Summary
SUMMARY

A brief summary of the thesis entitled “Structural and Optical Properties of some Rare-Earth doped Nanophosphors” is presented here. The thesis comprises of six chapters which are summarized as follows:

Chapter 1: Introduction

This chapter throws light on the developmental aspect of rare earth doped nanophosphors in recent years accompanying the detailed description about the luminescence phenomenon. The various modes of luminescence based on source of excitation and emission are also listed. The mechanism responsible for the luminescence phenomenon occurring in rare earth doped nanophosphors and mechanistic view of luminescence phenomenon in specific rare earth ions i.e. Sm$^{3+}$, Eu$^{3+}$, Tb$^{3+}$ and Er$^{3+}$ has been described in the thesis. A detailed literature survey regarding the synthesis and optical properties of relevant literature published on the rare earth doped nanophosphors has been provided. The practical implementation of rare earth doped nanophosphors in various fields ranging from display to the life saving medical applications have also been described at the end of the chapter.

Chapter 2: Materials and methods

This chapter presents an overview of various synthetic routes available for the development of rare earth doped nanophosphors and various instruments used to characterize these synthesized nanophosphors. The high purity starting chemicals utilized for nanophosphor synthesis are listed in this chapter. A detailed description of the solution combustion method employed by the author along with the brief account of different methods is mentioned. The powder characterization techniques such as X-ray diffraction studies (XRD), transmission electron microscopy (TEM) and luminescence spectroscopy (PL) have also been described in this chapter.

Chapter 3: Structural and optical properties of some rare earth doped SrGd$_2$Al$_2$O$_7$ nanophosphors

This chapter deals with the structural and optical properties of some rare earth doped SrGd$_2$Al$_2$O$_7$ nano-crystalline phosphors. SrGd$_2$Al$_2$O$_7$ host matrix is found to crystallize in tetragonal lattice with space group $I4/mmm$ (139). The host lattice doped distinctly with varying concentration of rare earth ions such as Sm$^{3+}$, Eu$^{3+}$, Tb$^{3+}$ ion
along with effect of sintering temperature have been examined in detail. The optical 
behavior of these rare earth doped nanocrystals has been elaborated through 
photoluminescence elucidation. This chapter comprises of three sections, discussed 
as follows:

Section-3.1: Sm\(^{3+}\) doped SrGd\(_2\)Al\(_2\)O\(_7\) Nanophosphors

SrGd\(_{2(1-x)}\)Sm\(_{2x}\)Al\(_2\)O\(_7\) (x = 0.5-10 mol\%) nanophosphor has been developed within 
the nano domain by approaching urea assisted solution combustion approach. X-ray 
powder diffraction data clearly reveal the stabilization of this nanophosphor in 
tetragonal lattice with homogenous diffusion of Sm\(^{3+}\) ion in host matrix and mere 
effect of dopant concentration on host lattice occupancy. The crystallization in nano 
regime is further confirmed by employing TEM and HR-TEM analysis. The 
nanophosphor shows some noticeable photoluminescent features accountable due to 
the nano range of crystallites. The presence of Gd\(^{3+}\) ion in the host matrix also helps 
in sensitization of Sm\(^{3+}\) ion. On irradiation with 407 nm wavelength, the 
nanophosphor displays efficient luminescence in orange-red region. Concentration 
dependency of luminescence behavior reveals SrGd\(_{1.9}\)Sm\(_{0.1}\)Al\(_2\)O\(_7\) as the optimum 
composition of nanophosphor. Critical distance determination undoubtedly infers the 
dipole-quadrupole (d-q) interactions solely accountable for non-radiative energy 
relaxation processes leading to concentration quenching. The chromatic color 
coordinates as well as nano dimension of particles with easy synthesis approach 
project this orange-red emitting efficient photoluminescent nanophosphor for 
application in display devices or near ultraviolet excited phosphor converted white 
light emitting materials.

Section-3.2: Eu\(^{3+}\) doped SrGd\(_2\)Al\(_2\)O\(_7\) Nanophosphors

SrGd\(_{2(1-x)}\)Eu\(_{2x}\)Al\(_2\)O\(_7\) nanophosphor (x = 0.5-15 mol\%) have been successfully 
synthesized by employing economically efficient and time saving urea assisted 
solution combustion approach. Single phased nanophosphors obtained by post heat 
treatment process accounts for maximum crystallinity at 1300°C. X-ray diffraction 
analysis depicts that the substitution of Gd\(^{3+}\) ion by Eu\(^{3+}\) do not have any observable 
effect on SrGd\(_2\)Al\(_2\)O\(_7\) host lattice. Photoluminescent analysis reveals that the 
nanophosphor can be successfully excited via host to metal charge transfer process 
(290 nm) and by different excitation wavelengths in near UV region yielding emission
centered at 628 nm attributed to transition of Eu$^{3+}$ ion unveiling its suitability for near UV excited white LEDs. Optimal composition for maximum luminescence is SrGd$_{1.8}$Eu$_{0.2}$Al$_2$O$_7$, after reaching this composition further increase in Eu$^{3+}$ concentration leads to decrease in luminescent efficiency. Morphological analysis of the synthesized powder is carried out by conducting TEM, HR-TEM analysis and performing selected area diffraction (SAED) pattern. The nanoscaling of crystallites is further advantageous for bearing efficient luminous properties by reducing internal scattering. Judd-Ofelt theory is utilized to determine radiative transition rate and the Judd-Ofelt intensity parameters of SrGd$_{1.8}$Eu$_{0.2}$Al$_2$O$_7$ nanophosphor for better understanding of spectral features. The CIE chromatic tuning from blue to red region proclaims this as an efficient nano-crystalline phosphor for single phased near ultraviolet excited white light emitting diodes.

**Section-3.3: Tb$^{3+}$ doped SrGd$_2$Al$_2$O$_7$ Nanophosphors**

Efficient color tunable SrGd$_{2(1-x)}$Tb$_{2x}$Al$_2$O$_7$ ($x = 0.5$-$10$ mol%) nanophosphor has been synthesized for the first time by employing a facile urea assisted solution combustion approach. X-ray powder diffraction study reveal purely single phased nanophosphor sintered at 1300°C for 3 h. The Rietveld refinement process depicts that SrGd$_{1.9}$Tb$_{0.1}$Al$_2$O$_7$ crystallized in tetragonal lattice with parameters: $a = 3.7034$ Å and $c = 19.7911$ Å, $V = 271.44$ Å$^3$, $Z = 2$ with the refinement finally converged to $R_p = 4.54\%$, $R_{wp} = 5.69\%$ and $\chi^2 = 2.102$. A very little effect of substitution of varying concentration of Tb$^{3+}$ ion on the crystallinity of SrGd$_2$Al$_2$O$_7$ host lattice. The nanoscaling of the Tb$^{3+}$ doped phosphor reveal average particle size in the range of 45-80 nm, analyzed by TEM analysis. The HR-TEM analysis further confirms the crystalline nature of the prepared nanophosphor. Photoluminescent features of SrGd$_{2(1-x)}$Tb$_{2x}$Al$_2$O$_7$ ($x = 0.5$-$10$ mol%) nanophosphor were explored and found to have remarkable luminescent properties owing to low phonon nature of host. Concentration directed luminescence behavior suggests the optimal composition of nanophosphor as SrGd$_{1.9}$Tb$_{0.1}$Al$_2$O$_7$ beyond which luminous efficiency decreases. Critical distance measurement claims dipole-dipole (d-d) interactions responsible for non-radiative energy transformation. The nanoscaling as well as the chromatic color tuning capability of the solution combustion synthesized nanophosphor proclaims an efficient green emitting nanophosphor suitable for application in solid state lighting materials.
Chapter 4: Structural and optical properties of some rare earth doped Ba$_2$YAlO$_5$ nanophosphors

This chapter illustrates the structural and optical properties exhibited by Eu$^{3+}$/Tb$^{3+}$ single doped Ba$_2$YAlO$_5$ phosphors developed in nano regime. The X-ray diffraction studies regarding substitution of Y$^{3+}$ by Eu$^{3+}$ or Tb$^{3+}$ individually on the Ba$_2$YAlO$_5$ host lattice is examined and the optical properties after successful incorporation of dopant ion have been analyzed via photoluminescent excitation and emission spectrum. This chapter has been divided into two sections, described as follows:

Section-4.1: Eu$^{3+}$ doped Ba$_2$YAlO$_5$ Nanophosphors

Color tunable Ba$_2$Y$_{(1-x)}$Eu$_x$AlO$_5$ nano-crystalline phosphor have been synthesized for the first time using economic and time saving urea assisted solution combustion approach. Single phased nanophosphor is obtained by heat treatment at 1225°C for 4 h. X-ray diffraction profile reveal that the doping with different amount of Eu$^{3+}$ ion does not have any considerable effect on the host lattice. The various phases present at different sintering temperatures are also discussed. The particle size in nano-domain in the range 40-90 nm analyzed via TEM analysis is in accordance with that calculated from Scherrer’s equation. HR-TEM analysis depicts the lattice fringes demonstrating crystalline behavior of the nanoparticles. Photoluminescence analysis indicates that this nanophosphor can be efficiently excited by NUV light unveiling its suitability for near UV excited white LEDs. The shifting of luminescent intensity from high energy $^5D_{3/2,1} ightarrow ^7F_j$ to $^4D_0 ightarrow ^7F_j$ transition levels as a function of europium concentration accounts for the blue to red chromatic tuning. The concentration controlled luminescent behavior depicts Ba$_2$Y$_{0.95}$Eu$_{0.05}$AlO$_5$ as optimal composition. The high value of critical distance claims quadrupole-quadrupole interactions responsible for non-radiative cross relaxation. The Judd-Ofelt intensity parameters and refractive index of the host are calculated by employing Judd-Ofelt theory to confirm the practical application of the synthesized nanophosphor. The CCT values and chromatic tuning from blue to red region proclaim this an efficient nanophosphor for NUV excited white light emitting materials.

Section-4.2: Tb$^{3+}$ doped Ba$_2$YAlO$_5$ Nanophosphors

Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ (x = 0.25-7 mol%) nanophosphor have been synthesized for the first time using facile urea assisted solution combustion method. After a heat
treatment processes single phased nanophosphor is obtained at 1225°C for 4 h. X-ray diffraction analysis confirm the crystallization of single phased Ba$_2$Y$_{(1-x)}$Tb$_x$AlO$_5$ nanocrystals in monoclinic lattice with $P2_1/ (11)$ space group irrespective of substitution of some Y$^{3+}$ ions by Tb$^{3+}$ ions from its coordinative sites. TEM studies shows the more or less spherical shaped particles in nano-domain with average size in the range 65-95 nm, which is in good correlation with that calculated from Scherrer’s equation. The excitation spectrum depicts the presence of maximum intensity peak at 368 nm attributed to $5^F_{6} \rightarrow 5^L_{10}$ suggesting that this nanophosphor can be efficiently excited by NUV light. On excitation at 368 nm, the emission spectrum displays the presence of $5^D_4 \rightarrow 7^F_j$ transitions with maximum intensity peak at 546 nm attributed to green emitting $5^D_4 \rightarrow 7^F_5$ transition. The concentration based luminescent behavior depicts Ba$_2$Y$_{0.97}$Tb$_{0.03}$AlO$_5$ as optimal composition for the maximum optical performance. The higher value of critical distance propose dipole-dipole multipolar interactions existing between the luminescent centres lead to concentration quenching beyond 3 mol% concentration by facilitating non-radiative cross relaxation. The chromatic index in the green region is further useful for application of this nanophosphor as one of the green components of tricolor based ultraviolet excited white LEDs.

Chapter 5: Structural and optical properties of some rare earth dopedBa$_2$LaAlO$_5$ nanophosphors

This chapter describes the structural and optical properties of Eu$^{3+}$/Tb$^{3+}$ single doped Ba$_2$LaAlO$_5$ nanophosphors. Ba$_2$LaAlO$_5$ host matrix exists in tetragonal lattice. The doping in this pre-existing host matrix with varying amount of Eu$^{3+}$ and Tb$^{3+}$ ions separately are examined and the respective optical properties are investigated in detail in this chapter. In the emission spectrum Eu$^{3+}$ shows the dominant peak around 626 nm indexed to $5^D_{0} \rightarrow 7^F_2$ transition whereas Tb$^{3+}$ exhibits dominant $5^D_4 \rightarrow 7^F_5$ transition at 544 nm responsible for red and green chromaticity, respectively. This chapter has been divided into two sections, summarized as follows:

Section-5.1: Eu$^{3+}$ doped Ba$_2$LaAlO$_5$ Nanophosphors

Ba$_2$La$_{(1-x)}$Eu$_x$AlO$_5$ nanocrystals ($x = 0.25$-10 mol%) have been synthesized for the first time by employing urea assisted solution combustion approach. X-ray diffraction profile of sample sintered at 1100°C shows complete resemblance with diffraction
profile of Ba$_2$LaAlO$_5$ host matrix revealing that the doping with different amount of Eu$^{3+}$ ion does not have any measurable effect on the host lattice and also confirming that single phased highly crystalline sample is achieved at 1100°C. The gain in crystallite size as a function of sintering temperature refers to the improved crystallinity of the synthesized nanophosphors. The TEM study depicts the slightly agglomerated particles with average particle size in the range of 40-90 nm which is consistent with calculations from Scherrer’s equation. The photoluminescence spectral scanning of Ba$_2$La$_{1-x}$Eu$_x$AlO$_5$ nano-crystalline phosphor reveal some good optical properties. The Photoluminescence excitation spectrum marks the transfer of electronic charge from filled 2p$^6$ orbital of O$^{2-}$ to the empty 4f orbital of Eu$^{3+}$ ion with the maxima positioned at 282 nm and some f-f transitions of Eu$^{3+}$ ion with maxima at 393 nm attributed to $^7$F$_0$→$^5$L$_6$ transition. On excitation at 393 nm, the emission spectrum is dominated by $^5$D$_0$→$^7$F$_2$ transition at 626 nm along with other $^5$D$_{1,0}$→$^7$F$_j$ transitions showing shifting of chromaticity from orange to red region as a change in europium concentration. The concentration dependent optical behavior reveals Ba$_2$La$_{0.95}$Eu$_{0.05}$AlO$_5$ as optimal composition. The dipole-dipole interactions are found to be responsible for non-radiative cross relaxation. The Judd-Ofelt intensity parameters and refractive index of the host are calculated by employing Judd-Ofelt theory to analyze the optical utility the synthesized nanophosphor. The CCT values and chromatic tuning in red region propose this as an efficient nanophosphor in the field of NUV excited white light emitting materials.

Section-5.2: Tb$^{3+}$ doped Ba$_2$LaAlO$_5$ Nanophosphors

Ba$_2$La$_{1-x}$Tb$_x$AlO$_5$ nanophosphor, where $x = 0.25$ to 7 mol% have been synthesized via economic and simple to execute, solution combustion approach using urea as an organic fuel in preheated furnace maintained at 500°C. The powder thus obtained is allowed to undergo heat treatment process for 3 h from 1000-1150°C. X-ray diffraction study elicits the crystallization of this Tb$^{3+}$ doped nanophosphor in tetragonal lattice with space grouping 14/mcm (140) irrespective of the varying concentration of dopant ion. The effect of sintering temperature on phase acquisition depicts that single phased highly crystalline sample is obtained at 1100°C. Morphological aspect examined via TEM analysis reveal nanoscaling of the sample with spherical shape with slightly agglomerated particles within 40-90 nm scale. The excitation spectrum marks the strong band with maxima at 301 nm is attributed to
spin allowed $4f^8 \rightarrow 4f^7 5d^1$ transition of Tb$^{3+}$ ion, inferring the availability of this Tb$^{3+}$ doped nanocrystals for ultraviolet excited phosphor converted white light emitting devices. On providing excitation wavelength as 301 nm, the emission spectrum is predominantly acquired by electric dipole driven $^5D_4 \rightarrow ^7F_3$ transition positioned at 544 nm along with $^5D_4 \rightarrow ^7F_1$ transitions which shows chromatic index in green region. Influence of concentration on optical behavior of Ba$_2$La$_{1-x}$Tb$_x$AlO$_5$ nano-crystalline phosphor reveal Ba$_2$La$_{0.97}$Tb$_{0.03}$AlO$_5$ as optimal composition. The measurement of critical distance claims dipole-dipole multipolar interactions accountable for non-radiative energy transformations causing concentration quenching. The decay dynamics shows mono-exponential nature of decay profile revealing homogenous diffusion of Tb$^{3+}$ ion in host lattice.

Chapter 6: Structural and optical properties of some rare earth doped BaY$_2$ZnO$_5$ nanophosphors

This chapter deals with the structural and optical characteristics of BaY$_2$ZnO$_5$ nanophosphors doped with Sm$^{3+}$ and Er$^{3+}$ ions. BaY$_2$ZnO$_5$ host matrix is found to crystallize in orthorhombic lattice with $Pbnm$ space group. The effect of doping of Sm$^{3+}$ and Er$^{3+}$ ions are analyzed on the host lattice and the respective optical properties exhibited by the two different rare earth doped nanophosphors are examined. Trivalent samarium ion displays reddish-orange chromaticity attributed to $^4G_{5/2}$ to $^6H_{7/2}$ transition while trivalent erbium shows predominant green emission around 545 nm corresponding to $^4S_{3/2}$ to $^4I_{15/2}$ transition. This chapter has been divided into two sections, summarized as follows:

Section 6.1: Sm$^{3+}$ doped BaY$_2$ZnO$_5$ Nanophosphors

BaY$_{2(1-x)}$Sm$_{2x}$ZnO$_5$ nanoparticles have been successfully synthesized via cost effective, single step urea assisted solution combustion process. The Rietveld refinement study reveals that BaY$_{2(1-x)}$Sm$_{2x}$ZnO$_5$ nanophosphors crystallizes in single phased orthorhombic lattice with space group $Pbnm$ and lattice parameters are found to be $a = 7.0735$ Å, $b = 12.3342$ Å, $c = 5.7107$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 498.2$ Å$^3$, $Z = 4$, the refinement finally converged to $R_p = 7.52\%$, $R_{wp} = 10.68\%$ and $\chi^2 = 5.95$. The cell volume increases due to the incorporation of Sm$^{3+}$ ion in the host lattice and resides in similar coordination environment as Y$^{3+}$ ion. The effect of sintering temperature on crystallite size reveals improvement in crystallinity. Surface
morphological studies reveal spherical shaped particles in nano regime accountable for prominent luminescence in visible range of spectrum. The PL spectrum illustrates dominant emission peak at 610 nm due to $^4G_{5/2} \rightarrow ^7H_{7/2}$ transition of Sm$^{3+}$ ions when excited at 411 nm wavelength proclaiming the significant orange-red component for WLEDs. Dipole-dipole interactions among dopant ions are primarily responsible for concentration quenching through non-radiative energy relaxation beyond 3 mol%. CIE color coordinates reflecting orange-red emission makes this nanophosphor a wonderful aspirant in NUV excited W-LEDs regime.

Section-6.2: Er$^{3+}$ doped BaY$_2$ZnO$_5$ Nanophosphors

BaY$_{2(1-x)}$Er$_x$ZnO$_5$ nanophosphors ($x = 0.5$-7 mol%) have been successfully synthesized via economical as well as eco-friendly urea assisted solution combustion approach. The structural analysis reveals crystallization of single phased nanophosphors by post heat treatment process in the orthogonal lattice with maximum phase purity and the doping with little amount of Er$^{3+}$ ion does not have any considerable effect on the host lattice crystallization. The unit cell parameters are found to be $a = 7.0699(3)$ Å, $b = 12.3351(5)$ Å, $c = 5.7088(2)$ Å, $V = 497.85(4)$ Å$^3$ and $Z = 4$ calculated by Rietveld refinement analysis. Photoluminescent analysis reveal that this nanophosphor can be successfully excited at 380 nm wavelength yielding green emission centered at 549 nm attributed to transition of Er$^{3+}$ ion manifesting the suitability for implementation in near UV excited white LEDs. Concentration dependent luminescence behavior reflects optimal composition as BaY$_{1.92}$Er$_{0.08}$ZnO$_5$ for achieving the maximum luminescence. The size of particles in nano domain accounts for the reinforced luminous efficacy by checking internal scattering. The critical distance measurement reveal that the dipole-quadrupole interactions among dopant ions are predominantly accountable for the concentration quenching which facilitate the non-radiative cross relaxation channel and responsible for the decline in the luminescence property beyond 4 mol%. The CIE color coordinates fall in the green region reflecting the candidature of this nanophosphor in near ultraviolet excited PC-WLED regime.

A list of publications and publications in refereed journals is given at the end of the thesis.
LIST OF PUBLICATIONS


8. Judd-Ofelt characterization and energy transfer mechanism of highly luminescent europium(III) complexes with 1-(5-chloro-2-hydroxyphenyl)-1,3-


10. Structural and photoluminescent aspects of reddish-orange SrGd$_{2(1-x)}$Sm$_{2x}$Al$_2$O$_7$ nanophosphor for Solid state lighting. Sangeeta Chahar, Mandeep Dalal, Sushma Devi, V.B. Taxak, S.P. Khatkar. (Communicated)

11. Judd-Ofelt analysis of color tunable nano-crystalline Ba$_2$Y$_{1-x}$Eu$_x$AlO$_5$ phosphor. Sangeeta Chahar, Mandeep Dalal, Avni Khatkar, Priti Boora, V.B. Taxak, S.P. Khatkar. (Communicated)