EXECUTIVE SUMMARY

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Titled

HYDROTHERMAL SYNTHESIS AND CHARACTERIZATION OF $ZnGa_2O_2$ BASED NANOPHOSPHORS

by

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Introduction

The manipulation of matter on an atomic or molecular scale has aroused an unprecedented excitement in the scientific and engineering communities over the last decade. Nanoscience involves research and technology development at the 1 nm to 100 nm range. The increased surface to volume ratio at the nanoscale leads to 'quantum confinement effects', whereby the electronic properties of solids are altered with great reductions in particle size. Wide band gap semiconductor nanomaterials containing a great number of defects, surface states or doped with optically active luminescence centers have attracted significant attention in research and applications in emerging technologies such as nanoelectronics, nanophotonics, energy conversion, non-linear optics, miniaturized sensors and imaging devices, solar cells, catalysis, detectors, photography and biomedicine.

Nanophosphors are 'light bearers' at the nanoscale. The wavelength emitted by the emission center is dependent on the atom itself, and on the surrounding crystal structure. An activator/co-activator impurity ion incorporation into the phosphor host material transfers the dominant recombination route from the surface state to impurity states. If the impurity induced transition can be localized as in the case of the transition metals or the rare earth elements, the radiative efficiency of the emission increases significantly. Obviously, all these attributes of a doped nanocrystalline phosphor material are very attractive for optoelectronic applications. Nanophosphor materials also find applications in plasma display panels, electroluminescence based displays and field emission displays; in light sources like fluorescent tubes, compact fluorescent lamps and cold cathode lamps and as detectors for x-rays.

Objective of the research problem

The synthesis of nanometre-sized phosphors has attracted much attention owing to their size-dependent electrical and optical properties originating from quantum confinement. Moreover, oxide materials have immense potential as chemically and thermally stable phosphor matrixes over the hygroscopic sulfides, against electron bombardment and hence possess excellent luminescent properties.

Synthesis of oxide phosphors are usually accomplished by solid-state reaction or by flux method. But this requires heat-treatment at higher temperatures (~ 1200 – 1400 ^{o}C) for several hours and

subsequent grinding. This may damage the phosphor surfaces, resulting in the loss of emission intensity. Various chemical routes have been developed to grow nanoparticles of such refractory ternary oxide materials. The research objective of this proposal shall be aimed at lowering the synthesis temperature of oxide phosphors by hydrothermal or microwave routes. These cost-effective techniques are quite simple and less time consuming.

The hydrothermal technique offers several advantages such as low-temperature synthesis, low cost, it is less hazardous and there is no need for the use of metal catalysts. The particles size and their distribution, phase homogeneity, and morphology could be well controlled. Microwave assisted synthesis of nanocrystalline materials has attracted much attention in recent years owing to its unique synthetic pathways, homogenous volumetric heating, rapid heating rates, short processing durations, uniformity and low power requirements. The technique, being cost effective, can be easily scaled up to processes for large scale synthesis.

The present project aims at synthesizing nanometre-sized AB_2O_4 based oxide phosphors and investigating their structural and optical properties.

Zinc gallium oxide, $ZnGa_2O_4$, is the matrix chosen for the study. It is a well-known low voltage ternary double oxide phosphor material used in flat panel displays. When undoped, it provides a high-quality blue emission and rare-earth doping gives the emission characteristics of RE ions and provides tunability over the whole visible spectra. Also, this multicolor cubic spinel has been investigated as a possible alternative to the ZnS-based low-voltage blue cathodoluminescent phosphor. But the synthesis of $ZnGa_2O_4$ spinel powders has been previously accomplished by solid-state reaction or by flux method. But this requires heat-treatment at higher temperatures for several hours and subsequent grinding. This may damage the phosphor surfaces, resulting in the loss of emission intensity. Various chemical routes have been developed to grow nanoparticles of such refractory ternary oxide materials.

Objectives

The objectives of the present project can be enlisted as follows.

1. ***Synthesis of nanopowders via hydrothermal route***
2. ***Characterisation of the nanopowders***
    a) Structural characterization
    b) Optical Absorption studies
    c) Luminescent studies
3. ***Correlation and Analysis of the results obtained***

Interdisciplinary relevance

Owing to its optical transparency and metallic conductivity, $ZnGa_2O_4$ is used as a transparent electrode in liquid crystal displays and solar cells. Up-converting and down converting phosphors in nanosizes have great promise in increasing efficiency of Si solar cells. Also, semiconductor quantum dots have been employed for biological labeling to provide real-time imaging of living cells with high resolution and in the field of quantum information processing.

Many research groups across the world are working on nanophosphor matrix systems and their novel applications in a multitude of functional devices and imaging applications. Moreover, hydrothermal / microwave synthesis is one of the chemical solution routes, which is of current interest and is attractive from environmental and ecological viewpoints. Hence a detailed investigation on the possibility for direct synthesis of luminescent oxide nanomaterials at relatively low temperatures has much relevance.

The aim of this research proposal is to investigate low temperature assisted economical routes towards refractory oxide phosphor and their films. Simple cost-effective techniques for synthesis of oxides would eventually widen the scope for their evolution into commercial materials that could be coated on a large scale on glass substrates. Above all, this work proposed in one of the frontier areas of nanoscience and nanotechnology is a primary motive of contributing my might to the cause of science and to the society at large.

Summary of the Project

ZnO and $ZnAl_2O_4$ nanoparticles could be synthesized via a green and inexpensive microwave assisted hydrothermal route. Pure and rare-earth doped $ZnGa_2O_4$ and $ZnAl_2O_4$ nanoparticles could be synthesized via hydrothermal route. Their structural, morphological and optical properties were characterized.

Zinc oxide nanoparticles were synthesized via two routes. Both the solvent free approach and green synthesis gave homogeneous fine white ZnO nanopowders that crystallized in the hexagonal wurtzite phase formation of ZnO. The average crystallite size and microstrain in the samples were calculated by W-H analysis. The optical band gap was determined from diffuse reflectance data analysis. Results obtained indicate that the microwave-assisted method is a promising low temperature, cheap, and fast method for the production of ZnO nanostructures with no need for expensive materials or complicated treatments.

Spinel $ZnAl_2O_4$ nanoparticles could be synthesized using a facile, environmentally benign and low cost microwave hydrothermal technique using *opuntia dilenii* haw plant extract. X-ray diffraction (XRD) analysis asserts the spinel phased growth of zinc aluminate in the as-prepared sample even

without any post-annealing treatments. The band gap was estimated from diffuse reflectance spectral data analysis to be 3.84 eV. The synthesis was not accompanied by severe mass loss as indicated by thermogravimetric analysis. It was evident from the results that the plant extract plays not only a role as a fuel, but it also has a chemical coordinating action contributing to the crystallization of $ZnAl_2O_4$ nanoparticles.

Pure and rare-earth doped $ZnAl_2O_4$ nanoparticles were synthesized by hydrothermally heating a homogenous precursor mixture with a pH 10 at 200^oC for 3 hours. The dopant used was Dy. X-ray diffraction analysis showed that nanoparticles with a cubic spinel structure could be grown. The average crystalline size corresponding to the dominant XRD peak (311) of the pure sample was estimated to be 11.38 nm. The bandgap of the samples were determined using diffuse spectral analysis. The red PL emissions from the intra-4f transition of Dy^{3+} ions are observed under an excitation of 545 nm. Luminescence quenching is observed in the nanoparticles as the dopant amount is varied. The project therefore proposes a low temperature synthesis of ternary aluminate phosphors.

Pure and rare-earth doped $ZnGa_2O_4$ nanoparticles were synthesized by hydrothermally heating a homogenous precursor mixture with a pH 10 at 200^oC for 3 hours. The dopants used were Eu and Dy. X-ray diffraction analysis showed that nanoparticles with a cubic spinel structure could be grown. The average crystalline size corresponding to the dominant XRD peak (311) of the pure sample was estimated to be 8.95 nm. The crystallite size of Eu doped samples were in the range 6-7 nm and that of Dy doped samples were 15-17 nm. The bandgap of the samples were determined using diffuse spectral analysis. The red PL emissions from the intra-4f transition of Eu^{3+} ions are observed under an excitation of 395 nm. Luminescence quenching is observed in the nanoparticles as the amount of Eu_2O_3 increases. The room temperature PL measurements of the Dy doped sample at an excitation wavelength of 270 nm showed that a bluish emission emerges in the 0.5 gm Dy doped sample on high temperature annealing. The project therefore proposes a low temperature synthesis of ternary oxide phosphors.

Achievements from the project

1. The microwave-assisted hydrothermal route is a promising low temperature, cheap, and fast method for the production of oxide nanostructures with no need for expensive materials or complicated treatments.
2. The hydrothermal synthesis strategy described in the present work provides a low temperature technique to synthesise ternary oxide phosphors.
3. Some red and blue nanophosphors were identified. The undoped and Dy doped sample $ZnGa_2O_4$ nanoparticles emitted in the blue region and the Eu doped sample showed an emission in the red

region of the electromagnetic spectrum. Undoped $ZnAl_2O_4$ nanoparticles gave a bluish emission whereas Dy doped sample emitted in the red region of the visible spectrum.

Contribution to the society

The work presents a microwave-assisted route to synthesise binary and ternary oxide phosphors saving both time and energy. It also presents the hydrothermal synthesis of luminescent ternary oxide phosphor materials from aqueous solutions at high vapour pressures. The method is particularly suitable for the growth of large good-quality crystals while maintaining control over their composition. Growing films using the hydrothermal technique can be investigated to develop the active layer for display devices. Co-doping in a single host lattice to get white emitting stable phosphors or multicolor emissions from a single luminescence center can be investigated. Further improvements in synthesis route can be made to obtain materials with better luminous efficiency for flat panel displays.