

Low Frequency Raman Spectra of Silica Aerogels with Double Fractal Structure

I. I. HINIĆ¹), G. M. STANIŠIĆ, S. B. KAJTEZ, and Z. V. POPOVIĆ

Institute of Physics, Pregrevica 118, 11080 Belgrade, Yugoslavia

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Silica aerogel samples with double fractal structure were synthesized. The samples were sintered at 1000 °C in different time intervals. In low frequency Raman spectra of the sintered samples, we observed two fractons caused by localization of vibration on clusters of two fractal substructures. During sintering the two fractal substructures become dense and, after 16 h of sintering, merge one into another.

1. Introduction

Fractal objects have the property of scaling, namely, every physical property can be presented as a power function x^s . For example, the mass of a fractal is $m \sim R^D$, while the surface is $S \sim R^{D_s}$, where R is a linear dimension of building structure particles, and D is the mass and D_s the surface fractal dimension, respectively [1]. The exponents D and D_s are real numbers [1].

Fractality of the structure of these materials is present in their vibrational spectra also. Low frequency Raman spectra (in the range from 10–150 cm^{-1}) of fractal materials attracted huge attention in the last few decades. Fracton or boson modes are found in spectra of many materials, such as glasses with different chemical composition, polymers, nanocrystals incorporated in an amorphous base, etc. [2–7]. Silica aerogel is a typical fractal material [8, 9]. The reduced Raman intensity for a disordered material can be expressed as [9]

$$I_r = \frac{I(\omega) \omega}{n(\omega) + 1} = C(\omega) g(\omega) = \omega^\nu, \quad (1)$$

where $n(\omega)$ is the Bose-Einstein distribution, $C(\omega)$ the light–vibration coupling (LVC) coefficient, $g(\omega)$ the density of phonon states, and ν is the Raman exponent. According to the Alexander-Orbach model [10–12], the Raman exponent for a non-coherent vibration in aerogels can be expressed as

$$\nu = d \left(\frac{2\sigma}{D} + 1 \right) - 1, \quad (2)$$

where d is the spectral fractal dimension (or fracton dimensionality), σ is a scaling exponent (so-called superlocalization exponent) which depends on the mechanical properties of the structure, and D is the mass fractal dimension of the structure [9, 13].

¹) Corresponding author; Tel.: +381 11 3160260 ext. 224; Fax: +381 11 3162190;
e-mail: HINIC@phy.bg.ac.yu

Alexander's calculations showed that values $\sigma \geq 1$ are in agreement with scaling theory, while $\sigma < 1$ violates self-similarity [10]. Theoretical calculations showed that σ is between 1 and 1.3 [13]. Equation (2) allows measuring of spectral fractal dimension. For silica aerogels, experiments show that ν is close to 1 and decreases as the density of the sample increases. Boukenter et al. obtained spectral fractal dimensions for three base-catalyzed aerogels in the interval from 0.88 to 1.05 [13]. The frequency of a fracton mode is connected with the average diameter of the building clusters L as

$$\omega_{FR} = \frac{S\nu}{L}, \quad (3)$$

where S is a constant depending on the cluster shape (for spherical clusters $S \approx 0.8$, and for stick clusters $S \approx 0.5$) and ν is the sound velocity [9, 14]. In this work we investigated low frequency Raman spectra of sintered silica aerogel series. The examined samples have very disordered fractal structure, which consists of two substructures with different fractal dimension. During sintering, these two structures merge one into another, fractality disappears, and the structure becomes homogeneous.

2. Experiment

The samples of silica aerogel with initial bulk density of 0.16 g/cm^3 were produced by mixing tetraethylortosilicate (TEOS), water, and ethyl alcohol in molar ratio 1:2:12. A two-step catalysis method was used. In the first step 10^{-3} mol of HCl and in the second step 0.2 mol of NH_4OH was added. Gelation time was very short, about 30 min. Samples were neutral ($\text{pH} = 7$) and were dried by supercritical extraction in Teflon tubes (critical parameters of ethyl alcohol are $p_c = 63.1 \text{ at}$ and $T_c = 243.1 \text{ }^\circ\text{C}$). Alcohol was extracted at a temperature and pressure far from the critical point ($p = 65 \text{ at}$ and $T = 250 \text{ }^\circ\text{C}$). The samples were isothermally sintered for 0, 2, 4, 6, 10, and 16 h at $1000 \text{ }^\circ\text{C}$ in air. The bulk density of each sintered sample was determined by measuring the mass and dimension of the cylindrical sample monolith.

Raman spectra in the spectral range from $3\text{--}150 \text{ cm}^{-1}$ were excited using a 514.5 nm line Ar ion laser and detected using a Jobin-Ivon U-1000 monochromator and photomultiplier as detector. The measurements were performed at 200 K , to avoid photoluminescence, without polarization. The laser power was below 100 mW .

3. Results and Discussion

Figure 1 shows low frequency Raman spectra in the spectral range from $3\text{--}60 \text{ cm}^{-1}$. The spectra were reduced using the Bose-Einstein distribution relation (Eq. (1)). Our previous investigations have shown that these samples of silica aerogel have double fractal structure. Using small angle X-ray scattering (SAXS) spectra, we observed two areas with different fractal dimensions in Porod's regime [15]. In Fig. 2a we present the fractal dimensions obtained for two Porod's areas versus bulk density. The existence of two Porod's areas and two fractal dimensions was explained by the fact that the structure of this silica aerogel consists of two substructures: the first one built of small clusters (linear dimension $\approx 40 \text{ \AA}$) which are, in the beginning of sintering, surface fractals, and the second one built of large clusters ($\approx 100 \text{ \AA}$) which are mass fractals [15].

The double fractal structure is reflected in the low frequency Raman spectra. The deconvolution of the low frequency Raman spectra is presented in Fig. 1 for each sam-

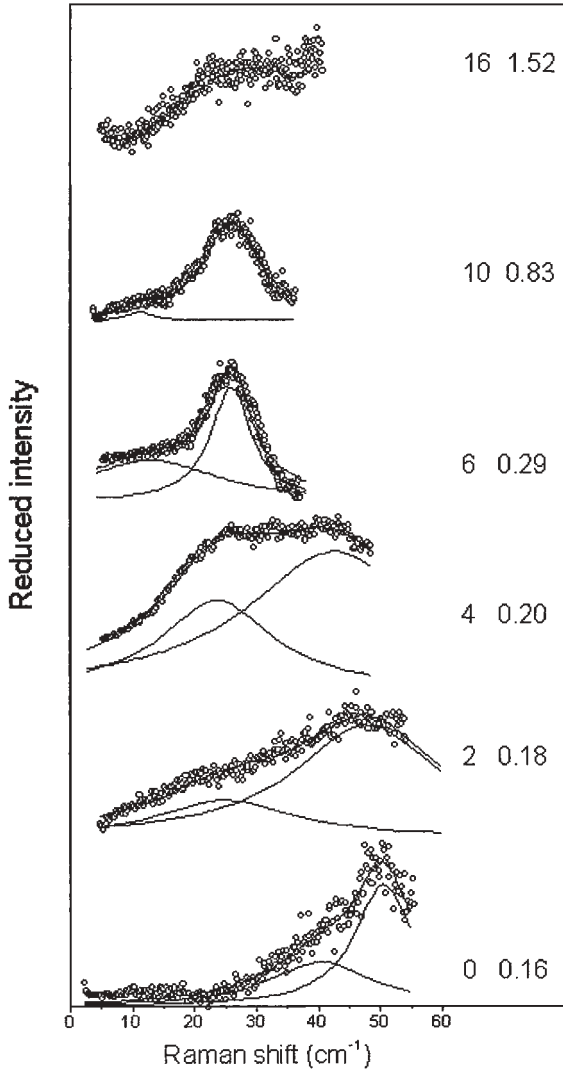


Fig. 1. Low frequency Raman spectra of silica aerogel samples. The time of sintering (in hours) and the bulk density (in g/cm³) of the sample are noted right to each spectrum. The Lorentzian profiles which were used for the deconvolution of the spectra are presented below each spectrum

ple of the series. Deconvolution was performed using one or two Lorentzian profiles. The lower frequency mode is denoted as fracton I, and the higher frequency mode as fracton II. We proved the nature of these modes using SAXS spectra. In the Porod's regime, the absolute value of the wave vector is inversely proportional to the average linear diameter of the building clusters [16],

$$q = A \frac{1}{L}, \quad (4)$$

where A is a multiplicative constant. If the limits of Porod's regimes are denoted as $q_{1,\min}$, $q_{1,\max}$

and $q_{2,\min}$, $q_{2,\max}$, we could estimate the average diameter of the building clusters in each substructure as

$$L_i = \frac{1}{\frac{(q_{i,\max} - q_{i,\min})}{2}}, \quad (5)$$

where $i = 1, 2$.

Figure 2b shows an estimation of the average diameter of the building clusters for Porod's regimes I and II, as well as the average diameter of the clusters estimated using the fracton frequency position according to Eq. (3). We assumed that clusters are spherical and the sound velocity is about 4000 m/s. As we can see in Fig. 2b,

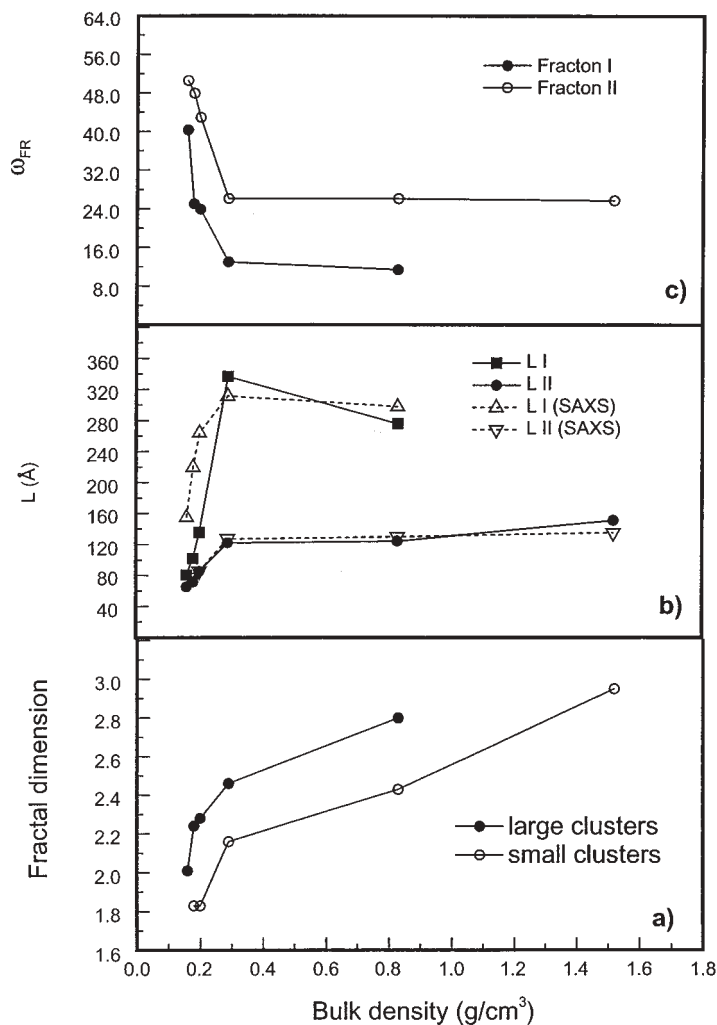


Fig. 2. a) Fractal dimension of the structure vs. bulk density for the two fractal substructures, b) estimation of the average cluster diameter obtained from SAXS and low frequency Raman spectra, and c) frequency position of fractons I and II vs. bulk density

both methods of estimation give nearly the same average cluster diameter. Thus we concluded that modes in the low frequency spectral range are really fractons, i.e. localized vibrations on clusters of two fractal substructures. Fracton I represents vibrations localized on large-cluster substructures, while fracton II is attached to small-cluster vibrations. By increasing the time of sintering, the fractons move to lower frequencies (Fig. 2c). As can be seen from Figs. 1 and 2, in the spectrum of the sample sintered for 16 h only one fracton exists. Consequently, in the SAXS spectrum of this sample, only one Porod's area is present with a unique fractal dimension. This means that after 16 h of sintering, the sample has no more double fractal structure.

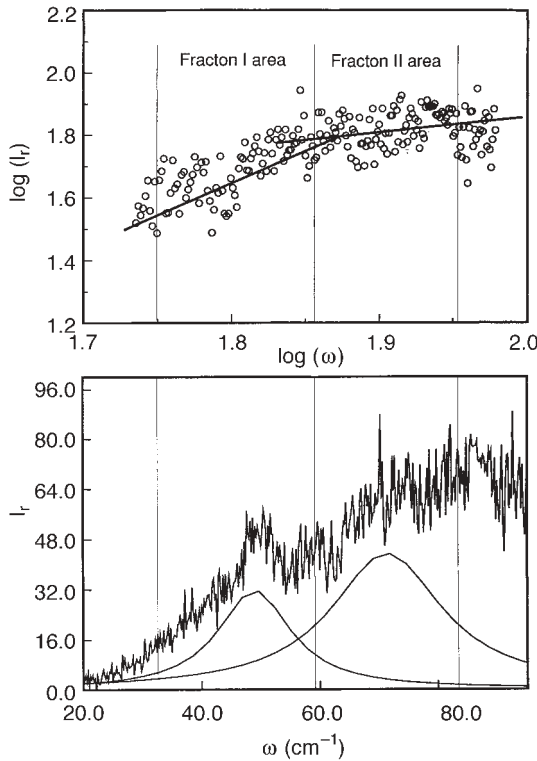


Fig. 3. Linear and double logarithmic plots of Raman spectra for the non-sintered sample

In order to extract the Raman exponent ν , we fitted a double logarithmic plot of the low frequency Raman spectra using a linear function. The limits of the fracton I and II areas in the double logarithmic plot were the limits for the fitting procedure (Fig. 3). The values of the spectral fractal dimension were obtained using Eq. (2). We used the value $\sigma = 1$ as superlocalization exponent, because all other combinations give non-physical values for the spectral fractal di-

mension. Table 1 shows the obtained values for structure fractal dimension, Raman exponent, and spectral fractal dimension for each sample in both substructures. Figure 4a presents the spectral fractal dimension versus sample bulk density.

As can be seen from Fig. 4a, the spectral fractal dimension changes non-uniformly during the first 6 h of sintering. We believe that during the first few hours of sintering, small clusters somehow dilute while large clusters become dense, as it is shown schematically in Fig. 4b. After 10 h of sintering, those two structures merge and their spectral fractal dimensions become close, leading to a single structure after 16 h of sintering.

Table 1

Obtained values for structure fractal dimension, Raman exponent, and spectral fractal dimension for each sample in both substructures

bulk density (g/cm ³)	sintering time (h)	parameters					
		D_1	D_2	ν_1	ν_2	d_1	d_2
0.16	0	2.01	1.81	1.18	0.93	1.095	0.917
0.18	2	2.24	1.81	1.07	0.65	1.093	0.780
0.20	4	2.28	1.83	1.03	0.53	1.081	0.730
0.30	6	2.46	2.16	0.73	0.85	0.950	0.960
0.83	10	2.80	2.43	0.79	0.76	1.044	0.965
1.52	16	—	2.95	—	0.73	—	1.030

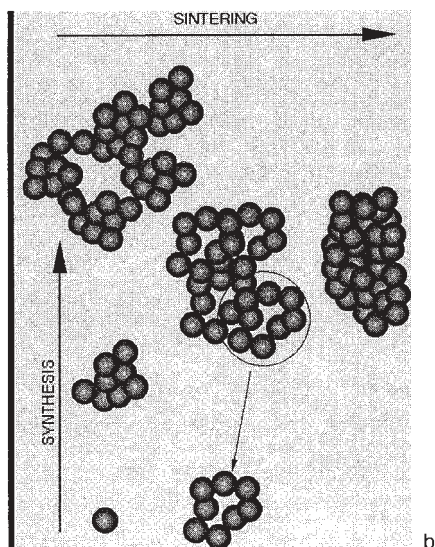
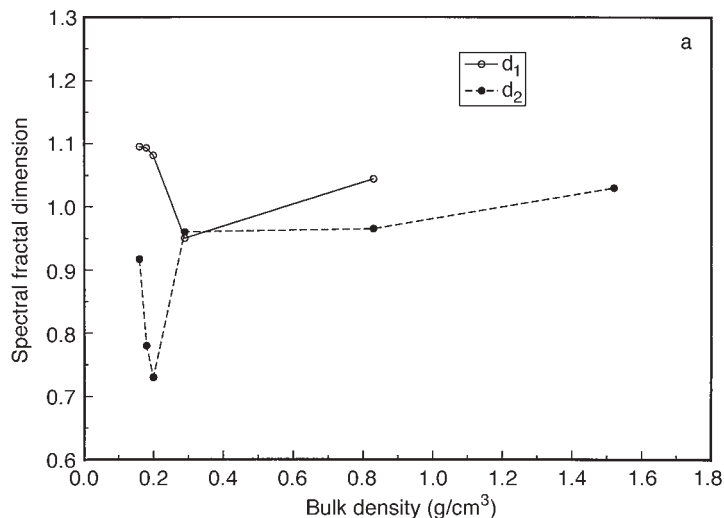


Fig. 4. a) Spectral fractal dimension vs. bulk density and b) schematically presented changes in cluster shape during sintering

4. Conclusion

We have shown that the double fractal structure of silica aerogel samples results in the appearance of two fracton modes in low frequency Raman spectra. As the sintering time increases, the double fractal structures merge and, consequently, the fracton modes become closer. At 16 h of sintering only one fracton exists. Our findings based on Raman spectra measurements are fully in agreement with results obtained from SAXS measurements on the same samples.

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