Summary of the thesis

This work comes under the general domain of condensed matter physics, more precisely optical properties of materials. However, within the ambit of optical properties, it is the field of luminescence to which this work exactly belongs.

Chapter 1: Introduction

Luminescent materials are a class of materials that give out light on being excited by different means like photons, electric field, cathode rays, chemical energy, X – rays, etc. They have extensive applications in diverse field like lighting, television, radiography, dosimetry, imaging, etc. These materials are also called phosphors.

A peculiar class of luminescent materials called up-conversion phosphors has found a wide range of applications. In such materials, absorption of two lower energy photons, usually in the near infrared region takes place to reach higher energy state and subsequent emission leads to yield a higher energy i.e. in the visible region. This up-conversion of energy is a nonlinear optical process characterized by the successive absorption of two or more pump photons (excitation) via intermediate long-lived energy states followed by the emission of output radiation at a shorter wavelength. The phenomena of up-conversion as a concept was first recognized and formulated by Auzel, Ovsyankin and Feofilov. Multiple approaches have been proposed for the process of upconversion. The phenomena of upconversion have led to generation of progressively novel areas of investigation.

The material generally consists of a host material with an activator or with a set of sensitizer and activator. Among the materials investigated to date, most of the studies performed involve rare earth ion sensitized and activated fluorides, sulphides and phosphates. However, their practical applications are limited due to several factors. Hence, there is a need to investigate new host materials. The rare earth ions used as sensitizers/activators are Holmium, Erbium, Ytterbium and Thulium.

The present study deals with relatively much less investigated host materials like Molybdates and Oxides. Erbium and Ytterbium have been used as activator and sensitizer respectively.

Among the prominent applications of up-conversion phosphors are light emitting diodes, solar cell and biological imaging. Unlike the light emitting diodes of past, which emitted in a limited range of visible spectrum, the modern versions can emit over a large range from ultraviolet to infrared wavelengths. Such LEDs which emit infrared radiation by passing current through it can be utilized for emitting visible radiation by coating of up-conversion phosphors on LED cover. These LEDs can be used instead of conventional LEDs and can be also used in the remote control units of many commercial products like television, DVD players and other applications.

The solar spectrum has a range of wavelengths including near infrared. The transmission of near infrared or sub band gap light causes major loss in conventional solar cells. A possibility to reduce such transmission losses is by insertion of impurities with energies located in the band gap of a solar cell material, which can upconvert the transmitted low energy photons from the solar spectrum to high-energy photons, which can then be utilized by the solar cell to generate additional electron-hole pairs. The upconverter can be present in the form of rare earth atoms implanted directly into the solar cell material itself.

The biological imaging techniques like X-ray, CAT Scan and MRI used in medical diagnosis to examine the structure and defects in biological tissues and living cells are limited by the harmful effects of radiation besides being unable to distinguish between benign and malignant tumors. These techniques do not provide real time response.

A bioimaging approach using up-conversion fluorescence can resolve these drawbacks of conventional bioimaging techniques. Up-conversion fluorescence technique with excitation in the near infrared region can be used for imaging of biological cells and tissues because it has several advantages including absence of photo-damage to living organisms, very low auto-fluorescence, non-harmful, real time response, high detection sensitivity and high penetration depth in biological tissues.

Major objectives of the study are:

- To synthesize new and relatively less investigated up-conversion phosphor material, particularly host materials with known activator and sensitizer.
- To authenticate the preparation of material using standard characterization techniques.
- To study the upconversion luminescence characteristics, particularly the spectral characteristics.
- To investigate the applications of theses materials particularly for solar cells.

The first chapter of the thesis deals with the introduction to the general phenomena of luminescence. It further elaborates the phenomena of upconversion and the various mechanisms through which the phenomena of upconversion can be explained. The chapter also gives details regarding the applications of upconversion materials. The theoretical explanation of upconversion phenomena has been given with depth. The chapter also deals with the general properties of materials used for the study.

Chapter 2: Instrumentation

The second chapter is on instrumentation. The chapter gives details of the various instrumentation techniques, particularly the techniques used for characterization of materials like X-ray diffraction, Scanning electron microscopy and Energy dispersive x-ray spectroscopy. The instrumentation used for investigating the spectral characteristics of upconversion luminescence and studying the IV characteristics has been also discussed in the chapter.

Chapter 3: Synthesis and characterization

The choice of host and activator/sensitizer plays an important role in the performance of a phosphor. Three host materials were chosen for synthesis with Yb^{3+} and Er^{3+} as the sensitizer and activator. These host materials are Lanthanum Molybdate, Bismuth Oxide and Cadmium Oxide. The amount of Ytterbium was kept constant while amount of Erbium was varied. Three samples were prepared for each of the hosts. The samples were prepared using precipitation method.

EDAX analysis of the samples confirms the presence of the activator and sensitizer as well as all elements of the host matrix.

XRD of the Lanthanum Molybdate samples shows that the samples have high degree of crystallinity. They are in monoclinic phase. Samples of Bismuth Oxide also show high degree of crystallinity. They are also in monoclinic phase. Results for Cadmium Oxide samples are similar. They are in cubic phase.

The average crystallite size of the samples is on the higher side. Bi_2O_3 samples have the highest size while CdO samples have the lowest.

SEM images of $La_2(MoO_4)_3$ show coarse grain structure with large variation in grain size. Higher resolution images show aggregation of rod like structures. Images of Bi_2O_3 samples clearly show rectangular rod structures of different size. Images of CdO sample exhibit coarse grain structure with a few occassional rods.

Chapter 4: Up – conversion luminescence study

The phosphor samples synthesized to study up-conversion characteristics were excited by 980 nm radiation.

All the samples give up-conversion luminescence. The samples of $La_2(MoO_4)_3$: Yb, Er give major emissions in the green and some emission in the red region. The emission with multiple peaks is attributed to the Er^{3+} ions, while Yb^{3+} acts as a sensitizer. There is splitting of peaks in the bluish green and green regions on account of the stark effect due to the crystal field of the host material. An increase in intensity is observed in the green region with increase in the Erbium content.

In case of Bi_2O_3: Yb, Er, all the samples exhibits a single narrow and intense peak at 510 nm. It is attributed to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions. Hence too, the intensity of the peaks increase with increase in the Erbium content.

The samples of CdO: Yb, Er give emission in the red region with a slight variation from 626 to 630 nm, which might be due to variation in crystal field. The intensity of the peak increases with increase in the Erbium content. Since these, phosphors have not been explored extensively, there is scope for further study.

Chapter 5: Application

One of the major applications of up-conversion materials is in dye sensitized solar cells, where it is expected that the use of up-conversion materials would increase the efficiency of the cells. To explore this aspect, DSSCs were fabricated in the laboratory using pure TiO_2 and mixture of TiO_2 with up-conversion materials synthesized for the study. The cell parameters were recorded using a conventional set up. The results show that the efficiencies of the cells fabricated by using the mixed samples give higher efficiencies. The best results are obtained for cells prepared by using $La_2(MoO_4)_3$:Yb, Er. Both the results are on expected lines.

Summary

The genesis of the work is in the fact that the most studied up-conversion materials, which are by and large rare earth based materials consisting of rare earth ions as hosts and rare earth ions as activators and sensitizers belong to the categories of fluorides, sulphides and phosphates, whose characteristics present some limitations in terms of low chemical stability, low mechanical strength and low laser induced damage threshold, due to which alternatives are needed in the form of more stable materials like oxides. Hence, the choice of Bismuth Oxide, Cadmium Oxide and Lanthanum Molybdate was made for this study, as the host materials. The pair of Ytterbium and Erbium as the sensitizer and activator respectively is also due to the success of this pair of ions in their trivalent state as an efficient due for up-conversion mechanism. The reasons have been explained.

All the samples were prepared using the precipitation method, which is simple and cost effective. Three samples for each host matrix were prepared with the amount of sensitizer (Yb^{3+}) being constant but variation in the amount of activator (Er^{3+}).

The presence of the elements was confirmed by EDAX. The characterization of the samples were done using XRD, which shows that all the samples are highly crystalline. The Lanthanum Molybdate and Bismuth Oxide samples are in monoclinic phase while the Cadmium Oxide sample is in cubic phase.

The morphology of samples was explored by SEM and several samples exhibit rod like structures.

For recording the Up-conversion spectra, the samples were excited by a 980 nm laser source. The Bismuth Oxide and Cadmium Oxide samples shows narrow band spectra in the bluish green (510 nm) and red region (626 – 630 nm) respectively. Lanthanum Molybdate sample give split peaks in bluish green and green region. The chromaticity points have been also displayed. The proposed mechanism of up-conversion in each case has been explained with diagrams.

For the application part, the phosphors were mixed with TiO_2 to make Dye Sensitized Solar Cells. Results show improvement in efficiency.