DIELECTRIC MEASUREMENTS OF SILICA AEROGELS

D. I. SANTOS, E. C. ZIEMATH, A. A. SILVA, H. C. BASSO
and M. A. AEGERTER

*Instituto de Física e Química de São Carlos, Universidade de São Paulo Cx.
Postal 369, 13560 São Carlos (SP) Brasil*

The dielectric response of aerogels of silica is measured down to 1.7 K and compared to a theoretical calculation using the Looyenga's relation applied to two different model structures. Helium atoms start to condense on the pore walls at $T \sim 13$ K and fill them at the liquefaction temperature. A drop of the dielectric constant accompanied by a large loss peak is observed near 35 K. The origin of the absorption lies in a thermally activated relaxation process and is probably due to a large number of structural defects similar to those proposed for bulk silica.

INTRODUCTION

Aerogels are a new and interesting class of materials prepared at room temperature by hydrolysis and polycondensation of metal or non metal-organic compounds. These materials can be prepared with a porosity of up to 99% and consequently low apparent density and high specific area (up to 1500 m²/g for SiO_2 aerogels). This confers to these materials interesting physical properties.[1-3] From the technological point of view aerogels are precursors for the preparation of new glasses and glass-ceramics without fusion, thin films, fibers and powders for ceramics of high technology having low sintering temperatures.[4,5]

In this paper we present preliminary results on the dielectric response of silica aerogels in the temperature range 1.7 K to 300 K.

PREPARATION OF THE SAMPLES[6]

Silica aerogels have been prepared by hydrolysis and polycondensation at 50°C of solution of $Si(OCH_3)_4$ (TMOS), H_2O and methanol in acid, neutral and basic conditions. The process of gelification is not well understood yet and parameters such as solution composition, pH and temperature have a strong influence on the gel structure.[7,8]

Simplified chemical reactions have been proposed to explain the inorganic polymerisation.

$$M(OR)_n + n(H_2O) \rightarrow M(OH_n) + nROH \quad \text{hydrolysis}$$

$$M(OH)_n \rightarrow MO_{n/2} + (n/2)H_2O \quad \text{polycondensation}$$
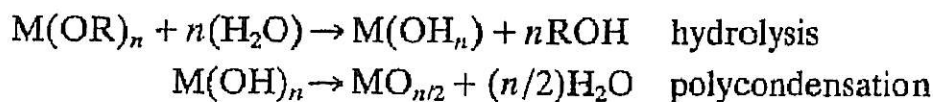
The gel obtained is a two phases material in which alcohol and water fill the pores of a silica skeleton. They were dried under hypercritical conditions.[6] The result is a monolithic, highly porous and amorphous SiO_2 material which can be visualized as a sponge formed by a SiO_2 skeleton.

The aerogels are practically free of inorganic impurities, but still contain a few % of organic material and chemically adsorbed water which can only be eliminated by heating at high temperature.

EXPERIMENTAL RESULTS

The elastic and dielectric behavior of amorphous solids at low temperatures differs completely from that of crystalline solids. A thorough review for inorganic glasses was recently written by Hunklinger and v. Schickfus.[9] At room temperature the dielectric constant of fused silica has a value of ~3.8 and this value decreases slightly ($\Delta\varepsilon' \sim 10^{-2}$) but steadily down to 5 K.[10] Below this temperature it rises again ($\Delta\varepsilon' \sim 1.5 \times 10^{-4}$) due to the presence of polar impurities. A large absorption peak independent of the OH content is found around 30 K at $f = 1$ KHz[11] and both acoustic and dielectric absorption data fit an Arrhenius law $\tau = \tau_0 \exp(U/KT)$ with $U = 49$ meV $\tau_0 = 10^{-15}$ s showing that the same mechanism is responsable for both phenomena. Microscopic models have been proposed to explain the relaxation process. The common assumption is the presence of localized structural defects existing in different double well potential configurations where the oxygen atoms can move from one well to the other by transverse or longitudinal motion (defect A and B[12]) or small angle rotation of the SiO_4 tetrahedron[13] (Figure 1).

Cylinders of aerogels have been sawed with a high precision diamond saw in disc form (ϕ 10 × 1.0 mm^3) and gold electrodes with guard rings have been deposited on both faces. The samples were placed on a special sample holder designed to avoid stresses on the material in a Supervaritemp Janis Cryostat. The samples were first evacuated at 10^{-3} mbar during several hours at room temperature. All the measurement have been performed in helium atmosphere with a General Radio bridge 1615-A (50–10^4 Hz). Figure 2 shows the results of ε' and tg δ for an aerogel prepared in neutral solution and having an apparent density $\rho_a = 0.35$ g/cm^3, overall porosity $P_i = 0.82 \pm 0.01$, porous volume $V_e = 2.41$ cm^3/g and specific BET Area $A_{BET} = 339$ m^2/g. The dielectric constant of the aerogel is much lower than that of amorphous bulk silica. Figure 3 shows a comparison of the values obtained for $f = 10$ KHz at 100 K for neutral gels of different composition with calculations based on the Looyenga's equation valid for a two components mixture.[14]

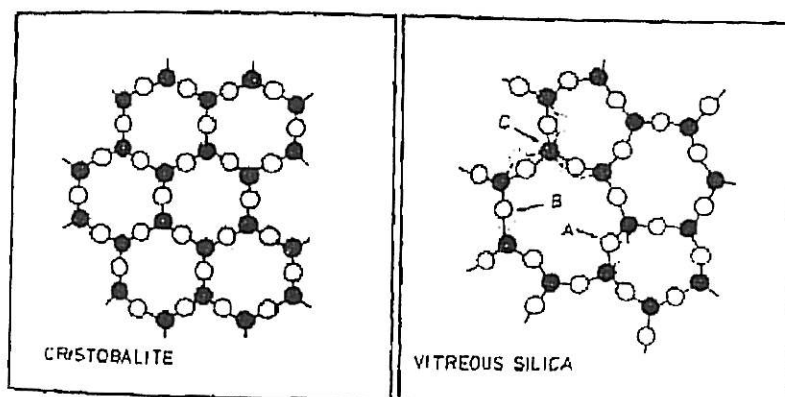$$\varepsilon_{(gel)} = [\varepsilon_0^{1/3} + (1 - P_i)(\varepsilon_i^{1/3} - \varepsilon_0^{1/3})]^3$$

FIGURE 1 Two dimensional representation of the structure of amorphous silica (● Si, ○ O) with three possible types of structural defects.[12,13]
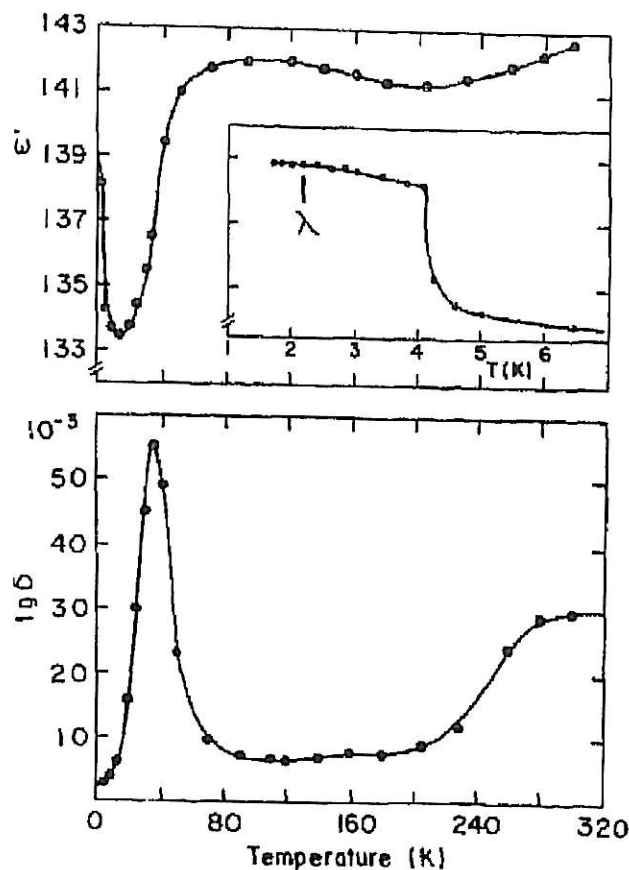
FIGURE 2 Dielectric response (ε', tg δ) of an amorphous silica aerogel prepared in neutral conditions as a function of temperature measured at $f = 10$ KHz. Aerogel specification: $\rho_a = 0.35$ g/cm^3, $A_{BET} = 339$ m^2/g.

In one model it is assumed that the low density material is composed of a solid SiO$_2$ skeleton having the same density ($\rho = 2.2$ g/cm^3) and dielectric constant ($\varepsilon_i = 3.8$) as the fused silica and empty macropores ($\varepsilon_0 = 1.0$). In a second and more realistic model, based on our recent SAXS studies,[7,8] we assumed that the neutral aerogel is composed of a light SiO$_2$ matrix containing empty and closed micropores in the 5–10 Å range which reduce its apparent skeletal density and
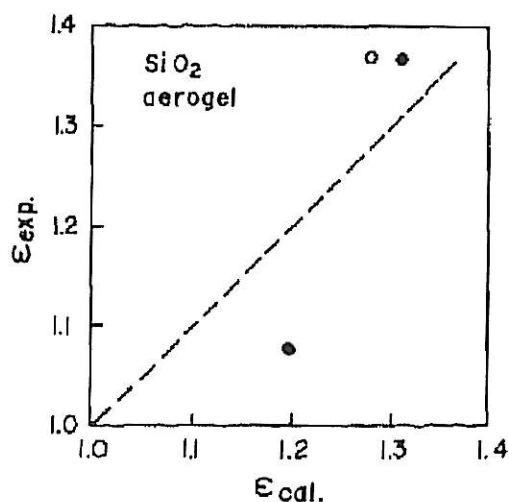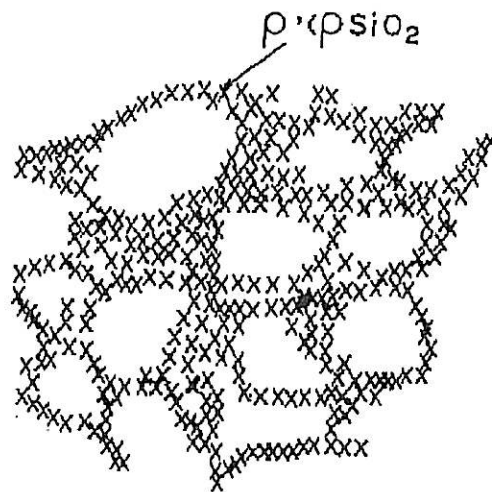

FIGURE 3 Comparison of the measured dielectric constant of neutral gels of different composition ($f = 10$ KHz, $T = 100$ K) with calculated dielectric constant using the Looyenga's relation applied to the first model (●) and to the second structure model (see text).

$$\rho'(\rho\, SiO_2$$

Structure of neutral aerogels

FIGURE 4   Neutral aerogels structure as derived from SAXS measurements (7, 8). The value of ρ' for the aerogel shown in Figure 2 is $\rho' = 0.415\, g/cm^3$.

dielectric constant to a value much smaller than bulk silica (0.415 g/cm³ and 1.28 respectively). This matrix still contains empty meso and macro pores (Figure 4). The values calculated for both models are not very different and the dispersion of the results does not allow to differentiate them.

A sharp decrease of ε' is observed near 35 K (for $f = 10$ KHz), accompanied by a large loss peak. Due to its similarity with the loss peak observed in bulk silica we deduce that it must have the same origin (Figure 1). The height of the loss peak is ~200 times larger and is narrower than that observed for bulk silica. It is an indication that aerogels contain a much larger density of structural defects than bulk silica; the formation of these defects if probably facilitated by the high specific area of the aerogel.

As the temperature is lowered, ε' passes through a minimum and then increases smoothly down to 4.2 K while the dielectric loss still decreases to practically unmeasurable values. We believe that He atoms start to condense at $T \sim 13$ K on the pores surfaces of the aerogel due to Van der Waals interaction; ε' reaches a maximum when liquid helium fills the pores. The variation of the dielectric constant due to the presence of liquid helium in the pores can be calculated with the Looyenga's relation; for both models $\Delta\varepsilon' \simeq 4.8 \times 10^{-3}$ for the gel presented in Figure 2 are in agreement with the experimental result. The slight increase of the dielectric constant at still lower temperatures can be accounted for by the temperature variation of the dielectric constant of ^{4}He.[15] The variation in ε' observed between 15 K and 1.7 K is therefore due to the gradual filling of the pores by He atoms contrary to what has been observed in bulk silica. The samples have micropores larger than the atomic dimension of He atoms, since no increase of ε' at the λ point has been observed.

Although gels of silica are known for many years, aerogels of silica (and other elements) are a new class of materials which are relatively easy to prepare in a wide range of porosity and specific area. Their dielectric response shows interesting features at low temperature; these materials are therefore promising for studies of the effect of He atoms on two-level systems (TLS) with acoustic and dielectric techniques[16] as the sound velocity may reach values as low as 10^4 cm/s

(35 times smaller than in conventional porous glasses) and consequently large effects should be observed when ^{3}He or ^{4}He fills the pores.

ACKNOWLEDGEMENT

REFERENCES

1. For a review see the Proceedings on "Glasses and Glass Ceramics from Gels", published in *J. Non Cryst. Solids,* **48** (1982), **63** (1984) and **82** (1986).
2. J. Frickc, *Aerogels,* Proc. of the 1st International Symposium, Würzburg 1985, Springer Verlag (1986).
3. O. El-Bayoumi and D. R. Uhlmann, ed. Proc. of the Symposium of "Glass Science and Technology, Problems and Prospects for 2004", Vienna 1984, *J. Non Cryst. Solids* **73** (1985).
4. C. J. Brinker, D. E. Clark and D. R. Ulrich, ed. "Better ceramics through chemistry", North-Holland 1984.
5. L. L. Hench and D. R. Ulrich, ed. Proc. International Conference "Ultra Structure Processing of Ceramics, Glasses and Composites", Gainesville (1983), J. Wiley (1984).
6. D. I. Santos, N. D. S. Mohallem and M. A. Aegerter. Cerâmica, Brasil, 1986.
7. A. Craievich, D. I. Santos, M. A. Aegerter, T. Woignier and J. Zarzycki. *J. Non Cryst. Solids* (in press) (1986).
8. A. Craievich, D. I. Santos, M. A. Aegerter, T. Lours and J. Zarzycki. Proc. 7º Cbecimat (Brasil) (1986).
9. S. Huncklinger and M. v. Schickfus, Acoustic and dielectric properties of glasses at low temperature. In: Amorphous Solids Low Temperature Properties, cap. 6, ed. W. A. Philips, *Topics in Current Physics,* **24** (1981), Springer Verlag.
10. R. D. McCammon and R. N. Work, *Rev. Sci. Instr.* **36,** 1169 (1965).
11. S. M. Mahle and R. D. McCammon. *Phys. Chem. Glasses* **10,** 222 (1969).
12. O. C. Anderson and N. E. Bömmel. *J. Am. Ceram. Soc.* **38,** 125 (1955).
13. R. E. Strakna. *Phys. Rev.* **123,** 2020 (1961).
14. J. B. Hasted. "Aqueous Dielectrics", Chapman and Hall (1973).
15. C. E. Chase, E. Maxwell and W. E. Millet. *Physica* **27,** 1129 (1961).
16. J. R. Beamish, A. Hikata and C. Elbaum. *Phys. Rev. Lett.* **52,** 1790 (1986).