PREFACE

Lanthanum phosphate ($LaPO_4$) possesses various properties of technological importance.

- Very low solubility in water.
- High thermal stability.
- High refractive index.

$LaPO_4$ has been found to be a suitable and effective deboning material for high-temperature oxide/ oxide composites, however, the properties of lanthanide compounds depend strongly on their composition and morphology. In addition, $LaPO_4$ based luminescent materials are currently used in devices such as cathode ray tubes and fluorescent lamps, with the luminescent properties being affected by the size and morphology of the $LaPO_4$ particles. To achieve a deeper understanding of the size-dependent properties and the synthesis conditions (e.g., temperature) on $LaPO_4$ particles, studies on the shape control of $LaPO_4$ nanocrystals have been performed. $LaPO_4$ powder can be synthesized from direct solid–liquid reaction of lanthanum oxide and phosphoric acid. Although it is a simple and effective synthesis route, the shape of the particles is hard to control and the morphology is heterogeneous.

Solid State Diffusion Reaction (SSR):

A solid state reaction route, also called a dry media reaction or a solvent less reaction, is a chemical reaction in which solvents are not used. In a normal reaction, the reacting agents, also called the reactants, are placed in a solvent before the reaction can take place. These reactants react to form a new substance. After the reaction is completed, scientists are able to remove the new product from the solvent. A solid-state reaction, however, allows the reactants to chemically react without the presence of a solvent.

The solid state reaction route is the most widely used method for the preparation of polycrystalline solids from a mixture of solid starting materials. Solids do not react together at room temperature over normal time scales and it is necessary to heat them to much higher temperatures, often to 1000 to 1500^{0}C in order for the reaction to occur at an appreciable rate. The factors on which the feasibility and rate of a solid state reaction include, reaction conditions, structural properties of the reactants, surface area of the solids, their reactivity and the thermodynamic free energy change associated with the reaction. After the reactants have been weighed out in the required amounts, they are mixed. For manual mixing of small quantities, usually an agate mortar and pestle are employed. Sufficient amount of some volatile organic liquid – preferably acetone or alcohol – is added to the mixture to aid homogenization. This forms a paste which is mixed thoroughly. During the process of grinding and mixing, the organic liquid gradually volatilizes and has usually evaporated completely after 10 to 15 minutes. For quantities much larger than ~20g, mechanical mixing is usually adopted using a ball mill and the process may take several hours. For the subsequent reaction at high temperatures, it is necessary to choose a suitable container material which is chemically inert to the reactants under the heating conditions used. Containers may be crucibles or boats made from foil. For low temperature reactions, other metals like Nickel (below 600–700^{0}C) can be used. The heating programme to be used depends very much on the form and reactivity of the reactants. In the control of either temperature or atmosphere, nature of the reactant chemicals is considered in detail. A good furnace is used for heat treatment. There are several conditions under which a solid state reaction can take place. Oven techniques use high temperatures to encourage reactions without solvents.

Solid State Reaction (SSR) method provides large range of selection of starting materials like, oxides, carbonates, etc. Since, solids do not react with each other at room temperature (RT). It is necessary to heat them at elevated temperatures as high as up to 1500^{o}C for the proper reaction to take place at appreciable rate. Thus, both, thermodynamic and kinetic factors are important in SSR. This synthesis route is very easy and does not require expensive as well as sophisticated equipments. The major advantage of SSR method is the final product in solid form is structurally pure with the desired properties depending on the final sintering temperatures. This method is environment friendly and no toxic or unwanted waste is produced after the SSR is complete. In this process the powders produced from SSR method is very fine as well as the cross contamination is very less. The phosphor was prepared with a conventional solid state reaction method. A stoichiometric mixture of these staring powders was thoroughly homogenized in an agent mortar for 1 hour and then put into an alumina crucible. The homogenized mixture was heated in air from room temperature to 1200^{o}C with a heating rate of 5°C/minute for 3 hours with several intermediate grindings. Each chapter is followed by the list of references and cross references.

By considering applications potential, around 41 phosphor samples are prepared and studied for their luminescence characteristics.

Characterization technique used to study the prepared phosphors:

- To identify the crystal structure and phase purity of the prepared phosphor materials, X-ray Diffraction analysis was carried out with a powder diffractometer using Cu Kα radiation at NCL, pune.
- The excitation and emission spectra of the synthesized phosphors have been recorded on a 'Shimadzu' system using Xenon lamp as excitation source at room temperature at M.S. University, Baroda. The Shimadzu Model RF-5301 PC is a high-resolution fluorescence spectrophotometer. The detector used is the Shimadzu make photomultiplier (type no R928 of multialkali. photocathode), which has a flat spectral response over the entire range of wavelength of measurement i.e. from 220 to 900 nm.
- The Thermoluminescence (TL) measurements were performed with Nucleonix make Windows Based thermoluminescence reader. The system consists of PMT housing with drawer assembly, high voltage module, D.C. amplifier module, Temperature controller unit, power supply unit, AD-DA card and a personal computer system along with required hardware and software.
- The microstructures of the samples were studied using a Scanning electron microscope (SEM).
- The FTIR spectra were recorded by FTIR spectrometer in the range from 500 to 4000 cm^{-1}.
- The particle size was measured by using Laser based particle size analyzer (Malvern Instrument Ltd (U.K).
- The CIE (Commission International de l'Eclairage) co-ordinates were calculated by the Spectrophotometric method using the spectral energy distribution.

About the present work:

In this thesis the effect of trivalent RE ions Ce-Tb, Tb-Ce, Eu-Tb and Ce-Eu-Tb with various concentrations of Tb, Ce, Eu doped in $LaPO_4$ is studied. These phosphors are synthesized using solid state reaction. The emission spectra of $LaPO_4$ sample doped with terbium and other combinations at different molar percentages were recorded with excitation wavelength of 254 nm at room temperature and their characterization like SEM, XRD, FTIR, EDAX and particle size analysis are discussed in this thesis.

In $LaPO_4$ doped Ce^{3+}, Eu^{3+} and Tb^{3+} phosphor due to the little difference between ionic sizes of Eu^{3+} ion and La^{3+} ion, Eu^{3+} ions can occupy La^{3+} ion sites, which gives rise to a characteristic crystal splitting of the energy levels. The Ce^{3+} and Eu^{3+} ions sensitize the luminescence of Tb^{3+} ions and good PL intensity is obtained. The materials studied are very attractive luminescent properties for the generation of the three primary colors, due to the red, green and blue emissions of $LaPO_4$:Eu^{3+}, $LaPO_4$:Tb^{3+} and $LaPO_4$:Ce^{3+}, respectively.

The most important rare earth phosphors are Y, Eu, and Tb, which are used to emit light at the wavelengths (colors) to which our eyes are most sensitive. These three elements are used in different combinations of phosphors to emit blue, red, and green light. The phosphors consisting of a rare earth phosphate (RE PO_4) (RE = La, Y, Eu, Tb, Gd) matrix doped with RE cations find important applications, especially in optoelectronic and biomedicine. For most of these applications, particles with uniform shape and narrow size distribution are highly desirable.

In this thesis the effect of trivalent RE ions Tb-Eu, Gd-Eu, Tb-Gd-Eu with various concentrations of Tb, Gd, Eu doped in $LaYPO_4$ is studied. These phosphors are synthesized using solid state reaction. The emission spectra of $LaYPO_4$ sample doped with Europium and other combinations at different molar percentages were recorded with excitation wavelength of 254 nm at room temperature and their characterization like PL, TL, SEM, XRD, FTIR, EDAX and particle size analysis are discussed in this thesis.

Synthesis of Lanthanum Phosphor:

List of materials used for the preparation of phosphors

- Lanthanum Oxide (La_2O_3).
- Ammonium Diahydrogen Phosphate ($(NH_4)_2$ HPO_4)
- Yttrium Oxide (Y_2O_3).
- Cerium Oxide (Ce_2O_3).
- Terbium oxide (Tb_4O_7).
- Gadolinium Oxide (Gd_2O_3).
- Europium Oxide (Eu_2O_3).

The samples of $LaPO_4$ and $LaYPO_4$ phosphor doped with rare-earth ions were prepared using solid state synthesis method. Stoichiometric proportions of raw materials namely, Lanthanum Oxide (La_2O_3), Yttrium oxide (Y_2O_3), Diammonium Hydrogen Phosphate [$(NH_4)_2$ H PO_4] with dopant rare earth materials are weighed and ground into a fine powder using agate mortar and pestle. The grounded samples were placed in an alumina crucible and fired at 1200^{o}C for 3 h in a muffle furnace with a heating rate of 5^{0}C/min. The samples are allowed to cool to room temperature in the same furnace for about 20 hours. The prepared samples were again powdered for taking the measurements.

The thesis consists of six chapters including conclusions. Chapters 1, 2 and 3 are the introduction, phosphor preparation and Phosphor Synthesis methods & Characterization Techniques. Chapters 4 and 5 are the results and discussions on the 41 prepared RE doped lanthanum phosphate phosphors and lanthanum yttrium phosphate phosphors. Each chapter is followed by references and cross references. Chapter 6 is the conclusions drawn from chapter 4 and 5 followed by brief suggestions for future work.