Formation of Irregular Rings in Silica Aerogel Structure During the Sintering Process

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Abstract: Samples of low-density, highly disordered silica aerogel with initial bulk density of 0.16 g/cm³, were sintered isothermally in different time intervals at 1000°C. Structural changes during the sintering process have been investigated by Raman spectroscopy. Defect modes of irregular three and four membered rings were observed in the Raman spectra of sintered samples.

Keywords: Silica Aerogel; Raman Spectroscopy; Infrared Spectroscopy; Sintering Process.

1. Introduction

Defect modes $D_1$ at ~ 490 and $D_2$ at ~ 607 cm⁻¹ appear in the Raman spectra of silica gels [1-2]. R. A. Bario et al. [3] suggested that the $D_1$ mode originates from vibrations of four membered puckered rings, while the $D_2$ mode can be attributed to the vibrations of planar three membered rings. This ring geometry corresponds to the minimum energy state of the silica gel structure. In Raman spectra of silica aerogels the $D_2$ mode is observed as a sharp
mode, due to planarity of three membered rings [3]. However, in real glasses such regularity can be destroyed which may result in shifting and/or broadening of defect modes [4]. Irregular three membered rings are not planar. Small differences in bond lengths and Si-O-Si angles along four membered puckered rings make them irregular.

During heat treatment in the sintering process, three membered rings close by condensation [5]. The formation of three membered rings is especially intensive at so called "medium" temperatures, above 600°C. As temperature increases, the reduced viscosity allows the surface to reconstruct in which stable five membered and higher order rings are formed on account of less stable, smaller rings [5].

Recent molecular orbital calculations performed by Uchino et al. [6] showed that defect modes frequency positions change when three and four membered rings are not completely regular. Using ab initio calculations, they obtained frequencies of the D₁ mode of irregular four membered rings and the D₂ mode of nonplanar three membered rings, as is shown in Tab. I.

**Tab. I** Frequencies of the D₁ mode of irregular four membered rings and D₂ mode of nonplanar three-membered rings according to ref. [6].

<table>
<thead>
<tr>
<th>Models</th>
<th>ω (cm⁻¹)</th>
<th>Assignation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model I</td>
<td>533</td>
<td>D₁</td>
</tr>
<tr>
<td></td>
<td>553, 644, 689</td>
<td>O₃₆Si(OH)ₓ, x = 1, 2</td>
</tr>
<tr>
<td></td>
<td>651</td>
<td>D₂</td>
</tr>
<tr>
<td>Model II</td>
<td>531</td>
<td>D₁</td>
</tr>
<tr>
<td></td>
<td>557, 684</td>
<td>O₃₆Si(OH)ₓ, x = 1, 2</td>
</tr>
<tr>
<td></td>
<td>652</td>
<td>D₂</td>
</tr>
<tr>
<td>Model III</td>
<td>526</td>
<td>D₁</td>
</tr>
<tr>
<td></td>
<td>553</td>
<td>O₃₆Si(OH)ₓ, x = 1, 2</td>
</tr>
<tr>
<td></td>
<td>645, 666</td>
<td>D₂</td>
</tr>
</tbody>
</table>

In our previous work [7] we concluded that application of a semiempirical method in computer simulations of silica aerogel structures could give good estimation of frequency positions in agreement with experimentally obtained infrared spectra. MNDO/d is one of the semiempirical methods. MNDO is a Modified Neglect of Diatomic Overlap method based on the neglect of diatomic differential overlap (NDDO) approximation. The MNDO/d method was expanded to include d-orbitals [7]. MNDO/d semiempirical calculations were applied on four models of the gel structure, which are summarized in Tab. II. We obtained similar results for D₁ and D₂ and many additional modes.

**Tab. II** Four models of the gel structure with different ring shapes and member numbers.

<table>
<thead>
<tr>
<th>Models</th>
<th>Model I</th>
<th>Model II</th>
<th>Model III</th>
<th>Model IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 members, regular</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>3 members, irregular</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4 members, regular</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>4 members, irregular</td>
<td>1</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5 members</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>6 members</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
These additional modes are connected with vibrations of irregularities that are randomly positioned, oriented and linked in the 3D gel structure. The model of the gel structure cannot be big enough to simulate the real structure in all details, so exact assignation of these vibrations is not possible. However, frequency distribution of the modes can be very useful in comparison with real experimental data, in order to estimate the type of structure, Si-O-Si rings and their population.

In this work, we used Raman spectroscopy to investigate samples of low-density silica aerogels synthesized to be very disordered and sintered in different time intervals at 1000°C. The types of the structure were identified using results of MNDOd calculations. Changes in the small ring populations during the sintering process were discussed.

2. Experiment

A sample of silica aerogel with initial bulk density of 0.16 g/cm³ was produced by mixing tetraethylorthosilicate (TEOS), water and ethyl alcohol in the molar ratio of 1:2:12. The two-step catalysis method was used. In the first step 3 10⁻³ mol of HCl and in the second step 0.2 mol of NH₄OH were added. Gelation time was very short, about 30 minutes. Samples were neutral (pH = 7) and were dried by supercritical extraction in Teflon tubes (critical parameters of ethyl alcohol are p_c = 63.1 at and T_c = 243.1°C). Alcohol was extracted at a temperature and pressure far from the critical point p = 65 at and T = 250°C).

The samples were isothermally sintered 0, 2, 4, 6, 10 and 16 hours at 1000°C in air. The bulk density of each sintered sample was determined from the mass and dimension of the cylindrical sample monolith.

Raman spectra excited by a 514.5 nm line of Ar ion laser were measured using a Jobin-Ivon U-1000 monochromator with a photomultiplier tube as detector. Incident beam power was 100-300 mW and measurements were performed at 200 K, without polarization. The observed samples have very intense photoluminescence (PL). At 200 K photoluminescence, which covers all Raman spectra [8], is minimal, and Raman spectra become visible.

3. Results and Discussion

The Raman spectra of the sintered sample series are shown in Fig. 1 in the spectral range from 400 to 1200 cm⁻¹.

These spectra were deconvoluted using a sum of up to 20 Lorentzian profiles. In the deconvolution process we obtained the frequency of peak maximum (ω), area below the Lorentzian (A) and width (w) of profile for each mode. In Fig. 2 an example of spectrum deconvolution in the case of the sample sintered for 16 hours is given.

The area below the Lorentzian profile is proportional to the number of vibrating modes. It is comparable with the intensity calculated using MNDOd. In Figs. 3 and 4 calculated intensities vs. Raman shift and areas below Lorentzians obtained by deconvolution from experimental Raman spectra are presented.

As we can see in Fig. 3 the structure of the non-sintered sample is in good agreement with model IV, which consists of bigger, four, five and six membered rings. The structure of the sample sintered 2 hours is something between models I and II. In Fig. 4 we can see that areas below Lorentzians of Raman spectrum do not agree with model I in the spectral range at
about 500 and at about 600 cm\(^{-1}\), which are connected with vibrations of regular three and four membered rings. The differences from model II are in the area of about 700 cm\(^{-1}\) containing modes caused by vibrations of links between three and four membered rings. We can conclude that the sample sintered for two hours did not have many regular small rings. The structure of the sample sintered for 4 hours is in good agreement with model III (Fig. 3).

![Graph showing Raman spectra](image)

**Fig. 1** Raman spectra of sintered sample series in the spectral range from 400 to 1200 cm\(^{-1}\). The bulk density of every sample is given on the right of the spectra. Experimental data are presented by circles, while the light gray line is the sum of Lorentzians obtained by deconvolution.

![Graph showing deconvoluted Raman spectrum](image)

**Fig. 2** Deconvoluted Raman spectrum of the sample sintered for 16 hours.

This model consists of both, small and big rings, without irregular three membered rings. The sample sintered for 10 hours has a structure between models III and IV, while the sample sintered for 16 hours is very like model IV. The structure of the sample sintered for 6 hours is not comparable with any model. Using this analysis we can reconstruct the evolution
of silica aerogel structure during the sintering process. The non-sintered sample structure consists of four, five-membered and higher order rings and does not have many three-membered rings. In the first two hours of sintering three-membered irregular rings form. In the next two hours these irregular rings become mostly regular and the number of four-membered rings increases. After six hours of sintering the structure reconstructs in such a way that stable five-membered and higher order rings form on account of less stable, smaller rings.

Fig. 3 A comparison of the intensity calculated using MNDOd and the area below Lorentzians obtained by deconvolution of experimental Raman spectrum. Structures of the non-sintered sample and the sample sintered for 16 hours are in good agreement with model IV that consists of four, five and six-membered rings. The best model for the structure of the sample sintered for 4 hours is model III, which has no irregular small rings.

This evolution model is approved by analysis of changes in Raman modes connected with small regular and irregular rings. Fig. 5a presents the areas below Lorentzians of $D_2$ mode for regular and irregular three-membered rings, vs. sample bulk density as log-log plot. The same dependence for $D_1$ mode for regular and irregular four-membered rings is presented in Fig. 5b.
The number of irregular three membered increases in the first two hours of sintering, while the number of regular three membered rings decreases (Fig. 5a). This can be explained by deformation of regular rings at the beginning of the sintering process. This process can explain disagreement of Raman spectrum of the sample sintered for two hours with model I for frequencies of three membered regular rings. The Raman spectrum has no regular three membered rings. Similar behavior is noted in the case of four membered rings (Fig. 5b). From the second to the fourth hour of sintering the number of irregular three membered rings suddenly decreases. The Raman spectrum of the sample sintered for four hours is in good agreement with calculations on model III, which have no irregular rings. The number of regular and irregular three membered rings reaches maximum for about six hours of sintering and then decreases. From the sixth hour of sintering the formation of higher order rings starts.

4. Conclusion

In this work we presented Raman spectra of sintered low-density silica aerogels with a very disordered structure. The structure of silica consists of Si-O-Si rings with different numbers of members. We determined the evolution of the structure and changes in the type and population of Si-O-Si rings during sintering process using semiempirical MNDOd computer simulations for several structure models. From these simulations we obtained exact positions of frequencies of regular and irregular three and four membered rings - small rings. Also, we analyzed changes in the Raman spectra of sintered sample series in the case of small ring modes. Both simulations and Raman spectra analysis show that in the first few hours of sintering deformation of regular three membered rings forms irregular rings. At the same time irregular four membered rings become formed. As sintering proceeds, higher order rings form on account of smaller ones.
Acknowledgments

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References