

REPORT DOCUMENT

AD-A254 566

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information, sending responses to the person to whom the collection of information should be addressed, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

Send all responses to the person to whom the collection of information should be addressed, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank) 2. REPORT DATE 29th Feb., 1992 3. REPORT TYPE AND DATES COVERED Final, 01 Sept. '90 to 31 Dec. '91

4. TITLE AND SUBTITLE
Laser densification and doping of sol-gel glasses

5. FUNDING NUMBERS
63224C 1693 06
2
6. AUTHOR(S)
TERENCE A. KING AEOsr-TR-3

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Manchester,
Oxford Road,
Manchester, U.K., M13 9PL

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR/NC
Building 410, Bolling AFB DC
20332 - 6448

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
AFOSR-90-0338

11. SUPPLEMENTARY NOTES

**DTIC
SELECTE
AUG 24 1992
S A D**

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release

12b. DISTRIBUTION CODE
Distribution is unlimited

13. ABSTRACT (Maximum 200 words)
An investigation into undoped and doped sol-gel glasses has been carried out for laser, optical and optoelectronic applications. Methods for the doping and characterization of sol-gel glasses have been developed. Lasers based on gel-silica glass doped with organic molecules and operating from the near UV to the near IR have been produced. The basic properties of the composite materials have been measured including dopant distribution, optical quality and photostability. Fundamental parameters and mechanisms for the doped systems of fluorescence lifetime, quantum efficiency and uniformity have been investigated. Controlled densification of the sol-gel glass to give increased refractive index has been demonstrated. This enables the writing of optical waveguides in bulk and thin films which open up many applications in optoelectronics and the surface densification of sol-gel glass for lightweight optics. New methods of densification of photosensitised sol-gel glass to give high spatial resolution micron size waveguides is described. Applications for the types of systems resulting from this work are reviewed and areas of future development described.

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT
UL
SAR

FINAL REPORT

Title: LASER DENSIFICATION AND DOPING OF SOL-GEL GLASSES

Principal Investigator: Professor Terence A. King

Contractor: University of Manchester

Contract Number: AFOSR - 90 - 0338

Report Period: 01 September '90 to 31 December '91

92 8 21 053

**T. A. King,
Physics Department,
Schuster Laboratory,
Manchester University,
Manchester. M13 9PL**

February 1992

92-23380



425411 SIP-8

CONTENTS

1. ABSTRACT
2. PROGRAMME ACHIEVEMENTS
 - 2.1 Sol-Gel Glass Lasers
 - 2.2 Laser Enhanced Densification
 - 2.3 Optical Properties of Undoped and Doped Sol-Gel Glasses
3. BACKGROUND
4. DOPED SOL-GEL GLASS LASERS
 - 4.1 Results
5. LASER ENHANCED DENSIFICATION OF SOL-GEL GLASSES
 - 5.1 Results
6. OPTICAL PROPERTIES OF DOPED SOL-GEL GLASSES
7. APPLICATIONS OF SOL-GEL GLASSES
8. REFERENCES

DTIC QUALITY COLLECTED 5

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Availability Codes
A-1	

ABSTRACT

An investigation into undoped and doped sol-gel glasses has been carried out for laser, optical and optoelectronic applications. Methods for the doping and characterization of sol-gel glasses have been developed. Lasers based on gel-silica glass doped with organic molecules and operating from the near UV to the near IR have been produced. The basic properties of the composite materials have been measured including dopant distribution, optical quality and photostability. Fundamental parameters and mechanisms for the doped systems of fluorescence lifetime, quantum efficiency and uniformity have been investigated. Controlled densification of the sol-gel glass to give increased refractive index has been demonstrated. This enables the writing of optical waveguides in bulk and thin films which opens up many applications in optoelectronics and the surface densification of sol-gel glass for lightweight optics. New methods of densification of photosensitised sol-gel glass to give high spatial resolution micron size waveguides is described. Applications for the types of systems resulting from this work are reviewed and areas of future development described.

2. PROGRAMME ACHIEVEMENTS

2.1 Sol-Gel Glass Lasers

This part of the programme demonstrated the following:

- (a) New tunable solid state lasers using organic dopants with laser wavelengths from the near UV to the near IR. Feasible laser action with inorganic ion dopants in the near IR.
- (b) Stable narrow linewidth outputs (100MHz) from pulsed sol-gel lasers in compact grazing incidence and distributed feedback laser cavities.
- (c) Enhancement of organic dopant operating lifetime when used in the sol-gel matrix.
- (d) Optimisation of doping methods to dope organic molecules into the porous sol-gel matrix. Doping is carried out on prepared sol-gel glass substrates using vacuum and controlled atmosphere conditions and with selection of sample temperature and time of the process.

2.2 Laser Enhanced Densification

In the programme it was demonstrated that controlled laser heating of the partially densified porous sol-gel glass matrix could achieve further densification. The increase in density also produces an increase in refractive index with increments in refractive index of up to 0.1 able to be laser written.

A summary of some of the achievements in this part of the programme includes the following aspects.

- (a) Production of permanent laser written waveguides in sol-gel glass substrates.
- (b) Laser writing of waveguides with long wavelength 10.6 μm carbon dioxide laser beams (waveguide width $\sim 100\mu\text{m}$) and with short wavelength 0.488 μm argon ion laser (waveguide width $\sim 2\mu\text{m}$) in sensitised sol-gel glass.
- (c) Determination of conditions for laser enhanced densification and threshold limits for the onset of laser damage to the substrate glass.

- (d) Characterisation of the laser densified material using microhardness, refractive index, and Raman spectroscopic techniques. New techniques for characterisation were developed based on reflection and ellipsometry.

2.3 Optical Properties of Undoped and Doped Sol-Gel Glass

With undoped glasses the programme achieved progress in the following:

- (a) Using light scattering and light transmission measurements demonstrated the dependence of optical quality on material preparation conditions.
- (b) Determined the parameters of the porous sol-gel glass influencing doping characteristics.
- (c) Initial demonstration of reduction in optical loss in sol-gel with active dopant and an index-matching third component. This involves the use of monomer impregnation followed by in-situ polymerisation to produce a composite material with minimal free volume.

A programme on the doping of sol-gel glass has been carried out and included the following achievements:

- (a) Effective doping with organic molecules.
- (b) Measurement of fluorescence lifetime and absorption and emission spectral features indicating modification of the radiative properties of the doped material when in the sol-gel glass. Demonstration of reduced non-radiative quenching and increased fluorescent lifetimes using picosecond lifetime measurements.
- (c) Enhancement of the photostability of organic molecules doped into sol-gel glass and the setting up of quantitative methods to determine photostability.

3. BACKGROUND

The existing proposal was formed by amalgamation of two proposals:

- (a) Laser densification of sol-gel glasses and,
- (b) Doped gel-silica glass lasers.

These proposals were funded as a single project under a combined title ref. AFOSR-90-0338, "Laser Densification and Doping of Sol-Gel Glasses". An extension formed an interim contract for the period 1 September to 31 December 1991. The existing contract (AFOSR-90-0338) was originally arranged for three years - 1 September 1990 - 31 August 1993.

The principal investigator had pursued a programme on "A Tunable Solid State Glass Laser" over the period from October 1987 to September 1990 funded within the US-UK research programme on advanced silica optics systems, contract F49620-88-C-0010. This project was conducted in association with the sol-gel silica optics research of Professor L. Hench in the Advanced Materials Research Center (AMRC) of the University of Florida and the GELTECH Inc. SDI-ISTO AFOSR funded programme.

The programme in the four-month period was to investigate tunable sol-gel lasers in new wavelength regions in the blue and near IR and to determine quantitative measurements and mechanisms of photostability important to long life sol-gel lasers. The dependence of laser densification on initial starting conditions of the glass for high stabilization temperatures and on the laser irradiation conditions were to be determined. Laser densification of sol-gel thin films for the fabrication of single mode waveguides or substrates could be developed from this investigation.

The ability to dope ultra high purity sol-gel derived silica hosts with controlled concentrations of a lasing element offers the possibility of the development of new solid state laser sources. When doped with organic molecules these could have good tunability over 50nm for each dopant and more limited but useful tunability for inorganic dopants common to glass lasers. These lasers would gain advantage from

the superior physical properties characteristic of gel-silica and the ease of manufacture and convenience in use common to glass lasers.

Within the previous programme laser action using organic molecule doping in gel-silica had been produced. Initial results showed that the system had great promise as a solid state medium giving tunable laser output. The medium gave evidence of being more photostable than that of lasers using organic molecules in solution. A programme was set out which included fundamental and applied topics in the investigation of (i) the adsorption and doping characteristics of organic molecule dopants into gel-silica. (ii) the laser characteristics of selected molecules doped into gel-silica, (iii) variation of doping characteristics with physical features of the gel-silica including pore size and distribution, and (iv) laser configurations and excitation methods. The previous study of inorganic doping of Nd ions with Al as a dispersant into the gel-silica matrix, could be extended into laser action in Nd/Al gel-silica. The use of co-doping could provide an energy transfer route and methods to reduce phonon quenching required to be determined.

This work offers the potential to realise solid state lasers tunable through the visible region and into the near UV and near IR, aided by the excellent optical transmission properties of gel-silica. Following on from this study advanced laser systems are considered which include compact high repetition rate lasers and high energy single pulse systems.

3.1 Organic Molecule Doped Gel-Silica as a Laser Medium

Laser action in organic molecules forms an important class of lasers since they give relatively wide tunability throughout the visible spectrum and into the near UV and near IR. Solutions of organic dyes for lasers are used extensively, although little work has been carried out on solid host media. The host medium can strongly influence the thermodynamic, spectroscopic and kinetic properties of the dye molecules. Particular features are thermal stability, absorption and emission spectral profiles and quenching mechanisms of the laser states. The solid gel-silica matrix holds promise for reduction of thermal degradation and impurity and molecule-molecule

concentration quenching, while also providing convenience in handling. There are a number of applications of the tunable organic dye laser where a solid medium would be advantageous.

Two methods of doping the gel-silica with organic molecules have been considered. In the sol-to-gel doping method hydrolysis and condensation of $\text{Si}(\text{OMe})_4$ incorporating the organic dye produces a gel which is dried to remove water and methanol. This method leads to a laser medium with the organic dye uniformly distributed through the gel-silica. It gives a reduction in intermolecular collisional quenching through reduction in concentration quenching, in quenching by photodecomposition products or impurities, reduced dimerization or aggregation and collisional self-quenching and an absence of migration of quenching molecules and impurities. Since the organic molecule is in a matrix cage they are isolated from organic solvents. This should give higher quantum yields of fluorescence. The greater thermal conductivity of glass over solvents maintains a more uniform temperature distribution throughout the active medium. Consequently there is reduced thermal lensing and laser-induced medium perturbations. The greater rate of removal of excess heat enables higher laser powers to be achieved. This method is also able to use higher dye concentrations leading to greater design flexibility and giving more compact and efficient laser cavities. There is a restriction in this method in the degree of densification of the gel-silica, this is set by the thermal stability of the organic molecules, such that the gel-silica is required to be almost undensified. A consequence of the low temperature densified glass is that it can only be dry polished. This type of gel-glass is also susceptible to fracturing and cracking when exposed to fluids or low temperature cycles.

The second method of doping the gel-silica has been investigated, termed adsorption doping, in which undoped gel glass densified to an intermediate temperature is immersed in a solution of the organic molecule. The organic molecules fill the pores in the glass and the sample is dried under carefully controlled conditions to prevent cracking. The molecules are then deposited on the walls of the pores. In

this method the gel glass can be almost fully densified and still adsorb the organic molecules, such that the samples have higher quality and can be machined and polished for laser fabrication. Trapping of the organic molecules in the pores, which are of typical nanometer dimensions, still allows some migration of impurities and may give a greater degree of quenching compared with the sol-to-gel doping method.

The glass matrix host provides a more stable medium thermally and chemically than the solution medium. Molecular migration through the medium is inhibited. There is an improvement in the optical quality of the medium and in the power handling capability. Increased concentrations of organic molecules can be used. An increase in the absorption-emission Stokes shift reduces molecular self-absorption and increases fluorescence efficiency.

Laser action had been observed in gel-silica glass doped with rhodamine 6G. The laser was excited by 248nm radiation from an excimer laser or by 507nm radiation from a flashlamp excited dye laser. A wide range of measurements on these systems included laser linewidths, pulse profiles and spectral lineshapes. There are several excitation geometries that can be used including transverse and longitudinal configurations. The projected improved photostability of the organic molecule doped gel-silica had been indicated in the initial samples studied.

3.2 Inorganic Doped Gel-Silica as a Laser Medium

Investigations in the previous research had been on Nd-doping into the gel-silica matrix. A wide range of physical characteristics were investigated which included absorption and emission spectra, fluorescent lifetimes, TEM and SEM measurements studying dopant dispersion through the medium and measurements of optical quality. Several sets of apparatus to determine these characteristics had been built up.

Gelsil samples doped with Nd over 0.5 to 5.0wt % showed relatively low emission efficiency and short fluorescent lifetimes ($< 10\mu\text{s}$), while the bandwidth was sufficiently broad to indicate scope for tunability. The TEM measurements showed that clustering of Nd was occurring and SEM-EDAX data indicated that all the Nd

was in clumps. When similar samples were co-doped with Nd and Al (in typical ratio Al/Nd > 4.5) longer excited state lifetimes ($\tau > 100\mu\text{s}$) and higher emission efficiency was observed. The TEM and SEM-EDAX measurements indicated that the Nd was uniformly distributed and that the co-doping had successfully produced regular dispersion of the active Nd. However the excited state lifetimes were still shorter than in phosphate or silicate glass giving evidence for a quenching mechanism being present. Absorption, FTIR and Raman spectroscopy showed that the samples had residual OH present to which the phonon quenching is attributed.

The previous work had shown that Nd-doped samples of gel-silica can be prepared which are uniform in the distribution of Nd. The results on excited states lifetimes and absorption and emission spectroscopy indicated that the kinetics of the populations of the laser levels can be regulated to allow laser action. Further work on the dehydration and densification methods is required to modify the excited states kinetics to allow laser action to take place.

3.3 Proposed Study of Sol-Gel Glass Lasers

The successful observation of laser action in organic molecule doping of gel-silica required to be fully investigated to understand the underlying physics and to determine the performance potential of the systems. Emphasis was given to organic doping in the programme over inorganic doping.

The following investigations were proposed.

- (i) A study to be made of the physical characteristics of a range of organic molecules doped into gel-silica, selected for their potential for laser studies. These include rhodamines, sulforhodamines, coumarins, oxanines and scintillator dyes. These have emission spectra from the UV through the visible to the near IR. This study could include spectral and kinetic measurements for doped gel-silica and comparison with solution data. Minimising photodegradation of the organic molecule is important for long life operation and a special study could be made to determine conditions under which this can be reduced.

- (ii) The nature of the molecular adsorption within the pores and the distribution of the organic molecules through the gel-silica medium was to be studied. Adsorption conformations could be studied by spectroscopy and NMR. The avoidance of clustering is important since this can affect quenching rates and also thermal properties.
- (iii) Methods of doping of organic molecules into the gel-silica require study. This work could include the sol-to-gel and adsorption doping methods, and methods to prevent sample cracking due to induced strain in the up-take and removal of solvent. The release of strain by controlled evaporation and low temperature annealing could be investigated.
- (iv) Adsorption doping into gel-silica matrices densified to various temperatures could be studied to determine the spectral, kinetic and laser properties with variation of pore sizes and distribution. Techniques for the polishing of samples with large pore fraction could be developed so that samples densified to low temperature could be explored for laser action. The role of pore size and laser properties requires investigation.
- (v) Excitation configurations can be compared for laser performance, thermal stability, molecular degradation and convenience in operation. The dependence of performance on the excitation method requires investigation. A variety of sources can be used including flashlamps and different types of lasers (doubled YAG, excimer, flashlamp dye and other solid state). With the present progress in semi-conductor diode lasers taking place consideration can be given to laser diode pumping of small structures by diode arrays to produce an all-solid-state (holosteric) laser. Various gel-silica geometries such as slab and rod can be studied. Excitation by diode pumped Nd:YAG at \sim kHz could give quasi-CW (50ns pulses to 10 - 10,000Hz) more easily than conventional CW argon ion pumping. With multi-flashlamp excitation in miniature laser cavities an extremely compact laser may be feasible which is operating at high repetition rates.

- (vi) Hermetic sealing of the gel-silica discs could be carried out to determine if an effective means of isolating the medium from the atmosphere can be devised. This would counter any tendency to take up moisture from the atmosphere. This also enables direct water-cooling of the gel-silica medium.
- (vii) Phonon quenching has been identified as a non-radiative loss mechanism in inorganic doped gel-silica. It is possible to investigate methods of removing OH contamination by chemical substitution. One route is the use of trimethylchlorosilane to substitute Me_3Si for hydrogen on the pore surface.

The use of energy transfer in a co-doped inorganic system such as Cr-Nd-gel-glass is of interest. These systems hold promise for a better match to excitation lamps, greater efficiency from the energy transfer mechanism and the improved thermal stability through reduced thermal loading on the medium.

The systems based on Nd with Al and P co-dopants to aid the dispersion of Nd could be investigated with variation of the Nd/Al or P ratio, and include studies of other dopants such as rare earths, Er and Ho, and Ti.

3.4 Laser Enhanced Densification

The objectives of the earlier research contract over the period from October 1987 to September 1990 had been

- (i) The investigation of the interaction of laser radiation with sol-gel glass.
- (ii) The study of the structure and properties of sol-gel glass densified by laser radiation.
- (iii) The study of aspects of the feasibility of laser-induced densification in the production of specialist optics.

Notable progress along those lines had been made. It had been shown that controlled densification of sol-gel glass is feasible with $10.6\mu\text{m}$ continuous wave carbon dioxide laser radiation. Lasers at other wavelengths had been used to investigate the densification. The thresholds for permanent (rather than transient) densification had been determined to be in the region of 4.5Jcm^{-2} . With increase in

laser fluence the thresholds for damage to the surface of sol-gel had also been determined. Theoretical models had been set up to describe these processes.

Methods had been built up to characterise the densified sol-gel glass. Reflectance methods to determine refractive index had been constructed. This is relevant to future studies in the characterisation of laser densified waveguides and laser-written tracks. The techniques of microhardness and microprobe Raman spectroscopy had been adapted to the characterisation of the densified medium.

It had been demonstrated that it was possible to write permanent tracks of densified material onto surfaces of partially dense sol-gel glass. Track widths to 100 μ m had been written and characterised in refractive index profile and with Raman and microhardness measurements. Initial studies of graded-index profiling with laser beams with a controlled transverse intensity profile had been carried out; this had included Gaussian beam profiles. The writing of waveguides with short wavelength UV radiation at 193nm from an excimer laser had been explored. This offers the possibility of writing waveguides only a few microns in width compatible with single mode laser beam propagation.

Initial studies had been made on large area surface densification using scanned laser beams. Provided the beam fluence is greater than the densification threshold area densification of sol-gel surfaces is feasible. With the application of these techniques the preparation of large area optical surfaces densified and with a defined refractive index could become possible. Thus a range of optical elements, including surface polishable components such as lightweight mirrors and holographic optical elements, would be feasible.

3.5 Proposed Study of Laser Enhanced Densification

The objectives of this programme were (i) to develop a thorough understanding of the process of laser densification of sol-gel matrices, extending from the initial theoretical model begun in the earlier contract, (ii) to establish practical methods of laser densification, both for narrow waveguide and large area surfaces, (iii) to characterise the physical, and particularly optical, properties of the laser densified

structures, and (iv) to explore the fabrication of selected optical elements using the data and methods developed within the programme.

The present model for the interaction of laser radiation was required to be extended from 1-D and 2-D to a 3-D form. The time characteristics of the laser irradiation could be included to allow for continuous (steady state) and pulsed (transient) modes. The optical and thermal characteristics for variation of the laser wavelength could be accounted for in order to model the changes in radiation condition. Within the model calculations on depth and transverse profiling could be developed, this is relevant to the formation of single mode waveguides.

The primary mechanism for heat deposition in the glass is by laser heating and secondary thermal heating via OH absorption. Hydrogen bonded water is removed by heating at low temperature while laser heating is able to remove OH groups. OH groups are also removed in the form of water by the condensation polymerisation, $\text{Si-OH} + \text{Si-OH} \rightarrow \text{Si-O-Si} + \text{H}_2\text{O}$. This work aimed to determine relations between dehydration and densification and relate the dehydration energy to the OH concentration. Spectroscopic methods were to be used to monitor OH concentrations at varying stages of laser densification. The detailed microscopic mechanisms occurring below and through the densification threshold could be considered.

The laser sources which have been used for densification had been the continuous wave carbon dioxide laser (10.6 μm), the excimer laser (193nm) and the erbium solid state laser (2.94 μm). Further laser sources at different wavelengths could be used to give a variation in the absorption, and hence densification, depth. Comparison of pulsed and continuous radiation indicates differences in the densification profile, this could be quantified. With short wavelength laser radiation the role of photoablative affects could be determined.

The studies in densification can be characterised using a range of physical measurements. The reflectance refractive index refractometer developed within the previous contract could be used for both microscopic and macroscopic measurement of waveguide tracks and surfaces and could be used in conjunction with microhardness

studies. Spectroscopic methods of FTIR and Raman techniques can be used to give structural detail.

The laser writing of waveguides with controlled refractive index profiles can be quantified. The optical attenuation and optical quality of the tracks could be determined, as this is important for device application. The use of laser beams of various beam profiles, such as Gaussian, super-Gaussian and top-hat can be used directly to control the refractive index profile. Writing waveguides down to single mode dimensions can be considered and these tested for propagation characteristics. Methods to determine depth profiles by prism coupling into waveguides modes and the use of a Moire reflectometer can be adopted in these studies.

The techniques developed can be used to evaluate their application in the fabrication of selected optical elements. These include surface densified components, lenses and GRIN lenses and interconnected waveguide meshes. Densification of doped gel-silica laser material can be developed to aid optical polishing to high quality surfaces in the associated gel-silica laser programme.

The objectives in this proposal are (i) to further the understanding of the underlying science of laser densification, (ii) to develop practical laser densification methods, (iii) to characterise surface and waveguide laser densified media, and (iv) to evaluate these methods for the fabrication of optical elements. The successful outcome of this work will be methods to control the density, optical properties such as refractive index and physical properties such as microhardness. The microscopic mechanism of laser heating through absorption and associated with dehydration and removal of OH groups is related to pore collapse and densification, these aspects can be explored. The technical feasibility could be investigated for densification of extended surface areas, profiled multimode and single mode waveguides and selected optical elements including mirror substrates, lenses, GRIN lenses and waveguide arrays.

4. DOPED SOL-GEL GLASS LASERS

Investigations on this contract from 1 September 1990 have been in several areas. Emphasis had been placed on organic dopants rather than inorganic dopants. Attention was paid in the first year's work to determining data for the following studies on lasers and specialist laser systems. An overview of the research is shown in Figure 1.

- (i) Measurements on the radiative properties of sol-gel glasses doped with selected organic molecules have been made and compared with the molecules in solution. Fluorescence lifetimes, quantum efficiencies and absorption and emission spectroscopy measurements were made to provide design data for laser systems.
- (ii) The photostability of organic molecules in the sol-gel glass host is important in determining the lifetime of the sol-gel glass laser. A quantitative measure for molecular degradation was set up since data in the literature and from other groups is not able to be intercompared because of the variety and undocumented nature of the information. A range of dopants including rhodamine 6G, rhodamine B, sulphorhodamine were measured.
- (iii) The tuning characteristics of the sol-gel laser doped with organic molecules, particularly rhodamine 6G, have been measured in a grazing incidence cavity. A wide tuning range similar to solution lasers has been found.
- (iv) The initial design of a sol-gel glass laser based on phenyl-biphenyl-oxadiazole (PBD) dye has been made in order to produce a short wavelength laser.
- (v) The nature of the molecular absorption within the pores was studied by fast subnanosecond excitation and fluorescent lifetime measurements. Some notable differences have been found in the fluorescent lifetime or linewidth for rhodamine 6G and methylene blue.
- (vi) Two large pore samples of sol-gel glass were investigated having a mean pore radius of 5nm compared with 1.2nm of earlier samples. A comparison of

GEL-SILICA LASERS AND OPTICS

Active medium : Gel silica with organic molecule/inorganic ion-polymer composite

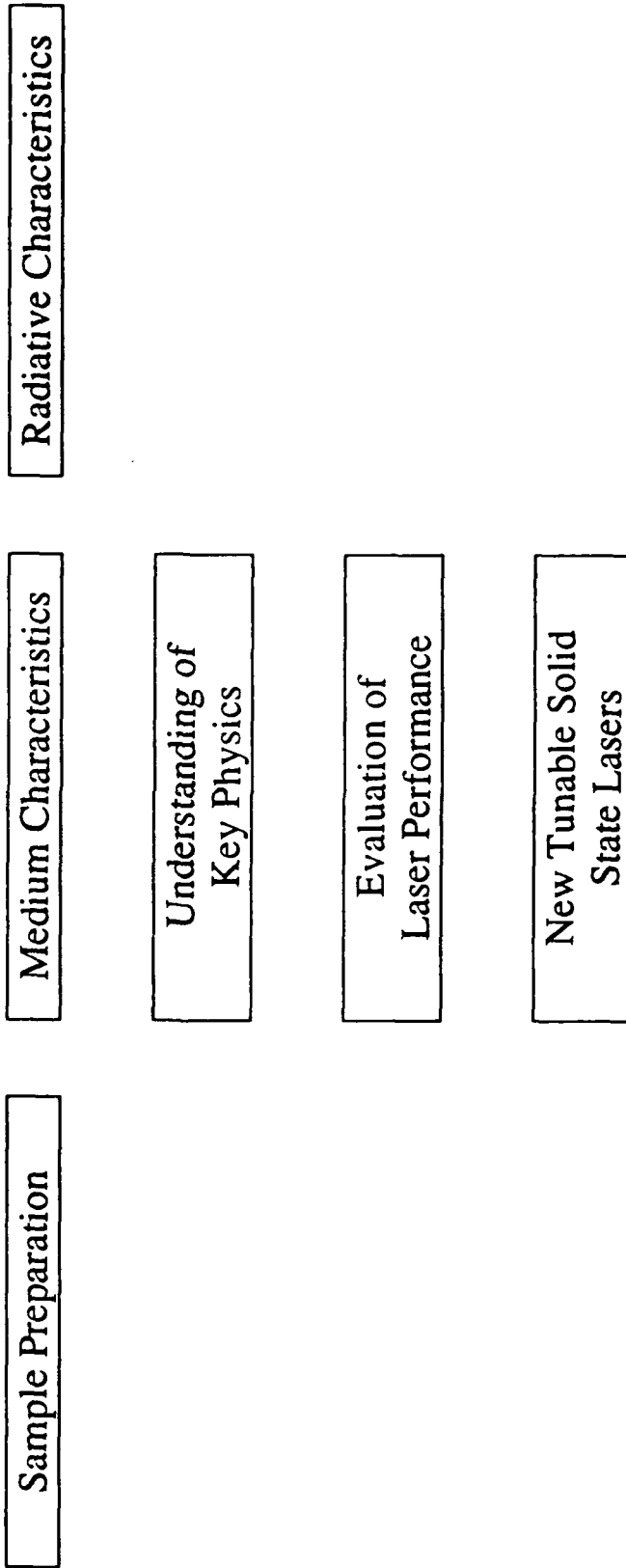


Figure 1

doping conditions, radiative and laser properties were made to compare with the small pore size samples.

- (vii) The assessment of tunable sol-gel glass lasers in various wavelength regions has been continued. In particular the short wavelength blue laser and longer wavelength 700-800nm region have been investigated. The range of laser parameters including operating wavelength range and tunability, efficiency and lifetime of the laser have been determined.

Quantitative data on photostability of the organic molecules has been derived. There are various factors which affect the dye molecule lifetime and which may be specific to classes of molecule. These factors have been explored and the implication for practical doped sol-gel glass laser systems.

4.1 Results - Gel-Silica Lasers

Work in this area has concentrated on the requirement to develop new and more practical gel-silica laser devices including improved performance from doped sol-gel lasers in various cavity configurations (Figure 2). The production of polymer and active dye gel-silica composites by a post doping method offers several potential advantages over the conventional ORMOSIL preparative methods, and should significantly enhance the basic mechanical and optical properties of undensified gel-silica.

The wavelength range of doped gel-silica lasers has been extended significantly in this project from 360nm using phenyl-biphenyl-oxadiazole (PBD) dye to 639nm with sulforhodamine 640 (Figure 3). The pump laser used was a Nd:YAG with harmonic generator assembly giving outputs of 20mJ per pulse at 255nm, and 200mJ per pulse at 532nm. In both cases the gel-silica block of dimensions 5x5x20mm was placed in a simple laser cavity consisting of a high reflector and output coupler of approximately 50% reflectivity. The output of the Nd:YAG laser was focused by a 20cm focal length cylindrical lens to a strip approximately 300 μ m wide at the surface of the gel-silica thereby producing a transversely pumped laser. Using pump energies of up to 5mJ per pulse, output efficiencies were ~ 1% (PBD) and ~ 5%

Gel-Silica Laser Developments

1. New Dyes
 - Phenyl-biphenyl-oxadiazole (P.B.D.)
 - Sulforhodamine 640

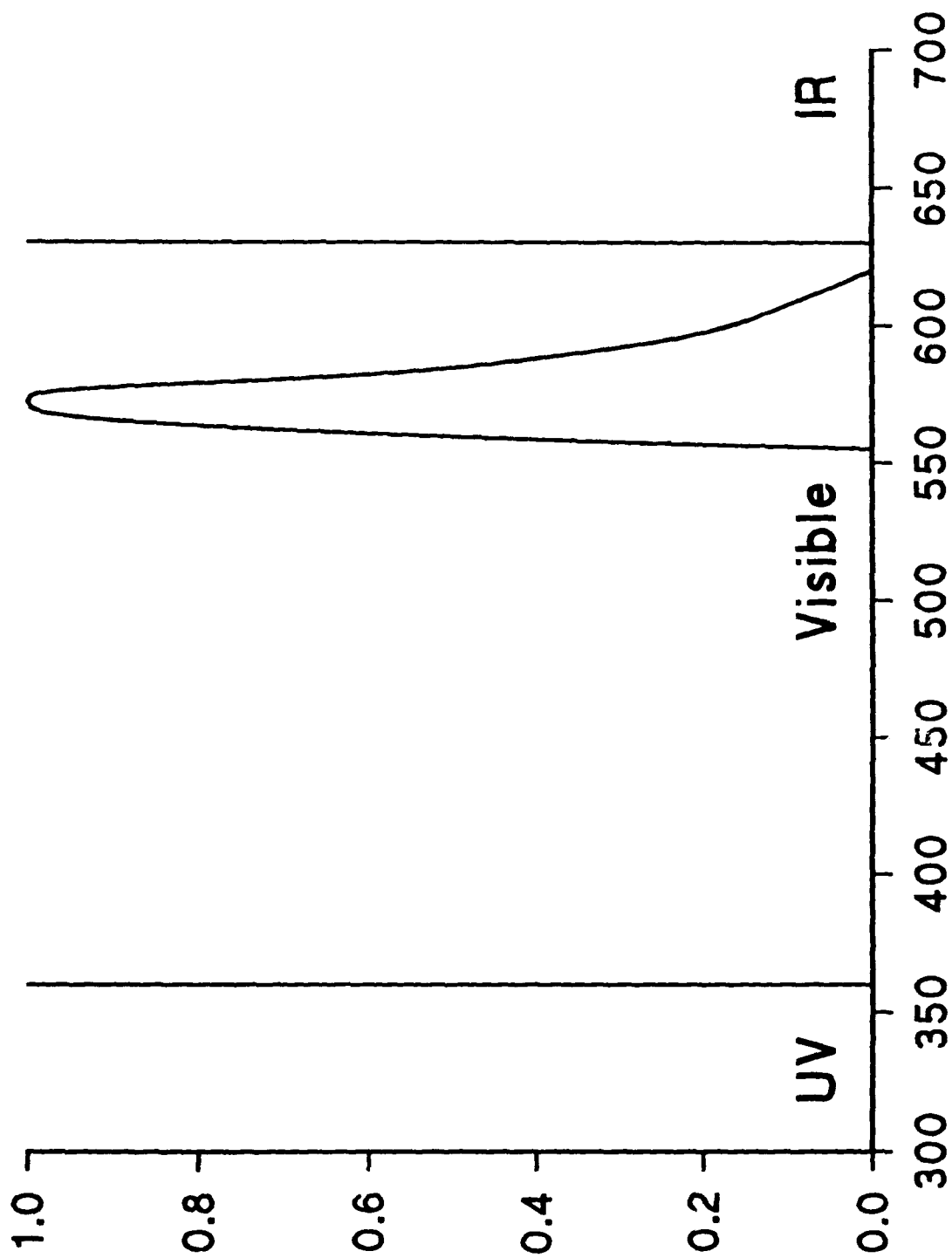
2. New Cavity Configurations
 - Littrow grating
 - Grazing incidence grating
 - Distributed Feedback

3. Determination of Dopant Distribution in Gel-Silica

4. Thin Film Doping

5. Doped Gel-Silica compared with doped ORMOSIL

PBD R6G Sulforhodamine 640



Wavelength (nm)

Gel-Silica Laser Development

Figure 3

(sulforhodamine), with significant shot to shot fluctuations and relatively poor photostability (< 500 shots). These results are preliminary and should be improved significantly by optimisation of the laser parameters.

Extensive work has been carried out on rhodamine 6G doped gel-silica including tuning operation, narrow linewidth performance, and photostability studies involving comparison with doped ORMOSIL samples. Using a Littrow mounted grating cavity and a frequency doubled Nd:YAG pump laser, the R6G doped (1×10^{-4} M) gel-silica laser was tuned from 560nm-620nm (Figure 3) with a maximum efficiency of 16% and a linewidth of 3nm.

In order to produce narrow linewidth performance another R6G doped sample (2×10^{-5} M) was placed in a Littman grazing incidence cavity designed for single mode operation and longitudinally pumped by the frequency doubled Nd:YAG laser. Although output efficiency was reduced significantly, the resulting linewidth was measured to be <0.05nm, a considerable improvement over the Littrow cavity result.

Dye photostability was measured by placing the doped gel-silica and ORMOSIL samples in a plane cavity consisting of high reflector and output coupler (R=80%), pumping the laser transversely with a frequency doubled Nd:YAG laser, and monitoring the laser output. The results for post-doped gel-silica (R6G) with and without the use of water as index matching fluid, ORMOSIL (R6G and RB) and a solution of R6G in methanol (all 1×10^{-4} M) are presented in Figures 4 and 5.

The apparent high photostability of the dye in solution is due to the large volume of the solution compared to the volume actually pumped (a factor of approximately 5000), and the mobility of dye molecules within the solution. From these results it is clear that index matched post-doped gel-silica compares favourably with the ORMOSIL host, giving similar peak efficiencies and greatly increased photostability of approximately 20,000 shots at a pump energy of 3mJ per pulse. This corresponds to a total input energy of 60J in a volume of approximately 0.5mm^3 or 120kJ/cm^3 compared to 10kJ/cm^3 for the R6G doped ORMOSIL sample (Figure 6). This result, together with the greater flexibility of the post-doping method and the

Laser Output versus Number of Shots

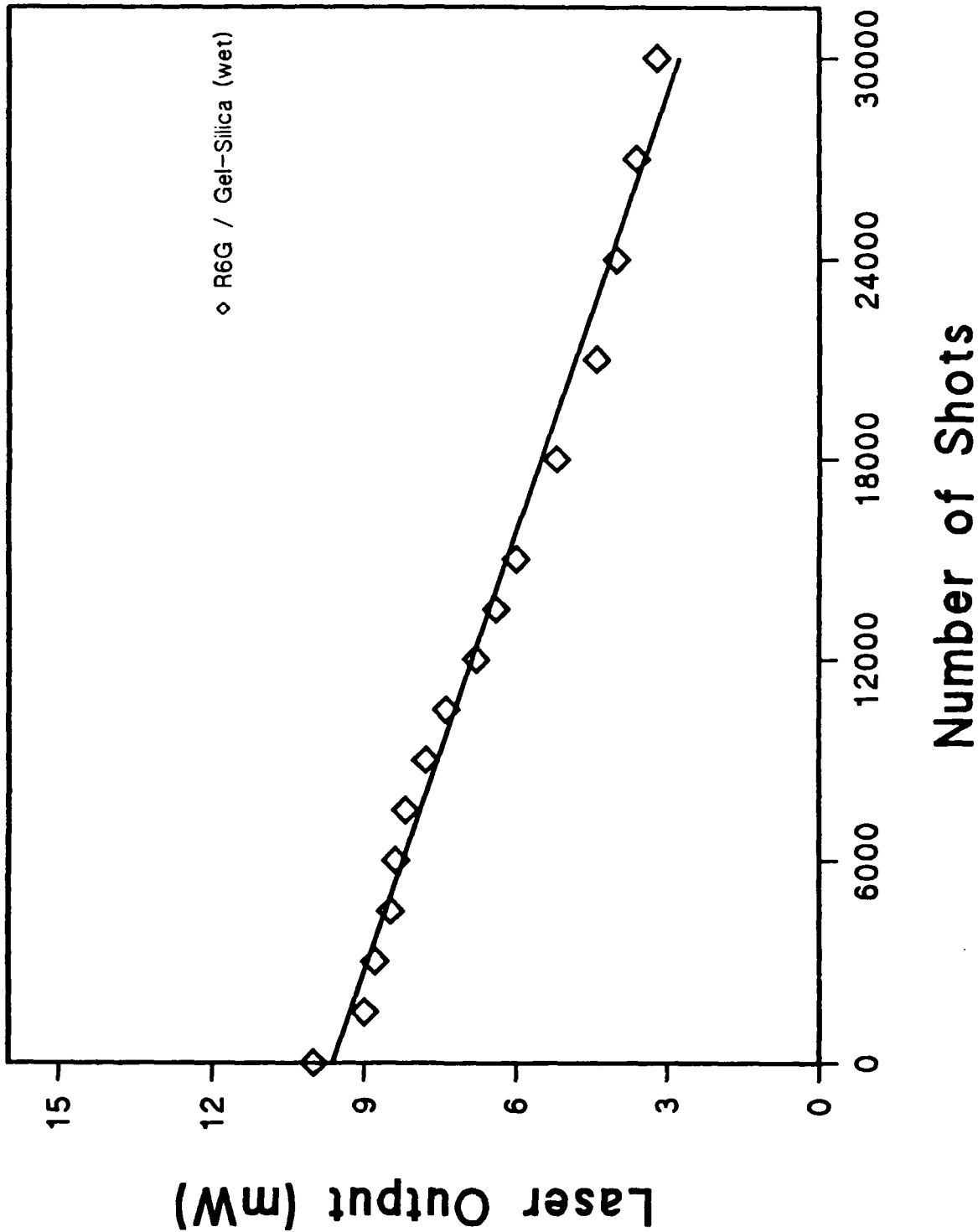


Figure 4

Laser Output versus Number of Shots

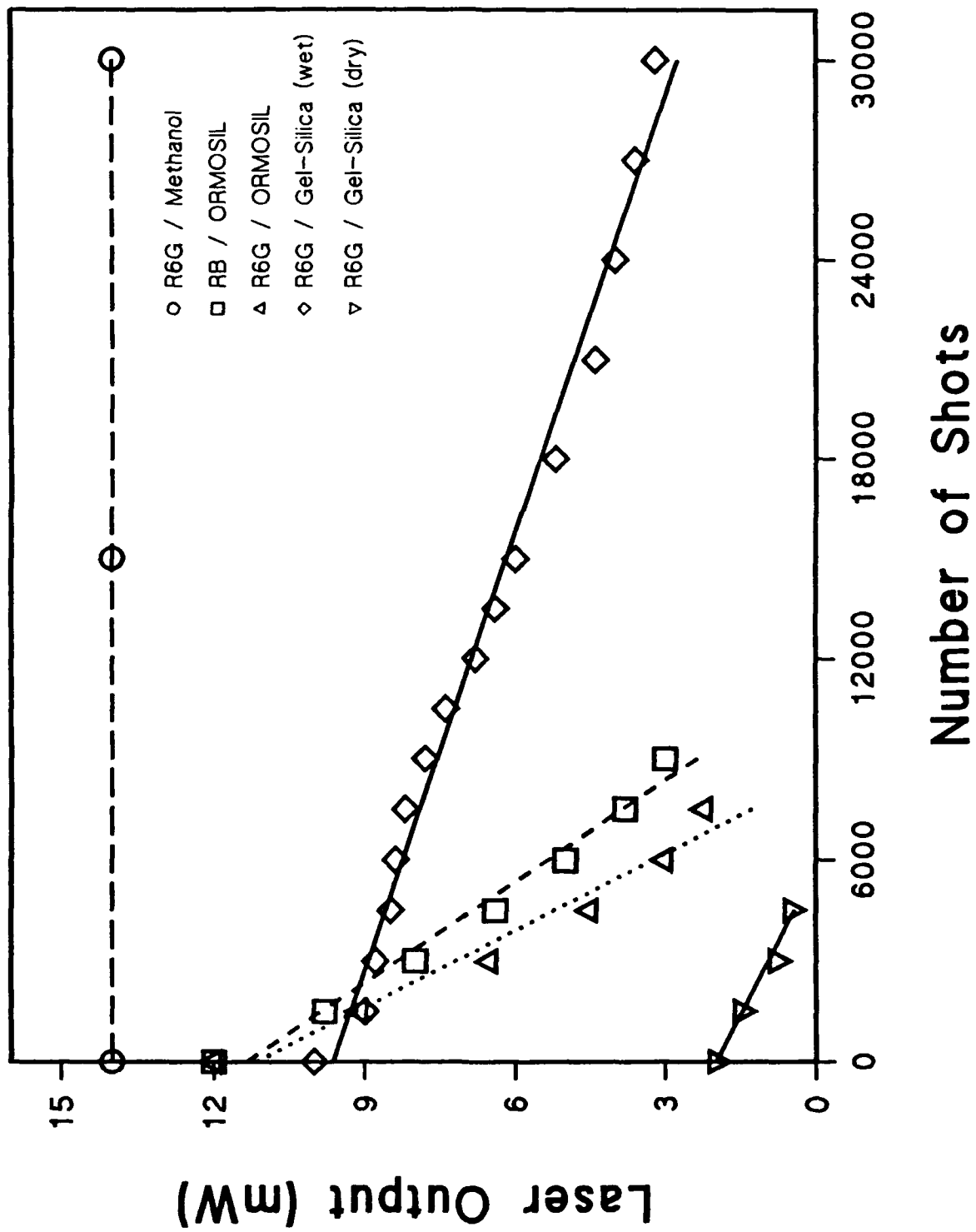


Figure 5

Comparison with ORMOSIL

	ORMOSIL	Gel-Silica (Index matched)
Dopant	1×10^{-4} R6G	1×10^{-4} R6G
Initial efficiency	40%	33%
No. of Shots	3200	19500
Volume (mm ³)	0.9	0.45
Energy Out (Jmm ⁻³)	4.2	43.3

possibility of including polymer index matching after the dopant has been introduced, highlights the advantages and potential offered by the post-doping method.

The results for the gel-silica lasers are summarised in Figure 7.

Another aspect of post-doping which has been studied is the distribution of dopant within the gel-silica sample and the dependence of the distribution on dopant size, doping conditions and gel-silica pore size (Figure 8). These aspects have been investigated using a fluorescence imaging technique to probe the dye concentration obtained within a gel-silica sample. The method involves the use of an argon ion laser ($\lambda=488\text{nm}$) as an excitation source and a scanning photodiode to detect the fluorescence as a function of position within the sample (Figure 9). This technique allows concentrations of up to 5×10^{-4} M R6G to be determined, as well as displaying the distribution of less concentrated samples. Using a solution of 2×10^{-4} M R6G in methanol and a standard 2.5nm pore size gel-silica sample it can be seen that the dye remains confined within 250 μm of the edge of the sample even after several days immersion in solution. In contrast, the results for a large pore size sample (4nm diameter) after 15 minutes and 7 hours immersion are presented in Figure 10. This clearly shows the slow time dependence of the diffusion process into the sample, despite the fact that the solvent penetrates to the centre in a matter of minutes. The importance of relative pore size and dopant size, the choice of solvent, the processing of the gel-silica and the possibility of tailoring dopant distributions to meet specific requirements and applications are still under investigation.

Gel-Silica Lasers

Summary

1. Lasers based on new dyes demonstrated with emission from ultraviolet to red.

- many other dye dopants possible
- properties can be inferred from solution data
- post doped dye / polymer composites are possible

2. New laser configurations

Grating cavities in grazing incidence (Littman) or Littrow configurations have produced efficient, tunable, and stable output.

- distributed feedback, slabs, rods and waveguide geometries being evaluated

3. Dopant distribution in gel-silica

Uniform distributions have been obtained and dependence on diffusion dynamics demonstrated.

- tailored dopant distributions realisable

Gel-Silica Lasers

Summary (cont)

4. Doped gel-silica thin films

Post doped gel-silica thin films have been produced.

- thin film waveguide laser cavities under investigation

5. Doped gel-silica compared with doped ORMOSIL

Photostability of index matched, post-doped gel-silica found to be superior to that of doped ORMOSIL. 20,000 laser pulses at 3mJ pump energy and maximum efficiency of 33% obtained.

- highly flexible post doping technique improved with polymer index matching and high mechanical stability of oxide matrix

Dopant Distribution in Bulk Porous Gel-Silica

- Determined by
- Molecular size and mobility
 - Pore size and interconnections
 - Densification temperature
 - Time in dopant solution
 - Choice of solvent
 - Temperature of solvent
 - Ion interactions

Possibility of tailored dopant distributions.

Experimental Arrangement to Monitor Dopant Distribution

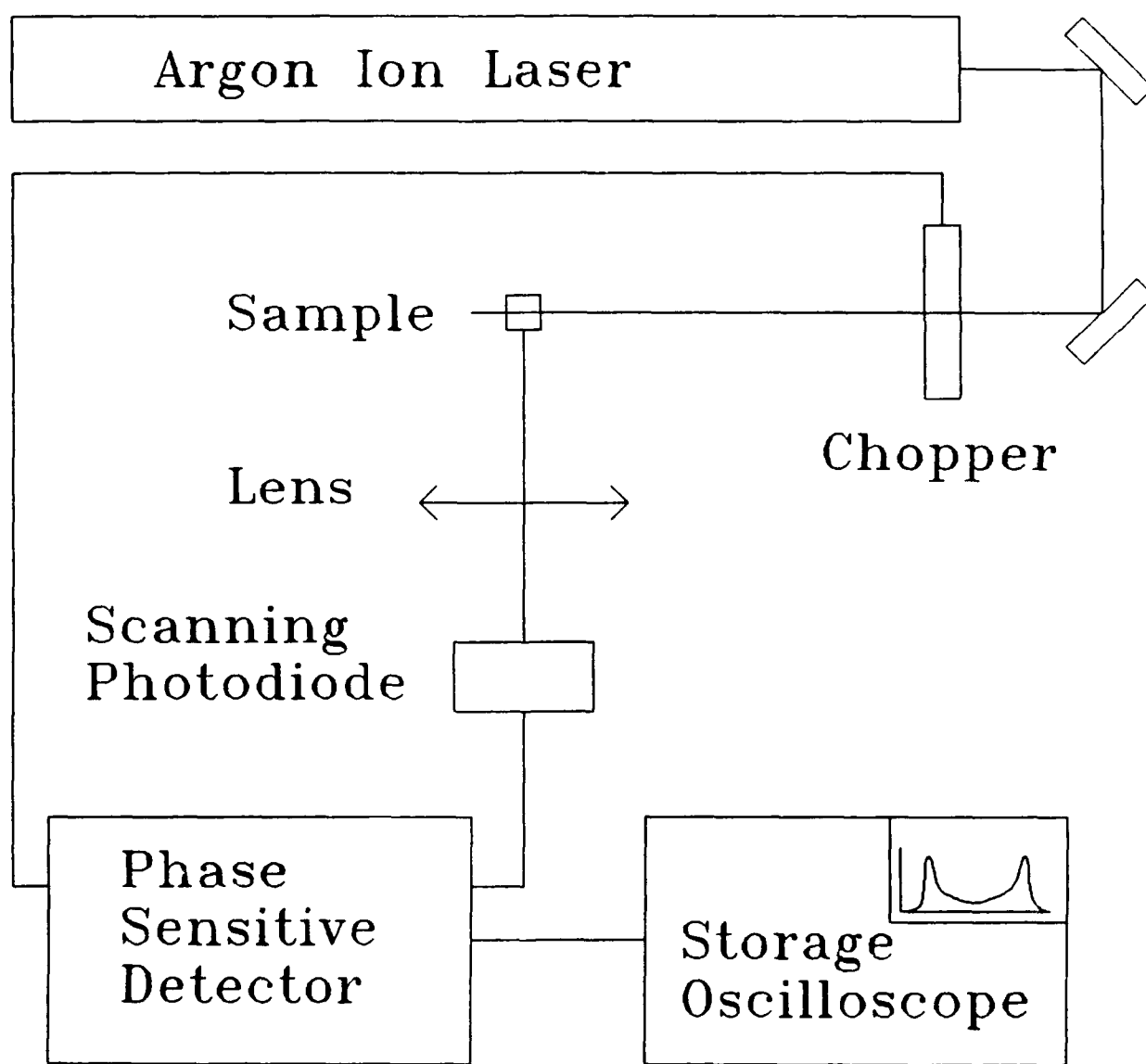
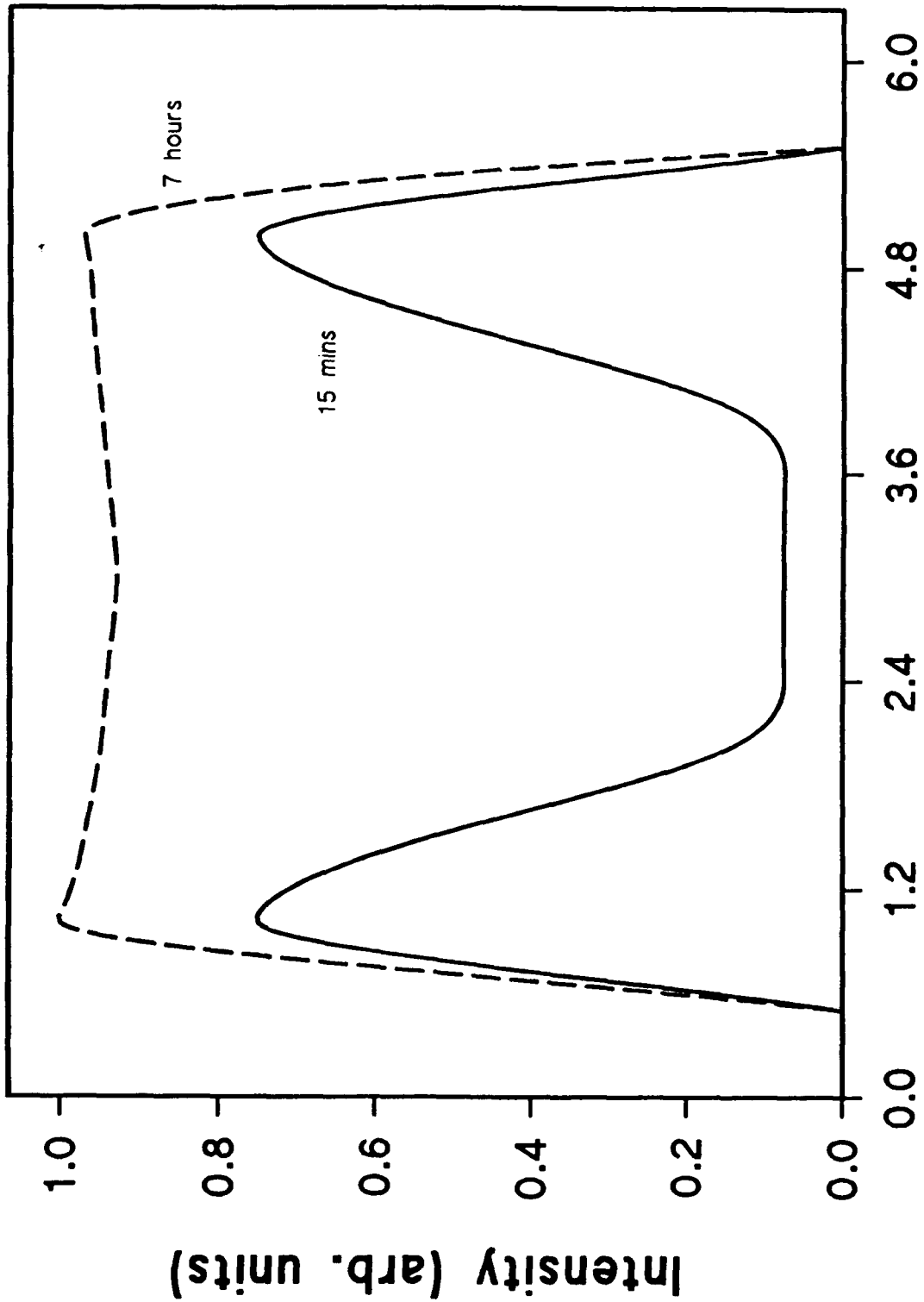


Figure 9

Fluorescence Intensity from Doped Gel-Silica Sample



Distance (mm)

Mean pore diameter : 4nm

Dopant : R6G

5. LASER ENHANCED DENSIFICATION OF SOL-GEL GLASSES

The theoretical model to describe laser densification of porous sol-gel glass developed in the previous programme has been extended and applied to the modelling of laser densification of gel-silica for various starting conditions and for variation of the laser irradiation conditions. It is found that the combination of laser intensity and exposure time are important values to be optimised in order to achieve densification without sample damage. For low intensity and long exposure times densification may not be obtained or the sample may crack due to lateral stresses set up by thermal conduction. These studies have been made with a 15W CW carbon dioxide laser. A higher power laser is required to investigate the higher incident intensity region.

The methods to characterise the densified samples have been further developed. The reflective refractometer has been refined to make routine measurement of refractive index. The Raman spectroscopy technique has been investigated to study partially and fully densified sol-gel glasses. These characterisation methods are important in providing reliable methods to determine the microstructure of the densified glass.

Methods have been under preparation for the laser densification of thin films of sol-gel glass prepared by spin coating. This is the beginning of the development of techniques to write thin film waveguides which will have many applications. Preparation of thin films of controlled thickness which are densified to set dimensions and refractive index is potentially feasible and enables the formation of single mode waveguides.

This part of the programme was aimed at developing the techniques, background data and model in order to evaluate the fabrication of selected optical elements. These elements include waveguides, interconnects, microlenses and microlens arrays and meshes of interconnections. In addition surface densification of large areas has application in large scale, lightweight optics and the sealing of porous doped sol-gel for laser and nonlinear optical application.

Determination of the relationship between the initial stabilisation of the porous sol-gel glass, the laser irradiation conditions and the exposure time has been made. A higher power carbon dioxide laser has been used to carry out densification at higher intensity.

Laser densification on samples which have been thermally pre-densified to higher temperatures in the region of 1000 - 1100°C has been made. The writing of small refractive index increments $\Delta n \sim 0.01$ under these conditions provide a device capability since the sample is nearer to the fully dense state with less sample fluctuation in uniformity.

Densification of thin films has been made with the aim of being able to write waveguide profiles for single mode guides at near IR wavelengths. Partially dense sol-gel thin films could be made by spin coating onto various substrates.

5.1 Results - Laser Enhanced Densification

Previous studies on laser enhanced densification of gel-silica using a CO₂ laser have proved successful and thresholds for densification and damage to the gel-silica have been determined at 4.3J/cm² and 6.4J/cm² respectively. The main limitation of this technique is the difficulty in focusing the CO₂ laser radiation to a spot significantly smaller than 100µm, thus limiting the spatial resolution and minimum size of waveguide produced. One way of reducing this minimum size is to dope the undensified gel-silica with a suitable species which absorbs radiation at shorter wavelengths, e.g. from an argon ion laser, where radiation can readily be focused to a spot size of 10µm or less. As well as producing greater resolution this also enables much higher intensities to be achieved with a modest power (3W) laser.

Initial developments of this technique have involved the use of rhodamine 6G as the absorbing species doped into gel-silica partially densified to 1000°C. The dopant concentration of 5x10⁻³ M leads to an absorption coefficient of approximately 500cm⁻¹ for the argon ion radiation, similar to that of CO₂ laser radiation in silica. The quantum efficiency of R6G is approximately equal to 1 and so the actual energy deposited in the dye is given by the energy difference between the excitation photon

($\lambda=488\text{nm}$) and the fluorescent photon ($\lambda=600\text{nm}$). This means that approximately 20% of the incident energy is transferred to heat and used to densify the gel-silica matrix, therefore the energy densities which follow have been adjusted to allow for this factor.

Using a 3W argon ion laser focused to a spot size of $100\mu\text{m}$, thresholds for damage to the gel-silica have been measured using two techniques. First the sample was held stationary and the exposure time and laser power varied to determine the damage threshold which in this way was measured at approximately $5\text{J}/\text{cm}^2$. The second technique involved translating the sample through a fixed laser beam at velocities between $10\text{cm}/\text{s}$ and $30\text{cm}/\text{s}$ to determine the velocity below which damage occurred. This was measured at $24\text{cm}/\text{s}$ corresponding to an energy density of $3.4\text{J}/\text{cm}^2$. These values agree well with those given for the CO_2 laser.

Reduction of the exposure energy below the thresholds determined above produced visible changes in the doped gel-silica samples in both the static and translation techniques. Preliminary measurements of the microhardness across these tracks and discs however showed no significant variation from the unexposed regions. These observations could be explained by one or more of the following:

1. The gel-silica sample at 1000°C was already near fully densified, allowing only a further 10% increase in microhardness - this is within the errors of the Riechart 2683 microhardness apparatus used.
2. The maximum temperature is produced below the surface of the gel-silica sample and so the surface hardness need not be significantly changed to produce densification below the surface. If this effect does occur then it suggests a method of producing cladded waveguide devices.
3. The damage produced is caused by evaporation of the organic species and does not necessarily correspond to a temperature sufficient to densify the gel-silica - reduction of the incident energy below this leads merely to a bleaching effect which can be observed optically.

Continuation work would be to explain in detail these results and to investigate the possibility of using inorganic species as an alternative dopant. Further studies could include densification at elevated temperatures (to ensure no water is trapped in the gel-silica matrix) and the laser densification of thin films leading to the potential for many optoelectronic components.

6. OPTICAL PROPERTIES OF DOPED SOL-GEL GLASSES

The radiative properties of dye molecules adsorbed into gel-silica hosts can exhibit significant differences from traditional solvent hosts due to molecular isolation and immobility. Studies of absorption spectra, emission spectra and excited state lifetimes have confirmed these differences and an experiment to measure dye photostability in terms of these parameters and quantum efficiency has been designed.

The two dyes studied were rhodamine 6G and methylene blue, and in each case three different hosts of methanol, water and gel-silica were used. The concentration of all the sample was only 2×10^{-6} M in order to minimise any concentration quenching effects which might otherwise distort the results. The properties measured were the absorption spectra using an absorption spectrometer, the emission spectra using an argon ion laser excitation source and an optical multichannel analyser, and the excited state lifetime using a mode-locked cavity dumped dye laser and photon counting technique (Figure 11).

In the case of rhodamine 6G no significant host dependent effects were observed, however with methylene blue there was a definite decrease in the absorption peak wavelength from water to methanol to gel-silica, and a similar decrease in the emission peak wavelength. The most striking effect was the increase in the excited state lifetime from 285ps in water to 1.8ns in gel-silica, an increase of 6.3 times (Figure 12). The measured lifetime in gel-silica actually had two components of 300ps and 1.8ns in approximately equal proportions, a fact which can be explained by the presence of residual water deliberately present in the gel-silica sample for index matching purposes and to reduce scattered light. The detailed results for both dyes in each of the three hosts are presented in table 1.

Experimental Arrangement to measure Fluorescence Lifetime

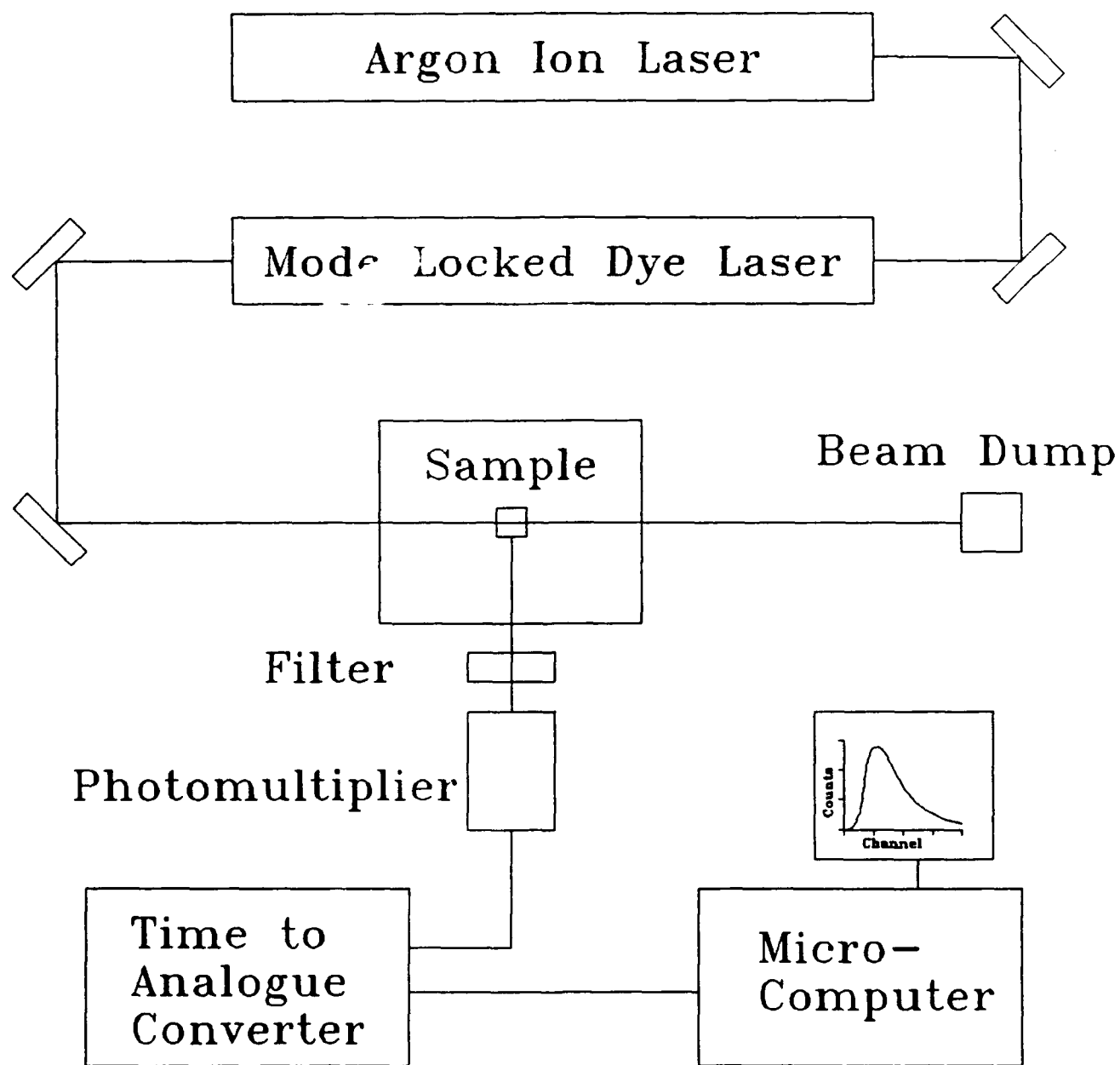


Figure 11

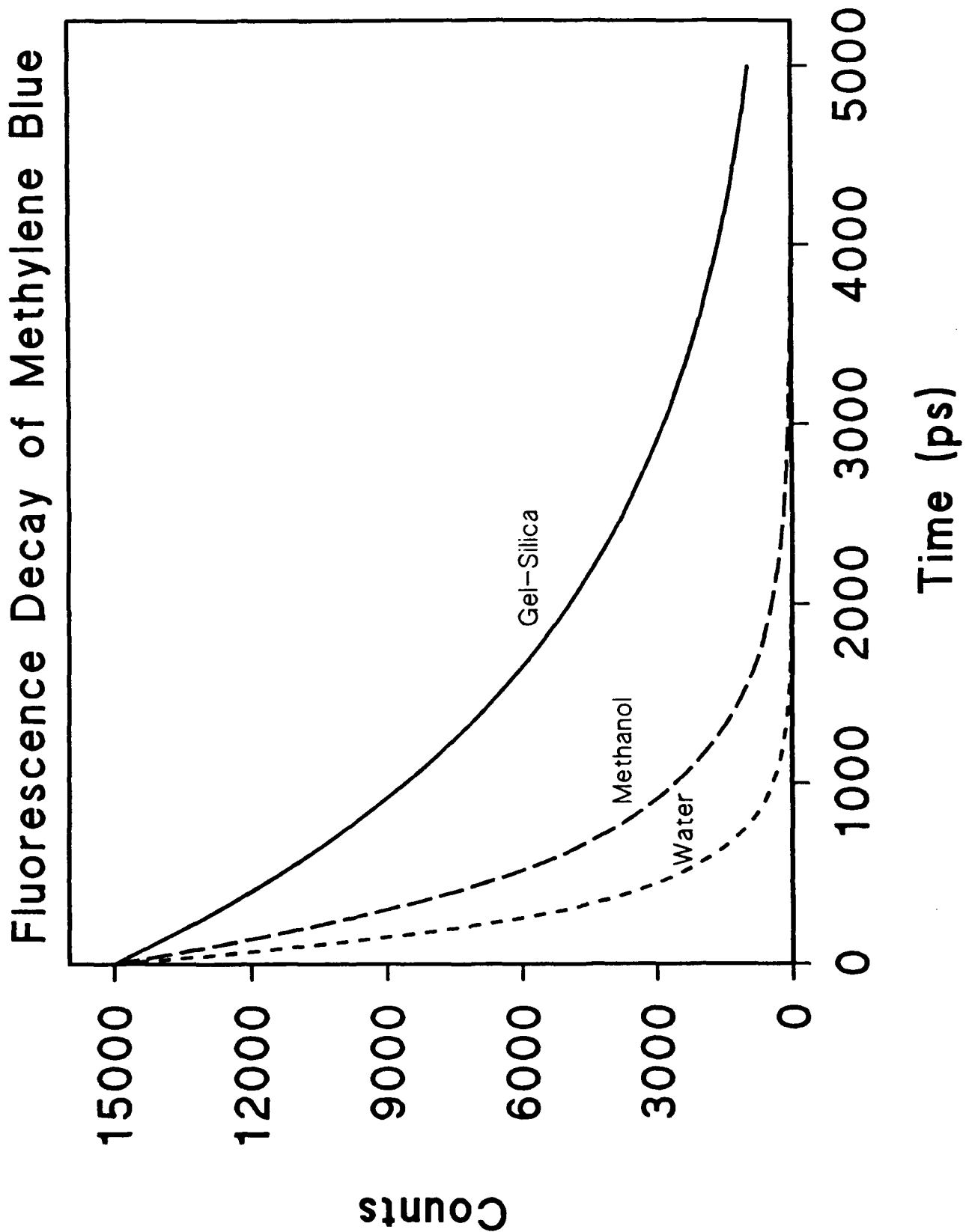


Figure 12

		Absorption Peak	Emission Peak	Lifetime
		+/- 1 nm	+/- 2 nm	ns +/- 10%
	Water	525	551	4.6
Rhodamine	Methanol	525	551	4.6
6G	Gel-silica	525	547	4.6
	Water	663	674	0.28
Methylene	Methanol	652	671	0.57
blue				
	Gel-silica	644	668	1.8

Table 1

Physical properties of dyes in water, methanol and gel-silica hosts.

These results are not unexpected because the high quantum efficiency of R6G in methanol cannot be improved significantly by molecular isolation, whereas methylene blue has a low quantum efficiency ~ 0.28 which is clearly increased in the gel-silica host. This is a significant result which demonstrates the importance of the interaction between the gel-silica host and the absorbed species as summarised in Figure 13. Further work could be directed at developing an experiment which directly measures the quantum efficiency of the absorbed dye as well as the excited state lifetime. This experiment will also monitor the dye photostability, allowing the most favourable gel-silica doped system to be selected as well as probing the basic physics of the interaction.

RADIATIVE PROPERTIES OF ADSORBED DYES

Perturbation of Excited States

Special shifts

- Stokes shift

Excited state lifetime increased

- Intersystem crossing reduced
- Collisional quenching reduced

Reduced intermolecular quenching

- Reduced aggregation

Reduced impurity quenching (incl. photodecomposition products)

Reduced rotational relaxation

Energy transfer by dipole-dipole interaction

Measurement

Spectra

- Absorption
- Emission

Excited state lifetimes

Quantum efficiency

Photostability

Photostability

Factors influencing photostability

- Dopant structure, internal conversion
- Host
- Irradiation wavelengths, intensity
- Ionic interaction
- Dopant mobility
- Oxygen

Measurement of photostability

- Required careful experimentation
- Defined irradiation and photostability monitoring apparatus designed and assembled

7. APPLICATIONS OF SOL-GEL GLASSES

7.1 Background

There is recent and growing interest in glasses prepared by the sol-gel process for applications in optics and optoelectronics. Several optical applications have been demonstrated, and there are many potential applications for novel devices. The Laser Research Group at Manchester has been involved in the background science and technology for many of these applications. The sol-gel process provides a low temperature route to the formation of high quality inorganic glasses which can be fabricated in bulk, thin film, coating or fibre forms. Most attention has been paid to silica gel-glass in which bulk porous gel-silica optical glass is produced from the sol by hydrolyzing a silica precursor, tetramethylorthosilicate TMOS with the action of a catalyst. The gel formed is then dried to produce a transparent gel-silica monolith; controlled heating of the gel removes solvent and organic products and gives densification of the material. For stabilization temperatures less than the full densification temperature the gel-silica is porous (Type VI) and is optically transparent and chemically and thermally stable. Fully dense gel-silica (Type V) has a high level of purity and homogeneity and excellent optical transmission in the visible, near UV and near IR, together with a low coefficient of thermal expansion and low dispersion. During the process heating stage the density, hardness and refractive index of the material increase.

Composite materials can be prepared in which optically active compounds are added at the sol stage or in the gel state. Organic molecules can be incorporated into the oxide network or held caged within the oxide matrix to form organically modified silicates (ORMOSILS) or post-doped into the partially densified porous gel-glass which provides a host matrix for the incorporation of organic or inorganic optically active compounds. Thin films and coatings can be prepared by dipping, spinning or spraying. Bulk materials can be formed in near net-shape sizes with high optical

transmission from the near UV to the near IR and with low coefficient of thermal expansion.

Many optical applications for sol-gel glass are being explored. The production of precision optics is possible with the sol-gel glass process being able to be used to cast near final shape and size optical components in the fully dense silica with reduction or elimination of grinding and polishing time. Gradient index optics can be produced by variation of the chemical composition, by leaching or by laser irradiation. Optically transparent thin films of ferroelectrics prepared by the sol-gel process have been used to demonstrate photovoltaic, photorefractive and two-wave mixing effects. High performance, broadband high damage resistance anti-reflection coatings are produced with the sol-gel method and scratch resistant Ormosil coatings. Organic molecule-oxide glass composites have been prepared in several ways to make dye-doped tunable lasers, photochromic media and optically nonlinear matrices.

A critical review of the properties and limitations of sol-gel glass for optical applications has been made by the Principal Investigator at Manchester. Application of inorganic ion or organic molecule doped sol-gel glass for laser and nonlinear optical applications is progressing. Relevant to this is the modification of spectral and radiative properties of the active components, photostability of the active dopants and the laser or optical performances. The modification of the optical properties of sol-gel partially densified glass by laser irradiation has been explored. It is of interest for the laser writing of optical interconnects and waveguides in bulk or thin films for surface densification.

Developments in optoelectronics and integrated optics require new photonic materials; glasses have valuable properties as substrates or to which functional elements can be added. The porous Type VI gel-silica is able to be formed with near net shape casting and replication of surface features which can largely eliminate grinding and polishing. The residual interconnected porosity is able to be used for thermally cooled optics, as substrates for diffusion or for laser-formed graded index optics such as GRIN lenses and optical waveguides. There is substantial interest in

optical waveguides for fast all-optical switching. Impregnation of glasses with dopants provides large nonlinear optical coefficients with fast response time and optical transparency giving low optical loss.

Gel-silica composites have been identified for nonlinear optical materials and the use of the sol-gel glass as a host for organic molecules with good NLO properties has been reported. Semiconductor quantum dots can be formed and incorporated into sol-gel films. Other optical elements include gradient index lenses and sol-gel coatings for displays and optoelectronic devices. Functional organic or polymer groups can be incorporated into sol-gel glass and second order $\chi^{(2)}$ and third order $\chi^{(3)}$ optically nonlinear molecules introduced into organically modified ceramics (ORMOCERS). The production of composites by pre-doping or post-doping into the interconnected nanometer pore network provides a medium for laser dyes, scintillators, fluorescence devices, wavelength filters and convertors, chemical sensors, nonlinear optical organics and polymers, liquid crystals, holographic elements and photopolymers. Sol-gel derived optical films have been micropatterned by embossing, laser writing and photolithography. The use of laser densification of porous gel-silica enables silica optical waveguides to be formed on silica substrates; these waveguides match the refractive index of silica optical fibres, providing low loss coupling.

7.2 Future Application Areas

Optical and optoelectronic applications for sol-gel glass are listed in Figures 14 and 15.

(a) Laser systems

The programme to date has shown that various types of new tunable laser sources which are of larger size and of high power or are compact and low power can be made which have new properties compared with existing lasers.

New laser systems can now be developed with the sol-gel matrices host with configurations giving enhanced output beam characteristics. These include large size rod or slab systems based on our ability to dope large volumes of sol-

SOL-GEL BASED OPTICAL DEVICES

DENSE BULK SILICA

**Net shape optics from precision moulding
(Tolerance ~25 μ m) Lenses, Aspheric, Fresnel lens
arrays, mirrors
Graded index optics**

OPTOELECTRONICS

**Novel high performance materials
Passive and active channel waveguides
modulators, switches, interconnects,
multiplexers, couplers**

**Lasers, nonlinear organics/polymers in gel,
semiconductor quantum dots
magneto-optical memories
optical fibres**

HOLOGRAPHIC ELEMENTS

**HOE optics
CD-ROM optical disc
displays**

FILMS AND COATINGS

**Optical sensors
photochromic, antireflection, electrochromic, thermochromic
'Smart' windows
protective (scratch, humidity, optical resistant)
ferroelectric, piezoelectric, electroconductive**

DEVICES

**Scintillator detectors, fluorescent converters, solar
concentrators
Optical filters, Faraday effect glasses**

OPTOELECTRONIC APPLICATIONS

***PASSIVE WAVEGUIDES**

- optical transmission, thick films

***NONLINEAR ACTIVE WAVEGUIDES**

$\chi^{(2)}$: poled organic films
frequency conversion (SHG)
electro -optic modulation

$\chi^{(3)}$: all-optical modulation (Mach-Zehnder interferometer)
optical switching (nonlinear directional coupler,
distributed feedback grating waveguide)

FERROELECTRIC FILMS

Piezoelectric transducers, SAW devices,
holographic memories, optical bistable elements,
pyroelectric IR detection
photorefractive, optical modulators

MULTIFUNCTIONAL MATERIALS

gel glass by selection of pore size and densification temperature. Tunable lasers based on organic dopants in rods and slabs of up to 12cm in size will generate output energies of 1J.

The achievement of the conditions for laser action for inorganic dopants such as Nd^{3+} enable a wide range of inorganic dopants to be considered for new laser systems particularly in the near UV, visible and near IR due to the good transmission of the silica sol-gel glass.

Ultra-compact laser systems based on doped thin films can be constructed using the techniques developed at Manchester for the doping of thin films. This will make lasers and amplifiers suitable for optoelectronics and optical communications.

The research to the present has indicated that flashlamp excited sol-gel glass lasers are feasible. At Manchester laser action with long duration excitation pulsed in the microsecond region have been demonstrated. Excitation by diode laser arrays and diode pumped solid state lasers should be able to be achieved and would open up new laser configurations.

At Manchester research on doped glass fibre lasers pumped by semiconductor diode lasers has been in progress. Sol-gel glass can be drawn into fibre form and this opens up fibre lasers based on doped sol-gel glass.

The sol-gel glass lasers are able to be considered for applications in laser radar, LIDAR, rangefinding, optical communications, optical sensors and optical signal processing. A valuable laser for laser radar, LIDAR and ranging is the Ho laser at $2\mu\text{m}$ in the eyesafe region. The Manchester group has studied this laser when doped in a crystal matrix; the silica sol-gel glass matrix would make a high power $2\mu\text{m}$ laser with energy output in the joule region.

(b) Nonlinear optical and photonic applications

At Manchester there has been demonstrated methods of doping sol-gel glass with organic molecules and also the enhancement of the glass optical quality by making index matched composite materials. When added to methods of thin film production this enables a wide range of systems to be created for photonic applications using nonlinear optical dopants as summarised in Figure 14 and 15..

The sol-gel based doped nonlinear optical waveguides can be used for

- (i) Frequency conversion, e.g. for second harmonic generation of diode laser radiation.
- (ii) Light modulation, using electro-optic $\chi^{(2)}$ molecules or optical $\chi^{(3)}$ material.
- (iii) Light switching. Optical switches of nonlinear directional coupler configuration are now possible with a configuration deposited and patterned by laser writing.

The sol-gel glass doped with organic molecules can be poled to create a large $\chi^{(2)}$ coefficient. This enables applications in second harmonic generation, electro-optic modulation and photorefractive processes to be developed. Doping the sol-gel glass with semiconductor quantum dot materials (quantum clusters, e.g. CdS, CdSe) is presently being studied. These systems show promise for enhanced $\chi^{(3)}$ nonlinear processes relevant to optical modulation, switching and limiting.

The sol-gel glass matrix doped with nonlinear optical materials is valuable for applications in photonics, optoelectronics and optical communications. The silica sol-gel glass is compatible with silica optical fibres.

(c) **Laser densification, writing and patterning of sol-gel glass**

The laser enhanced densification developed at Manchester can be used to write waveguides into the basic partially dense sol-gel or into sensitised material.

Applications for laser densification which are possible are in the following areas:

- (i) Thin films of sol-gel material deposited by spin coating or dipping which can be densified to write waveguides or interconnects for photonic applications.
- (ii) Micro-optical elements can be created by laser densification. Microlens arrays and Fresnel lenses can be produced for optical signal processing applications.
- (iii) Large area densification can be used in large area optical substrates and light weight mirrors, and in the hermetic sealing of sol-gel glass surfaces.

The sol-gel films have been shown to have large optical damage levels. For example, they make excellent antireflection coatings for high power laser applications.

7.3 The Manchester Laser Research Group

The Laser Research Group at Manchester is well set up to carry out research and applications programmes based on sol-gel glass materials. It has substantial experience in the sol-gel glass covering a wide range of basic research and optical studies. It is well equipped with characterization equipment, including spectroscopy, fluorescent lifetime measurements, light scattering, thin film ellipsometry and refractive index techniques and access to x-ray diffraction and electron microscopy. It has twenty five years' experience in laser physics and has available a wide range of optical and laser based equipment. The research staff are experienced in collaborative projects and research in both fundamental science and applications.

7. **REFERENCES**

A. **Optical Glass and Macromolecular Materials (OGAMM) Meetings**

- 1(a) A. J. Berry and T. A. King "Development of tunable doped gel-silica glass lasers"

Proc. 1st OGAMM meeting, 13-26, Pitlochry, June 1988.

- 1(b) D. J. Shaw, A. J. Berry and T. A. King "Laser densification of sol-gel matrices"

Proc. 1st OGAMM meeting, 170 - 175, Pitlochry, June 1988.

- 2(a) T. A. King, D. J. Shaw, A. J. Berry "Laser enhanced densification of gel-silica optics"

Proc. 2nd OGAMM meeting, 110-117, Ilkley, Aug. 1989.

- 2(b) T. A. King, D. J. Shaw and C. Whitehurst "Doped gel-silica laser hosts"

Proc. 2nd OGAMM meeting, 145 - 165, Ilkley, Aug. 1989.

3. D. J. Shaw, C. Whitehurst, A. Charlton and T. A. King "Laser developments in sol-gel glass".

Proc. 3rd OGAMM meeting, Keswick, Aug. 1990.

4. A. Charlton, M. A. Meneses-Nava, D. J. Shaw and T. A. King "Gel-silica lasers and optics", Proc. 4th OGAMM meeting, 105 - 113 Ilkley, Aug. 1991.

B. Journal References

1. D. J. Shaw and T. A. King "Densification of sol-gel silica glass by laser irradiation"
Proc. SPIE Vol. 1378 'Sol-Gel Optics', 474, 1990
2. T. A. King "Lasers and Ultrastructure Processing" in 'Chemical Processing of Advanced Materials'
Ed. L. L. Hench and J. West, Wiley 1992.
3. C. Whitehurst, D. J. Shaw and T. A. King "Sol-gel solid state lasers doped with organic molecules"
Proc. SPIE Vol. 1328, 'Sol-Gel Optics', 1990.
4. D. J. Shaw, A. J. Berry and T. A. King "Laser densification of sol-gel silica glass"
IOP Phys. Conf. Ser. No. 103, Pt. 1, p. 85, 1989.
5. A. J. Berry and T. A. King "Characterization of doped sol-gel derived silica hosts for use in tunable glass lasers"
J. Phys. D., 22, 1419, 1989.
6. T. A. King "Infrared solid-state lasers"
Proc. SPIE Vol. 1277 'High Power Solid State Lasers and Applications', 2, 1990..
7. A. Charlton, I. T. McKinnie, M. A. Meneses-Nava and T. A. King "A tunable visible solid state laser"
J. Mod. Opt. 39, 1992.