Spectroscopic Study of R101 Dye Liquid in and Solid Media

دارسه طيفيه لصبغة R101 في الأوساط السائله والصلبة

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Abstract

The purpose of this study is to choose a laser dye (R101), and study its absorption and fluorescence spectra in visible region before and after mixing with polymer and doping this mixture with metal oxides. These oxides may work as micro resonator, and a solid random laser may be obtained

ألخلاصه

ان غرض هذه الدراسة يكمن في اختيار صبغة ليزرية (R101) ودراسة أطياف الامتصاص والانبعاث لها ثم تحديد أمكانية عملها بوصفها وسطاً ليزرياً في المنطقة المرئيه بعد تغير الوسط الجامع لها سائلاً كان ام صلباً، وإدخال دور الاكاسيد الفلزية لما له من دور فاعل في أنشاء مجموعة من المرنانات الليزرية المايكروية الداخلية ومن ثم أمكانية الحصول على ليزرات عشوائية صلبة صغيرة الحجم.

Introduction

Organic dyes dissolved in suitable solvents have been extensively used as lasing media for several decades [1]. Their extensive wavelength coverage and tunability coupled with a significant fluorescence yield had contributed to their widespread use.
However, certain limitations e.g. inflammability and toxicity of some solvents, their evaporation and fluctuations in flow rate are some of the points which have limited their applications in certain applications. Use of solid hosts to entrap the dye molecules has been suggested as a viable alternative and in recent years extensive and intense efforts have been devoted to use polymers or silica gel as host materials [2, 3].

The Dye color nature belongs to existence of chromospheres, and it represents the responsible chemical group for the color of the molecule i.e. its ability to absorption. The most important dyes used in dye lasers scopes are xanthenes group dyes which contain on 3 benzene cycles such as Rhodamine 101 [3, 4].

The solid dyes, which have been used, are composed of organic dye lasers. The use of solid dyes was a source of interest for researchers in field of developing active media for dye laser. The solid solutions of dyes have been studied in polymer solid solutions which form the active media in harmonic lasers and they are used more than liquid solutions. When the dyes join inside the polymer solution, the displacement of the spectra of absorption and fluorescence takes place relative to the methanol solution [5, 6]. The study of interaction between light and laser dye in solid polymers solutions has concluded that the Rhodamine in solid media shows photo
Physical behavior similar to that in liquid solutions. The photo stability increases clearly when the chloroform joints with polymer series [7].

Experimental Section

Absorption Spectra Measurement

UV-Visible absorption spectra of the laser dyes were carried out using UV-Visible double-beam computerized spectrophotometer Cintra 5 (supplied from GBC scientific Equipment) was used in this experiment for absorption measurements, as illustrated in figure (1).

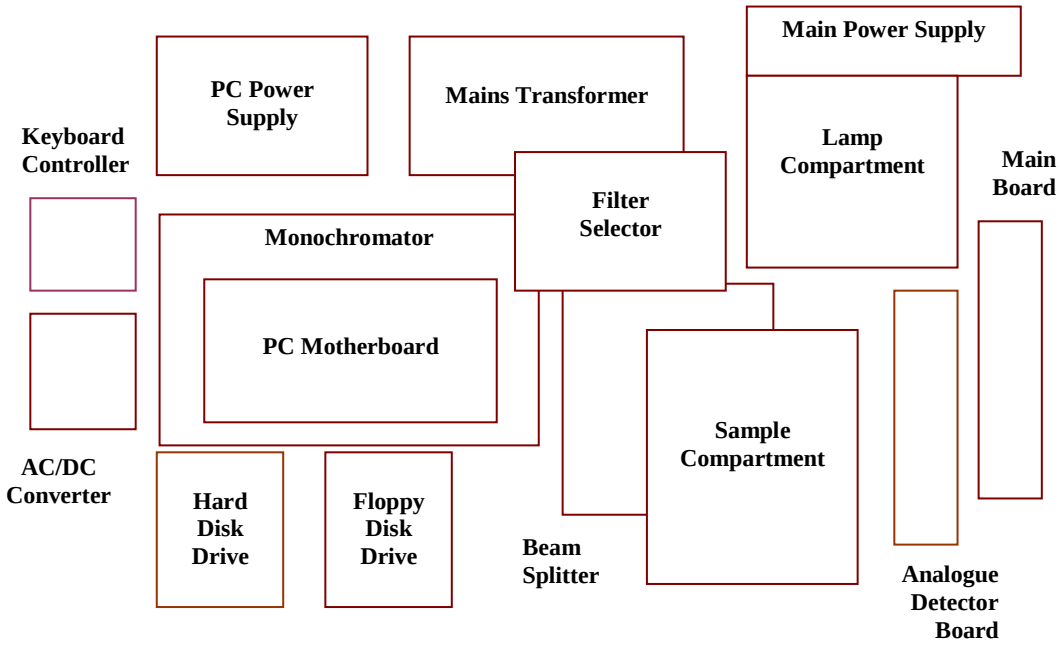

Figure (1) Schematic diagram of the absorption spectrum arrangement

Fluorescence Spectra Measurement

The fluorescence set up illustrated in Fig. (2) was applied in this study. Laser induced fluorescence of the dyes have been recorded through the spectrophotometer using a diode pumped solid state green laser of 531nm, CW output power of 10 mw with line width <2 nm and beam diameter <2 mm. The laser has a suitable wavelength that lies within the peak absorption band of the dye used in our experiment. The dye fluorescence output was detected through a Jarrell ash monochromatic model 82-000. This unit is an Ebert scanning spectrometer, 0.5 meter focal length, with eight speed electric drive, plane reflection grating, of 1180 groove/mm and counter. The detection unit was a photomultiplier PMT (type R666 Hamamatsu) which was connected to an X-Y recorder (Siemens) to detect the output signal

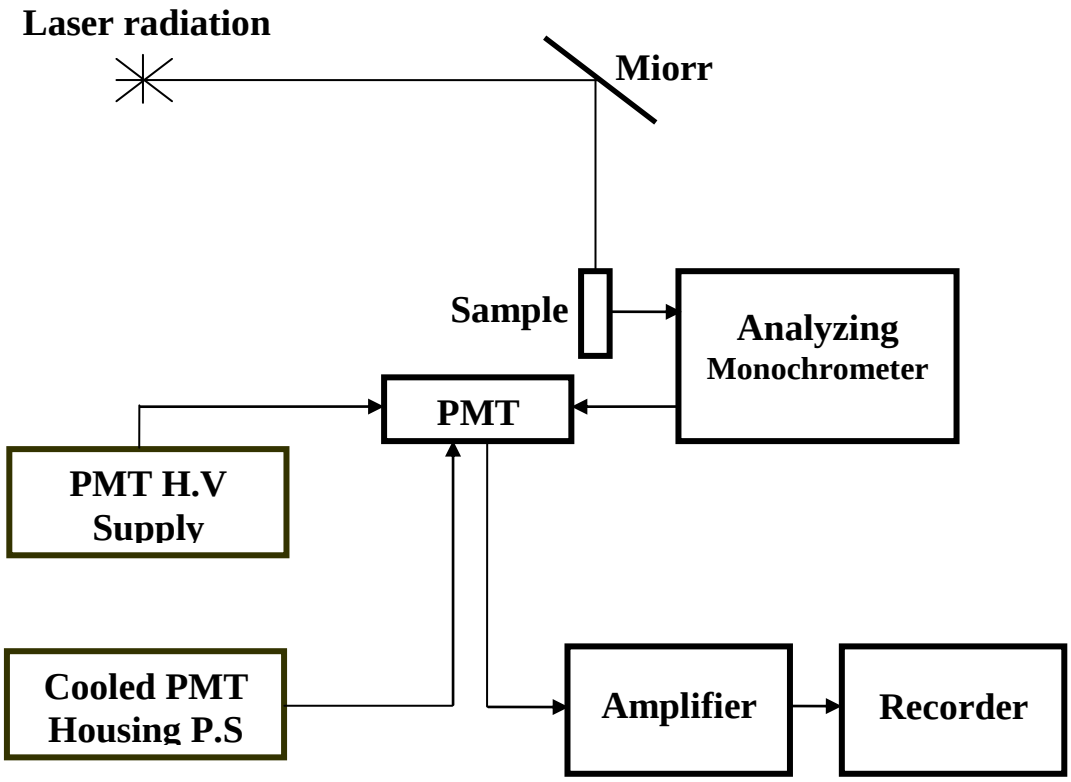

Figure (2) Schematic diagram of the fluorescence spectrum set up

Materials and Method

Materials

Dyes

The dye used was R101 (Rhodamine 101) laser dye ($C_{32}H_{31}N_2O_7CL$), from Xanthenes family, molecular weight 591.06 gm/M supplied by Lambda Physics LC (6400). R101 was used as received without further purification.

Polymer

Methylmethacrylat (MMA) with chemical form ($CH_2CH_3COOCH_3$) was used as a monomer supplied by Fulka (Switzerland) to obtain a solid polymer to be used as a host for laser dyes.

Oxides

Some oxides had been used as they received from (Matthey Johnson Co. limited) with spectroscopic standard purity:

1- Silver Oxide (Ag_2O).
2- Beryllium Oxide (BeO).
3- Cadmium Oxide (CdO).

Solvents

The following solvents were used:

1-Methanol (CH_3OH) with spectroscopic grade purity supplied by Gainland Chemical Company.
2-Methyl chloroform (CH_3CCL_3) with spectroscopic grade purity supplied by Philip Harris chemical company U.K.

Preparation of Dye Solutions

Preparation of Liquid Samples

The solutions of the dye were prepared by dissolving the required amount of the dye into the solvent, then after obtaining high concentration of dye solutions it was diluted by applying the diluting equation: $\mathbf{C_1 V_1 = C_2 V_2}$

Where $\mathbf{C_1}$**:** Primary Concentration**,** $\mathbf{C_2}$**:** Final Concentration

$\mathbf{V_1}$**:** Primary Volume**,** $\mathbf{V_2}$ Final Volume

Preparation of Solid Samples

The PMMA polymer (Poly Mehta MethyleAcrylate) was prepared by dissolving MMA (Metha MethyleAcrylate) in Methylcloform with mixing ratio 1:1 then the product was mixed with the solution.

Preparation of Solid Samples with Oxide

The prepared R101 dye solution in methyl chloroform was mixed with a concentration of silver oxide which was added with quantity equals to half of dye weight. The same way was applied for R101with beryllium oxide and cadmium oxide. Then, 0.5ml of R101 dye solution with silver oxide was dissolved in chloroform methyl solvent and 4.5 ml of PMMA was then added. The same step was repeated for R101 dye solution with beryllium oxide and cadmium oxide.

Results and Discussion

Absorption Spectra of R101 Dye Solution

Fig. (3) Shows the absorption spectra for R101 dye-oxides in mixture methyl chloroform, using two different concentrations of 10^{-4} M and 10^{-5} M. For solutions of 10^{-4} M concentration: The peak absorbance occurs at 562.9, 562.4, and 562.2 nm for Ag_2O, BeO, and CdO oxide solutions respectively. And for 10^{-5} M: The peak absorbance occurs at 560.8, 560.3, and 560 nm for Ag_2O, BeO, and CdO solutions respectively. The absorption spectra are shown in Fig. (4), for R101 dye-oxide solutions when PMMA polymer was added to these solutions. For solutions of 10^{-4} M concentration: The peak absorption intensity (peak absorbance) occurs at 569.5, 569.3, and 569 nm for Ag_2O, BeO, and CdO oxide solution respectively. And for 10^{-5} M: the peak absorbance occurs at 567.6, 567.4, and 567 nm for Ag_2O, BeO, and CdO solutions respectively.

From the above results one can see that the peak absorbance is shifted towards the shorter wavelength (blue shift) as the concentration decreased, this is because the increase of concentration means an increase in the number of the molecules per unit volume and hence this will cause a change in energy levels as a result of increasing of perturbing effect of molecules. Also we can notice that the absorbance increases with the increase of concentration as expected from Beer-Lambert law.

The results show that adding PMMA to R101 dye-oxide solution causes the spectra of absorption to be shifted to the longest wave length (red shift) compared with solution without PMMA, this is because of the increasing of perturbing effects between the molecules, as well as, the dimer formation (which results from accumulation of dye molecules).

The results are tabulated in table (1), where the peak absorbance wavelengths are given for R101 dye-oxide solutions in liquid phase (before adding PMMA polymer), and in solid phase (after adding PMMA polymer).

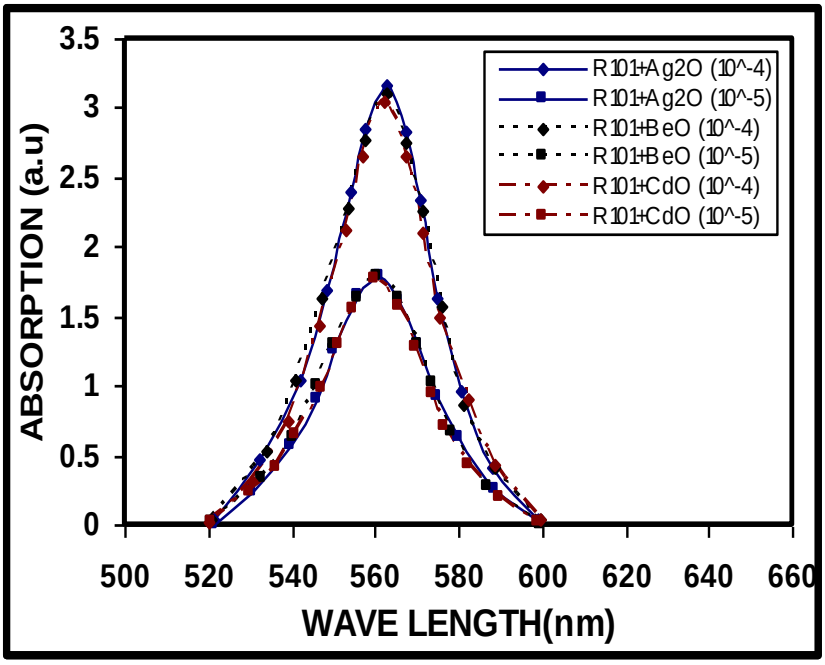

Figure (3) Absorption spectra of R101 dye with oxides [Ag_2O, BeO, and CdO] in methyl chloroform at different concentrations

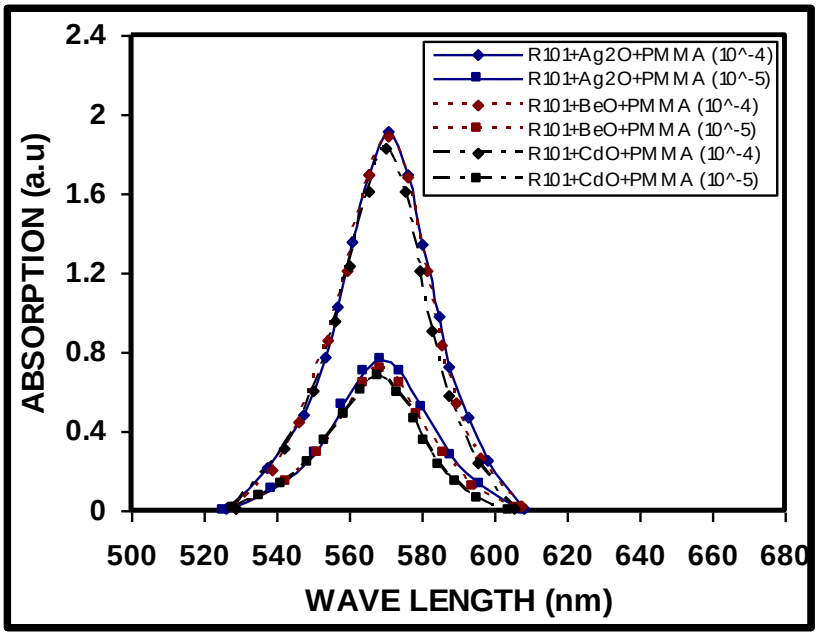

Figure (4) Absorption spectra of R101 dye with oxides [Ag_2O, BeO, and CdO] and polymer PMMA in methyl chloroform at different concentrations

Fluorescence Spectra of Dye-Oxide Solution

The fluorescence spectra of R101 dye-oxide mixtures dissolved in methyl chloroform are displayed in Fig (5) for 10^{-5} M and 10^{-4} M concentrations. The pumping power of laser used to excite the samples was 10 mW. It has been noticed that there was no shift of the peak fluorescence wavelength when the Ag_2O, BeO, and CdO oxides were used and there was an increase of the fluorescence intensity compared with oxide free solutions of R101 dye.

Fig. (6) shows the fluorescence spectra of R101 dye-oxide mixtures in PMMA polymer solid solutions. It was noticed that there was a decrease of the fluorescence intensity of the PMMA solid solution compared to that of liquid solutions. In addition to that there was a clear red shift of

the fluorescence spectra of PMMA solution compared to that of liquid solution. The results are listed in table (2) for comparison.

One can conclude from the fluorescence spectra that the fluorescence efficiency increases and the half width decreases of R101 dye-oxide liquid solutions compared to that of PMMA solid solution. Generally speaking the fluorescence intensity of liquid solutions was a bout as twice as that of PMMA solid solution. So, it is clarified here the reason behind adding oxides to R101 dye solutions, to act as strong scattering centers, which increase the inner reflections in R101 dye solution, hence increase the light path and number of absorbing molecules, and consequently increase number of emitted photons, hence the fluorescence in intensity will in crease.

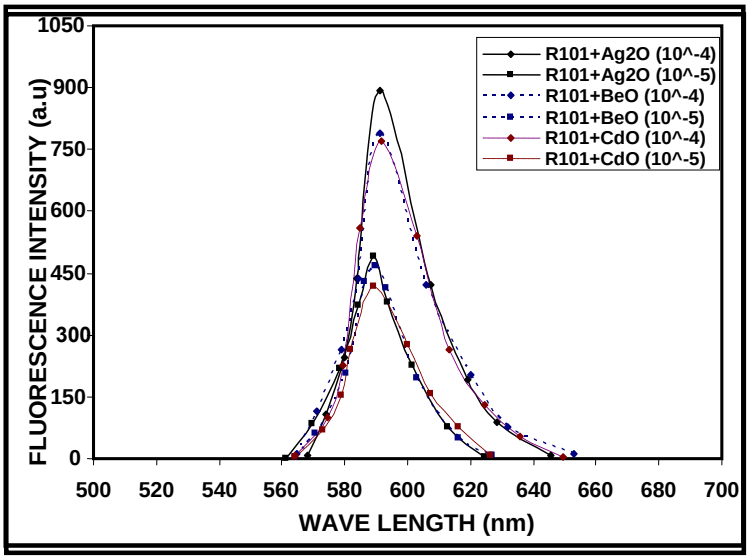

Figure (5) Fluorescence spectra of R101 dye with oxides [Ag_2O, BeO, and CdO] in methyl chloroform at different concentrations

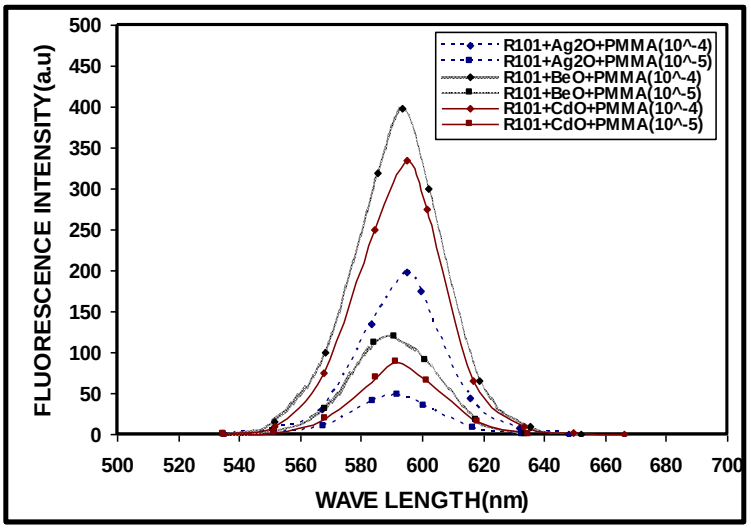

Figure (6) Fluorescence spectra of R101 dye with oxides [Ag_2O, BeO, and CdO] and polymer PMMA in methyl chloroform at different concentrations

Table (1) Peak of absorbance wavelengths for R101 dye-oxide solution, with out adding PMMA (liquid solution), and with adding PMMA (solid solution)

Oxides	Concentration (M)	peak absorbance wavelength (nm)	
		Liquid solution	Solid solution
Ag_2O	10^{-4}	562.9	569.5
	10^{-5}	560.8	567.6
BeO	10^{-4}	562.4	569.3
	10^{-5}	560.3	567.4
CdO	10^{-4}	562.2	569
	10^{-5}	560	567

Table (2) Peak of fluorescence wavelengths for R101 dye-oxide solution, with out adding PMMA (liquid solution), and with adding PMMA (solid solution)

Oxides	Concentration (M)	peak fluorescence wavelength (nm)	
		Liquid solution	Solid solution
Ag_2O	10^{-4}	591.4	595
	10^{-5}	589.2	591.2
BeO	10^{-4}	591.4	595
	10^{-5}	589.2	591.2
CdO	10^{-4}	591.4	595
	10^{-5}	589.2	591.2

Conclusions

The spectral characteristics of Rhodamine 101 dye- oxide solutions in the liquid and the solid polymer environment have been studied. The absorptivity of R 101 dye solution is increase by adding the metal oxides with blue shift compared to dye-oxide solution with PMMA (solid solution). Also, the adding of metal oxides leads to increase the efficiency of fluorescence spectrum of R 101 dye solution through the decreasing of the FWHM compared to dye-oxide solution with PMMA. Finally, the intensity of the fluorescence bands of dye-oxide solution with PMMA is decrease with time, because of the bleaching of dye molecules.

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