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DIELECTRIC RESPONSE OF SILICA AEROGELS

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The dielectric response of porous silica aerogel prepared by hypercritical drying of gels from hydrolysis of TMOS - Methanol solution have been measured between 1.6 K to 300 K and frequencies between 50 and 10^5 Hz. The ε' value of the porous gels is found practically constant between room temperature and 100K but smaller than of fused silica. A sharp decrease of ε' is observed near 35 K and accompanied by a large loss peak (tg δ). A small increase of ε' for $T < 13$ K is attributed to the adsorption of He atoms on the porous superficies.

1. INTRODUCTION

Aerogels are a new and interesting class of materials which can be prepared at room temperature by hydrolysis and polycondensation of organometalic compounds. The possibility to obtain amorphous materials in a large range of porosity (typically 0 to 99 %) and specific area (up to 1500 m^2/g for SiO_2 aerogels) confers them interesting physical properties. On the other side aerogels are also precursors for the preparation of new glasses and glass ceramics without fusion, thin films, fibers and ultra fine monodisperse powders for ceramics which can be usually sintered at relatively low temperatures. Greater purity and homogeneity are also possible. There is little information in the literature[1,2,3] about the electrical properties of the gel derived materials despite the fact that the high porosity offers the possibility to form materials with low dielectric constant.

In this paper we present preliminary results of a study of the dielectric response of silica aerogels in the temperature range 1.8 K to 300 K and frequencies 50 to 10^5 Hz.

2. PREPARATION OF AEROGELS

Silica aerogels have been prepared from solutions of tetramethoxysilane (TMOS, Fluka) dissolved in methanol. The composition was C = 40, 50, 60 vol % of TMOS. To this solution 4 moles of

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bidistilled water was added to each mol of TMOS. The sols have been also catalysed by adding to the water HNO_3 (pH ≈ 2) or NH_4OH (pH ≈ 9) in order to prepare gels under acidic, neutral and basic conditions. After 20 min of vigorous stirring at room temperature the sols have been transferred into Pyrex tubes, hermetically closed and let to gel at 55°C. Immediately after the gelation, the tubes have been opened and placed in an auto-clave for drying under hypercritical solvent evacuation[4]. The critical conditions P_c ≈ 200 bar and T_c ≈ 300°C have been reached by addition of methanol in the autoclave. These aerogels still contain a few weight % of adsorbed water and organic materials (carbon) which can only be eliminated by heating at high temperature.

The samples used for dielectrics measurements have been cut with a precision diamond saw into thin slices with parallel surfaces and 0.8 - 1 mm thickness and 10 mm diameter. Gold electrodes with guard rings (diameter ≈ 6 mm) have been deposited on both faces. The samples were mounted in a Janis Supervaritemp Cryostat allowing temperature variation between 1.7 K and 300 K (in helium atmosphere). The dielectric measurements have been performed using a General Radio Model 1615 A capacitance bridge between 50 Hz and 10^5 Hz. Some measurements have also been realized using a home-made automatic low frequency bridge (10^{-2} - 50 Hz)[5]. Prior any low temperature measurements the samples have been thoroughly evacuated at 10^{-3} mbar during several hours at room temperature.

Most of the aerogels have been also characterized by other techniques such as SAXS, BET, porosimetry and densitometry[6-9].

3. EXPERIMENTAL RESULTS AND DISCUSSION

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 given by Hunklinger and Schickfus[10]. At room temperature the dielectric constant of amorphous fused silica is $\varepsilon' \approx 3.8$ and its value decreases slightly but steadily down to 5 K ($\Delta\varepsilon' \approx 10^{-2}$). Below this temperature it rises again ($\Delta\varepsilon' \approx 10^{-4}$) due to the presence of polar impurities[11]. A large absorption loss peak independent of the OH constant is found around 30 K at f = 1 KHz[12]. Both acoustic and dielectric absorption data fit an Arrhenius law $\tau = \tau_o \exp(U/KT)$

with U = 49 meV and $\tau_o = 10^{-13}$ s showing that probably the same mechanism is responsible for both relaxation processes. The common assumption is that these phenomena are due to the presence of localized structural defects existing in different double well potential configuration (figure 1) where the oxygen atoms can move from one well to the other by transverse or longitudinal motion (defect A and B), or small angle rotation of SiO_4 tetrahedra (defect C)[13-14].

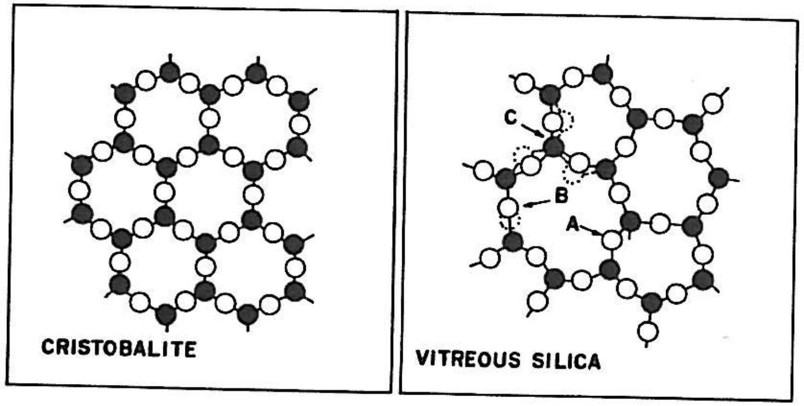

FIGURE 1
Two dimensional representation of the structure of amorphous silica (● (Si), o (O)) with three possible types of structural defects[13-14].

Recently the dielectric properties of various amorphous and porous gels have been analysed at room temperature between 10^3 and 10^6 Hz by Chandrashekhar and Shafer[3]. These gels were mainly xerogels prepared from TMOS alcoxide or Cabosil M-5 silica fume and consequently have a different structure and porosity than our aerogels. They found a considerable anomaly in the dielectric constant of the organic gel derived glasses without any corresponding changes in the dielectric loss factor or dc resistivities when compared to fused silica glass. This anomaly is reflected by a much higher dielectric constant ($\varepsilon' \sim 6.5 - 7.0$) and a slightly higher dielectric loss factor ($1.5 - 2.10^{-3}$) as compared to $\varepsilon' \approx 3.8$ and tg $\delta < 1.10^{-3}$ for fused silica; it is suggested that these differences are caused by the presence of traces of elemental carbon (up to 500 ppm).

Figure 2 shows a typical results of ε' and tg δ found for our aerogels measured at f = 10KHz. In this example the SiO_2 aerogels have been prepared under neutral condition with a TMOS concentra-

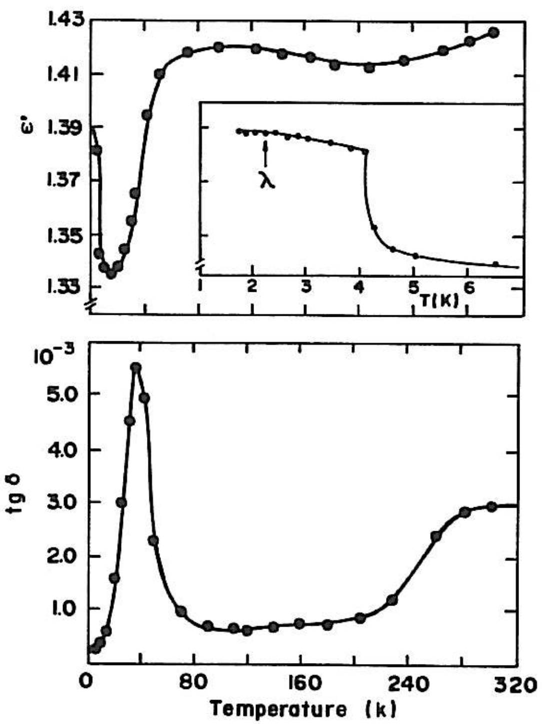

FIGURE 2
Dielectric response ε' and tg δ of a silica aerogel prepared under neutral conditions measured at 10 KHz (see text for physical parameters).

tion C = 50 vol %; it has an apparent density of ρ_a = 0.35 g/cm³ an overall porosity P_i = 0.82 ± 0.01, a porous volume V_e=2.41cm³/g and a specific BET area A = 339 m²/g. All aerogels prepared so far by us either in acid, basic or neutral conditions are thought to have a structure described as a sponge of apparent density ρ_a and

formed by a light SiO_2 matrix occupying a volume fraction (1-Φ) and which contains essentially closed micropores in the 5-10 Å range; its apparent skeletal density is reduced to values $\rho = \rho_a/(1-\Phi)$ smaller than 2.2 g/cm³ and open meso and macro pores occupying the remaining volume fraction Φ [6,7,15].

As foreseen the dielectric constant ε' measured for T > 120 K is lower than that of amorphous fused silica (ε' ~ 3.8) while the tg δ value is slightly higher ($< 10^{-3}$). Various theoretical models are available in order to calculate the dielectric constant of a two components compound, in our case a SiO_2 sponge of dielectric constant ε_1 and open pores (air or vacuum) of dielectric constant ε_2 = 1. Figure 3 gives the results of the mean value of ε' taken for T > 120 K for four aerogels as a function of the

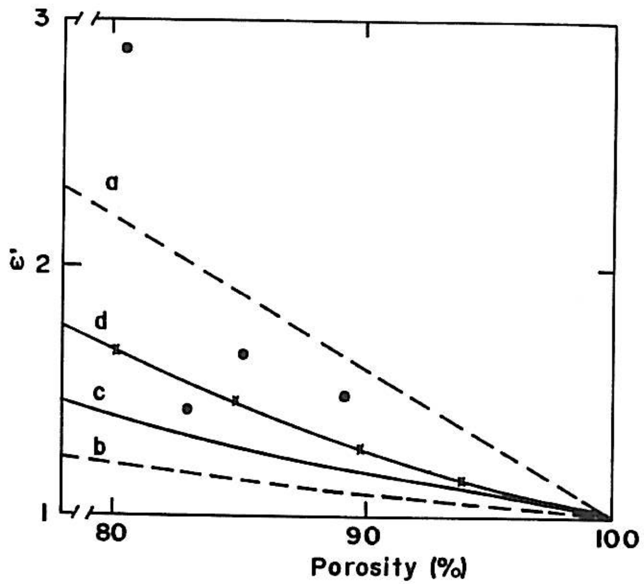

FIGURE 3
Measured dielectric constant ε' of aerogels as a function of the porosity (o). The curves are theoretical models (see text).

the porosity P defined as $P = (1 - \rho_a/\rho)$ where ρ is the density of fused silica.

The theoretical curve (c) of the figure refers to the Looyenga's equation[16] ε' (gel) = $[\varepsilon_2^{1/3} + (1-P)(\varepsilon_1^{1/3} - \varepsilon_2^{1/3})]^3$ calculated using the values $\varepsilon_1 = 3.8$ (SiO_2) and $\varepsilon_2 = 1.0$. All the experimental data have higher values. Curve (d) refers to the same model but using the values proposed by Chandrashekhar et al[3] $\varepsilon_1 = 7.0$ and $\varepsilon_2 = 1.0$. Except for one measurement the fit appears much better and confirms that elemental carbon or the remaining organic compounds alter probably the dielectric constant of the SiO_2 matrix. The two other curves refer to two other simpler models for which $\varepsilon' = (1-P)\,\varepsilon_1 + P\varepsilon_2$ (curve a) corresponding to a porosity normal to the capacitor plates and $1/\varepsilon' = (1-P)/\varepsilon_1 + P/\varepsilon_2$ (curve b) corresponding to a porosity along the capacitor plates. The curves have been calculated again for the values $\varepsilon_1 = 7.0$. As in reference 3 the results lay in between the two curves; however the Looyenga's relation seems to give a better fit. A discrimination between the different models should be obtained with gels of lower porosity which can be obtained by progressive densification at higher temperatures (T ~ 1100°C). Such measurements are underway.

At lower temperature a sharp decrease is observed around 35 K accompanied by a large loss peak. Due to its similarity with the loss peak observed in fused silica we deduce that it must have the same origin. The height of this peak is however ~ 300 times larger and somewhat narrower, indicating that aerogels may contain a much larger density of structural defects. Moreover a frequency and temperature analysis in term of a Debye model shows that the mean relaxation time follow also an Arrhenius type behavior $\tau = \tau_o \exp(U/KT)$ with U = 20.2 meV and $\tau_o = 2.3 \cdot 10^{-8}$ s compared to U=49meV and $\tau_o = 10^{-13}$ s for fused silica (figure 4).

As the temperature is lowered, ε' passed by a minimum and then increases smoothly down to 4.2 K while the dielectric loss still decreases to unmeasurable values ($< 10^{-4}$). We believe that He atoms start to condense at T ~ 13 K on the aerogels pores superficies due to Van der Waals interaction. At T = 4.2 K, ε' reaches a maximum when liquid helium fill all the open pores. The increase of ε' between 10 and 4.2 K is in good agreement with a calculation based on the Looyenga's relation substituting $\varepsilon_2 = 1$ (vacuum) by the dielectric constant of liquid helium ($\varepsilon_2 = 1.049$). the slight variation observed at T < 4.2 K can be accounted by the

temperature variation of the dielectric constant of ^4He [17]. No increase of ε' is detected at the λ point; this confirms that the micropores are either closed or have a size smaller than the atomic dimension of He atoms.

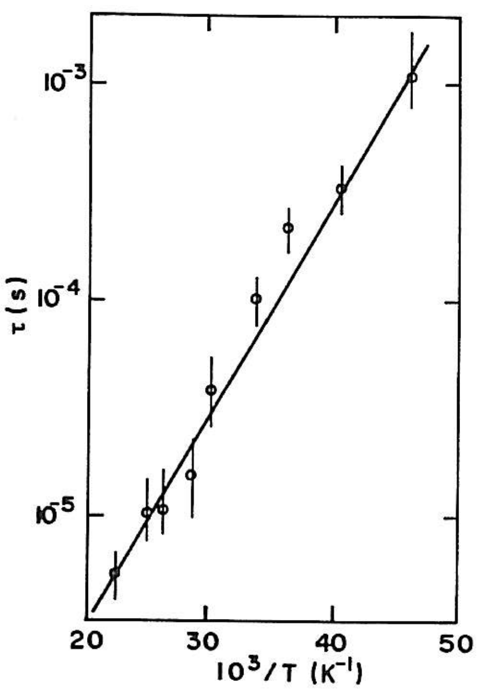

FIGURE 4
Arrhenius behavior $\tau = \tau_o \exp(U/KT)$ of the low temperature relaxation peak; U = 20.2 meV, $\tau_o = 2.3 \cdot 10^{-8}$ s.

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