Fluorescent Dyes in Sol-Gel Glasses

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We review the sol-gel technology and the methods by which fluorescent dyes can be incorporated into inorganic glasses and organic-inorganic composites. The performance of the dyes in solar concentrators, tunable lasers, and active waveguides is presented.

INTRODUCTION

The sol-gel technology by which inorganic or composite organic-inorganic materials are made at relatively low temperature consists of hydrolysis of the constituent molecular precursors and subsequent polycondensation to glass-like form. The technology allows for the incorporation of organic and inorganic additives. Based on the sol-gel process a large number of sophisticated materials have been prepared and studied.

The first successful attempt to incorporate organic dyes and stabilize them within a sol-gel matrix started in 1984, together with my colleagues David Avnir and David Levy. This was the beginning of number of studies aiming to understand the fundamental mechanisms, improve the doped materials, and develop successful applications in many industrial areas [1–6].

We shall describe the sol-gel process and the fluorescent dyes that can be incorporated into glasses by using the process. Examples of solar concentrators, tunable laser, and active waveguides will be given.

REVIEW OF SOL-GEL MATERIALS

The sol-gel method is a low-temperature technique for creating solid glass bulks or thin films. Using this method, coatings on glass, ceramic, metal, or other solid substrates are easily fabricated. In addition, the relatively gentle synthetic conditions allow for the addition of various dopants such as organic dyes or inorganic ions which convert the resulting glass/dopant combination into an active material that may be used in various optical or sensing applications. The incorporation of organic materials into glasses prepared using sol-gel methods was first described in 1984 [5], followed by a paper describing incorporation of inorganic ions into sol-gel glasses [2] and thin-film sol-gel coatings [7,8].

The precursor solution for sol-gels consists of various alkoxides or inorganic sols that can be applied to surfaces by dip coating, spin coating, or laminar coating. The most common precursor molecules result in silicate, titania, germanate, alumina, zirconia, tungstate vanadates, or ormosil [7] glasses.

In this section we first provide a description of the "generic" sol-gel process. A number of specific sol-gel or composite sol-gel/polymer systems will be described.

GENERAL DESCRIPTION OF THE SOL-GEL PROCESS

The sol-gel process is based on hydrolysis and polycondensation reactions of metalorganic compounds such as silicon alkoxide compounds. A common example for a silicon alkoxide is the family of tetra alkoxysilanes that have the general form $Si(OR)_4$, where R is an alkyl group

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and therefore *OR* is an alkoxy group, mainly ethoxy or methoxy. The names tetraethoxysilane (TEOS) and tetra-methoxysilane (TMOS) are given to these liquid compounds. TEOS or TMOS is used as a component in a starting mixture that contains water as the second reactant. Basically, the sol-gel process can be realized without using any solvent, but in most cases it is preferable to use a solvent in the starting mixture to control the reaction rate of the process. Alcoholic solvents are commonly used for this, but there are other possibilities (e.g., acetone). The molar ratio between the different components of the starting mixture has a great influence on the final product.

For a starting mixture that includes tetra alkoxysilane and water, hydrolysis reactions of the form $\equiv$Si-OR + $H_2O \rightarrow \equiv$Si-OH + ROH occur. This is the first stage of the sol gel process. A complete hydrolysis of a tetra alkoxysilane molecule has the form $Si(OR)_4 + 4H_2O \rightarrow Si(OH)_4 + 4ROH$, and a solution of silanol groups, $Si(OH)_4$, in alcohol is obtained. The hydrolysis can be catalyzed by acidic catalysts in electrophilic mechanism. The reaction rate of the hydrolysis is increased with the strength of the acid, therefore HCl and HNO_3 are common catalysts. On the other hand, a base also can catalyze the reaction, by a nucleophilic mechanism. The reaction rate of the hydrolysis is also influenced by stearic considerations and is decreased with the size of the alkoxy group. For this reason, TMOS hydrolysis is faster then TEOS hydrolysis.

The second stage of the process consists on polycondensation inter(e)actions of the hydrolysis products. Each condensation reaction of two hydrolysis products have the form: $\equiv$Si-OH + HO-Si$\equiv$ $\leftrightarrow$ $\equiv$Si-O-Si$\equiv$ + H_2O

If we consider, for simplicity, an ideal model in which condensation reactions take place only after a complete hydrolysis, we assume that the reactants are silanols; a general form that describes the polycondesation stage is $nSi(OH)_4 \rightarrow (SiO_2)_n + 2nH_2O$

The result of the polycondensation reactions is the creation of an inorganic three-dimensional cross-linked polymer, leading to formation of sol particles. Farther condensation reactions link between the sol particles, forming wet gel. Evaporation of the liquids leads to dry gel (xerogel).

The glass obtained by the sol-gel process is porous [9]. The polycondensation can be catalyzed by hydrofluoric acid (HF), because F^- ions can replace hydroxyl ion in the hydrolysis product $Si(OH)_4$, and being more electronegative than the hydroxyl, they increase the attraction to other silanols, leading to Si$-$O$-$Si bonds. In a similar way, the polycondensation can be catalyzed by base. The rate of the condensation reaction influences glass porosity. Higher condensation reaction rates result in higher porosity.[9] Therefore, the choice of catalyst (acid or alkaline) allows a degree of control of the porosity of the glass. For example, when HF is used as a catalyst, the porosity increases with increasing concentration of HF.

$$\equiv Si-O-Si\equiv \ + \ H_2O \leftrightarrow \ \equiv Si-OH \ + \ HO-Si\equiv$$

Heating the glass to high temperatures evaporates the water, leading to dehydroxylation and complete condensation, which stabilizes the glass. A thermal treatment at more than 800°C makes the glass completely impenetrable for water, but many applications require penetration of liquids into the glass. For this purpose it is common to heat the glass up to 500°C; this produces a glass structure that enables penetration of liquids only into the pores, while preventing damage to the glass.

Zirconia Based Glass

Zirconia based glasses prepared by the sol-gel method makes them attractive for incorporation of fluorescent dyes for use as waveguides sensors and other optoelectronic materials:

1. The high refractive index of the films enables their use as waveguides deposited on ordinary glass substrate.
2. To use the waveguides for environmental, biological, or industrial sensing purposes, special consideration must be given to the matrix stability to chemical damage in solution. Zirconia-containing glasses have long been known to be alkali-resistant.
3. Unlike titania, ZrO_2 causes no catalytic photo-degradation of organic dopant. The energy gap between valence and conduction bands is much higher, so the photocatalytic stage:

$$M^* \rightarrow M^+ + e^-CB) \qquad (1)$$

where *M** is a photoexcited molecule and *e*-(*CB*) is the electron in the conduction band of the semiconductor, is less favorable.

It was, therefore, the aim of our work to prepare high optical quality waveguiding films based on zirconia or zirconia-polymer composites at a temperature that allows the incorporation of organic analytical reagents.

In ref. [10] we described the preparation of zirconia and hybrid zirconia-ormosil planar waveguides by sol-gel technology at room temperature. Acetic acid was used as chelating agent to stabilize the zirconia precursor. Multimode light guiding was demonstrated for the first

time in zirconia films prepared by the sol-gel method. The properties of the films: refraction index, thickness and transparency, as well as structural characterization using Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy (XPS), thermal analysis, and X-ray diffraction (XRD) were studied. The zirconia film contains propoxy, acetate, and hydroxyl ligands. In the zirconia-ORMOSIL films Zr-O-Si bonds were found although homocondensation bonds are favored. The mechanism proposed for the structural results involves condensation of oligomeric species that react by ligand exchange. XRD show wide peaks at small angles. These peaks can be attributed to oligomeric structures with a lattice constant of about 10 Å. The hybrid films are hydrophobic, and XPS measurement shows that the surface is covered mainly by organic groups of the ormosil. Films doped by pH indicator methyl red showed reversible response to acid and base vapors; this opens the possibility to use such films as waveguide based optical sensors and hosts for a number of dopants [11,12].

ORMOSILS Hosts

Organically modified silicates (ORMOSILs) usually exhibit lower porosity and enhanced mechanical properties that allow cutting, grinding, and polishing before heat treatment. A typical ORMOSIL gel network contains a significant amount of organic functionalities, which offers great flexibility with respect to the chemical compatibility of the gels with the dye to be incorporated. Various organic laser dyes have been incorporated into ORMOSILs, derived from polydimethylsiloxane and tetraethoxysilane. These sol-gel–derived PT-ORMOSILs proved to be good hosts for laser dyes.

The mechanical and optical properties of glasses prepared by sol-gel can be improved by modifying the sol process and using a variety of organofunctional silicane alkoxides. Modified alkoxide precursors $RSi(OEy)_3$ where R is a non-hydrophobic group such as methyl, vinyl, or amyltriethoxysilane (denoted as MTEOS, VTEOS, and ATEOS, respectively) lead to organic–inorganic hybrid matrices. The covalently bonded organic groups decrease the mechanical tensions during the drying process. Functionalized alkoxides $F-R'-Si(OEt)_3$, where F is a chemical function such as an amino or isocyanate group and R' is an alkyl spacer, allow to covalently graft onto the xerogel matrix to avoid phase separation and consequently to increase the concentration of the guest molecules. After drying, optically clear and dense inorganic–organic hybrid xerogels (30 mm diameter and 15 mm thick) were obtained and described in 1988 [12].

Recently we have prepared a matrix of polyethylene urethane silica [13]. The purpose was to synthesize a new matrix material that could incorporate a wide range of dyes. The matrix described below possesses the high mechanical and thermal stability and high refractive index of zirconium oxide. By combining the strength and hardness of sol-gel matrices with the processability and ductility of polymers, novel transparent hybrid material can be obtained. Polyethylene urethane silane (PEUS) was synthesized from 3-isocyanatopropylthriethoxysilane (ICTEOS) and polyethylene glycol (PEG); chlorobenzene was used as a solvent. The epoxy-silica-ormosil (ESOR) precursor was obtained from tetramethoxysilan (TMOS) and 3-glycid oxypropyl trimethoxysilane (GLYMO). These two types of ORMOSILS were combined with zirconium oxide matrix, which was used as an inorganic hetero network and as an efficient catalyst for the epoxy polymerization. ZrO_2 is the best promotor for epoxy polymerization [14]. However, reaction at room temperature is limited (about 27% unreacted epoxy groups) as is reaction at high temperature 70°C/8 hour (about 24%), but the part of unreacted epoxy groups is still lower than in cases of SiO_2/TiO_2 (70–57%) or in case of SiO_2 (100%). In the case of ZrO_2 unreacted epoxy groups (at least 24%) can be reacted with secondary amino groups in urethane linkage of PEUS. Because of strong chemical bonding between organic and inorganic parts, the hybrid materials offer superior mechanical properties (elasticity, flexibility) and are suitable for incorporation of organic dyes.

The hybrid materials were obtained by using three precursor composites. (1) poly(ethylene)glycol chain covalently linked by urethane bridges with thriethoxysilane groups synthesized separately, (2) epoxy-silica ORMOSIL precursor, and (3) a zirconium oxide precursor. The solubility of most laser dyes is limited in pure hydrophobic or hydrophilic matrices, which can cause aggregation and excitation energy migration within aggregates of dye molecules of the dyes, resulting in decreased efficiency when used in a laser. The novel organic–inorganic ORMOCER matrix can efficiently solubilize many laser dyes. It was shown that the combination of two types of clusters creates two subphases with different degrees of hydrophilicity/hydrophobicity and results in an active interface. Polymethylmetacrylate (PMMA), polyurethane (PU), and various epoxides have been also used as polymer hosts for solid state dye lasers.

ORGANIC LASER DYES

Organic laser dyes generally contain extended conjugated pi bonds that determine the resonant optical absorp-

tion bands of the dye molecule. To a first approximation, the conjugated pi-electrons can be analyzed as a quantum mechanical particle in a potential well [15]. However, the spectra can be significantly modified by adding functional groups with various electronegativities (e.g., electron-withdrawing groups such as ketones) to the basic conjugated system.

Organic dyes tend to have very broad spectra, which are affected by solvent polarity. Dye molecules tend not to be water soluble unless charged or highly polar side groups are added. In addition, their large size (as compared to ions) lends itself to various photochemical processes that result in photobleaching. They also tend to form dimers or aggregates, often resulting in large changes in their spectral properties.

Organic dyes come in families, which are characterized by a basic structure to which various substituent groups are added. A recent review of the visible-light organic dyes can be found in ref. [16]. In this paper we describe four dye systems that were used in our laboratory.

Perylimide Dyes

Figure 1 shows the structure of perylene orange, which is a perylimide dye. Its excitation and emission spectra have been extensively studied [17]. The mirror image character of these spectra is a common feature of fluorophores [18]. Perylene orange and related perylimide dyes were among the first dyes to be incorporated into sol-gel hosts [19,20] and has been found to be very photostable. A family of dyes with varying spectral properties is created by adding substituent groups to the original dye molecule.

Pyrromethene (PM) Dyes

Pyrromethene dyes are a highly efficient family of dyes based on a substituted pyrromethene-BF_2 core. The generic structure of this family of dyes appears in Fig.
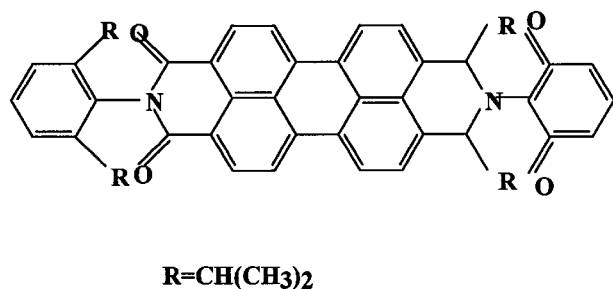
2. Typical members of this family are also used as fluorescent labels in biological imaging, where they are known as Bodipy dyes. The lasing and photophysical properties have been extensively studied [21]. Although they are very efficient, they are less photostable than perylimide dyes. Much effort has been invested in improving the longevity of pyrromethene-based solid-state dye lasers [22], particularly by removing oxygen from the immediate environment of the dye. Laser longevity in excess of 1 million pulses has been reported [23].

Rhodamine Dyes

The rhodamine dye family is based on the xanthene structure (Fig. 3) [16]. Again, a large family of rhodamine dyes has been created. One of the most common dye in this family is rhodamine 6G (R6G), also called rhodamine 590, shown in Fig. 4. Rhodamine 6G has been found to be an efficient but not very stable dye. The rhodamine family is created by varying the substitutents, especially at the amino groups at position 3 and 6. Of particular interest is sulforhodamine 101 (Fig. 4) in which aliphatic rings rigidize the amino end groups. This increases the quantum efficiency and reduces the temperature sensitivity of the dye.

PM 580
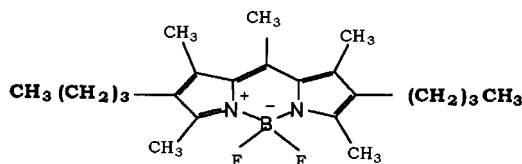

PM 597

R=CH(CH₃)₂

Fig. 1. Perylene orange.
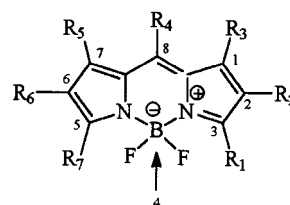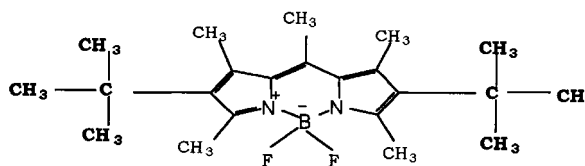
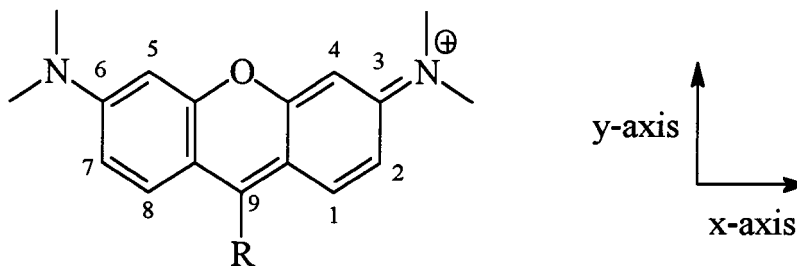**Fig. 2.** Generic structure of pyrromethene dyes.

Fig. 3. Generic xanthene chromophore.

Cyanine Dyes

The cyanine dye family spans a very large range of wavelengths, from green to infrared [16]. The general formula of cyanine dyes is presented in Fig. 6. In this figure Hal stands for the halogen anion and C = 5 and C = 7 is the number of carbons in the connecting chain. The number of methane groups that join the two imidazole determine the wavelength range of the dye, while the substituent (Fig. 6) has a smaller but still significant effect on the wavelength range of the dye. These dyes have been extensively characterized in the past when they were used as voltage-sensitive membrane probes. Cyanines are popular as biological labels, because of the wide choice of emission wavelength and also because the two "tails" of the molecule can be altered (e.g., by adding hydrophobic chains) to create any desired physical property (hydrophobicity) without affecting the spectral behavior. Photophysical properties of cyanine dyes in sol gel glasses can be found in ref. [24].

AN EXAMPLE OF APPLICATION OF FLUORESCENT DYES IN LUMINESCENT SOLAR CONCENTRATORS (LSC)

One way of lowering the photovoltaic, PV, price of electricity using solar energy is to concentrate the solar radiation, particularly that part that is most efficient in PV energy conversion, on high-efficiency solar cells,

which are expensive; however, their amount and cost can be considerably diminished by using concentrated solar light on their small areas. The light emitted as fluorescence from the edges of the concentrator can be matched to about 50% efficiency of solar cells.

The operation of an LSC is based on absorption of solar radiation in a collector containing a fluorescent species in which the emission bands have little or no overlap with the absorption bands. The fluorescence emission is trapped by total internal reflection and concentrated at the edges of the collector, which is usually a thin glass plate. LSCs have the following advantages over conventional solar concentrators: They collect both direct and diffuse light; there is a good heat dissipation of non-utilized energy by the large area of the collector plate in contact with air so that essentially "cold light" reaches the PV cells; tracking the sum is unnecessary; the luminescent species can be chosen to allow matching of the concentrated light to the maximum sensitivity of the PV cells. The main advantage is that the large area to be covered by the solar cell is reduced to the area of the edges.

The theory of LSC, which is based on internal reflection of fluorescent light that is subsequently concentrated at the edges has been discussed in detail for inorganic
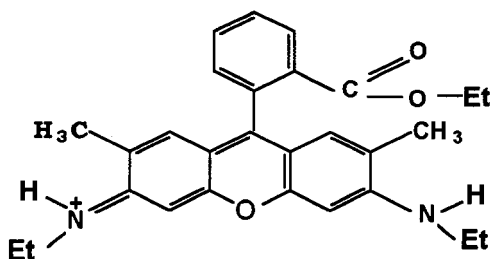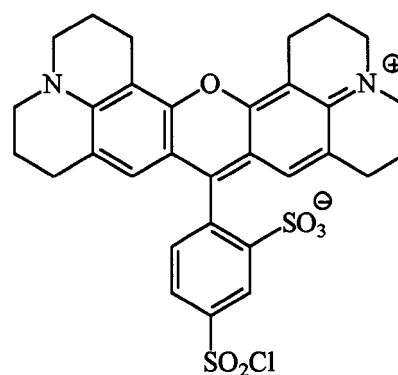

Fig. 4. Rhodamine 6G (Rh6).

Fig. 5. Sulforhodamine 101-sulphonyl chloride.

(a)... X=C(Me) 2 ; R=Me ; C=5
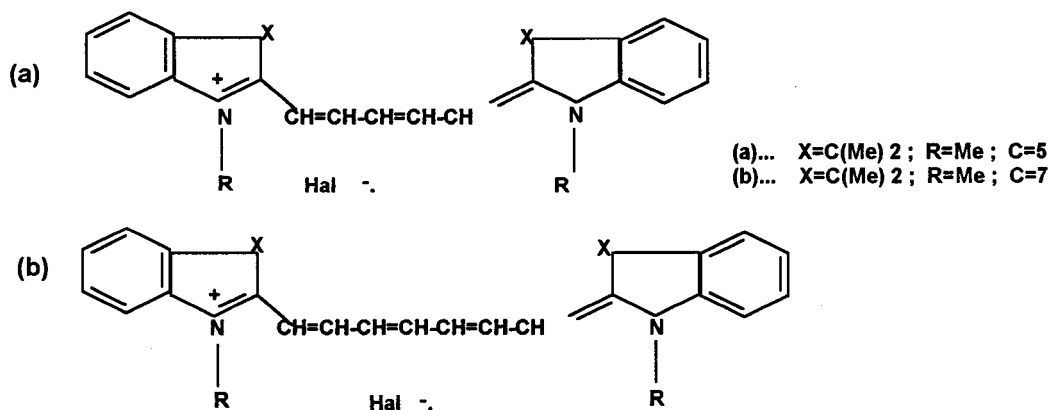(b)... X=C(Me) 2 ; R=Me ; C=7

Fig. 6. Cyanine dyes.

materials and organic dyes incorporated in bulk polymers [25].

A transparent plate doped by fluorescent species absorbs in the visible (solar part of the spectrum). The resulting high-yield luminescence should then be evolved at the longer wavelengths part of the spectrum. About 75%–80% of the luminescence is trapped by total internal reflection in the plate having a refractive index about 1.5. Repeated reflections of the fluorescent light carry the radiation to the edges of the plate, where it emerges in the concentrated form. The concentration factor is proportional to the ratio of the surface of the plate to its edges and the optical efficiency of the plate. Photovoltaic cells can be coupled to the edges and receive the concentrated light. Such an arrangement should decrease substantially the amount of photovoltaic cells needed to produce a given amount of electricity and thus reduce the cost of the system of photovoltaic cells.

Parameters determining the optical plate efficiency depend on the following factors [25]:

1. The fraction η_{abs}, which is the ratio of photons absorbed by the plate to the number of photons falling on the plate;
2. The quantum efficiency Φ, which is the ratio between the number of photons emitted to the number of photons absorbed;
3. The Stokes efficiency η_s, which is the ratio of the average energy of emitted photons to the average energy of the absorbed photon and is given by:

$$\eta_s = \nu_{em}/\nu_{abs} \qquad (2)$$

4. The fraction η_t of the light trapped in the collector, given by:

$$\eta_t = (1 - 1/n^2)^{1/2} \qquad (3)$$

where n is the refractive index of the light-emitting medium;

5. The transport efficiency η_{tr}, which takes into account the transport losses resulting from matrix absorption and scattering;
6. The efficiency η_{self}, which results from losses arising from self-absorption of the colorants.

The optical efficiency of the plate, which is the energy coming out of the edges of the plate divided by the energy falling on the plate, including reflection is given by:

$$\eta_{Opt} = (1 - R)\eta_{abs}\Phi\eta_s\eta_t\eta_{tr}\eta_{self} \qquad (4)$$

where R is Fresnel reflection coefficient and is about 4% for ordinary glass.

The energy output, E_{out}, is given by:

$$E_{out} = E_{in}\ \eta_{opt}\eta PV^{(\lambda)} \qquad (5)$$

where E_{in} is the energy falling on the plate and $\eta PV^{(\lambda)}$ is the efficiency of the PV cell at a wavelength λ. The efficiency of PV cells can be increased from about 12% for total solar spectrum to more that 50% at the emission wavelengths of the perylimide dyes, *vide infra*. In addition, it is easier to prepare antireflective coatings for such a narrow wavelength range. Finally, the factor of decrease of surface of the PV cells coupled to the edges of the LSC plate compared to the full coverage of the surface is:

$$F = \eta_{opt}(A_{surf}/A_{edge}) \cdot (\eta PV^{(\lambda)} \cdot /\eta_{solar}) \qquad (6)$$

where A_{surf} is the area of the collector, A_{edge} is the area of its edges to which the photovoltaic cells are coupled, and η_{solar} is the efficiency of the photovoltaic cells in respect to total solar spectrum.

Although a large number of papers have been published about luminescent plates in which the dye is incorporated in the entire bulk of the plate, the configuration in which the plate is covered by a thin film incorporating the colorant deposited in close contact with the plate is relatively new. The advantage of doped thin sol-gel films having optical contact with the transparent plate is that the luminescence emitted from the thin film is trapped in the plate. Parasitic losses resulting from self-absorption and scattering from impurities thus can be greatly reduced compared to bulk doped plates. As an example of such a system, we may examine rhodamine 6G incorporated in sol-gel film. Based on the experimental data of absorption and emission of rhodamine 6G in sol-gel glass, its quantum efficiency of 0.95, molar extinction coefficient of 82000 M^{-1} cm^{-1}, and the overlap of absorption of Rh6G with the solar spectrum using a 50-micron-thick film deposited on a plate having refractive index of 1.51, Monte-Carlo computations were performed for an optical efficiency of a plate having dimensions of 1 M^2. The optical efficiencies of such plates are approximately 15%. Although Rh6G is not stable enough to be used in practical device for LSCs, it can serve as a model for computation in sol-gel glasses. Much better results can be obtained with the photostable perylimide dyes, provided they can be introduced into the sol-gel system.

In a recent work we indeed have been able to introduce the dyes into a composite polymer/sol-gel glass system and into a glass using the sol-gel procedure. A combination of two dyes increases the overlap of absorption with the solar spectrum followed by an increase in optical efficiency.

The main requirements for luminescent solar concentrators (LSC) are their efficiency, photostability, and ease of fabrication. This has been achieved here by deposition of organically modified sol-gel films doped by photostable perylimide dyes on glass substrate. The absorption spectra of these dyes extends from 420 to 620 nm, covering the visible part of the solar spectrum, and the emission is between 550 and 750 nm, close to the optimum response of silicon and germanium arsenide solar cells. The efficiency of such type of collector was calculated from the absorption coefficients, quantum efficiency of the fluorescence, and overlap between emission and absorption spectra, by the method of Monte-Carlo and found to be close to 20%. Optimum concentrations are shown to be strongly dependent on the extent of overlap between the absorption and the emission spectra, which also appears to be the limiting factor in respect to the efficiency of the concentrator [25].

Tunable Lasers in the Visible Based on Sol-Gel Technology

Incorporation of perylimide and pyrromethene dyes into glasses prepared by the sol-gel method enables the design of new types of visible, stable, solid lasers tunable in the visible range [2]. These can be prepared either in the form of slabs or rods or as waveguiding active media deposited on glass or polymer supports. The difference between the refractive indices of the film and its support determines whether waveguiding occurs in the film or a leaking waveguide laser is formed. The defficiency of the lasers obtained recently is up to 70% when appropriate optical pumping is designed.

We discuss the chemical and physical aspects of the photostability of the dyes in glasses, phenomena responsible for non-radiative relaxation of their excited state, and energy efficiencies of laser.

The recently developed tunable dye lasers in the visible range are obtained by incorporation of stable laser dyes into glasses prepared by the sol-gel method. For the lasers to be photostable and more efficient it is essential that the dye molecules penetrate the glass matrices in a unimolecular form and be protected from the surroundings.

Until recently, liquid dye lasers were the main systems used to achieve tunability in the visible and the only commercial choice for tunable lasers between 400 and 660 nm. However, in the last few years an intensive effort was devoted to produce embedded organic dyes in various solid matrices, with the goal of achieving solid-state dye laser devices that may replace the liquid dye lasers; for example, laser dyes were incorporated into silica-gels, xerogels, alumina gels, ORMOSILS, and composite glasses. A solid-state dye laser has advantages over a liquid dye laser by not being a volatile solvent, being non-flammable, toxic, and having compact size and mechanical stability. Still, for applications that require high powers, at either continuous wave or pulsed high-repetition-rate operation, the problem of heat dissipation is a serious impediment for their utilization. In liquid dyes, on the other hand, a jet or a flowing solution is handy practical ways of solving the heat problem. In both cases, photostability is a feature of prime importance in selecting a laser dye. Lasers obtained by impregnation of the perylimide dyes into sol-gel glasses, where the dyes are enclosed in the pores of the glass, seem to be so far the most photostable system.

In 1989 we succeeded for the first time to prepare a photostable tunable laser by impregnating the orange perylene derivative (perylimide) dye "BASF-241" dissolved in MMA, into a silica gel. The method of Pope and

Mackenzie [26], which allows polymerization of MMA in the pores of the glass, was applied here. The dye, which is orders of magnitude more stable than the conventional laser dyes impregnated in the glass, provided an efficient solid-state laser material. This laser was tunable in the range of 568–583 nm.

The extension of the lasing range picking around 613 nm was performed by impregnating the red perylimide dye into composing silica gel PMMA glasses. This wavelength is important for medical PDT and diagnostics. Human blood and tissue absorption is small in the red, range allowing the preferential absorption of light by a photoactive cancer therapeutic agent, such as hematoporphyrin derivative, which concentrates in tumors.

The perylimide dyes were dissolved in a methylmethacrylate (MMA) monomer to form solutions of various concentrations in the range 10^{-6}–10^{-3} mol/L. Highly porous silica-gel bulk glasses (density about 0.7 g/cm^3) were prepared by the sol-gel method and were dried by slow heating (100°C/day) from room temperature to 500°C. Then, the bulks were immersed in the dye-doped solution of the MMA monomer, which was simultaneously catalyzed by the addition of 2% benzoyl peroxide. The MMA-dye solution thus diffused into the silica-gel glass pores and polymerized therein. After this process of dye impregnation, the bulks were reimmersed in an MMA-dye solution, which at this stage was catalyzed for full polymerization by 0.5% benzoyl peroxide and kept in a sealed container at 40°C for about a week. The samples were then withdrawn, cleaned, and polished, to obtain parallel-piped slabs of approximate dimensions 10 × 10 × 3 mm^3, with clear smooth surfaces. For this class of glasses we give the name composite glass.

The density of the composite glass was $d = 1.447 \pm 0.005$ g/cm^3, and the refractive index $n = 1.472 \pm 0.003$.

Later solid-state dye lasers were made by incorporating photostable laser dyes in ORMOSIL and composite glass matrices. Three different types of pyrromethene (PM) were used: PM 567, PM 580, and PM 597. Their formulae are presented in Fig. 2. The ORMOSIL glass samples were prepared by a one-step process at room temperature by sol-gel technology, which led to the formation of hybrid organic–inorganic materials. The composite glass samples are made by biphase process: (a) preparation of porous silica gel, (b) impregnation of the dye dissolved in MMA into the silica gel and polymerization of the MMA.

Various glass compositions were tested and their efficiencies and half output energy lifetimes were measured. The optimal slope efficiency for the lasers pumped transversally, by frequency-doubled Nd-YAG laser, approaches 42% in PM 597 in composite glass.

ORMOSILs usually exhibit lower porosity and enhanced mechanical properties that allow cutting, grinding, and polishing before heat treatment. A typical ORMOSIL gel network contains a significant amount of organic functionalities, which offers great flexibility with respect to the chemical compatibility of the gels with the dye to be incorporated.

Various organic laser dyes have been incorporated into ORMOSILs, derived from polydimethylsiloxane and tetraethoxysilane. These sol-gel derived PT-ORMOSILs proved to be good hosts for the laser dyes in terms of stability and optical gain.

The mechanical and optical properties of glasses prepared by the sol-gel are being improved constantly by modifying the sol process and using a variety of organo-functional silane alkoxides. Modified alkoxide precursors, $RSi(OEt)_3$ or $RSi(OMet)_3$ (where R is a non-hydrophobic group), such as methyltriethoxysilane (MTEOS), vinyltriethoxysilane (VTEOS), amyltriethoxysilane (ATEOS), 3-(trimethoxysilyl)propylmethacrylate (TMSPMA), methyltriethoxysilane (MTEOS), 3-glycidoxypropyltrimethoxysilane (GLYMO), or methyltrimethoxysilane (MTMOS) lead to organic-inorganic hybrid matrices.

The permanent organic group decreases the mechanical tensions during the drying process. Functionalized alkoxides $F-R'-Si(OEt)_3$, where F is a chemical function such as an amino or isocyanate group and R' is an alkyl spacer, allow covalently graft onto the xerogel matrix to avoid phase separation and consequently to increase the concentration of the guest molecules. After drying, optically clear and dense inorganic–organic hybrid xerogels (30 mM diameter and 15 mM thick) were obtained in our laboratory.

Discussion of a large number of fluorescent dye-doped glasses, their efficiencies, and their photostabilities can be found in ref. [21] and references therein.

Planar Active Wave Guides

Planar optical waveguides hold considerable potential in the field of integrated optics. Doped material with optically active spectra can be of interest for the realization of active planar devices such as optical amplifiers of lasers. Other advantages of pure or doped thin films, which are waveguiding, are to enable the use of both the light guiding for structural investigations and the fluorescence properties of the dopants and thus to correlate the microstructural and optical properties of these waveguides.

The forming of active planar waveguides by the sol-gel method is feasible by incorporation of a variety of

laser dyes at room temperature. Light amplification in a dye-doped in these devices is achieved.

The combination of the tunability and high efficiency of laser dyes with the high power density that easily can be achieved in planar waveguide makes devices based on dye-doped waveguides very promising, for example: Glass waveguiding films were prepared from titania and modified silica using the sol-gel method and doped by the laser dye rhodamine B. The guided and amplified fluorescence (pumped by a double-frequency Nd-YAG laser) was coupled out either by static grating written on the film or by a prism. The gain of the emitted superradiance was determined from the amplified spontaneous emission intensity dependence on the pumped strip length. A maximum net gain of 54 ddB/cm was measured [27–30].

CONCLUSIONS

In this short review I tried to give an outline of the sol-gel process for preparation of glasses either totally inorganic or composed of organic parts–inorganic. The process allows incorporation of varieties of fluorescent dyes leading to many applications in optics, biosenvsors, sensors, luminescent, solar concentrators, etc. Most of the references cited are from the work of my own group. However numerous publications were performed on the subject all over the world. These are cited in the papers referred above.

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