

Sol-gel method preparation silica gel-glasses, doped trivalent rare-earth ions for fiber optics applications

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ABSTRACT

Optical materials prepared by the sol-gel process are of current technological interest. Sol-gel silica glasses doped with rare-earth (RE^{3+}) ions are an important class of optical materials with applications including solid-state lasers, optical waveguides, fiber amplifiers and devices for optical communications. In this paper, we describe the preparation of rare-earth-doped silica-gel glasses and discuss the infrared properties of silica structure as a function of heat treatment. The samples were prepared from tetraethoxysilane (TEOS), water, ethanol, fumed silica and soluble in a water or ethanol the salts of the RE^{3+} (Er^{3+} , Nd^{3+} , Sm^{3+} , Pr^{3+} , Eu^{3+}) elements.

Keywords: sol-gel process, silica gel-glasses, silica structure, rare-earth ions, infrared spectroscopy

1. INTRODUCTION

There is currently a great deal of interest in the development of active glass devices that derive their important optical properties from organic or inorganic species doped into the glass. Among inorganic dopants, several of the trivalent rare earth ions are being investigated for use in lasers and devices for optical communications.

Because of the high melting temperature of SiO_2 , it is difficult to prepare rare-earth doped silica glasses using the traditional technique involving the quenching of an oxide melt. The sol-gel process provides a convenient alternative method for preparing doped glass samples without melting. The sol-gel method is a low-temperature solution method for glass preparation based on the inorganic polymerization of hydrolyzed metal alkoxides. Metal ion dopants to be incorporated in the final glass product are added to the initial solution in the form of inorganic salts, metal alkoxides or encapsulated metal complexes. The hydrolysis and condensation reactions driving polymerization continue, leading to the formation of a porous gel extending throughout the reaction vessel at the gel point. The porous gel is then dried and densified to form glass [1].

The optical properties of Er^{3+} are particular interest in the pursuit of lasers operating at eye-safe wavelengths and in the fabrication of fiber amplifiers for optical communication signals. The electronic transition from the $^4\text{I}_{13/2}$ energy level manifold to the $^4\text{I}_{15/2}$ of Er^{3+} produces light at a wavelength of approximately 1.5 μm , which is outside the range of wavelengths focused on the human eye, and is close to the wavelength of lowest signal attenuation in a low-loss silica glass fiber [2]. Nd^{3+} -doped glasses are of interest in the development of high powered glass lasers for inertial confinement research, and both Nd^{3+} - and Pr^{3+} -doped systems are being investigated for amplification of optical signals at 1.3 μm . Eu^{3+} it is possible to use as an optical probe of gelation and densification of sol-gel glasses.

A potential problem associated with rare-earth-doped silica-gel glasses is clustering of the rare earth ions due to the low solubility of rare earth oxides in SiO_2 . Concentration quenching among clustered rare-earth ions leads to a decrease of fluorescence efficiencies and shorter lifetimes through cross-relaxation or energy transfer processes.

An understanding of the influence of glass composition and structure on the optical properties of rare earth dopants depends on determining the environment of rare earth ions in glass. Our objectives are to prepare sol-gel glasses with a spatially uniform distribution of rare-earth dopants, to determine the local bonding environments of rare-earth dopants in sol-gel glasses. In this paper, we describe the preparation of RE^{3+} -doped sol-gel silica glass and discuss the infrared properties of silica structure as a function of heat treatment at various temperatures.

2. EXPERIMENTAL

The silicon alkoxide precursor used to prepare all of the RE^{3+} -doped samples for this study was TEOS (tetraethoxysilane ($\text{Si}(\text{OC}_2\text{H}_5)_4$, Fluka) and fumed silica (aerosil T-30, Wacker-Chemie GmbH, Germany). Samples of the RE^{3+} -doped xerogels and glass were prepared by sol-gel process including the following stages (fig. 1): TEOS hydrolysis in the system $\text{Si}(\text{OC}_2\text{H}_5)_4:\text{C}_2\text{H}_5\text{OH}:\text{H}_2\text{O}:\text{HCl}$ with mole ratio 1:2:16:0.01 by vigorous mixing in fluoroplastic reactor in air atmosphere, addition the fumed silica with a specific surface 200 cm^2/g into the sol as filler, ultrasonic dispergation with vigorous stirring and centrifugal separation from agglomerates and dust particals. Then, the sol-colloid system was neutralised up to $\text{pH}=6.5$ with help of ammonia solution and was cast into fluoroplastic moulds to prepare the solid gels shaped as disks and rods. The wet gels were formed during 20-30 min in sealed containers; then the containers were opened and the gels were washed by distilled water. The resulting gels were dried slowly at 30-60 $^\circ\text{C}$ in the period 7-14 days in air. After drying for

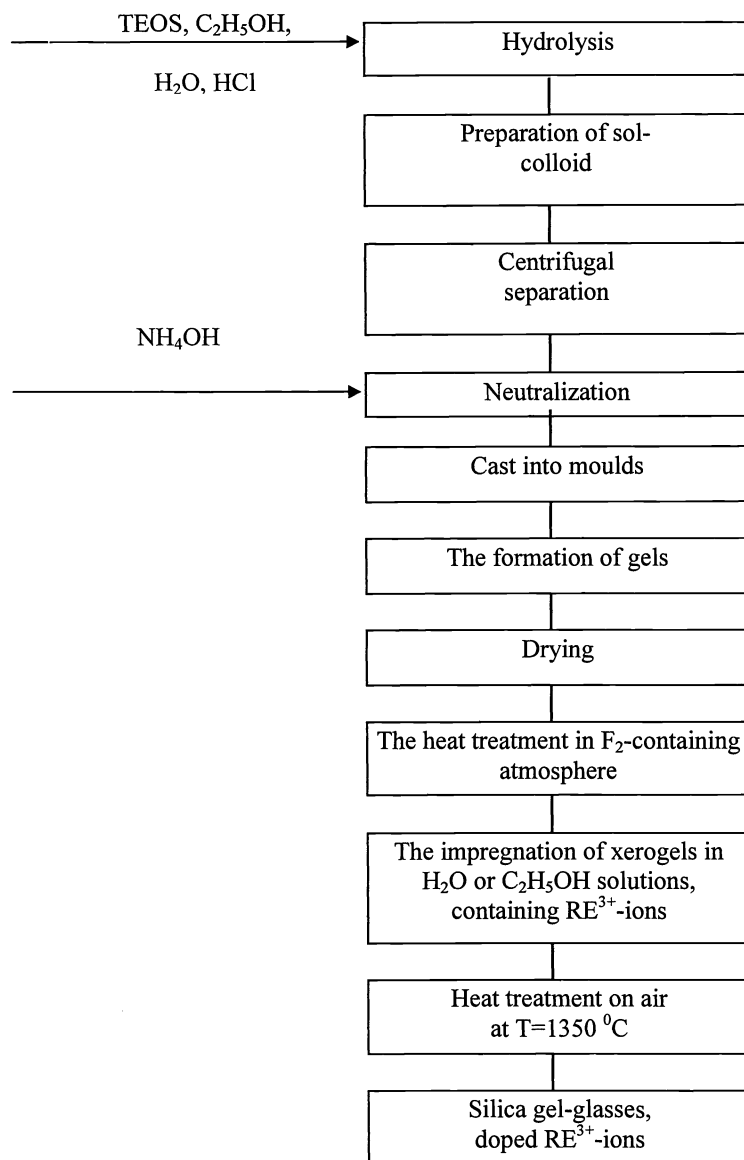


Fig.1. The circuit of technological process of manufacturing silica gel-glasses, doped rare-earth ions (Er³⁺, Nd³⁺, Sm³⁺, Pr³⁺, Eu³⁺).

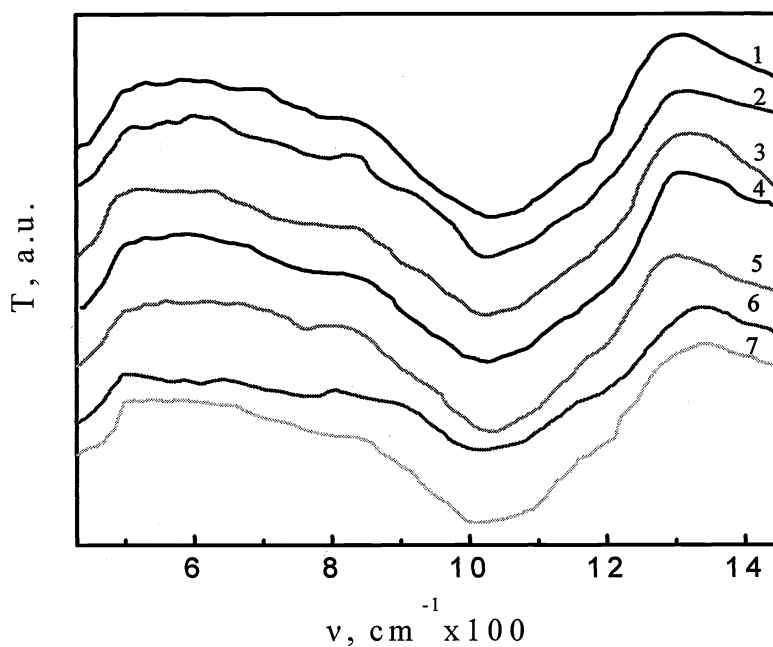


Fig. 2. The transmission IR-spectra of xerogel and glass doped with rare-earth ions, obtained by direct sol-gel method and temperatures processed at following: 60 °C (1), 100 °C (2), 300 °C (3), 600 °C (4), 800 °C (5), 1100 °C (6) and 1180 °C (7).

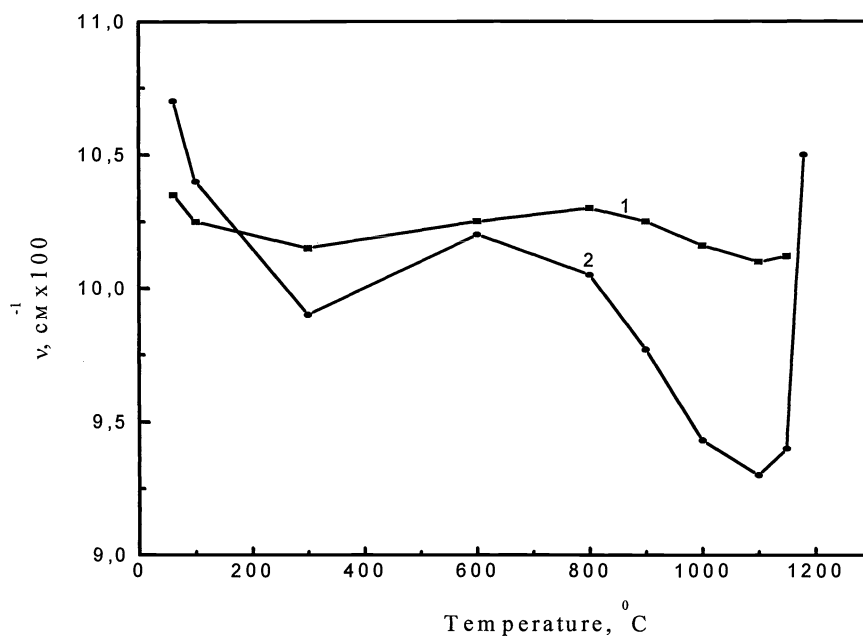


Fig. 3. The situation of minimum a IR of bands transmission of valence vibrations Si-O-Si, depending on temperature of processing: 1-silica xerogels and gel-glasses, doped rare-earth elements; 2-undoped silica xerogels and gel-glasses.

removal of OH-groups the further heat treatment xerogels is conducted in fluor-containing atmosphere. The source of fluor was freon ($\text{C}_2\text{Cl}_3\text{F}_3$). The mixture of freon/oxygen was used for the technique of gaz-phase doping. After the monolithic xerogel samples, doped fluorine, were impregnated in water or ethanol solutions, containing the salts of the RE^{3+} (Er^{3+} , Nd^{3+} , Sm^{3+} , Pr^{3+} , Eu^{3+}) elements. The final heat treatment samples was conducted on air at temperature 1350°C before the reception transparency glasses. The measurements of the infrared spectra of silica structures were made on SPECORD 75IR.

3. RESULTS AND DISCUSSION

The result of measurements of transmission IR-spectra of monolithic xerogel and silica gel-glasses were obtained. In the field of $1300\text{--}2200\text{ cm}^{-1}$ and $400\text{--}900\text{ cm}^{-1}$ frequent curves have not characteristic changes and are located in the field of 90–95% transmission. In a range $900\text{--}1300\text{ cm}^{-1}$ minimum of a transmission band is observed. The transmission in a minimum does not exceed 30%. From $400\text{--}1300\text{ cm}^{-1}$ of the special changes in a spectrum is not observed.

Analyzing the area of transmission minima, it is easy to notice the displacement of a transmission minimum.

The fig. 2 show the transmission IR-spectra of xerogel and glass with the identical doping contents, obtained by direct sol-gel method at temperatures: 60°C , 100°C , 300°C , 600°C , 800°C , 1100°C and 1180°C . On these spectra bands of absorption with a maximum in the field of frequencies 1100 cm^{-1} (ν -vibration of Si-O-Si-band) are observed.

As is known [3], these vibration are sensitive to change of a silica network configuration: the shift of a minimum of a transmission band to the higher vibration frequencies corresponds to a more ordered structure (so, for a quartz glass this significance makes 1120 cm^{-1} [4]).

The obtained spectral curves enable to make some conclusions relatively the structure evolution of xerogel during heat treatment. For convenience of the analysis a fig. 3 is resulted, on which situation of minima of transmission bands depending on temperature of heat treatment are represented. As we can see, for xerogel and then glass of a contain RE^{3+} it is possible to allocate some characteristic areas of silica network formation.

So, at 60°C xerogel has reasonably ordered structure, the further displacement of a minimum of a transmission band in the party of low frequencies testifies about a disorder of a xerogel structure. It occurs at temperature $100\text{--}300^\circ\text{C}$ and is connected with removing of physically and chemically adsorbed water and partially—with removing of organic connections.

The further displacement of a minimum of a transmission band testifies to xerogel densification and structure ordering. More one minimum (in the field of 1100°C) is connected, as appears, to final formation of Si-O-Si bands in exchange of Si-OH band. Further ordering of a structure corresponds to formation of a silica glass (1180°C).

For pure xerogel and glass (not containing any additives) the curve character is the same, as xerogel and glass, doped RE^{3+} ions ($940\text{--}1070\text{ cm}^{-1}$), fig .3, curve 2.

4. CONCLUSIONS

We have described the preparation of rare-earth-doped silica-gel glasses and discuss the infrared properties of silica structure as a function of heat treatment.

The IR measurements results two main steps of final formation of three-dimentional frame may be distinguished. After the monomer to polimer transition (about 1000°C) heat treatment temperature increasing (1180°C) the conversion of the porous structure into a fully densified and homogeneous structure is observed. In summary it is necessary to note, that significance of frequency of a transmission minimum band for sol-gel structures is less, than for quartz glass, that is because of large number of defects.

The silica gel-glasses, doped trivalent rare-earth ions can used for fiber optics and other applications.

5. REFERENCES

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