Preparation and Spectral Investigations of Neodymium Oxide doped Polymethylmethacrylate based Laser Material

Monika Chahar*, Vazid Ali*, Sushil Kumar**

*Polymers and Advanced Materials Research Lab., Department of Chemistry, Chaudhary Devi Lal University, Sirsa-125 055, India.
**Materials Science Lab., Department of Physics, Chaudhary Devi Lal University, Sirsa-125 055, India.

Abstract- The modifications in structural and optical properties by incorporating rare earth oxide in polymethylmethacrylate (PMMA) matrix may open up the possibility of the development of smart tunable laser materials. In the present work, neodymium oxide is embedded in synthesized PMMA matrix by chemical doping process. The spectral investigations of neodymium oxide doped PMMA matrix has been carried out using FTIR, UV-visible and photoluminescence spectrophotometers. Infrared study has shown that the absorption band region 1800-1000 cm^{-1} becomes sharper as concentration rare earth oxide increases in PMMA matrix. UV-visible spectra show that the absorption peaks occurred in the UV range 211-228 nm. The photoluminescence study has shown that reasonably sharp fluorescence emission peak is observed in region 380-390 nm whose position changes as concentration of rare earth oxide varies in PMMA matrix.

Index Terms- Chemical doping, tunable laser materials, neodymium oxide, PMMA, Spectral investigations.

I. Introduction

Laser materials are that type of substances in which the majority of atoms or molecules are in the excited energy states. Many solid, liquid, gaseous substances have been studied, including synthetic ruby crystal, helium-neon gas mixture and organic laser dyes, capable of continuous operation, but at a low power. Among all laser materials, the tunable laser materials show great impression because they can continuously change their emission wavelength, or color, in a given spectral range. As such, these quantum devices have found numerous applications in many diverse fields. In particular, tunable lasers have played a crucial and sustained role in advancements of materials science. Among basic fields that employ tunable lasers are use of rare earth oxides and organic dye as the gain medium and their wide spectrum, which makes it highly tunable or to produce very short duration pulses. Tunable laser materials have numerous applications in optics, electronics, photodynamic therapy, non-linear optics, dye chemistry, material processing, atmospheric and underwater sensing, local area communications network, sensors [1-4], spectroscopy, birthmark removal, isotope separation and industry [5] etc. A lack of toxicity and flammability, lower costs and, essentially, compactness would make them useful for medical applications or research work [6-8]. Laser materials made by polymerization of rare earth oxides in the polymer host matrix are an advanced class of materials with great deal of future promise for potential applications as high performance materials. Several research groups are engaged in the development and interpretation of these types of advanced materials. Fan Rongwei et al. [9] have reported the solid state dye lasers based on LDS 698 doped in modified polymethylmethacrylate. Schultheiss Slike et al. [10] have reported rhodamines in silica-zirconia materials, Scott J. Brian et al. [11] have reported mesoporous and mesostructured materials for optical applications. Purificacion et al. [12] have been reported photonic and nanobiophotonic properties of luminescent lanthanide-doped hybrid organic-inorganic materials. In the present study, we want to make efforts to synthesize the thin film shaped tunable laser material. For this, we use polymethylmethacrylate (PMMA) as a host matrix for the dispersion of rare earth oxide molecules in it. Choice of PMMA as host material for rare earth oxide doping due to their good transparency, resistivity, mechanical strength and optical homogeneity which can play an important role to built up the tunable laser material or advanced optical materials. The thin film shaped neodymium oxide doped PMMA based material has been prepared by casting method. The concentration of neodymium oxide in polymethylmethacrylate matrix varies as $0.6x10^{-3}$, $1x10^{-3}$, $1.2x10^{-3}$, $1.3x10^{-3}$ and $1.4x10^{-3}$ mol/L. The structural and optical characterizations of prepared samples are made by spectroscopic techniques such as FTIR, UV-visible and photoluminescence (PL) spectroscopy. We have recorded the IR absorption spectra and fluorescence emission spectra at different concentrations of rare earth doped in PMMA matrix and analyzed them with regard to their applications as tunable luminescent laser materials for device fabrication.

II. Experimental Details

A. Chemicals used

Perspex (PMMA) (Ruchi Enterprises Mumbai, India), Acetone (Spectrochem Pvt. Ltd., Mumbai, India), neodymium oxide (Sigma Aldrich).

B. Methodology and chemical doping

The neodymium oxide doped polymethylmethacrylate based material have been prepared by dissolving perspex 17.0g in acetone and stirring has been done for four days with the help of a magnetic stirrer. Chemical doping of neodymium oxide has been carried out by making solution of rare earth oxide in acetone. The samples have been synthesized by adding dopant solution with different concentration into solution of perspex during polymerization process. The neodymium oxide concentration in synthesized PMMA matrix varies as $0.6x10^{-3}$, $1x10^{-3}$, $1.2x10^{-3}$, $1.3x10^{-3}$ and $1.4x10^{-3}$ mol/L. The resultant reaction mixture doped with neodymium oxide was cast into petridishes and put them in an oven at 42ºC for about 15 days so that the evaporation of acetone from the samples took place for the sake of homogeneous incorporation of neodymium oxide (dopant). The temperature was increased slowly up to 80ºC for 24 h for final ageing to achieve good physical and mechanical strength of prepared material.

III. RESULTS AND DISCUSSION

A. FTIR study

Spectroscopic characterization is an essential tool which is useful to understand the optical properties and behavior of interacting groups after the doping of synthesized materials. Prepared PMMA based material has been characterized by IR spectroscopy using FTIR spectrophotometer (Nicolet 360). IR spectra of undoped and neodymium oxide doped PMMA, exhibit several peaks as shown in Figure1 (a), (b) and (c). To explain the effect of dopant, we have taken FTIR spectra of polymethylmethacrylate at different rare earth oxide concentrations such as 1.2×10^{-3}, 1.4×10^{-3} mol/L. The absorption band in the region 3015-3010 cm^{-1} is mainly due to C-H stretching of PMMA. The main band in the region 1800-1000 cm^{-1} is associated with the combination of vibrations of CH_3-CO_2-C-CH_3 network of polymethylmethacrylate. Region appears in 1697-1650 cm^{-1} is due to the stretching of C=O group. The absorption band appears at 1500-1430 cm^{-1} is due to C-H deformation of $–CH_3$ group. The absorption band in the region 2843-2810 cm^{-1} is due to C-H stretching of C-O-CH_3 group. The absorption band appears at 1459-1440 cm^{-1} is due to C-H deformation of $–CH_2$ group. The absorption band appears at 841-800 cm^{-1} due to stretching of C-C group. The absorption band appears 1395-1386 cm^{-1} is due to C-H deformation of $C(CH_3)_2$ group. It has been clear from the IR spectra of undoped and neodymium oxide doped samples that the absorption band region 1800-1000 cm^{-1} becomes sharper as the concentration of dopant increases in PMMA matrix and it may be due to the homogeneous dispersion of neodymium oxide molecules in the PMMA matrix. It has been observed that the prolonged heat treatment at moderate temperature of the samples increases mechanical strength, abrasion resistance, transparency etc. which may be due to improvement in bonding in PMMA network.

B. UV-visible study

The UV-visible study of neodymium oxide doped polymethylmethacrylate based material has been done by recording optical absorption using Spectrophotometer (Perkin Elmer Lambda). The absorption spectra of pure PMMA and neodymium oxide doped PMMA are shown in Figure 2. It has been observed that the absorption peaks appears at wavelengths 223, 222, 228, 211 and 218nm as the concentration of dopant varies as $0.6x10^{-3}$, $1x10^{-3}$, $1.2x10^{-3}$, $1.3x10^{-3}$ and $1.4x10^{-3}$ mol/L in PMMA matrix respectively. The shifting shifting occurred in the spectra may be due to the polarity of solvent used in the synthesis or may be due to the dispersion of rare earth oxide particles in the PMMA matrix.

C. Photoluminescence study

Photoluminescence spectra of undoped and neodymium oxide doped samples are shown in Figure 3a and 3b. PL study of neodymium oxide doped PMMA in which the concentration of dopant varies as $1x10^{-3}$, $1.2x10^{-3}$ and $1.4x10^{-3}$ mol/L shows emission peaks at wavelength 389, 380 and 390 which lie in UV region. It has been observed from fluorescence spectra that the emission peak has maximum intensity at concentration $1.4x10^{-3}$ mol/L corresponding to wavelength 390nm. A slight shifting has been observed in the spectra as concentration of dopant changes in the host matrix.

IV. CONCLUSION

In summary, neodymium oxide doped PMMA based thin film shape tunable laser material has been prepared and characterized by FTIR, UV-visible and photoluminescence (PL) spectroscopic techniques. The absorption band region 1800-1000 cm^{-1} of IR spectra becomes sharper as concentration of rare earth oxide increases in the PMMA matrix which may be due to homogeneous dispersion of neodymium oxide atoms/molecules in the PMMA matrix. The UV-visible study of rare earth oxide doped PMMA thin plastic films shows that the absorption peaks are observed at wavelengths 223, 222, 228, 211 and 218nm as concentration varies from $0.6x10^{-3}$to$1.4x10^{-3}$ mol/L. The fluorescence spectra show that the prominent emission peak is observed at ~ 590 nm at concentration $1.4x10^{-3}$ mol/L of rare earth oxide. The photoluminescence study shows a slight shifting in emission peak as concentration of rare earth changes in the PMMA matrix. All these factors make the possibility of the development of rare earth doped PMMA tunable laser materials.

V. FIGURES AND TABLES

ISSN 2250-3153

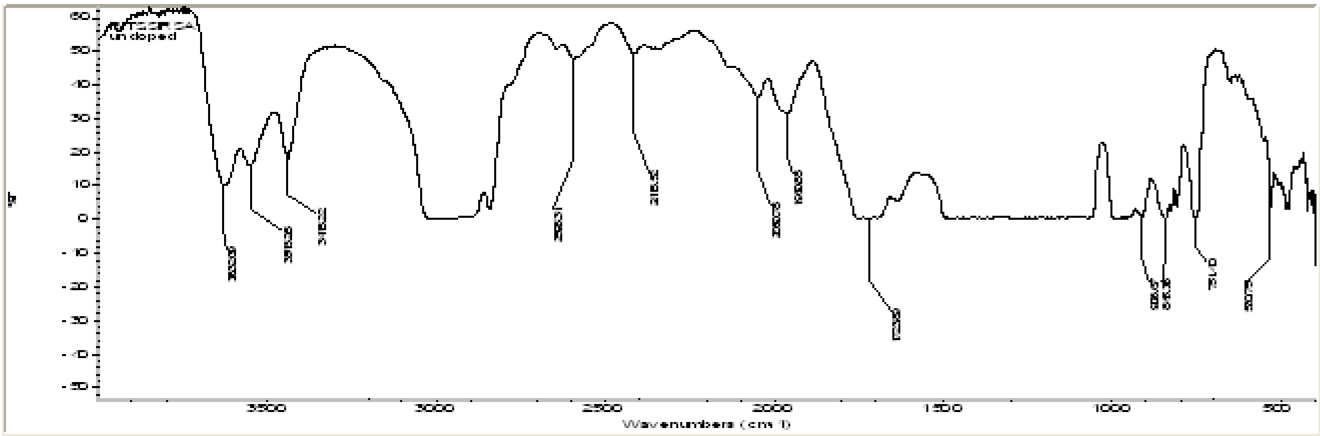

Figure 1a: IR spectra of Undoped PMMA

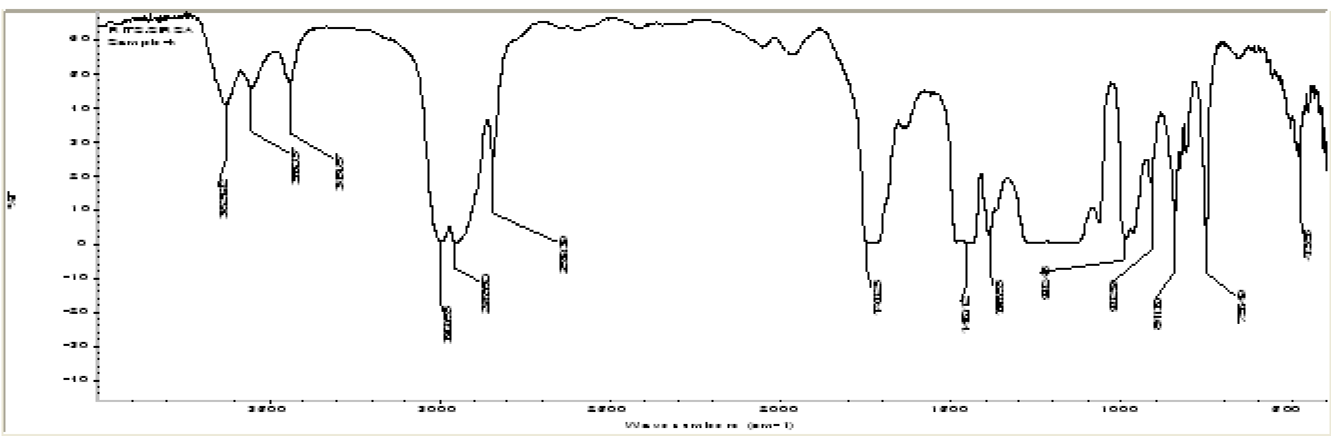

Figure 1b: IR spectra of neodymium oxide doped PMMA with concentration 1.2×10^{-3} mol/L

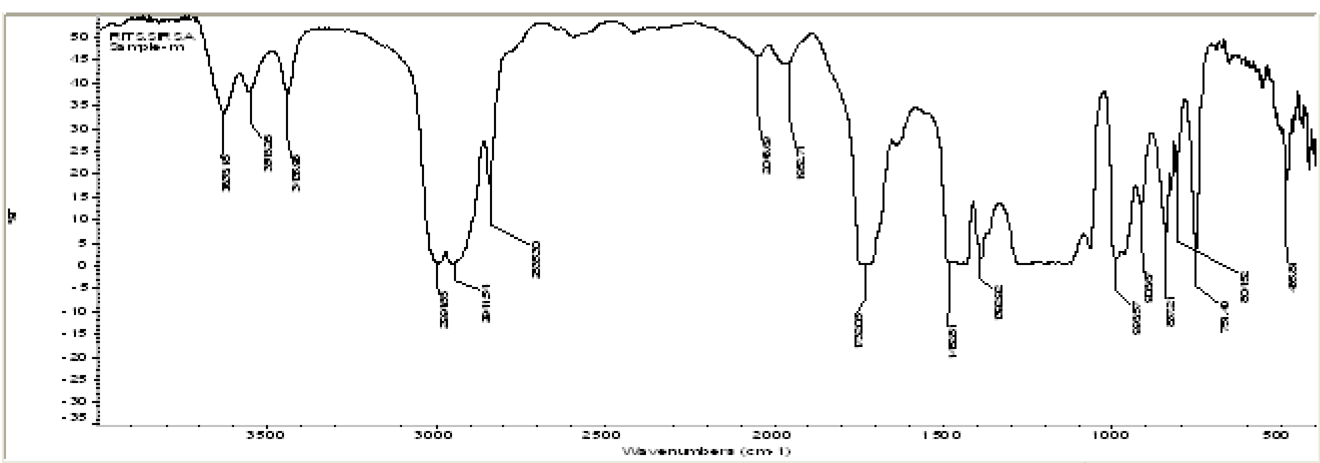

Figure 1c: IR spectra of neodymium oxide doped PMMA with concentration 1.4×10^{-3} mol/L

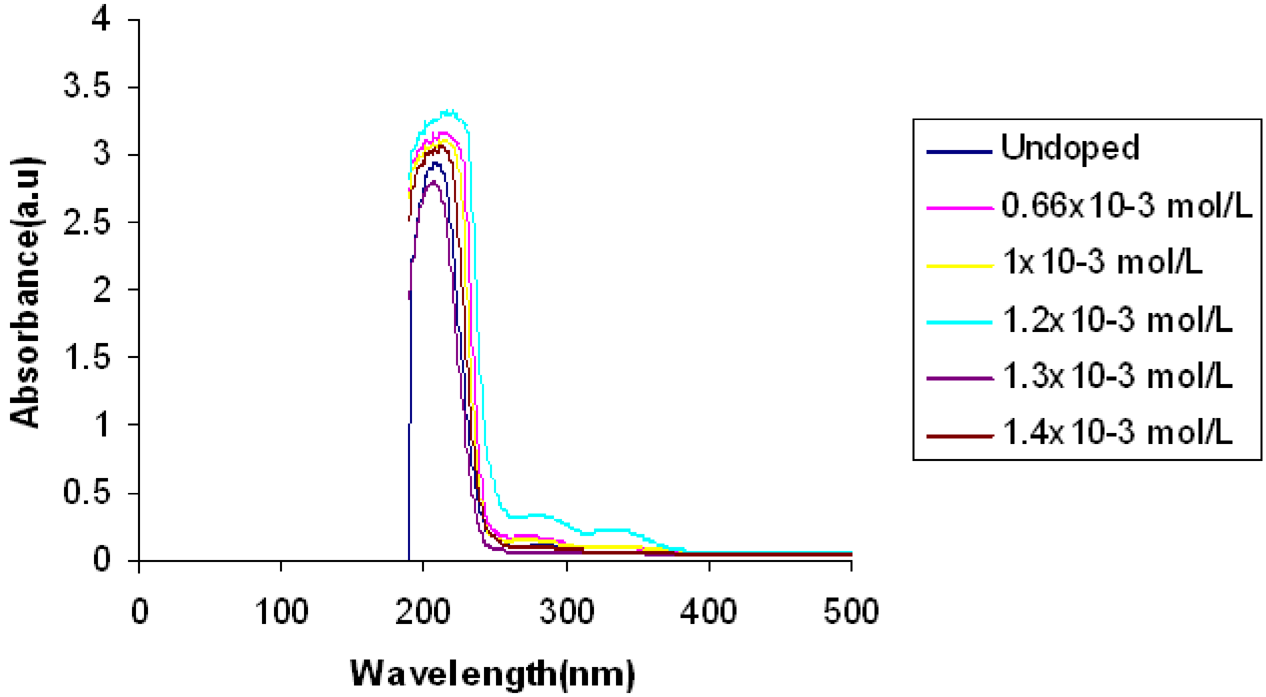

Figure 2: Absorption spectra of undoped and neodymium oxide doped PMMA

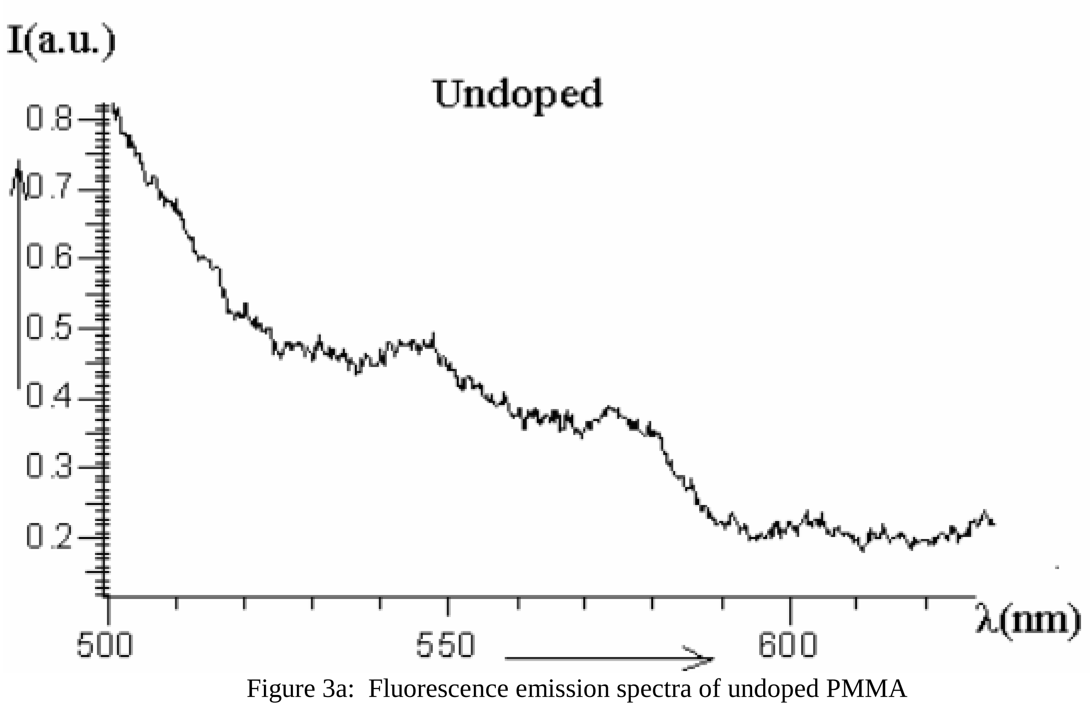

Figure 3a: Fluorescence emission spectra of undoped PMMA

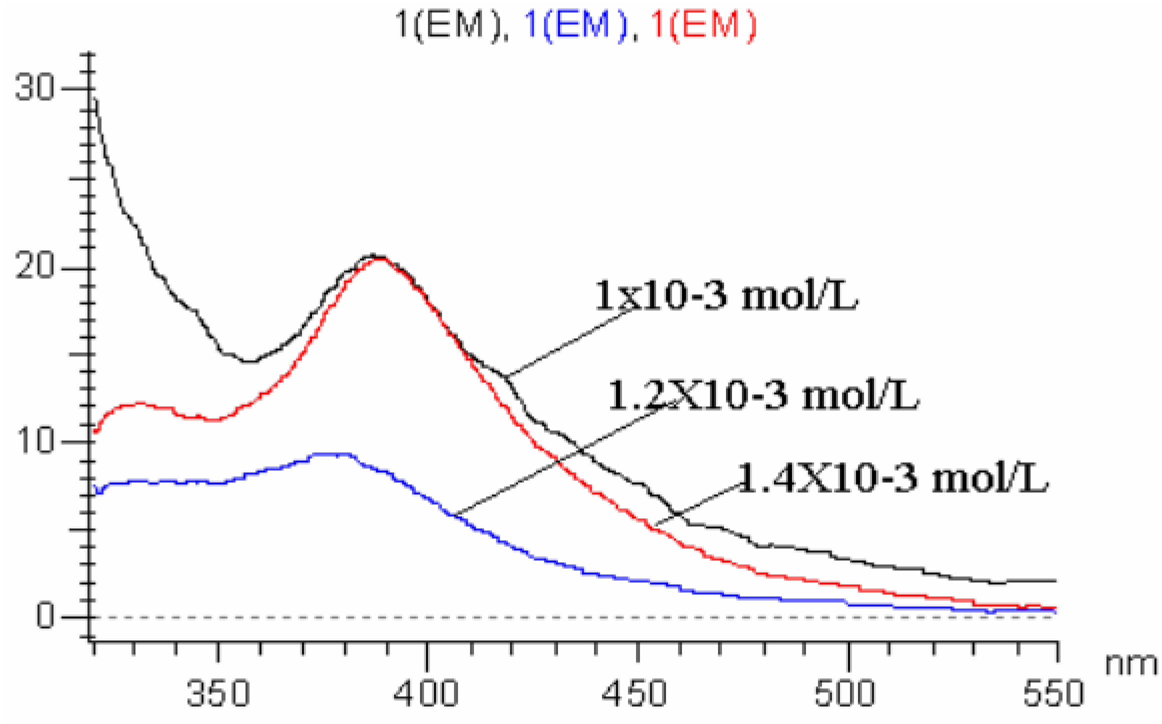

Figure 3b: Fluorescence emission spectra of neodymium oxide doped PMMA

Table 1: Photophysical properties of neodymium oxide doped PMMA based material

Concentration of dye (mol/L)	λ_{abs}^{max} (nm)	λ_{em}^{max} (nm)	Stokes shift (nm)
1×10^{-3}	222	389	167
1.2×10^{-3}	228	380	152
1.4×10^{-3}	218	390	172

ACKNOWLEDGEMENT

Authors wish to express their grateful thanks to Materials Science Laboratory, Department of Physics, Jamia Millia Islamia (Central University), New Delhi, India and Department of Chemistry, Maharshi Dayanand University, Rohtak, India for providing research facilities during this work.

REFERENCES

[1] F. J. Duarte, Solid-state multiple-prism grating dye-laser oscillators, Appl. Opt., Vol. 33, No. 18, 1994, pp.3857-3860.

[2] D. A. Gromov, K. M. Dyumaev, A. A. Manenkov , A. P. Maslyukov, G. A. Matyushin , V. S. Nechitalio and A. M. Prokhorov, Efficient plastic-host dye lasers, J. Opt. Soc. Am.B., Vol. 2, No. 7, 1985, pp.1028-1031.

[3] N. K. Chaudhury, R. Gupta and S. Gulia, Sol-gel technology for sensor applications Defence Science Journal, Vol. 57, No. 3, 2007, pp. 241-253.

[4] H. Podbielska and Ulatowska – Jarza, "Sol-gel technology for biomedical Engineering, Bulletin of The Polish Academy of Sciences Technical Sciences, Vol.53, No.3, 2005, pp. 261-271.

[5] F. J. Duarte, Organic dye lasers: brief history and recent developments." Opt. Photon. News, Vol. 14, No. 10, 2003, pp. 20-25.

[6] H. Aldag., Solid State Dye Lasers for Medical Applications, Proc. SPIE-Int. Soc. Opt. Eng. (Visible and UV Lasers), Vol. 184, 1994, pp. 2115.

[7] M. D. Rahn and T. A. King, Comparison of laser performance of dye molecules in sol-gel polycom host media, Appl. Phys. B, Vol. 34, No. 36, 1995, pp. 8260-8271.

[8] R. Reisfeld, "The state of the art of solid state tunable lasers in the visible, Opt. Mater., Vol. 4, No.1, 1994, pp. 1-3.

[9] R. Fan, Y. Xia and D. Chen, Solid state dye lasers based on LDS 698 doped in modified polymethylmethacrylate, Optics express, Vol. 16, No.13, 2008, pp. 9804-9810.

[10] S. Schultheiss, E. Yariv, R. Reisfeld and H. D. Breuer, Solid state dye lasers: Rhodamines in silica-zirconia materials, Photochem. Photobiol. Sci, Vol.1, No. 5, 2002 pp. 320-323.

[11] B. J. Scott, G. Wirnsberge and G. D. Stucky, Mesoporous and Mesostructured materials for optical applications, Chem.Mater., Vol. 13,, No. 10, 2001, pp. 3140- 3150.

[12] Purificacion Escribano and Beatriz Julian-Lopez, Photonic and nanobiophotonic properties of luminescent lanthanide-doped hybrid organic-inorganic materials J. Mater. Chem.,18 (2008) 23-40.

AUTHORS

First Author: Ms. Monika Chahar, Research Scholar, Department of Chemistry, Chaudhary Devi Lal University, Sirsa- 125 055, Haryana, India.
Email id - monikachahar2009@gmail.com

Second Author and corresponding Author Dr. Vazid Ali, Assistant Professor, Department of Chemistry, Chaudhary Devi Lal University, Sirsa- 125 055, Haryana, India.
Email id - vazid61@yahoo.com, monikachahar2009@gmail.com

Third Author: Dr. Sushil Kumar, Associate Pofessor, Department of Physics, Chaudhary Devi Lal University, Sirsa- 125 055, Haryana, India.
Email id - sushil_phys@rediffmail.com

,