

Synthesis of SiO_2 matrices doped with some inorganic compounds

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The properties of silicon dioxide xerogels doped with salts and nanoparticles of inorganic compounds have been studied. Optimization of the synthesis and annealing conditions of SiO_2 matrices made it possible to increase essentially the microhardness of the doped samples. Using the aquametry technique, there was established the distribution mechanism of the of titanium oxide nanoparticles in the xerogel matrix intended to develop the new generation of luminescent materials. To obtain a moisture-resistant material, with increased service life, it has been proposed to dope the xerogel matrices with titanium oxide nanoparticles or to treat the undoped matrices with nitrocellulose lacquer.

Изучены свойства ксерогелей на основе оксида кремния, допированного солями и наночастицами неорганических соединений. Оптимизация условий синтеза и отжига SiO_2-матриц позволила значительно увеличить микротвердость легированных образцов. С привлечением акваметрии установлен механизм распределения наночастиц оксида титана в матрице ксерогеля, являющейся основой для создания люминесцентных материалов нового поколения. Для получения влагостойкого материала с увеличенным сроком эксплуатации предложено легировать матрицы ксерогеля наночастицами оксида титана или проводить обработку нелегированных матриц цапон-лаком.

Oxide glass-ceramic SiO_2 matrices containing micro- or nanoparticles of light-emitting rare-earth compounds are a promising photonic media with high chemical stability and mechanical strength [1]. Rare-earth elements may be a good alternative for thermally unstable dyes being applied widely to dope SiO_2 matrices for laser facilities. However, no detailed information on the conditions of the synthesis of such materials and their physico-mechanical properties is available in literature [2, 3].

The aim of this work was to investigate the properties of silicon dioxide xerogels doped with salts or nanoparticles of inorganic compounds and possessing high microhardness and cracking resistance.

SiO_2 matrices were synthesized by the sol-gel method [4] in modified conditions of tetramethoxysilane hydrolysis and polycondensation of the formed compounds. In particular, while running the sol-gel process, the medium acidity was varied, and volatile components were simultaneously removed. The tetramethoxysilane (TMOS) chosen as a precursor was hydrolized in aqueous methanol solution using hydrochloric or nitric acid as a catalyst. The inorganic dopants were incorporated into the matrix at room temperature using either aqueous solutions of nitrates of rare-earth elements $Re(NO_3)_3$, where $Re = Ce^{3+}$, Tb^{3+}, La^{3+}, Eu^{3+} (with 0.15 mass. % salt concentration), or colloid aqueous solutions of terbium-doped cerium orthophosphate $CePO_4{:}Tb$ (20 mol. %), and europium-doped lanthanum orthophosphate $LaPO_4{:}Eu$ (20 mol. %), as well as titanium oxide nanoparticle powder dispersed in water or in methanol. The size of cerium orthophosphate and titanium oxide particles was approximately 2 nm and 15 nm, respectively.

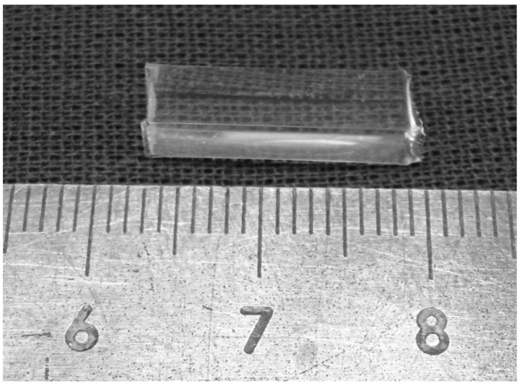

Fig. 1. SiO_2 matrix sample.

It has been found that homogeneous distribution of the inorganic components in the matrix was achieved in the cases when the doping additions were introduced in the form of true solutions of lanthanoid salts, colloid solutions of the orthophosphates, or titanium oxide nanoparticles in the course of TMOS hydrolysis. To avoid phase separation [5], the concentrations of the additives were not higher than 3.0 mass. %.

To obtain the xerogel, the reaction mixture was mixed thoroughly together with a filler and cast into plastic containers of different size and shape, then the containers were hermetically sealed. The gel formation lasted 20–24 hrs. Ageing and drying were realized at 40–50°C during 2–4 weeks, depending on the sample initial volume. The dried samples were annealed at 750–900°C either in air or in vacuum, depending on the dopant type.

The sample mass loss which amounted ~85 % was determined from the mass difference before and after drying and calcination of SiO_2 matrices. The use of such data while calculating the initial concentration of the introduced additives to ensure that the threshold concentration in the ready material (3 mass. %) will not to be exceeded, thus avoiding the matrix layering.

Fig. 1 presents a photo of transparent SiO_2 matrix synthesized by the described technology. As seen from the microphotographs obtained using an Olimpus IX71 microscope, this matrix is a highly porous material (Fig. 2). The porosity and density of the synthesized material were determined by hydrostatic weighing [6]. Depending on the heat treatment conditions, the porosity ranged between 54 and 25 %, the density was within limits of 0.98 to 1.40 g/cm^3, which agreed with the literature data [7, 8].

Microhardness measured usually by Vickers diamond pyramid is a significant mechanical characteristic of xerogels. As has been established in this work, doping with inorganic salts and particles by the proposed technology does not cause any deterioration of the said parameter, since under external load of 100 g the microhardness value for the additive-free xerogels and that for the doped samples differ insignificantly, and on the average amounts 170 kg/mm^2. The microhardness data available in the literature are lower and do not exceed 85 kg/mm^2, therefore, it may be concluded that optimization of the synthesis conditions allows to obtain doped xerogels with improved mechanical properties [2, 9].

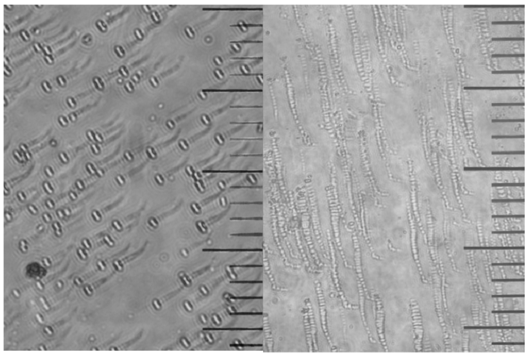

Fig. 2. Microphotos of the SiO_2 matrix in two planes in transmitted light (1 graduation line is 0.01 mm).

The undoped xerogel matrices stored during 14 days in air became cloudy. In our opinion, such a worsening of the optical properties is connected with saturation of the xerogel pores with water from air. Presented in the Table are the study results of water absorption properties of SiO_2 matrices, including the xerogel samples treated with nitrocellulose lacquer which isolates the matrix from ambient air. The water content in the investigated xerogel samples was determined by titration with visual indication of the end point by the K.Fischer method, using the setup providing protection of the reagent and the sample against atmospheric moisture according to the procedure described in [10]. As an extraction agent, methanol was applied into which water was extracted during continuous stirring the mixture by a magnetic mixer. It was established that complete water extraction from the non-annealed and annealed xerogel samples lasted 15 minutes. The Table data testify that non-annealed xerogel dried at 45–50°C to a constant mass contains a rather high (20.5±0.1 mass. %) water amount. Moreover, the use of nitro-

Table. Water content in the xerogel samples as titrated by the Fischer method

Sample	Storage time, days	Found water, mass. %
Non-annealed xerogel	1	20.5±0.1
Annealed xerogel	30	1.42±0.02
	90	12.7±0.2
Annealed xerogel coated with nitrocellulose lacquer	30	1.2±0.1
	90	5.4±0.3
Annealed xerogel after storage in water	1	13.4±0.7
Annealed xerogel coated with nitrocellulose lacquer after storage in water	1	10.8±+0.5

cellulose lacquer efficiently protects the xerogel matrix against humidification both while storing it in air and immersion in water.

The aquametry technique was also used to clear up the distribution mechanism of the of titanium oxide nanoparticles in the xerogel matrix. Using the K.Fischer method, it has been established that after 90-day storage, the xerogel samples doped with titanium oxide (irrespective of the solvent used for its dispersion) contain 5.2±0.2 mass. % of water. Such a fact is in good agreement with the moisture content in the xerogel samples treated with nitrocellulose lacquer and stored in air during the same time (see the Table). In this connection, it should be concluded that the nanoparticles are located mainly at the solid/air interface and, similar to nitrocellulose lacquer, block the pores homogeneously over the whole xerogel volume. Thus, the titanium oxide introduction into the xerogel matrix allows not only to obtain advanced luminescent materials, but also to reduce essentially their water absorption property.

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Синтез SiO_2-матриць, допованих деякими неорганічними сполуками

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Досліджено властивості ксерогелів на основі оксиду кремнію, допованого солями та наночастинками неорганічних сполук. Оптимізація умов синтезу та відпалу SiO_2-матриць дозволила значно збільшити мікротвердість легованих зразків. Способом аквametрії встановлено механізм розподілу наночасток оксиду титану у матриці ксерогелю, яка є основою для створення люмінесцентних матеріалів нового покоління. Для отримання вологостійкого матеріалу з подовженим строком експлуатації запропоновано легувати матриці ксерогелю наночастинками діоксиду титану або обробляти нелеговані матриці цапон-лаком.