Chapter 7

Summary and Scope for future prospectus

7.1 Summary

Phosphors are the inorganic nanomaterials which are highly essential for the fabrication and improvement of high resolution optical and plasma panel display systems, imaging devices and lamps. Rare earth (RE) ions doped phosphors, have found to be excellent luminescent materials because of their marked improvements in lumen output, color rendering index, energy efficiency and greater radiation stability.

Preparative routes are now increasingly becoming important to prepare phosphor materials with better purity and homogeneity. The present study is mainly focussed on the PL properties of pure and rare earth doped Zn_2TiO_4 phosphors. Zn_2TiO_4, suitable host materials due to their properties such as high chemical and thermal stability. Also, crystal structure of the host material and dopant ion is greatly affect the luminescencent properties of phosphors. Rare earth elements are generally been used to enhance the luminescent property of the phosphor due to their rich emission colors based on their 4f $\rightarrow$4f or 5d $\rightarrow$ 4f transitions.

In the current work, we report here solution combustion synthesis as a part of our study on nanophosphors. It is a simple and rapid process which not only yields nanosize materials but also allows homogeneous mixing of rare-earth impurity ions in a single step. Synthesis route provides number advantages over the conventional synthetic routes such as simple experimental setup, low cost, energy saving, choice of a wide variety of fuels, rapid cooling leads to nucleation of crystallites without any growth and also has the potential to scale up because of the gas evolution, large particles or agglomerates can be disintegrated during the process and the products formed are of high purity. $Zn_2TiO_4:Eu^{3+}$ (1- 11 mol %) , Zn_2TiO_4: Tb^{3+} (1- 11 mol %), $Zn_2TiO_4:Dy^{3+}$ (1- 11 mol %) and $Zn_2TiO_4:Sm^{3+}$ (1- 11 mol %) nanophosphors were synthesized by solution combustion route using ODH fuel.

The Stiochiometric amount of raw materials were dissolved in a minimum quantity of doubled distilled water in a cylindrical pyrex dish and mixed thoroughly using magnetic stirrer for about 5 min. The pyrex dish containing the solution was placed in a pre-heated muffle furnace maintained at 500 ± 10 ^oC. The solution boiled resulting in a transparent gel. Then the reaction was initiated and a flame appeared on the surface of the foam and spreads rapidly throughout the entire volume, and a white powder was left behind within 5 min. Further, the sample was calcined at 1000

^{o}C for 3 h. The final product used for characterization and luminescent studies after grinding into a fine powder by agate mortar and pestle.

Presence of Prominent diffractions peaks in the PXRD pattern indicates the formation of cubic phase with JCPDS File No. 70-1677. The average crystallite size were estimated (~ 15-50 nm) for all the prepared samples using Debye- Scherer's formula. SEM studies confirms the highly porous, agglomeration, large voids and cracks irregular morphology of the prepared products and TEM picture confirms the spherical nature of the particles with size in the range 20-50 nm and polycrystalline behaviour of the prepared samples.

UV–Vis Diffused reflectance spectra were obtained in the wavelength 200 - 700 nm for all the samples, revealed that Tb^{3+} ions doping leads to a blue shift in the absorption edges. Wood and Tauc relation was employed to estimate the energy gap and was found to be in the range 3.0-3.2 eV, the variation in the energy gap is attributed to dopant impurities. Bands in the FTIR spectroscopy confirms the presence C–OH, M–O vibrations ((M = Zn, Ti)) in the cubic structure.

The response of dopant ion concentrations on luminesense properties of Zn_2TiO_4 nanophosphor was studied. The PL emission spectra of Zn_2TiO_4: Eu^{3+} (1-11 mol %) nanophosphor was measured under 395 nm excitation wavelength. Emission peaks at 578, 592, 613 and 654 nm which were attributed to Eu^{3+} transitions $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_3$ respectively. The emission peak centered at 613 nm was called characteristic red emission, confirms energy transfer from Zn_2TiO_4 to Eu^{3+}. 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.

The PL emission spectra of Zn_2TiO_4: Tb^{3+} (1-11 mol %) nanophosphor was measured under 415 nm excitation wavelength. The peaks at 493, 514, 545, 580 and 620 nm were attributed to $^5D_3 \rightarrow ^7F_3$ (blue), $^5D_4 \rightarrow ^7F_6$ (blue green), $^5D_4 \rightarrow ^7F_5$ (green), $^5D_4 \rightarrow ^7F_4$ (orange) and $^5D_4 \rightarrow ^7F_3$ (red) respectively. Among, green emission corresponding to $^5D_4 \rightarrow ^7F_5$ transition at 545 nm was the most dominant one which has the largest probability for both electric-dipole and magnetic-dipole induced transitions. CIE chromaticity diagram confirmed that the present phosphor exhibit green luminescence with excellent CCT (5173 K) value and colour purity indicates

Zn_2TiO_4: Tb^{3+} promising materials in green region for WLEDs, ceramic color pigments and solid state display applications.

The PL emission spectra of Zn_2TiO_4: Dy^{3+} (1-11 mol %) nanophosphor was measured under 420 nm excitation wavelength. The peaks at 496 nm (blue region), 570 nm (yellow region) and 685 nm (red region) corresponds to the transitions $^4F_{9/2}\rightarrow{}^6H_{15/2}$, $^4F_{9/2}\rightarrow{}^6H_{13/2}$, $^4F_{9/2}\rightarrow{}^6H_{11/2}$ respectively. .the transition $^4F_{9/2}\rightarrow{}^6H_{15/2}$ is magnetic dipole which and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ is related to the hypersensitive transition which is strongly affected by the crystal environment. The CIE chromaticity co-ordinates are located in the white region and the CCT was found to be 4449 K. indicates Zn_2TiO_4:Dy^{3+} was the potential phosphor for warm WLEDs, solid state lighting, biological imaging applications.

The PL emission spectra of Zn_2TiO_4: Sm^{3+} (1-11 mol %) nanophosphor was measured under 420 nm excitation wavelength. it consists of four prominent emission peaks in the range 550 - 750 nm were attributed to the intra-4f orbital transitions $^4G_{5/2}\rightarrow{}^6H_{5/2}$ (591 nm), $^4G_{5/2}\rightarrow{}^6H_{7/2}$ (611 nm), $^4G_{5/2}\rightarrow{}^6H_{9/2}$ (677 nm) and $^4G_{5/2}\rightarrow{}^6H_{11/2}$ (736 nm) [39–41]. Among, the transition centered at 611 nm ($^4G_{5/2}\rightarrow{}^6H_{7/2}$) was having the highest intensity, was partially magnetic and partially forced electric-dipole (ED) transition. The transition $^4G_{5/2}\rightarrow{}^6H_{5/2}$ was magnetic dipole (MD) and the transition $^4G_{5/2}\rightarrow{}^6H_{9/2}$ was purely ED sensitive to the crystal field. CIE coordinate of (0.59508, 0.4041) revealed that 3 mol % sample exhibits highest intensity in orange red region. CCT value of 1750 K show that the sample can be used for the fabrication of warm white light emitting devices

7.2. Scope for further work

The present research work is mainly focused on the luminescence properties of pure and few rare earth elements doped Zn_2TiO_4 nanomaterials. However, there is scope for further investigation such as

1. Preparation of materials with Green combustion route using various plants extracts (bark/ leaf/ milky/seed) as an eco-friendly fuels which avoids the use of toxic chemicals and high energy inputs.
2. Synthesis of Zn_2TiO_4 nanopowders by sonochemical route using different fluxes.

3. Comparison study of PL properties with Chemical and Green synthesized routes.
4. Comparison of PL properties with Chemical and Green synthesized routes.
5. Effect of PL has to be studied with various fluxes, activators and co-activators.

Low cost production is a central attraction of any product and it is believed that Zn_2TiO_4 has much potential to introduce low cost white LEDs in the market. Investigation of the luminescence from Zno-TiO_2 system is very essential for the future possible application in the development of white LEDs to replace conventional light sources.