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Mutual influences of sol-gel matrices and dopants on the materials optical properties

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The optical properties of doped sol-gel derived materials were studied. Two types of materials were examined; thin films doped with titanium dioxide and bulks doped with pH indicators: Bromothymol Blue and Nile Red. Different amounts of TiO_2 (in concentrations: 20, 40, 60 and 80 mol%) were entrapped into the silica sol-gel thin films. The refractive indices of the films were measured. A linear increase of refractive index with increasing addition of TiO_2 was observed. Bromothymol Blue and Nile Red pH indicators were entrapped into the sol-gel bulks. Two methods of dye immobilization were used. In the first method, indicators were mixed with liquid hydrolyzate used for bulk preparation. In the second one, the dried sol-gel bulks were impregnated with liquid dye solutions. The absorption spectra in visible range were examined for dyes in solutions and sol-gel bulks. Changes in absorption spectra were observed depending on the way of dopant entrapment.

1. Introduction

Transparent glass-like materials can be prepared in a process of controlled hydrolysis and polycondensation of various precursors at low temperatures. The most popular precursors are metal oxides, whereas TEOS (tetraethoxysilan) or TMOS (tetramethoxysilan) are used to produce silica based gels. The sol-gel method for preparation of solids is being regarded as an important technology along with solid-state reaction, melt quenching and vapour-phase deposition methods [1]. A schematic route for obtaining the target gel material from liquid source compounds is depicted in Fig. 1

As can be seen from this figure, the sol-gel process comprises several steps that chemistry is well described in the literature [2], [3]. First, silicate precursor is mixed with water and/or alcohol and catalyst and stirred for a few hours. This process leads to hydrolysis of the Si–O–R bonds. Acids or bases catalyze the hydrolysis reaction.

The preparation of sol-gel material enables to add various compounds into the liquid mixture of precursors. This is a very attractive feature of sol-gels which can be taken advantage of in a number of practical applications. The matrices doped with photosensitive molecules can be used for construction of optical chemical sensors [4]. Entrapment of metals enables the preparation of special antireflection coatings [5] and other optical elements [6]. Immobilization of chemial compounds in the sol -gel matrix can also be performed post synthesis by impregnating the prepared

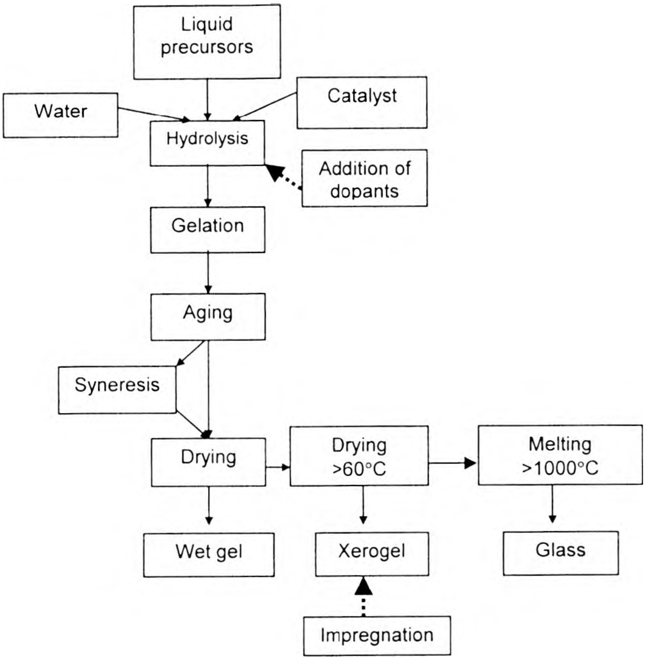

Fig. 1. Schematic representation of the route for preparation of sol-gel derived materials.

matrix. Addition of dopants influences optical properties of both matrix as well as entrapped compounds. These mutual influences will be discussed in this paper.

2. Sol-gel material preparation

For the purpose of this study two types of sol-gel matrices, thin films and bulks were produced by means of the acid catalyzed route. After hydrolysis pH of the obtained homogenous hydrolyzate was gradually brought up to ca. 6, *e.g.*, by means of a diluted ammonia solution. This resulted in quick (several minutes) gelation and formation of so called "wet" gel.

The precursors for the sol-gel films were TEOS mixed with EtOH (ethanol) with addition of 0.1N HCl as a catalyst. The proportions were: 24 ml water : 74.42 ml TEOS : 18.80 ml EtOH : 0.285 ml HCl. These precursors were mixed together by means of magnetic stirrer for 4 h at room temperature. During the hydrolysis process the titanium oxide was gradually added to the solution, so as to obtain 20, 40, 60, 80 mol% concentrations. After hydrolysis, the early polycondensation began and the liquid gel was placed on the clean pure silica substrate with a dip-coating method. The samples were then heated at 200 °C for 12 h. The layers obtained were 1 μm thick.

The precursors for the bulks were TEOS and water mixed in the following proportions: 24 ml water : 19 ml TEOS. These bulks were doped with photosensitive dyes often used in optical sensors for pH measurement [7]. Bromothymol Blue and

Nile Red indicators were studied, whereas liquid solutions were added to the mixture of precursors. The water solutions of 5 g dye in 100 ml had pH equal 10.

3. Examination of refractive index of titanium doped sol-gel films

Recently, the structure and spectroscopic features of silica-titania based sol-gels have been the subject of many examinations, not only due to the general problem of amorphous materials, but also because of potetial applications [8]. One of the fundamental parameters characterizing the sol-gel films is the refractive index. Controlling the porosity allows us to control the refractive index in porous materials. Adding various dopants to the sol-gel matrix can also change the refractive index.

Here, the addition of titanium dioxide was studied. The dopant was added to the liquid hydrolyzate, as it was already described. Different ratios of dopants were used (20, 40, 60, 80 mol%) and their influence on refractive index was examined. Three

Table 1. Mean value of refractive index dependent on the amount of TiO_2 added to the silica sol-gel films. The measurements were performed for yellow He line d, $\lambda = 587.56$ nm.

TiO_2 [mol%]	Mean value of refractive index			
	Sample I	Sample II	Sample III	**Mean value**
20	1.5524	1.5528	1.5526	**1.5526**
40	17016	17018	1.7020	**1.7018**
60	1.8552	1.8549	1.8546	**1.8549**
80	2.0013	2.0017	2.0024	**2.0018**

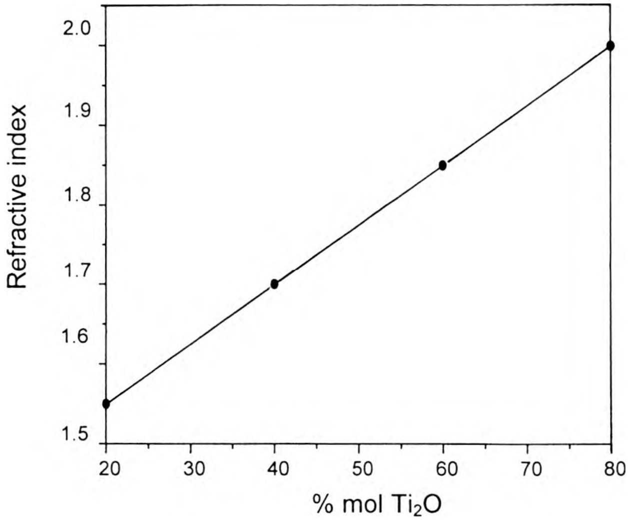

Fig. 2. Refractive index of thin sol-gel layer as a function of molar concentration of TiO_2.

samples of thin xerogels were prepared for each molar ratio of TiO_2 and the refractive index was measured at four different points of each sample. The mean values of the measured indices are presented in Tab. 1.

The mean value from the measurement of all three samples, as shown in Tab. 1, is presented graphically in the diagram of Fig. 2. One can see that the value of refractive index growths linearly with an increasing amount of dopant.

All the measurements discussed here were performed on freshly prepared samples, that is, just after completing the heating process.

4. Influence of sol-gel matrix on absorption characteristics of doped materials

One of the attractive features of sol-gel matrices is their porosity, which enables the various sensitive molecules to be entrapped. Generally, silica based sol-gels are transparent and chemically inert. In some cases, the optical properties of dopants do not change while immobilized in sol-gel bulks or films [7]. However, in many cases the matrix strongly modifies the optical response of entrapped dyes [9]. The method of immobilization can also influence spectroscopic properties of entrapped compounds. In this study, we prepared silica based sol-gel bulks, according to the explanation given in section dealing with material preparation. As the examined dyes the following pH indicators were used: Bromothymol Blue and Nile Red. In solutions with pH of 10, they show absorption maxima at 600 and 580 nm, correspondingly.

Two methods of entrapment were applied. In the first one, the indicators were added to the liquid precursors and the bulks prepared were already doped with these dyes. In the second method, first the sol-gel bulks were produced and then placed in the indicator solutions, so as to impregnate the materials. The absorption

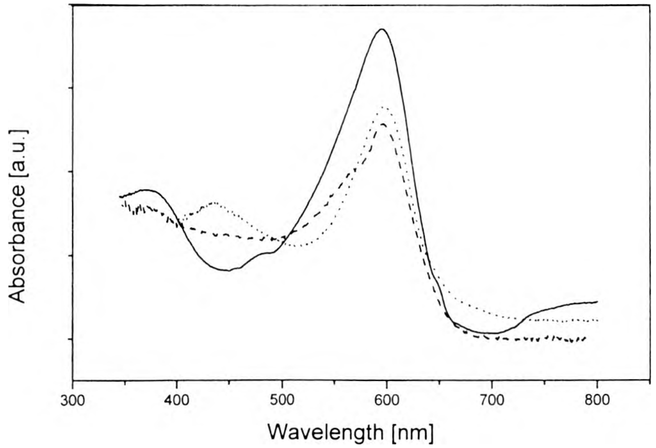

Fig. 3. Absorption spectra in visible range of Bromothymol Blue doped bulks. The absorption maximum is observed near 600 nm. This maximum is not influenced by the method of dye entrapment.

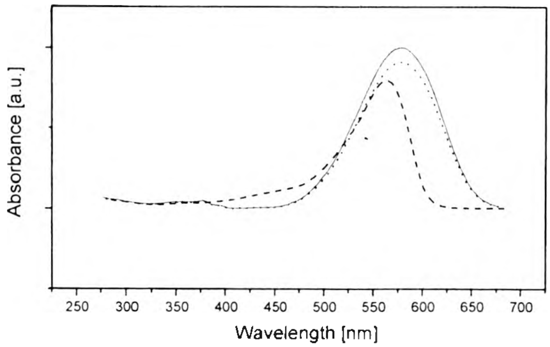

Fig. 4. Absorption spectra in visible range of Nile Red doped bulks. The absorption maximum is shifted in the case when indicator was added during the hydrolysis (—— NR in solution, – – – NR in sol-gel (add to hydrolyzate), ···· NR in sol-gel (impregnated)).

spectra of dye solutions, sol-gel doped bulks on the way of hydrolysis, and impregnated bulks were measured. These spectra are visualized in Fig. 3 and Fig. 4.

Analyzing the absorption function, one can see that in the case of Bromothymol Blue the maximum absorption is observed for the same wavelength, independent of whether it was measured in solution or in bulks. The other dye—Nile Red shows, however, the shift of the absorption peak towards the shorter wavelengths, in case of immobilization during the hydrolysis. These results are collected in Tab. 2.

Table 2. Changes of absorption maximum depending on the doping method. In all the cases dyes have pH = 10.

Indicator	Absorption maximum [nm]	Object of examination
	600	Water solution
BT	600	Impregnated sol-gel matrix
	600	Indicator added during hydrolysis
	580	Water solution
NR	580	Impregnated sol-gel matrix
	564	Indicator added during hydrolysis

This experiment demonstrated that the method of immobilization might influence the optical properties of immobilized compound. Some expriments show that the absorption spectrum is solvent dependent [10]. This probably can explain why some indicators when solved in the mixture of liquid precursors and then entrapped in the matrix, change the spectral characteristics. The other reason might be the structural changes due to the changing dimensions of pores during drying.

Such changes are observed not only for absorption of pH indicators, but also for photoluminescent molecules. We have also proved that the life time of oxygen sensitive Ruthenium compound in 20% water solution is in the range (5.0±0.1) μs, while, when entrapped in sol-gel in nitrogen atmosphere, it shows 0.5 μs longer life time. Both of the experiments were performed at 20 °C and in nitrogen atmosphere (no oxygen in the environment) [11].

5. Final remarks

Sol-gel materials due to their high chemical homogeneity, low processing temperatures, possibility of entrapping various molecules are very attractive for many applications. One of the areas where these features are extensively investigated is the field of optical chemical sensors. Since the sol-gel derived materials provide excellent matrices for a variety of organic and inorganic compounds, they can be used for construction of optodes.

Generally, silica based doped sol-gel materials are capable of preserving the chemical and physical properties of dopants. Many researches underline that these materials are chemically inert. However, as it was shown in this paper, the optical characteristics can be changed in some cases. Especially, the sol-gel matrix can influence some pH sensitive indicators. This depends on the method of molecules immobilization. This conclusion should be taken into account when constructing an optode for optical sensors.

We also demonstrated that dopants influence the matrix properties, *e.g.*, refractive index. This is an interesing feature, which enables us to construct materials with the tailored unique parameters.

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