Synopsis of the Thesis entitled

Synthesis, Characterization and Applications of Upconversion Phosphors

to be submitted to

The Maharaja Sayajirao University of Baroda

for the degree of

Doctor of Philosophy

in

Applied Physics

by

Sohankumar M. Chauhan

under the supervision of

Dr. Bishwajit S. Chakrabarty

Applied Physics Department

Faculty of Technology & Engineering

The M. S. University of Baroda

Vadodara

April 2018

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 third chapter is on the synthesis and characterization of material. This chapter gives the process of synthesizing the phosphors materials. Three host materials namely Lanthanum Molybdate ($La_2(MoO_4)_3$), Bismuth Oxide (Bi_2O_3) and Cadmium Oxide (CdO) were synthesized. Erbium (Er) was used as an activator and Ytterbium (Yb) was used as a sensitizer. Three samples were prepared for each of the host material varying the proportion of activator and sensitizer.

These samples were characterized using X-ray diffraction. The XRD results of samples of $La_2(MoO_4)_3$ confirm the presence of the material in monoclinic phase with high degree of crystallinity and matching with JCPDS file no. 70 – 1382. Some peaks of Ytterbium were also observed. The XRD peaks of Bi_2O_3 confirmed its presence in the monoclinic phase. This sample also shows high degree of crystallinity. The d-values matched with JCPDS file no. 71 – 2274. XRD results of CdO are in confirmation with JCPDS file no. 05 – 0640. This sample is also in cubic phase with high degree of crystallinity.

EDAX analysis was carried out to confirm the presence of respective elements. The scanning electron microscopy shows a wide variation of the grain size. There are rod like structures and aggregation of these structures in the samples of $La_2(MoO_4)_3$. The samples of Bi_2O_3 show distinct rectangular rod structures along with coarse grains and a few plate like structures. The samples of CdO do not show any rod like structures. The crystallite size calculated by Scherrer formula using XRD data puts the size in the order of micrometers. This is corroborated by the SEM images.

Chapter 4: Photoluminescence study

The fourth chapter is on the luminescence characteristics of the samples under study. As a preliminary investigation, the samples were checked for their emission and color of emission using a 980 nm near infrared pen. The Lanthanum Molybdate and Bismuth Oxide samples exhibited greenish glow. However, the hue was different for both these samples with Bismuth Oxide showing slightly bluish green color. The Cadmium Oxide samples gave red color.

The phosphors were investigated for their upconversion emission characteristics on a set up specially meant for the same. The excitation wavelength for all the samples was fixed at 980 nm.

The Lanthanum Molybdate samples gave multiple peaks of emission from 523 nm to 555 nm in the green region with good intensity. There are peaks between 644 nm and 672 nm in the red region also. However, the intensity of these peaks is very low.

All the samples of Bi_2O_3 exhibited a sharp and intense peak at 510 nm, again in the green region. Apart from this, there are low intensity peaks at 474 nm and 664 nm.

The Cadmium Oxide samples give a sharp and intense peak around 627 nm, which in the red region.

The spectroscopic transitions and mechanism for upconversion luminescence has been also discussed in this chapter.

Chapter 5: Application

The chapter 5 is an attempt to investigate a potential application of the synthesized materials. As mentioned earlier one of the applications of upconversion phosphors is to minimize the

transmission losses in a solar cell by converting the infrared component of the solar spectrum into visible light and there by provide a means for generation of additional electron-hole pairs, which could enhance the current generation in the solar cell. However, this pertains to conventional solar cell and it was not possible to do that in the laboratory. As an alternative these materials were tested in a dye sensitized solar cell (DSSC). In DSSC, the electrolyte used is TiO2, which generates electron-hole pairs by absorbance in the visible region. In this case also, the infrared component remains unutilized. Hence, the synthesized samples of upconversion phosphors, which can convert infrared into visible, were added to TiO_2 and DSSC was fabricated.

The V-I characteristics of this DSSC were recorded to study the changes in the V-I characteristics in comparison to pure TiO_2. The chapter deals with the results and discussion of theses V-I characteristics.

References:

[1] Auzel F, "Upconversion and Anti-Stokes Processes with f and d Ions in Solids", *Chem. Rev*., 104 (2004), pp. 139-173.

[2] V. V. Ovsyankin and P.P. Feofilov, *Sov. Phys. Jetp Lett.*, 4 (1966), pp. 317.

[3] Wang F, Liu X, "Recent Advances in the Chemistry of Lanthanide-Doped Upconversion Nanocrystals", *Chem. Soc. Rev.* 38 (2009), pp. 976-989.

[4] Feng W., Debapriya B., Yongsheng L., Xueyuan C. and Xiaogang L., "Upconversion nanoparticles in biological labeling, imaging and therapy", *Analyst*, 135 (2010), pp. 1839-1854.

[5] Patra A, Friend CS, Kapoor R, Prasad PN, "Fluorescence Upconversion Properties of Er^{3+} Doped TiO_2 and $BaTiO_3$ Nanocrystallites", *Chem. Mater.* 15(2003), pp. 3650-3655.

[6] Wang G, Peng Q, Li Y, "Upconversion Luminescence of Monodisperse CaF_2: Yb^{+3}/Er^{+3} Nanocrystals", *J. Am. Chem. Soc.,* 131 (2009), pp.14200-14201.

[7] Stephan Heer, Olaf Lehmann, Markus Haase, and Hans-Ulrich Gudel, "Blue, Green, and Red Upconversion Emission from Lanthanide-Doped $LuPO_4$ and $YbPO_4$ Nanocrystals in a Transparent Colloidal Solution", *Angew. Chem. Int. Ed.,* 42 (2003), pp. 3179–3182.

[8] S. K. Singh, K. Kumar and S. B. Rai, "Multifunctional Er^{3+} – Yb^{3+} codoped Gd_2O_3 nanocrystalline phosphor synthesized through optimized combustion route", *Appl Phy B,* 94 (2009), pp. 165-173.

[9] Huijuan Liang, Guanying Chen, Long Li, Yuan Liu, Feng Qin, Zhiguo Zhang, "Upconversion luminescence in Yb^{3+}/Tb^{3+}-codoped monodisperse $NaYF_4$ nanocrystals", *Optics Communications,* 282 (2009), pp. 3028–3031.

[10] Hyppanen I, Holsa J, Jouko K, Lastusaari M, Pihlgren L, "Up-conversion Luminescence Properties of Y_2O_2S: Yb^{3+}, Er^{3+} Nanophosphors", *Opt. Mater.,* 31 (2009), pp. 1787-1790.

[11] T. Trupke, M. A. Green, P. Wurfel, "Improving solar cell efficiencies by up-conversion of sub-band-gap light", *Journal of applied physics,* Vol 92, 7 (2002), pp. 4117-4122.

[12] S. Mavengere, H. M. Yadav and J. S. Kim, "Photocatalytic properties of nanocrystalline TiO_2 coupled with up-conversion phosphors", *Journal of Ceram. Sci. Tech,* 8, 1 (2017) pp. 67 – 72.

[13] Rong Huang, Qi Wang, J. Liao, W. You, "Microwave hydrothermal synthesis and upconversion luminescence properties of Yb^{3+}/Tm^{3+} co-doped $NaY(MoO_4)_2$ phosphor", *Bull. Mater.Sci.*, 7 (2017), pp. 1447-1453.

[14] Martina Marin-Dobrincic, E. Cantelar and F. Cusso, "Temporal dynamics of IR-to-visible up-conversion in $LiNbO_3:Er^{3+}/Yb^{3+}$: a path to phosphors with tunable chromaticity, *Optical Mat. Express*, 2, 11 (2012), pp. 1529.

[15] S. Basu, P. S. Devi and H. S. Maiti, "Lanthanum molybdenum oxide: Low temperature synthesis and characterization", *J. Mater. Res.*, 21, 5 (2006), pp. 1133.

[16] S. P. Hargunani, "Synthesis and up-conversion properties of Er^{3+}-Yb^{3+} co-doped $LiBaBO_3$ phosphor", *IARJSET*, 3, 11 (2016), pp. 216.

[17] H. Shen, F. Wang, X. Fan and M. Wang, "Synthesis of LaF_3: Yb^{3+}, Ln^{3+} nanoparticles with improved upconversion luminescence, J. Experimental Nanoscience, 2, 4 (2007), pp. 303.

[18] Y. Tian, B. Chen, R. Hua, J. Sun, L. Cheng and H. Zhong, "Optical transition, electron-coupling and fluorescent quenching of $La_2(MoO_4)_3$: Eu^{3+} phosphor", *J. Applied Phy.*, 109 (2011), pp. 053511-1.

[19] N. Li, J. Zhou and Y. Sun, "Synthesis of $La_{2(1-x)}(MoO_4)_3:RE_{2x}$ (RE=Eu, Tb) phosphor powders via a sol-gel combustion process and their photoluminescent properties", *J. Appl. Spectroscopy*, 81, 5 (2014), pp. 885.

[20] Z. Fu, Qi Wu, W. Gong, L. Shi, W. Li and Z. Dai, "Photoluminescence properties and analysis of spectral structure of $R_2(MoO_4)_3$: Eu^{3+} (R = La, Gd) phosphors", *J. Opt.Soc. Am. B.*, 28, 4 (2011), pp. 709.

[21] Chang Sung Lim, "Microwave –modified sol-gel preparation of $La_2(MoO_4)_3$: Er^{3+}/Yb^{3+} particles and their upconversion photoluminescence properties", *Analytical science and technology*, 27, 6 (2014), pp. 314.

[22] Qianqian Huang, Suning Zhang, Chenxin Cai, Bo Zhou, *Materials Letters*, 65, 2011, pp. 988-990.

[23] Ming-Guo Ma, Jie-Fang Zhu, Run-Cang Sun, Ying Jie Zhu, *Materials Letters*, 64, 2010, pp. 1524-1527.

[24] Xiao-Ping Shen, Shi-Kui Wu, Hui Zhao, Qi Liu, *Physica E*, 39, 2007, pp. 133-136.

[25] V. Fruth, A. Ianculescu, D. Berger, S. Preda, G. Voicu, E. Tenea and M. Popa, "Synthesis , structure and properties of doped Bi2O3", *J. European Ceram. Soc.*, 26 (2006), pp. 3011.

[26] K. Shitara, T. Moriasa, A. Sumitani, A. Seko, H. Hayashi, Y. Koyama, R. Huang, D. Han, H. Moriwake and I. Tanaka, *Chem. Mater.*, 29 (2017), pp. 3763.

[27] A. Walsh and G. W. Watson, *Physical Review B*, 73 (2006), pp. 235104-1.

[28] A. S. Lanje, R. S. Ningthoujam, S. J. Sharma and R. B. Pode, *Indian Journal of Pure and Applied Physics*, 49 (2011), pp. 234.

[29] Heidari A and Brown C, *J. Nanomed. Res.*, 2, 5 (2015), pp. 00042.

[30] A. Salem, *Eur. Phys. J. Plus.*, 129, 263 (2014), pp. 1-12.

[31] A. Chithambararaj, D. B. Mathi, N. R. Yogamalar and A. C. Bose, *Mater. Res. Express*, 2 (2015), pp. 055004.

[32] G. Blasse and B. C. Grabmeir, Luminescent Materials, Springer, Berlin, 1994.

[33] Y. Liu, W. A. Pisarski, S Zeng, C. Xu and Q. Yang, "Tri-color upconversion luminescence of rare earth doped $BaTiO_3$ nanocrystals and lowered color separation", *Optics Express*, 17, 11 (2009), pp. 9089.

[34] Y. Wang and J. Ohwaki, "High-efficiency infrared to visible upconversion of Er^{3+} in $BaCl_2$", *J. App. Phy.*, 74, 2 (1993), pp. 1272.

[35] L. XiXian and CAO WangHe, "Blue, green, red upconversion luminescence and optical characteristics of rare earth doped rare earth oxide and oxysulfide", *Sci China Ser B-Chem*, 50, 4 (2007), pp. 505.

[36] Leyu Wang and Yadong Li, "Controlled synthesis and luminescence of lanthanide doped $NaYF_4$ nanocrystals", *Chem. Mater.*, 19 (2007), pp. 727-734.

[37] F. Vetrone, J. C. Boyer, J. A. Capobianco, A. Speghini and M. Bettinelli, "Effect of Yb^{3+} codoping on the upconversion emission in nanocrystalline Y_2O_3:Er^{3+}", *J. Phys. Chem. B*, 107, 5 (2003), pp.1107.

[38] T. Soukka, K. Kuningas, T. Rantanen, V. Haaslahti and T. Lovgren, "Photochemical characterization of up-converting inorganic lanthanide phosphors as potential labels", *Journal of Fluorescence*, 15, 4 (2005), pp. 513.

[39] E. De la Rosa, L. A. Diaz-Torres, P. Salas and R. A. Rodriguez, "Visible light emission under UV and IR excitation of rare earth doped ZrO_2 nanophosphor", *Optical Materials*, 27 (2005), pp.1320.

[40] S. K. Singh, A. K. Singh, D. Kumar, O. Prakash and S. B. Rai, "Efficient UV-visible upconversion emission in Er^{3+}/Yb^{3+} co-doped La_2O_3 nanocrystalline phosphor", *Appl. Phys. B*, 98 (2010), pp. 173.

[41] T. Sandrock, H. Scheife, E. Heumann and G. Huber, "High power continuous wave upconversion fiber laser at room temperature", *Optics Letters*, 22, 11 (1997), pp. 808.

Publications:

[1] *Effect of thermal annealing on the thermoluminescent properties of nano-calcium fluoride and its dose-response characteristics*, J. K. Mundupuzhakal, R. H. Biswas, **S. Chauhan**, V. Varma, Y. B. Acharya and B. S. Chakrabarty, (Radiation Protection Dosimetry (2014), pp. 1-6).

[2] *Lead (Pb) doped fluoride nanocrystals: Structural and optical properties*, **Sohan M. Chauhan** and B. S. Chakrabarty, (International Journal of Advanced Research (2014), Vol. 2, Issue 7, pp. 607-614).

[3] *Dielectric property and conductivity study of Polyaniline – CaF_2 nanocomposites*, **Sohan M. Chauhan,** Jayveer Mahida and B. S. Chakrabarty, (J. Nano Adv. Mat. (2016) 4, No. 1, pp. 9-16).

[4] *Synthesis and characterization of rare earth (Yb, Er) doped Bi_2O_3 phosphors*, **Sohan M. Chauhan** and B. S. Chakrabarty, (J. Nano Adv. Mat. (2017) 5, No. 2, pp.41-47).