Study of Optical properties & fabrication route for PMMA films doped with Nile Blue Laser dye

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ABSTRACT. In this research work optical properties and fabrication route has been studied for five different series . A comparative study is also done with undoped PMMA matrix and four sample with different concentration of dye solution . Acetone is used as a solvent for both dye and PMMA. Acetone is the best solvent that can easily break down and dissolved other substances. The films were synthesized by using casting method . The optical properties of these synthesized films were characterized with UV Spectrophotometer , FTIR Spectrophotometer testing's. From UV Study we have find out the absorbance bands pattern ofthese films . From FTIR we have find out the changes occur in polymer matrix due to presence of dye molecule or vice versa . Shifting in peaks of absorption spectra has been observed from the data with increase of dye concentration in PMMA matrix **.**

Keywords : Nile Blue , PMMA , Dye doped film , Optical Properties

1.INTRODUCTION. Poly (methyl methacrylate) (PMMA) is the most commonly used polymer matrix for solid state dye laser materials because of its excellent optical transparency & resistivity[1]. It has good mechanical strength and also have good optical homogeneity . PMMA is used for synthesis of advanced optical laser materials [2,3].Solid state dye laser materials have many applications in optics , underwater sensing , medical field ,local area communication networks and in industries . These materials are non-toxic, fire-proof , economical range and the most important thing is that it is user friendly nature which made them strong contenders in markets [4]. PMMA Based dye laser materials are synthesized by polymerization of laser dyes in polymer host matrix , and such type of materials are the most advanced class of optical materials with great deal of future promise for potential application as high performance optical laser materials[5,6,] .

First time in 1967 Soffer and McFarland and Peterson and Snavely report about the stimulated emission from solid state matrix doped with organic dyes, but that time the biggest problems was due to organic dyes chemical properties, only few dyes are completely miscible in solution and due to less miscibility they show low lasing efficiencies and photodegradation occur in dye molecules which cause distortion in synthesized materials physical and spectral properties [7,8]

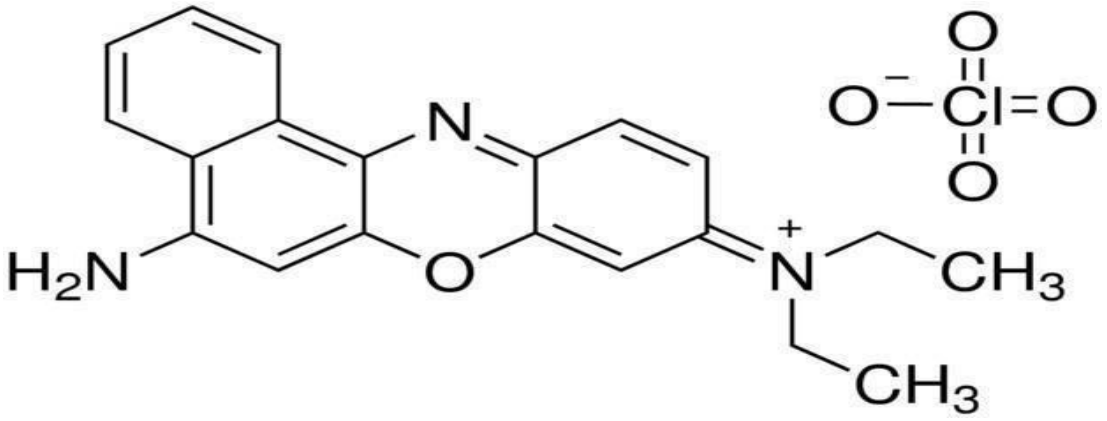
.After trails of many years new organic dyes were synthesized which show high performance and some innovations were also implemented for trapping of laser dye in

solid matrix . Laser dyes which shows full absorbance in uv- visible region which are stable and having gd solubility properties are used for doping in these materials processes as Aggregation Caused Quenching (ACQ), Aggregation-Induced Emission (AIE) [9] and Aggregation Enhanced Emission (AEE) [10] might take place affecting the emission properties of these synthesized materials PMMA based solid state dye laser materials are the one of those materials that have been synthesized as fruitful advanced optical materials [11] . Polymethyl methacrylate (PMMA) is frequently used as the host material for solid-state optical limiting filters . This polymeric material is widely used in the fields of defense and aerospace and optical industries, e.g., In terms of properties, PMMA is the most common organic glass, and it has a small chromatic dispersion, a high linear transmittance in the VIS ranges, and excellent optical properties [12]. As a result, PMMA has a high hardness, excellent chemical stability, and excellent polishing / processing performance toward optical-grade quality [13]. When it comes to giving polymers an optical limiting character, dyes are frequently used. PMMA based materials gave a platform for the production of active elements which can properly control the characteristics of laser radiation [14.15].

Nile Blue A Perchlorate is one of the high performance dye for benzo[a]phenoxazine family which is highly fluorescent and photostable organic dye. It is a cationic dye and it has unique photophysical properties . This dye also have different property of self association in stock solution and the use of Nile Blue in many applications in medical fields have attract my interest in this laser dye The absorption spectra of this dye depend upon the solvent used. Absorbance wavelength shown by Nile Blue slightly shifts depending upon the of solution in which it is dissolved for ethanol it will show absorbance near byat 600 nm For acetone it is near by 620 nm [16].

In our present study one concentration is undoped PMMA and other four concentrations are 0.33×10^{-4}mol/l , 0.50×10^{-4}mol/l , 0.61×10^{-4}mol/l , 0.73×10^{-4}mol/l . Prepared samples were characterized by using spectroscopic techniques such as UV Spectrophotometer and FTIR

2.MATERIALS AND EXPERIMENTAL. Nile blue is the laser dye which is used for doping in PMMA based dye laser materials. The Empirical formula of dye is $C_{20}H_{20}ClN_3O_5$ & the molecular weight of dye is 417.84 . The chemical structure of laser dye is shown in figure 1 . The raw material PMMA (Krishna Enterprises Delhi, India) Acetone (AR GRADE) , Nile Blue A Perchlorate (Sigma Aldrich) . The polymethylmethacrylate thin films doped with Nile Blue lase dye have been prepared by dissolving the 27 gm of PMMA in mixture of acetone and 7% of the volume of methanol is also added to mixture of solid PMMA and liquid solution . Acetone and methanol both are best solvent for both dye and PMMA . After preparation of this solution mixture the mixture is poured into beaker and beaker is placed on magnetic stirrer at a temperature of 10 degree and solution is stirred for seven days and after seven days PMMA is completely dissolved and a homogeneous solution is formed . For the doping process a standard amount of dye is dissolved in mixture of acetone and methanol .The concentration of dye in PMMA solution varies as 0.33×10^{-4}mol/l , 0.50×10^{-4}mol/l , 0.61×10^{-4}mol/l ,0.73×10^{-4}mol/l . After that the PMMA chemical mixture is casted into thin glass slides and flat bottom Petri dishes and then the glassware carrying the solution is placed in oven at 30 degree temperature almost for 23 days for the complete evaporation of solvent because it is necessary for proper trapping of dye in PMMA matrix . After 23 days for almost 32 hours the temperature of oven is raised up to 70 degree for the final step to attain the good outlook and mechanical strength synthesized solid state dye laser films.



Chemical structure of Nile Blue A Perchlorate
Figure 1

3. RESULTS AND DISCUSSION.

3.1 UV – VIS STUDY

The absorption spectra of undoped PMMA and four different synthesized PMMA thin films are shown in fig 2 from this obtained data we can say that as the concentration of dye is goes on increasing the intensity of absorbance band going on increasing and the peaks are becoming very clear .As it is clear from the sharpness of peak that there is loss of some dye molecule is also occur at high temperature because at low dye concentration the peak of is broad but as concentration increases the peaks are sharpened .

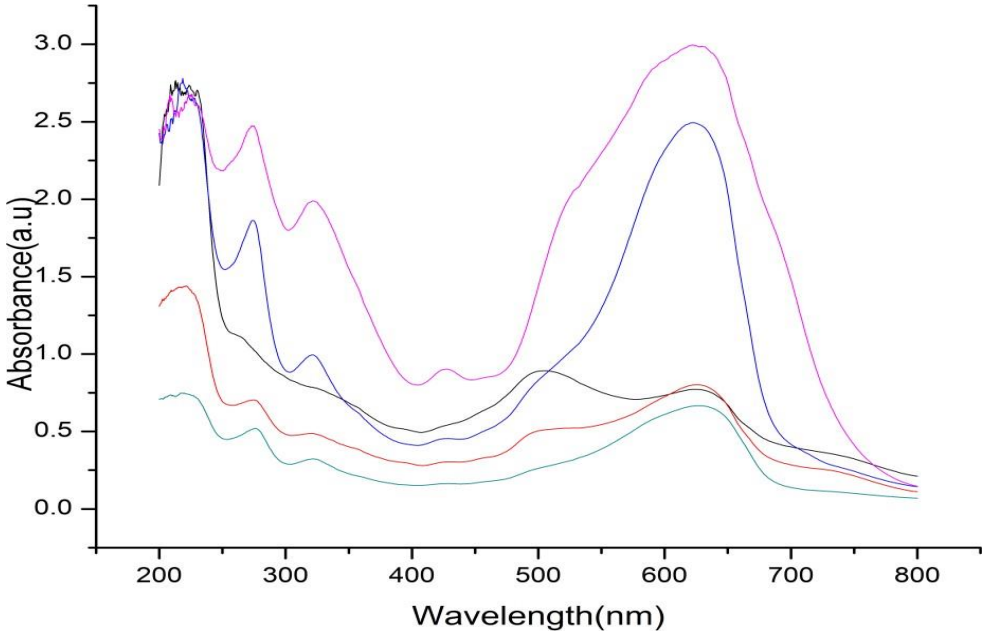


Figure 2

Absorbance spectra of undoped PMMA film and dye doped film with different concentrations

Peaks observed from all five series are depicted below :

1. From undoped PMMA we get peak at 220 nm another at 340 nm at 1.5 intensity.
2. From 0.33 $\times 10^{-4}$ mol/l concentration we observe peak at230 nm ,270nm, 320 nm,620 nm at 0.7 intensity .
3. From 0.50 $\times 10^{-4}$mol/l concentration we observe peak at 230 nm ,270 nm , a little peak at 500 nm ,broad peak at 630 nm at 1.3 intensity.
4. From 0.61$\times 10^{-4}$mol/l concentration we observe peak at 235 nm ,280 nm, 330 nm , 635 nm at 2.4 intensity .The peak observed from this concentration are clear and somewhat sharp also ascompare to above series .
5. From 0.71 $\times$ 10^{-4}mol/l concentration peak observe at 220 nm , 230 nm , 260 nm , 340 nm,440 nm , 640 nm at 2.4 intensity but the height of peak at 640 nm is near by the 2.8 intensity.

As from data its very clear that a slight shifting is observed in all concentration and peaks are becomingclear and these spectral properties of these synthesized PMMA films confirms that PMMA based solid state dye laser materials have good optical properties they show good absorbance inUV-VIS region and they are best optical laser materials .

3.2 FTIR STUDIES. The IR spectra of undoped PMMA films and dye doped PMMA films , is shown infigures from fig 3 (a) – (e) .

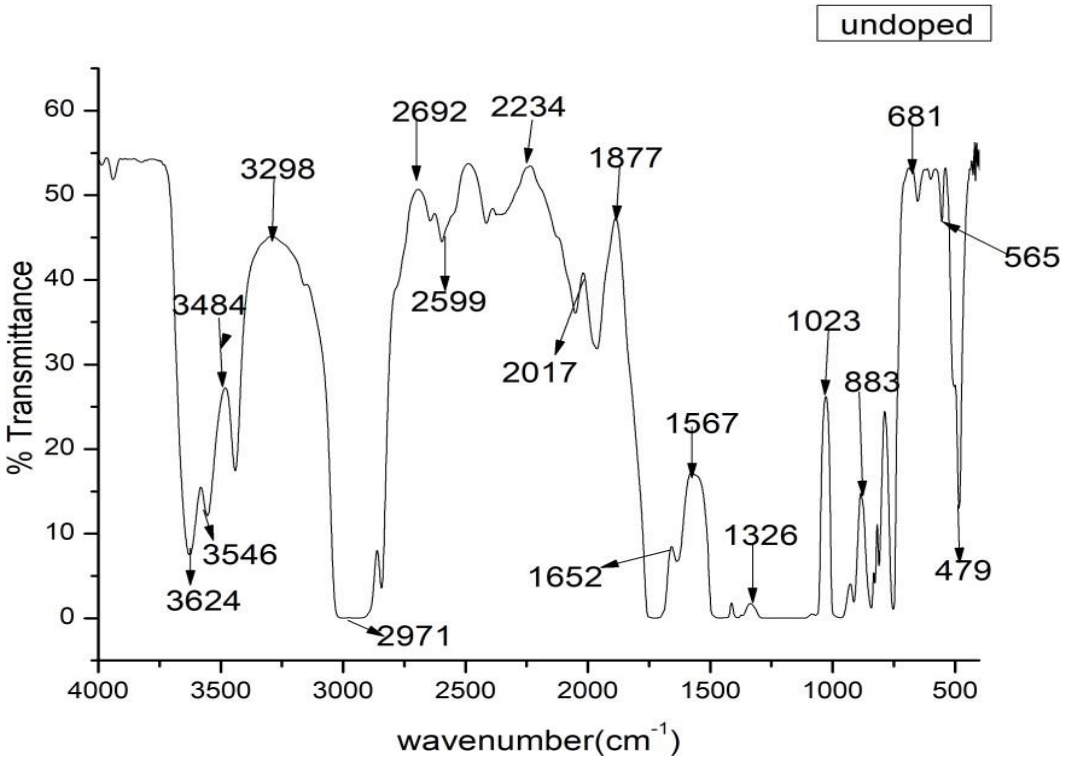


Figure 3
IR Spectra of undoped PMMA

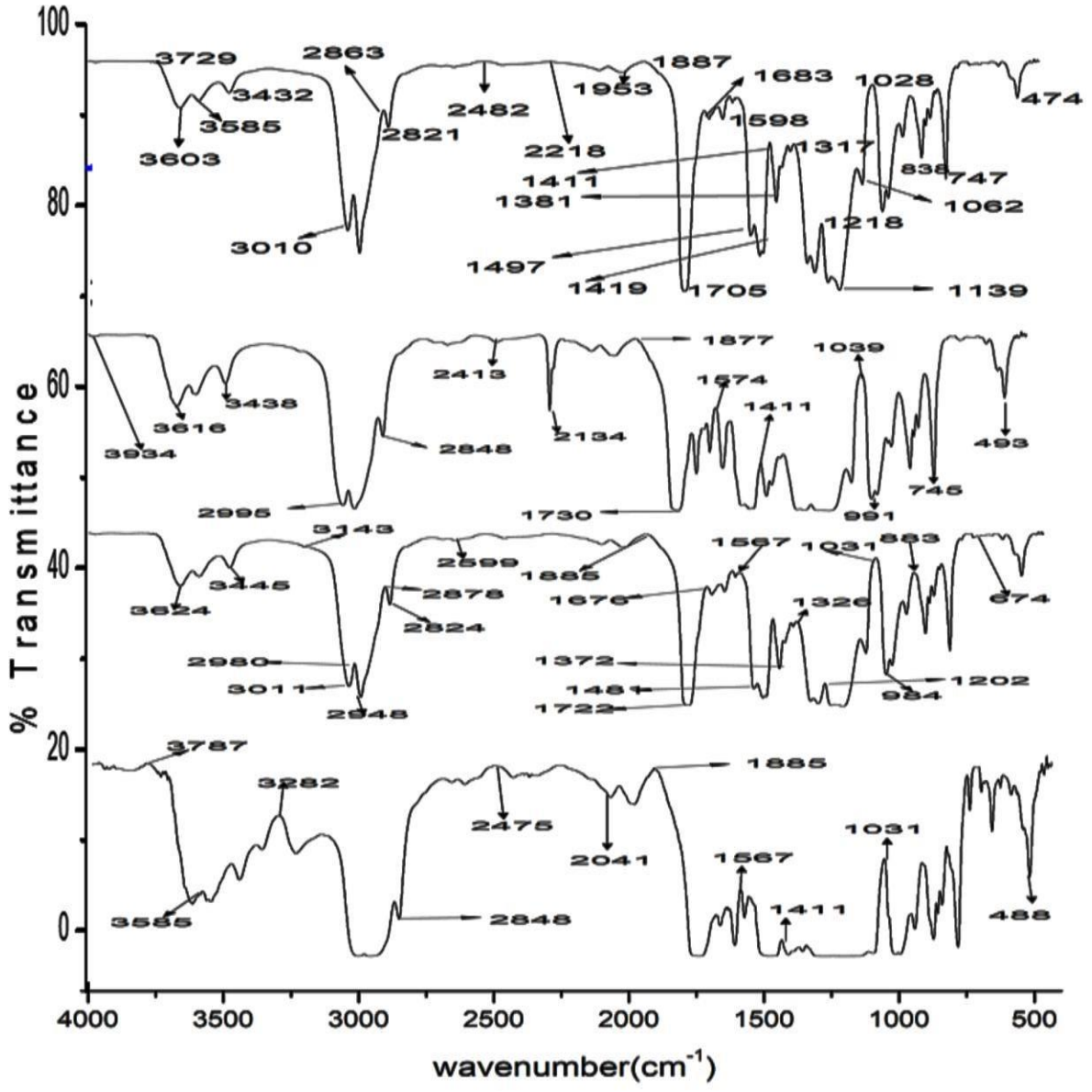


Figure 4
FTIR Spectra of laser dye doped PMMA films with concentration0.33× 10^{-4} mol/l , 0.50 × 10^{-4} mol/l , 0.61 × 10^{-4} mol/l , 0.73 × 10^{-4} mol/l

To examine the variation in spectra due to concentration of dye. We had synthesized films of different dye concentration and from results we concluded it very clearly that yes variation in dye concentration creates a change in molecular structure occurs due to stretching and bending occur in different bonds . The absorption band appear in region 2995- 3010 cm^{-1}shows two band one is due to C-H stretch and another is due to asymmetrical stretching in two C-H bond of methylene groups . the bands found at 1705 ,1722,1730 cm^{-1} are very strong at different intensities. The region from 1700 - 1730 cm^{-1} is assigned for free lateral stretching of c=o(saturated) . The peaks appeared in 1411 – 1481 cm is due to methylene C-H bend . The curve appear at 1326- 1372 $cm^{-1}$is due to O-CH stretching and here deformation of PMMA took place .The region from 700-1300 cm-1 is due to c-c vibration. A wide band is formed in 3570-3200 cm^{-1} region and this is due to presence of Hydroxyl group and OH Group creates stretching . The region from 3603 – 3525 cm^{-1} show narrow band due to non bonded hydroxyl group. The band appear in 1411-1320cm^{-1}refers to carboxylic salts .

The other most important bands are aromatic ring vibration that are centered about 1600-1500cm^{-1}. O-H band out of plane bend at 690 -590 cm^{-1} The intensity of bands appear in region 3010-2990 c^{-1} region increased with increasing concentration of dye in PMMA film. The band appear at 1700-1730 cm^{-1} region intensity decreasing with increasing dye concentration. The intensity of band appear at 1031-1039 cm^{-1},1500- 1595 cm^{-1} region going on increasing with increasing concentration of dye . In many regions we have noticed the some intensity goes on increasing while some are decreasing. We can easily conclude that presence of dye molecule in different concentration in these doped film alter the pattern of spectrum because increasing concentration of dye molecule in PMMA leads to disappear some peaks and show some other peaks that is confirmed from the above FTIR spectrum.

4. CONCLUSION. In this present research work , Nile Blue doped PMMA based solid state dye laser materials has been synthesized and characterized by using UV and FTIR spectroscopic techniques . IR spectroscopy is used to study the structural changes that happens in PMMA matrix . The UV - VIS data of dye doped PMMA film gives the maximum absorption peak at 640 nm and a slight shifting patterns seen with increase in dye concentration . The intensity of absorption band in region 3010 – 2990 cm^{-1} of IR spectra goes on increasing with increasing concentration of dye and the absorption band appears in 1800- 1000 cm^{-1} Become sharper with the increasing concentration of dye in matrix . the presence of dye molecule in PMMA matrix may disappear some peaks and enhance some other new peaks these two studies are very helpful for more innovations in solid state dye laser materials . These two studies tells about the absorbance trend and structural changes that occur due to presence of different concentration of dye molecule in PMMA thin films.

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