ACKNOWLEDGEMENTS

First and foremost, I would like to express my heartfelt thanks to the **Vice-chancellor, Director (R and D)**, **Registrar, HOD-Physics, all teaching and non teaching staff members Physics deperatment** of Bharathiar University, Coimbatore for giving me permission to do the research work.

It is a great privilege to put on record my profound sense of gratitude and indebtedness to my research guide **Dr. Prashantha S.C, Professor and Head, Department of Physics, East West Institute of Technology, Off Magadi Main Road, Bangalore-91** for his consistence guidance, constant encouragement and suggestions given during the course of this endeavor. His pleasing nature will always be a pleasant memory in my life.

I am very much thankful to the Principal, **Dr. B.R. Lakshmikantha,** and **Management,** Dayananda Sagar Academy of Technology and Manegement, Bangalore-82, for providing me the necessary support during my research work.

My sincere thanks and gratitude to **Dr. H. Nagabhushana**, Professor & Chairman, Department of Physics, C.N.R Rao center, Tumkur University, Tumakuru for his valuable motivation, immense support, valuable suggestions, help and guidance starting from the formulation of the problem to the final shaping of the thesis. His advice has been valuable at each and every stage of work.

My sincere thanks to **Dr. Nagabhushana B.M**, Professor & Head, Department of Chemistry, M.S.R.I.T for his valuable motivation, support, help and guidance at each and every stage.

I am very much thankful to the Principal, **Dr. K. Channakeshavalu,** and **Management** EWGI, for providing me the necessary facilities and support during my research work.

I am immensely thankful gratitude to **Dr. H.P. Nagaswarupa** Dept. of Chemistry EWIT Bengaluru, **Dr. K S Anantharaju** Dept. of Chemistry, Dayanand Sagar College of Engineering Bengaluru, **Dr H.B. Premakumar** Professor, Dept of Physics,

M.S.R.U.A.S, Bengaluru and **Mr. Ramachandra Naik** Department of Physics, New Horizon College of Engineering, Bengaluru and **Dr. Vishnu Mahesh,** Assistant Advisor, NAAC, Bengaluru for their immense support and valuable suggestions.

.I deeply express my heartfelt thanks to **Dr. R.V Anantha murthy, Dr. M.C Radhakrishna**, **Dr. Vijaya kumara K**, **Mr. Madhusudhana H.C**, **Mr. Deepak kumar B.N**, **Mr. Ashok kumar M.S**, **Mr. Shylesh K.S**, **Mr. Hareeshkumar, Mr. Anoop G.L, Mr. Amith**, **Mr. Sreenidhi B.S**, **Mr. Nagesh O.S, Mrs. Lavanya R** and all my colleagues of DSATM, Bangalore, as they provided a very friendly and enthusiastic environment during the course of research.

My sincere thanks to **Dr. Anilkumar, Dr. Ravikumar, Dr. K. Gurushantha**, of East West Institute of Technology and **R B. Basavaraju** research scholar C N R Rao center, Tumkur University, Tumkur for their help and support.

I express my sincere thanks to **Dr. D.M. Jnaneshwara, Dr. M. Chandrashekar, Dr. P.B. Devaraj, B. Daruka Prasad, R. Harikrishna, G.P. Darshan, Mr. Suresh C, Mr. Yogananda** and all my research colleagues for their valuable suggestions and help during my research work.

My sincere thanks to **Mr. Harish H.G, Mr. Hemantha Reddy M.V, Mrs. Swetha J, Mr. Madhu R, Mr. Avinash K.S, Mr. Sunil E** and all my friends for their support during my research work.

I am ever grateful to my parents **Smt. Manjula** & **Sri. Mallesh K.H** and my brother **Naveena M** & my sister **Sudha M** who are supportive and given inspiration in all walks of my life.

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Date: **Girish K.M**

PREFACE

The preparation and study of nano size materials are gaining a tremendous interest in the field of material science from the last few decades. The particles with nano size have better properties like large surface area, quantum confinement and high sinterability etc. Particularly in the area of optics: emission lifetime, luminescence quantum efficiency and concentration quenching were found to strongly depend on the particle-size in the nanometer range. The surface properties and chemical composition of the phosphors plays a vital role in the development of high definition projection TV and color plasma panel displays. In this context, undoped and doped rare earth ions have been widely used to synthesize phosphors with high quantum efficiency, effective excitation and absorption, color parity, longer lifetime, which are required for the progress of modern luminescence devices.

It was noticed that the crystal structure of the host lattice and dopant ion plays a major role on the luminescence properties of the phosphor. In this manner titanium based inorganic materials have been studied vigorously due to their excellent properties and potential applications in various fields. In Zno-TiO_2 system three major forms known to exist are: Zn_2TiO_4 (cubic), $ZnTiO_3$ (hexagonal) and $Zn_2Ti_3O_8$ (cubic). Among these, cubic Zn_2TiO_4 is a prominent host candidate for various applications due to their few important properties like good chemical, thermal stability, mechanical resistance, particularly high permittivity, low dielectric losses etc. Also, it is a versatile luminescent host material due to the extensive range of multi-colors that can be obtained from various dopant ions.

An enhancement in the emission efficiency of the host materials were noticed by adding with very small quantities of dopants or co-dopant ions. In recent years, luminescent phosphors were gaining importance in white light generation for future application technologies. Efforts have been put to build novel luminescent materials for WLEDs and lighting applications for the replacement for fluorescent and incandescent lamps.

Various synthesis routes such as solution combustion, solid-state reactions, sol-gel, chemical co-precipitation, hydrothermal, spray paralysis etc were utilized to prepare pure and rare earth doped Zn_2TiO_4 nanophosphors. Among the various synthesis techniques, combustion route provides a number of advantages; such as inexpensive raw materials, low synthesis temperature, relatively simple preparation process, molecular level of mixing, high degree of homogeneity, short reaction time and homogenous product with fine particles.

The present thesis consists of seven chapters: **Chapter-1** deals the brief introduction about nanomaterials, Phosphors, synthetic routes and the present work. **Chapter-2** reports experimental and characterization techniques. **Chapter-3** describes the structural, self explosive route and photometric studies of Eu^{3+}doped Zn_2TiO_4. **Chapter-4** focuses on the structural, band-gap analysis and optical properties of Tb^{3+} doped Zn_2TiO_4. **Chapter-5** presents structural, optical studies and forensic finger and lip print applications of Dy^{3+} doped Zn_2TiO_4. **Chapter-6** describes morphological, PL, photocatalytic, CV studies and forensic finger print sensor applications of Sm^{3+} doped Zn_2TiO_4. **Chapter-7** ends with summary, conclusion and scope of the future prospectus.

Chapter 1: It provides the outline of introduction, applications, properties, significance, different synthesis routes of nanophosphors. Also gives advantages of combustion synthesis over other synthesis routes. It deals with types of luminescence, light emission mechanism in phosphors and review of literature along with scope of the present work.

Chapter 2: It describes the combustion synthesis of pure and RE^{3+} ions (Eu, Dy, Tb,Sm) doped Zn_2TiO_4 nanophosphor prepared using lab made Oxalyl di-hydrazide (ODH) as a fuel. It also deals with principle and instruments used for characterization such as powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV-Visible spectrophotometer (DRS), CHI604E electrochemical working station and photoluminescence (PL) technique.

Chapter 3: Deals with synthesis of different mol concentration of Eu^{3+} (1-11 mol %) doped Zn_2TiO_4: nanophosphors by solution combustion method for

the first time using ODH as a fuel and the obtained sample was calcined at 1000 ^{o}C for 3h. PXRD patterns Confirms the cubic phase. Electron micrograph studies show that the particles are nano size in the range 20-45 nm which is well comparable to the results obtained via Scherer's method and W-H plots. The phosphor exhibits different emission (in the range 540 nm to 660 nm) due to Eu^{3+} corresponding to $^{5}D_{0}\rightarrow{}^{7}F_{j}$ (j = 0,1,2,3,4) transitions when excited by NUV (395 nm) photons. The transition centered at 613 nm ($^{5}D_{0}\rightarrow{}^{7}F_{2}$) is strong and gives red emission. The excellent red emission properties and the estimated CIE chromaticity co-ordinates (x, y) are nearer to NTSC standard values and CCT values of this phosphor suggest that it may be used for display and solid state lighting applications

Chapter 4: Cubic $Zn_2TiO_4:Tb^{3+}$ nanoparticles were successfully synthesized via solution combustion route using ODH as a fuel. The crystallite size of the nanoparticles in the range 40–65 nm, which was in good agreement with the TEM results. UV-Visible diffuse reflectance spectra revealed that Tb^{3+} ions doping leads to a blue shift in the absorption edges. The PL spectra consist of characteristic emission peaks of Tb^{3+} which were assigned to transition of $^{5}D_{3,4} \rightarrow {}^{7}F_{J}$. The PL emission intensity at 545 nm ($^{5}D_{4} \rightarrow {}^{7}F_{5}$) is higher than other emissions indicating that Tb3+ ions were located at high symmetry local sites with an inversion center in Zn_2TiO_4 host lattice. CIE chromaticity diagram confirmed that the present phosphor exhibit green luminescence with excellent CCT (5173 K) value and colour purity. The obtained CIE values are very close to NTSC CIE standard illuminant for green light. The highly luminescence properties of $Zn_2TiO_4:Tb^{3+}$ nanophosphors can be promising materials in green region for WLEDs, ceramic color pigments and solid state display applications.

Chapter 5: Deals with synthesis, characterization, PL and forensic finger print studies of $Zn_2TiO_4:Dy^{3+}$ (1-11 mol %) nanophosphors. All the characteristic emissions $^{4}F_{9/2} \rightarrow {}^{6}H_{j\ (j=15/2,\ 13/2,\ 11/2)}$ of Dy^{3+} ion in a Zn_2TiO_4 matrix were confirmed by the PL emission studies. The estimated branching ratio was found to be ~ 74 %, indicating the usefulness of the present nanophosphor for display device applications. From the CIE chromaticity co-ordinates, the detection of fingerprint marks on different surfaces and lip

print images indicates that $Zn_2TiO_4:Dy^{3+}$ is very promising for warm WLEDs, solid state lighting, forensic sciences and Cheiloscopy applications.

Chapter 6: This chapter deals with solution combustion synthesis of novel reddish orange emitting $Zn_2TiO_4:Sm^{3+}$ doped nanophosphors. PL spectra and CIE coordinate of (0.59508, 0.4041) revealed that 3 mol % sample exhibits highest intensity in orange red region. CCT value 1750 K of the sample show that, it can be used for the fabrication of warm white light emitting devices. Decay time was estimated to be 6.41 ms. Temperature sensing capability of these optimized nanophosphors was demonstrated over the range of 25 to 400 ^oC. The latent fingerprints detected by using optimized sample show relatively well defined characteristics for finger ridge details resulting in good contrast for enhanced detection which may find application in forensic science for individual identification. Also, series of Sm^{3+} (1-9 mol %) doped Zn_2TiO_4 nano powders were characterized as electrode material for solid state flexible supercapacitors and catalyst for dye degradation. Electrochemical studies show high reversible electrode reaction, high charge transfer resistance and exhibit high sensitivity for detection of Paracetamol. Also, Photocatalytic activity shows the enhanced activity in the degradation of TY dye under UV light irradiation, the obtained results suggest that prepared material is highly useful for supercapacitors, battery, energy storage devices and prominent material for degradation of organic dye pollutants.

Chapter 7: It summarizes the results obtained in the present research work and the scope for the future work. Solution combustion technique is an instantaneous, single step, energy saving process with many advantages over other wet chemical outs. All the PL emissions in the present investigation are attributed to the f–f or 4f-5d transitions of rare earth ions in the host lattice. Based on the results reported in the present investigations some important conclusions and suggestions for further studies in this direction are also made.

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GLOSSARY OF TERMS

FTIR	Fourier Transform Infrared Spectroscopy
FWHM	Full Width Half Maximum
HRTEM	High Resolution Transmission Electron Microscope
ODH	Oxalyl di-hydrazide
PL	Photoluminescence
PLE	Photoluminescence Excitation
PXRD	Powder X-Ray diffraction
RT	Room Temperature
SCS	Solution Combustion Synthesis
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
TL	Thermoluminescence
JO	Judd o felt
UV-VIS	Ultra violet visible spectroscopy
VB	Valence band
CB	Conduction Band
EDAX	Energy dispersive X-ray analysis
EDS	Energy dispersion spectroscopy
SAED	Selected Area Electron Diffraction
NPs	Nanoparticels
NUV	Near Ultra -violet
NIR	Near Infra-red
LED	Light emitting diode

WLED	White light emitting diode
JCPDS	Joint Committee on Powder Diffraction Standards
RE	Rare-earth
DRS	Diffuse Reflectance Spectra
NTSC	National Television System Committee
CIE	Commission Internationale de l'Eclairage
LEP	Latent Finger Prints
CCT	Correlated color temperature
ET	Energy transfer

SYMBOLS

α	Alpha
β	Beta
k	Boltzmann constant
γ	Gamma
λ	Wavelength
ε	Strain
υ	Frequency
s	Second
hr	Hour
kg	kilogram
cm	Centimeter
a.u.(arb. unit)	Arbitrary units
nm	Nanometer
Å	angstrom
mg	Milligram
ml	Millilitre
mm	Millimeter
^{o}C	Degree Celsius
eV	Electron volt
E_g	Energy gap or Band gap
R_c	Critical distance
e	Electron charge
m_e	Electron mass
h	Planck's constant
c	Speed of light in air or vacuum