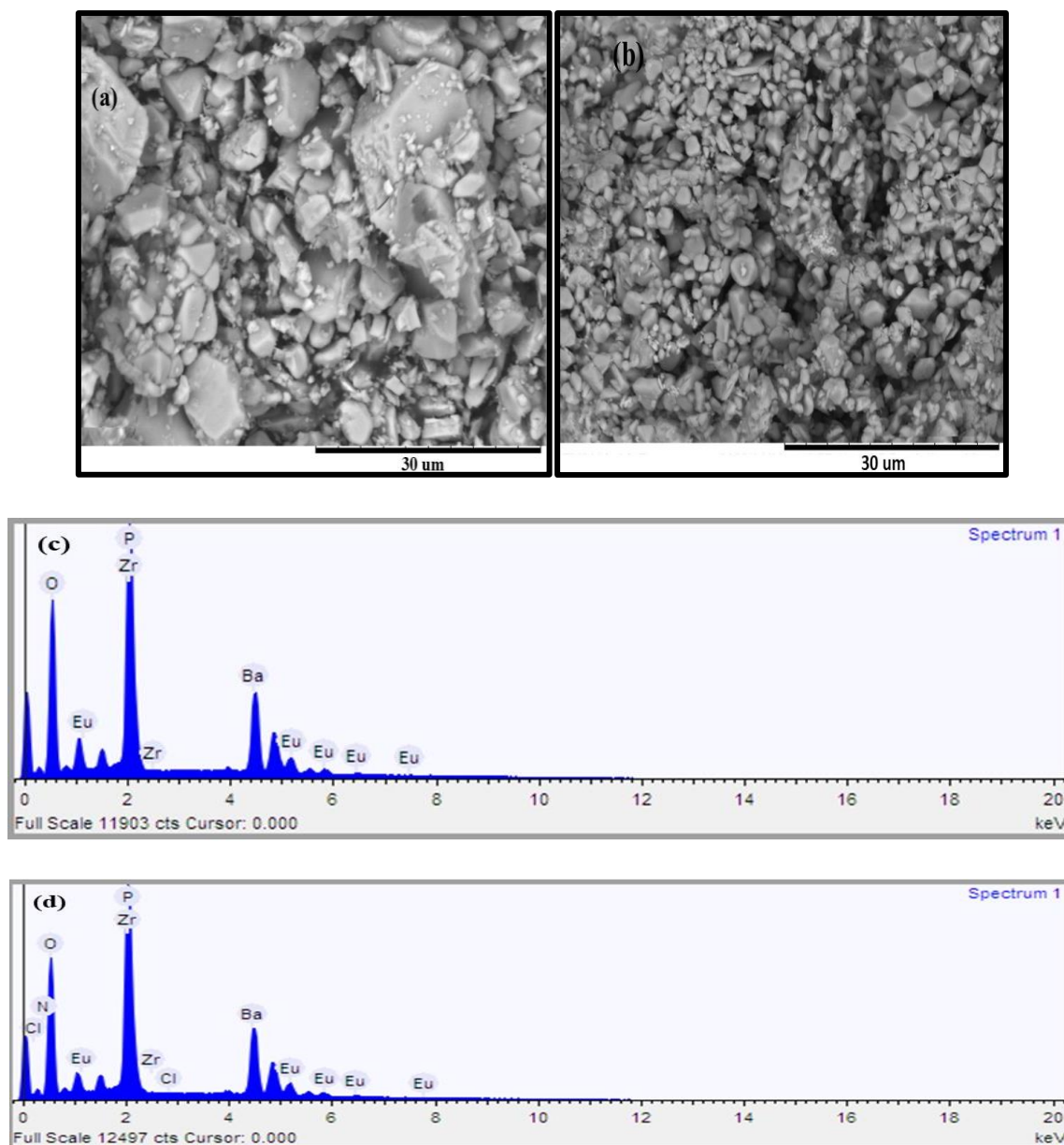


Fig.3.3.(a)The SEM image of $\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$ prepared 0 wt% of NH_4Cl **(b)** The SEM image of $\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$ prepared 5 wt% of NH_4Cl **(c)** EDS profile of $\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$ prepared 0 wt% of NH_4Cl **(d)** EDS of $\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$ prepared 5 wt% of NH_4Cl

Fig.3.3(c) and (d) shows the energy dispersive spectrometer (EDS) graph for the $\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$ synthesized with 0 and 5 weight percent of NH_4Cl (AC6) depicting their elemental composition. The peaks in the graphs reveals that Ba, Zr, O, P and Eu are present in both the samples and no elemental impurity peaks were observed. Moreover, in both the samples the peak profiles are similar indicating that flux elements dissipated due to high

temperature calcination as shown in Fig.3.3 (c) & (d). Thus, EDS finding also affirms that Eu^{3+} got incorporated in the host lattice effectively.

3.3.3 FTIR studies

The FTIR spectrum of $\text{BaZr}(\text{PO}_4)_2$ recorded for wave number spanning 500 to 1500cm^{-1} is depicted in Fig.3.4. The two bands in $1120\text{--}940\text{ cm}^{-1}$ and $650\text{--}540\text{ cm}^{-1}$ region are characteristic IR absorption band of $(\text{PO}_4)^{3-}$ [150]. The recorded spectrum has bands present in both the ranges. The band around 940 cm^{-1} and 1020 cm^{-1} is attributed to symmetric and antisymmetric stretching vibrations respectively of PO_4 tetrahedra [151]. Similarly, the bands at 530 cm^{-1} , 580 cm^{-1} , and 635 cm^{-1} are due to asymmetric deformation mode of phosphate groups [152]. Thus, FTIR studies support the presence of phosphate groups in the phosphor.

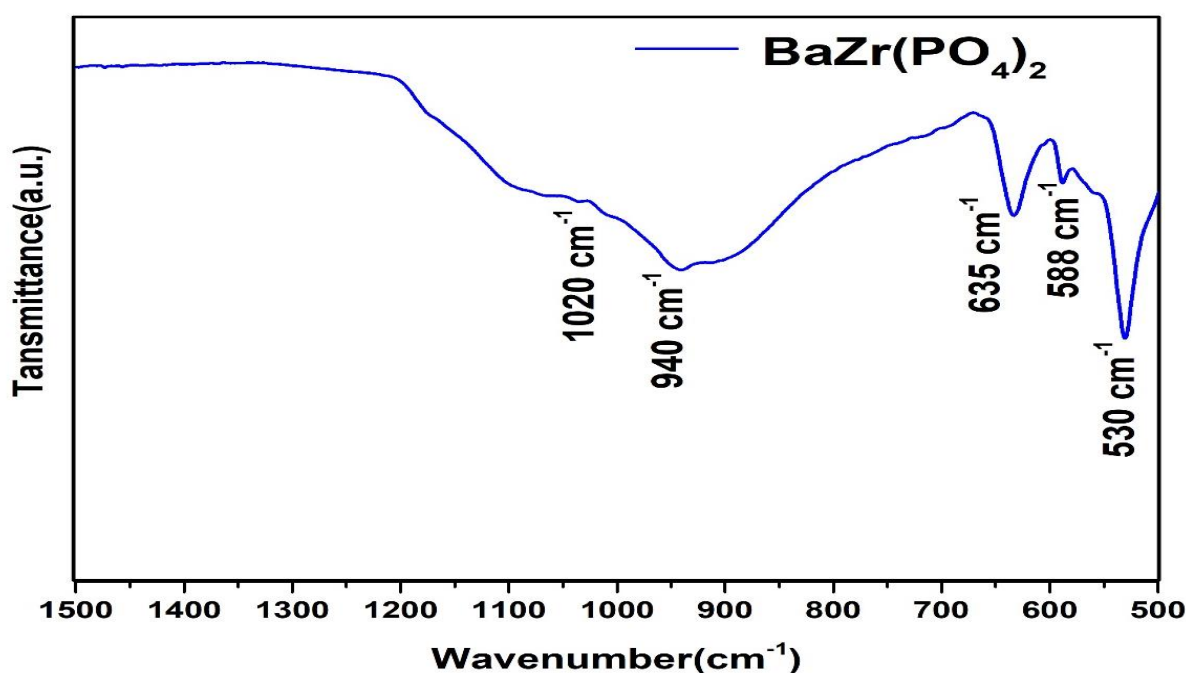


Fig. 3.4. FTIR spectrum of $\text{BaZr}(\text{PO}_4)_2$

3.3.4 Thermogravimetric Diffuse Reflectance Spectroscopy:

The diffuse reflectance spectroscopy graph of $\text{BaZr}(\text{PO}_4)_2$ along with the $\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$ is shown in Fig.3.5(a). The contamination by impurity ions alters the optical properties of the semiconductors [153]. Both the samples show an absorption band in the 250–350 nm range peaking around the same point, which corresponds to the charge transition band.

of $(\text{PO}_4)^{3-}$ octahedra in the $\text{BaZr}(\text{PO}_4)_2$ host matrix. Past this range clearly apparent additional small drops are present in $\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$ spectra which are missing in undoped sample. These are located at 394 nm and 463 nm corresponding to ${}^7\text{F}_0-{}^5\text{L}_6$ and ${}^7\text{F}_0-{}^5\text{D}_2$ transitions of Eu^{3+} respectively well in agreement with excitation spectra. Moreover the reflectance spectrum for $\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$ shifts to a lower value relative to $\text{BaZr}(\text{PO}_4)_2$ owing to $\text{Eu}^{3+}-\text{O}^{2-}$ charge transfer band [154].

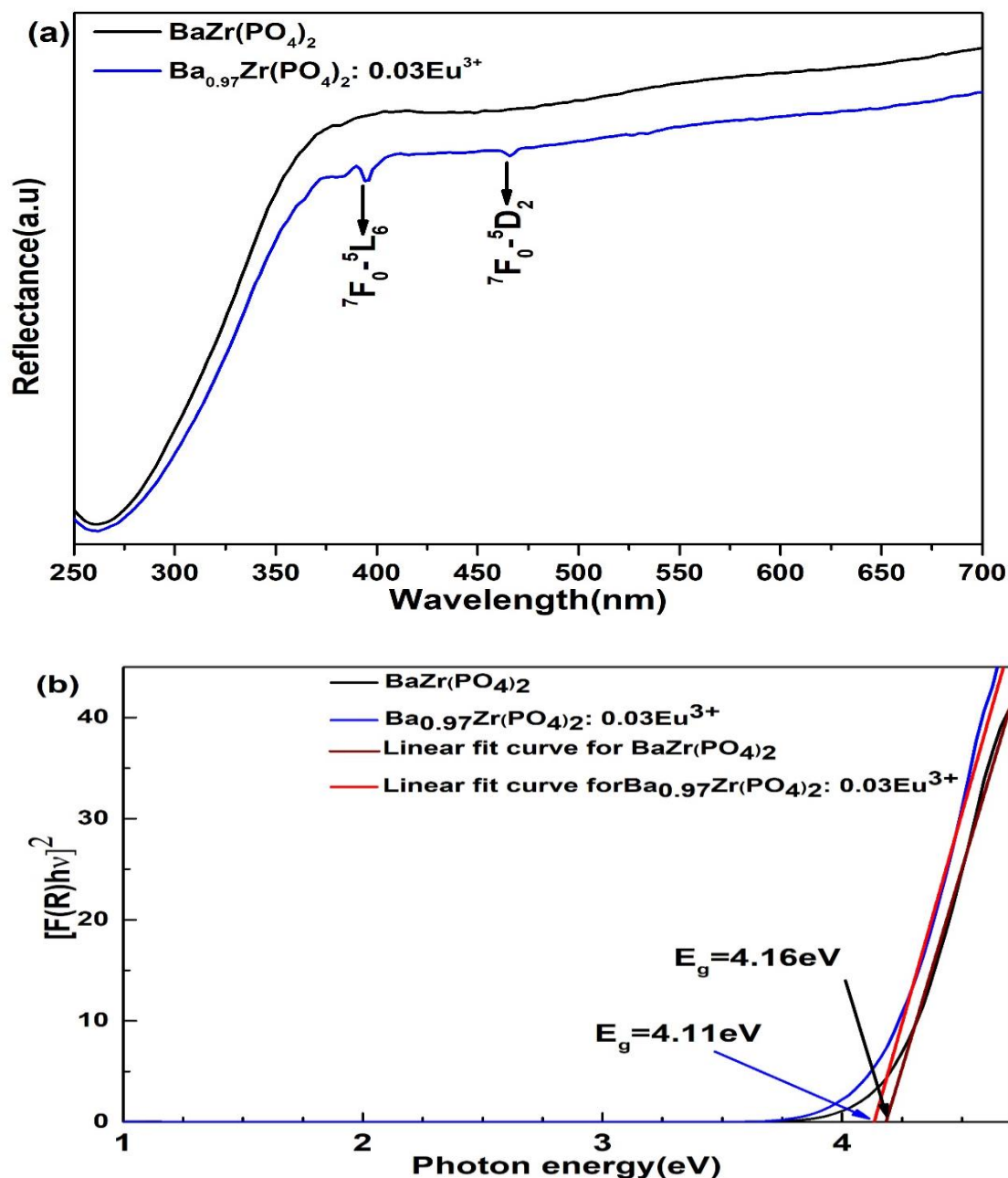


Fig.3.5 (a): Diffuse Reflectance Spectra of $\text{Ba}_{(1-x)}\text{Zr}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($x = 0$ and 3.0 mol%) **(b):** Tauc Plot for band gap determination for $\text{Ba}_{(1-x)}\text{Zr}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($x = 0$ and 3.0 mol%)

The Tauc equation for determining the optical band gap E_g of a semiconductor using absorption coefficient (α) is given by:

$$\alpha h\nu = C(h\nu - E_g)^n \quad (3.1)$$

Where h is Planck's constant, ν is frequency of photon, C is a constant, E_g is band gap, $n=1/2, 2, 1/3$ and 3 for direct transition, indirect transition, inhibitory direct transition and inhibitory indirect transition respectively. Moreover, α can be replaced with Kubelka Munk function, $F(R)$ by Kubelka Munk approximation:

$$F(R) = \frac{K}{S} = \frac{(1-R)^2}{2R} \quad (3.2)$$

where R , K and S are reflectance, absorption and scattering coefficients [155]. For α is proportional to $F(R)$, the Tauc relation becomes

$$F(R)h\nu = C(h\nu - E_g)^n \quad (3.3)$$

Fig.3.5(b) shows Tauc plot between $(F(R)h\nu)^2$ vs $h\nu$ for $BaZr(PO_4)_2$ and $Ba_{0.97}Zr(PO_4)_2:0.03Eu^{3+}$. Band gap is then calculated from intercept of linear fit of linear portion of graph as shown. The band gap for $BaZr(PO_4)_2$ and $Ba_{0.97}Zr(PO_4)_2:0.03Eu^{3+}$ is extrapolated to 4.16 eV and 4.11 eV respectively. This red shift in optical band gap due to presence of dopant ion is attributed to generation of intermediate energy levels around valence and conduction band leading to narrowing of band gap.

3.3.5 Photoluminescence Investigations:

Fig.3.6 illustrates the photoluminescent excitation spectra of $Ba_{(1-x)}Zr(PO_4)_2:xEu^{3+}$ ($x = 1.0-5.0$ mol%) monitored at emission corresponding to 7F_0 to 5D_2 transition of Eu^{3+} at 612nm. Several intense peaks ascribed to 4f-4f transitions of Eu^{3+} can be clearly seen. These peaks centred around 360, 380, 392, 414 and 463 nm corresponds to ${}^7F_0-{}^5D_4$, ${}^7F_0-{}^5L_7$, ${}^7F_0-{}^5L_6$, ${}^7F_0-{}^5D_3$ and ${}^7F_0-{}^5D_2$ transitions respectively and are consistent with those obtained in diffuse reflectance spectra of $Ba_{0.97}Zr(PO_4)_2:0.03Eu^{3+}$ [141,144,156]. Among these peaks the most intense corresponds to ${}^7F_0-{}^5L_6$ transitions at 392 nm which is four times intense than ${}^7F_0-{}^5L_7$ peak and 3.6 times intense than ${}^7F_0-{}^5D_2$ peak. Moreover, it is apparent that increasing Eu^{3+} ion concentration enhances the spectral intensity initially till $x = 3.0$ mol% where it is maximum,

thereafter it decreases on subsequent addition of Eu^{3+} ion, without altering the emission spectra peak profile.

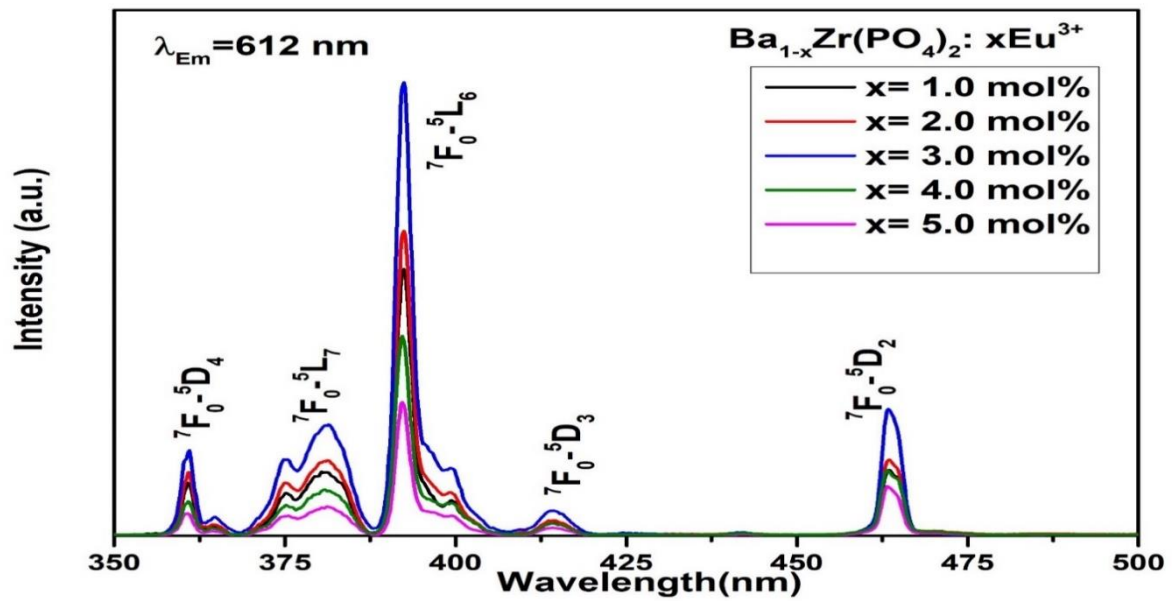
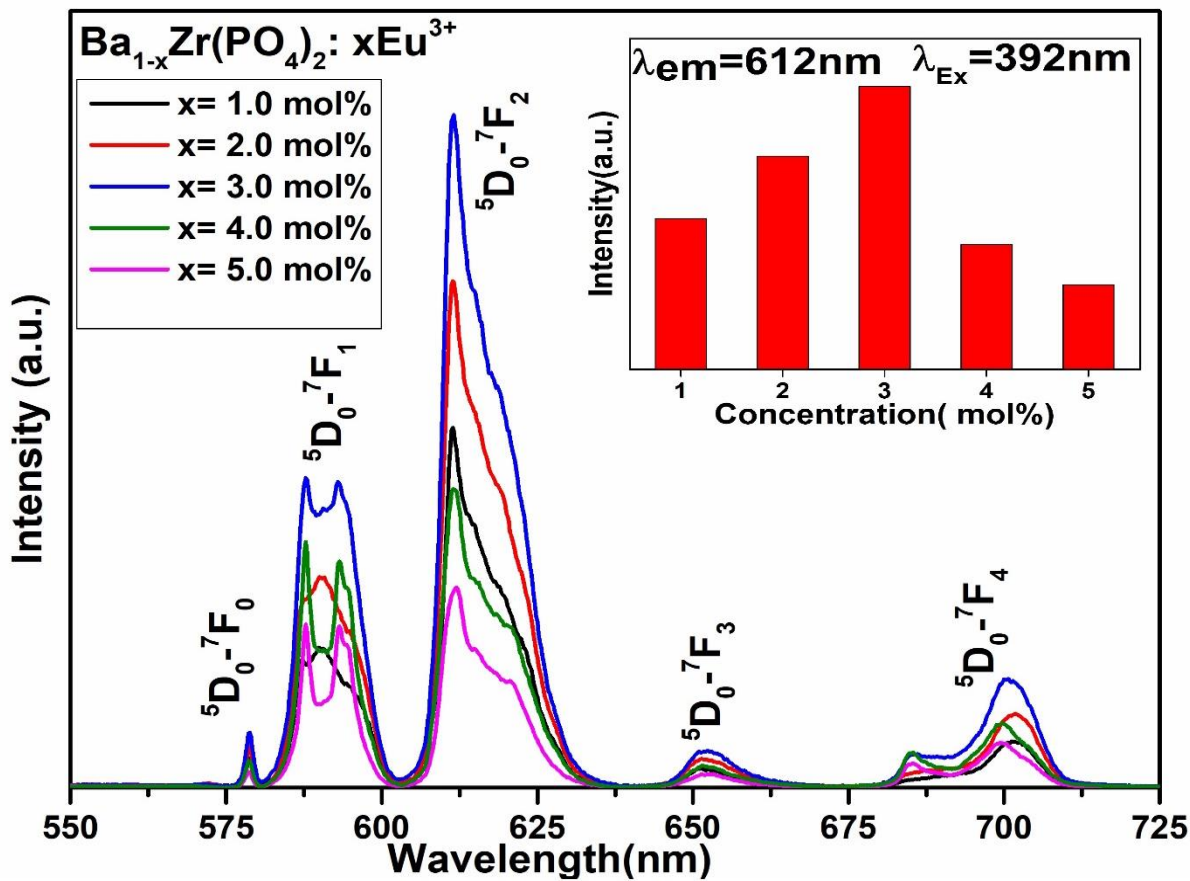
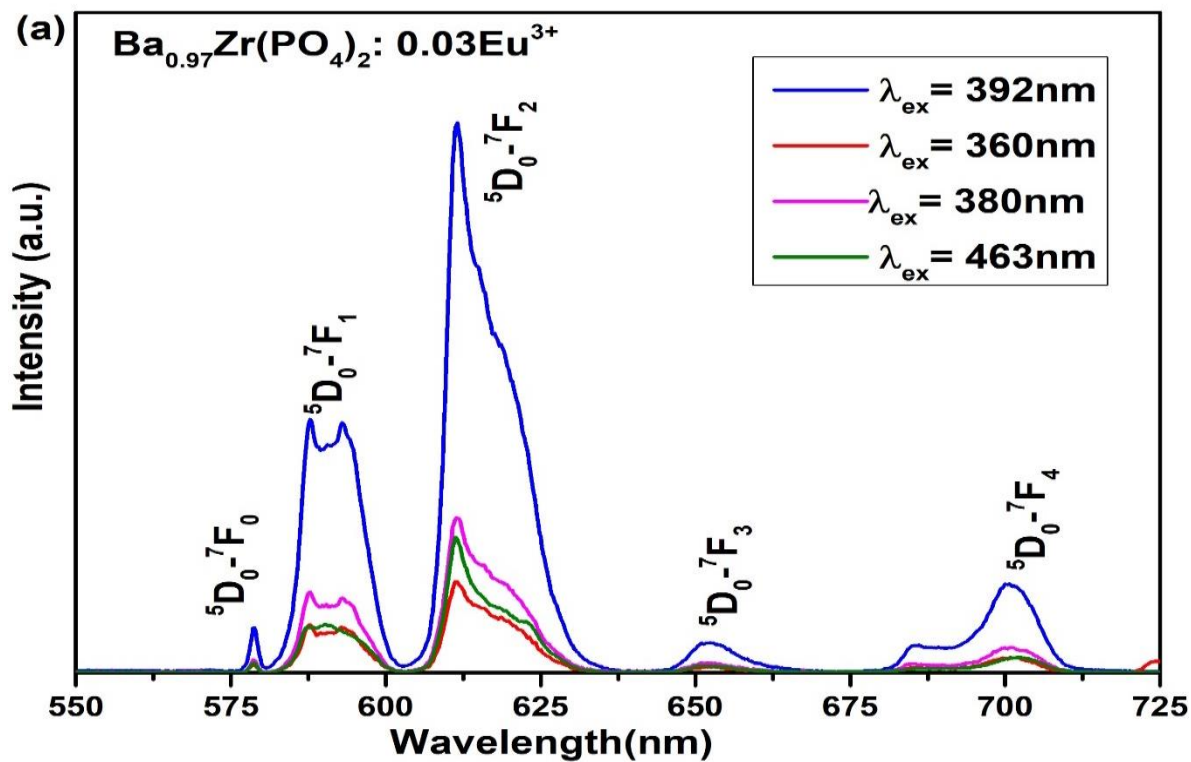


Fig.3.6. The excitation spectra of $\text{Ba}_{(1-x)}\text{Zr}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($x = 1.0, 2.0, 3.0, 4.0$ and 5.0 mol%) at 612nm emission wavelength.



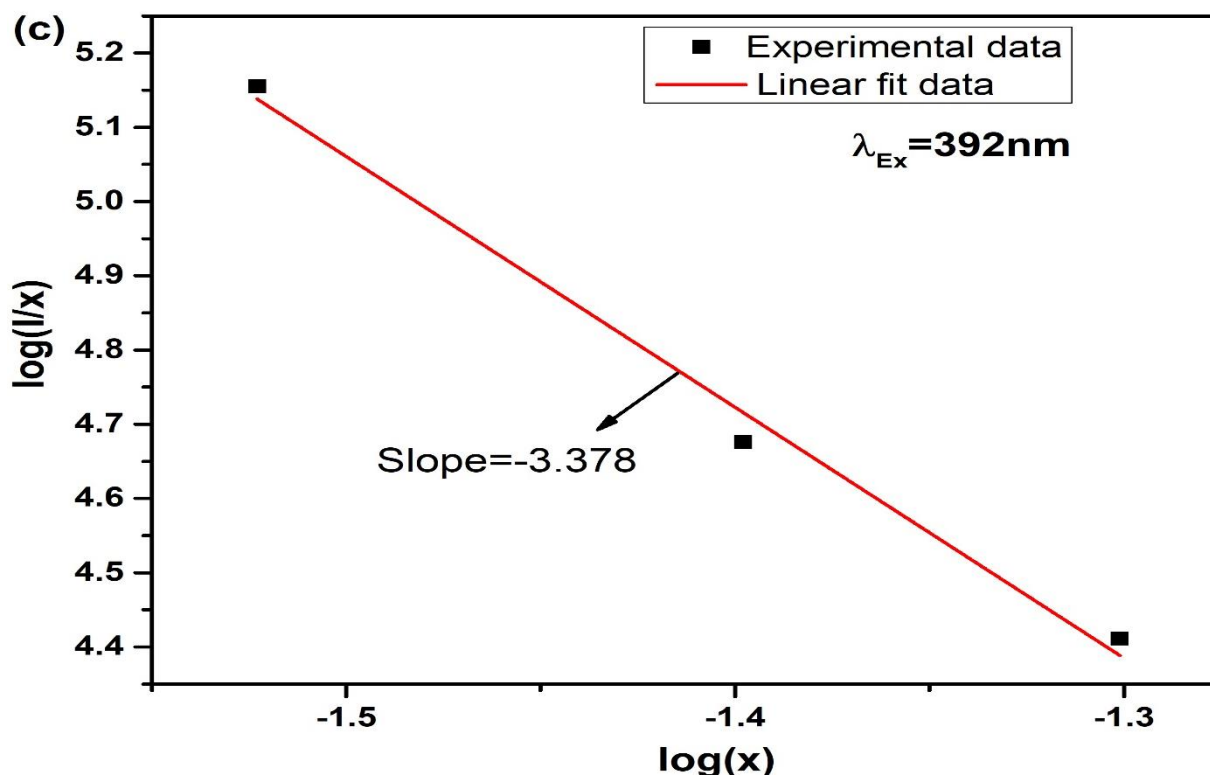


Fig.3.7. (a): The emission spectra for $Ba_{(1-x)}Zr(PO_4)_2:xEu^{3+}$ at ($x = 3.0$ mol%) monitored at different excitation wavelengths. **(b):** The emission spectra of $Ba_{(1-x)}Zr(PO_4)_2:xEu^{3+}$ ($x = 1.0, 2.0, 3.0, 4.0$ and 5.0 mol%) under 392 nm excitation wavelength. **(c):** Plot of $\log(I/x)$ versus $\log(x)$ for $Ba_{(1-x)}Zr(PO_4)_2:xEu^{3+}$ ($x = 1.0, 2.0, 3.0, 4.0$ and 5.0 mol%)

Fig.3.7 (a) shows emission spectra of $Ba_{0.97}Zr(PO_4)_2:0.03Eu^{3+}$ excited under $360, 380, 392$ and 463 nm wavelengths. It is clear that the spectrum monitored at 392 nm wavelength is most intense, indicating that a UV-LED chip can be used as an effective excitation source for $Ba_{(1-x)}Zr(PO_4)_2:xEu^{3+}$ phosphor. Fig.3.7 (b) shows emission spectra of $Ba_{(1-x)}Zr(PO_4)_2:xEu^{3+}$ ($x = 1.0- 5.0$ mol%) when samples were excited to 5L_6 levels by 392 nm wavelength. The emission profile comprises of narrow bands centred around $579, 591, 612, 652$ and 700 nm ascribed to $^5D_0-^7F_{0-4}$ electronic transitions of trivalent Europium ion. The peak profile (position and shape) remains unaltered for different concentrations of Eu^{3+} due to shielding of $4f^6$ electrons of Eu^{3+} by outer $5s$ and $5p$ electrons [157].

The emission transition $^5D_0-^7F_0$ (597 nm), identified as electric dipole, as per Judd–Ofelt theory it is strictly not allowed (as $\Delta J = 0$). A low intensity peak corresponding to this may be attributed to J-mixing arising from perturbation in crystal field giving rise to mixing of wavefunctions of sublevels of different levels [41,158]. The transition $^5D_0-^7F_1$ (591 nm), lying in orange emission region, is a magnetic dipole transition and is permissible as per selection

rules($\Delta S = 0$, $\Delta L = 0$, $\Delta J = 0, \pm 1$, with $0 \leftrightarrow 0$ forbidden) [41]. The probability of this transition is not constrained by crystal environment around Eu^{3+} ion and doesn't vary significantly with host [159]. So, the peak corresponding to this transition dominates when Eu^{3+} takes inversion symmetry sites. The ${}^5\text{D}_0\text{-}{}^7\text{F}_2$ (612 nm) transition corresponding to red emission is hypersensitive electric dipole transition allowed by the selection rules $|\Delta S| = 0$, $|\Delta L| < 2$, and $|\Delta J| \leq 2$, when Eu^{3+} occupy a low symmetry site. So, with the reduction in symmetry in local environment of Eu^{3+} the strength of emission of this transition increases. So asymmetry ratio (A_{21}) which can be obtained from the ratio of electric dipole transition integral intensity to that of magnetic dipole transition (i.e. $A_{21} = I_{\text{ED}}/I_{\text{MD}}$), gives good judgement about symmetry around Eu^{3+} as well the red colour purity of phosphor. A high value of this ratio is a clear indication of low symmetry of Eu^{3+} site [160–163]. The emission spectra clearly show the dominating ${}^5\text{D}_0\text{-}{}^7\text{F}_2$ peak indicating presence of most of activator ions located at the asymmetric sites. The computed A_{21} values for different samples are tabulated in Table 3.2. A decrease in A_{21} value with increasing concentration indicates that Eu^{3+} ions present at two different symmetry sites [164]. Moreover, the stark splitting of ${}^5\text{D}_0\text{-}{}^7\text{F}_2$ level into two peaks centred at 587 nm and 593 nm indicates presence of some Eu^{3+} ions in sites having inversion symmetry [77].

Sample	A21
$\text{Ba}_{0.99}\text{Zr}(\text{PO}_4)_2:0.01\text{Eu}^{3+}$	2.6
$\text{Ba}_{0.98}\text{Zr}(\text{PO}_4)_2:0.02\text{Eu}^{3+}$	2.4
$\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$	2.2
$\text{Ba}_{0.96}\text{Zr}(\text{PO}_4)_2:0.04\text{Eu}^{3+}$	1.66
$\text{Ba}_{0.95}\text{Zr}(\text{PO}_4)_2:0.05\text{Eu}^{3+}$	1.63
AC6	2.79

Table 3.2. Value of asymmetry ratio for various samples

The bar graph in Fig.3.7(b) reveals the variation of intensity of the ${}^5\text{D}_0\text{-}{}^7\text{F}_2$ peak with Eu^{3+} ion concentration. The intensity is maximum for 3 mol% concentration of Eu^{3+} ions and falls off with variation on either side. As concentration of Eu^{3+} is increased the nearest activator ion distance decreases, and the probability of energy transfer among Eu^{3+} ions becomes more than probability of emission thereby leading to non-radiative loss of excitation energy among the Eu^{3+} ions [161]. This non-radiative loss can be in generally attributed to three different mechanisms viz. exchange interaction, multipole–multipole interaction and radiation

reabsorption [61,132]. The critical distance between the nearest activator ions gives a good estimation of the energy loss mechanism involved, which can be evaluated using Blasse formulae mentioned elsewhere [160,165].

For $\text{BaZr}(\text{PO}_4)_2$ lattice, the value of R_c for Eu^{3+} in this system was found to be 22.44 Å, which being above 5 Å suggesting that multipole-multipole interaction mechanism accounts for non-radiative energy transfer. Further the nature of multipole interactions can be investigated by employing Dexter's relation [161]. A plot of $\log(I/x)$ vs $\log(x)$ is shown in fig.3.7(c) from where the value of Q is computed to be 10.13, thereby establishing quadrupole-quadrupole interactions contributing to non-radiative energy transfer.

3.3.6 Influences of Fluxes on Emission Spectra

The role of fluxes in lowering the sintering temperature, augmenting the luminescent properties and improving the morphology of phosphors has been reported by many authors [166–170]. Fig.3.8 shows emission spectra of $\text{Ba}_{0.99}\text{Zr}(\text{PO}_4)_2:0.01\text{Eu}^{3+}$ phosphor monitored under 392 nm excitation for BZP1, AC2, NC, LC and KC samples. It reveals that emission intensity increases only when NH_4Cl (AC2) is added as a flux while for rest of chlorides the emission intensity declines. The addition of NH_4Cl not only lowers the sintering temperature to 1223 K but also boost the luminescence of the phosphor by boosting the diffusion of Eu^{3+} ions in host lattice. The peak intensity for $^5\text{D}_0-^7\text{F}_2$ level of AC2 sample was found to be 1.31 times that of BZP1 sample and the spectrum profile was found to be similar for both AC2 and BZP1.

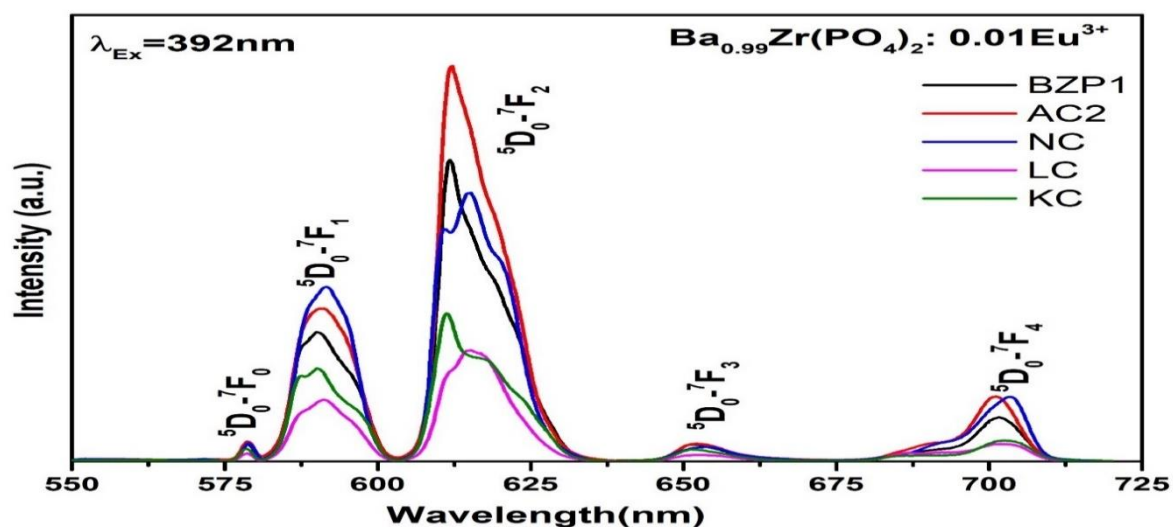


Fig. 3.8. Emission spectra of $\text{Ba}_{0.99}\text{Zr}(\text{PO}_4)_2:0.01\text{Eu}^{3+}$ with different fluxes under 392 nm excitation wavelength.

Further, the decline in luminous intensity of NaCl, KCl and LiCl assisted samples is attributed to crystal deformation and incorporation of impure phase in crystal structure which can be seen in Fig. 3.9 depicting the XRD profile of these phosphors. The higher amount of these fluxes further deteriorated the crystal structure so were not considered for further investigation. Also, the XRD pattern for NH_4Cl assisted sample clearly shows no such impurity peaks and any significant variation in XRD pattern is observed. Thus, among all the chlorides under investigation NH_4Cl emerges out as an obvious choice to be used as flux. With this, the amount of NH_4Cl was increased to identify the best possible amount of flux that can be used in the prepared phosphor. Further the correlation between luminescence and the quantity of flux was studied. The Fig.3.10 shows the variations in emission of $\text{Ba}_{0.99}\text{Zr}(\text{PO}_4)_2:0.01\text{Eu}^{3+}$ with variation in quantity (weight %) of NH_4Cl added as flux. It is clear from the Fig.3.10 that 5 weight % is the optimum quantity of flux as any variation on either side leads to fall in PL intensity.

Fig.3.11 depicts the XRD profiles for different NH_4Cl assisted samples to look for any variation in the crystal structure with the addition of flux in the host. As it is seen in Fig.3.11 that for AC1, AC3, AC4 and AC5 samples remarkable variation in peak intensity is clearly visible suggesting the phase distortion leading to decline in PL intensity for these samples [169–171]. Fig.3.12 shows variation in intensity of PL spectra for optimised quantity of flux for 3.0 mol % Eu^{3+} doped $\text{BaZr}(\text{PO}_4)_2$. The obtained spectral profile is same for both the samples indicating that crystal phase is not distorted, which can be verified from the XRD profile of AC6 sample in Fig.3.11. The mean crystallite size for AC6 sample using Debye Scherrer formula as done earlier was found to be around 35.87 nm which was 37.66 nm for BZP3 sample indicating that addition of NH_4Cl as flux leads to better crystallinity of the sample. It was found that intensity for $^5\text{D}_0\text{-}^7\text{F}_2$ transition got enhanced by 1.43 times in AC6 sample compared to BZP3 sample. The asymmetry ratio for BZP3 and AC6 samples was found to be 2.2 & 2.79 respectively indicating that flux assisted samples have more asymmetric nature of Eu^{3+} occupied sites. Moreover, for AC6 sample $^5\text{D}_0\text{-}^7\text{F}_2$ peak exhibits stark splitting with a shoulder peaked at 621 nm. The $^7\text{F}_2$ level is degenerate, so it can split in to a maximum of $(2J+1)$ levels due to crystal field splitting [172]. The flux assistance led to better incorporation of rare earth inside the host composition, thus altering the magnitude of local field acting on the rare earth ion resulting in stark splitting of the degenerate levels [173,174]. Thus, the presence of spectral splitting in a dominant $^5\text{D}_0\text{-}^7\text{F}_2$ transition further affirms the presence of Eu^{3+} ions in asymmetric

environment for flux assisted AC6 sample [175]. Hence, it can be concluded that NH_4Cl as a flux enhanced the luminescent performance of the phosphor.

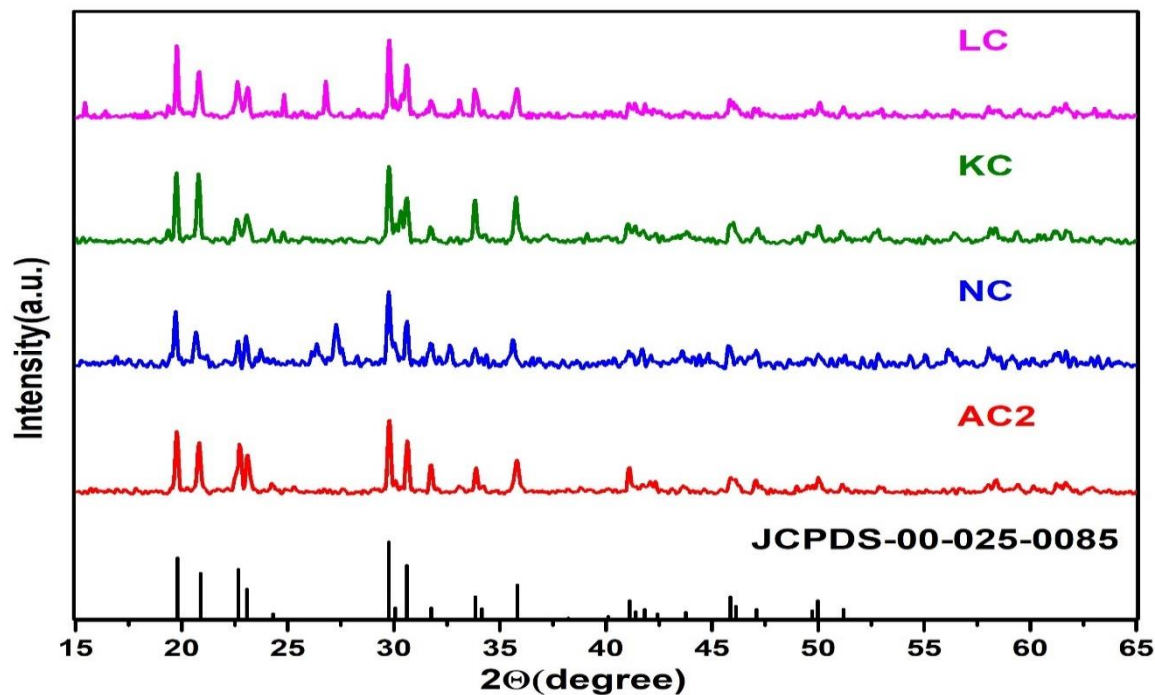


Fig.3.9. X-ray diffraction pattern of various flux blended $\text{Ba}_{0.99}\text{Zr}(\text{PO}_4)_2:0.01\text{Eu}^{3+}$ phosphors

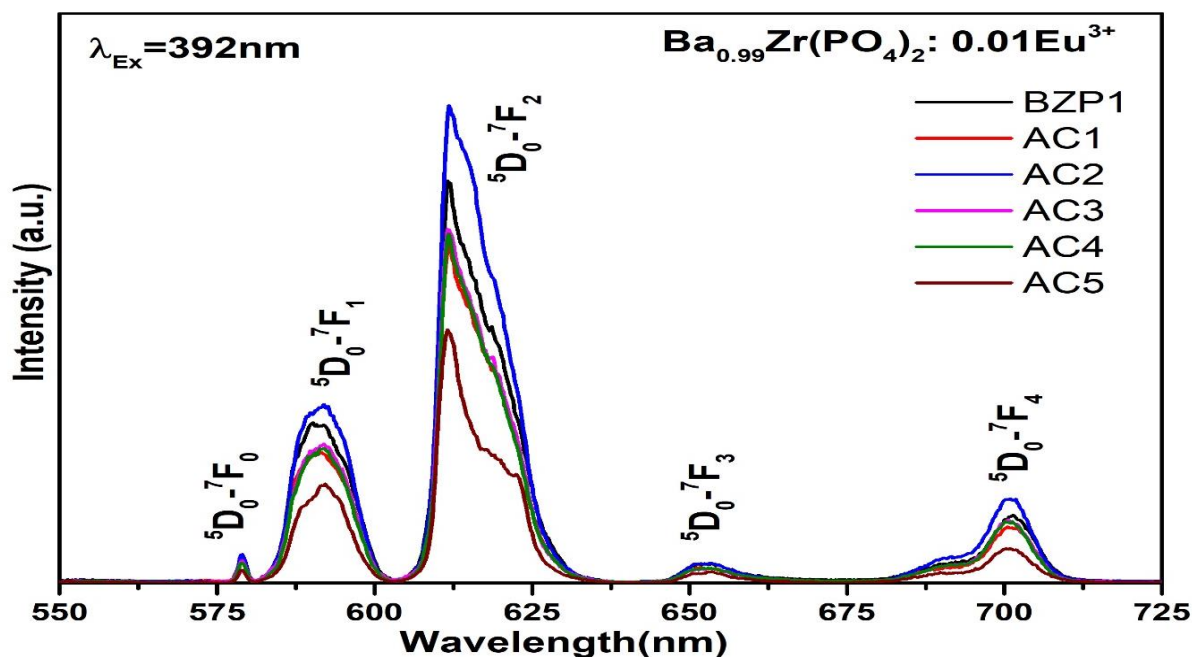


Fig.3.10. Emission spectra of $\text{Ba}_{0.99}\text{Zr}(\text{PO}_4)_2:0.01\text{Eu}^{3+}$ with different wt% of NH_4Cl under 392 nm excitation wavelength.

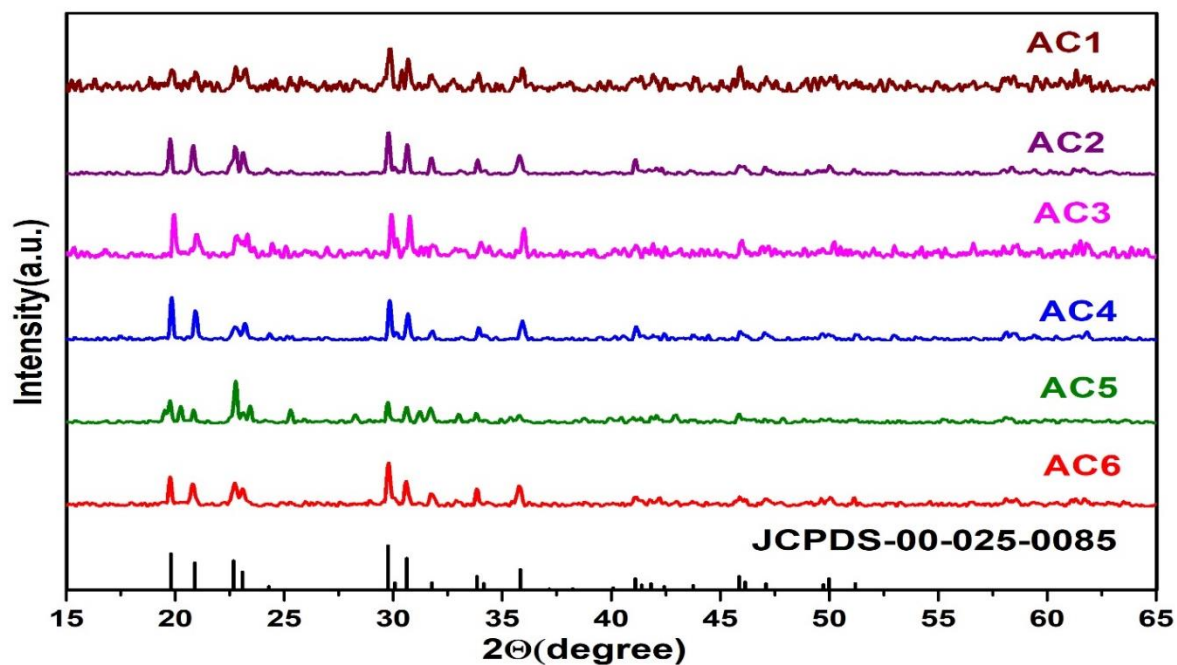


Fig.3.11. X-ray diffraction pattern with different weight % of NH₄Cl assisted BaZr(PO₄)₂:xEu³⁺ phosphors

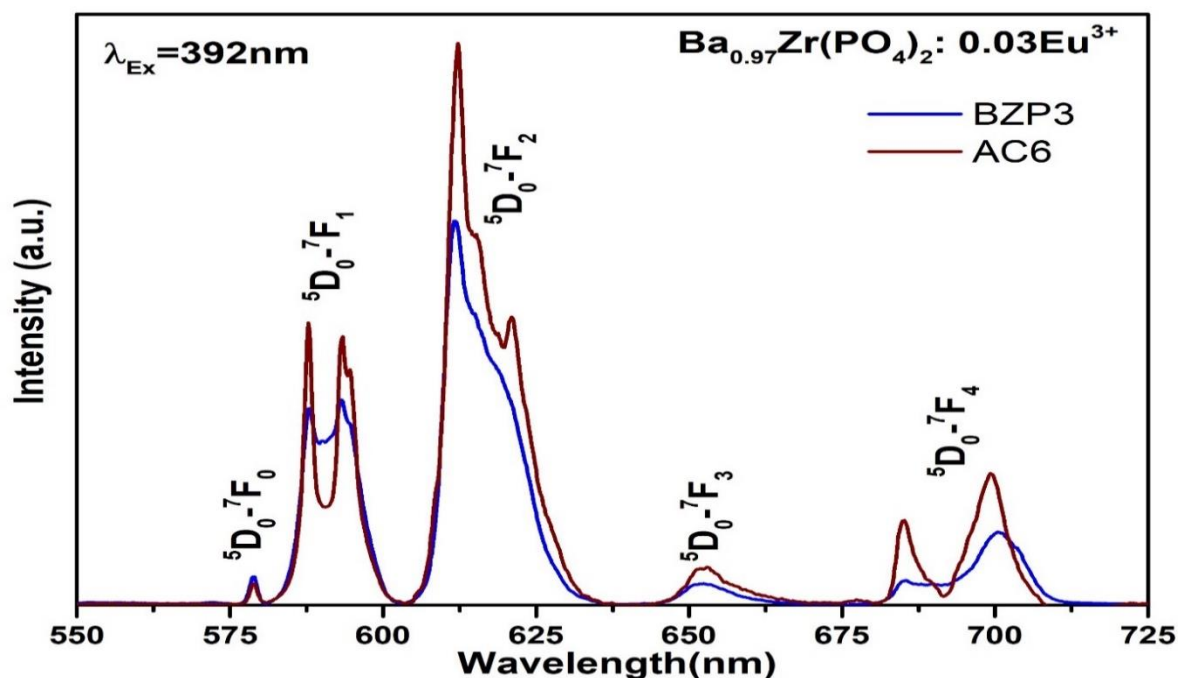


Fig.3.12. Emission spectra of Ba_{0.97}Zr(PO₄)₂:0.03Eu³⁺ without flux and with 5 wt% NH₄Cl under 392 nm excitation wavelength.

3.3.7 Temperature Dependent PL

The variation of the luminescent properties of a phosphor with temperature for assessing its thermal stability need to be investigated for considering commercial application of phosphor for wLEDs specially the high power one [62,72,132]. Fig.3.13(a) depicts the temperature dependent photoluminescence of $\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$ for temperatures in range 300-420 K monitored at an excitation wavelength of 392 nm.

The thermal quenching behaviour of the phosphor is indicated by the observed decrease in luminescence as temperature rises. Moreover, the spectral profile remains unaltered at higher temperatures. Fig.3.13(b) shows the normalised PL intensity at various temperatures and it is found that at 420 K the phosphor retained 75% emission intensity. The reason for declining intensity can be related to the mechanism of temperature induced transition from excited state to the ground state and multiphonon relaxation [176,177]. Moreover, the dependence of luminescence on temperature is governed by the Arrhenius equation [72]:

$$I_T = I_0 [1 + A \exp(-\Delta E/KT)]^{-1} \quad (3.4)$$

Where I_T is intensity of emission at temperature T , I_0 represents intensity of emission monitored at ambient temperature, A is arbitrary constant, ΔE is activation energy, K represents Boltzmann constant (8.629×10^{-5} eV/K). So, if a graph is plotted for $\ln((I_0/I_T)-1)$ against $1/KT$, as displayed in Fig.3.13(c), a straight line whose slope will give value of activation energy will be obtained. According to Fig.3.13(c), the value of activation energy for $\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$ phosphor is 0.333 eV, which is significantly better than the other reported Eu^{3+} activated phosphors like $\text{Sr}_{1.7}\text{Zn}_{0.3}\text{CeO}_4:0.3\text{Eu}^{3+}$ and $\text{Ca}_2\text{YZr}_2\text{Al}_3\text{O}_{12}:0.08\text{Eu}^{3+}$ ($E_a = 0.1788$ eV and 0.16 eV) [62,154].

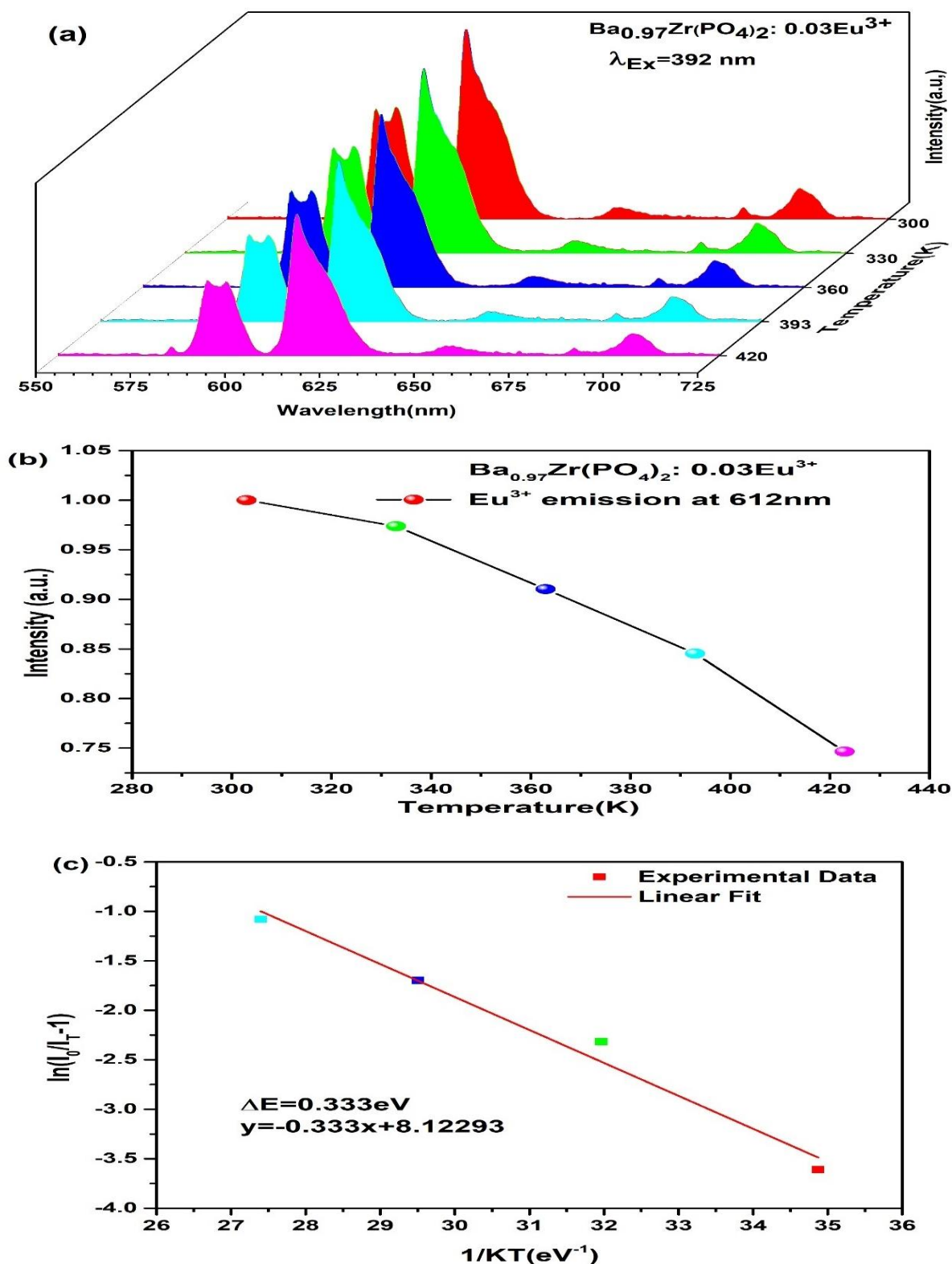


Fig.3.13 (a): Temperature dependent PL spectra for $\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$ phosphor at different temperatures between 300K to 420 K under 392 nm excitation. **(b):** Normalised PL intensity of $\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$ Phosphor at different temperatures. **(c):** linear fit plot of $\ln[(I_0/I)-1]$ versus $1/kT$ for $\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$ phosphor.

3.3.8 Colorimetric analysis

The Commission Internationale de L'Eclairage (CIE) coordinate of phosphor is another measure to quantify the performance of phosphor. Therefore, using emission spectra monitored at 392 nm excitation, CIE coordinate for $\text{BaZr}(\text{PO}_4)_2:\text{xEu}^{3+}$ ($x = 1.0, 2.0, 3.0, 4.0, 5.0 \text{ mol}\%$) were calculated and are shown in Table 3.3. Fig.3.14 reveals that the CIE coordinates of all the samples belongs to pure red region of the plot thus indicating the pure red emission from the prepared sample.

Sample	CCT(K)	CIE Co-ordinates (x,y)	Color purity(%)	Decay Time(ms)
$\text{Ba}_{0.99}\text{Zr}(\text{PO}_4)_2:0.01\text{Eu}^{3+}$	2292.485	(0.641, 0.358)	92.22	1.414
$\text{Ba}_{0.98}\text{Zr}(\text{PO}_4)_2:0.02\text{Eu}^{3+}$	2325.111	(0.642, 0.357)	92.56	1.381
$\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$	2301.994	(0.642, 0.357)	92.37	1.361
$\text{Ba}_{0.96}\text{Zr}(\text{PO}_4)_2:0.04\text{Eu}^{3+}$	2177.306	(0.637, 0.362)	91.30	1.294
$\text{Ba}_{0.95}\text{Zr}(\text{PO}_4)_2:0.05\text{Eu}^{3+}$	2144.021	(0.636, 0.363)	90.96	1.280
AC2	2407.064	(0.645, 0.354)	93.20	1.365
AC6	2582.470	(0.650, 0.354)	94.35	1.191

Table 3.3. CCT, CIE Co-ordinates, Color purity and decay time for of $\text{Ba}_{(1-x)}\text{Zr}(\text{PO}_4)_2:\text{xEu}$ phosphors

The CIE chromaticity coordinates for flux assisted $\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$ were (0.650,0.354) which are close to that of commercial red phosphor $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (0.655,0.345) [178]. Also the CIE coordinates of all the samples are proximate to the standard red color coordinates value (0.67,0.33) of National Television standard Committee(NTSC) system [61]. The color purity for red emission was computed employing the following equation [140]:

$$\text{Color purity} = \frac{\sqrt{(x-x_i)^2 + (y-y_i)^2}}{\sqrt{(x_d-x_i)^2 + (y_d-y_i)^2}} \times 100\% \quad (3.5)$$

where (x,y) are the color-coordinates of the sample, (x_i,y_i) corresponds to white point, and (x_d,y_d) are the coordinates corresponding to dominant wavelength point. Correlated color temperatures (CCT) were calculated using the McCamy's polynomial formula [77]. Both the CCT and color purity are tabulated in Table 3.3. The results suggests that the as prepared phosphor has a warm red emission and is a potential candidate for applications in wLEDs as a red component.

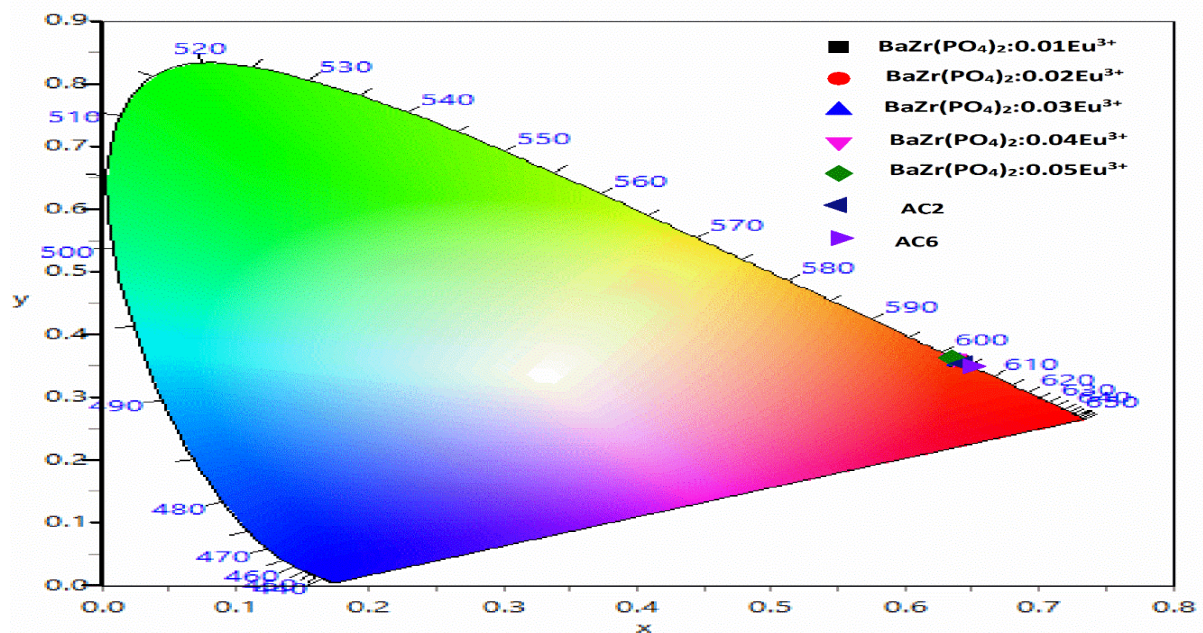


Fig 3.14. CIE chromaticity coordinates diagram of $\text{Ba}_{(1-x)}\text{Zr}(\text{PO}_4)_2:\text{xEu}^{3+}$ phosphors.

3.3.9 Decay Curve

The photoluminescent decay traces was recorded for the $\text{Ba}_{(1-x)}\text{Zr}(\text{PO}_4)_2:\text{xEu}$ ($x = 1.0, 2.0, 3.0, 4.0, 5.0$ mol%), AC2, and AC6 samples monitored for $^5\text{D}_0\text{-}^7\text{F}_2$ emission at $^7\text{F}_0\text{-}^5\text{L}_6$ excitation and are depicted in Fig.3.15. The curves were fitted employing the biexponential fit equation which relates the luminescence intensity at time t , I_t with that at time $t=0$ as:

$$I_t = I_0 + C_1 e^{\left(\frac{-t}{\tau_1}\right)} + C_2 e^{\left(\frac{-t}{\tau_2}\right)} \quad (3.6)$$

Where C_1 and C_2 are constants, τ_1 and τ_2 are fast and slow lifetimes respectively. The average lifetime τ , for the phosphors was calculated from the fitted parameters using the relation:

$$\tau = \frac{C_1 \tau_1^2 + C_2 \tau_2^2}{C_1 \tau_1 + C_2 \tau_2} \quad (3.7)$$

The average lifetime values are tabulated in the Table 3.3. The biexponential fit function with two different lifetimes suggests the presence of Eu^{3+} ions at more than one sites [179]. A decreasing trend for lifetime values with increasing concentration of Eu^{3+} ions is observed which is due to increase in non-radiative transitions among Eu^{3+} ions as the distance between them decreases [169].

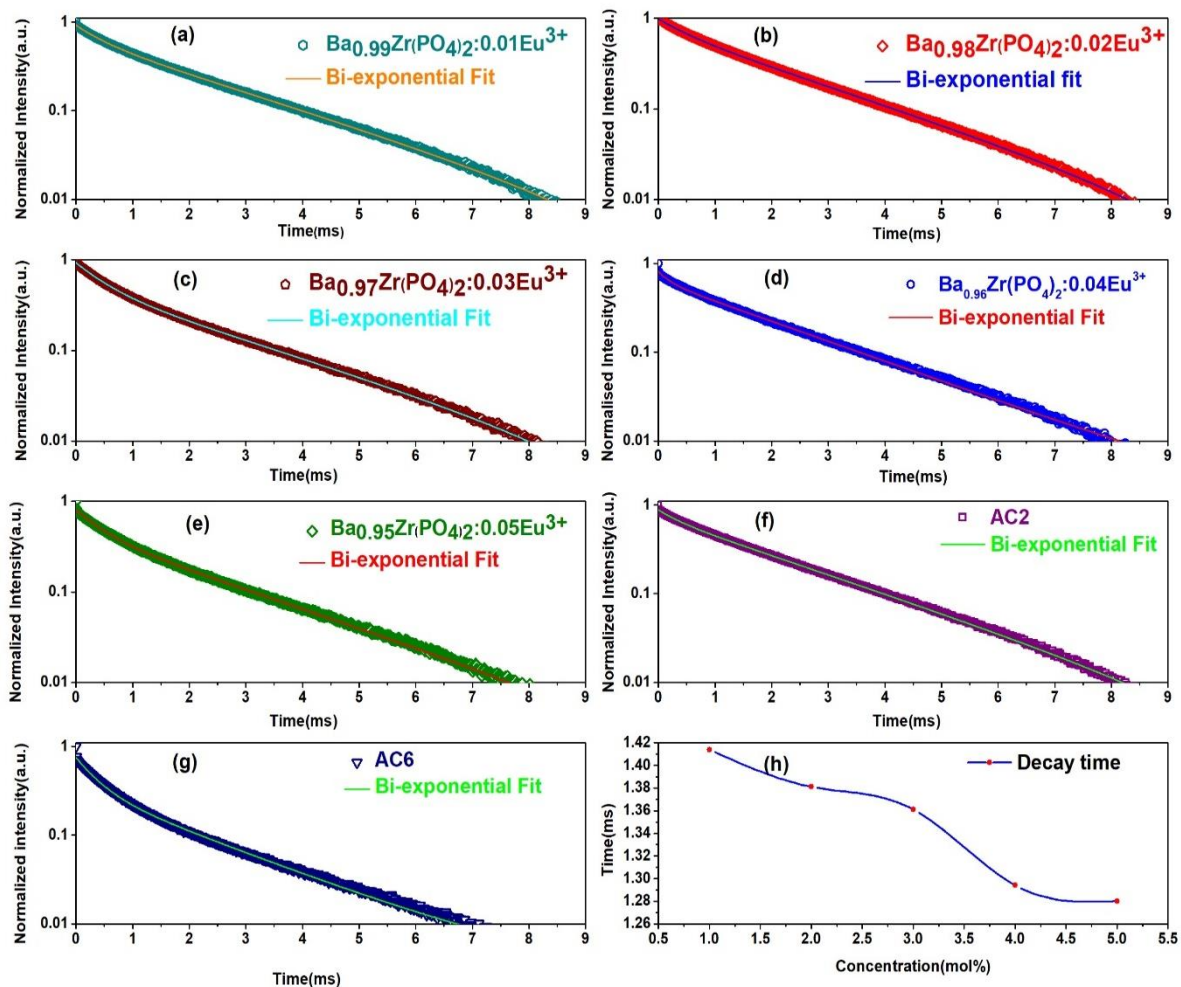


Fig.3.15. (a–g): PL decay curve of all the phosphors ($\lambda_{\text{ex}} = 494 \text{ nm}$ and $\lambda_{\text{em}} = 612 \text{ nm}$).

(h): Variation of decay time with Eu^{3+} ions concentration.

3.3.10 Judd-Ofelt Analysis of Radiative Properties

The Judd-Ofelt (J-O) theory provides significant insight about the spectroscopic behavior of trivalent rare earth ions in a particular coordination environment. The J-O Intensity parameters Ω_λ ($\lambda=2, 4$, and 6) are evaluated to conclude radiative potential of RE ions in different hosts, and identifying bonding and local structure in vicinity of RE ions. Usually, these intensity parameters are derived from absorption spectrum but in case of Eu^{3+} activated host matrices

we can evaluate Ω_2 and Ω_4 using emission spectrum due to special energy level structure of Eu^{3+} ions [53].

The transition 5D_0 to 7F_1 is magnetic dipole transition and is untrammelled from crystal field. As per J-O theory its spontaneous transmission probability (A_{01}) is related to magnetic dipole strength by following relation [53–55].

$$A_{01} = \frac{64\pi^4\nu^3n^3s_{md}}{3h(2J+1)} \quad (3.8)$$

where ν is energy in cm^{-1} corresponding to 5D_0 to 7F_1 transition, h is Planck's constant, $(2J+1)$ is degeneracy of initial state, s_{md} is magnetic dipole strength and n the refractive index for $\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$ was estimated to be 1.85 using the formula [56] :

$$\frac{n^2-1}{n^2+1} = 1 - \sqrt{\frac{E_g}{20}} \quad (3.9)$$

where, E_g the optical band gap is obtained from DRS.

The transitions 5D_0 to 7F_J ($J= 2,4$ and 6) corresponds to electric dipole transitions and their corresponding spontaneous transmission probability(A_{0J}) is related to electric dipole strength by following relation

$$A_{0J} = \frac{64\pi^4\nu^3e^2n(n^2+2)^2}{3h(2J+1)9}\sum_{\lambda=2,4,6}\Omega_{\lambda}\left|\langle 5_{D_0}||U^{(\lambda)}||7_{F_J}\rangle\right|^2 \quad (3.10)$$

where ν is energy in cm^{-1} corresponding to 5D_0 to 7F_J transition, n is refractive index, $J = 0$ for 5D_0 state , e is electronic charge (4.8×10^{-10} esu) and $\left|\langle 5_{D_0}||U^{(\lambda)}||7_{F_J}\rangle\right|^2$ is the squared reduced matrix elements, which are zero for all electric dipole transition originating from 5D_0 level except for $j'= 2, 4$ and 6 with values 0.0032 ,0.0023 and 0.0002 respectively. The ratio of radiative transition probability can be expressed in terms of ratio of integral intensity of corresponding peaks in emission spectra and hence Ω_{λ} can be obtained as per following equation [57] :

$$\Omega_{\lambda} = \frac{s_{md}\nu_1^2}{e^2\nu_{\lambda}^2}\frac{9n^3}{n(n^2+2)^2\left|\langle 5_{D_0}||U^{(\lambda)}||7_{F_J}\rangle\right|^2}\frac{\int I_{\lambda}(\nu)d\nu}{\int I_1(\nu)d\nu} \quad (3.11)$$

The value of transition energy for calculation of JO parameters has been obtained as an average over the selected transition region from emission spectra:

$$\nu_{\lambda} = \frac{\int \nu I(\nu) d\nu}{\int I(\nu) d\nu} \quad (3.12)$$

Thus obtained values of J-O Ω_2 and Ω_4 for $\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$ and flux assisted AC6 sample are listed in Table 3.4. The value of Ω_6 parameter cannot be estimated because the emission corresponding to $^5\text{D}_0$ to $^7\text{F}_6$ is located in Infrared region and could not be experimentally detected in our sample. However, the influence of Ω_6 on radiative property of Eu^{3+} can be neglected [57].

sample	$\Omega_2 (\times 10^{-20}) \text{ cm}^2$	$\Omega_4 (\times 10^{-20}) \text{ cm}^2$
$\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$	3.36	1.33
AC6	4.31	1.96

Table 3.4: J-O parameters (Ω_2 , Ω_4) of BZP3 and AC6 phosphors

The Ω_2 parameter which is associated with hypersensitive electric dipole transition $^5\text{D}_0$ to $^7\text{F}_2$ is responsive to crystal field. The high value of Ω_2 is related to higher covalence of metal ligand bonds and indicates lower symmetry of Eu^{3+} sites which is consistent with the obtained higher asymmetry ratio. The parameters Ω_4 and Ω_6 on the other hand are attributed to macroscopic bulk properties such as rigidity and viscosity of the compounds [58]. The increasing trend in value of Ω_2 from $\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$ to flux assisted AC6 sample indicates more covalency of Eu-O bond and low local symmetry of Eu^{3+} in AC6 sample. These findings are identical with the increasing trend in asymmetry ratio thus reaffirming more asymmetric nature of Eu^{3+} occupied sites in flux assisted AC6 sample.

The fluorescent branching ratio, which gives the ratio of emission of a level with respect to other levels, and is a measure of potential of emission of a level, for $^5\text{D}_0$ to $^7\text{F}_j$ transitions can be obtained using the following relation [59]:

$$\beta = \frac{A_{J-J'}}{\sum A_{J-J'}} \quad (3.13)$$

The observed fluorescent lifetime (τ_{obs}) can be related to total transition rate (A_T), radiative transition rate (A_R) and non-radiative transition rate (A_{NR}) as:

$$\frac{1}{\tau_{\text{obs}}} = A_T = A_R + A_{NR} \quad (3.14)$$

The radiative transition rate can further be used to evaluate non-radiative transition rate. The quantum efficiency defined as fraction of photons emitted to those of absorbed by Eu^{3+} ion can thus be obtained by following equation:

$$\eta = A_R / (A_R + A_{NR}) \quad (3.15)$$

The evaluated radiative transition rates and branching ratios for $^5\text{D}_0$ to $^7\text{F}_j$ transitions and quantum efficiency for $\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$ and flux assisted AC6 sample are listed in Table 3.5. It can be observed that incorporation of flux marginally improves the branching ratio for $^5\text{D}_0$ - $^7\text{F}_2$ transition. The branching ratio for $^5\text{D}_0$ - $^7\text{F}_2$ transition in BZP3 and AC6 sample is coming out to be greater than 0.5 thus indicating that they can be a potential candidate for laser action for the said transition [59].

	$^5\text{D}_0$ - $^7\text{F}_j$	Energy(cm^{-1})	Radiative Transition Rate(A_{0-j}) (s^{-1})	β	A_R (s^{-1})	A_{NR} (s^{-1})	A_T (s^{-1})	$\eta(\%)$ (s^{-1})
BZP3	$^5\text{D}_0$ - $^7\text{F}_1$	16905	92	0.28	332	402	734	45.23
	$^5\text{D}_0$ - $^7\text{F}_2$	16224	201	0.60				
	$^5\text{D}_0$ - $^7\text{F}_4$	14329	39	0.12				
AC6	$^5\text{D}_0$ - $^7\text{F}_1$	16900	92	0.23	408	433	841	48.51
	$^5\text{D}_0$ - $^7\text{F}_2$	16217	257	0.63				
	$^5\text{D}_0$ - $^7\text{F}_4$	14344	59	0.14				

Table 3.5: Radiative transition rates, Branching ratio and quantum efficiency of BZP3 and AC6 phosphors

3.4 CONCLUSIONS

Single phased $\text{Ba}_{(1-x)}\text{Zr}(\text{PO}_4)_2:x\text{Eu}$ ($x = 1.0$ - 5.0 mol%) without and with added chloride fluxes having monoclinic structure belonging to C2/m space group has been synthesized via simple solid-state route. The morphological studies and crystal structure of the prepared phosphors was investigated using XRD and SEM. The band gap of the $\text{BaZr}(\text{PO}_4)_2$ and $\text{Ba}_{0.97}\text{Zr}(\text{PO}_4)_2:0.03\text{Eu}^{3+}$ samples was computed to be 4.16 eV and 4.11 eV respectively. The photoluminescent studies revealed that UV LED chip can be used as a source of excitation for the prepared phosphor and have most dominant emission peak is in red region (612 nm). The

critical activator concentration for Eu^{3+} was found to be 3.0 mol %, with quadrupole-quadrupole interaction contributing to radiation quenching. The incorporation of NH_4Cl as flux improved the luminescent performance of the phosphor without deforming the spectral profile as well as the crystal structure. The variation of photoluminescence with temperature revealed that the prepared phosphor exhibits superior thermally stable luminescent characteristics with 0.333 eV activation energy. The calculated CIE coordinates for the prepared samples lie proximate to NTSC standard for red colour. The J-O theory was employed for evaluation of J-O parameters, transition rates branching ratio and quantum efficiency. The branching ratio value for $^5\text{D}_0$ - $^7\text{F}_2$ transition indicate the prepared phosphor as a promising prospect in laser and solid state lighting application. All the studies establish that 5 weight % NH_4Cl assisted 3 mol% Eu^{3+} activated $\text{BaZr}(\text{PO}_4)_2$ is a promising red emitter for wLEDs.

4

CHAPTER

Tunability of photoluminescent properties and energy transfer behaviour of thermally stable BaZr(PO₄)₂: Dy³⁺, Eu³⁺ Phosphor for warm white LEDs and indoor lighting applications

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- *Dy³⁺ and Dy³⁺/Eu³⁺ co-doped BaZr(PO₄)₂ phosphors were synthesized via solid-state reaction, forming a pure monoclinic phase.*
 - *The BZP:Dy³⁺ phosphor exhibited blue (482 nm) and yellow (576 nm) emissions, resulting in white light.*
 - *Co-doping with Eu³⁺ introduced red emission at 612 nm, enabling tunable color from cool to warm white.*
 - *Energy transfer from Dy³⁺ to Eu³⁺ occurred through dipole–dipole interaction as per Dexter and Reisfeld's theory.*
 - *The co-activated BZP phosphor showed 87.87% intensity retention at 420 K with 0.267 eV activation energy, confirming suitability for white LEDs.*
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4.1 INTRODUCTION

Past decades have witnessed replacement of traditional lighting sources like incandescent lamps, halogen lamps and fluorescent lamps which were less efficient and detrimental to environment by white light emitting diodes (w-LEDs) [77–79]. The w-LEDs have emerged as a viable alternative by dint of their superior attributes of being more efficient, affordable, less power consuming, more durable and friendly to environment [60,80,81]. Currently most prevalent technique to realize w-LEDs is to couple blue InGaN LED chip with YAG: Ce phosphor having broad yellow emission. Though this technique yields LEDs with high luminous efficacy and good chromaticity but due to absence of red light component these devices emit cold white light having upraised correlated color temperature and modest color rendering index [77,79,82]. The aforesaid demerits are addressed using a strategy which involves coating of three different multiphase phosphor having emission in red, green and blue region on an ultraviolet or near UV LED chip. However, this method exhibits low luminescence efficiency as blue emitted photons suffers reabsorption by red and green phosphors [83–85]. Therefore development of a single phased co-doped phosphor that can be coupled with UV or NUV chip can provide a viable way out for warm white light with high luminous efficacy [80,84,86]. Among the rare earths Dy^{3+} due to its distinctive characteristic spectrum with bands in yellow and blue region is a promising dopant for white light emission when excited by near UV wavelength due to presence of intra 4f electronic configurational band [34,87]. However here again due to lack of red component, Dy^{3+} doped phosphor will not be suitable for indoor lighting application. Nevertheless, addition of Eu^{3+} ions to compensate for red component can help in achieving better CRI and CCT for warmer emission. In this regard many works has been reported where Eu^{3+} owing to its characteristic red emission resulting from intra 4f transitions from $^5\text{D}_0$ to $^7\text{F}_j$ ($j=1,2,3,4,5$) has been added to overcome the red deficiency [88–91]. Therefore, by co-doping Eu^{3+} ions in Dy^{3+} activated phosphor we can explore energy transfer between Dy^{3+} and Eu^{3+} to achieve lower CRI value for white light having tunable CCT shifting towards warm region from cool region.

The choice of host material plays a crucial role in development of single-phase phosphor material as crystal field of host matrix influence the optical properties of phosphor [92]. So far many host matrices notably aluminates, phosphates, oxides, zincates, molybdates, tellurites, silicates etc. have been exploited for the generation of white light by different workers. The luminescent properties of $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped SrLaLiTeO_6 phosphor synthesized via solid state

route has been studied for obtaining white light by spectral adjustment achieved by varying doping concentrations [93]. Chen et al. have obtained the tunability from cold to warm white light in $\text{SrLa}_{0.97-x}\text{AlO}_4: 0.03\text{Dy}^{3+}, x\text{Eu}^{3+}$ phosphor by varying relative concentration of Dy^{3+} and Eu^{3+} [94]. Blue to white colour tuning in $\text{BaY}_2(\text{MoO}_4)_4: \text{Dy}^{3+}/\text{Eu}^{3+}$ with good thermal stability has been achieved by Yifan et al [95]. Deepali et al. have synthesized $\text{Na}_4\text{Ca}_4\text{Si}_6\text{O}_{18}:\text{Dy}^{3+}/\text{Eu}^{3+}$ phosphor via solid state reaction technique and investigated its optical properties [78]. Among the inorganic oxides, like silicates, the phosphates have been a popular choice as a host material due to their significant attributes such as remarkable physical and chemical stability, excellent thermal and optical stability, low temperature synthesis, cost effectiveness, eco- friendliness and a large optical band gap [73]. Therefore, oxide-based phosphate host matrix has been chosen to investigate luminescent properties by subsequent addition of dopant ions. The $\text{BaZr}(\text{PO}_4)_2$ (BZP) belongs to orthophosphate family having 3-D rigid framework of polyhedrons of BaO_{10} , ZrO_6 , and PO_4 which possess stability at high temperatures, low thermal conductivity, fast ionic conductivity and low thermal expansion. Their structure provides flexibility to accommodate different cations with in their framework or inter-framework positions without disturbing the basic structure of their lattice [74–76].

The present study focuses on development of monophase white radiant $\text{BaZr}(\text{PO}_4)_2$ (BZP) phosphor with color tunability attained by varying parameters wavelength of excitation and relative concentration of dopant ions. In this study, solid state reaction route has been exploited for synthesizing BZP: Dy^{3+} and BZP: $\text{Dy}^{3+}/\text{Eu}^{3+}$ phosphors. The crystallographic phase, microstructural, photoluminescent, decay kinetics and energy transfer studies have been carried out. The colorimetric properties and stability of the phosphor luminescence at elevated temperatures has been investigated in detail for prospective use of BZP: $\text{Dy}^{3+}/\text{Eu}^{3+}$ phosphor in w-LEDs for indoor lighting application.

4.2 SAMPLE PREPARATION AND CHARACTERIZATION

4.2.1 TECHNIQUES:

The solid-state synthesis route was followed for preparing BZP: Dy^{3+} and BZP: $\text{Dy}^{3+}/\text{Eu}^{3+}$ samples. Firstly, a series of Dy^{3+} doped BZP phosphor were synthesized by taking stoichiometric amount of Dy_2O_3 , BaCO_3 , ZrO_2 and $(\text{NH}_4)\text{H}_2\text{PO}_4$ as raw materials and mixing together in acetone in Agate mortar followed by manual grinding for 90 minutes. The obtained grounded powder was then sintered at 1373 K in a programmable high temperature furnace

followed by a natural cooling to room temperature. The sintered hard mass was then grounded again in Agate mortar to obtain fine powder sample, which was used for subsequent characterizations and analysis. The samples with 0.0, 1.0, 1.5, 2.0, 2.5, 3.0 and 3.5 mol % of Dy^{3+} were labelled as BZP, BPD1, BPD1.5, BPD2, BPD2.5, BPD3 and BPD3.5 respectively. For the co-doped samples along with above mentioned precursors Dy_2O_3 in stoichiometric ratio were taken and the same route and conditions were followed. For the co-doped samples, the doping concentration of Dy^{3+} was fixed at 2.5 mol% and amount of Eu^{3+} in mol% was varied from 1.0 mol% to 5.0 mol% and were labelled BPDE1, BPDE2, BPDE3, BPDE4 and BPDE5 respectively. Additionally, the sample having composition of 1.0 mol% of Dy^{3+} with 1.0 mol% of Eu^{3+} was labelled BPD1E1.

The structural studies for pure BZP and BZP: $\text{Dy}^{3+}/\text{Eu}^{3+}$ phosphor has been carried out on PANalytical X'pert PRO X- Ray diffraction system which utilizes Cu-K_α radiation ($\lambda = 1.54 \text{ \AA}$). The microstructure studies and elemental analysis has been carried out utilizing JEOL Japan JSM 6610LV model of Scanning Electron Microscope. The photoluminescent studies has been carried out on Spectro-fluorophotometer of JASCO FP-8300. The decay kinetics has been studied using Edinburgh FL920 Fluorescence Life Time Spectrometer instrument. The temperature dependent spectrometer of FLAME-S-XR1-ES recorded the variation in photoluminescence with temperature in 300 K to 450 K range.

4.3 RESULT AND DISCUSSION:

4.3.1 Phase identification, estimation of crystallite size and surface morphology

The Purity of phase of pure, Dy^{3+} activated and $\text{Dy}^{3+}/\text{Eu}^{3+}$ bi-activated BZP phosphors was authenticated by XRD examination. As depicted in Fig.4.1 diffraction pattern of all the samples are well matched to the standard ICDD PDF card no 01-074-8689 which corresponds to the monoclinic phase of $\text{BaZr}(\text{PO}_4)_2$ belonging to space group $\text{C2/m}(12)$ having lattice constants $a=8.531 \text{ \AA}$, $b=5.293 \text{ \AA}$, $c = 7.875 \text{ \AA}$ and $\beta = 93.8^\circ$. Fig. 4.1(b) shows the 3-dimentional ball and stick model of the crystal structure produced by VESTA software using the data retrieved from the Materials Project for $\text{BaZr}(\text{PO}_4)_2$ (mp-556139) from database version v2023.11.1. . The structure consists of alternate layers of $\text{Zr}(\text{PO}_4)_2$ group formed by corner sharing of ZrO_6 octahedra with PO_4 tertrahedra and of Ba cations, which are parallel to (011) plane. So bigger ZrO_6 and BaO_{10} polyhedra are intercalated along c axis. The smaller PO_4 tetrahedra is tilted and shares corner with three ZrO_6 octahedra and one BaO_{10} polyhedra Since no impurity peak

appeared in the diffraction patterns of Dy^{3+} activated and $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-activated samples thus establishing that incorporation of Dy^{3+} and Eu^{3+} did not bring any structural deviations. The probable substitution of dopant ions can be speculated on the basis of percentage radius difference D_r given by following equation [96]:

$$D_r = \frac{R_m(\text{CN}) - R_d(\text{CN})}{R_m(\text{CN})} \quad (4.1)$$

Where R_m and R_d are ionic radii of the original and dopant ions in the matrix and CN is the coordination number. The D_r for Dy^{3+} ions ($R = 0.91 \text{ \AA}$, $\text{CN} = 6$) for host cations $\text{Ba}^{2+}/\text{Zr}^{4+}$ ($R = 1.35/0.72 \text{ \AA}$, $\text{CN} = 6$) were calculated and it being less than 30% for Dy^{3+} and Zr^{4+} suggests substitution of Zr^{4+} ions by Dy^{3+} ions. Moreover, as displayed in the right panel of Fig. 4.1(a) a shift in diffraction peak towards smaller diffraction angles is observed as the concentration of Dy^{3+} ions is increased which may be attributed to substitution of smaller ionic radii Zr^{4+} ions by larger ionic radii Dy^{3+} ions [97].

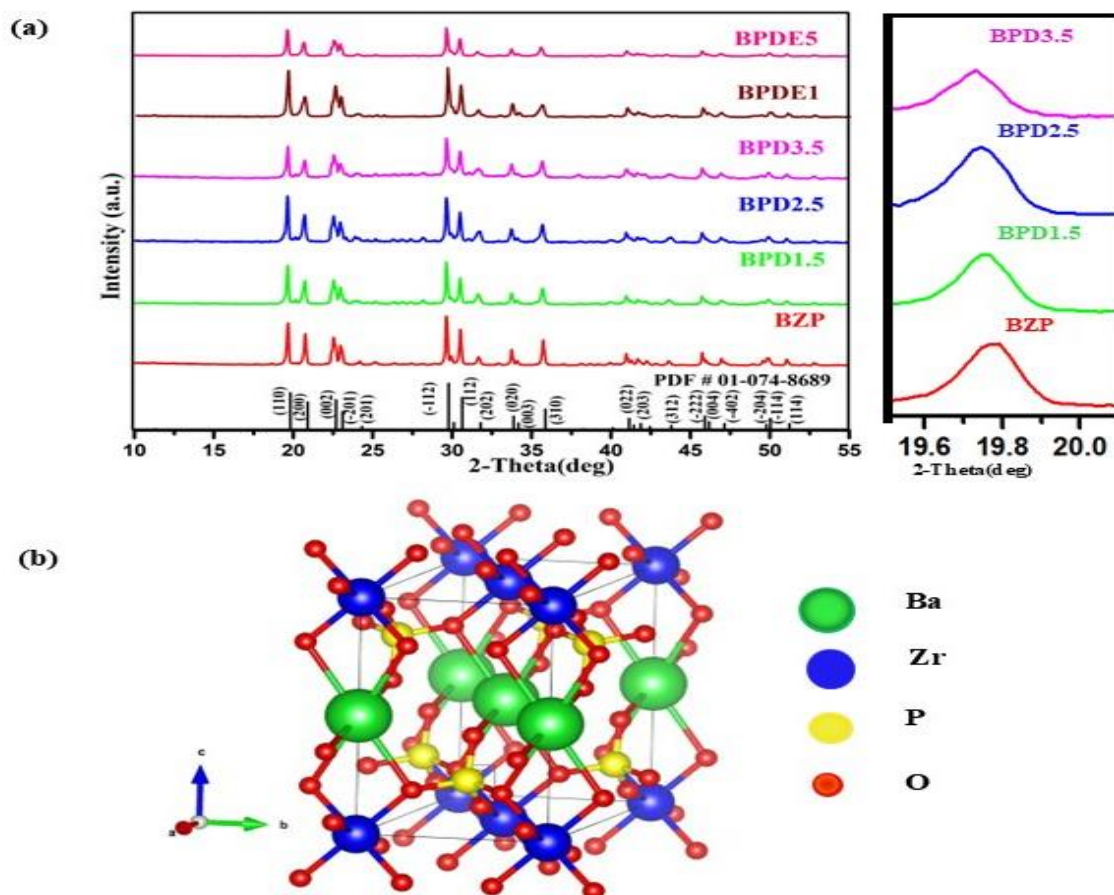


Fig.4.1. (a) XRD pattern for un-doped, Dy^{3+} singly doped and $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped BZP phosphors along with standard diffraction pattern. **(b)** Crystal structure of $\text{BaZr}(\text{PO}_4)_2$

Sample	Debye-Scherrer Method D (nm)	Williamson Hall Method (nm)		Dislocation Density δ (nm^{-2})	
		D(nm)	Microstrain	Debye-Scherrer Method	Williamson Hall Method
BZP	42.96	55.91	0.00065	0.00054184	0.00032
BPD1.5	34.91	55.01	0.00164	0.00082054	0.00033
BPD2.5	33.32	51.35	0.00216	0.00090072	0.000379
BPD3.5	32.28	46.84	0.00152	0.00095969	0.000456
BPDE1	30.08	42.016	0.00103	0.00110521	0.000566
BPDE5	27.47	34.75	0.00165	0.0013252	0.000828

Table 4.1. Crystallite size (D), microstrain and dislocation density (δ) of pure and doped $\text{BaZr}(\text{PO}_4)_2$

The crystallite size of the phosphor is an important parameter which influences its photoluminescent properties [98]. Evaluation of crystallite size provides an insight about the crystallinity of the prepared phosphor as well as the structural dislocations introduced in the lattice which impacts the luminescence of the phosphor. The mean size of the crystallites of the phosphors was estimated from physical broadening of diffraction peaks using Debye-Scherrer formula for all the major peak planes [99]:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (4.2)$$

Where D, K, β and λ are crystallite size, Scherrer constant (= 0.9), fullwidth at half maxima conforming to Bragg's angle θ and wavelength of X-rays. The obtained value of average crystallite size varied in range 27– 43 nm for different compositions and the values are given in Table 4.1. The Scherrer equation underestimates the crystallites size because as per Scherrer formula the crystallite size is independent of microstrain in lattice arising due to intrinsic defects and dislocation density.

Since Scherrer equation doesn't take into account intrinsic defects and strain effects so Williamson Hall approach which incorporates strain induced widening thus giving more accurate and comprehensive perception of the variation in crystal structure with incorporation of dopants. The Williamson Hall plots are obtained using the equation given by [100]:

$$\beta \cos \theta = \frac{K\lambda}{D} + 4\varepsilon \sin \theta \quad (4.3)$$

where, ε is the lattice strain. So, a plot of $\beta \cos \theta$ and $4 \sin \theta$ will be a straight line whose slope will equate to lattice strain and the intercept, $K\lambda/D$ will yield the value of crystallite size (D). Such plots are portrayed in Fig.4.2 for undoped, Dy^{3+} doped and $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped samples. The average crystallite size and lattice strain values obtained using Williamson Hall approach are summarized in table 4.1. The values of lattice strain contemplate the level of distortions and defects in the lattice which is dependent on the type and extent of doping level [101]. It is clear from table 4.1 that undoped sample exhibits the minimum strain value and it increases as dopants ions are introduced suggesting increment in strain as small size Zr^{4+} is substituted by larger Dy^{3+} ions [102]. Further the Williamsons and Smallman's formulae given below was utilised for estimation of dislocation density (δ) from crystallite size D [103]:

$$\delta = \frac{1}{D^2} \quad (4.4)$$

It can be observed from table 4.1 that the result retrieved from both the formulations are consistent and as dopant concentration increases the crystallite size diminishes. This decreasing trend is attributed to lattice distortions and defects arising due to introduction of dopant ions inside host lattice thus inhibiting growth of larger crystallites [104]. These structural distortions resulting from dopant ions may influence the local crystal field environment and are likely to improve the optical properties of the phosphor by altering the electronic transitions and facilitating energy transfer between dopant ions [101,105]. The crystallite size values obtained from Williamson Hall approach were moderately higher than Scherrer formula because the former approach took in to account the strain broadening [106].

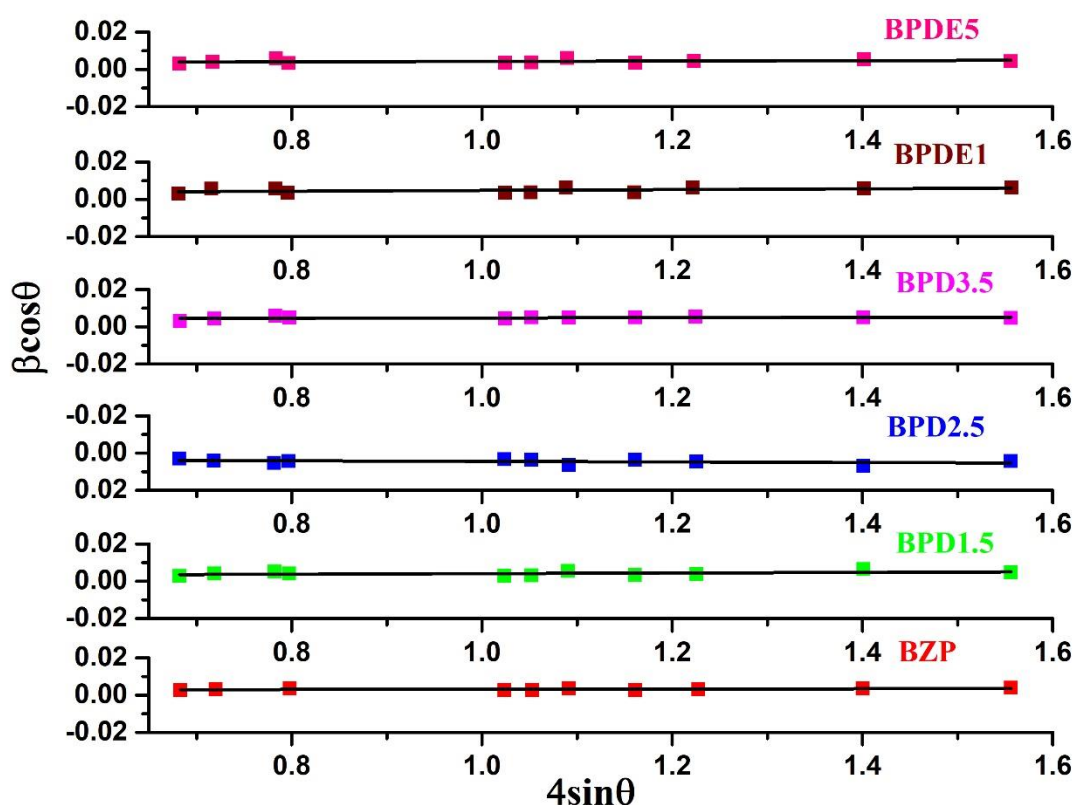


Fig. 4.2. Williamson hall plot for un-doped, Dy^{3+} singly doped and $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-doped BZP phosphors

4.3.2 Microstructure characteristic and elemental analysis (SEM and EDS:

The surface morphology along with the elemental composition of the prepared samples has been analyzed via SEM and energy dispersive spectrometer (EDS) spectrum. Fig. 4.3(a) and (b) depicts the SEM images for BPD2.5 and BPDE1 phosphor. The images reveal uneven and asymmetrical size and morphology of the particles which are gloomed on to each other. The phosphor material's particle size, which is related to the luminescent performance and is a crucial parameter for its assessment for the application, varies in a range of 1-5 μm for both the samples [107,108]. The particle size examination reveals that it is conformable to the commercial phosphors [109]. The EDS spectrum depicted via Fig.4.3(c) and (d) reveals characteristic peaks corresponding to Ba, Zr, O, P, Dy and Eu thus verifying presence of these elements in the samples. Moreover, absence of any other element or contaminant implies high

purity of the prepared phosphors. Thus, the effective incorporation of Eu^{3+} and Dy^{3+} ions inside host matrix is confirmed by energy dispersive spectrometer.

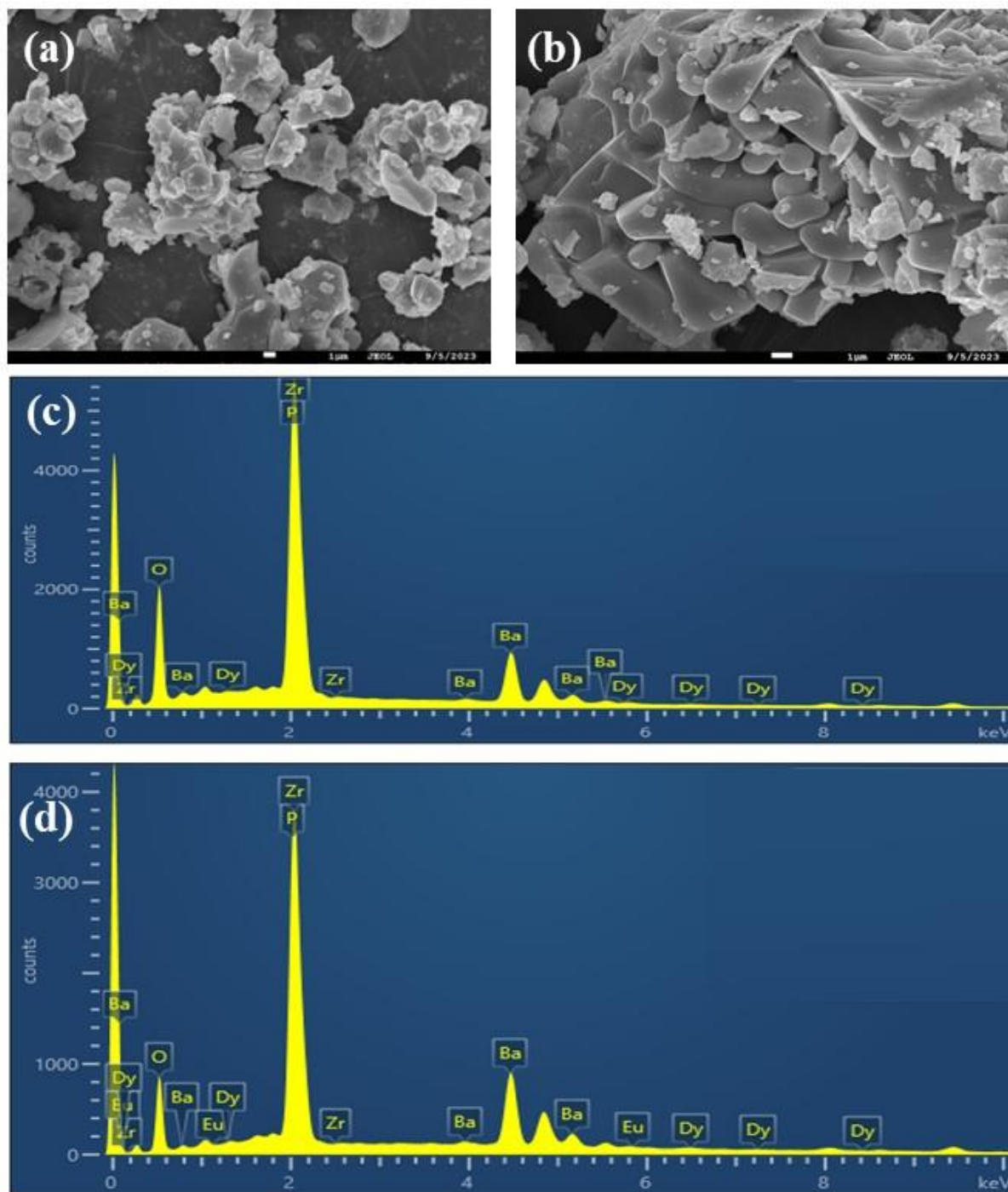


Fig.4.3.(a)The SEM image of $\text{BaZr}(\text{PO}_4)_2:0.025\text{Dy}^{3+}$ (b) The SEM image of $\text{BaZr}(\text{PO}_4)_2:0.025\text{Dy}^{3+}, 0.01\text{Eu}^{3+}$ (c) EDS profile of $\text{BaZr}(\text{PO}_4)_2:0.025\text{Dy}^{3+}$ (d) EDS profile of $\text{BaZr}(\text{PO}_4)_2:0.025\text{Dy}^{3+}, 0.01\text{Eu}^{3+}$

4.3.3 Spectroscopic studies of BaZr(PO₄)₂: Dy³⁺ Phosphors

Fig.4.4(a) depicts the photoluminescence excitation spectra for BZP: Dy³⁺ with different concentrations of Dy³⁺ monitored for ⁴F_{9/2} to ⁶H_{13/2} emission of Dy³⁺ conforming to 576 nm wavelength. All samples exhibited sharp peaks arising due to intra f-f characteristic electronic transitions of Dy³⁺ from ⁶H_{15/2} ground state to different excited states located at 349 (⁶P_{7/2}), 386 (⁴I_{13/2}), 363(⁶P_{5/2}), 452(⁴H_{15/2}), 324 (⁶P_{3/2}), 424 (⁴G_{11/2}) and 475 nm (⁴F_{9/2}) in decreasing order of their intensity [110,111]. The presence of most intense peak at 349 nm suggests that Dy³⁺ doped BZP can be excited using emission from UV LED chip thus it is appropriate for fabrication of w-LEDs. Moreover, the excitation spectrum is most intense when the doping concentration is 2.5 mol% wherein peak profile remains unaltered with variation in concentration of Dy³⁺. Fig.4.4(b) depicts the emission spectra of BZP: xDy³⁺ (x=1.0 -3.5 mol%) phosphor excited via 349 nm photon corresponding to ⁶H_{15/2} to ⁶P_{7/2} transition of Dy³⁺. When stimulated with UV light the 4f electron of Dy³⁺ ions gets excited from ⁶H_{15/2} ground state to various excited states from ⁴F_{9/2} to ⁶P_{7/2}, from where they get relaxed to the lowest excited state ⁴F_{9/2} state via cascaded non radiative transition process. Thereafter, electronic transitions from ⁴F_{9/2} state to ⁶H_{13/2} and ⁶H_{15/2} ground state generates characteristic emissions as described in Fig.4.7 [112]. As shown in Fig. 3.4(b) the PL spectra include three peaks where two peaks are intense which are positioned at 482 nm and 576 nm conforming to ⁴F_{9/2} to ⁶H_J (J = 15/2 and 13/2 respectively) transition belonging to the Dy³⁺ and one weaker band at 667 nm conforming to ⁴F_{9/2} to ⁶H_{11/2} transition. Among these transitions, the one falling in blue region at 482 nm is magnetic dipole transition whereas the transition falling in yellow region at 586 nm is electric dipole transition. The electric dipole transition is highly responsive to the environment around Dy³⁺ while magnetic dipole transition is unresponsive to the location of Dy³⁺ [113,114]. The PL spectra reveal more pronounced electric dipole transition indicating the presence of Dy³⁺ ions at low symmetry locations having non-inversion centers [115]. Hence the asymmetry ratio which is yellow to blue (Y/B) intensity ratio is key indicator of environment around Dy³⁺ ions. So, if Y/B value is less than 1 it indicates high symmetry location about Dy³⁺, while a value of greater than one suggests reduced symmetry environment at Dy³⁺ locations. Moreover when Y/B ratio is close to one, it indicates white emission of phosphor. [116]. The calculated Y/B ratio with respect to different concentrations of Dy³⁺ are tabulated in Table 4.2. Moreover, concentration dependent spectral analysis from Fig. 4.4(b) reveals that the shape and location of spectral peaks remain unaltered with variation in concentration and only intensity variation is observed. Further, it is evident from the bar graph in Fig. 4.4(c) that increasing Dy³⁺

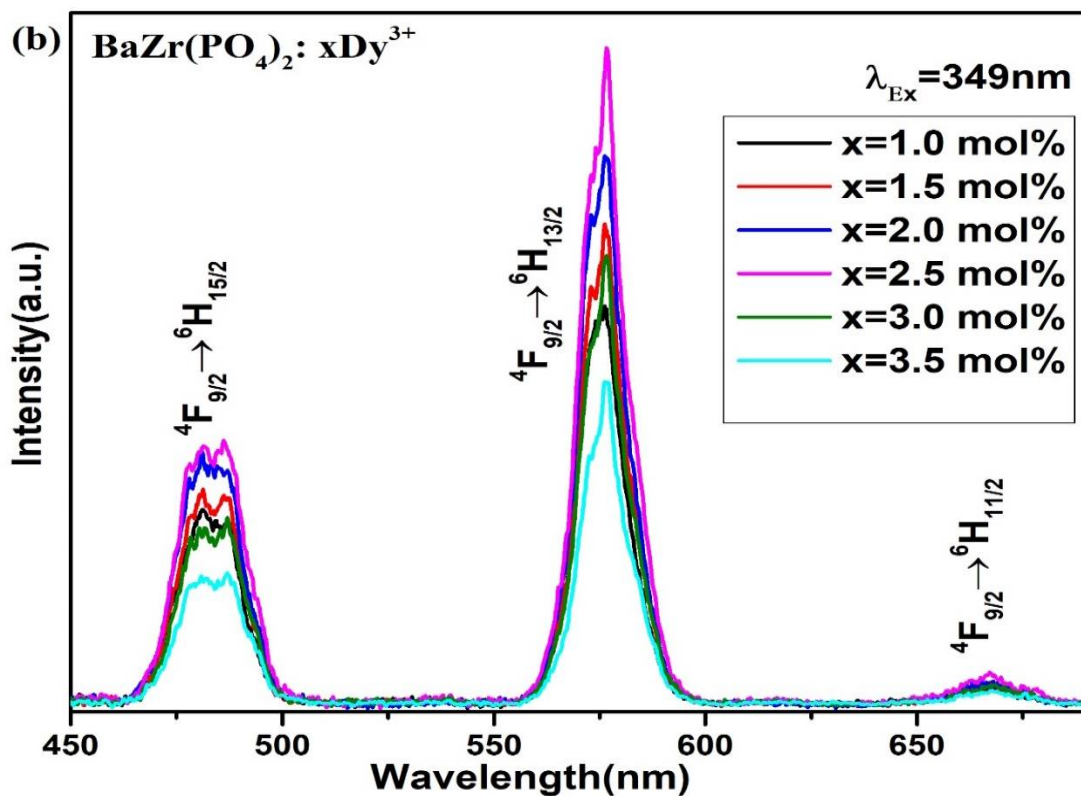
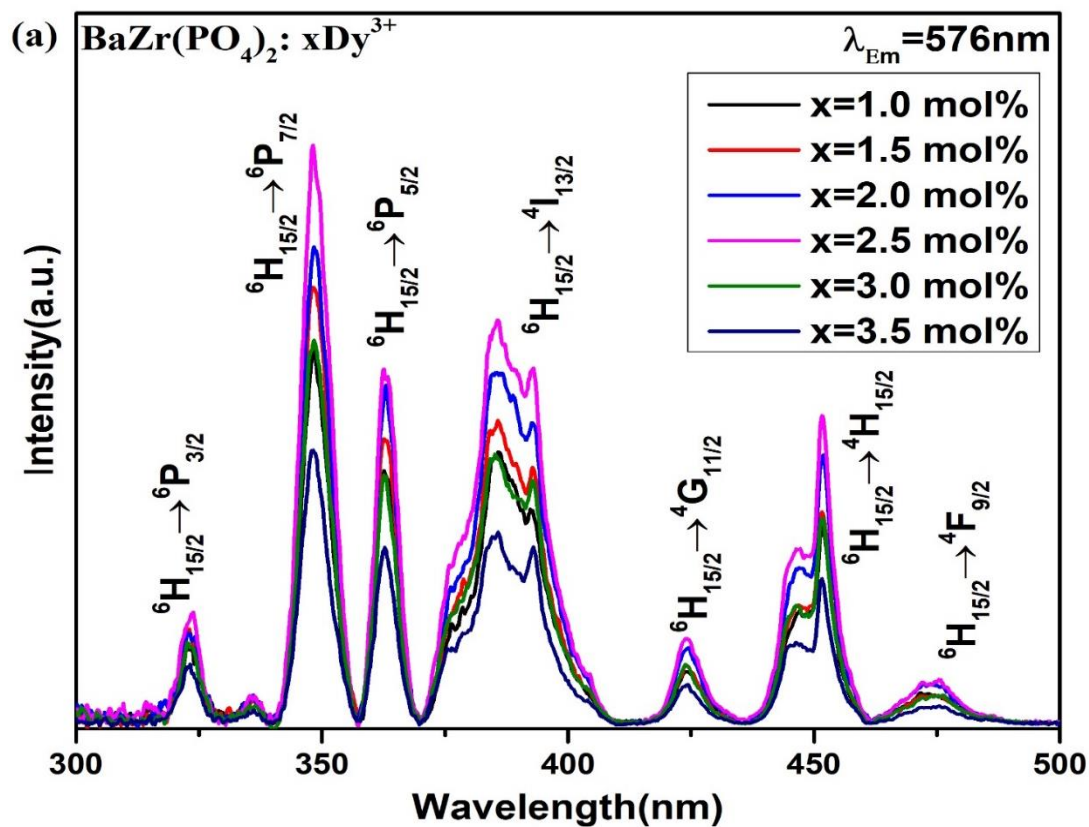
concentration enhances the spectral intensity and a maximum intensity is achieved for a concentration of 2.5 mol%, beyond which increase in Dy^{3+} concentration turns down the spectral intensity. This decline in emission intensity is accredited to phenomenon of concentration quenching occurring due to cross relaxation mechanism depicted in Fig.4.7. The non-radiative energy exchange process amidst proximate Dy^{3+} ions gives rise to concentration quenching [117,118]. The critical distance R_c is obtained to further investigate the origin of energy loss mechanism involved, which is given by Blasse's formulae [110]:

$$R_c = 2 \sqrt[3]{\frac{3V}{4\pi x_c N}} \quad (4.5)$$

Where, V is unit cell volume ($V=354.81 \text{ \AA}^3$), x_c is critical concentration ($x_c=0.025$) and N is available cation sites in unit cell ($N=2$). The calculated value of R_c for BZP: Dy^{3+} phosphor comes out to be $23.85 \text{ \AA}$. Since the obtained value of critical distance is exceeding $5 \text{ \AA}$, exchange interaction is not the main channel liable for concentration quenching. The larger value of R_c suggests that concentration quenching mechanism occurs via multipolar interaction, which can further be investigated for its character by employing Dexter's theory using the equation [32,33,81]:

$$\log\left(\frac{I}{x}\right) = -\frac{\theta}{3}\log(x) + A \quad (4.6)$$

where, x is relative amount of dopant ion present in phosphor, I is emission intensity, θ is constant of multipolar interactions which takes value equal to 6, 8 and 10 for dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions in their respective order and A is a constant. So, a plot for Equation 1 would be a straight line for $\log(x)$ as abscissa and $\log(I/x)$ as ordinate with slope equal to $\theta/3$. Fig.4.4(d) depicts such a plot for BZP: $x\text{Dy}^{3+}$ ($x = 2.5, 3.0$ and $3.5 \text{ mol\%}$) which is a straight line with slope equal to -2.1833 thus giving value of θ around 6 thus establishing dipole-dipole interactions responsible for non-radiative energy loss.



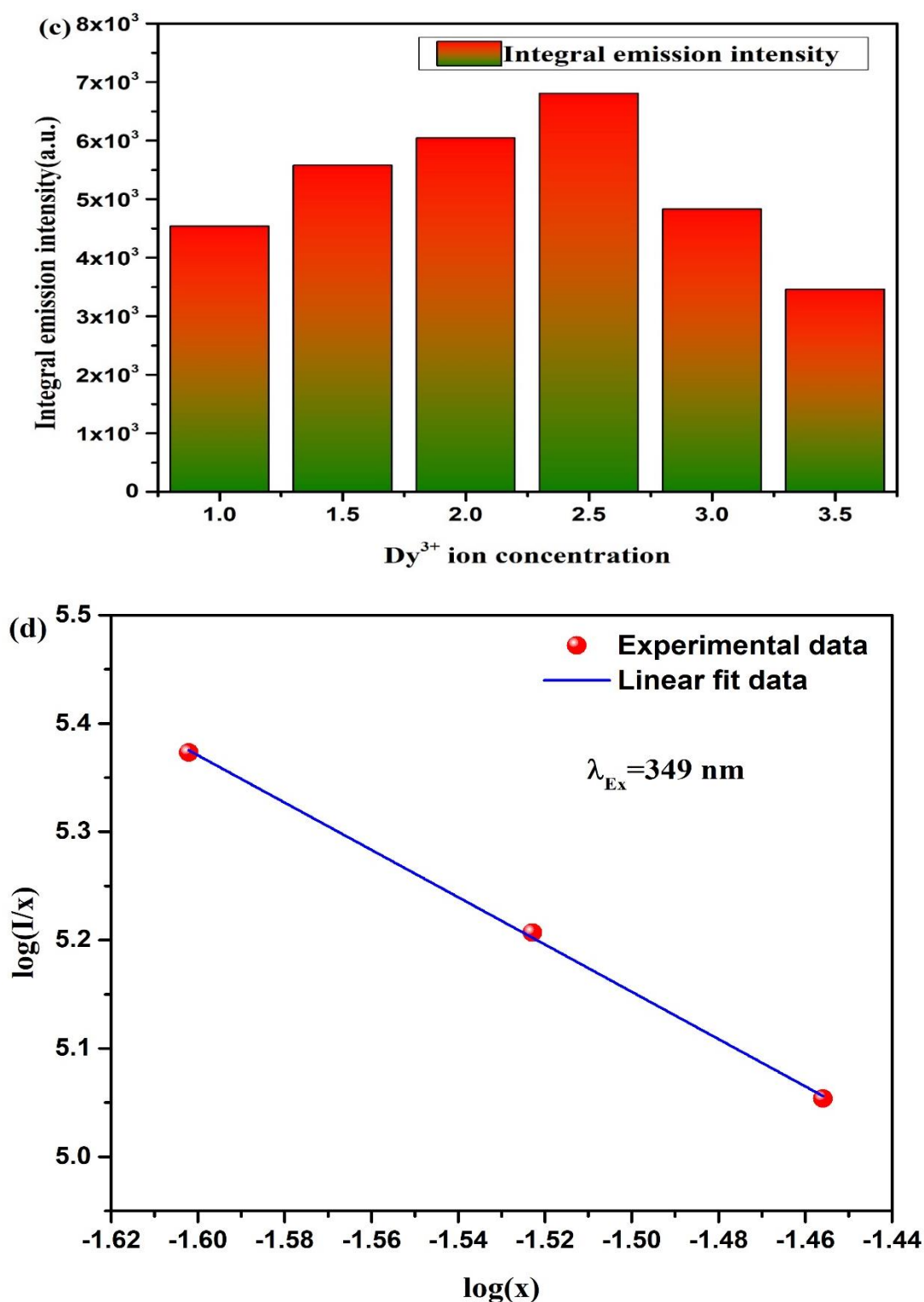


Fig.4.4. (a): The excitation spectra of $\text{Ba}_{(1-x)}\text{Zr}(\text{PO}_4)_2:x\text{Dy}^{3+}$ ($x = 1.0, 1.5, 2.0, 2.5, 3.0$ and 3.5 mol%) at 576 nm emission wavelength. **(b):** The emission spectra of $\text{Ba}_{(1-x)}\text{Zr}(\text{PO}_4)_2:x \text{Dy}^{3+}$ ($x = 1.0, 1.5, 2.0, 2.5, 3.0$ and 3.5 mol%) under 349 nm excitation wavelength. **(c):** Relationship between Emission intensity and Dy^{3+} ion concentration. **(d):** Plot of $\log(I/x)$ versus $\log(x)$ for $\text{Ba}_{(1-x)}\text{Zr}(\text{PO}_4)_2:x \text{Dy}^{3+}$ ($x = 2.5, 3.0$ and 3.5 mol%)

Sample	Y/B Ratio	Fluorescent life time (ms)	PL Quantum efficiency (%)	Non radiative relaxation rate (s ⁻¹)
BPD1	1.610813	0.680761	95.38476	67.79537
BPD1.5	1.695854	0.667595	93.54	96.76521
BPD2	1.675745	0.658766	92.30293	116.8408
BPD2.5	1.746408	0.647743	90.75844	142.6732
BPD3	1.778809	0.628739	88.09566	189.3369
BPD3.5	1.712595	0.61355	85.96749	228.7101

Table 4.2. Y/B Ratio, Fluorescent lifetime, quantum efficiency and non-radiative rates for Ba_(1-x)Zr(PO₄)₂: xDy³⁺ (x = 1.0, 1.5, 2.0, 2.5, 3.0 and 3.5 mol%) phosphors.

4.3.4 Spectroscopic studies of BaZr(PO₄)₂: Dy³⁺, Eu³⁺ Phosphors:

Hence the most effective concentration of Dy³⁺ ions in BZP host matrix is 2.5 mol% for which emission intensity is maximum with two intense peaks in blue (482 nm) and yellow (576 nm) and a very faint peak in red region (667 nm). Since these Dy³⁺ ions doped phosphor has a negligible red emission so they have been co-doped with Eu³⁺ ions with optimize Dy³⁺ concentration in order to enhance emission in red region for attaining pure white emission and achieve color tunability. Moreover, the presence of closely matched excitation levels of Eu³⁺ ions and Dy³⁺ ions within near ultraviolet region facilitates excitation of phosphor by a near ultraviolet excitation source.

The PL excitation spectra of BZP: 1.0Eu³⁺, BZP: 1.0Dy³⁺ and BZP: 1.0 Dy³⁺, 1.0 Eu³⁺ phosphor monitored at most intense emission wavelength of Dy³⁺ (576 nm) and Eu³⁺ (612 nm) has been compared in Fig.4.5. In PLE spectrum monitored for 612 nm emission for BZP: 1.0Eu³⁺ phosphor only 4f-4f transition peaks corresponding to characteristic transitions of Eu³⁺ centred at 360nm (⁷F₀-⁵D₄), 380nm (⁷F₀-⁵L₇), 392nm (⁷F₀-⁵L₆), 414nm (⁷F₀-⁵D₃) and 463 nm (⁷F₀-⁵D₂) are present. Similarly, the PLE spectrum for BZP: 1.0Dy³⁺ phosphor monitored for 576 nm exhibited 4f-4f transition peaks corresponding to Dy³⁺ ions only as discussed above. While it can be observed that for 1 mol% of Eu³⁺ - 1 mol% of Dy³⁺ co-doped BZP phosphor that the PLE spectrum monitored at 612 nm wavelength exhibits not only characteristic 4f-4f transitions corresponding to Eu³⁺ but the excitation peaks belonging to Dy³⁺ at 349 nm (⁶H_{15/2}

to ${}^6P_{7/2}$) and 363 nm (${}^6H_{15/2}$ to ${}^6P_{5/2}$) are also present indicating that absorbed excitation energy by Dy^{3+} ions is partially moved to Eu^{3+} ions. So, the presence of excitation bands of Dy^{3+} in excitation spectrum when it is monitored at emission wavelength corresponding to Eu^{3+} indicates some transfer of energy from Eu^{3+} to Dy^{3+} . An alike excitation spectrum is observed when monitored at 576 nm wavelength with Dy^{3+} characteristic peaks being more pronounced. The common excitation band range lying in near UV region of electromagnetic spectrum shared by Dy^{3+} and Eu^{3+} ions allows the co-doped phosphor to be driven with a photon with n-UV wavelength.

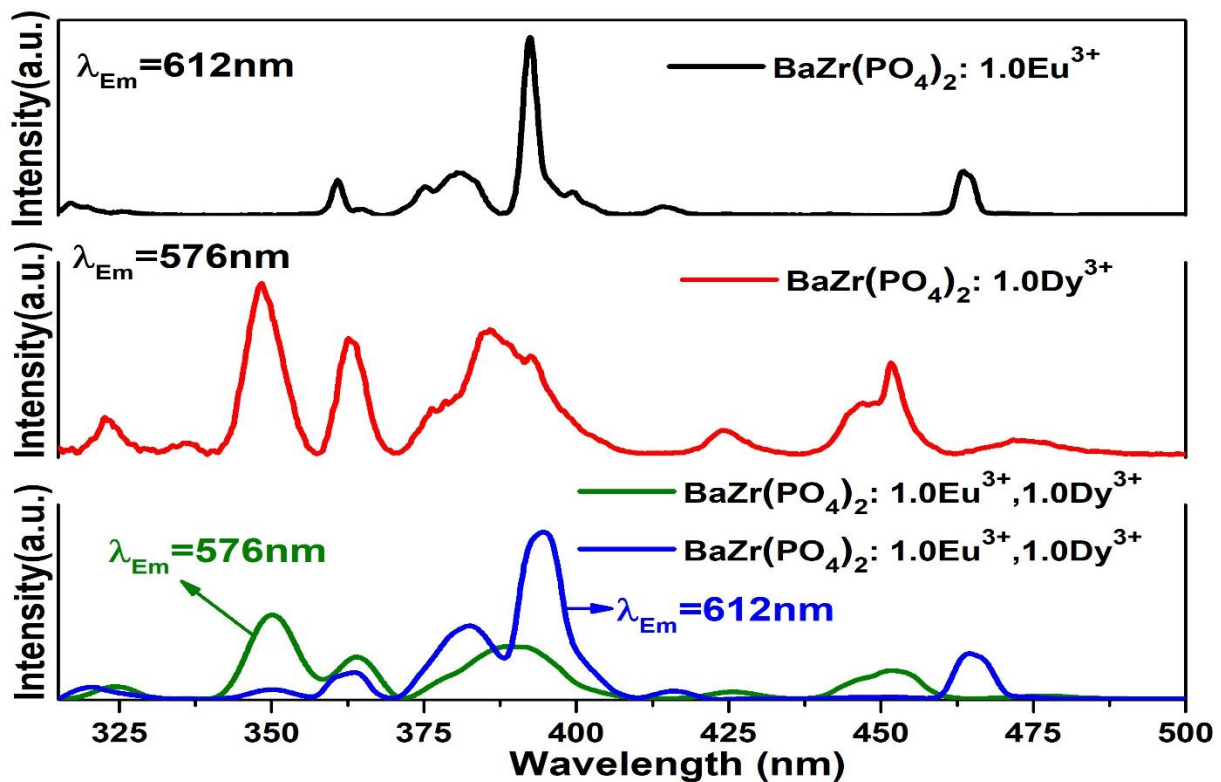


Fig.4.5. The photoluminescence excitation spectra of $BaZr(PO_4)_2:1.0 Eu^{3+}$, $BaZr(PO_4)_2:1.0 Dy^{3+}$ and of $BaZr(PO_4)_2:1.0 Eu^{3+}, 1.0 Dy^{3+}$ co-doped phosphor by monitoring with emission wavelengths at both 576 nm (yellow) and 612 nm (red)

Furthermore, to examine the process of energy transference among Eu^{3+} ions and Dy^{3+} ions, a set of samples of bi-activated phosphors $BZP: 2.5Dy^{3+}, yEu^{3+}$ were prepared. The photoluminescence spectra of these co-doped phosphors have been investigated by varying excitation wavelengths at 349, 363, 380 and 394 nm to manifest the energy transfer mechanism and colour tunability. Fig.4.6(a-d) illustrates PL emission spectra of $BZP: 2.5Dy^{3+}, yEu^{3+}$ ($y =$

1-5 mol%) phosphors when excited at wavelength of 349, 363, 380 and 394nm respectively. The simultaneous presence of characteristics bands of Eu^{3+} and Dy^{3+} ions can be seen distinctly in emission profile. The bands placed at 482 and 576 nm belongs to $^4\text{F}_{9/2}$ to $^6\text{H}_J$ ($J = 15/2$ and $13/2$ respectively) Dy^{3+} ion transitions, while the ones at 591, 612, 652 and 700 nm are ascribed to $^5\text{D}_0$ - $^7\text{F}_{1-3}$ transitions of Eu^{3+} ions. It is conspicuous from Fig.4.6 that excitation wavelengths and relative Dy^{3+} and Eu^{3+} ions concentrations can remarkably influence the strengths of emission bands of Eu^{3+} and Dy^{3+} . Fig.4.6(a) displaying emission profile monitored by exciting samples with pure Dy^{3+} characteristic excitation of 349 nm, clearly shows that the emission profile of BZP:2.5 Dy^{3+} , x Eu^{3+} co-doped phosphor has dominance of Dy^{3+} characteristic peaks at 482, 576 and 667 nm over relatively weak emission accredited to $^5\text{D}_0$ to $^7\text{F}_2$ Eu^{3+} ion transition sited at 612 nm. Moreover, since the $^4\text{F}_{9/2}$ to $^6\text{H}_{13/2}$ band of Dy^{3+} partially overlaps with $^5\text{D}_0$ to $^7\text{F}_1$ band of Eu^{3+} so under excitation at 349 nm due to dominance of $^4\text{F}_{9/2}$ to $^6\text{H}_{13/2}$ band of Dy^{3+} over a feeble $^5\text{D}_0$ to $^7\text{F}_1$ band of Eu^{3+} the latter is not visible in the emission spectra. Under 363 nm excitation (which again corresponds to Dy^{3+}) in Fig.4.6(b) the Dy^{3+} emission are more pronounced as compared to Eu^{3+} emission further the Eu^{3+} emissions are improved as compared to 363nm excitation as there exist an excitation band in vicinity if 363 nm in excitation spectrum of Eu^{3+} . The emission profile recorded under excitation of 380 nm which is overlap of Dy^{3+} excitation band tail ascribed to $^6\text{H}_{15/2}$ - $^4\text{I}_{13/2}$ transition centred at 386 nm with $^7\text{F}_0$ - $^5\text{L}_7$ excitation band of Eu^{3+} , as shown in Fig.4.6(c) reveals overall dominance of Dy^{3+} peaks over Eu^{3+} peaks. Further as the composition changes with Eu^{3+} quantity being raised from 1 mol% to 2 mol% Eu^{3+} emission becomes more prominent and start decreasing on further increasing the Eu^{3+} concentration demonstrating concentration quenching at these levels. [119]. Fig.4.6(d) displays emission spectra corresponding to excitation of $^7\text{F}_0$ - $^5\text{L}_6$ transition of Eu^{3+} and reveals that Eu^{3+} emission peaks overshadow Dy^{3+} emission. Moreover, the effect of Eu^{3+} ions concentration with fix Dy^{3+} concentration on the intensity of different band can also be investigated from Fig.4.6. It is observed that irrespective of excitation wavelength as concentration of Eu^{3+} ions are increased, all the peaks ascribed to f-f transitions of Dy^{3+} ions follow a decreasing trend of intensity. Furthermore, it is observed that Eu^{3+} characteristic peak increases in intensity as concentration is increased from 1 mol% to 2 mol% and thereafter it declines as Eu^{3+} ion concentration is increased further due to concentration quenching. This observation is common in all the emission profiles monitored at different excitation wavelengths. The above observations reveal that both Eu^{3+} and Dy^{3+} ions compete for equivalent positions in BZP host lattice and as concentration of Eu^{3+} ions rises depressed

number of sites are available for Dy^{3+} ions thus resulting in diminished intensity of Dy^{3+} ions [120,121]. Moreover enhanced energy transmission from Dy^{3+} ions to Eu^{3+} ions is evident from the observation that strength of Dy^{3+} emission diminishes and Eu^{3+} emission grows with rise in Eu^{3+} ions concentration, thus revealing Dy^{3+} acting as a sensitizer absorbing energy from photon and shifting it to Eu^{3+} ions which is further emitted as visible light [34,60,121].

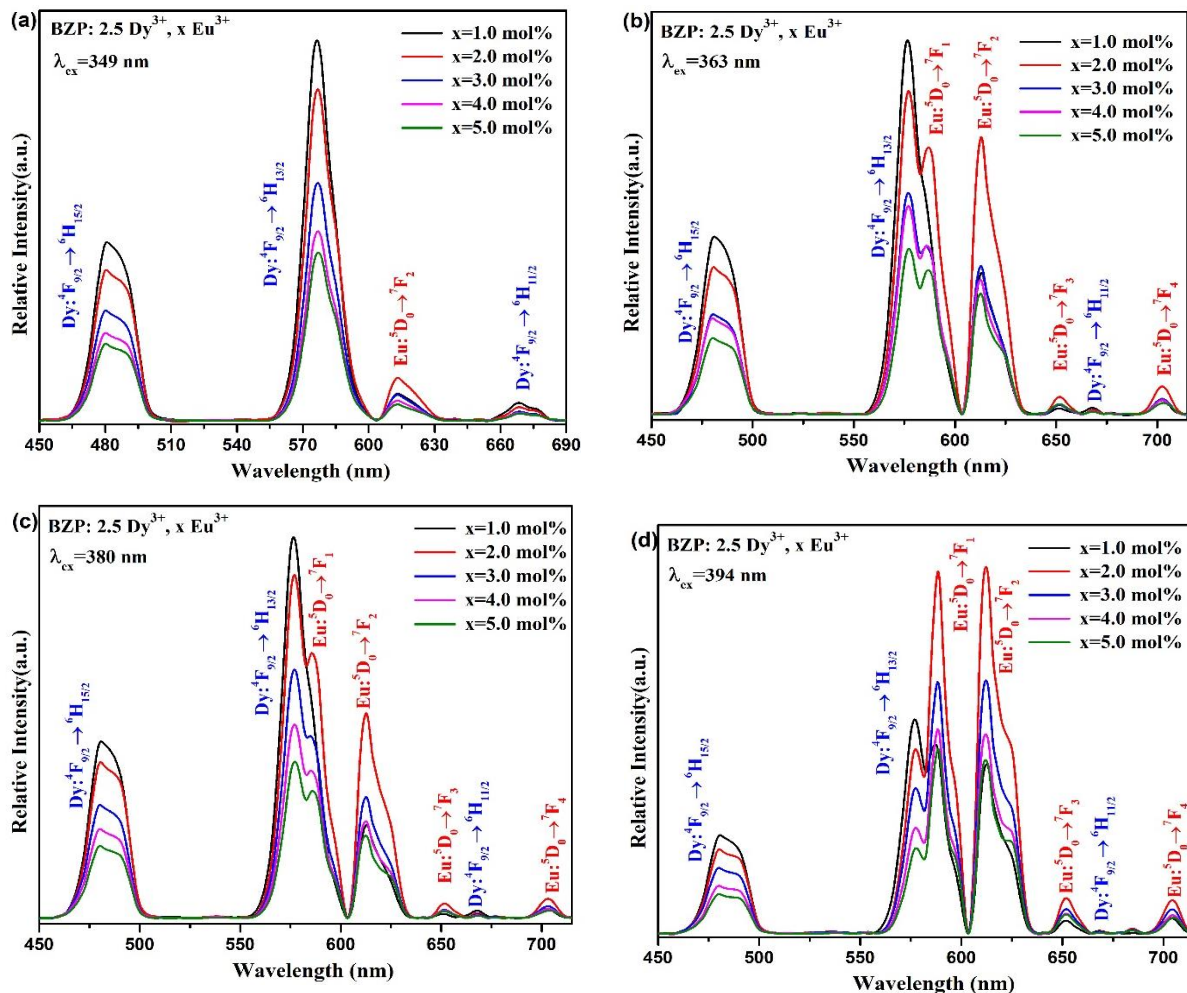


Fig.4.6. (a-d). The photoluminescence emission spectra of $\text{BaZr}(\text{PO}_4)_2:2.5 \text{ Dy}^{3+}, x \text{ Eu}^{3+}$ ($x=1.0-5.0 \text{ mol\%}$) co-doped phosphor monitored at excitation wavelengths of 349,363,380 and 389 nm

Therefore, we can modulate the relative intensity of characteristic emissions of Eu^{3+} and Dy^{3+} by varying the wavelength of excitation photon and relative amount of Eu^{3+} and Dy^{3+} ions, which makes it possible to achieve colour tunability in BZP phosphor.

The Partial energy level diagram in Fig.4.7 depicts different energy states of trivalent Europium and Dysprosium ions involved in radiative and nonradiative transitions and possible energy

transfer scheme. The electrons are pumped to excited levels ${}^6P_{7/2}$, ${}^6P_{5/2}$, ${}^4I_{13/2}$, ${}^4G_{11/2}$, ${}^4I_{15/2}$ and ${}^4F_{9/2}$ from the ground level ${}^6H_{15/2}$ by absorbing photons of suitable wavelength from excitation source. These excited electrons then non radiatively relax to ${}^4F_{9/2}$ level (depicted with zigzag arrows), from where they jump to ground state ${}^6H_{15/2}$ and ${}^6H_{13/2}$ giving emission in blue and yellow region respectively. In a Parallel process a part of energy from ${}^4F_{9/2}$ level of Dy^{3+} is transferred to 5D_2 , 5D_J ($J = 0$ and 1) levels of Eu^{3+} by virtue of phonon assisted non radiative relaxation (depicted with dashed arrows) and finally electrons from 5D_0 levels of Eu^{3+} are relaxed to ground state emitting radiation in red region. The proximate location of ${}^4I_{15/2}$, ${}^4F_{9/2}$ and 5D_2 , 5D_J ($J = 0$ and 1) levels of Dy^{3+} and Eu^{3+} respectively is visible in the energy chart [60,79,91]. The non radiative transmission of energy between a sensitizer and activator involves either multipolar interaction or exchange interaction depending on average critical distance (R_c) between Dy^{3+} and Eu^{3+} ions. If R_c has a value close to $5\text{\AA}$ then exchange interactions are accountable for energy transfer process and if R_c is greater than $5\text{\AA}$ then multipolar interactions are responsible. The equation (4.3) was utilised for evaluating value of R_c where all the parameters have same values as used earlier but for the co-doped system x_c will have a value that equates to sum of we will use x_c the critical concentration as the sum of concentration of both the ions at which intensity corresponding to Dy^{3+} is fifty percent of that sans Eu^{3+} [60,90]. Fig.4.8 depicts variation of emission intensity of BZP: $2.5 Dy^{3+}$, yEu^{3+} with concentration of Eu^{3+} , from where concentration of Eu^{3+} corresponding to critical concentration is estimated to be 0.04. Thus critical distance has a calculated value of $17.34\text{\AA}$, which is quite larger than $5\text{\AA}$ thus implicating multipolar interactions as mechanism for energy transfer process. In order to evaluate the class of multipolar interaction Riesenfeld's and Dexter theory can be utilized which relates the quantum efficiencies η_0 and η_s to total concentration C of Eu^{3+} and Dy^{3+} by relation (2) [34]

$$\frac{\eta_0}{\eta_s} \propto C^{\frac{n}{3}} \quad (4.7)$$

Where, η_0 is emission quantum efficiency of Dy^{3+} sans Eu^{3+} and η_s being its value in the presence of Eu^{3+} and n takes different values for dipole-dipole ($n = 6$), dipole-quadrupole ($n = 8$) and quadrupole-quadrupole interactions ($n = 10$). The ratio of quantum efficiencies η_0/η_s can be approximated to the ratio I_{s0}/I_s , where I_{s0} and I_s represents integrated emission intensity of ${}^4F_{9/2}$ to ${}^6H_{13/2}$ transition of Dy^{3+} without and with co-dopant ions. Therefore equation (5) can be transformed to equation (6)

$$\frac{I_{s0}}{I_s} \propto C^{\frac{n}{3}} \quad (4.8)$$

Fig.4.9 shows plots for equation (4.3) for $n = 6, 8$ and 10 and it is apparent that the best fit curve is obtained for $n = 6$ thus suggesting dipole-dipole interactions accountable for energy transference to Eu^{3+} from Dy^{3+} . Additionally the efficiency of energy transference taking place from sensitizer Dy^{3+} to activator Eu^{3+} can be evaluated using the relation [122]:

$$\eta_T = 1 - \frac{I_S}{I_{S0}} \quad (4.9)$$

The evaluated values of transfer efficiency are tabulated in table 4.3. The energy transfer efficiency for $\text{BaZr}(\text{PO}_4)_2:\text{Dy}^{3+}/\text{Eu}^{3+}$ phosphor are superior to thermally stable $\text{KCaY}(\text{PO}_4)_2:\text{Dy}^{3+}, \text{Eu}^{3+}$ and $\text{Sr}_3\text{Gd}(\text{PO}_4)_3:\text{Dy}^{3+}, \text{Eu}^{3+}$ phosphors [80,88].

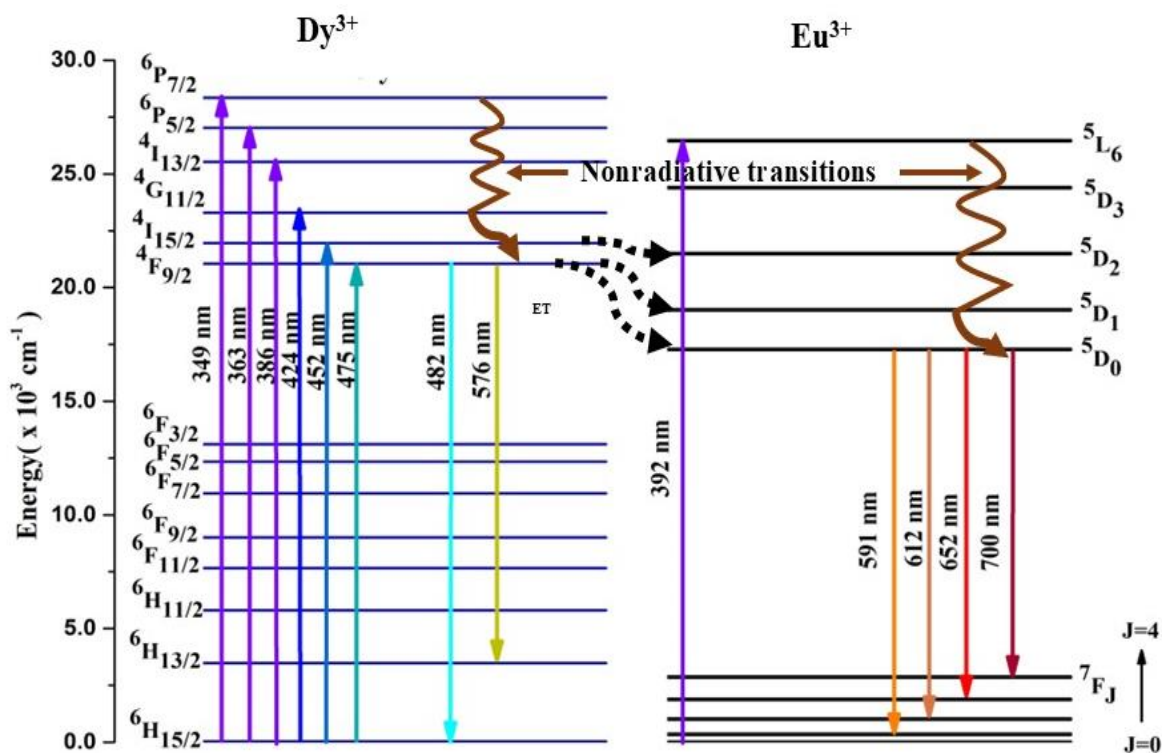


Fig.4.7. Partial energy level diagram demonstrating possible energy transfer scheme from Dy^{3+} to Eu^{3+} ions in BZP Phosphor.

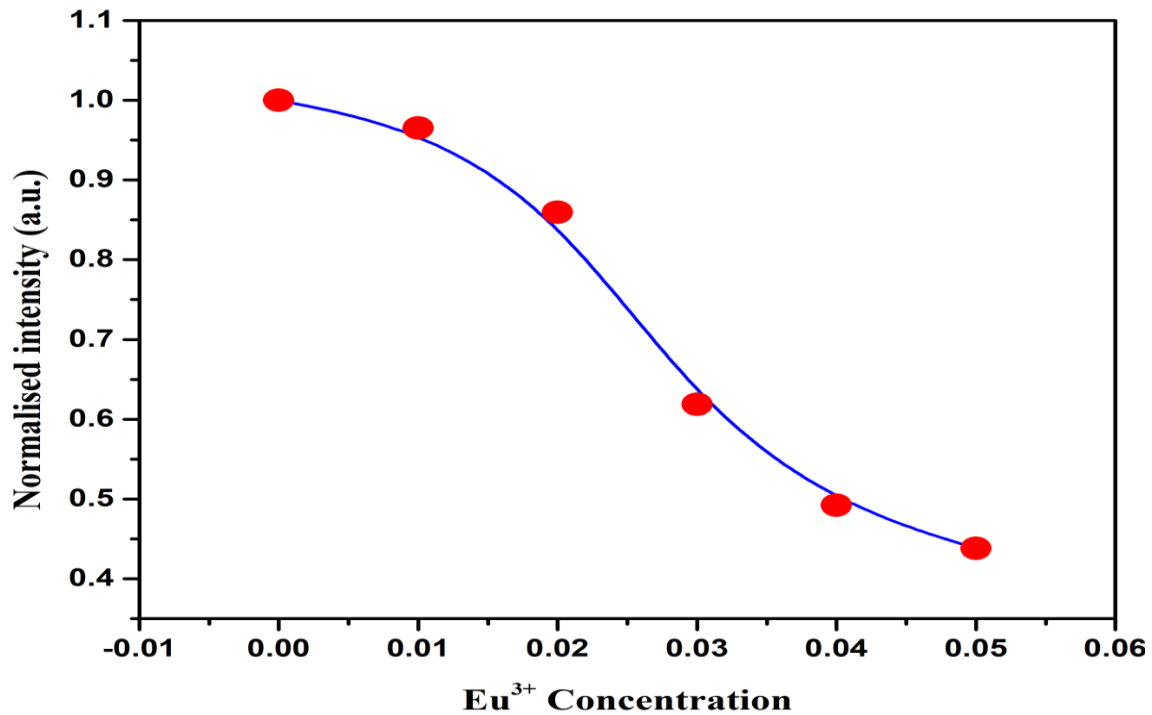


Fig.4.8. The dependence of the relative Dy³⁺ emission intensity in BaZr(PO₄)₂: 0.025Dy³⁺, yEu³⁺ (y = 0.01, 0.02, 0.03, 0.40, 0.50), on the content of Eu³⁺

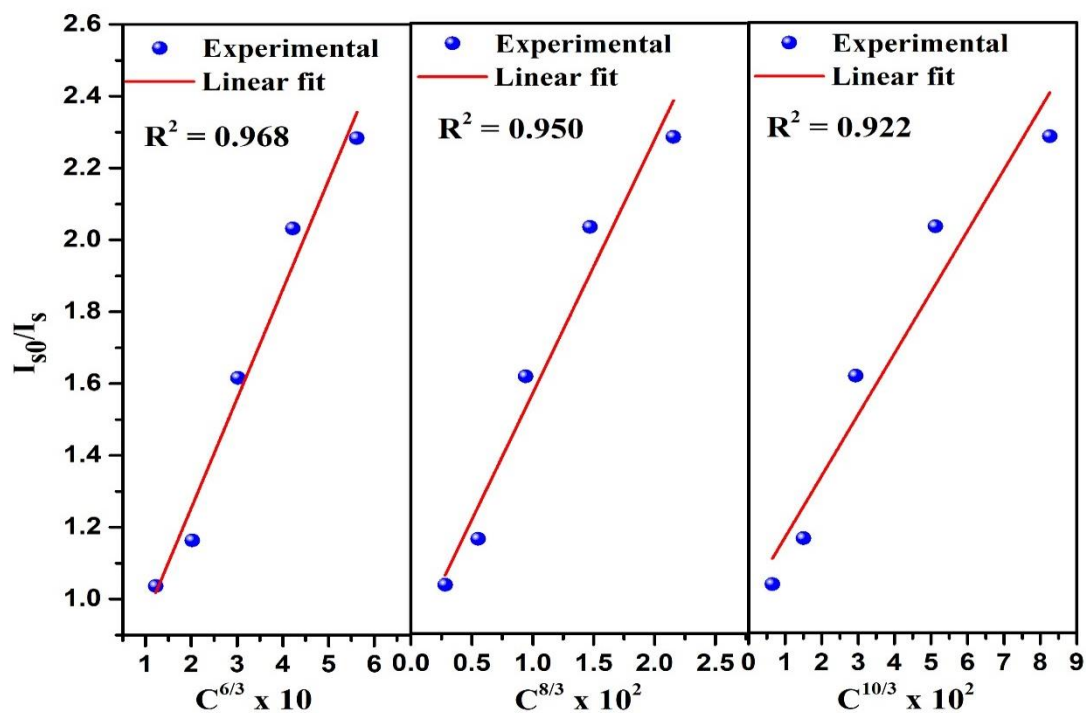


Fig.4.9. The variation of I_{s0}/I_s on $C^{n/3}$ (n=6, 8 and 9) in BaZr(PO₄)₂: 0.025Dy³⁺, yEu³⁺ (y = 0.01, 0.02, 0.03, 0.40, 0.50).

Sample	Fluorescent life time (ms)	Energy transfer probability (P)	Energy transfer efficiency (%)
BPDE1	0.579	0.18	3.45
BPDE2	0.575	0.19	14.0
BPDE3	0.539	0.31	38.1
BPDE4	0.524	0.36	50.8
BPDE5	0.455	0.65	56.2

Table 4.3. Fluorescent lifetime, energy transfer probability and energy transfer efficiency for $\text{BaZr}(\text{PO}_4)_2:2.5 \text{ Dy}^{3+}, x \text{ Eu}^{3+}(x=1.0-5.0 \text{ mol\%})$ phosphors

4.3.5 Lifetime analysis of $\text{BaZr}(\text{PO}_4)_2: \text{Dy}^{3+}$ Phosphors:

In order to study the relaxation dynamics of BZP: $x\text{Dy}^{3+}$ phosphors fluorescent decay curves for $^4\text{f}_{9/2}$ level recorded at excitation wavelength of 349 nm were analyzed and are depicted in Fig.4.10. A third order -exponential decay function has been used for fitting the curves given by equation [123,124]:

$$I_t = I_0 + A_1 e^{\left(\frac{-t}{\tau_1}\right)} + A_2 e^{\left(\frac{-t}{\tau_2}\right)} + A_3 e^{\left(\frac{-t}{\tau_3}\right)} \quad (4.10)$$

Where A_1 , A_2 and A_3 are constants, I_0 and I_t are emission intensity values at time $t = 0$ and t respectively, τ_1 , τ_2 and τ_3 are lifetime components. The fitted parameters yield the average lifetime τ as per the relation:

$$\tau_{av} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2 + A_3 \tau_3^2}{A_1 \tau_1 + A_2 \tau_2 + A_3 \tau_3} \quad (4.11)$$

The Table 4.2 depicts thus obtained lifetime values. It can be noted that as Dy^{3+} concentration is increased from 1 mol% to 3.5 mol% average lifetime values decreases indicating increased probability of nonradiative transitions arising due to decreased space among adjacent Dy^{3+} ions. The relation between average lifetime and concentration of Dy^{3+} ions has further been investigated using Auzel's model, where the experimental data is fitted using Auzel's relation which relates fluorescent lifetime to the concentration of dopant as per equation [125,126]:

$$\tau(c) = \frac{\tau_0}{1 + \frac{c}{c_0} e^{\frac{-N}{3}}} \quad (4.12)$$

Where, $\tau(c)$ is the computed fluorescent lifetime value at concentration c of dopant ion, τ_0 is radiative lifetime, N is no of phonons generated via cascade multiphonon process in quenching ${}^6\text{H}_{13/2}$ level of Dy^{3+} and c_0 is a constant with dimensions same as that of concentration. As shown in Fig.3.11 the experimental lifetime values fit well with Auzel model yielding values of τ_0 , N and c_0 to be 0.7137, 4.59 (~ 5) and 5.02 respectively. The obtained value of τ_0 can be further used to determine PL quantum efficiency and non-radiative transition probability of ${}^6\text{H}_{13/2}$ level of Dy^{3+} in BZP phosphors. The PL quantum efficiency(η) is an important parameter of a phosphor with application in solid state lighting and is given as the ratio of observed lifetime τ_{av} to radiative lifetime τ_0 expressed mathematically as:

$$\eta = \frac{\tau_{av}}{\tau_0} \quad (4.13)$$

The non-radiative transition rate (A_{NR}) can be computed using below relation:

$$\frac{1}{\tau_{av}} = \frac{1}{\tau_0} + A_{NR} \quad (4.14)$$

The value of η and A_{NR} evaluated using Equation 4.11 and 4.12 for the samples are enlisted in Table 4.2.

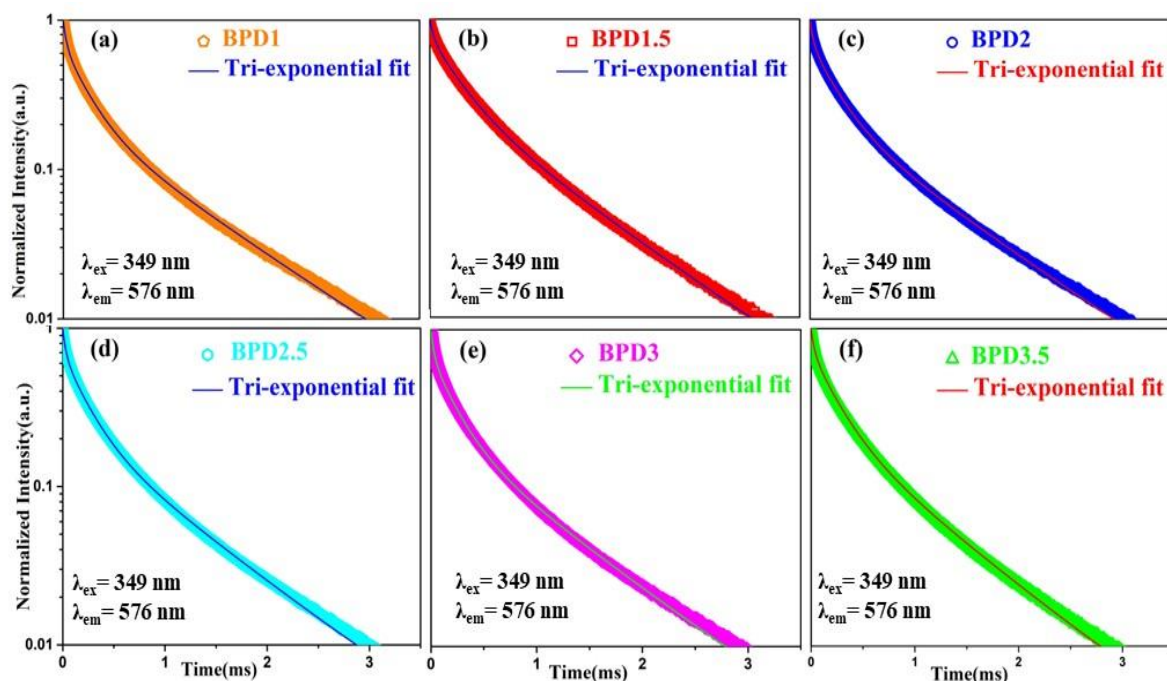


Fig.4.10. (a-f) Decay curves of $\text{Ba}_{(1-x)}\text{Zr}(\text{PO}_4)_2:\text{x}\text{Dy}^{3+}$ ($x = 1.0, 1.5, 2.0, 2.5, 3.0$ and 3.5 mol%) for ${}^4\text{f}_{9/2}$ level monitored at excitation wavelength of 349 nm

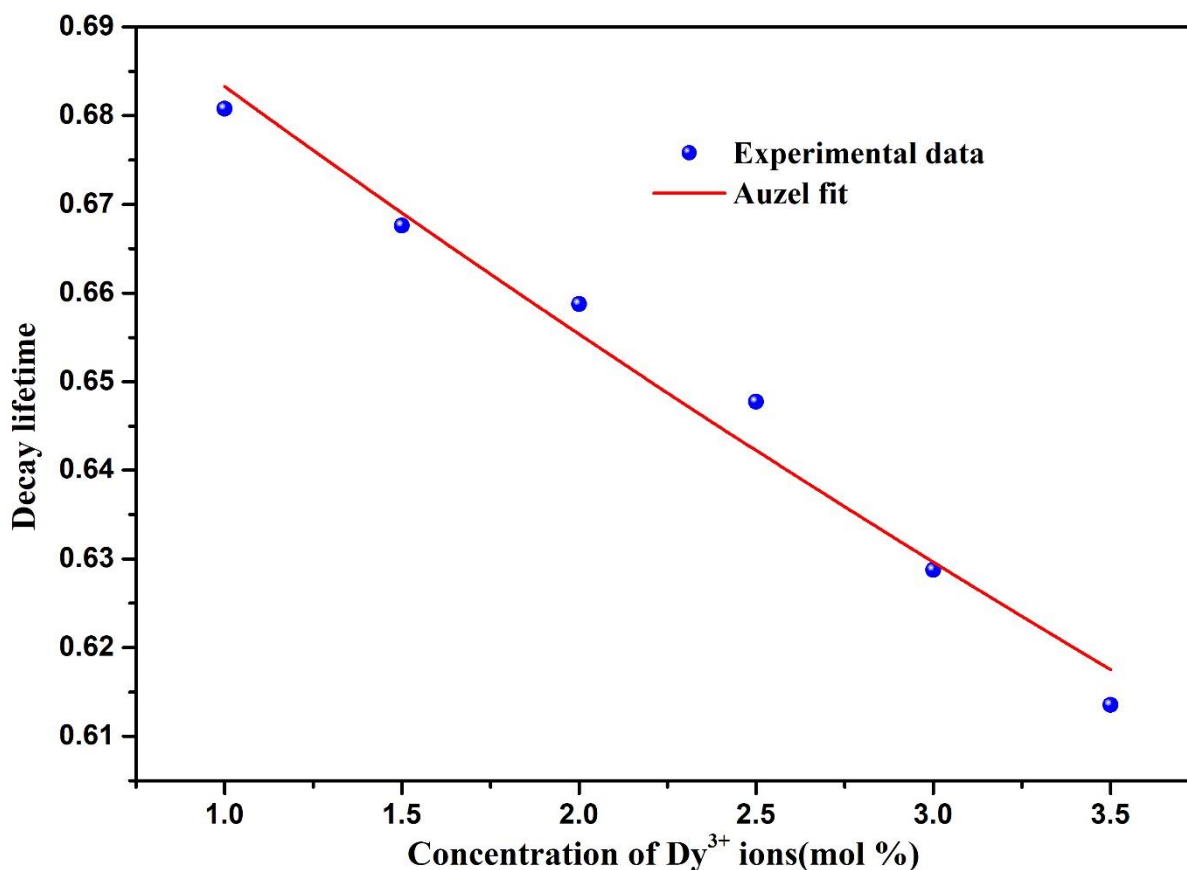


Fig.4.11. Auzel's fitting of decay lifetime of $\text{Ba}_{(1-x)}\text{Zr}(\text{PO}_4)_2:x\text{Dy}^{3+}$ ($x = 1.0, 1.5, 2.0, 2.5, 3.0$ and 3.5 mol%) with concentration of Dy^{3+} ions.

4.3.6 Lifetime analysis of $\text{BaZr}(\text{PO}_4)_2: \text{Dy}^{3+}, \text{Eu}^{3+}$ Phosphors:

To further analyze the non-radiative transfer of energy from Dy^{3+} to Eu^{3+} the decay curves for $^4\text{f}_{9/2}$ level recorded for 349 nm excitation wavelength for BZP: 2.5 Dy^{3+} , y Eu^{3+} ($y = 1-5$ mol %) phosphors were plotted and are displayed in Fig.4.12(a-e). The plots have been fitted well using a triexponential function as mentioned in eq. (8). The decay lifetimes evaluated using eq. (4.9) is tabulated in Table 4.3. Fig.4.12(f) shows the correspondence between lifetime values and concentration of Eu^{3+} and it is evident that lifetime values fall as the relative quantity of Eu^{3+} gets larger starting from 0.0 mol% to 5.0 mol %. The decrease in value of lifetime further confirms the energy transference from Dy^{3+} to Eu^{3+} . Additionally the probability rate (P) of energy transfer for dipole-dipole interaction between sensitizer and activator can be evaluated from lifetime values using relation mentioned elsewhere [62]. The calculated P values are listed in Table 4.3. Fig.4.12(f) shows the plot of P values with concentration of Eu^{3+} and it can be seen that the energy transfer probability increases as concentration of Eu^{3+} increases.

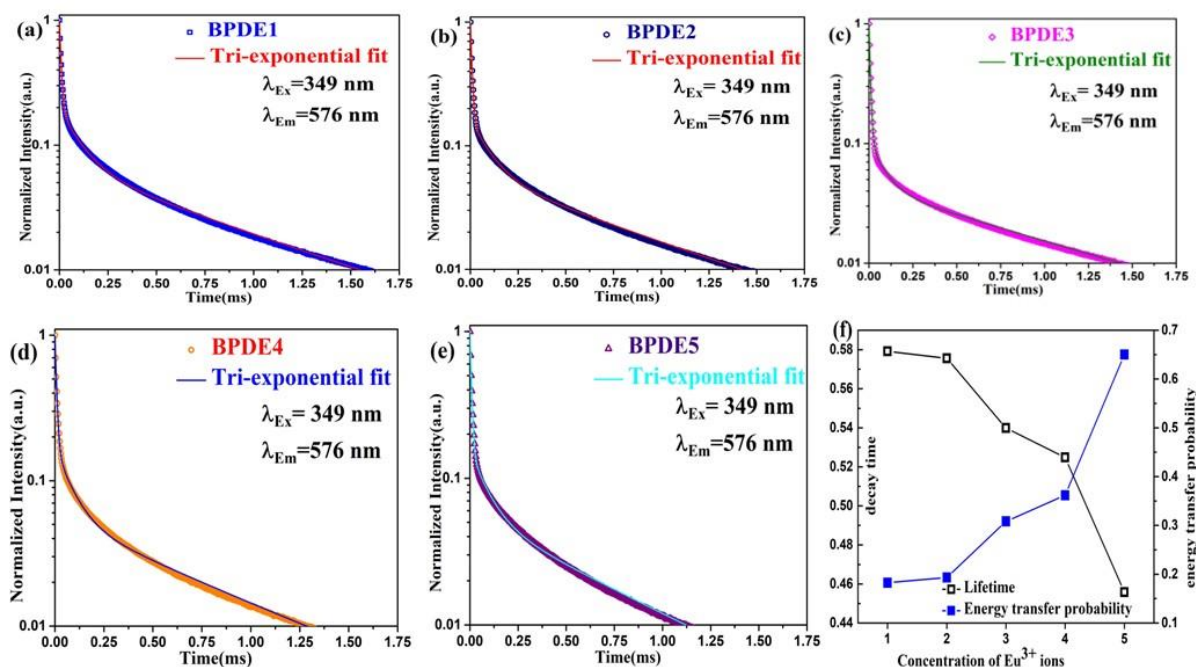


Fig.4.12. (a-e) Decay curves of BaZr(PO₄)₂:2.5 Dy³⁺, x Eu³⁺ (x=1.0-5.0 mol%) co-doped phosphor for ⁴f_{9/2} level monitored at excitation wavelength of 349 nm. **(f)** lifetime and energy transfer probability versus concentration of Eu³⁺ ions.

4.3.7 Photometric characteristics of BaZr(PO₄)₂: Dy³⁺, Eu³⁺ Phosphors

To evaluate the prospects of the thus prepared phosphor in terms of quality of white emission and colour modulation by varying activator and sensitizer ratio the chromaticity coordinates are evaluated to express the color emission with quantitative values. The chromaticity coordinates are obtained from emission spectra as per CIE 1931 standard. The emission intensity data are transformed to trichromatic colour space with the help of tristimulus values obtained by using [60,67]:

$$X = \int L(\lambda) \bar{x}(\lambda) d\lambda, \quad (4.15)$$

$$Y = \int L(\lambda) \bar{y}(\lambda) d\lambda, \quad (4.16)$$

$$Z = \int L(\lambda) \bar{z}(\lambda) d\lambda \quad (4.17)$$

Where $L(\lambda)$ denotes spectral radiance and $\bar{x}, \bar{y}, \bar{z}$ are standard CIE observer curves. CIE coordinates (x,y) are then calculated using following equation:

$$x = \frac{X}{X+Y+Z}, \quad y = \frac{Y}{X+Y+Z} \quad (4.18)$$

The thus obtained x, y values were used in McCamy's empirical formula mentioned elsewhere to calculate the correlated color temperature (CCT) values [65]. Fig.4.13 (a-e) depicts the plot

of CIE coordinates of Dy^{3+} activated and $\text{Dy}^{3+}/\text{Eu}^{3+}$ co-activated BZP phosphor on chromaticity diagram. The absolute calculated values of color coordinates and the CCT values are presented in Table 4.4. Fig.4.13(a) shows that the color co-ordinates of Dy^{3+} doped BZP phosphor at 349 nm excitation wavelength lies in white region with CCT values moving towards warmer region with increase in Dy^{3+} concentration thus emission shifting towards warmer light with Dy^{3+} concentration. Fig.4.13(b) depicts the variation in colour coordinates of BPDE1 phosphor from white to red under different excitation wavelength. Fig.4.13(c) reveals that CIE coordinates move more towards inner region of white domain by co-doping with Eu^{3+} ions under 349nm excitation. It is clear from Fig.4.13(c-f) that by adjusting concentration of Eu^{3+} ions and excitation wavelength we can tune colour co-ordinates from white to red and CCT from cooler to warmer region. It is conspicuous from the Table 4.4 that CCT values decreases with increasing Eu^{3+} concentration under different excitations and varied from 4247 to 1775 K. The CCT values obtained in present work for various samples have warmer values compared to the CCT values of the thermally stable $\text{Ca}_{6.92}\text{Mg}_2(\text{PO}_4)_6$: Dy^{3+} , Eu^{3+} phosphor, $\text{NaSrBi}_2(\text{PO}_4)_3$: Dy^{3+} , Eu^{3+} phosphor and SrLaLiTeO_6 : Dy/Eu phosphor reported by other workers [85,93,127]. These observations suggest that color tunability can be realized in these phosphors by tuning composition with variation in concentration of co-dopant as well as by variation of excitation wavelength thus making them potential candidate for color tunable displays and light emitting devices.

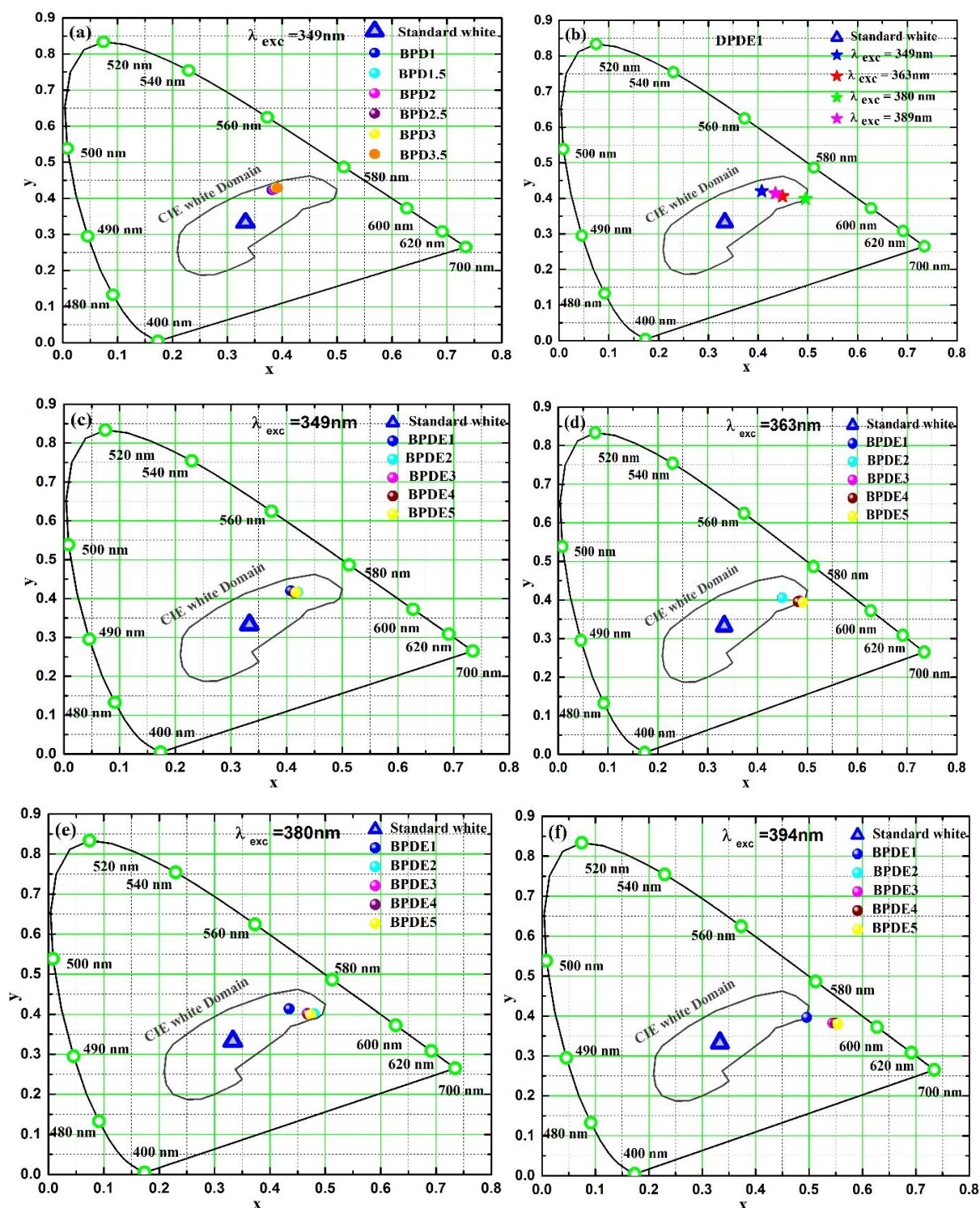


Fig. 4.13. (a): CIE chromaticity co-ordinates of $\text{Ba}_{(1-x)}\text{Zr}(\text{PO}_4)_2:\text{x}\text{Dy}^{3+}$ ($x = 1.0, 1.5, 2.0, 2.5, 3.0$ and 3.5 mol%) at 349 nm excitation wavelength. (b): CIE chromaticity coordinates of DPDE1 at different wavelengths (349, 363, 380 and 389 nm) (c–f): CIE coordinates of D2.5E1, D2.5E2, D2.5E3, D2.5E4, and D2.5E5 under 349, 363, 380 and 394 nm excitation wavelength, respectively.

Excitation			CCT
Wavelength (nm)	Sample	CIE co-ordinates (x,y)	(K)
349	BPD1	(0.381,0.423)	4247.723
	BPD1.5	(0.386,0.427)	4165.758
	BPD2	(0.385,0.424)	4174.558
	BPD2.5	(0.388,0.428)	4121.105
	BPD3	(0.390, 0.429)	4099.216
	BPD3.5	(0.392,0.429)	4051.053
	BPDE1	(0.408,0.420)	3670.553
	BPDE2	(0.420,0.416)	3408.49
	BPDE3	(0.415,0.415)	3493.424
	BPDE4	(0.414,0.415)	3504.809
	BPDE5	(0.417,0.416)	3460.591
363	BPDE1	(0.449,0.406)	2823.514
	BPDE2	(0.449,0.406)	2823.211
	BPDE3	(0.484,0.398)	2290.612
	BPDE4	(0.481,0.396)	2319.807
	BPDE5	(0.491,0.394)	2191.416
380	BPDE1	(0.435,0.414)	3118.888
	BPDE2	(0.480,0.401)	2370.683
	BPDE3	(0.468,0.402)	2527.273
	BPDE4	(0.468,0.400)	2506.681
	BPDE5	(0.474, 0.399)	2422.219
394	BPDE1	(0.496,0.396)	2160.43
	BPDE2	(0.553,0.381)	1738.769
	BPDE3	(0.544,0.383)	1765.37
	BPDE4	(0.550,0.382)	1748.921
	BPDE5	(0.554,0.380)	1733.459

Table 4.4. CIE Co-ordinates and CCT values for BaZr(PO₄)₂: xDy³⁺ (x = 1.0, 1.5,2.0, 2.5,3.0 and 3.5 mol%) and BaZr(PO₄)₂:2.5 Dy³⁺, x Eu³⁺(x=1.0-5.0 mol%) phosphors

4.3.8 Thermal stability of BaZr(PO₄)₂ : Dy³⁺, Eu³⁺ Phosphors

Since the light output and CRI of LEDs is affected by the heat generated by LEDs especially those operating at high powers [34]. So, the performance of phosphor material at higher temperatures and their thermal stability needs to be evaluated for considering them for commercial applications in high powered LEDs. Fig.4.14(a) depicts variation of emission spectra of BPDE1 phosphor with temperature in a range from 300 to 450 K under excitation wavelength of 349 nm. It is apparent from the graph that the peak position doesn't vary with rise in temperature suggesting the ability of phosphor maintain structural and chemical stability resulting in steady state emission at elevated temperatures. However, the intensity falls gradually with increase in operating temperature due to thermal quenching effect resulting from thermally excited cross relaxation of electrons [99,128]. Fig. 4.14(b) displays the normalized PL intensity at 576 nm for different temperatures and it can be observed that BPDE1 phosphor retains 87.87% and 79.28% of emission intensity at 420 and 450 K respectively indicating the good thermal stability of the phosphor as compared with other reported works presented in Table 4.5 [34,78,131,80,84,85,88,93,127,129,130]. The thermal stability can be further assessed by evaluating activation energy (E_a) from the Arrhenius formula which relates fluorescence intensity at temperature T (I_T) to other parameters as [79]:

$$\ln \left(\frac{I_0}{I_T} - 1 \right) = C - \frac{E_a}{KT} \quad (4.19)$$

Where I_0 is intensity measured at room temperature, C is a constant and K is Boltzmann constant. A graph plotted for Equation 4.17 is displayed in Fig 4.14(c). By linear fitting the graph E_a comes out to be 0.267 eV which is notably higher than other reported work as shown in Table 4.5. The activation energy of BPDE1 phosphor is better than Na₄Ca₄Si₆O₁₈:Dy³⁺/Eu³⁺ phosphor even though both phosphors retain almost equal emission at 423 K. Moreover, for BPDE1 sample not only the activation energy is better than the phosphate phosphor Sr₃Gd(PO₄)₃:0.03Dy³⁺, xEu³⁺ reported by Bin et al. but also the energy transfer efficiency from sensitizer to activator is superior [88]. Therefore, above mentioned results established the promising luminescent properties of the phosphor at elevated temperatures and its potential for applicability in high powered wLEDs.

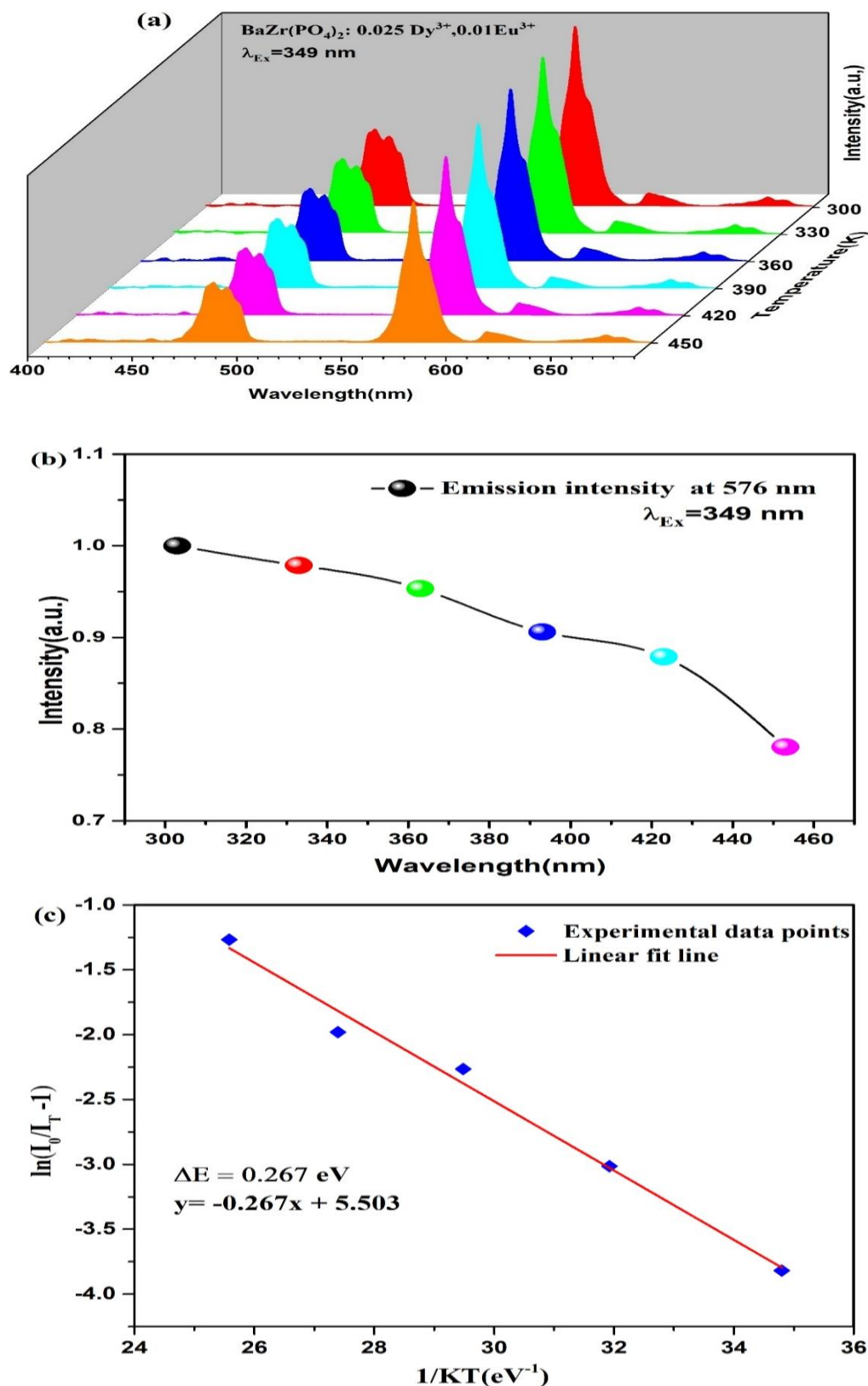


Fig.4.14 (a): Temperature dependent PL spectra for BPDE1 phosphor monitored at an excitation wavelength of 349 nm. (b): Normalised PL intensity of BPDE1 Phosphor at different temperatures. (c): linear fit plot of $\ln[(I_0/I)-1]$ versus $1/kT$.

Sample Name	Emission intensity sustained at 423 K (%)	Activation Energy (eV)	References
BDE1	87.87	0.267	PRESENT WORK
CDE3	85.68	0.267	[59]
Na ₄ Ca ₄ Si ₆ O ₁₈ :Dy ³⁺ /Eu ³⁺	88.71	0.25	[2]
Sr ₃ Gd(PO ₄) ₃ :0.03Dy ³⁺ , 0.085Eu ³⁺	80	0.1883	[14]
BBP: 8at.%Dy ³⁺ , 0.8at.%Eu ³⁺	76	0.23	[9]
KCYP:3%Dy ³⁺ , 7%Eu ³⁺	~70	0.174	[4]
Na ₃ Gd (PO ₄) ₂ : 0.05Dy ³⁺ , 0.03Eu ³⁺	82	-	[13]
KSGP:5%Dy ³⁺	85	0.245	[61]
Ca _{6.92} Mg ₂ (PO ₄) ₆ :0.05Dy ³⁺ , 0.03Eu ³⁺	~87	0.24718	[10]
SLLT: 7%Dy/15%Eu	71.3	0.224	[62]
NSBP-0.09Dy ³⁺	75	0.199	[64]
CMW: xDy ³⁺ (x = 3mol%)	75	0.21	[66]

Table 4.5. Comparison of thermal stability parameters of BDE1 phosphor with other reported phosphors.

4.4 CONCLUSIONS:

Single phased Dy³⁺ activated and Dy³⁺/ Eu³⁺ coactivated BZP phosphors has been prepared via solid state reaction route. The XRD pattern indicate pure monoclinic phase which matched well with standard ICDD PDF card no 01-074-8689 with space group C2/m(12). The FE-Sem images reveal asymmetrical agglomerated particles in micrometer size range. The PL studies reveals that a UV light source can be used as source of excitation for the phosphors. The singly doped BZP: Dy³⁺ phosphors exhibit emission in white region with presence of strong emission bands in blue and yellow region with a feeble peak in red region. The phosphors coactivated with Dy³⁺/Eu³⁺ show color tunability by varying wavelength as well relative concentration of activator and coactivator revealing shift of CCT from cooler to warmer region with presence

of co-activator. The decay profiles revealed decrease in lifetime value with increase in relative quantity of dopants for both single doped and co-doped phosphors. The co-activated BZP: $\text{Dy}^{3+}/\text{Eu}^{3+}$ phosphor exhibit superior stability at operating temperatures with activation energy of 0.267 eV. The above studies altogether demonstrate the promising potential of the BZP phosphor singly activated with Dy^{3+} and bi activated with $\text{Dy}^{3+}/\text{Eu}^{3+}$ in w-LEDs and color tunable devices.

5

CHAPTER

Photoluminescent properties of Bi³⁺ doped BaZr(PO₄)₂ and Energy Transfer in Bi³⁺, Tb³⁺ codoped phosphors

- Synthesis of Bi³⁺-doped and Bi³⁺/Tb³⁺-codoped BaZr(PO₄)₂ phosphors using the solid-state reaction method.
 - Structural and optical analyses confirmed pure phase formation and effective dopant incorporation in the BZP host.
 - Bi³⁺-activated phosphors exhibited a prominent blue emission around 468 nm under 313 nm excitation.
 - Energy transfer from Bi³⁺ to Tb³⁺ was validated through PL spectra and decay curves with dipole–dipole interaction as the main mechanism.
 - The critical energy transfer distance between Bi³⁺ and Tb³⁺ was calculated to be 21.85 Å with CIE coordinates (0.157, 0.213) for Bi³⁺-only phosphor.
 - Tunable blue–green emission was achieved in codoped samples, indicating suitability for solid-state lighting applications.
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5.1. INTRODUCTION

In the recent decades there has been upsurged demand of White light-emitting diodes (w-LEDs) for lighting applications because of their superior energy efficiency, extended lifespan, and environmental benefits [180,181]. There are two primary approaches for commercial fabrication of w-LEDs. The predominant one comprises of collaborating blue emission from InGaN chips with yellow-emitting YAG: Ce³⁺ phosphors. Though employment of this approach is facile and economical, it has critical drawbacks of low color rendering index (CRI < 75), high correlated color temperature (CCT > 6000 K), and poor luminous efficiency [182]. These limitations which are due to missing red components in their emission, undermine their use in applications requiring warm, comfortable lighting. The alternate approach requires mixing of multiple-coloured phosphors to generate white light which has improved color rendering and better color temperatures [183]. The missing emission in the cyan region (480-520 nm), commonly referred to as the "cyan gap," represents another critical challenge in current w-LED based technology [184]. This cyan gap results in inferior color rendering index with low color vividness, thus introducing barriers in achieving full-spectrum luminescence comparable to natural sunlight. The traditional approaches of employing Ce³⁺ or Eu²⁺ doped phosphors to fill up this gap results in reabsorption in the visible region, where intense absorption bands overlap with emission spectra, further complicating the achievement of optimal performance [185]. Therefore, for the improved performance of w-LEDs it is crucial to develop red, green and blue emitting phosphors having efficient absorption in near ultraviolet region. The phosphors having emission in green region have greater significance compared to red and blue phosphors as they have a disproportionately large impact on the overall luminous efficiency of w-LED devices. The reason for this is that the sensitivity curve of human eye matches the emission peak of green phosphors. The trivalent terbium ions (Tb³⁺) having an electronic configuration of ([Xe]4f¹⁴5d¹⁰6s²) is an established green-emitting activator for phosphor applications due characteristic 4f-4f emissions, with the ⁵D₄→⁷F₅ transition providing the dominant contribution to green luminescence around 545 nm [186]. However, Tb³⁺ ions because of forbidden f-f transitions suffer from weak absorption in the near-ultraviolet area which significantly reduce their direct excitation efficiency under UV-LED illumination which can be improved in a co-doped system having Bi³⁺ as sensitizer [187]. Bismuth as a transition ion (Bi³⁺) with an electronic configuration of ([Xe]4f¹⁴5d¹⁰6s²), have exposed 6s and 6p electrons that are highly sensitive to crystal field environments [188].

Therefore, Bi^{3+} activated phosphors possess diverse luminescent properties across a broad spectral range from ultraviolet to near-infrared regions, depending on the host matrix. Consequently, luminescence in blue region can be obtained from Bi^{3+} -doped materials by choosing the right host matrix and appropriate excitation parameters [185]. Moreover, Bi^{3+} having a strong and broad absorption characteristics in the ultraviolet and near-ultraviolet region have a distinct upside over the weak and narrow absorption characteristics of traditional lanthanide activators. Apart from being an activator, Bi^{3+} ions can also take role of sensitizer to enhance luminescence performance and achieve tunable emission [189]. Consequently, Bi^{3+} ions can effectively capture excitation energy and transfer it to nearby activator ions in a co-doped system. Furthermore, having minimal absorption in the visible range Bi^{3+} ions doesn't encounter the reabsorption problems which is common with traditional lanthanide activators. Hence, the energy transfer process between Bi^{3+} as a sensitizer and Tb^{3+} as an activator can be exploited in development of high-performance phosphor materials. The use of phosphate materials as an effective host material for luminescent materials is well documented attribute to their merits of having favourable phonon energy, large band gap, good chemical and mechanical stability, cost effectiveness and environment friendliness. In the present work, we have chosen $\text{BaZr}(\text{PO}_4)_2$ belonging to orthophosphates as host matrix with a crystal structure comprising of the alternating layers of barium cations and $\text{Zr}(\text{PO}_4)_2$ structural units that are stacked parallel to the (011) crystallographic plane. This layered structural framework provides stability and mechanical properties to the crystalline lattice [73,190]. The monophase Bi^{3+} activated and $\text{Bi}^{3+}/\text{Tb}^{3+}$ coactivated blue to green emitting $\text{BaZr}(\text{PO}_4)_2$ (BZP) phosphor has been obtained through solid state route. The color tunability has been attained by modulating the concentration of dopant ions and wavelength of excitation. Detailed examinations have been conducted on the crystal structure, microstructure, luminescence, energy transfer, photometric parameters and decay kinetics studies for the prepared phosphors.

5.2. Material synthesis and characterization:

The powder samples of undoped BZP, BZP: Bi^{3+} and BZP: $\text{Bi}^{3+}/\text{Tb}^{3+}$ phosphors with nominal composition were made utilizing solid phase reaction technique. The stoichiometric amount of raw materials Bismuth(III) Oxide (Bi_2O_3), Terbium(III,IV) oxide (Tb_4O_7), Barium Carbonate (BaCO_3), Zirconium(IV) oxide (ZrO_2) and Ammonium dihydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) were weighed and mixed together using acetone as a fluid media in Agate mortar. The precursor mixture was then grinded for 90 minutes manually and resultant mix powder was moved to an

alumina crucible inside a programmable high temperature furnace to be sintered at 1373 K . The rate of heating was kept controlled at 5 K per minute and after sintering it was left to cool down naturally to ambient temperature. A fine powder was obtained by grinding the sintered hard mass in an Agate mortar, to use it for characterisation and analysis. The labelling for samples with 0.0, 1.0, 2.0, 3.0, 4.0 and 5.0 mol % of Bi^{3+} was done as BZP, BZPB1, BZPB2, BZPB3, BZPB4 and BZPB5 respectively. The co-doped series was prepared keeping concentration of Bi^{3+} at 3.0 mol % and Tb^{3+} content was kept at 0.25, 0.50, 0.75 and 1.0 mol% and samples were named BZPB3T0.25, BZPB3T0.50, BZPB3T0.75 and BZPB3T1 respectively. Additionally, one sample of single doped 1.0 mol% of Tb^{3+} and one co-doped sample for composition of 1.0 mol% of each Bi^{3+} and Tb^{3+} was prepared and labelled BZPT1 and BZPB1T1 respectively.

The analysis of the formed phase and structural parameters for selected phosphor samples has been done employing Bruker D8-Advanced X- Ray diffraction machine with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). The microstructural imaging with Energy dispersive X-ray spectrum has been carried out using JEOL JSM7610 Scanning Electron Microscope (SEM) instrument which employs Schottky emitter electron gun. The Spectro-fluorophotometer JASCO FP-8300 with 150 W Xenon lamp as source of excitation and having a resolution of 1 nm has been used to carry out luminescence measurements. The decay kinetics analysis was done using Cary–Eclipse Spectrofluorometer instrument equipped with 150 W Xenon lamp.

5.3. RESULT AND DISCUSSION:

5.3.1. Phase identification and crystal structure of $\text{BaZr}(\text{PO}_4)_2:\text{Bi}^{3+}/\text{Tb}^{3+}$ Phosphors

The XRD patterns for $\text{BaZr}(\text{PO}_4)_2$ host matrix, $\text{BaZr}(\text{PO}_4)_2:\text{Bi}^{3+}$ and $\text{BaZr}(\text{PO}_4)_2:\text{Bi}^{3+}/\text{Tb}^{3+}$ powder samples along with standard ICDD PDF card no 01-074-8689 data for monoclinic phase of BZP are displayed in Fig.5.1(a). The diffraction peak positions and the relative intensity of peaks align closely with the standard data conforming to C2/m (12) space group with lattice constants values a , b , c and β as $8.531 \text{ \AA}$, $5.293 \text{ \AA}$, $7.875 \text{ \AA}$ and 93.8° in corresponding order. The absence of any extraneous peaks in the X-ray diffraction of Bi^{3+} -doped and $\text{Bi}^{3+}/\text{Tb}^{3+}$ co-doped samples confirms that the incorporation of Bi^{3+} and Tb^{3+} ions does not cause any significant structural distortions or secondary phase formation. Fig. 5.1(b) presents the 3-D polyhedron structure of $\text{BaZr}(\text{PO}_4)_2$ which has been constructed using the

Vesta software. The crystal structure comprises of the alternating layers of barium cations and $\text{Zr}(\text{PO}_4)_2$ structural units that are stacked parallel to the (011) crystallographic plane. The $\text{Zr}(\text{PO}_4)_2$ layers consist of a three-dimensional network where ZrO_6 octahedra and PO_4 tetrahedra are interconnected via corner-sharing arrangements thus creating a robust framework that forms one type of layer in the structure. Barium cations are intercalated between these $\text{Zr}(\text{PO}_4)_2$ layers -creating a layered architecture. When the structure is viewed along the c-axis direction, a stacked pattern can be observed where the larger coordination polyhedra - specifically the ZrO_6 octahedra and BaO_{10} polyhedra - are distributed throughout the structure. The PO_4 tetrahedra assume a tilted orientation to serve as linking units that connect multiple coordination polyhedra simultaneously. Each PO_4 tetrahedron shares corners with three different ZrO_6 octahedra and one BaO_{10} polyhedron, thereby creating an extended three-dimensional network that stabilizes the entire crystal structure. The smaller PO_4 tetrahedra therefore act like a bridge in the overall connectivity between the tetrahedral and polyhedral coordination units thus providing the primary structural framework that governs stability and mechanical properties of the crystalline lattice [74–76]. The conceivable substitution sites of the dopant ions can be deduced through evaluation of the percentage ionic radius gap D_r between the host ions $\text{Ba}^{2+}/\text{Zr}^{4+}$ ($R = 1.35/0.72 \text{ \AA}$) with respect to the dopant ions $\text{Bi}^{3+}/\text{Tb}^{3+}$ ($R = 1.03/0.923 \text{ \AA}$). The percentage difference being less than 30% for Bi^{3+} and Ba^{2+} also for Tb^{3+} and Zr^{4+} suggests the probable substitution of Ba^{2+} by Bi^{3+} and Zr^{4+} by Tb^{3+} [148].

The crystallite size is an important microstructural parameter that need to be investigated as the photoluminescent efficiency and spectral characteristics of phosphor materials are correlated with the crystallite size. Evaluation of crystallite dimensions provides better understanding of the crystallinity and the structural defects present within the host lattice. These structural attributes have significant influence on the radiative and non-radiative recombination processes that govern the luminescence features of the phosphor system [98]. The average value of crystallite dimension was evaluated employing Debye-Scherrer formulation from the observed broadening of the diffraction peaks for major planes [83]. The obtained values for average crystallite size are given in Table 5.1. It can be observed from Table 1 that as the content of Bi^{3+} is increased in the host matrix the crystallite size plummets which could be attributed to lattice contraction arising from replacement of larger ionic radii Ba^{2+} with smaller ionic radii Bi^{3+} . For the co-doped samples, it can be seen that as Tb^{3+} content is raised with Bi^{3+} content fixed the crystallite size increases due to replacement of smaller Zr^{4+} ion by the larger Tb^{3+} ion [191].

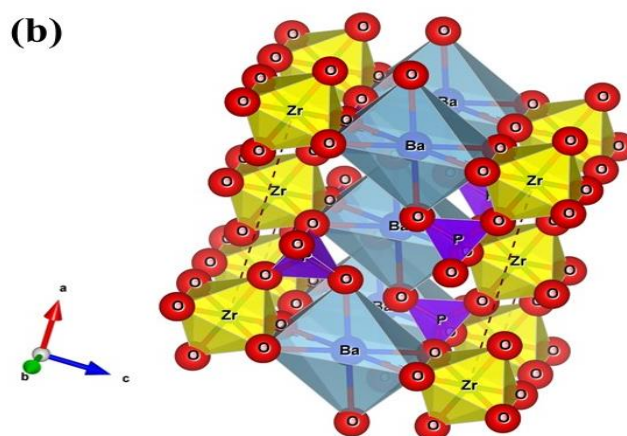
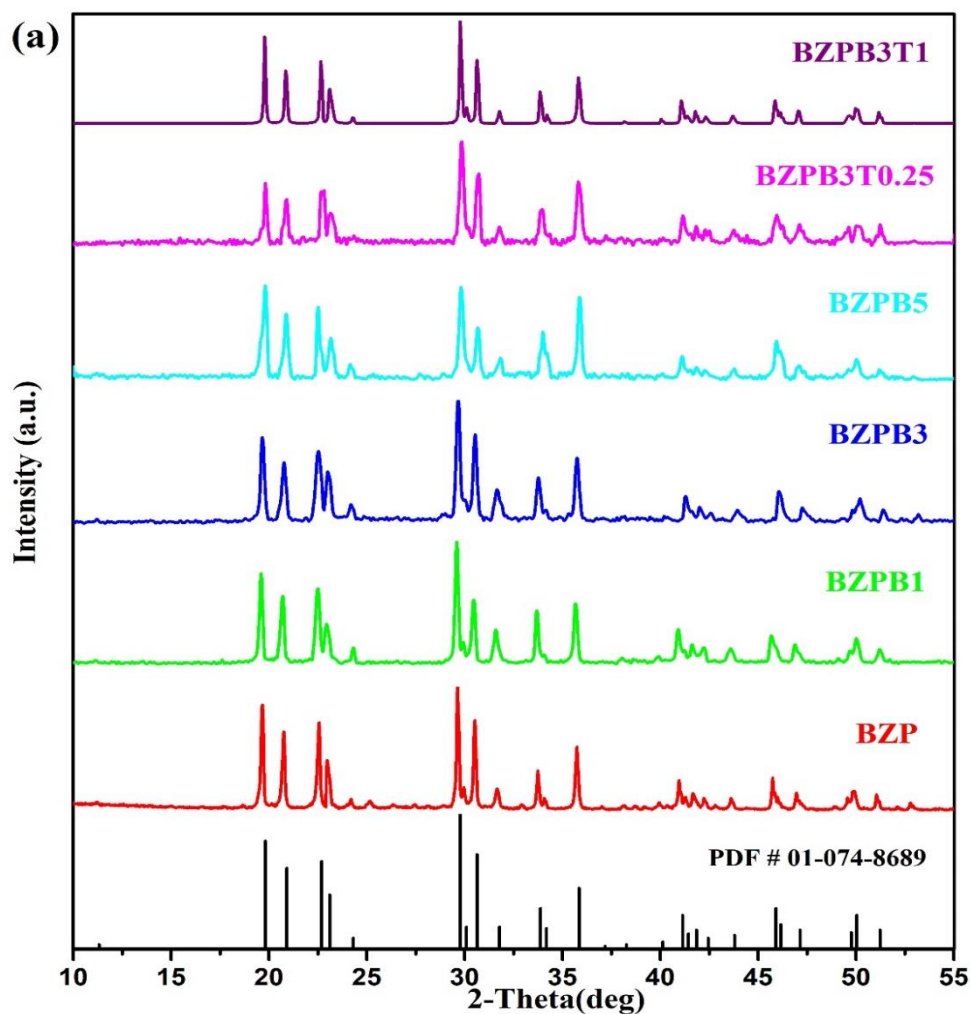


Fig. 5.1. (a) XRD graph for pure phase, Bi^{3+} doped and $\text{Bi}^{3+}/\text{Tb}^{3+}$ co-doped BZP phosphors along with standard diffraction pattern; **(b)** Crystal structure unit cell depicting polyhedron coordination for of $\text{BaZr}(\text{PO}_4)_2$

5.3.2. Microstructure studies and elemental analysis:

The microstructural studies of selected phosphor samples have been carried out by employing SEM to obtain high resolution SEM micrographs, to generate elemental maps and energy dispersive spectrometer (EDS) spectrum. Fig. 5.2 (a) and (b) displays the SEM micrograph along with elemental mapping for the BZPB3 and BZPB3T0.50 phosphor samples. The figures reveal inhomogeneous shape and size of the particles formed by agglomeration of smaller cluster due to high temperature calcination. [192]. The grain size varies in range of 2- 10 μm . The EDS spectrum depicted in Fig.5.2(c) reveals the signals from Ba, Zr, P, O, Bi and Tb elements thus confirming their presence in the samples. Moreover, the elemental mapping images in Fig.5.2 (c) and (d) reveals that they are evenly distributed throughout the sample. The microstructural studies of selected phosphor samples have been carried out by employing

Sample Name	Crystallite Size (nm)
BZP	42.96
BZPB1	41.67
BZPB3	35.65
BZPB5	30.43
BZPB3T0.25	33.23
BZPB3T1	45.54

Table 5.1. Crystallite size of pure and doped $\text{BaZr}(\text{PO}_4)_2$

SEM to obtain high resolution SEM micrographs, to generate elemental maps and energy dispersive spectrometer (EDS) spectrum. Fig.5.2 (a) and (b) displays the SEM micrograph along with elemental mapping for the BZPB3 and BZPB3T0.50 phosphor samples. The figures reveal inhomogeneous shape and size of the particles formed by agglomeration of smaller cluster due to high temperature calcination[192]. The grain size varies in range of 2- 10 μm . The EDS spectrum depicted in Fig.5.2(c) reveals the signals from Ba, Zr, P, O, Bi and Tb elements thus confirming their presence in the samples. Moreover, the elemental mapping images in Fig. 5.2 (c) and (d) reveals that they are evenly distributed throughout the sample.

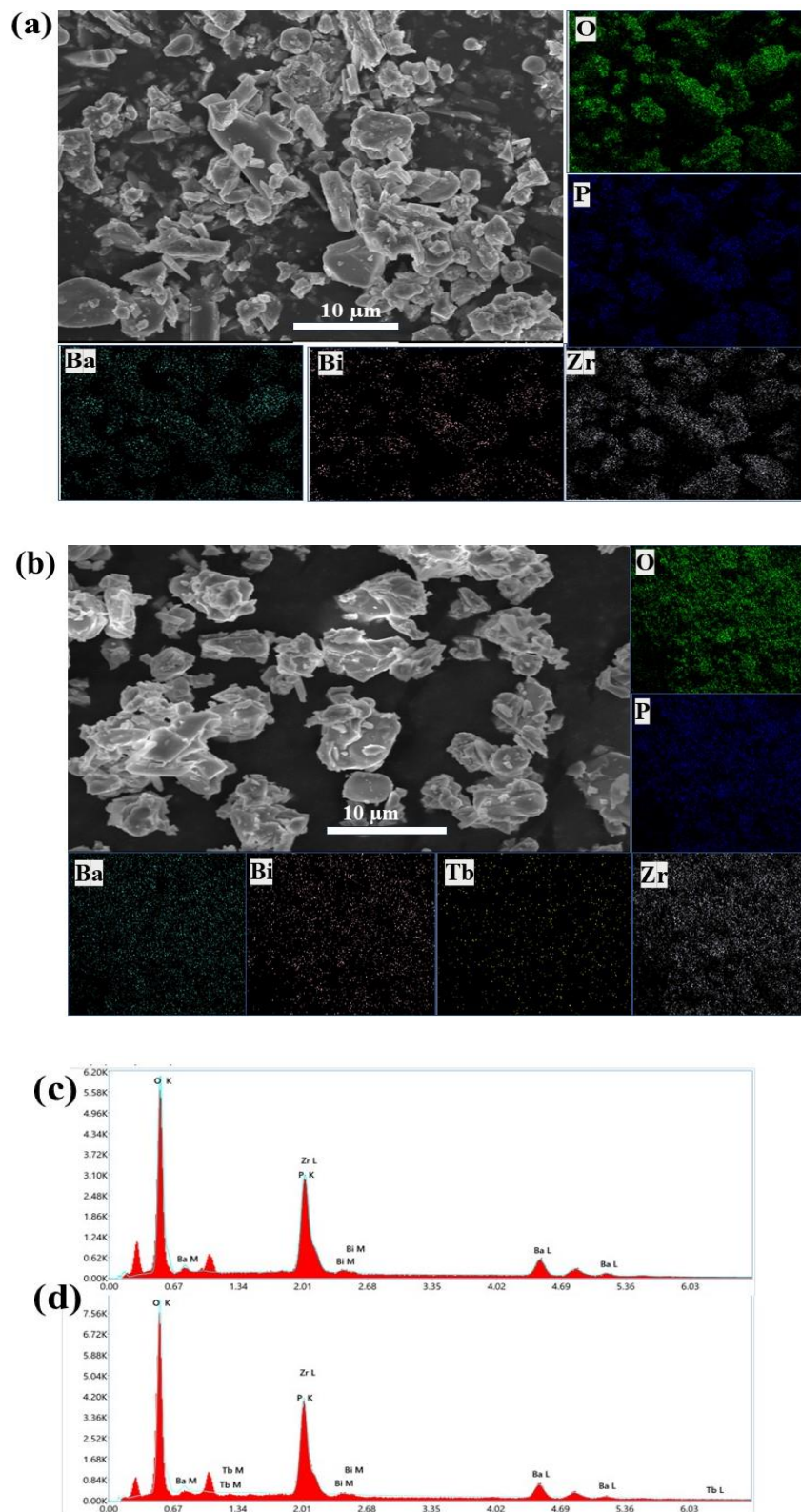


Fig.5.2. The SEM micrograph along with elemental maps of **(a)** BaZr(PO₄)₂:0.03Bi³⁺ ; **(b)** BaZr(PO₄)₂: 0.03Bi³⁺, 0.005Tb³⁺ ; **(c)** EDS profile of BaZr(PO₄)₂:0.03Bi³⁺ ; **(d)** BaZr(PO₄)₂: 0.03Bi³⁺, 0.005Tb³⁺

5.3.3. Spectral analysis of $\text{BaZr}(\text{PO}_4)_2:\text{Bi}^{3+}$ Phosphors

The excitation and emission spectra of BZPB3 phosphor are shown in Fig. 5.3(a). It can be observed that excitation profile when recorded at an emission wavelength of 468 nm consist of band spanning the range 275-350 nm centered at 313 nm. The emission profile recorded by monitoring the excitation wavelength at 313 nm comprise of an asymmetrical broad band peaking at 468 nm with a weak shoulder present at 521 nm spanning the range 385 nm to 600 nm. The asymmetric nature of emission band indicates that Bi^{3+} ions are present at multiple lattice sites in the BZP host [193]. To further analyze the emission spectrum Gaussian fitting was employed to deconvolute the emission spectrum in to two distinct bands centered at 468 and 521 nm as shown in Fig. 5.3(b) thus confirming presence of two emission centers. Fig. 5.3(c) depicts the transitions between electronic states that are accountable for the emission and excitation bands of Bi^{3+} ions in PLE and PL spectra. The ground state of Bi^{3+} with $6s^2$ electronic configuration is $^1\text{S}_0$ while excited state originates from $6s6p$ configurations and consist of a singlet $^1\text{P}_1$ state and triplet levels $^3\text{P}_0$, $^3\text{P}_1$, and $^3\text{P}_2$. The transitions through $^1\text{S}_0$ ground state to $^3\text{P}_0$ and $^3\text{P}_2$ are prohibited by spin selection rules, whereas the ones from ground state to $^3\text{P}_1$ and $^1\text{P}_1$ are allowed with high absorption strength owing to spin orbit coupling [183,194]. So, the band in excitation spectrum around 313 nm corresponds to $^1\text{S}_0 \rightarrow ^3\text{P}_1$ transitions and emission band results from $^3\text{P}_1 \rightarrow ^1\text{S}_0$ transition of Bi^{3+} as shown in Fig. 5.3(c).

Fig. 5.3(d) illustrates the PL spectra of BZP: $x\text{Bi}^{3+}$ phosphor with different concentration of Bi^{3+} monitored by exciting samples with 313 nm photons. It is evident from Fig. 5.3(e) that as the content of dopant Bi^{3+} ions is raised from 1.0 to 3.0 mol% the emission peak tends to elevate while after this level any subsequent addition of Bi^{3+} a decrement in emission intensity is observed. Thus, the optimized content of Bi^{3+} ions in BZP phosphors is considered to be 3.0 mol%. The concentration quenching effect can be held accountable for this fall in intensity which occurs when the distance between the dopant ions is less than the critical distance (R_c) which is given by Blasse's formula mentioned elsewhere [195]. The calculated R_c figure for BZP phosphor is 22.44 Å which being greater than 5 Å indicates that electronic interactions are accountable for concentration quenching. The nature of the involved electronic interaction could be either dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole which depends on constant of multipolar interaction parameter Q which take value 6, 8 and 10 for respective interaction. The value of Q can be obtained using Van Uitert's equation from Dexter's theory given by equation (5.1) [83]:

$$\log\left(\frac{I}{c}\right) = -\frac{Q}{3}\log(c) + A \quad (5.1)$$

Where I is Intensity of emitted photons, c is concentration of dopant ion and A is a constant. Using graph for Equation (5.1) is plotted and is depicted in Fig.5.4(f). The Slope of graph equals $Q/3$ which is calculated to be 3.41 thus yielding value of Q to be 10.2 thereby establishing that quadrupole-quadrupole interactions are accountable for the concentration quenching phenomenon. The above results reveal that BZP: Bi^{3+} phosphors exhibit the broad absorption in UV region and emission band in blue region attributed to transitions among $^3\text{P}_1$ and $^1\text{S}_0$ bands thus appropriate to act as sensitizer for co-doping.

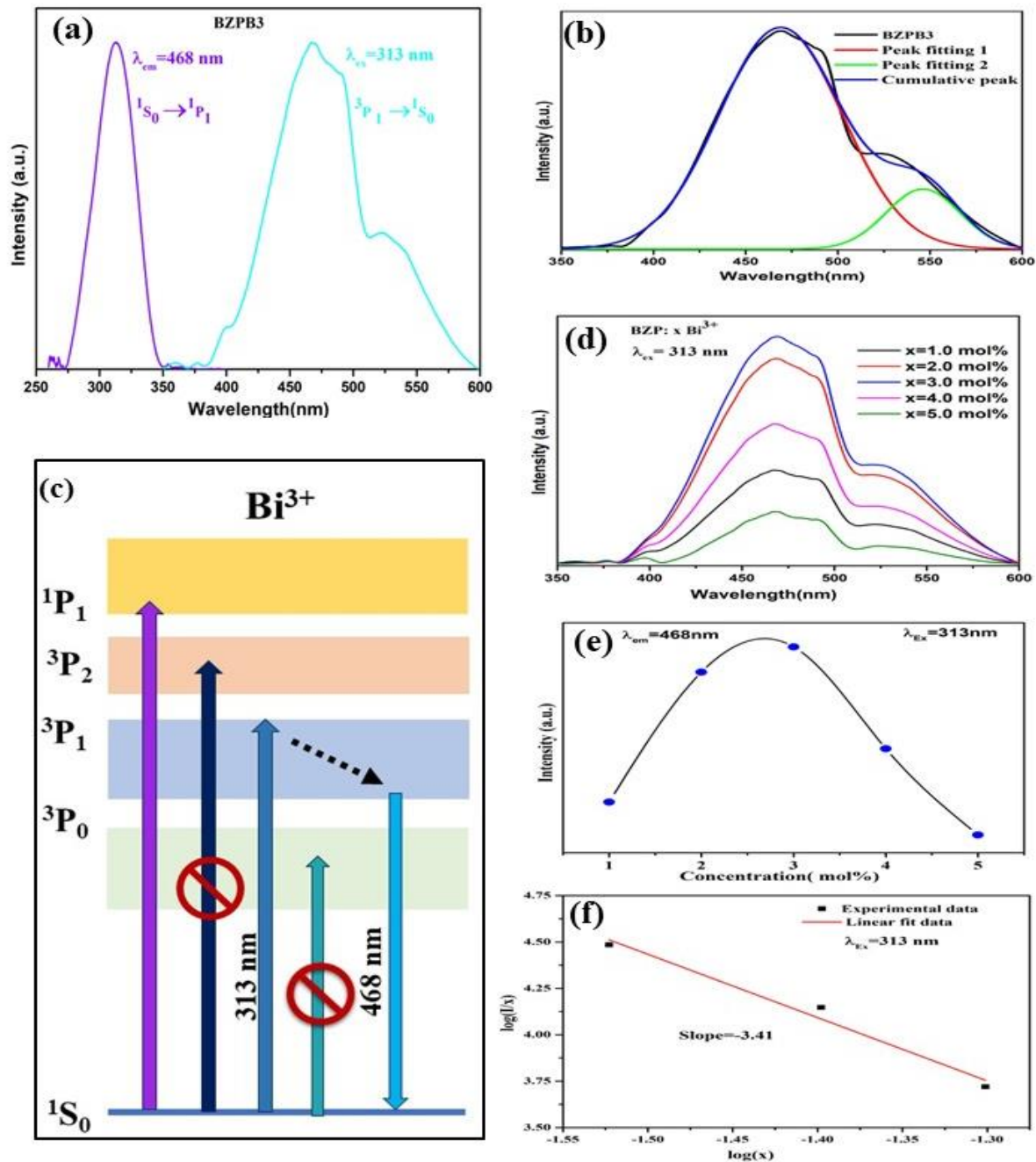


Fig.5.3. (a) The excitation and emission spectra of BZPB3 phosphor; (b) The emission spectra of BZP: xBi³⁺ (x = 1.0-5.0 mol%) under 310 nm excitation wavelength; (c) The partial energy level diagram of Bi³⁺ depicting possible electronic transitions; (d) The emission spectra of BaZr(PO₄)₂:x Bi³⁺ (x = 1.0-5.0 mol%) under 310 nm excitation wavelength; (e) Luminescence intensity in relation to the doping concentration of Bi³⁺; (f) Plot of $\log(I/x)$ versus $\log(x)$ for BZP: xBi³⁺ (x = 1.0-5.0 mol%).

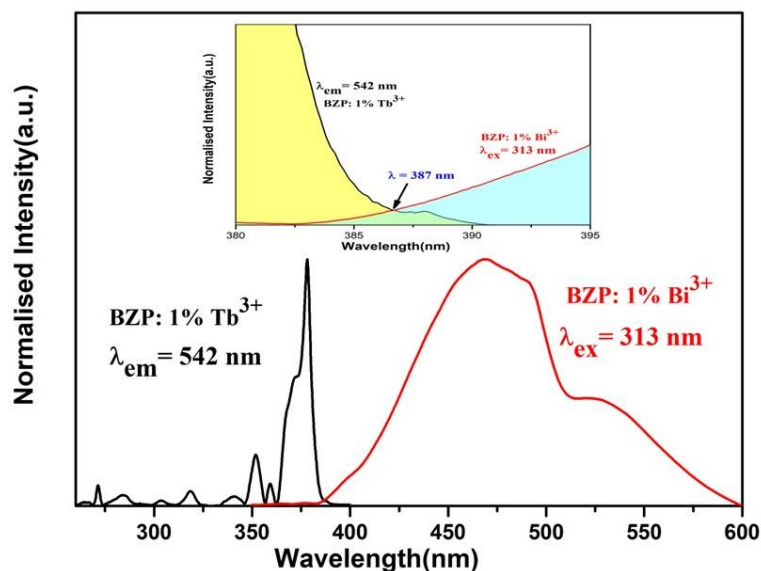


Fig.5.4. The spectral overlap spectral overlap of excitation spectrum of BZP: 1% Tb³⁺ and emission spectrum of BZP: 1% Bi³⁺.

5.3.4 Photoluminescence Properties of BaZr(PO₄)₂: Bi³⁺, Tb³⁺ Phosphors

Bi³⁺ generally have a broad UV absorption while Tb³⁺ despite having sharp emission peaks in yellow green region have weak absorption in UV range due to spin forbidden transitions in UV and NUV range so, Bi³⁺ ions can be employed as sensitizer to stimulate Tb³⁺ ions as activators and improve luminescence and obtain color tuning via energy transfer from Bi³⁺ to Tb³⁺ [186]. The Forster-Dexter theory provides the requisite for energy transfer between ions and highlights that such transfer takes place when emission spectrum of sensitizer overlaps with excitation of activator [78,196]. Fig.5.4 depicts the spectral overlap of excitation band ⁷F₆–⁵D₆ of Tb³⁺ centered at 378 nm with the ³P₁ → ¹S₀ emission band of Bi³⁺ indicating possible energy transfer from Bi³⁺ to Tb³⁺ in a co-doped BZP system. Therefore, we synthesized Bi³⁺ and Tb³⁺ co-doped phosphors to study energy transfer between them in order to achieve color tunability.

The emission spectrum of single Tb³⁺ doped BZP phosphor sample BZPT1 recorded by keeping excitation wavelength at 378 nm is presented in Fig.5.5. The emission spectrum comprises of characteristic emission bands of Tb³⁺ with peaks at 417 (⁵D₃→⁷F₅), 436 (⁵D₃→⁷F₄), 489 (⁵D₄→⁷F₆), 542 (⁵D₄→⁷F₅), 583 (⁵D₄→⁷F₄) and 622 nm (⁵D₄→⁷F₃) with most intense peak present at 542 nm. Among these ⁵D₄→⁷F₅ transition located at 542 nm is magnetic dipole transition and obeys selection rule ΔJ = ±1. While the ⁵D₄→⁷F₆ transition centred at 489

nm is electric dipole in nature and obeys selection rule $\Delta J = 2$. The PL excitation profiles of BZPB1, BZPT1 and BZPB1T1 phosphors are compared in Fig. 6. The excitation spectrum of singly Bi^{3+} doped BZP phosphor as shown in Fig. 6 (a) exhibits the characteristic $^1\text{S}_0 \rightarrow ^3\text{P}_1$ transition band in range 275-350 nm centered at 313 nm. Fig.5.6 (b) shows the excitation spectrum of single Tb^{3+} doped BZP phosphor monitored at emission of 542 nm and it reveals various narrow peaks belonging to electronic transitions of Tb^{3+} ions. The small band present at 271 nm corresponds to 4f-5d transition of Tb^{3+} while all other results from 4f-4f transitions [197]. The band centered around 283, 304, 319, 340, 352, 359, 370 and 378 nm corresponds to transitions from $^7\text{F}_6$ ground state to $^5\text{H}_4$, $^5\text{H}_6$, $^5\text{H}_7$, $^5\text{L}_9$, $^5\text{L}_0$, $^5\text{G}_3$ and $^5\text{G}_6$ levels of Tb^{3+} and the most intense band corresponds to 378 nm wavelength [180,181,198]. It can be observed from the Fig.5.6 (c) that for BZPB1T1 phosphor when excitation spectrum is monitored at 468 nm emission which is characteristic Bi^{3+} emission not only excitation band corresponding to Bi^{3+} at 313 nm is present but also weak Tb^{3+} band around 378 nm can be seen. Similarly, when excitation is recorded with characteristic Tb^{3+} emission at 542nm a band in range 275-350 nm corresponding to Bi^{3+} emission is clearly visible. The above observations indicate energy transfer between Bi^{3+} and Tb^{3+} ions [186]. In order to investigate the course of transfer of energy in detail the co-doped phosphor samples of BZP: 0.03 Bi^{3+} , x Tb^{3+} (x=0. 25, 0. 5, 0. 75 and 1.0 mol %) were prepared and photoluminescent analysis has been carried out. The PL emission spectra of codoped BZP:3.0 Bi^{3+} , x Tb^{3+} phosphors has been analyzed by exciting with different wavelengths of 313 nm (Tb^{3+} excitation), 378 nm (Bi^{3+} excitation), 387 nm (spectral overlap of excitation band $^7\text{F}_6 \rightarrow ^5\text{D}_6$ of Tb^{3+} with the $^3\text{P}_1 \rightarrow ^1\text{S}_0$ emission band of Bi^{3+}) and 468 nm (Bi^{3+} emission) to comprehend the energy transfer process and achieve the color tunability.

Fig.5.7 (a) depicts the emission spectra for BZP:3.0 Bi^{3+} , x Tb^{3+} phosphors samples when monitored at an excitation wavelength of 313 nm which is pure Bi^{3+} excitation. For the co-doped phosphors, it can be observed that along with characteristic emission band of Bi^{3+} resulting from $^3\text{P}_1 \rightarrow ^1\text{S}_0$ transition, multiple peaks centered at 436, 488, 542, 583 and 622 nm corresponding to the 4f-4f transitions of Tb^{3+} are also present. The peak in green region centered around 542 nm which belongs to $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of Tb^{3+} is the dominant peak. The emission spectra for the co-doped samples can be looked upon as the superposition of emission spectra of BZP: Tb^{3+} ions on the emission spectra of BZP: Bi^{3+} ions. The emission intensity of blue band resulting from $^3\text{P}_1 \rightarrow ^1\text{S}_0$ transition of Bi^{3+} can be observed to decrease as the content of Tb^{3+} is increased. Moreover, the emission intensity of the peaks resulting from

Tb³⁺ 4f-4f transitions are seen to be increased initially as content of Tb³⁺ ions is raised from 0.25 mol% till 0.75 mol %, thereafter due to phenomenon of concentration quenching it falls. Fig.5.7 (b) displays the variation in the intensities of blue band (³P₁ → ¹S₀ transition of Bi³⁺) and green emission (⁵D₄→⁷F₅ transition of Tb³⁺) with variation in concentration of Tb³⁺ for BZP:3.0 Bi³⁺, x Tb³⁺ co-doped phosphors. The intensity of blue emission due to Bi³⁺ falls off rapidly with incorporation of Tb³⁺ ions while the green emission becomes more intense steadily attaining maximum intensity when Tb³⁺ concentration is 0.75 mol% and it falls thereafter due to concentration quenching. The above observations demonstrate the phenomenon of energy transfer where Bi³⁺ assumes the role of sensitizer by imbibing energy from the UV photon which it transfer to Tb³⁺ activator that emits energy in form of green photon [182,199].

Fig.5.8 shows the emission profile of BZP:3.0 Bi³⁺, x Tb³⁺ (x= 0.25, 0.5, 0.75 and 1.0 mol%) phosphors recorded by keeping the excitation wavelength at 378 nm which is pure Tb³⁺ excitation. It is apparent that the emission spectra of co-doped samples exhibit the peaks corresponding to ⁵D₃→⁷F_J (J = 5 and 4) and ⁵D₄→⁷F_J (J = 6, 5, 4 and 3) transitions of Tb³⁺ located at 417, 436, 489, 542, 583 and 622 nm while the Bi³⁺ emission band is not visible indicating negligible energy transfer from Tb³⁺ to Bi³⁺. Moreover, as the Tb³⁺ concentration is increased the emission intensity increases from 0.25 mol% of Tb³⁺ till 0.75 mol% of Tb³⁺, thereafter it decreases owing to concentration quenching effects.

Fig.5.9 depicts the emission profile of BZP:3.0 Bi³⁺, x Tb³⁺ (x= 0.25, 0.5, 0.75 and 1.0 mol%) phosphors by exciting them via 387 nm photons which corresponds to the overlap of Tb³⁺ excitation with Bi³⁺ emission. It can be observed that with 387 nm excitation the emission band of Bi³⁺ though is visible but is not as strong as it was observed under 313 nm. Further Tb³⁺ peaks are also present with the one corresponding to its ⁵D₄→⁷F₅ transition being the most intense peak. The emission intensity follows the same trend as with other excitations attaining maximum intensity at 0.75 mol % and falling after that indicating concentration quenching has been achieved.

The emission spectra recorded for excitation wavelength corresponding to the emission of sensitizer Bi³⁺ at 468 nm is displayed in Fig.5.10. It reveals that ⁵D₄→⁷F₅ transition which usually is the most intense has become so feeble that it is just noticeable whereas ⁵D₄→⁷F₆ level turned in to the most intense exhibiting stark splitting in to two bands located at 482 and 495 nm. The weak presence of ⁵D₄→⁷F₆ band in the spectra can be observed in the inset of the Fig.

5.10. The above observations may be accounted by the preferential population of 5D_4 Stark level due to transfer of energy to Tb^{3+} from Bi^{3+} .

The possible mechanism behind the transfer of energy from Bi^{3+} to Tb^{3+} can be explained from Fig.5.11 depicting the partial energy diagram. The Bi^{3+} electrons absorb UV photons and get transitioned to 3P_1 excited level from 1S_0 ground level. These electrons are then relaxed to a sublevel of 3P_1 state via non radiative transitions. Some of electrons then return to 1S_0 ground state emitting photons in blue region while, another batch of electrons transmits energy to 5D_3 level of Tb^{3+} ions via phonon assisted non radiative relaxation. The electrons then may reach to 5D_4 level from 5D_3 level of Tb^{3+} . Ultimately electrons return to 7F_J levels emitting photons in green region.

Further to understand the process of energy transfer between sensitizer and activator in detail in detail the average critical distance (R_c) between Bi^{3+} and Tb^{3+} was evaluated using Blasse's formula [60]. The value of R_c came out to be 21.85 Å indicating multipolar interactions responsible for energy transfer. Further Riesfeld's and Dexter theory was employed to investigate the nature of multipolar interactions. The equation (5.2) relates the ratio of emission intensity of Bi^{3+} without Tb^{3+} ions (I_0) and emission intensity of Bi^{3+} with Tb^{3+} ions (I_s) [200]:

$$\frac{I_0}{I_s} \propto C \frac{n}{3} \quad (5.2)$$

The above equation can be plotted for dipole-dipole ($n = 6$), dipole-quadrupole ($n = 8$) and quadrupole-quadrupole ($n = 10$) interactions. Such a plot for different values of n is shown in Fig. 12. It can be observed from Fig.5.12 that the curve with best fit is the one with $n = 6$ establishing energy transfer via dipole-dipole interactions.

Further the efficiency of energy transference from Bi^{3+} to Tb^{3+} is estimated exploiting the following equation (5.3) [95]:

$$\eta_t = 1 - \frac{I_s}{I_0} \quad (5.3)$$

Fig. 5.13 depicts the calculated values of energy transfer efficiency for BZP:3.0 Bi^{3+} , x Tb^{3+} co-doped phosphors. The maximum value of energy transfer efficiency is 64.4 % for BZP:3.0 Bi^{3+} , 1.0 Tb^{3+} phosphor.

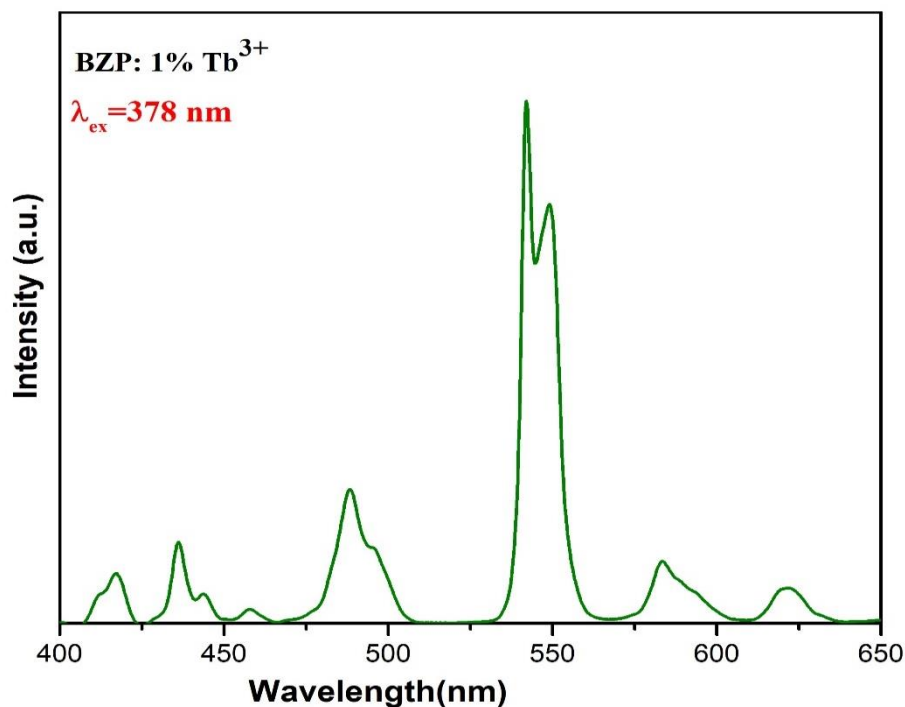


Fig.5.5. The photoluminescence emission spectra of BaZr(PO₄)₂:1.0 Tb³⁺ at excitation wavelength of 378 nm.

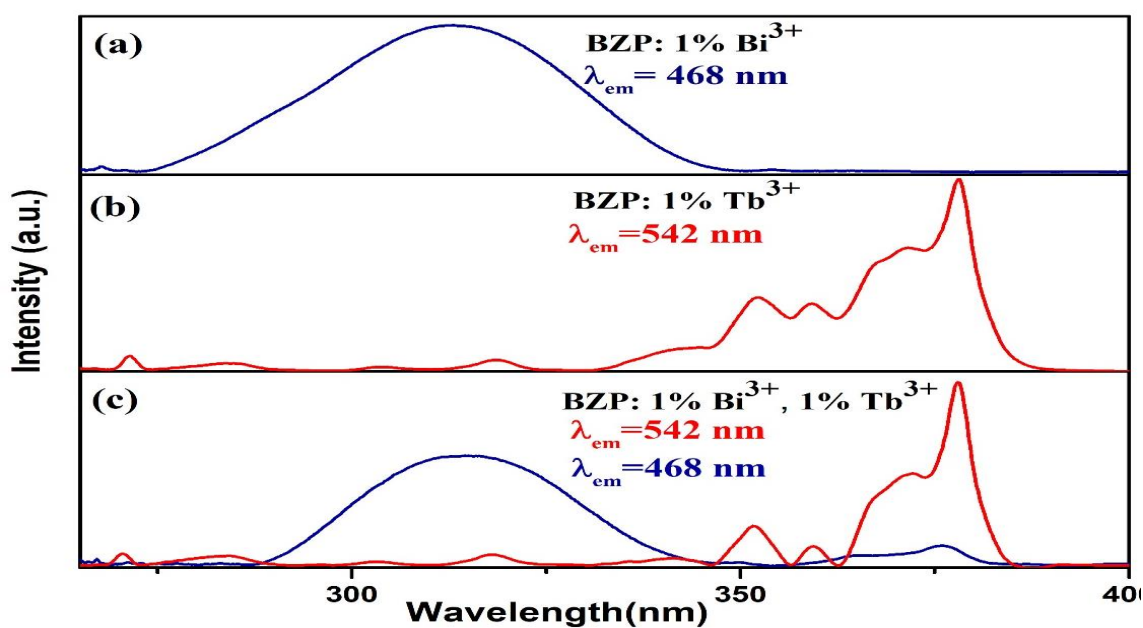


Fig.5.6. The photoluminescence excitation spectra of (a) BaZr(PO₄)₂:1.0 Bi³⁺; (b) BaZr(PO₄)₂:1.0 Tb³⁺; (c) BaZr(PO₄)₂:1.0 Bi³⁺, 1.0 Tb³⁺ co-doped phosphor by monitoring with emission wavelengths at 468 nm (blue) and 542 nm (red).

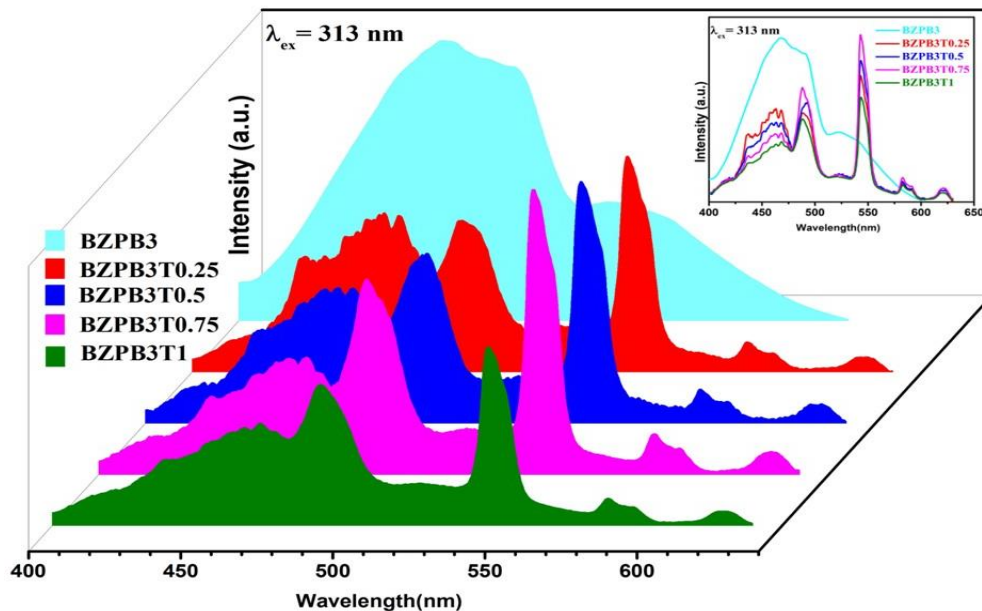


Fig.5.7 (a). The photoluminescence emission spectra of $\text{BaZr}(\text{PO}_4)_2:3.0 \text{ Bi}^{3+}, x \text{ Tb}^{3+}$ ($x = 0.0, 0.25, 0.5, 0.75$ and 1.0 mol%) at excitation wavelength of 313 nm .

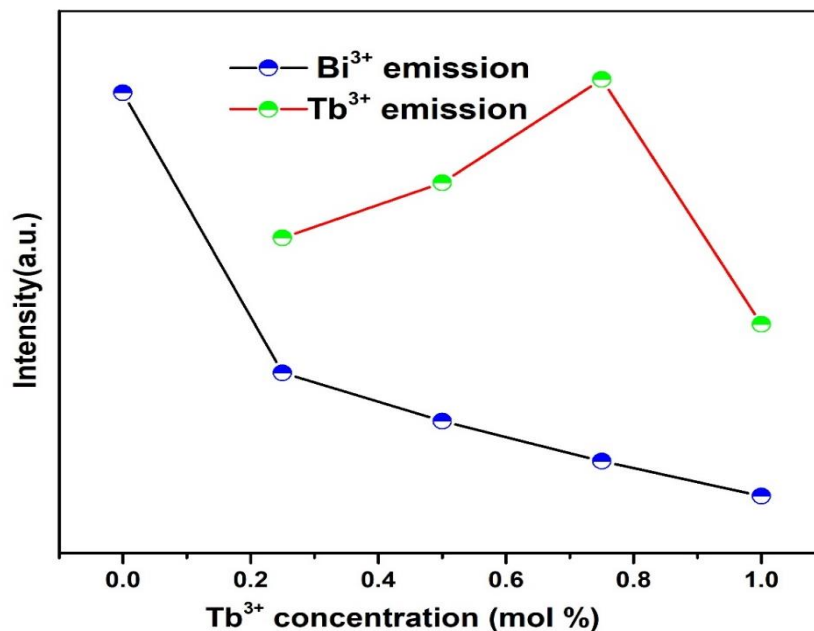


Fig.5.7 (b). The variation in intensity the intensities of blue band ($^3\text{P}_1 \rightarrow ^1\text{S}_0$ transition of Bi^{3+}) and green emission ($^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of Tb^{3+}) with variation in concentration of Tb^{3+} for $\text{BaZr}(\text{PO}_4)_2:3.0 \text{ Bi}^{3+}, x \text{ Tb}^{3+}$ ($x = 0.0, 0.25, 0.5, 0.75$ and 1.0 mol%) at excitation wavelength of 313 nm .

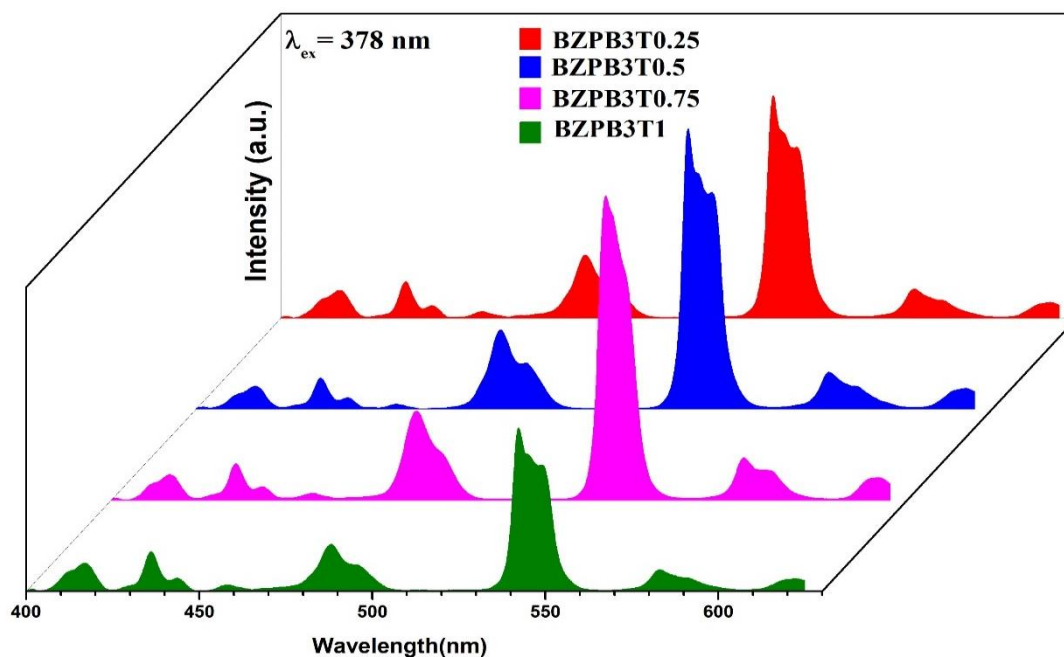


Fig.5.8. The photoluminescence emission spectra of $\text{BaZr(PO}_4)_2: 3.0 \text{ Bi}^{3+}, x \text{ Tb}^{3+}$ ($x = 0.0, 0.25, 0.5, 0.75$ and 1.0 mol%) at excitation wavelength of 378 nm.

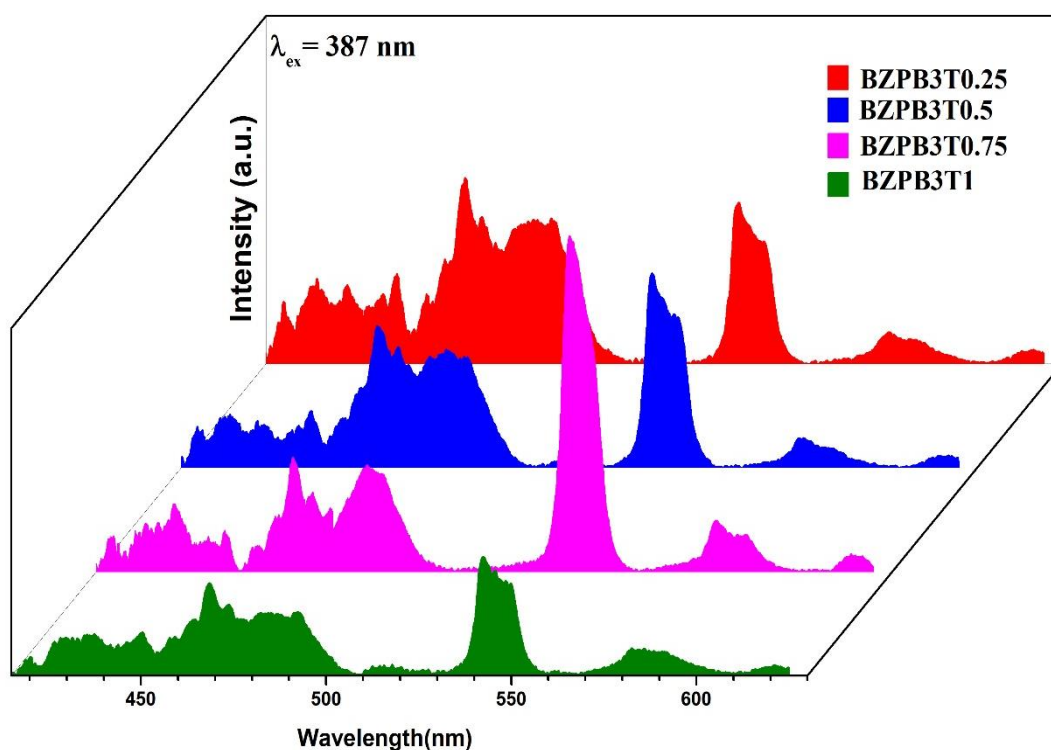


Fig.5.9. The photoluminescence emission spectra of $\text{BaZr(PO}_4)_2: 3.0 \text{ Bi}^{3+}, x \text{ Tb}^{3+}$ ($x = 0.0, 0.25, 0.5, 0.75$ and 1.0 mol%) at excitation wavelength of 387 nm.

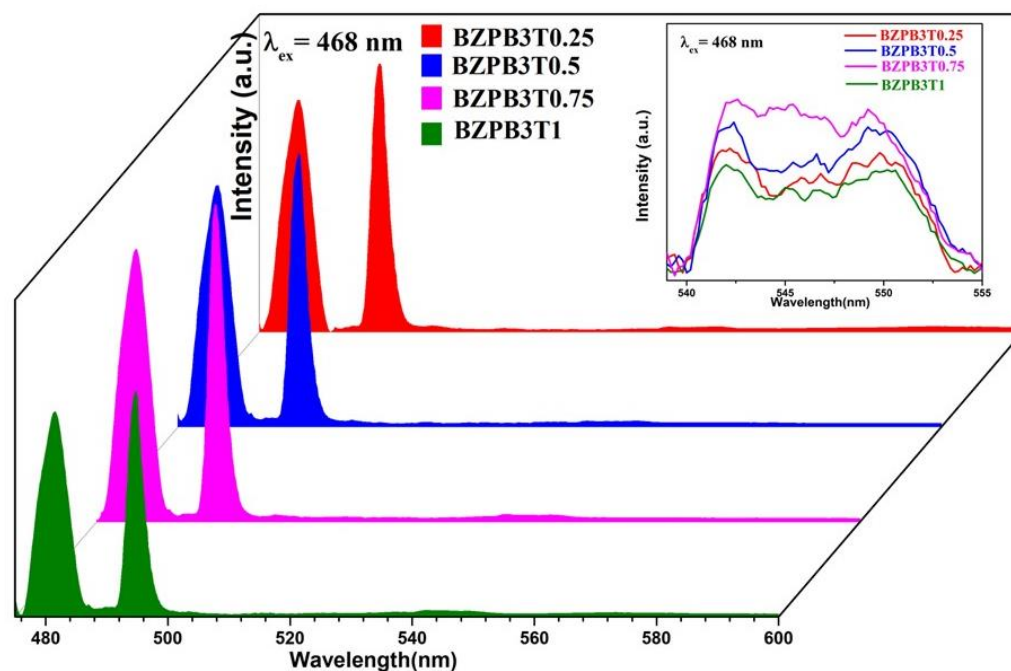


Fig.5.10. The photoluminescence emission spectra of $\text{BaZr}(\text{PO}_4)_2: 3.0 \text{ Bi}^{3+}, x \text{ Tb}^{3+}$ ($x = 0.0, 0.25, 0.5, 0.75$ and 1.0 mol%) at excitation wavelength of 468 nm .

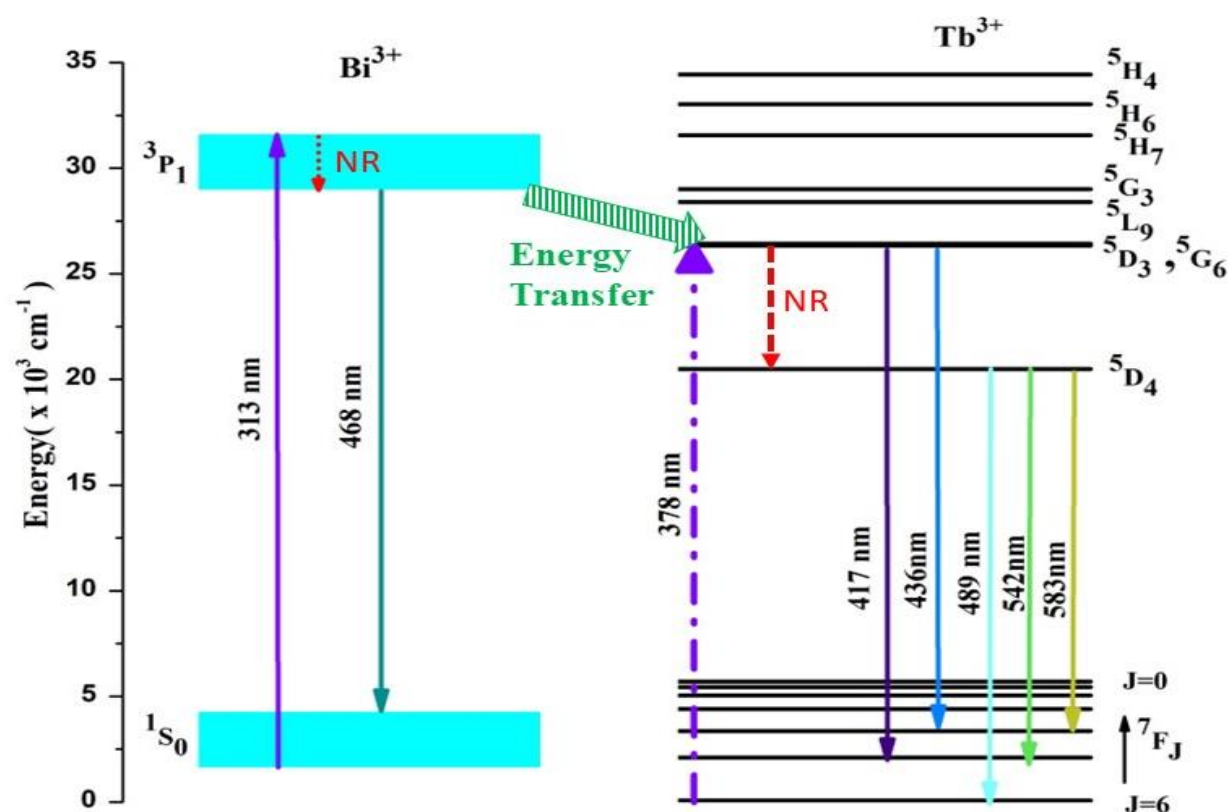


Fig.5.11. Partial energy level diagram demonstrating possible energy transfer scheme from Bi^{3+} to Tb^{3+} ions in BZP Phosphor

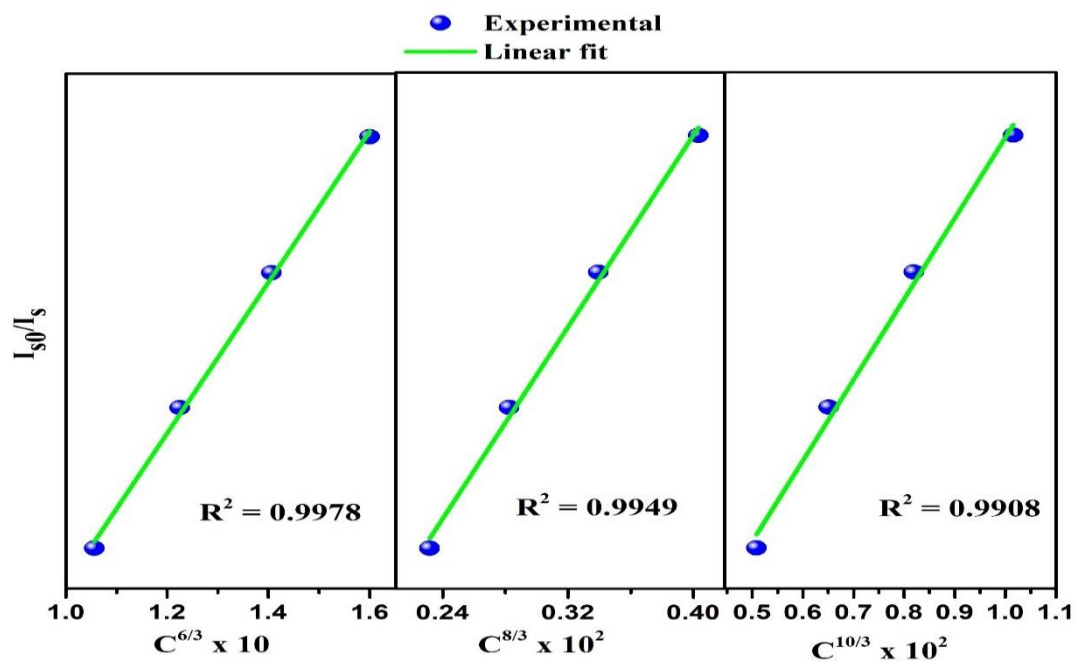


Fig.5.12. The variation of I_{s0}/I_s on $C^{n/3}$ ($n=6, 8$ and 9) in $BaZr(PO_4)_2: 0.023Bi^{3+}, yTb^{3+}$ ($y = 0.0025, 0.005, 0.0075, 0.01$).

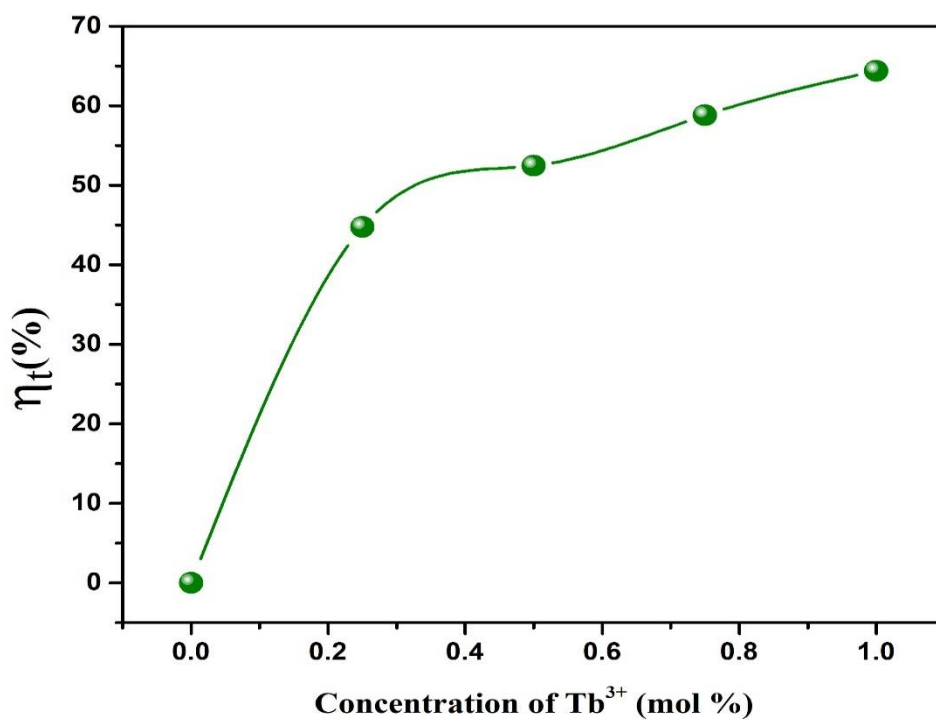


Fig.5.13. Plot of energy transfer efficiency from Bi^{3+} to Tb^{3+} in $BZP:0.03 Bi^{3+}, yTb^{3+}$ phosphors.

5.3.5 Decay Kinetics of BaZr(PO₄)₂ : Bi³⁺, Tb³⁺ Phosphors:

To further prospect the energy transfer from Bi³⁺ to Tb³⁺ the lifetime measurements have been carried out for Bi³⁺ in BZP:3.0 Bi³⁺, x Tb³⁺ (x= 0.0, 0.25, 0.5, 0.75 and 1.0 mol%) phosphors by exciting with a wavelength of 313 nm monitored at 468 nm emissions. The obtained decay traces which are fitted using bi-exponential decay function are depicted in Fig.5.14. The lifetime values were obtained as 6.209, 5.161, 4.266, 4.211 and 2.632 ms for x=0.0, 0.25, 0.50, 0.75 and 1.0 mol% respectively in BZP:3.0 Bi³⁺, x Tb³⁺ phosphors using equation mentioned elsewhere [87]. It is evident from the Fig.5.14(e) that the lifetime value for Bi³⁺ emission falls with rising concentration of Tb³⁺ ions in the co-doped samples which signals towards the migration of absorbed energy Tb³⁺ from Bi³⁺ and further strengthen the claim of transfer of energy from Bi³⁺ to Tb³⁺. Further the efficiency of energy transfer η_T to Tb³⁺ from sensitizer Bi³⁺ can be evaluated using the value of Bi³⁺ sensitizer lifetime sans activator Tb³⁺ (τ) and its lifetime value in presence of the activator (τ_0) using expression given by equation (5.4).

$$\eta_T = 1 - \frac{\tau}{\tau_0} \quad (5.4)$$

Moreover, the probability rate of energy transfer can also be obtained from lifetime values τ and τ_0 from the equation (5.5)

$$P = \frac{1}{\tau} - \frac{1}{\tau_0} \quad (5.5)$$

The obtained values for energy transfer efficiency and probability rate of energy transfer are tabulated in Table 5.2. Therefore, the findings of decay kinetics further affirm the transfer of energy transfer to Tb³⁺ sites from Bi³⁺ in BaZr(PO₄)₂: Bi³⁺, Tb³⁺ Phosphors.

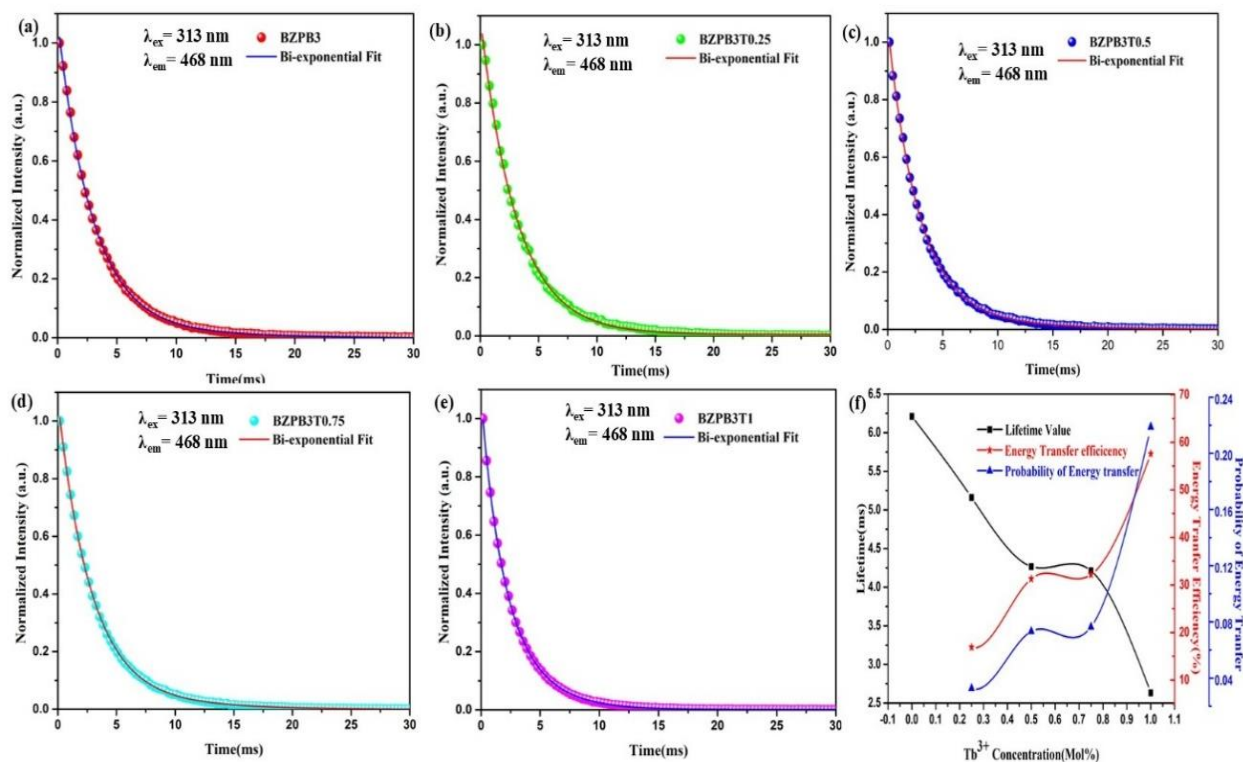


Fig.5.14. (a-e) Decay plots for BaZr(PO₄)₂: 3.0 Bi³⁺, x Tb³⁺ (x=0.0, 0.25, 0.50, 0.75 and 1.0 mol %) phosphors for 468 nm emission monitored at excitation wavelength of 313 nm; **(f)** lifetime, energy transfer efficiency and probability of energy transfer.

Sample	Fluorescent lifetime (ms)	Probability of energy transfer (P)	Energy transfer efficiency (%)
BZPB3	6.209	-	-
BZPB3T0.25	5.161	0.03	16.9
BZPB3T0.5	4.266	0.07	31.3
BZPB3T0.75	4.211	0.08	32.2
BZPB3T1	2.632	0.22	57.6

Table 5.2. Fluorescent decay lifetime values, probability of energy transfer and energy transfer efficiency for BZP:3.0 Bi³⁺, x Tb³⁺ (x = 0.0, 0.25, 0.50, 0.75 and 1.0 mol%) phosphors

5.3.6 Chromaticity of $\text{BrZr(PO}_4)_2\text{:Bi}^{3+},\text{Tb}^{3+}$ Phosphors

In order to analyze the color perception of the emission from the phosphors the emission spectra data has been used to determine the Commission International de l'Eclairage (CIE) coordinates of the phosphors using formulation from the literature [60] and the obtained coordinates are tabulated in Table 5.3. Fig.5.15 (a) reveals CIE Coordinates diagram for of BZP: x Bi^{3+} phosphors and it is evident that the emission lies in the blue region of CIE plot. Fig.5.15(b) illustrates the coordinates for BZP:3.0 Bi^{3+} , 0.25 Tb^{3+} phosphor for different excitation wavelengths of 313, 378, 387 and 468 nm and it can be seen that under different wavelengths the CIE coordinates vary from blue to green region. It can be seen from Fig.5.15(c) that for excitation wavelength of 313 nm the incorporation of Tb^{3+} along with Bi^{3+} leads to shift of the CIE coordinates from blue region towards green region on the chromaticity plot. Fig.5.15(d) reveals that for the excitation wavelength of 378 nm the colour coordinates for co-doped samples lie in green region of the chromaticity plot. Further Fig.5.15(e) shows the CIE plot for excitation wavelength of 387 nm and it reveals that the coordinates modulate from blue region to green region of the colour diagram as Tb^{3+} content is varied. As shown in Fig.5.15(f) when samples are excited with 468 nm the phosphor emission moves towards cyan region of the chromaticity plot. All these observations reveals that by varying the concentration and the excitation wavelength the emission color can be modulated in varied hues from blue to green and color and thus revealing the potential of the prepared phosphors to modulate emission color for a UV excited light emitter.

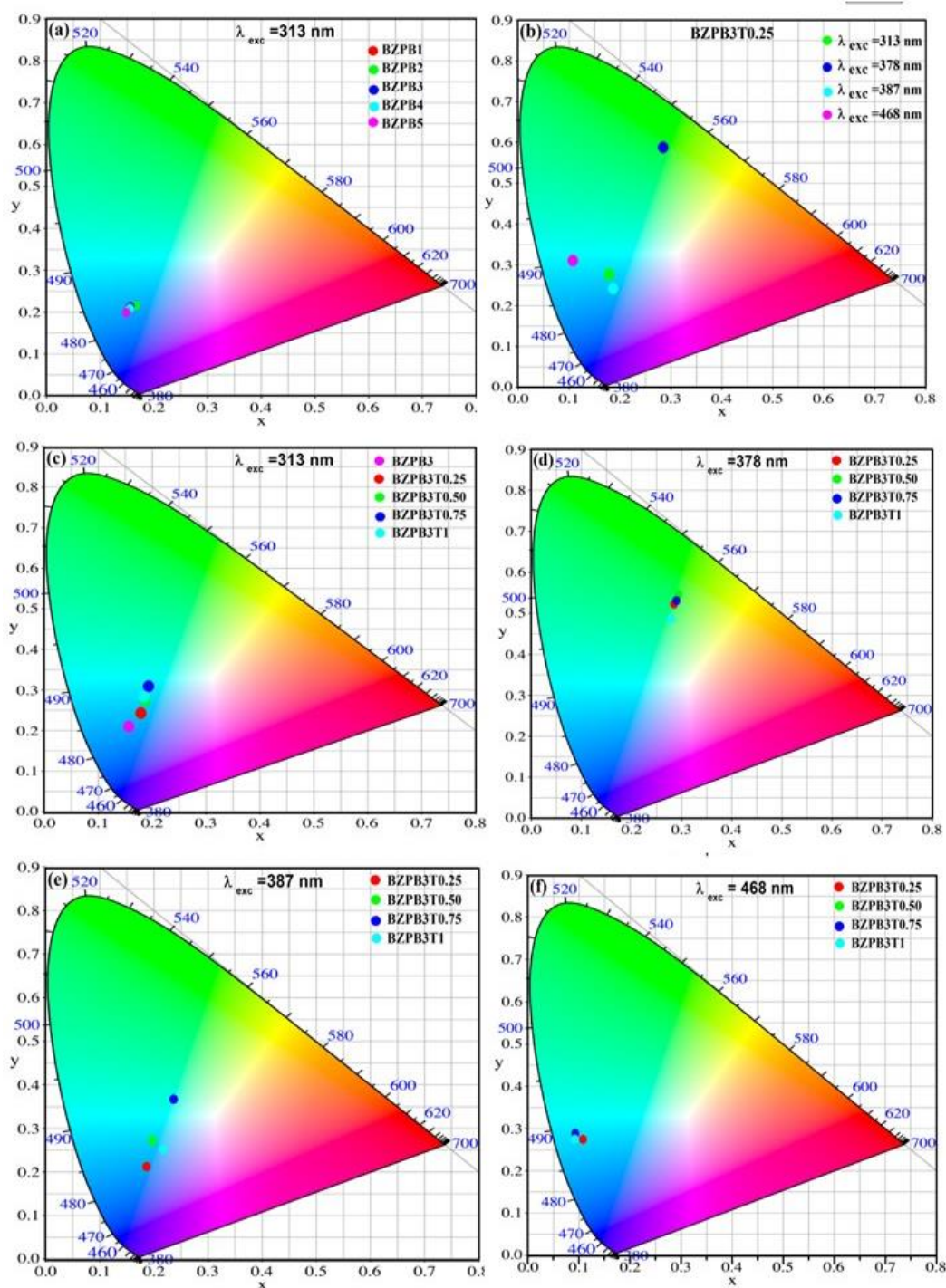


Fig.5.15. (a) CIE chromaticity co-ordinates of $\text{BaZr(PO}_4)_2:\text{xBi}^{3+}$ ($x = 1.0, 2.0, 3.0, 4.0$ and $5.0 \text{ mol\%}$) at 313 nm excitation wavelength; (b) CIE chromaticity coordinates of BZPB3T0.25 at different wavelengths ($313, 378, 387$ and 468 nm); (c–f) CIE coordinates of BZPB3T0.25, BZPB3T0.50, BZPB3T0.75 and BZPB3T1 under $313, 378, 387$ and 468 nm excitation wavelength, respectively.

Excitation Wavelength (nm)	Sample	CIE co-ordinates (x,y)
313	BZPB1	(0.155,0.211)
	BZPB2	(0.167,0.215)
	BZPB3	(0.157,0.213)
	BZPB4	(0.156,0.209)
	BZPB5	(0.149, 0.198)
	BZPB3T0.25	(0.180,0.246)
	BZPB3T0.5	(0.188,0.278)
	BZPB3T0.75	(0.194,0.312)
	BZPB3T1	(0.185,0.287)
378	BZPB3T0.25	(0.285,0.522)
	BZPB3T0.5	(0.294,0.546)
	BZPB3T0.75	(0.290,0.531)
	BZPB3T1	(0.279,0.486)
387	BZPB3T0.25	(0.187,0.215)
	BZPB3T0.5	(0.198,0.275)
	BZPB3T0.75	(0.237,0.370)
	BZPB3T1	(0.218,0.255)
468	BZPB3T0.25	(0.108,0.276)
	BZPB3T0.5	(0.092,0.282)
	BZPB3T0.75	(0.093,0.290)
	BZPB3T1	(0.092,0.276)

Table 5.3. CIE Co-ordinates for BaZr(PO₄)₂: xBi³⁺ (x = 1.0-5.0 mol%) and BaZr(PO₄)₂:3.0 Bi³⁺, x Tb³⁺(x= 0.0, 0.25,0.50, 0.75 and 1.0 mol%) phosphors.

5.4 CONCLUSIONS:

Monophasic BaZr(PO₄)₂: Bi³⁺ and BaZr(PO₄)₂: Bi³⁺/Tb³⁺ phosphors were prepared by using solid phase route. The X-Ray Diffraction studies revealed successful incorporation of Bi³⁺ and Tb³⁺ ions in pure monoclinic matrix corresponding to standard ICDD PDF card no 01s-074-8689 belonging to C2/m(12) space group. The microstructure studies show uneven micro sized

particles. The photoluminescent studies reveal that BZP: Bi³⁺ phosphors exhibit the broad excitation band in UV region and emission band in blue region attributed to transitions among ³P₁ and ¹S₀ bands. The PL studies in BZP: Bi³⁺/Tb³⁺ Phosphor demonstrate energy transfer from Bi³⁺ as a sensitizer to Tb³⁺ activator where dipole-dipole interactions being reason behind energy transfer mechanism. The maximum value of energy transfer efficiency is 64.4 % for BZP: 3.0Bi³⁺, 1.0Tb³⁺ phosphor. The findings of decay kinetics further affirm the transfer of energy to Tb³⁺ sites from Bi³⁺ in BaZr(PO₄)₂: Bi³⁺/Tb³⁺ Phosphors. The coactivated Bi³⁺/Tb³⁺ phosphor exhibits tunability in emission by adjusting concentration of activator and coactivator and the excitation wavelength. Thus, all these findings indicated that the BZP: Bi³⁺ and BZP: Bi³⁺/Tb³⁺ phosphor is a promising candidate for solid-state lighting and color tunable devices.

6

CHAPTER

Conclusion, Future Scope of Work and Social Impact

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- ❖ ZP phosphors doped with rare-earth ions were successfully synthesized with phase purity and stable monoclinic structure.
 - ❖ The doped and co-doped samples exhibited strong blue, yellow, orange, and red emissions suitable for white and tunable lighting.
 - ❖ The phosphors showed excellent thermal stability and sustained luminescence at elevated temperatures.
 - ❖ Energy transfer among activator ions enhanced colour tuning and overall emission intensity.
 - ❖ Future work includes exploring new dopants, host modifications, nano-structuring, and LED device fabrication.
 - ❖ The research supports energy-efficient lighting, environmental sustainability, and technological advancements.
 - ❖ The developed phosphors offer social benefits through reduced energy consumption, rural illumination, and national self-reliance.
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6.1 CONCLUSION

The present work focused on the systematic synthesis, structural characterization, photoluminescence investigation, and performance evaluation of $\text{BaZr}(\text{PO}_4)_2$ (BZP) based phosphor materials doped with different rare-earth ions for their applicability in solid-state lighting (SSL) systems. The motivation behind developing these phosphors arose from the growing global demand for energy-efficient, cost-effective, and thermally stable luminescent materials capable of supporting high-power LEDs. The $\text{BaZr}(\text{PO}_4)_2$ host, owing to its high chemical stability, wide band gap, rigid phosphate framework, and excellent thermal endurance, offered an ideal matrix for hosting various activator ions and for exploring their luminescent behaviour.

In this research, the phosphors were synthesized successfully through a conventional high-temperature solid-state reaction method. The synthesis process allowed the formation of uniform, phase-pure structures free from impurities, as confirmed through detailed X-ray diffraction and Rietveld refinement analyses. The results established that the incorporation of Dy^{3+} , Eu^{3+} , Sm^{3+} , and co-dopants did not disrupt the monoclinic crystal structure of the BZP lattice. Lattice distortion introduced by dopants remained within tolerable limits, demonstrating the host's ability to accommodate a wide range of activator ions without structural instability.

Morphological studies revealed that the phosphors possessed a well-defined microstructure with grain sizes suitable for good light scattering and emission enhancement. The dense microstructure supported efficient radiative transitions, indicating the suitability of the synthesis technique and the host environment.

Photoluminescence investigations provided comprehensive insights into the excitation-emission behaviour of each doped system. The Dy^{3+} -doped phosphors displayed characteristic blue and yellow emissions resulting from transitions associated with the excited 4f states. The observed spectral features enabled the generation of near-white or warm-white light depending on concentration. Eu^{3+} -activated samples emitted intense red light attributed to hypersensitive electric dipole transitions, and the corresponding colour purity demonstrated the potential of these phosphors for red components in wLEDs. Sm^{3+} doped samples exhibited orange-red emissions, which became increasingly intense as the concentration approached the optimized level before concentration quenching appeared.

Co-doped systems, particularly $\text{Dy}^{3+}/\text{Eu}^{3+}$ combinations, showed efficient energy transfer processes that improved or tuned the emission characteristics. This cooperative behaviour offered opportunities for multicolour emission tuning using a single host lattice.

Concentration quenching analyses highlighted the significance of maintaining an optimal activator concentration to prevent non-radiative losses. The decrease in luminescence beyond the threshold was attributed to dipole–dipole or multipolar interactions, confirming the theoretical predictions. Lifetime decay curves provided additional evidence of radiative and non-radiative channels existing in various doped systems. The single or biexponential nature of the decay further supported the understanding of energy transfer dynamics and ion–ion interactions.

Thermal stability studies, carried out by measuring temperature-dependent photoluminescence, indicated that the BZP host exhibited excellent thermal quenching resistance. Samples retained a large percentage of their room-temperature emission even at higher temperatures, which is a crucial requirement for phosphors to function reliably in LED devices. Activation energy values derived from thermal quenching behaviour reinforced the thermal robustness of the phosphor materials.

CIE chromaticity coordinates and colour purity measurements established that the emission of the doped phosphors could be tailored across blue, yellow, orange, and red regions by suitable dopant combinations. With appropriate tuning, the phosphors demonstrated potential for generating warm white, cool white, or colour-tunable light sources.

Overall, this research successfully demonstrated that $\text{BaZr}(\text{PO}_4)_2$ is a highly competitive host matrix capable of enabling strong emission intensities, good colour purity, thermal stability, and long-term luminescence reliability. These factors mark the doped BZP phosphors as promising candidates for applications in solid-state lighting, display technology, and a range of optical devices.

6.2 FUTURE SCOPE OF THE WORK

Exploration of New Dopant Ions and Co-Doping Strategies:

While the study examined Dy^{3+} , Eu^{3+} , and Sm^{3+} ions, several other rare-earth ions such as Tb^{3+} , Er^{3+} , Tm^{3+} , Ho^{3+} , and Yb^{3+} may produce desirable luminescent effects due to their unique 4f–

4f transitions. Incorporating these ions can expand the colour palette into green, blue, or near-infrared regions. Additionally, multi-ion co-doping strategies can be implemented to create tunable white light or warm-white emissions with improved colour rendering.

Development of Broadband and Deep-Red Emissions:

To enhance LED performance, achieving deep-red emissions with high colour purity is crucial for horticultural lighting and medical applications. Transition metal ions such as Cr^{3+} , Mn^{4+} , and Bi^{3+} can be introduced into the BZP lattice to obtain broadband or high-intensity deep-red emission. These dopants respond strongly to crystal field variations, enabling engineering of tailored spectral bands.

Band Gap Engineering Through Host Modification:

Future work may involve partial substitution of Ba, Zr, or phosphate groups with similar ions to fine-tune crystal field strength. This band-gap engineering can significantly alter the emission wavelengths, enhance quantum yield, or improve excitation response to near-UV or blue LED light. Mixed phosphates or solid solutions may provide new luminescent behaviours.

Application of Nano-Structuring and Morphology Control:

Phosphors with controlled particle size, shape, and surface characteristics can demonstrate improved scattering, better excitation absorption, and higher luminescence. Methods such as sol-gel, hydrothermal, flame spray pyrolysis, or microwave-assisted synthesis may produce nanoscale or uniform particles with improved efficiency. Coating or core-shell structures may also help suppress surface defects and reduce thermal quenching.

Integration Into Prototype LED Devices:

To translate laboratory findings into commercial applications, future research should focus on fabricating phosphor-on-chip (POC) or phosphor-in-package (PIP) LED modules using the synthesized materials. Measurements such as correlated colour temperature, luminous flux, colour rendering index, and long-term stability under electrical stress will provide practical validation of phosphor performance.

Advanced Photophysical and Time-Resolved Studies:

More detailed time-resolved spectroscopic studies using microsecond or nanosecond pulsed excitation can offer deeper insight into energy transfer pathways, defect levels, and relaxation

mechanisms. Theoretical modelling using quantum mechanical tools can predict optimum dopant sites, energy level splitting, and multipolar interaction strengths.

Computational Simulations and First-Principles Analysis:

Density functional theory (DFT)-based simulations can be carried out to analyse electronic structure, band-gap variations, and defect chemistry of the host lattice. These calculations can aid in predicting luminescence efficiency, preferred dopant substitution sites, and stability of charge states, thereby guiding experimental synthesis more effectively.

6.3 SOCIAL IMPACT

The development of rare-earth doped $\text{BaZr}(\text{PO}_4)_2$ phosphors carries broad societal significance due to the central role of lighting technologies in daily life, industry, and national energy consumption. The following points detail the major social impacts of this research:

❖ Contribution to Energy Conservation and Sustainability

Solid-state lighting based on efficient phosphors reduces global electricity consumption significantly, as lighting forms an integral part of domestic, commercial, and industrial power use. The phosphors developed in this research can improve LED efficiency, thereby helping reduce power loads on national grids, lower electricity bills, and conserve natural resources.

❖ Environmental Protection Through Non-Toxic Materials

Traditional lighting technologies such as fluorescent lamps require mercury-based materials, which pose severe environmental and health risks. The synthesized BZP-based phosphors are free from toxic or hazardous components, making them environmentally sustainable alternatives that reduce landfill pollution and ecological harm.

❖ Support for Smart Cities and Technological Advancement

High-efficiency phosphors play a crucial role in enabling smart lighting systems, sensor-based illumination, and intelligent energy management. Their adoption can support the development of smart infrastructure in urban areas while improving the quality, reliability, and adaptability of public lighting.

❖ Enhancement of Rural Electrification Initiatives

Efficient white LEDs built using these phosphors can offer high luminance at low energy consumption, making them suitable for remote and rural areas where electricity supply is limited. This can support rural education, healthcare facilities, street lighting, and night-time safety with affordable long-lasting light sources.

The research presented in this thesis has contributed significantly to the understanding and development of $\text{BaZr}(\text{PO}_4)_2$ -based phosphor materials. Through detailed analysis, the work demonstrates that BZP is a technically superior and versatile host matrix capable of enabling high-efficiency, thermally stable, and colour-tunable luminescence suitable for next-generation LED systems. The findings pave the way for future innovations in phosphor materials and their applications, providing both scientific and societal benefits.

❖ **Contribution to Domestic Research and Industrial Self-Reliance**

The successful development of indigenous phosphors contributes to national self-reliance and reduces dependency on imported phosphor materials. This strengthens the domestic optoelectronics industry and encourages the growth of local manufacturing and research facilities.

Applications Beyond Lighting

These phosphors have diverse applications, including displays, agricultural lighting, bio-imaging, sensing devices, emergency signage, and decorative lighting. Their use in multiple fields contributes to advancements in science, medicine, security, and communication.

Economic Benefits Through Cost-Effective Lighting

High-performance LEDs offer long lifetimes, low energy consumption, and minimal maintenance, resulting in economic benefits for households, industries, and government bodies. The adoption of cost-effective phosphor materials can further reduce the production cost of LED devices.

Improved Quality of Life

Better illumination improves night-time visibility, enhances road safety, reduces accidents, and supports learning environments. High-quality lighting impacts psychological comfort, productivity, and health, making it a vital social aspect.

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