

Review

Fluorescence-active Waveguides by the Sol-Gel Method. Theory and Application

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Z. Naturforsch. **2014**, *69b*, 131 – 140 / DOI: 10.5560/ZNB.2014-3301

Received November 14, 2013

Active waveguides can be applied in environmental sensors, telecommunication, medicine, computers and electronic convertors. The sol-gel technology allows formation of planar and fiber waveguides incorporating fluorescent organic and inorganic dopants. Several sol-gel matrices which enable the incorporation of lanthanides and their complexes and fluorescent organic molecules are presented. A short description of the theory of luminescence of lanthanides is outlined and examples of active waveguides known today are given. The mechanisms for infrared to visible light conversion are explained. Suggestions for practical approach to novel active waveguides are given. Increase of fluorescence as a result of an interaction of fluorescent species with metal nanoparticles is presented.

Key words: Sol-Gel Method, Waveguides, Fluorescence

Introduction

Active waveguides are of great importance in designing environmental and biological sensors, active components in telecommunication, medicine, computers and electronic convertors [1 – 3].

They may be formed as fiber waveguides or plates. The ways by which they can be prepared are numerous. One of the easiest ways is the sol-gel method which allows at relatively low temperature an incorporation of organic molecules [4, 5] or metal ions [6].

The worldwide needs for optical components are growing exponentially in the fields of optical amplifiers, sensors, biological and medical applications, electrooptic modulators and non-linear optical materials. In this respect sol-gel-derived materials may find an important role as a variety of compositions can be prepared at relatively low temperature, and the sol-gel matrices can incorporate fluorescent ions, complexes and noble metal nanoparticles (NPs) which increase the fluorescence properties if properly designed.

In this paper the sol-gel methods are briefly described, and the synthesis of a variety of host matrices are given. The theory of absorption and luminescence of the rare earth ions is outlined. Several examples of active waveguides prepared by the sol-gel method are presented, and some ideas for further development in the field are proposed.

General Description of the Sol-Gel Process

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 which 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 reference [4], followed by a paper describing incorporation of metal

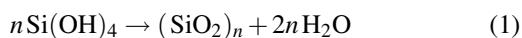
ions into sol-gel glasses [6] and thin-film sol-gel coatings [5]. The precursor solution for sol-gels contains various metal alkoxides or inorganic sols [7]. These solutions can be applied by dip coating, spin coating or laminar coating. The most common precursors result in silicate, titania, germanate, alumina, zirconia, tungstate vanadates, and ormosils [8].

The sol-gel process is based on hydrolysis and polycondensation reactions of metalorganic compounds such as alkoxy silanes. Most common examples are the family of tetraalkoxysilanes which have the general form Si(OR)_4 , where OR is an alkoxy group, mostly, ethoxy or methoxy. The names tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS) are given to these liquid compounds. TEOS or TMOS are used as components in starting mixtures which contain also 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 (alcohol for example) in the starting mixture in order to control the reaction rate of the process. The molar ratio between the different components of the starting mixture has a great influence on the final product.

In the starting mixture which includes a tetraalkoxysilane and water, hydrolysis reactions of the form $\equiv\text{Si}-\text{OR} + \text{H}_2\text{O} \rightarrow \equiv\text{Si}-\text{OH} + \text{ROH}$ occur. This is the first stage of the sol-gel process. The complete hydrolysis of a tetraalkoxysilane molecule proceeds according to $\text{Si(OR)}_4 + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4\text{ROH}$. The hydrolysis can be catalyzed by following an 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, base also can catalyze the reaction, by a nucleophilic mechanism. The reaction rate of the hydrolysis is also influenced by steric considerations and is decreased with the size of the alkoxy group. For this reason, TMOS hydrolysis is faster than TEOS hydrolysis.

The second stage of the process consists of a polycondensation of the hydrolysis products – according to $\equiv\text{Si}-\text{OH} + \text{HO}-\text{Si}\equiv \rightleftharpoons \equiv\text{Si}-\text{O}-\text{Si}\equiv + \text{H}_2\text{O}$.

If we consider, for simplicity, an ideal model in which condensation reactions take place only after a complete hydrolysis, a general form which describes the polycondensation stage is:



The result of the polycondensation reactions is the creation of an inorganic three-dimensional crosslinked polymer, leading to the formation of sol particles. Further condensation reactions link the sol particles forming wet gels. Evaporation of the solvents leads to a dry gel (xerogel).

The glass obtained by the sol gel process is porous [9, 10]. In the preliminary stage the polycondensation can be catalyzed by hydrofluoric acid (HF), since the more electronegative F^- ions can replace hydroxyl ions in the hydrolysis products. The rate of the condensation reaction influences the glass porosity. Higher condensation reaction rates result in higher porosity. 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.

Heating the glass to high temperatures evaporates the water leading to de-hydroxylation and 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 , to produce a glass structure which enables penetration of liquids only into the pores, while preventing damage of the glass. The mechanical and optical properties of glasses prepared by the sol-gel can be improved by modifying the sol process and using a variety of organo alkoxides. The modified organo alkoxide precursors RSi(OEt)_3 where R is a non-hydrolyzable group such as methyl, vinyl or amyl (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 $\text{X}-\text{R}'-\text{Si(OEt)}_3$, where X is a chemical function such as an amino or isocyanato group and R' is an alkanediyl spacer, allow to covalently graft onto the xerogel matrix to avoid phase separation and consequently to increase the concentration of the guest molecules.

Zirconia is a suitable host for active waveguides because of its high damage threshold and its superior properties in terms of mechanical strength, fracture toughness, and mechanical durability. Its high refractive index is barely affected by thermal expansion and low phonon energy [11]. Zirconia causes no photocatalytic degradation of the organic dopants taking into

account the large gap between valence and conduction bands [12].

Organic-inorganic matrices

The various characteristics of the sol-gel process (organometallic precursors, organic solvents, low processing temperatures, processing versatility of the colloidal state.) allow the introduction of 'fragile' organic molecules inside an inorganic network. Inorganic and organic components can be mixed at the nanometer scale, in virtually any ratio, leading to the formation of the so-called hybrid organic-inorganic nanocomposites. These hybrids are extremely versatile in their composition, processing and optical and mechanical properties. The properties of hybrid materials do not depend only on the interface between both phases. The general tendency is to increase the interfacial interactions by creating intimate mixing and/or interpenetration at the nanometer scale between both components. The nature of the interface between the organic and inorganic components allows classifying these hybrid nanocomposites into two groups. Class I corresponds to all those systems where organic and inorganic components show only weak interactions based on Van der Waals, hydrogen bonding or electrostatic forces. On the contrary in class II materials, at least parts of the organic and inorganic components are linked through strong chemical bonds (covalent or iono-covalent).

Among hybrid compounds, siloxane-based materials present several advantages for the design of materials for photonics: firstly, many precursors are commercially available or can be easily modified or synthesized; secondly, the control of the precursor reactivity can be achieved by using acidic, basic or nucleophilic catalysts; thirdly, transparent films or monoliths having a good mechanical integrity can be easily processed; and fourthly, the resulting materials are generally not toxic.

Numerous siloxane-based hybrid organic-inorganic materials have been developed in the past few years. They are yielding many interesting new materials, with improved mechanical properties tunable between those of glasses and those of polymers. Sol-gel processed hybrid materials for optical devices, new sensors and biosensors, new catalysts or membranes have been reported to have high efficiency, good selectivity and stability [8, 13].

A new matrix of zirconia-silica-polyurethane (ZSUR) was reported by us [14]. This matrix allows incorporation of a wide range of photonic molecules and possesses high mechanical and thermal stability and a high refractive index [15].

The matrix of polyethylene-urethane-silica also possesses high mechanical and thermal stability and a high refractive index. By combining the strength and hardness of sol-gel matrices with the processability and ductility of polymers, novel transparent hybrid materials can be obtained. Diurethane siloxane (DURS) is synthesized from 3-isocyanatopropyltriethoxysilane (ICTEOS) and polyethyleneglycol (PEG), chlorobenzene being used as a solvent. The epoxy-silica-ormosil (ESOR) precursor was obtained from tetramethoxysilane (TMOS) and 3-glycidoxypipropyl trimethoxysilane (GLYMO). These two types of ormols were combined with a 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. However, the reaction is limited at room temperature (about 27% unreacted epoxy groups) and still slow at a temperature of 70 °C/8 hours (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 the urethane linkages of DURS. Due to strong chemical bonding between organic and inorganic parts, the hybrid materials offer superior mechanical properties (elasticity, flexibility) and are suitable for the incorporation of organic dyes.

The hybrid materials can be obtained by using three precursor composites: a) a polyethyleneglycol chain covalently linked by urethane bridges with triethoxysilane groups synthesized separately, b) an epoxy-silica ormosil precursor and c) a zirconium oxide precursor. The solubility of most laser dyes is limited in pure hydrophobic or hydrophilic matrices, which can cause migration and aggregation of the dyes, resulting in decreased efficiency when used in a laser. The novel organic-inorganic ORMO-CER 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. Polymethylmethacrylate (PMMA), polyethyleneglycol dimethacrylate

(PEGDM), polyurethane (PU) and various epoxides have been also used as polymer hosts for solid state dye lasers [16].

List of common precursors for the preparation of optical materials

1) *Tetraalkoxysilanes* (general form: Si(OR)_4):

TEOS – Tetraethoxysilane, $\text{Si}(\text{OC}_2\text{H}_5)_4$
TMOS – Tetramethoxysilane, $\text{Si}(\text{OCH}_3)_4$

2) *Organoalkoxysilanes* (general form: $\text{R}'-\text{Si-(OR)}_3$):

TMSPMA – 3-(Trimethoxysilyl)propylmethacrylate, $\text{C}_7\text{H}_8\text{O}_2-\text{Si}(\text{OCH}_3)_3$
GLYMO – 3-Glycidoxypropyltrimethoxysilane, $\text{C}_6\text{H}_{11}\text{O}_2-\text{Si}(\text{OCH}_3)_3$
MTMOS – Methyltrimethoxysilane, $\text{CH}_3\text{Si}(\text{OCH}_3)_3$

3) *Zirconia precursor:*

Zirconium-*n*-propoxide, $\text{Zr}(\text{OC}_3\text{H}_7)_4$

4) *Organic monomers for polymerization:*

MMA – Methyl methacrylate, $\text{CH}_2\text{C}(\text{CH}_3)\text{COOCH}_3$
EGDM – Ethyleneglycol dimethacrylate, $\text{CH}_2\text{C}(\text{CH}_3)\text{COO}-\text{CH}_2-\text{CH}_2-\text{OOC}(\text{CH}_3)\text{CH}_2$

Hosts for the incorporation of fluorescent dyes

The matrices used for preparation of solid-state dye lasers in our laboratory are:

- 1) Composite sol-gel glass/PMMA polymer system
- 2) Organically modified silicates (ORMOSIL)
- 3) Zirconia-silica-polyurethane (ZSUR) ormoser

Composite glass/polymer hosts

First, a standard sol-gel glass is prepared using acidic catalysis, then MMA with 1.5×10^{-4} M dye laser dye is allowed to diffuse into the porous glass. The monomers are polymerized by drying for a few weeks at 40 °C, after which the impregnated samples are polished to obtain high optical quality [17].

Organically modified silicates

ORMOSIL: TMOS, MTMOS and GLYMO are commonly used as precursors to create a sol-gel glass in which the dyes are incorporated in a one-step process [18].

Zirconia-silica polyurethane (ZSUR)

The procedure for the preparation of a novel OR-MOCER hybrid matrix ZSUR can be found in reference [19]. The final solution of ZSUR was obtained from DURS (di-urethane siloxane), ESOR (epoxy-silica ormosil) and ZrO_2 precursor solutions.

The DURS oligomer precursor was synthesized by reacting ICTEOS (3-isocyanatopropyltriethoxysilane) and PEG-600 (polyethylene glycol) with the molar ratio of 2 : 1. The reagents were stirred in chlorobenzene under reflux for 3 h. The residual solvent was evaporated, and a DURS inorganic-organic hybrid oligomer material was obtained. Isocyanato-functionalized siloxanes coupled with a polyol to form urethane linkages are known as systems improving bond strength. The immobilization of laser dyes in such polymer hybrid matrices is expected to be important for their use as laser gain media for the visible and near infrared wavelength regions.

The epoxy-silica-ormosil (ESOR) precursor was obtained from TMOS and GLYMO with a molar ratio of 1 : 1. First, TMOS was hydrolyzed at room temperature for two hours (TMOS : $\text{CH}_3\text{OH} : \text{H}_2\text{O} : \text{CH}_3\text{COOH} = 15.0 : 12.8 : 7.2 : 2.4$), then GLYMO was added and the mixture stirred for 3 h at room temperature.

Zirconium-*n*-tetrapropoxide was hydrolyzed using a procedure similar to that reported in reference [20]. In order to obtain ZSUR, these two composites, DURS and ESOR, were combined with a zirconium oxide (ZrO_2) matrix, which was used as an inorganic hetero network and as a promoter catalyst for the epoxy polymerization. The nominal molar ratio in the final sol was $\text{SiO}_2 : \text{ZrO}_2 = 69 : 31$; for urethane : epoxy it was 24 : 76.

Due to strong chemical bonding between the inorganic coupling agent (isocyanatoalkyl)triethoxysilane and the organic polymer (polyethylene glycol), GLYMO and zirconium oxide, it was 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.

Organic fluorescent dyes

Organic fluorescent dyes generally contain extended conjugated π -bond systems which determine the resonant optical absorption bands of the dye molecule. To a first approximation, the conjugated π electrons can be analyzed as a quantum mechanical particle in a potential well. 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 usually 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 metal ions) lends itself to various photochemical processes that result in photobleaching. They can also form dimers or aggregates, often resulting in large changes in their spectral properties.

Active Fluorescent Materials Based on Sol-Gel Technology

Active fluorescent materials are prepared by doping sol-gel glasses during their preparation with stable luminescent organic dyes, lanthanide complexes or lanthanide ions. The obtained materials can be applied either as chemical sensors or active waveguides excited by a light-emitting diode (LED). The infrared fluorescence can be upconverted to visible light.

The theory of fluorescent properties of organic dyes can be found in the book by F. P. Schäfer [21].

Chemical sensors and biosensors are small devices capable of continuously and sometimes reversibly recording the concentration of a (bio)chemical species. Sol-gel-based chemical sensors are the chemical equivalent to physical sensors which, for instance, measure the light intensity, temperature and pressure. Typical chemical species, for which a current interest exists in terms of sensing, include pH, oxygen and pollutants. Typical species for which biosensors have been developed include glucose, cholesterol, phenytoin, immunoglobulins, and pollutants such as atrazine.

The increasing popularity of sol-gels in sensor applications results from a number of interesting features including the following: (a) a sol-gel can be manufactured at low temperatures and physiological pH values; (b) their microstructure can be controlled to

some extent; (c) they are optically transparent from the UV to the near infrared; (d) the index of refraction can be varied to some extent; (e) they provide a certain permeation selectivity in that only small ions and molecules can enter their network, while large molecules such as proteins and whole cells remain outside the matrix (hence, interactions inside the matrix are usually limited to small molecules and ions); (f) they are chemically and mechanically stable; and (g) the fabrication procedure enables any desired geometric shape to be tailored. Typical configurations of doped sol-gel glasses are, for example, thin films deposited onto glass plates or microscope slides, tubes, powders or monolithic discs, and especially optical waveguides [22].

Sol-gel matrices doped with organic or bio-organic molecules are used as optically active materials, including filters and lightguides, luminescent materials and laser components.

Sol-gels are considered to be of particular use in connection with evanescent-wave optical-fiber or integrated optical waveguide sensing.

Sol-gel technology was applied in optical fiber sensor technology in which the fluorophore indicator was immobilized in a gel coated on a fiber, and its characteristic optical spectra were analyzed as a function of pH. A response to pH was obtained in the range of pH 5–9. The sol-gel process for low-temperature fabrication of porous glass has been used to entrap chemically sensitive dyes for fiber sensor applications. Evanescent wave fluorescence excitation was used to examine the behavior of an unclad fiber which was dip-coated with a thin layer of dyed sol-gel cladding which was entrapped within the indicator [22].

Some examples of active sensors prepared by the sol-gel method

Active waveguides based on visible light excitation

Active fluorescent waveguides can be prepared in different configuration in which the fluorescent species can be excited by visible light utilizing the transparency of the glassy waveguide matrix or by infrared light created by the an LED.

Some examples of systems excited by visible light are presented in reference [23].

A silica glass plate prepared by the sol-gel method loaded with malachite green [24] was exposed to acid

atmosphere and the fluorescence measured as a function of time of penetration. A reversible behavior of the proton in and proton out process was observed during several hours [11]. A similar behavior was found also in zirconia glass waveguides [25]. Optical waveguide sensors using visible light excitation by an argon laser were proposed for evanescent light excitation. In this configuration the molecules of the investigated material were incorporated in the cladding on a transparent waveguide which was excited by an argon laser. The evanescent light allowed exciting of the fluorescent material. This system was proposed as a sensor for pH [26].

Active waveguides based on infrared (IR) excitation

A modern trend of scientific and technical solutions is aimed on the miniaturization of systems. Therefore it is clear that the future waveguiding-based systems will be designed in this direction. Much of the present research is based on small excitation and detection sources such as LEDs in lasers and nanosized semiconductors. The classical work by Auzel [27] allows conversion of infrared to visible light by the processes shown in Fig. 1.

As can be seen from the figure a realistic solution is the energy transfer from a donor ion, usually Yb, to an emitting ion such as Er, Tm, Pr, Ho following upconversion to their higher electronic state and resulting in visible emission.

In this direction large effort is presently extended to prepare sol-gel-based glasses co-doped with Er and Yb that have the potential to absorb the IR light coming from an LED. AlGaAs is emitting between 750–850 nm, InGaAs between 900–1100 nm and GaInAsP between 1300–1500 nm. The reason for

that can be seen from Fig. 2. The emitted light is absorbed by Yb, Tm, Er, Ho, followed by an energy transfer to the emitting ions in the visible, like Tb, Ho, Er, and Tm.

Some examples of infrared to visible light upconversion are waveguides prepared by the sol-gel method as listed below. Almeida *et al.* [28] prepared silicatitania by the sol-gel method doped with Er^{3+} and Ag nanoparticles (NPs) and determined the potential of this material for planar active waveguides.

Guglielmi *et al.* have prepared Er^{3+} -doped planar waveguides based on a $\text{GeO}_2\text{-SiO}_2$ matrix and measured the fluorescence at 1530 nm following the excitation at 980 nm. This material has a possibility for an upconversion in addition to Yb-doped systems [29].

Among the rare earth ions much attention has been given to research and the development of Nd^{3+} ($1.05 \mu\text{m}$), Pr^{3+} ($1.3 \mu\text{m}$) and Er^{3+} ($1.5 \mu\text{m}$) doped glass fibers for telecommunication systems. This interest is associated with excellent transmission parameters in the telecommunication regions of silica low-loss windows. Among the different practical solutions of optoelectronic structures appropriate for construction of rare earth-doped amplifiers, planar glass light-guides and glass fibers most often find application. For manufacturing optical fibers the most popular material is fluoride glass ZBLAN [30] which is characterized by low energy vibrations leading in consequence to reduced nonradiative transitions. Another critical parameter limiting optical efficiency is clustering of lanthanide ions and contamination by hydroxyl groups. The OH^- vibrations not only limit the performance of erbium-doped fiber amplifiers by several orders of magnitude, but limit also the appearance of an upconversion effect (green emission). To avoid aggregation of metal ions the active glass is co-doped with alu-

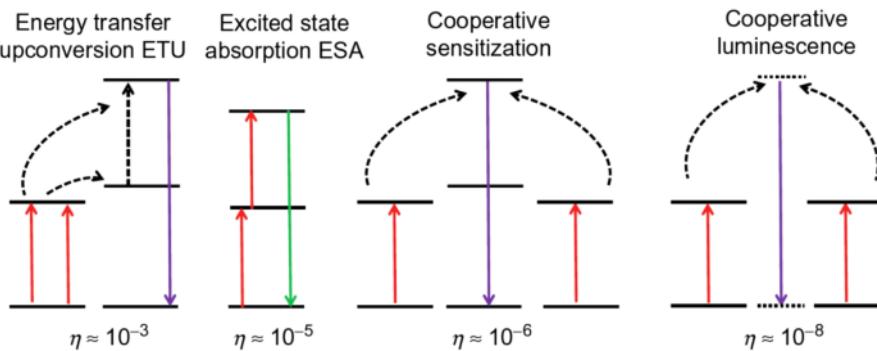


Fig. 1 (color online). Upconversion mechanisms and estimated relative efficiencies reproduced by kind permission of J.-C. G. Bünzli from ref. [1]. Note that the second mechanism, ESA, is more precisely described as GSA-ESA, ground state absorption followed by excited state absorption.

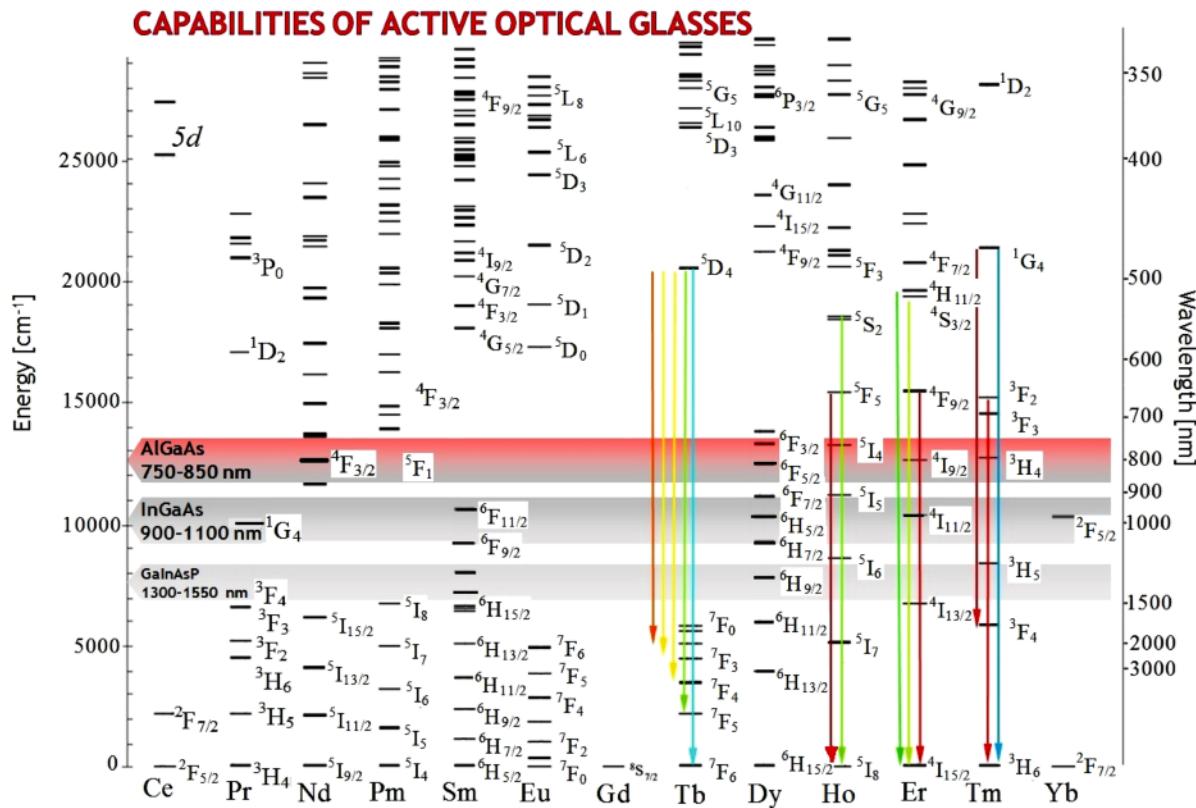


Fig. 2 (color online). Capabilities of active optical glasses. This picture was kindly provided by D. Dorosz.

minimum ions, however, the synthesis of such glasses is difficult to control. The OH^- vibrations lower the fluorescence intensities of the emitting species by multi-phonon relaxation.

The group of Strek prepared Nd^{3+} -doped sol-gel silica fibers of $125\ \mu\text{m}$ in diameter, which are pulled from the preform with a concentration of active ions of 0.03 mol-%. The optical properties of such fibers were investigated and compared to that of monolithic samples. The attenuation factor for this fiber was determined at $1.08\ \mu\text{m}$ to be $90\ \text{dB/km}$. The difference in emission spectra between Nd^{3+} -doped sol-gel silica bulk samples and fibers is manifested in a significant shift of the peak emission of the ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$ transition. The fluorescence of a Nd^{3+} -doped silica gel fiber was measured as a function of the length of the fiber and the excitation power. It was found that the fluorescence intensities and lifetimes are slightly dependent on the fiber length. Moreover it was noted that the intensity of the fluorescence increases linearly with the power [31].

One of the problems in the preparation of luminescent waveguides by the sol-gel method are the OH^- groups left after the formation of the material. This problem has been elaborated by the group of Almeida and Ferrari [32].

Suggestions for Future Work

Based on the existing knowledge we can propose what should be done now in order to utilize the sol-gel process for more efficient fluorescent waveguides.

The optical absorption of rare earth ions is low as the f-f transitions are forbidden by the Laporte rule. The transitions become partly allowed when the symmetry around the rare earth is lowered or when a chemical bond is formed between the rare earth ions and their ligands [33–35].

To circumvent this difficulty, the emitting rare earth ions have to be incorporated into structures where the symmetry around the ion is low and the rare earth emission enhanced. A number of complexes prepared by

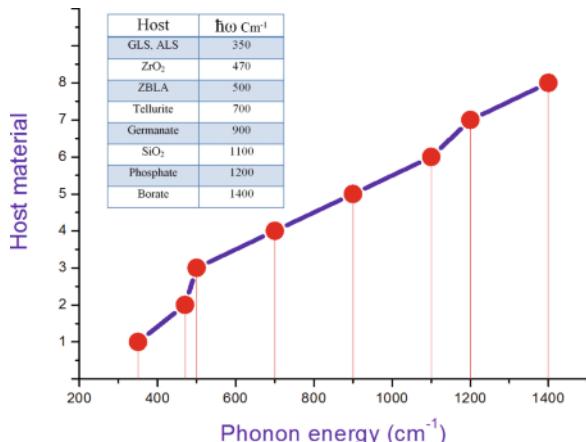


Fig. 3 (color online). Graph of phonon energy in some hosts. Abbreviations: GLS: 3 Ga₂S₃·La₂S₃; ALS: 3 Al₂S₃·La₂S₃; ZBLA: 57% ZrF₄ – 34% BaF₂ – 4% AlF₃ – (5 – x)% LaF₃ – x% PrF₃ with 0 < x < 5.

the sol-gel method have been studied [36–41], and it has been shown that the stability of the prepared materials is strongly increased as compared to the solution. The emission intensities increase significantly as compared to the aqueous solution where the non-radiative relaxations are assisted by the OH⁻ vibrations. The non-radiative relaxations are higher in silicate glasses than in zirconia glasses as seen from Fig. 3 [34, 35]. Thus a good solution is to use zirconia glasses as a basis of optical materials.

Of special interest is the Yb podate complex [1] incorporated in a silica matrix [42]. Yb is predominantly used for upconversion. Another important complex for upconversion may be the NaNd(SP)₄ chelate [43]; its behavior in sol-gel glasses is presently under investigation.

Recently very interesting results of upconversion were obtained in the group of Dorosz. Antimony-germanate glasses doped with Yb, Tm and Ho excited by a laser diode emitting at 976 nm showed white upconversion. The emission consisted of the blue part originating from ¹G₄ → ³H₆ (Tm³⁺), green ⁵F₄ → ⁵I₈ (Ho³⁺) and red ⁵F₅ → ⁵I₈ (Ho³⁺) [44]. In germanate glasses strong luminescence at 489, 543, 586, and 621 nm corresponds to ⁵D₄ → ⁷F_J (*J* = 6, 4, 3) transitions and luminescence at 381, 415 and 435 nm results from ⁵D₃, ⁵G₆ → ⁷F_J (*J* = 6, 5, 4) transitions [45]. In tellurite glasses doped with Yb and Tm blue luminescence at 477 nm arising from the transition ¹G₄ → ³H₆ was obtained from upconversion from Yb³⁺ [46].

Another promising approach for efficient active waveguides is the possibility to increase the rare earths luminescence in sol-gel prepared glass by their interaction with noble metal nanoparticles [47]. Such an approach can be found in references [48–52].

Metal nanoparticles embedded in a dielectric are known to exhibit interesting optical properties resulting from collective electronic excitations at the interface between the metal and the dielectric matrix, the result being a surface plasmon resonance (SPR). This may lead to another type of mechanism responsible for PL enhancement effects, based on a local field enhancement around the Er³⁺ ions, due to surface plasmon resonances of the metal nanoparticles. Active planar waveguides and bulk glasses doped with Er³⁺ and Ag NPs have been prepared by sol-gel processes. Two different procedures were used for dopant incorporation, with Ag⁰ nanoparticles being precipitated by thermal reduction of Ag⁺ ions in both cases. The presence of Ag⁰ nanoparticles in silica-titania planar waveguides and in Er-doped silica bulk glass, with average sizes ranging from 2 to 15 nm, as evidenced by visible absorption spectroscopy and TEM, caused a significant enhancement of the Er³⁺ photoluminescence, irrespective of the method used for silver incorporation, but the photoluminescence intensification was particularly remarkable, up to nearly 60 times, in planar waveguides prepared by sol-doping with Er³⁺ and Ag⁺ ions (followed by Ag⁰ precipitation).

The dominant mechanism responsible for PL intensification in the Ag-containing samples studied in this work is believed to be a local electric field enhancement around the Er³⁺ ions, due to SPR of the Ag⁰ nanoparticles, as it was shown to occur only for resonant excitation [48–55].

Conclusion

Promising materials for a new generation of active waveguides are stable lanthanide complexes incorporated in transparent matrices obtained by the sol-gel method. Zirconia glasses with low phonon energy and high photostability may find applications in this direction. Such glasses will prevent thermal- and photo-degradation of the fluorescent species. Production of future active waveguides will therefore be based on the sol-gel method. Addition of nanoparticles of silver [49], gold [52] and copper [53] to the system will increase their performance.

In this chapter I have concentrated mainly on the results arising from our own research. Most of the investigations of other groups have been cited in the references below.

Acknowledgement

My gratitude is extended to my colleagues and friends for many helpful discussions and exchange of illuminating

ideas (in alphabetic order): Francois Auzel, David Avnir, Georges Boulon, Jean-Claude Bünzli, Dominik Dorosz, Anna Grabowska, Jean-Marie Lehn, Janina Legendziewicz, Voicu Lupei, Marek Grinberg, Marek Pietraszkiewicz, Oscar Malta, Shlomo Magdassi, Shlomo Rushin and last but not least Wieslaw Strek. My thanks go to my assistant Viktoria Levchenko for her important help in preparation of the manuscript.

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