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Doped polymeric systems produced by sol-gel technology: optical properties and potential industrial applications

Summary — A review of the studies on sol-gel technology application to the production of doped polymeric systems, which can be applied as new optical materials: tunable lasers, sensors, waveguides, photochromic or electrochromic materials and semiconductors. Sol-gel method based on hydrolysis and subsequent polycondensation of precursors, such as organo-silicon alkoxides (Scheme A), leading to formation of porous glass was described. The matrices for incorporation of organically active dopants in are produced from this glass. The matrices can be the glass/polymer composites, organically modified silicates (ORMOSIL) or hybrid materials zirconia — silica — polyurethane (ZSUR) (Schemes B—E). The characteristics of examples of laser dyes forming the solid tunable lasers are given. Finally, the description of semiconductors produced by incorporation of nanoparticles into the matrices discussed has been presented.

Key words: sol-gel technology, doped polymeric systems, glass/polymer composites, laser dyes, tunable lasers, nanoparticles, semiconductors.

DOMIESZKOWANE UKŁADY POLIMEROWE WYTWARZANE METODĄ ZOL-ŻEL: WŁAŚCIWOŚCI OPTYCZNE I POTENCJALNE ZASTOSOWANIE PRZEMYSŁOWE

Streszczenie — Przedstawiono przegląd prac poświęconych wykorzystaniu technologii zol-żel do wytwarzania domieszkowanych układów polimerowych mogących mieć zastosowanie jako nowe materiały optyczne: lasery przestrajalne, sensory, falowody, materiały fotochromowe i elektrochromowe oraz półprzewodniki. Opisano metodę zol-żel opartą na hydrolizie i następującej po niej polikondensacji prekursorów, takich jak alkoholany krzemoorganiczne (schemat A) prowadzącą do otrzymywania porowatego szkła. Z tego szkła wytwarza się matryce do wbudowywania aktywnych organicznie domieszek. Matryce mogą być kompozytami szkło/polimer, organicznie modyfikowanymi krzemianami (ORMOSIL) lub materiałami hybrydowymi tlenek cyrkonu-krzemionka-poliuretan (ZSUR) (schematy B-E). Podano charakterystykę przykładowych barwników laserowych tworzących stałe lasery przestrajalne. Na zakończenie przedstawiono opis półprzewodników otrzymanych przez osadzenie nanocząstek na omówionych wcześniej matrycach.

Słowa kluczowe: technologia zol-żel, domieszkowane układy polimerowe, kompozyty szkło/polimer, barwniki laserowe, lasery przestrajalne, nanocząstki, półprzewodniki.

Recently a major effort has been centered on introducing optically active organic materials into a photostable mediums such as polymers, silica-gels, xerogels, organically modified silicates (ORMOSIL), composite films and composite glasses [1—4]. The sol-gel process is a solution synthesis technique which provides a low temperature chemical route for the preparation of rigid transparent matrices. Sol-gel processes provide techniques for the preparation of materials which contain silicate and organic groups in a single amorphous phase. The preparation procedure at room temperature allows introduction of "fragile" organic molecules inside an inorganic network, involving inorganic and organic components that can be mixed at the nanometer scale and leading to the formation of organic-inorganic nanocomposites. These hybrids are extremely versatile in their composition, processing and optical and mechanical properties. Such materials can possibly show a resultant combination of beneficial physical and chemical properties of silicate glass and organic polymeric materials. Also, silica glasses containing organic components in their network can more readily dissolve organic dyes, and therefore be used in a variety of optical materials.

In addition to sol-gel glasses based mainly on silica, other materials such as ZrO_2, SiO_2/TiO_2, ZrO_2, ORMOSIL and zirconia-silica urethane matrix have been investigated.

DESCRIPTION OF SOL-GEL PROCESS

The sol-gel method is a low-temperature technique for the formation of solid glasses or thin-films. Using this method, the coatings on glass, ceramic, metal or other solid substrates are easily fabricated. In addition, the relatively gentle synthetic conditions allow the addition of dopants such as organic dyes or inorganic ions, which convert the resulting glass/dopant combination into an active material which may be used in optical or sensing applications. The incorporation of organic materials into glasses prepared using sol-gel methods was first described in 1984 [5] followed by the paper describing incorporation of inorganic ions into thin-film sol-gel coatings [6].

The precursor solution for sol-gels consists of various alkoxydes or inorganic sols. This solution can be applied by dip coating, spin coating or laminar coating [7]. The most common precursors are used to produce silicates [8], titania, germanates, alumina, zirconia, tungstates, vanadates and ORMOSIL.

In this section, we first provide a description of the "generic" sol-gel process. Then, a number of specific sol-gel or composite sol-gel/polymer systems are described. For each of these systems a typical synthesis is given and properties specific to that system are summarized.

The sol-gel process is based on hydrolysis and polycondensation reactions of metalorganic compounds such as silicon alkoxides. Commonly used silicon alkoxides include the family of tetra alkoxysilanes, which have the general formula $Si(OR)_4$, where R is an alkyl group, and therefore OR is an alkoxy group (usually ethoxy or methoxy). Examples include tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS). TEOS or TMOS are used as the components in an initial mixture which also contains water as the second reactant. The sol-gel process can be realized without using any solvent, but in most cases, it is preferable to use a solvent in the initial mixture in order to control the reaction rate of the process. Alcohol based solvents are commonly used, but there are also another possibilities (*e.g.* acetone). The molar ratio between the different components of the initial mixture significantly influences the final product.

For an initial mixture which includes tetraalkoxysilane and water, hydrolysis reaction in the form:

$$\equiv Si\text{-}OR + H_2O \rightarrow \equiv Si\text{-}OH + ROH \qquad (1)$$

occurs. This is the stage of the sol-gel process. Complete hydrolisis of a tetraalkoxysilane molecule produces a solution of $Si(OH)_4$ in alcohol:

$$Si(OR)_4 + 4H_2O \rightarrow Si(OH)_4 + 4ROH \qquad (2)$$

The hydrolysis can be catalyzed by acidic catalysts *via* an electrophilic mechanism. The reaction rate of the hydrolysis increases with the strength of the acid. Therefore, HCl and HNO_3 are commonly used catalysts. On the other hand, the reaction can also be base-catalyzed *via* a nucleophilic mechanism [8]. The reaction rate of the hydrolysis is also influenced by steric effects and decreases with the size of an alkoxy group. For this reason, TMOS hydrolysis is faster then TEOS one.

The second stage of the process is a polycondensation of the hydrolysis products. Each condensation reaction of two hydrolysis products has the form:

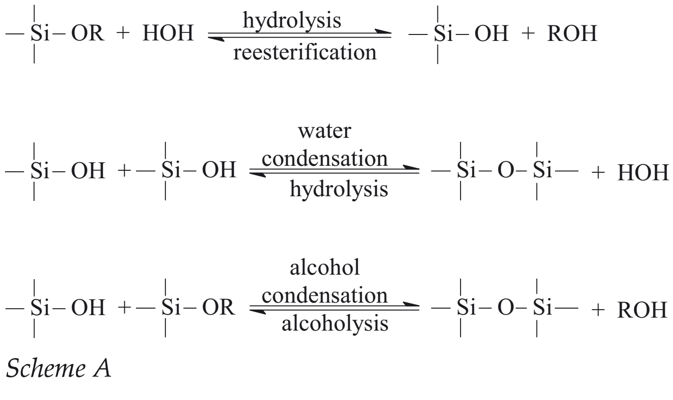
$$\equiv Si\text{-}OH + HO\text{-}Si\equiv \leftrightarrow \equiv Si\text{-}O\text{-}Si\equiv + H_2O \qquad (3)$$

If we consider, for simplicity, an ideal model in which condensation reactions take place only after a complete hydrolysis, so that the reactants are silanols, then a general form which describes the polycondensation stage is given by:

$$nSi(OH)_4 \rightarrow (SiO_2)_n + 2nH_2O \qquad (4)$$

The result of the polycondensation reactions is the formation of three dimensional crosslinked polymer network, leading to formation of sol particles. Further condensation reactions link the sol particles, forming a wet gel. Evaporation of the liquid leads to a dry gel (xerogel), which is porous glass. The polycondensation can be catalyzed by hydrofluoric acid (HF), since F^- ions can replace hydroxyl ion in the hydrolysis product $Si(OH)_4$ and being more electronegative than the hydroxy one, they increace the attraction to other silanols, leading to Si-O-Si bonds [9]. 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. Therefore, the choice of catalyst (acid or alkaline) allows to control a degree of the glass porosity. For example, when HF is used as a catalyst, the porosity increases with increasing concentration of HF [10, 11].

One of the main problems of sol-gel glasses is cracking, which is attributed to inhomogeneous drying [12]. Furthermore, even uncracked glasses suffer from a tendency to develop cracks when introduced into liquids. Since the reaction described by equation (3) is reversible, the presence of water in the glass prevents complete condensation, and large amounts of penetrating water can cause hydrolysis, resulting in cracking of the glass. Heat-



Scheme A

ing the glass to high temperatures causes an evaporation of 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 which enables penetration of liquids only into the pores, while preventing damage to the glass.

The scheme A is a schematic representation of the classical sol-gel process, in which also reversible reaction of alcohol condensation was taken into consideration.

COMPOSITE GLASS/POLYMER HOSTS

Composite glasses are the materials in which organic polymers fill the pores of porous glass. Thus, composite glass contains two different phases, an inorganic skeleton of porous glass and an organic phase. The thermal dehydroxylation described above is followed by impregnation and then polymerization of the organic monomers in the glass' pores. A composite glass was first obtained by Pope and Mackenzie [13], who used methyl methacrylate (MMA) together with a porous silica gel glass. Polymerization of the impregnated MMA was initiated with benzoyl peroxide at 40 °C, leading to the production of a composite glass of high optical and mechanical quality.

A laser gain medium is formed by dissolving of organic dyes in the monomer solution prior to diffusion of the monomer into the porous glass and polymerization. A typical synthesis of a composite glass matrix is described in [14] and [15] and is briefly summarized here.

Composite glass samples were made using a two step process:

— preparation of porous silica gel;

— impregnation of silica gel with dye/MMA solution and polymerization of the MMA.

The dyes were dissolved in MMA monomer to form the solutions of different concentrations in the range of 10^{-6}—10^{-3} mol/liter. Highly porous silica gel bulk glasses (density about 0.7 g/cm^3) were prepared by the sol-gel method and dried by slow heating (100 °C/day) from room temperature to 500 °C. Then the samples were immersed into the dye-doped solution of MMA monomer, which was simultaneously catalyzed by the addition of 2 % of benzoyl peroxide. MMA-dye solution thus diffused into the silica gel glass pores, and polymerized there. After this process of glass impregnation with a dye, the samples were reimmersed in MMA-dye solution, which at this stage was catalyzed for full polymerization by addition of 0.5 % of 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. The density of the composite glass was d = 1.447±0.005 g/cm^3 (measured by Archimedes method) and the refractive index n = 1.472±0.003 [15].

ORMOSIL HOSTS

ORMOSIL usually exhibit lower porosity and enhanced mechanical properties which allow cutting grinding and polishing prior to 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 dyes to be incorporated. Various organic laser dyes have been incorporated into ORMOSIL, derived from polydimethylsiloxane (P) and tetraethoxysilane (T). These sol-gels derived PT-ORMOSIL proved to be good hosts for the laser dyes.

The mechanical and optical properties of a glass, prepared by the sol-gel process, can be improved by modifying of the sol process and using a variety of organofunctional silicone alkoxides. Modified alkoxide precursors [RSi(OEt)$_3$ where R is an organic group such as methyl, vinyl or amyl (methyl-, vinyl- or amyltriethoxysilane) are 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 [16]. Functionalized alkoxides F-R'-Si(OEt)$_3$, where F is a functional group such as amino or isocyanate and R' is an alkyl spacer, enable the dopants to be covalently grafted onto the xerogel matrix, in order to avoid phase separation. After dying optically clear and dense inorganic-organic hybrid xerogels were obtained (30 mm diameter and 15 mm thick) [17, 18]. In our lab ORMOSIL glass samples were prepared by a one step process at room temperature which led to the formation of hybrid organic–inorganic materials. Below the preparation of a typical ORMOSIL laser host is described [19].

ORMOSIL based lasers were prepared by stirring a mixture of tetramethoxysilane (TMOS), methyltetramethoxysilane (MTMOS), 3-glycid opropoxytrimethoxysilane (GLYMO) and water in molar ratio of 1:1:1:5. A few drops of HCl were added to the mixture in order to catalyze the hydrolysis until a completely transparent solution was obtained. After one hour a solution of rhodamine 6G/ethanol or Pyrromethene 597/MMA a few drops of triethoxysilanepropylamine (TESPA) were added to the stirred solution, such that the dye concentration was about $2 \cdot 10^{-4}$ M. After additional stirring, the solution was cast into polyethylene containers with pinholes in the cover and dried in an oven at 40—45 °C. The solution was gelled, aged and dried during 4—6 weeks. Finally the samples were polished. The density of these samples was measured, by Archimedes method, to be 1.33—1.35 g/cm^3.

The use of TESPA or another base is essential for pyrromethene dye samples, since these dyes will not act at low pH [20]. TESPA was chosen for reasons which are now described. Being an aminoorganotriethoxysilane, TESPA takes part in the sol-gel process, and its silicon is incorporated into the silicate array during the polycondensation reactions. Additionally, its amine can be covalently bonded to an epoxide group, which is bonded to the silicate array. This mechanism may increase the degree of cross-linking of the material. However, since TESPA is a condensation catalyst, its molar fraction in the mixture has to be limited, since fast polycondensation increases the porosity.

POLYURETHANE

A new organically modified zirconia silica polyurethane was found to be an excellent host for organically active species [1].

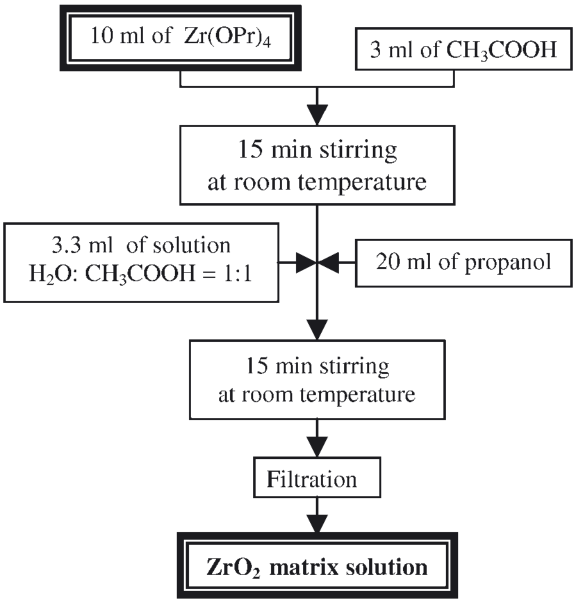
The hybrid material zirconia-silica-polyurethane (ZSUR) was obtained by using three precursors:

— poly(ethylene glycol) chain covalently linked by urethane bridges with triethoxysilane groups synthesized separately,

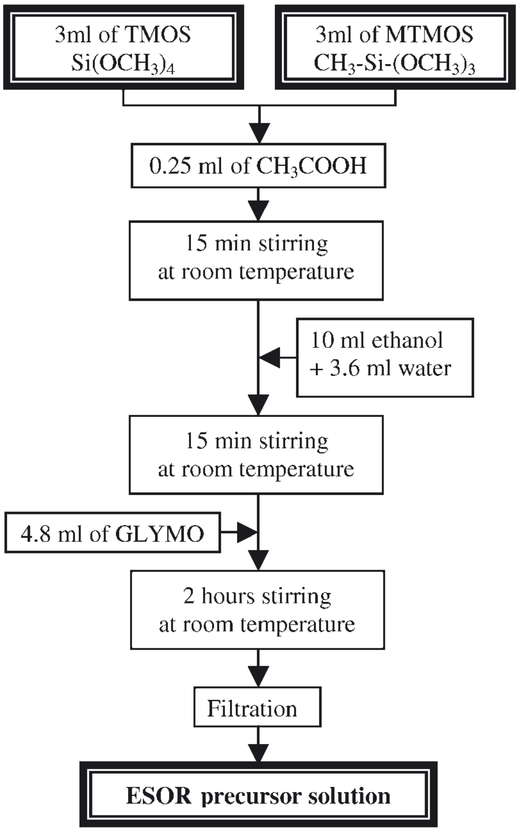
— epoxy-silica-ORMOSIL precursor,

— a zirconium oxide precursor.

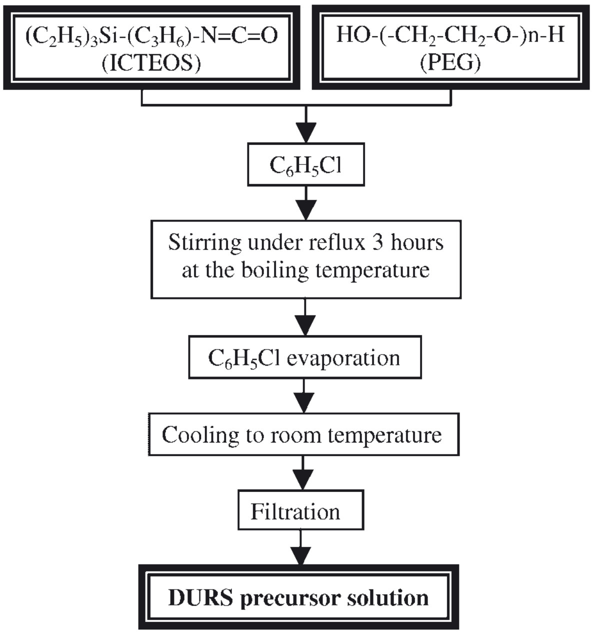
The procedure of ZSUR preparation is shown in the schemes B—E. The final solution of ZSUR was obtained from diurethane siloxane (DURS), epoxy-silica-ORMOSIL (ESOR) and ZrO_2 precursor solutions. ZrO_2 matrix solution was obtained from zirconium n-tetrapropoxide in propanol and acetic acid was used as a chelating agent to stabilize the zirconium oxide precursor. DURS-oligomer precursor was synthesized by reaction of 3-isocyanatopropyltriethoxysilane (ICTEOS) and poly(ethylene glycol) (PEG-600) in the molar ratio 2:1. The reagents were stirred in chlorobenzene at boiling temperature under reflux for 3 hours. The residual solvent was evaporated and DURS inorganic-organic hybrid oligomer material was obtained. Isocyanate functionalized siloxane coupled with the polyol to form urethane linkage is known as a system improving bond strength. The epoxy-silica-ORMOSIL (ESOR) precursor was obtained from MTMOS and GLYMO in molar ratio 1:1:1. In order to obtain ZSUR, these two composites, DURS and ESOR were combined with a zirconium oxide



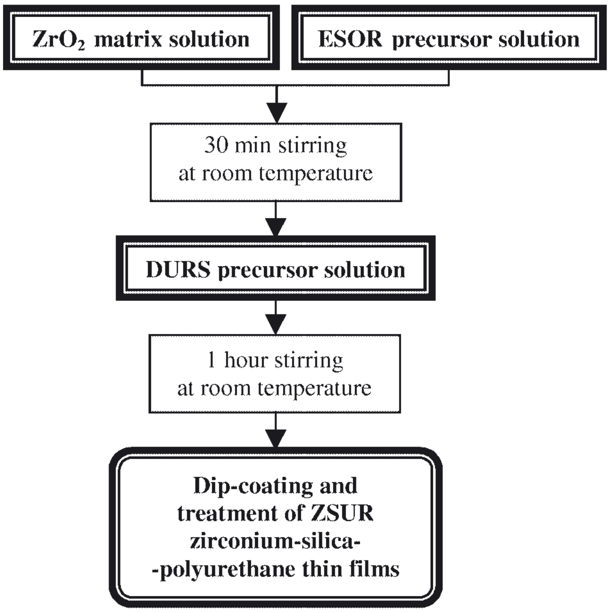
Scheme B



Scheme C



Scheme D



Scheme E

(ZrO_2) matrix, which was used as an inorganic hetero network and as a promoter catalyst for the epoxy polymerization. Although the reaction at room temperature between zirconium and epoxy groups is limited (about 27 % of unreacted epoxy groups) as well as at high temperature (70 °C/8 hours, about 25 % of unreacted epoxy groups), in the case of ZSUR unreacted epoxy groups (at least 24 %) can be reacted with secondary amino groups in urethane linkage of DURS. The nominal molar ratio in the final sol SiO_2:ZrO_2 was 69:31; and of urethane of epoxy was 24:76.

Due to the strong chemical bonding between the inorganic coupling agent isocyanatotrietoxysilane and the organic polymer — poly(ethylene glycol), GLYMO and zirconium oxide, it is possible to combine the strength and hardness of sol-gel matrices with the processibility and ductility of polymers which offer better mechanical properties (elasticity, flexibility) and higher chemical stability.

TUNABLE LASERS BASED ON SOL-GEL PROCESS

Solid state tunable dye lasers which use laser dyes embedded in a sol-gel matrix as their gain medium were first prepared in 1989 [21, 22]. The first lasers were based on the orange perylene derivative BASF-241 dissolved in methyl methacrylate (MMA), which was able to diffuse into porous glass and then undergo polymerization. Thus, the resulting laser host was a composite of porous sol-gel glass with poly(methylmethacrylate) (PMMA)/ dye filling the pores [22, 23].

Since then, many variations of these lasers have been demonstrated, including the use of different dyes (*e.g.* rhodamines, polymethenes, perylimides) [24], and different solid state matrices such as ORMOSIL, silica gels, xerogels, alumina gels and composite glass/polymer matrices [24]. Thin films of dye doped sol-gel formed using a simple dipping procedure have been shown to function as thin-film lasers [25, 26] and active waveguides [27]. A narrow linewidth sol-gel based dye laser was demonstrated by Lo *et al.* [28]. Although there are now many new fixed wavelength solid state lasers available (*e.g.* various diode lasers and diode-pumped solid state lasers), organic-dye lasers are still one of the simplest continuously tunable lasers, and they remain an area of active study [29, 30]. Organic dye lasers have generally been based on liquid-dye solutions. Such lasers often use a flowing volatile solvent, which may be messy, flammable, and can present a health hazard to the operators of these lasers. This motivates the development of solid state dye lasers, which do not suffer from the problems mentioned above. While high power dye-lasers require a flowing liquid dye system to dissipate heat, solid state dye lasers have very good prospects for replacing liquid dye systems in low and medium power applications, as well as in low repetition rate pulsed systems. There are other applications for sol-gels doped with organic dyes, such as light sources and sensors, but in this paper we focus on their use in lasers.

Both the solid state host and the organic dyes used in solid state dye lasers must be optimized in order to achieve good laser performance. The solid host materials should show high optical quality and transparency, and must also have appropriate thermal properties (for example, the ability to dissipate heat as quickly as possible). The dyes must be selected for appropriate spectral properties (to match the desired laser wavelengths), compatibility with the solid state hosts and photostability.

The first sol-gel/dye lasers were based on the perylimide dye perylene orange (Reisfeld R. 1989 cited in [33]). This dye is known as showing high photostability. The threshold energy (the minimal pump energy/pulse needed for laser) and slope efficiency for three different solid hosts are given in Table 1.

Table 1. Laser performance of BASF 240 (perylene orange) [3]

Matrix	Threshold energy	Slope efficiency
Composite	0.21 mJ	36 %
ORMOSIL	0.22 mJ	30 %
PMMA	0.31 mJ	11 %

Lasers based on the pyrromethene family of dyes have been very actively studied due to the high reported efficiency of these dyes [1].

The results obtained with a number of transverse pumped sol-gel/dye lasers are presented in Table 2. In each case, the lasers were pumped with the second harmonic output of a Q-switched Nd:YAG laser, which emitted pulses of about 10 nsec width at 532 nm. The pump pulse energy was controlled and varied between 1 and 30 mJ/pulse.

The transverse pumping arrangement provides a simple means for obtaining lasing.

However, we note that at the dye concentrations used, most of the pump energy is absorbed within the first 100 microns of the surface. As the dye is photobleached, the pump beam can move farther into the bulk, and the laser beam position and shape will change. For this reason, much of the recent works on such lasers use a longitudinal pumping arrangement [1]. Nevertheless, comparative studies between laser systems can be done with the simpler transverse arrangement by using longitudinal pumping with frequency doubled Q switched Na YA6 laser 86 % slope efficiency was reported [1].

Laser performance of pyrromethene (PM) dyes in several matrices is presented in Table 2 [31].

Table 2. Laser efficiency and photostability (longevity) of pyrromethene (PM) in glass matrices [32]

Dye	Matrix	Threshold energy	Initial slope efficiency	Half-life longevity (number of 6 mJ pump pulses)
PM 567	ORMOSIL 1	0.23 mJ	32 %	9500
PM 580	ORMOSIL 1	0.22 mJ	31 %	11 000
PM 580	ORMOSIL 2	0.21 mJ	38 %	20 500
PM 580	Composite	0.24 mJ	30 %	9000
PM 597	ORMOSIL 1	0.21 mJ	38 %	11 500
PM 597	ORMOSIL 2	0.20 mJ	43.3 %	22 000
PM 597	ORMOSIL 3	0.21 mJ	36 %	63 000
PM 597	Composite	0.21 mJ	42 %	29 000

From the tables we can learn that all the three PM dyes are efficient, but in our conditions, PM 597 shows the best performance with the highest efficiency (43.3 % in ORMOSIL 2 and 42 % in composite glass). The photostability results can be normalized by calculating the accumulated energy pumped for 1 mol of dye in the active region, during the decay of the dye laser output energy to 50 % of the initial value. In this case considering the data, the results of 135,000 pump pulses half life longevity of PM 597/PMMA and 63,000 pulses for PM 597/ORMOSIL 3, correspond, respectively, to the impressive values of 120 GJ/mol and 55 GJ/mol.

Lasers obtained by impregnation of sol-gel glasses with perylimides where the dyes are enclosed in the pores of the glass, seem to be far the most photostable system.

PROSPECTS FOR IR LASERS

So far no laser performance in IR range has been reported. However several recent reports provide information on incorporation of several IR dyes into sol-gel glasses in [3]. Report concerns IR dye 1,1″,3,3,3′,3′-hexamethylindotricarbocyanine incorporated into several sol-gel matrices of silica, aluminum, titanium and zirconium oxohybride organic coating. The emission of the glasses occurred around 800 nm. Dyes emitting at longer wavelength one micron incorporated in composite glasses have been extensively studied by the group Casalboni as described in [3]. The authors studied four infrared polymethine dyes absorbing in near IR region (0.8—1.1 μm) and emitting around 1.2 μm. The molecules were embedded in ORMOSIL material synthesized by a sol-gel method. The samples investigated were prepared as films, deposited on glass substrates. Steady-state absorption and emission measurements have been accomplished for the chromophores in solution as well as in hybrid organic-inorganic films in order to determine the effect of the solid cage on the optical properties of the chromophore.

A near infrared dye laser (HITC) was incorporated in a wide variety of different transparent sol-gel matrices such as silica or aluminum, titanium and zirconium oxo polymers and inside hybrid organic-inorganic coatings. Absorption and emission properties are reported. The chemical stability of HITC depends on the residual water content and the acidity of the matrix. Better stability is obtained when the dye is embedded in silica gels or hybrid organic-inorganic matrices made of a siloxane network crosslinked with nanosized zirconium oxo particles (Lebeeau 1993 cited in ref. [3]).

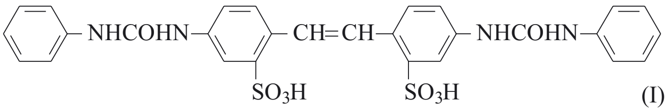
BLUE AND UV LASERS

The research for blue and UV operating sol-gel lasers began in the middle of nineties (Gvishi R. 1995 cited in [3] report on spectroscopic study of blue laser dyes). The dyes: didecyl para-polyphenyl heptamer (DDPPH), didecyloxy para-polyphenyl heptamer (DDOPPH) and bisbenzothiazole 3,4-didecyloxy-thiophene (BBTDOT) were studied. No laser operation could be detected that time.

Blue laser operation was reported by Lam cited in [3]. This was achieved by silica slabs doped by coumarin 460 (C460). The tuning range of the doped silica laser extended from 468 to 494 nm. The conversion efficiency of the blue laser was 5.5 %.

We have studied recently the spectroscopic properties of a fluoroscence laser dye 4,4′-dibenzylcarbamidostilbene -2,2′-disulfonic acid [called Direct White (DW), formula (I)] [32] incorporated into hybrid matrices as a potential blue laser dye.

The choice of DW as a blue laser dye is based on stilbene derivatives (which are known as color with high photostability) and the presence of isolating groups,



(I)

such as one ethylene (-CH=CH-) and two carbamide groups (-NHCOHN-) leading to the intermolecular color shift effect [13] to UV range of spectrum and allowing the emission in the blue region. Detailed description of this blue laser dye can be found in [32].

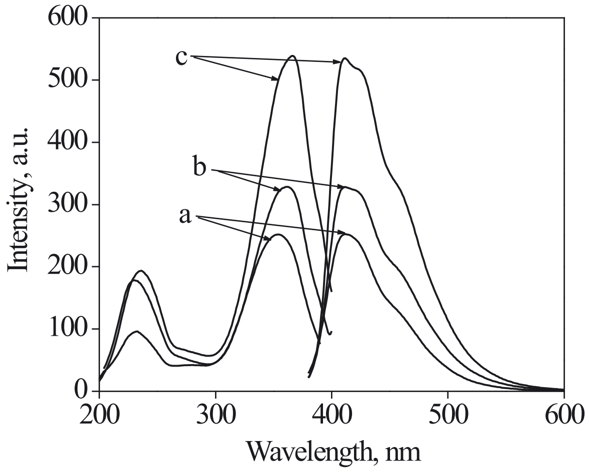


Fig. 1. Excitation and emission spectra of DW dye incorporated in zirconia (a), zirconia-GLYMO (b) and ZSUR (c) thin films [31]

The emission and excitation spectra of DW incorporated in zirconia, zirconia-GLYMO and ZSUR thin films are shown in Fig. 1.

NANOPARTICLES IN GLASSES PREPARED BY SOL-GEL METHOD — QUANTUM SIZE EFFECTS

Semiconductor nanocrystals (NCs) in transparent media have recently attracted attention due to their properties and promising applications in the non linear optics and optical switching. Nanocrystalline semiconductors exhibiting quantum size effects have been prepared and studied in a number of different forms, mainly as dispersed colloidal particles in a liquid or solid matrix but also in thin films. The incorporation of CdS into silica film and into zirconia film prepared by sol-gel method has been reported previously [33—37].

When the diameter of a semiconductor crystallite approaches, or becomes smaller than the bulk exciton diameter, changes occur in the energy band structure. Since the levels are confined to potential wells of small lateral dimensions, quantization occurs, resulting in increased spacing between levels as crystal size becomes smaller. The effect is observed as blue shift in the absorption and emission spectra with decreasing crystal size. These changes in the absorption spectrum of materials with changing particle size have been used to illustrate the quantum size effect (QSE).

From theoretical point of view these materials provides the models for three dimensional quantum confinement and allow identification of the excited states. The energy states of the quantum dots are positioned between the discrete energy levels of atoms or bands of molecules, and the broad band of the condensed phase.

The basic ideas of quantum confinement or quantum wells were introduced in 1970s. In these nanoclusters, the dimensions of the wave functions of the electron-hole pair (exciton) in the lowest excited state of the nanocluster are comparable to the physical size of the particle. This quantum confinement of the exciton means that the continuum band of energies becomes more molecular in character, with narrow ranges of energy and line structure in the optical spectra. From chemical point of view, less delocalization means less energy stabilization; a reflection of this is that the absorption band for direct transmissions of nanosized semiconductor clusters is shifted to higher energies than in the extended bulk parent materials. The "photo charging" of the semiconductor particle, that is, photo inducting high electron concentration into a narrow conducting band with a small effective density of states, also changes the band gap and the resulting absorption edge.

Generally, the blue shift of the exciton absorption peaks in discussed in two cases: one is valid for the excitons having an effective Bohr radius (R) much larger than the crystal size (a_0) and the other is for exciton having an effective radius much smaller than the crystal size ($a_0/R>4$). These two regimes are named the "electron-hole confinement" and the "exciton confinement", for which energies are approximately given by:

$$E = E_g + (\hbar^2\pi^2)/(2\mu a_0^2) \tag{5}$$

$$E = E_g + (\hbar^2\pi^2)/(2Ma_0^2) \tag{6}$$

where: μ — *reduced mass*, M — *translation mass of the exciton.*

Many theoretical models for the expected variation of effective bandgap have been proposed. The most commonly used, at least until recently, was the effective mass approximation, based on parabolic energy bands, used by Efros and Efros [38] and Brus [39]. This model treats the particles as a sphere-boy confining the electrones and holes with an infinite potential barrier, including a correction for coulombic interaction between electrons and holes. In general, the lower excited state energies can be calculated within the effective mass approximation using the different mass for the conduction and valence bands. In addition, the Coulomb interaction can be included to give an approximate expression for the lowest energy [40].

$$E^* = E_g + \frac{\hbar^2\pi^2}{2a_0^2}\left[\frac{1}{m_e}+\frac{1}{m_h}\right]-\frac{1.8e^2}{\varepsilon a_0} \tag{7}$$

where: ε — *dielectric constant of the semiconductor,* E_g — *band gap of the bulk material,* e — *electron charge.*

The quantum size effect is dependent on the crystal size a_0. The effect increases with the decreasing crystal size [41, 42].

Compared to the well-known II-VI and III-V materials, PbS have larger exciton radius (a_B = 18 nm) and a small fraction of atoms at the surface at the same carriers confinement regime. The absorption edges of PbS nanocrystals cover the 0.5—2.5 μm wavelength range which are important for telecommunication. More recent reports discuss the incorporation of PbS nanocrystals into polymers [43], glasses [44] and into sol-gel materials [45—49].

The sol-gel process extends the conventional glass melting methods, as it allows incorporation of semiconductor NCs at low temperatures and predetermined concentration and size. Furthermore, the sol-gel technology has advantages in the formation of films with controllable thickness, three-dimensional protection of NCs, prevention of NCs growth, aggregation and oxidation. The widely investigated matrix materials are SiO_2, ZrO_2, SiO_2/TiO_2 and ZrO_2/ORMOSIL. PbS NCs of sizes 2—4 nm in ZrO_2 [46], 2—3.5 nm in SiO_2/TiO_2 [47] and 4—8 nm in ZrO_2/ORMOSIL matrix [48] have also been studied recently.

We have reported [49] the incorporation of PbS NCs ranging between 4—8 nm into ZSUR matrix obtained by sol-gel method. The sizes of the particles were controlled by temperature treatment and by concentration of PbS in ZSUR matrix. PbS NCs sizes were determined by transmission electron microscopy (TEM) measurements. The quantum size effect could also be extracted from optical absorption and photoluminescence spectra. The new matrix allows incorporation of 5—50 % of PbS forming a characteristic structure of dendrite by reaction of lead acetate with ammonium thiocyanate in sol-gel matrix. The sol precursors of the matrix for ZSUR contained zirconium oxide (ZrO_2) matrix solution, TMOS, GLYMO or DURS were synthesized separately. ZrO_2 matrix solution was obtained from zirconium *n*-tetrapropoxide in propanol, and acetic acid was used as a chelating agent to stabilize the zirconium oxide precursor.

Table 3 summarizes the energy of the first exciton transition and particles size as a function of annealing temperature and mole per cent of PbS material within the different matrices. Particle size as calculated as described in [50].

In [51] preparation of indium arsenide (InAs) was described. The use of a hydrophobic polymer, polystyrene serves to encapsulate the nanocrystals inside the sphere while maintaining many of their original properties. The obtained nanospheres were characterized by transmission electron microscopy and scanning electron microscopy, chemically by energy dispersive X-ray spectroscopy, and optically by a single particle fluorescence spectroscopy.

Indium arsenide nanocrystals embedded in silica glasses was also obtained by Yang *et al.* [52].

III-V semiconductor InAs NCs embedded in silica glasses was synthesized by combining of sol-gel process and heat treatment in hydrogen gas. The size of InAs NCs can be easily controlled *via* changing In and As contents in the initial materials and the heating temperature in hydrogen gas atmosphere. Absorption measurements indicate a blue shift in energy with a reduction of In and As contents in SiO_2 gel glasses as a result of quantum confinement effect. A near-infrared photoluminescence with peak at 3.40 μm was observed at 6 K under 514.5 nm Ar+ laser excitation from InAs NCs embedded in the silica gel glasses.

Table 3. Optical properties of PbS NCs in ZSUR and ZrO_2 sol-gel films

Content of PbS in ZSUR films mole %	T_{an} °C	Energy of first exition transition eV	Particle size nm	Content of PbS in ZrO_2 films mole %	T_{an} °C	Energy of first exciton transition eV	Particle size nm
20	130	2.4	2.5	20	200	2.05	2.7
	170	1.65	3.0		250	1.65	3.0
	200	1.35	3.3		300	1.2	3.6
	220	1.92	2.7		350	1.35	3.3
30	130	1.3	3.5	30	200	1.1	4.0
	170	1.1	4.0		250	1.02	4.7
	200	1.35	3.3		300	0.92	5.7
	220	1.70	2.9		350	1.0	5.0

CONCLUSIONS

We have presented the variety of host matrices prepared by the sol-gel method. Examples of laser dyes forming solid tunable lasers in the host materials and their laser characteristics are given. A short description of nanoparticles in the variety of host matrix mainly deals with II and VI semiconductors and the most recent findings concerning III and VI semiconductor in silica matrix were presented.

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