

A Study of Preparation of Luminescent Phosphors Characterization Techniques and Lanthanide Doped Nanophosphors

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Abstract

The aim of this study is to the best of one's knowledge, this is the first time that blue light emitting flexible AC powder electroluminescence (ACPEL) devices have been fabricated with undoped and Europium incorporated ZnGa₂O₄ as well as undoped CaWO₄ phosphors and their characteristics were tested. Technologically important materials are the ones which are directly or indirectly used for the advancement of the existing technology or development of new technology. It can be achieved through, improvement of performance, enhancement of activity or by modifying the overall behavior of a device in terms of accuracy, cost, handling and safety etc. In the recent years, an extensive advancement in the field of phosphors has been explored by introducing transition metal ions and trivalent rare earth ions (lanthanides) as luminescent centers (dopants) in different host matrices to produce phosphors for solid state lighting applications. In general, most of the phosphors are usually made up of a host material which consists of a family of sulphides, phosphates, aluminates, oxides, molybdates, tungstates, silicates and so on with or without suitable dopant (transition metal ions and lanthanides). The luminescent host lattice is normally an insulator or wide bandgap semiconductor and it serves to accommodate the dopant ions. The host compound also controls few of the physical and chemical behaviors of the luminescent phosphors such as emission intensity and lifetime properties. In most cases, the dopant ions or activator ions are usually present in concentration levels varying from a few ppm up to one to five moles of the host lattice.

Keywords: Preparation, Luminescent, Phosphors Characterization, Lanthanide Doped, Nanophosphors, AC powder electroluminescence

1. INTRODUCTION

Synthesis of various Gallates (Ga₂O₃, ZnGa₂O₄) and Tungstates (CaWO₄, Ca₃WO₆) based luminescent phosphors and its characterization techniques employed for analyzing the several properties of the luminescent phosphor materials were discussed in this chapter. The gallates and tungstate based nanophosphors have been synthesized using different methods such as low-temperature polyol route, solution combustion method, co-precipitation method, sol-gel method, solid state synthesis etc [1-6]. Among them, low temperature synthesis route is commonly used for the present study. This chapter mainly demonstrates the preparation of undoped and doped Ga₂O₃, ZnGa₂O₄, CaWO₄ nanophosphors via low-temperature synthesis method, allowing the production of fine particles in the nano-regime. Also, undoped, Eu ions doped ZnGa₂O₄ and undoped Ca₃WO₆ phosphors have been prepared using conventional solid state synthesis route for large scale production of bulk materials. These materials can be used for the fabrication of AC powder electroluminescent devices using screen printing technique. In this regard, the development of the solid state lighting system through the identification of an effective light conversion Nano phosphor is of vital importance. A luminescent Nano phosphor literally "light bearing materials" is a material capable of absorbing energy and re-emitting it in the form of light (ultraviolet, visible or Infrared). In practice, there are many challenges at every step of the way and efficiently creating light from semiconductor materials with band-gaps that span the visible spectrum is extremely challenging. Lot of research is going on to develop novel mercury-

free inexpensive Nano phosphors that convert longer wavelength Ultra Violet (UV) to blue light eventually into white-light and are eco-friendly with improved luminous efficacy, energy-saving, long-lifetime and low-power consumption characteristics.

2. LITERATURE REVIEW

Recently, Yu et al. in (2018), prepared Eu²⁺ and Eu³⁺ co-doped Ga₂O₃ nanocrystals (NC) in an organic phase at a low temperature of 300°C. Authors tried to synthesize Ga₂O₃:Eu nanocrystals by using the organic phase synthetic method and it is applied to inorganic phosphor systems for the generation of white light. From the PL analysis, the presence of a broad absorption band was mainly attributed to the ligand to the metal charge transfer transition at ~370nm, f-f (Eu³⁺) allowed 7F₀ → 5L₆ transition at 395nm, and 7F₀ → 5D₂ transition at 465nm, as well as the efficient electronic transition of 4f → 5d (Eu²⁺) at ~400nm. Ga₂O₃:Eu NCs were coated onto 395nm near-ultraviolet chips to fabricate a white light emitting diode. It exhibits a luminous efficiency of 34 lm/W, CIE colour coordinate of (0.2964, 0.2831), high color rendering index of 80 and color correlated temperature of 8528 K. Shin et al. in 2018, demonstrated that the green LEDs using In₂O₃ nanorods or p-type GaN based pn junction with insertion of Ga₂O₃ thin layer. In this study, In(OH)₃ nanorods were uniformly grown on plasma treated p-GaN surface using a hydrothermal route. XPS analysis clearly revealed the formation of Ga₂O₃ on the p-GaN surface via O₂ plasma treatment. The electroluminescence spectra of fabricated LEDs using n-In₂O₃/Ga₂O₃/p-GAN heterojunction showed green emission at a wavelength of ~554nm at forward bias condition. The authors proposed a possible light emission mechanism for the fabricated heterostructure and various energy states mediated through green emissions were suggested with suitable band diagram.

Chikoidze et al. (2017), reviewed that the importance of intrinsic majority hole conduction can exist and emerge in nominal undoped β-Ga₂O₃, via a wide range of characterization techniques. The study also investigated a prudent methodology for fabricating wafers of β-Ga₂O₃ of both p and n-type nature afforded new avenues and perspectives for high power and deep-UV optoelectronic applications.

Sawada et al. (2016), had examined that the structural and optical properties of Tb³⁺ and Eu³⁺ co-doped β-Ga₂O₃ crystals synthesized by Metal-Organic decomposition (MOD) method and further calcined at 800°C. The luminescence properties were investigated by PL analysis and decay measurements. This literature explained that the β-Ga₂O₃ doped with Tb³⁺ and Eu³⁺ samples when excited at a wavelength of λ_{ex} ~350 nm exhibits energy transfer from Tb³⁺ to Eu³⁺ sample, resulting in the decreased Tb³⁺ and enhanced Eu³⁺ emissions. The authors explained the temperature dependent study of Eu³⁺ emission intensity from T= 20 to 450 K using developed models. Authors also studied their interaction between Tb³⁺ and Eu³⁺ emissions using decay measurements which were supported by PL analysis.

Patil et al. (2014), prepared a single Gallium oxide nanoparticles co-doped with rare earth metals using simple precipitation method and followed by a calcination step. Gallium oxide nanoparticles with an average size of 4~5nm were synthesized. Undoped Gallium oxide powder was found to emit strong blue light. The green and red emissions induced from the respective doped Tb and Eu were counterbalanced in a corresponding single powder by controlling the doping level against blue emission by host defects. The Tb and Eu incorporation into Gallium oxide host enabled the single powder to generate white light. One of the great advantages of this co-doped phosphor could be provided to control the color chromaticity of phosphors by merely varying the internal composition of the single powder. Spinel structured β-Ga₂O₃ nanoparticles doped with Al₂O₃ (different compositions) were prepared directly from the aqueous precursor solutions of the source material, using ammonia in the presence of citric acid by the mild-hydrothermal method at 180°C. XRD pattern of as-prepared precipitates imparted the spinel structured cubic phase with an average crystallite size of 4-5nm. Spinel structure of nanoparticles in all composition ranges was maintained after heating at 600°C. The structural transformation of the β-Ga₂O₃ structure into spinel structure has been observed in the nanomaterials with compositions ranging from Ga₂O₃ to (Al_{0.50}Ga_{0.50})₂O₃ after annealed at 1000°C. A broad violet-blue emission band with a peak wavelength centered at 415 nm under UV excitation at 325nm was observed from the luminescence studies have been reported in 2015.

Kim et al. (2013), proposed and investigated the electrical and optical properties of undoped Ga₂O₃ nanoparticle (NP) layer combined with single-walled carbon nanotube (SWNT) via simple spin and dip-coating methods for deep UV LEDs. From the current voltage (I-V) curve characteristics, the Ga₂O₃ NP/SWNT layer showed a high current level of 0.4×10⁻³ A at 1V. Compared with the undoped Ga₂O₃ NP layer, the optical transmittance of Ga₂O₃ NPs/SWNT layer after 15times of dipping was decreased by only 15% at 280nm. By adjusting the dipping times in

the Ga₂O₃ NP/SWNT layer, an improved optical transmittance of 77.0% at 280nm after 15times of dip-coating processes was obtained. In 2013, Cabello et al prepared the Ga₂O_{3-x} – Tb and Ga₂O_{3-x} –Tb/M thin films (where M=Mn or Cr), by a simple photochemical method, using β-diketonate complexes as precursors. The structural and compositional characterization of the films were carried out using XPS and XRD respectively, revealed the formation of Ga₂O_{3-x} as a host material, Tb as activator and Mn and Cr as co-dopants. The amorphous nature of the films strongly determines the non-crystalline nature of the as-photo-deposited samples. From the PL spectra, under excitation at 254nm, the doped films showed characteristic emissions associated to 5D₄- 7F_J (J=6, 5, 4, 3) transitions of Tb ions, but these emissions decrease and deteriorate with co-doping and annealing of the films. Nevertheless, more investigation has been required in order to study the influence of the defects and the annealing temperature on the PL properties of photo-deposited thin films. In 2013, Kang et al. studied on undoped β-Ga₂O₃ and Tb³⁺ doped β-Ga₂O₃ hollow nanostructures with various Tb³⁺ concentrations prepared by the hydrothermal method and followed by the calcination process. The XRD analysis demonstrated that as prepared samples shown the core-shell structure with amorphous nature. It was crystallized while calcined at 800°C. The HRTEM and FE-SEM investigations observed that β-Ga₂O₃ hollow nanostructures with diameters of 200nm and thickness of about 20-30nm. The green emission spectra of Tb³⁺ doped β-Ga₂O₃ hollow nanostructures as a function of Tb³⁺ ions were observed due to the 5D₄ → 7F₁ transitions. The Tb³⁺ doped β-Ga₂O₃ hollow nanostructures showed the highest green emission intensity at 7mol% of Tb³⁺ ions.

Tokida et al. (2013), demonstrated the synthesis of β-Ga₂O₃:Eu³⁺ red-emitting films by a metal-organic deposition method. The XRD results showed that β-Ga₂O₃ which was observed at calcination temperature T_c ranges from 200°C to 1200°C. The PL measurements indicated that calcined at T_c ~ 800-900°C makes possible the strong Eu³⁺ related red emission peaks at λ = ~600-700nm. No noticeable strong lattice-temperature dependences of the Eu³⁺ related red emission and decay time (~0.5ms) was obtained. This report suggested that new insight for further exploiting and extending towards the applications of semiconducting β-Ga₂O₃:Eu³⁺ films in various fields. In 2013, Shanmugan et al. studied the optical and surface properties of Al-doped Ga₂O₃ thin film using thermal evaporation method by high temperature annealing process. The optical absorbance spectrum was the evidence of Al-doping into Ga₂O₃ lattice with decreased absorbance for increased temperature. The surface of Ga₂O₃ thin film was modified by Al diffusion at high temperatures. The grain growth was also observed as a result of Al diffusion. The elemental composition of Al-doped Ga₂O₃ thin film was showing the behavior of elemental diffusion during the annealing process as O deficient. Noticeable surface roughness and particle size were achieved in the post-annealing process at a high temperature as a result of Al diffusion.

Marwoto et al. (2012) reported on the growth of Europium doped Gallium Oxide (Ga₂O₃:Eu) thin films via direct current (DC) magnetron sputtering technique. The absorption studies showed that the variation of Eu doping concentration inflicted no change in the optical band gap of the growing films. The optical band gaps of undoped and Eu doped Ga₂O₃ samples exhibited relatively similar values i.e., 3.4eV. The existence of Eu (2%) doping in the Ga₂O₃ configuration leads the luminescence peak to the shorter wavelength region (blue-shift). In contrast, Eu (5%) leads the luminescence peak to the longer wavelength region (red-shift). PL emissions of all samples were observed in the red region with the emission peak in the range of 593 to 602nm.

Lopez et al. (2012), had reported that In-doped Gallium Oxide micro and nanostructures are grown through thermal oxidation of metallic Gallium in the presence of Indium Oxide. The cathodoluminescence (CL) studies revealed that the Indium incorporation modifies the native defect structure. A blue, defect-related luminescence band was found to be strongly increased when Indium content increases. From spatially resolved Raman spectroscopy, the inclusion of Indium ions in the octahedral Gallium sites does not result in a strong modification of the vibrational modes of the crystal up to 6% In, with the exception of an intensity increase of the 651cm⁻¹ Ag mode and broadening of some peaks.

3. SYNTHESIS OF LUMINESCENT PHOSPHORS

The chemicals and raw materials used in the synthesis of luminescent phosphors and electroluminescence device fabrication are listed under the Table 1.

Table 1. Raw materials used for the preparation of luminescent phosphors

| S. No. | Raw Materials | Chemical Formula | Grade and Company | Purity (%) |
|--------|--|---|---|------------|
| 1 | Zinc Nitrate Hexahydrate | Zn(NO ₃) ₂ .6H ₂ O | AR, Sigma Aldrich | 99 |
| 2 | Zinc Oxide | ZnO | AR, May and Baker Ltd. | 99 |
| 3 | Zinc Acetate | Zn(OOCCH ₃) ₂ .2H ₂ O | AR, Merck | 99.9 |
| 4 | Gallium Nitrate Hydrate | Ga(NO ₃) ₃ .xH ₂ O | AR, Sigma Aldrich | 99 |
| 5 | Gallium Oxide | Ga ₂ O ₃ | AR, Alfa Aesar | 99 |
| 6 | Gallium Metal | Ga | --- | 99.99 |
| 7 | Calcium Nitrate | Ca(NO ₃) ₂ .4H ₂ O | AR, Sigma Aldrich | 99 |
| 8 | Calcium Carbonate | CaCO ₃ | AR, Sigma Aldrich | 99 |
| 9 | Sodium Tungstate dihydrate | Na ₂ WO ₄ .2H ₂ O | AR, Sigma Aldrich | 99.5 |
| 10 | Tungsten Oxide | WO ₃ | AR, Sigma Aldrich | 98.99 |
| 11 | Manganese Chloride Tetrahydrate | MnCl ₂ .4H ₂ O | AR, Sigma Aldrich | 99 |
| 12 | Dysprosium Oxide | Dy ₂ O ₃ | AR, Sigma Aldrich | 99 |
| 13 | Europium Oxide | Eu ₂ O ₃ | AR, Alfa Aesar | 99 |
| 14 | Terbium Oxide | Tb ₄ O ₇ | AR, Sigma Aldrich | 99 |
| 15 | Organic Binder | -- | PH-745 binder, M/s. Conductive compounds, USA | -- |
| 16 | Barium Titanate paste | BaTiO ₃ | BT-101 Paste, M/s. Conductive compounds, USA | -- |
| 15 | Silver paste | Ag | M/s. Conductive compounds, USA | -- |
| 16 | Indium Tin Oxide coated Polyethylene terephthalate Substrate | ITO - PET | M/s. Conductive compounds, USA | -- |
| 17 | Acetone | C ₃ H ₆ O | LR, Merck | 99.5 |
| 18 | Methanol | CH ₄ O | LR, Merck | 99.5 |
| 19 | Hydrochloric acid | Con. HCl | LR, Merck | 99 |
| 20 | Nitric acid | Con. HNO ₃ | LR, Merck | 99 |
| 21 | Urea | CO(NH ₂) ₂ | AR, Sigma Aldrich | 99 |
| 22 | Ethylene glycol | C ₂ H ₆ O ₂ | LR, Merck | 99.5 |

4. POLYOL SYNTHESIS OF UNDOPED AND LANTHANIDE DOPED NANOPHOSPHORS

The nanophosphors were synthesized by low temperature polyol route in different organic solvents. A typical clear synthesis procedure is given below. Starting materials such as chlorides or nitrates were dissolved in solvents like ethylene glycol or glycerol or water. Some solvents like ethylene glycol and glycerol can act both as a solvent as well as a stabilizing agent. These solvents were chosen as they are stable upto a temperature of 180°C and most of the inorganic metal salts (acetates, chlorides, nitrates, etc.) are soluble in them. Further, they are easily available, quite stable under ambient conditions and are non-toxic in nature. Precipitating agents depends on the type of the nanophosphor material, which is being prepared. For preparing the metal oxide nanoparticles/ nanomaterials, urea was used as a precipitating agent. It is superior over other bases like ammonia, NaOH, etc. as it decomposes at above 85°C and generates OH ions uniformly throughout the solution leading to homogeneous precipitation. Initially a hydroxide phase will be formed and subsequently it is converted into oxide by increasing the reaction temperature or by heating the product in a furnace at high temperatures.

Procedure for synthesizing nanophosphors

In a general, soluble metal salt was dissolved in an appropriate solvent and the solution was heated in a silicon oil bath under stirring upto-desired temperature. The precipitating agent was added to the reaction medium at high temperatures depending on the actual material to be synthesized. Temperature of the reaction medium was raised to a value close to reaction temperature so that the nanomaterials/ precursor for nanomaterials start precipitating. The solvent molecules also act as stabilizing ligands to prevent aggregation of small particles.

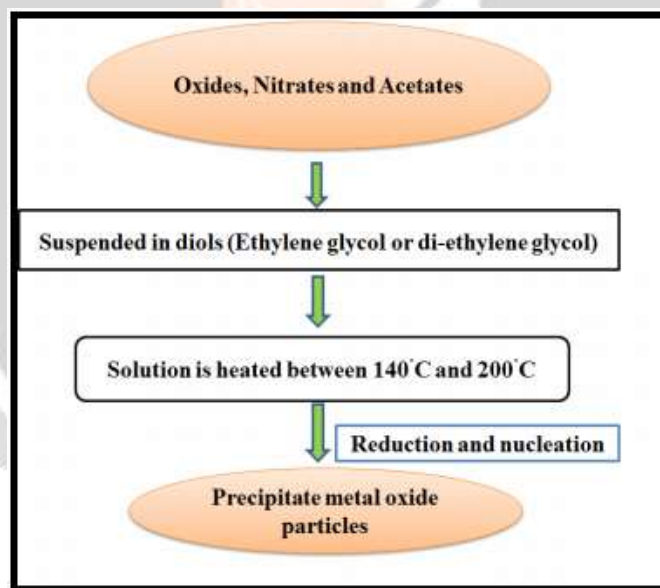


Figure 1 Schematic flowchart for the synthesis of nanophosphors by polyol method

The precipitate was separated by centrifugation, washed with ethanol and acetone to remove unreacted species, and dried under ambient conditions. Schematic flowchart for the synthesis of metal oxide nanophosphors through polyol method are depicted in figure 1.

5. SYNTHESIS OF BINARY OXIDE NANOPHOSPHORS

1. Preparation of Undoped ZnO Nanophosphors

The stoichiometric amounts of Zinc acetate source material was added with 10ml of distilled water. The solution was stirred continuously until a transparent solution was obtained. This solution was transferred into a two-necked round bottom flask, containing ethylene glycol (20 ml) and distilled water (5 ml) were added to this mixture. The

solution was slowly heated up to 100°C followed by the addition of approximately 3g of urea, it was completely dissolved in 20ml of ethylene glycol. It was then slowly heated to 140°C and maintained at that temperature over 2 hours for the nucleation and growth of the nanoparticles. After the reaction, the precipitate was collected by centrifugation and then washed two times with acetone and three times with methanol followed by drying under ambient conditions. The resultant white colored product was further heated in a muffle furnace at 900°C for 5 hrs.

2. Preparation of Undoped Ga₂O₃ and Lanthanide Ions Doped Ga₂O₃ Phosphors

The schematic representation for the preparation of undoped and Dy³⁺ ion doped Ga₂O₃ nanophosphors are shown as in figure 2.

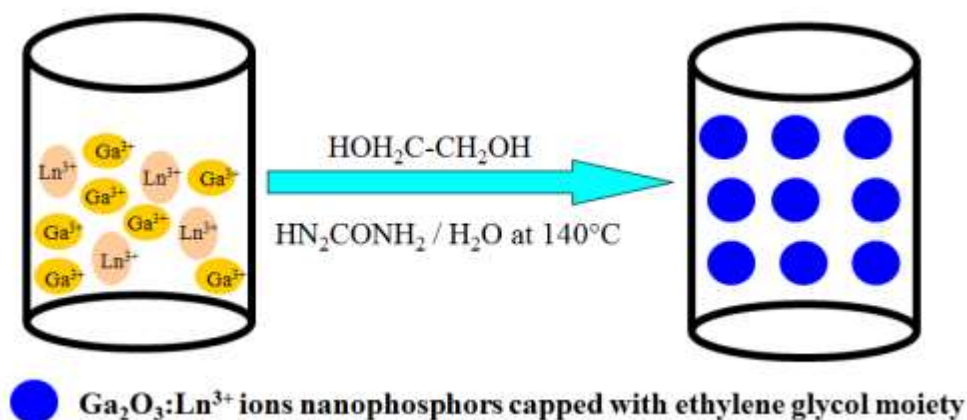


Figure 2 Schematic representation for the synthesis of undoped and Ln³⁺ ion doped Ga₂O₃ nanophosphors

The similar procedure has been employed for preparing Ga₂O₃ samples, appropriate amounts of Ga metal were dissolved in con. HCl and con. HNO₃ mixture in a beaker and the excess acid was removed by repeated evaporation by adding water. This solution was transferred into a two-necked round bottom flask, containing ethylene glycol (20 ml) and distilled water (5 ml) were added to this mixture. The solution was slowly heated upto 90°C in a silicon oil bath while stirring followed by the addition of urea (5.0 g). Temperature was raised to 120°C and refluxed until a slightly turbid solution was obtained. At this temperature, the sufficiently high concentration of OH⁻ is generated in the medium leading to high concentration of GaOOH nuclei, which facilitates growth of the nuclei into nanoparticles. The temperature was maintained at this value for 2 hours. After the reaction, the precipitate was collected by centrifugation and was then washed two times with ethyl alcohol and three times with acetone followed by drying under ambient conditions.

6. SYNTHESIS OF TERNARY OXIDE NANOPHOSPHORS

1. Preparation of Undoped ZnGa₂O₄ and Eu³⁺, Tb³⁺ Doped ZnGa₂O₄ Phosphors

Gallium metal and Zinc acetate were used as starting materials for the preparation of ZnGa₂O₄ nanophosphors. Undoped ZnGa₂O₄ and ZnGa₂O₄:Eu³⁺, Tb³⁺ nanophosphors were synthesized through simple low temperature polyol route. Appropriate amounts of Gallium metal (0.2 g) was dissolved in concentrated HCl containing few drops of HNO₃ in a beaker and the excess acid was removed by repeated evaporation by adding water. This solution was transferred into a round bottom flask, containing appropriate amount of zinc acetate. Ethylene glycol (25 ml) and distilled water (5ml) were added to this mixture. The solution was slowly heated up to 100°C followed by the addition of ~3g of urea dissolved in ethylene glycol. It was then heated to 120 °C whereupon turbidity appeared and maintained for 2 hrs to complete the reaction. The precipitate was collected by centrifugation and then washed with acetone and ethyl alcohol followed by drying under ambient conditions. The resultant white colored as-prepared product was further dried in an oven for about 10-15 mins at 100°C. For Eu³⁺, Tb³⁺ doped ZnGa₂O₄ samples, same procedure were followed except the addition of appropriate amounts of Eu₂O₃ and Tb₄O₇ was carried out while dissolving Ga metal in con. HCl. The final white colored as-prepared sample was further heated in a furnace for about 5 hrs at different temperatures viz., 300, 600 and 900°C.

2. Preparation of Undoped ZnGa₂O₄ and Mn²⁺ Doped ZnGa₂O₄ Phosphors

Undoped and Mn²⁺ doped ZnGa₂O₄ phosphor materials were prepared by solution combustion method. Undoped ZnGa₂O₄ sample has been synthesized by using Zinc nitrate hexahydrate (1.61g), Gallium nitrate hydrate (3g) and urea (2.19g) as starting materials. Metal nitrates (oxidizers) and urea (fuel) were used in the process of combustion. Starting materials were crushed and ground in a china dish with a minimum quantity of the de-ionized water to form a transparent solution. It was then inserted in a preheated furnace maintained at 500°C. The prepared solution undergoes rapid dehydration and decomposition with an evolution of large amount of gaseous by-products. The solution undergoes ignition, burns completely, yielding a voluminous solid mass. The entire combustion process was over in less than five minutes. The dish was immediately removed from the furnace. The resultant voluminous product was crushed into the fine powder using pestle and mortar.

7. CO-PRECIPIATION METHOD FOR THE SYNTHESIS OF UNDOPED AND LANTHANIDE DOPED NANOPARTICLES

A clear picture of the synthesis procedure for this method is given in figure 3.

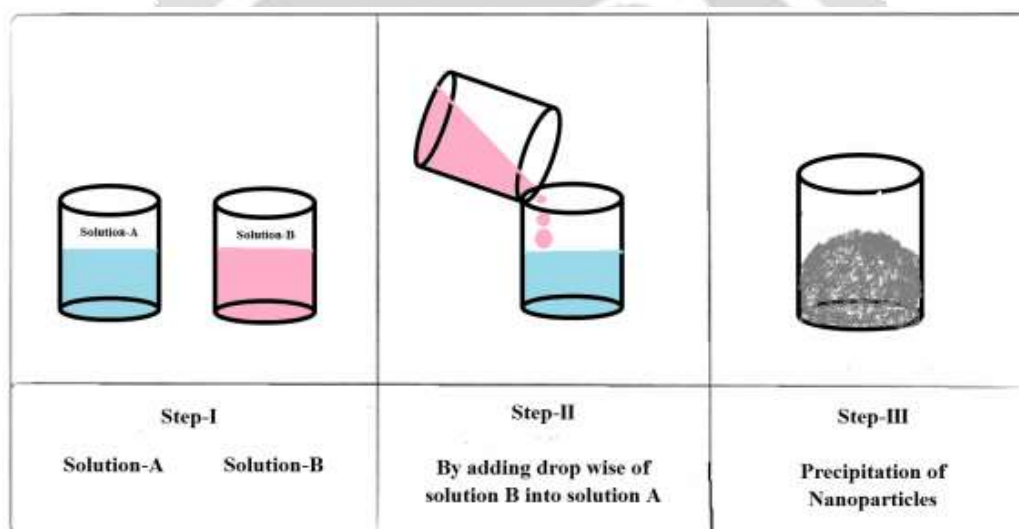


Figure 3 Schematic view for the synthesis of nanoparticles by Co-precipitation route

In the co-precipitation method, a mixed precipitate of two or more insoluble species is simultaneously removed from the solution. The precursor materials homogeneously dissolved in suitable solvents are reduced by reducing agents and results in precipitate. These precipitates are collected, washed and dried by any suitable modes. Several advantages observed with co-precipitation methods such as low cost, low reaction temperature, uniform particle distribution, and low agglomeration with low particle size make it desirable in the synthesis of nano particles. In this work, considering its advantages, co-precipitation method has been adopted for the synthesis of undoped and Eu³⁺ doped CaWO₄ nanoparticles in powder form.

Preparation of Undoped CaWO₄ and Eu³⁺ Doped CaWO₄ Nanoparticles

Undoped and 1% Eu³⁺ doped CaWO₄ samples were prepared at room temperature by simple co-precipitation method. In a typical synthesis process of undoped CaWO₄, 10 ml aqueous solution of 0.56g Ca(NO₃)₂·4H₂O (metal nitrates) and 0.80g Na₂WO₄·2H₂O (reducing agent) were prepared separately and mixed with each other at room temperature under continuous stirring. The turbid solution was then stirred vigorously for two hours to obtain a white coloured precipitate which was then washed three times with methanol followed by acetone. The as-prepared product is then dried and ground well to yield undoped CaWO₄ nanoparticle. CaWO₄:1% Eu³⁺ sample was synthesized using the same protocol by taking the stoichiometric amount of europium precursor. For this, the

stoichiometric amount of Eu_2O_3 salt was dissolved in nitric acid and the excess acid was evaporated by repeatedly adding deionized water followed by heating at 100°C . As-prepared powders of undoped CaWO_4 and Eu^{3+} - doped CaWO_4 were annealed at different temperatures viz., 300, 500, 700 and 900°C for 5h in air to check the thermal stability of synthesized products.

8. SOLID STATE REACTION SYNTHESIS ROUTE FOR UNDOPED AND LANTHANIDE DOPED PHOSPHORS

In the solid-state reaction route, the manual mixing of two or more solid reagents can be ground thoroughly using an agate mortar and pestle are required for the preparation of crystalline materials. The figure 4 shows the detailed flowchart for the synthesis of phosphors through solid state method. Sufficient amount of some volatile organic liquid such as acetone, methanol etc. is added for the purpose of homogeneous mixing of solid reagents. During the process of grinding, the organic liquid gradually volatilizes and evaporates completely after 10 to 15 minutes. Solids do not react together at room temperature over normal time scales and it is required to heat them too much higher temperatures say 1000 to 1300°C . The rate of the solid-state reaction and feasibility depends on the factors such as reaction conditions, structural properties of the reactants, surface area of the solids, their reactivity and the thermodynamic free energy change associated with the reaction.

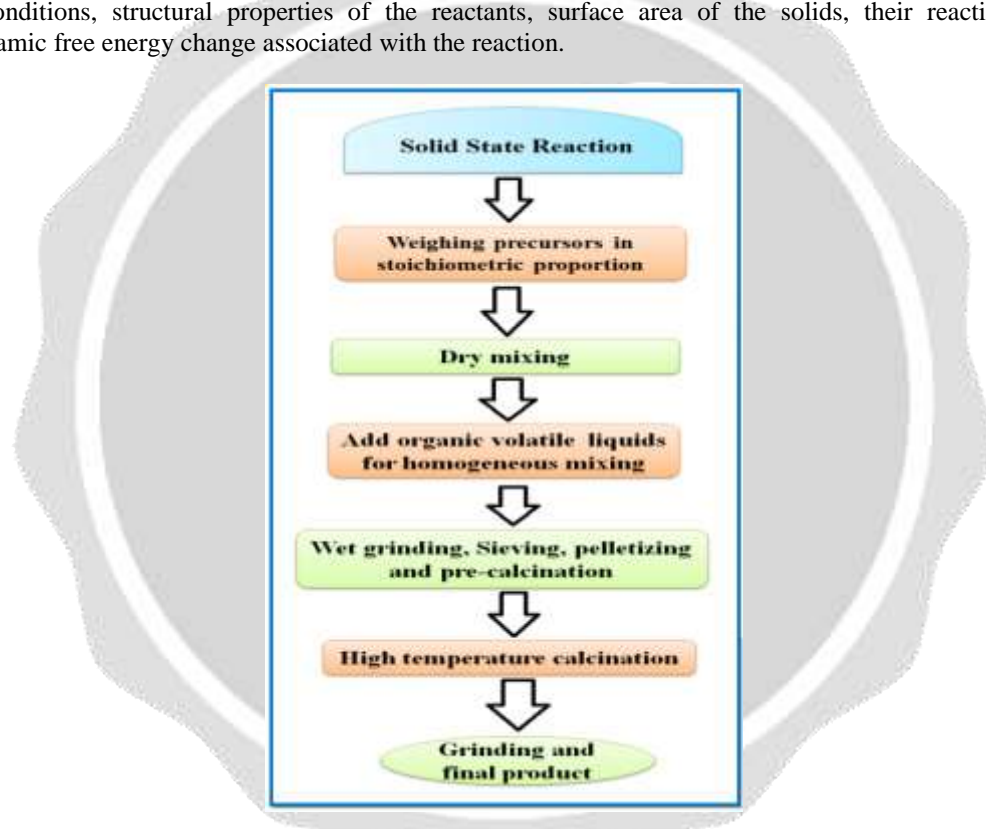


Figure 4 Flowchart for the synthesis of phosphors by solid state reaction route

The merits of SSR is that, it has higher productivity in terms of large-scale material synthesis and less expensive. Main demerits are: the size of nanoparticles is not found in the nano-regime. By taking advantages of this method, the present study has been opted to synthesize the ternary phosphors with large-scale mass production. These samples can act as a phosphor/active layer for both powder and thin-film electroluminescence (EL) devices.

9. CONCLUSION

As discussed in detail, lanthanide-based luminescent materials are known to be better candidates for w-LED applications. They are prepared either by complexing Ln^{3+} ions with suitable organic ligands or by doping Ln^{3+} in an appropriate inorganic lattice having different dimensions. Luminescent properties of such materials depend on their synthesis methods, composition and more importantly on the structure as well as chemical bonding. Therefore, it is required to have prior fundamental information about the structure to accomplish better insight about the

property and functionality. Perovskiteoxide materials have profound structural flexibility in terms of the constituent elements, covering most of the periodic table, and exhibit predictable-structure-property relations. As phosphors, most of the perovskite-oxide matrices have their characteristic emission peaks in the blue region of the visible spectrum. Perovskite-oxide phosphors also have compatibility of operation at much higher temperatures and oxidizing atmospheres. Luminescent properties of phosphors with trivalent rare earth ions showed the maximum number of existing transitions ranging from the deep ultraviolet to the mid-infrared make those appropriate candidates for lamp phosphors and device display applications. The synthesis of such compounds in the bulk or Nano form with the desired properties is a challenging task. Therefore, in the present work, in addition to the conventional solid-state synthesis, a number of soft-chemical methods have also been employed. The soft-chemical routes are low-temperature synthesis technique that allows better compositional homogeneity of the reacting constituents. However, the synthesis feasibility, chemical and thermal stability of certain compounds like transition-metal and rare earth based oxide are a matter of concern. Thus, a prudent selection of the preparative techniques and fine-tuning of process parameters is required to obtain these technologically important materials.

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