

Influence of the synthesis conditions on the photoluminescence of silica gels

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Abstract: The photoluminescence spectra of silica xerogel samples synthesized with ethanol as solvent and xerogel where the ethanol was exchanged by water before drying are reported. In addition, the photoluminescence spectrum of a silica cryogel synthesized with *tert*-butanol as solvent was investigated. The samples were modified by formamide. Bands at 2.00, 2.20, 2.32 and 2.46 eV were identified. In the photoluminescence spectra of all samples. The band at 2.00 eV is caused by the presence of silane, and the band at 2.20 eV is connected with the nonstoichiometric composition of silica. The photoluminescence band at 2.32 eV was found to originate from the organic groups of the solvent. The origin of this band are E' defect centers, which is a prominent paramagnetic defect in conventional α -SiO₂.

Keywords: silica gel, luminescence, infrared spectroscopy.

INTRODUCTION

The sol-gel process is a simple chemical procedure for making many different materials, among them silica gels. Silica gels are prepared by a chemical reaction employing a metal alkoxide (for example tetraethylorthosilicate (TEOS)) and water in an alcoholic solvent. The first reaction is hydrolysis which induces the substitution of OR groups linked to silicon by silanol Si–OH groups. These chemical species may react together to form Si–O–Si (siloxane) bonds which lead to silica network formation. This reaction of condensation establishes a 3D network which invades the whole volume of the container. The liquid used as solvent to perform the different chemical reactions remains within the pores of the solid network and has to be removed. Silica aerogel samples can be dried by simple evaporation at temperatures close to room temperature and atmospheric pressure, whereby so called *xerogels* (a word derived from the Greek word “xeros” which means dry) are obtained. By sublimation of frozen solvent *cryogels* are obtained. An *aerogel* results from a supercritical drying process. The drying step is performed inside an autoclave which allows the critical point (p_C , T_C) of the solvent to be overpassed.

A major problem during drying is cracking of the samples. Zarzycki showed that drying stress is a function of pore size and rate of evaporation of the pore liquor, which depends on the liquor vapor pressure.¹ Only by using supercritical extraction can large monoliths without cracks be obtained. However, because of the high costs and risk of this method, processes for preparing monolithic xerogels at ambient pressure have in recent years been developed.^{2,3} One of these methods involves the addition of a drying control chemical additive (DCCA) to the sol. The DCCA changes the structure of the gel during gelation in such a way as to equalize the pores dimension, so the difference in the surface tension of the pores is lower and the sample can be dried under normal conditions.³ The DCCA must also be removable during densification before pore closure.³

The structure of the sol-gel derived oxide networks and defects in the structure are strongly affected by the concentration of the interacting species, their ratios, the reaction medium solvent, the pH, the catalyst and the temperature during condensation. Silica gels have several microstructure defects which are responsible for the appearance of photoluminescence (PL). One such defect is a non-bridged oxygen hole center (NBOHC) described by the relation $\text{SiOH} = \text{SiO}\cdot + \cdot\text{H}$ where the dots denote uncoupled electrons. In PL spectra of Si/O systems, this defect is connected with the bands at about 1.80 eV⁴ or 1.90 eV.^{5,6} The band which appears at 2.00 eV originates from the presence of silan (SiH and/or SiH_2).⁷ The band at 2.20 eV is caused by the non-stoichiometric structure SiO_x where $1 < x < 2$.⁷⁻⁹ The origin of the PL of silica gels can be organic compounds which remain from the synthesis. Thermal treatment results in the formation and/or removal of various defect centers.¹⁰

In this work the PL spectra of silica gels synthesized and dried by different methods were investigated. First sample was a xerogel synthesized with ethanol as the solvent and DCCA-formamide modified (XG sample). The second sample was obtained by the exchange of ethanol by water in the XG sample before drying (sample XGW). Both xerogels were dried by evaporation under ambient conditions. The examined cryogel sample (CG) was synthesized using *tert*-butanol as solvent and freeze-dried. The PL spectra were compared with the PL spectra of two silica aerogels synthesized without DCCA, in ethanol solvent and dried by supercritical extraction: the first was not sintered (AG sample), and the second was sintered for 15 h at 1000 °C (AGS sample). These samples were described in a previous paper.⁷

EXPERIMENTAL

The silica gel samples were made by the sol-gel process using tetraethylorthosilicate (TEOS), water, different solvents (ethanol and *tert*-butanol), acid catalyst HCl and DCCA - formamide. The amounts of the initial compounds are presented in for each sample (Table I).

The sample XGW was washed after gelation in water for 47 days. The parameters of gelation and drying are shown in Table II.

TABLE I.

Sample	TEOS/cm ³	Solvent/cm ³		H ₂ O/cm ³	HCl/cm ³	Formamide/cm ³
		Ethanol	<i>Tert</i> -butanol			
XG	7.5	6.0	–	4.2	0.7	4.2
CG	7.5	–	6.1	6.6	0.7	4.2

TABLE II.

Sample	Gelation time/h	Gelation temperature/°C	Drying method	Drying time/days	Drying temperature/°C
XGW	1	60	Evaporation	139	20
XG	1	60	Evaporation	9	20
CG	24	40	Sublimation	1	25

The PL spectra were recorded using a Jobin-Ivon U1000 monochromator and photomultiplier as detector. The samples were excited by the 4.88 nm line of an Ar ion laser. The measurements were performed at room temperature in air. The infrared (IR) reflection spectra of all samples were measured using BOMEM DA8 spectrometer at room temperature in the spectral range from 400 to 1500 cm⁻¹. For these measurements, the KBr pellet technique was used.

RESULTS AND DISCUSSION

The PL spectra of the samples XGW, XG and CG are presented in Fig. 1 while the PL spectra of the samples AG and AGS are shown in Fig. 2. The PL spectra were deconvoluted using a sum of 4 or 5 pseudovoit profiles, which are also shown in Figs. 1, and 2.

The IR spectra of the same samples are shown in Fig. 3. The IR spectra were fitted using a three-parameter model of the dielectric function:

$$\varepsilon(\omega) = \varepsilon_{\infty} + \sum_j \frac{S_j}{\omega_j^2 - \omega^2 + i\gamma_j^2 \omega^3}$$

where S_j , ω_j and γ_j are respectively the oscillator strength, resonance frequency and damping parameters of j -th oscillator, and ε_{∞} is the high frequency dielectric constant.

From the deconvolution procedure of PL spectra, the band positions, width and area below each band were obtained. The areas below the PL bands for each xerogel, cryogel and aerogel sample are shown in Fig. 4.

The PL spectra of xerogels exhibit four bands at about 2.00, 2.20, 2.32 and 2.46 eV. In the PL spectra of the aerogels an additional band at 1.80 eV appears. As was discussed in our previous work,⁷ the band at about 1.80 eV is connected with NBOHC centers at the surface of the gel. The band at 2.00 eV is assigned to the presence of silane, while the band at 2.20 originates from the non-stoichiometric composition of the gel structure.⁷ In the PL spectra of xerogels and cryogel, bands at 2.00 and 2.20 eV are also present. From the behavior of the band at 2.20 eV, in-

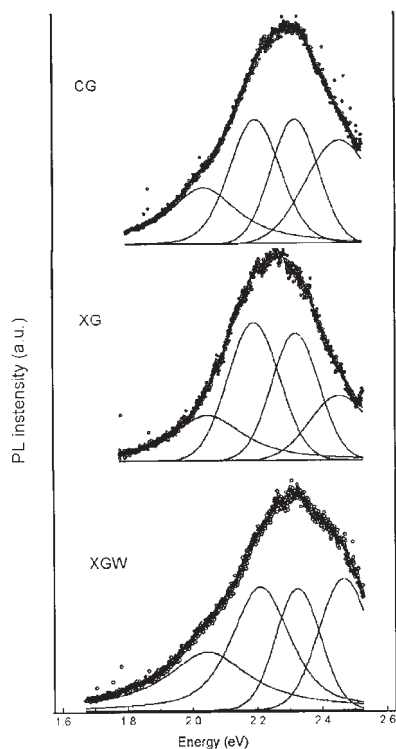


Fig. 1. PL spectra of the xerogel made with ethanol (XG), xerogel washed in water (XGW) and the cryogel made with *tert*-butanol.

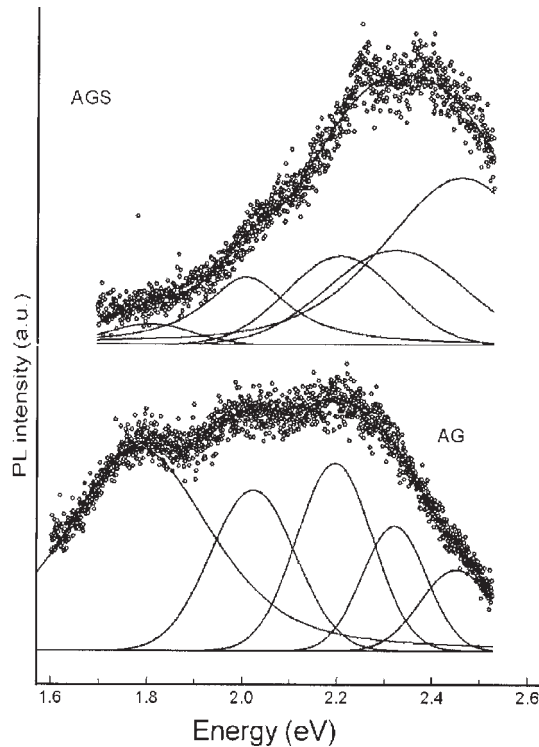


Fig. 2. PL spectra of the aerogels: non-sintered (AG) and sintered 15 h at 1000 °C.

formation about the non-stoichiometric composition of the gel structure can be obtained. The exchange of the organic solvent by water allows the polymerization reaction to go more to completion so the composition of the sample washed in water is less non-stoichiometric. The process of sintering has the same effect so the area below the 2.20 eV band is low in the case of the sintered aerogel.

After drying by evaporation or sublimation, a certain amount of solvent remains in the closed pores of the sample. The presence of the organic solvent (ethanol or *tert*-butanol) is visible in the IR spectra. The mode connected with ethanol is at about 1050 cm^{-1} while the mode of *tert*-butanol is at about 1150 cm^{-1} . From the fitting procedure of the IR spectra, the oscillator strengths of these modes, which are proportional to the amount of vibrating molecules or residues can be obtained. As can be seen in Fig. 5a, the area below the PL band at 2.32 eV changes in a similar manner as the oscillator strength of the organic solvents in the silica gel samples.

For example, in the sample XGW, which had been washed in water, the amount of solvent is very low, as is the case of the sintered AGS sample where the organic material had been removed by sintering at high temperature. In the case of

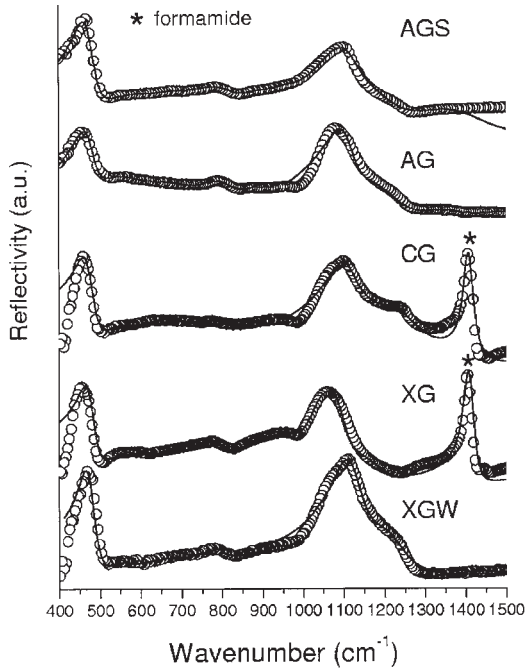


Fig. 3. IR Spectra of the xerogels, cryogel and aerogels. Experimental data are presented by circles, while the fit curve is the solid line.

these two samples the area below the band at 2.32 eV is low. It can be concluded that this band originates from the organic compounds in silica gels structure. Note that washing in water removes all the formamide. This can be seen from Fig. 3, where in the spectrum of the XGW sample the mode at about 1400 cm⁻¹ connected with formamide is absent.

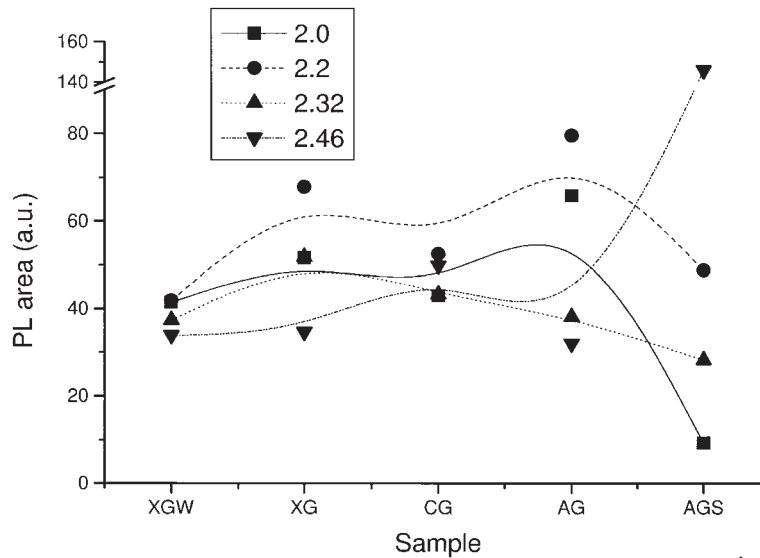


Fig. 4. Areas below the PL bands in the spectra of all the samples.

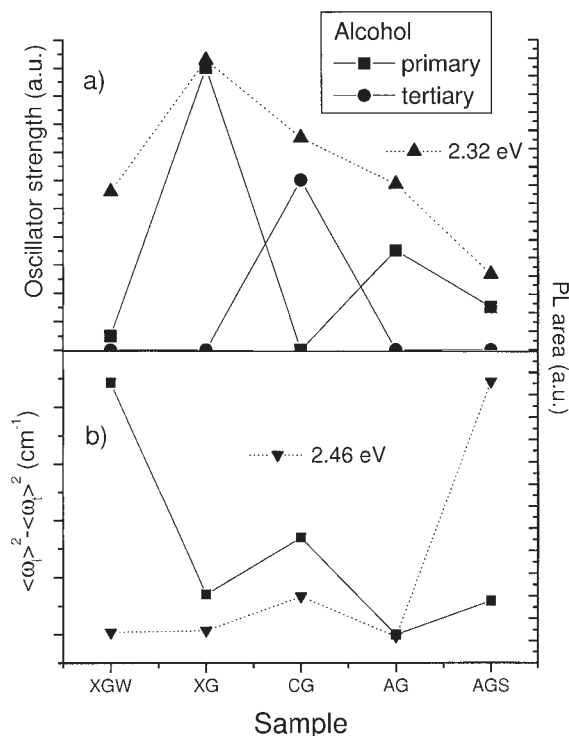


Fig. 5. a) Oscillator strengths of the alcoholic modes compared with the area below the PL mode at 2.32 eV; b) spectral activity of the IR modes connected with the antisymmetric vibration of the Si–O–Si bonds compared with the area below the PL mode at 2.46 eV.

For each sample the spectral activity in spectral range where the antisymmetric modes connected with the Si–O–Si bonds are positioned were calculated. This spectral activity increases with increasing network connectivity.¹¹

The area below the band at 2.46 eV and the measure of spectral activity of IR spectra in the region connected with the antisymmetric vibrations of Si–O–Si are shown. The presence of water during washing (in the case of the XGW sample) allows the condensation process to continue and so the number of Si–O–Si bond increases. The sintering process affects the structure of the silica aerogel in a similar way (AGS sample). The area below the band at 2.46 eV is higher in the PL spectra of the XGW and AGS samples. It can be concluded that increasing the network connectivity increases number of defects too. There are probably E' centers which are prominent defects in conventional α -SiO₂.

CONCLUSIONS

The method of synthesis, precursors and drying procedure affect the defects which can be formed in the structure of silica gel. The PL spectra of silica xerogels and cryogels consist of four bands at 2.00, 2.20, 2.32 and 2.46 eV. The band at 2.00 eV originates from the presence of silane at the surface of the sample. The non-stoichiometric composition of the structure of the gels produces a PL band at 2.20 eV.

The band at 2.32 eV is connected with the presence of organic residues which remain in the gel pores after drying. Increasing the network density allows the formation of E' paramagnetic defect centers which produce a PL band at 2.46 eV.

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ИЗВОД

УТИЦАЈ УСЛОВА СИНТЕЗЕ НА ФОТОЛУМИНЕСЦЕНЦИЈУ СИЛИКА ГЕЛОВА

ИВАНА ХИНИЋ, ГОРАН СТАНИШИЋ и ЗОРАН ПОПОВИЋ

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Приказали смо фотолуминесцентне спектре узорка силика ксерогела синтетисаног са етанолом као растварачем и узорка ксерогела у коме је етанол замењен са водом пре сушења. Осим тога, истраживали смо фотолуминесцентни спектар силика криогела синтетисаног са *tert* бутанолом као растварачем. Узорци су модификовани формамидом. У фотолуминесцентном спектру свих узорка идентификоване су траке на 2,00, 2,20, 2,32 и 2,46 eV. Трака на 2,00 eV је узрокована присуством силана док је трака на 2,20 eV везана за нестехиометријски састав силике. Установили смо да фотолуминесцентна трака на 2,32 eV потиче од органских група из растварача. Узрок траке на 2,46 eV су E' центри који су чести парамагнетни дефекти код конвенционалног α -SiO₂.

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