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DIELECTRIC RESPONSE OF SILICA AEROGELS

A.A. da Silva, D.I. dos Santos and M.A. Aegerter

Instituto de Física e Química de São Carlos
University of São Paulo
C.P. 369, 13560 São Carlos, São Paulo, Brasil

The dielectric response of porous silica aerogel prepared by hypercritical drying of gels from hydrolysis of TMOS-Methanol solution have been measured between 1.8 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 100 K but smaller than that of fused silica. A sharp decrease of ϵ' is observed near 35 K and accompanied by a large loss peak (Fig 6). A small increase of ϵ' for $T < 13$ K is attributed to the adsorption of He atoms on the porous superficies.

INTRODUCTION

Aerogels are a new and interesting class of materials which can be prepared at room temperature by hydrolysis and polycondensation of organometallic compounds and are precursors for the preparation of new glasses and glass ceramics without fusion, thin films, fibers and ultra fine monodisperse powders for ceramics sintered at low temperatures. 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.

The elastic and dielectric behavior of amorphous solids at low temperatures differs completely from that of crystalline solids. A review for inorganic

glasses was recently given by Hunklinger and Schickfus [4]. At room temperature the dielectric constant of amorphous fused silica is $\epsilon' \approx 3.8$ and its value decreases slightly steadily down to 5 K ($\Delta\epsilon' \approx 10^{-2}$). Below this temperature it rises again ($\Delta\epsilon' \sim 1.5 \cdot 10^{-4}$) due to the presence of polar impurities [5]. A large absorption loss peak independent of the OH content is found around 30 K at $f = 1$ KHz [6]. Both acoustic and dielectric absorption data fit an Arrhenius law $\tau = \tau_0 (U/KT)$ with $U = 49$ meV and $\tau_0 = 10^{-13}$ 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 configurations where the oxygen atoms can move from one well to the other by transverse, longitudinal or small angle rotation of SiO_4 tetrahedra [7,8].

Recently the dielectric properties of various amorphous and porous xerogels have been analysed at room temperature between 10^3 and 10^6 Hz [3]. They found an anomaly in their dielectric constants without any corresponding changes in the dielectric loss factor or dc resistivities when compared to fused silica glass. This anomaly is reflected by a higher dielectric constant ($\epsilon' \sim 6,5 - 7,0$) and a slightly higher dielectric loss factor ($1,5 - 2,0 \cdot 10^{-3}$) probably caused by the presence of traces of elemental carbon incorporated into these glasses as a result of the combustion of organic matter held in micropores. The mechanism of this enhancement is not yet understood.

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.

PREPARATION OF AEROGELS

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

to $\approx 2,5 \cdot 7$ or 9 was added to each mol of TMOS. After 20 minutes of vigorous stirring at room temperature the sols have been transferred into Pyrex tubes hermetically sealed and left to gel at 55° C. Aerogels have been prepared by hypercritical evacuation [9]. 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 into thin shaped slices of 0.8 - 1mm 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 Supertemp Cryostat allowing temperature variation between 1.8 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. Prior any measurements the samples have been thoroughly evacuated at 10^{-3} mbar for several hours at room temperature.

EXPERIMENTAL RESULTS

Figure 1 shows a typical result of ϵ' and $\text{tg } \delta$ found for our aerogels. In this example the neutral SiO_2 aerogels has been prepared with a TMOS concentration C = 50 vol % and has an apparent density $\rho_a = 0,35$ g/cm³, an overall porosity $P = 0,82 \pm 0,01$, a porous volume $V_p = 2,41$ cm³/g and a specific BET area $A = 339$ m²/g.

All aerogels prepared so far are thought to have a structure described as a sponge of apparent density ρ_a , formed by a light SiO_2 matrix occupying a volume fraction $(1 - \phi)$ and which contains essentially closed micropores in the 5-10 Å range; its apparent skeletal density is reduced to volume $\rho_p \rho_a / (1 - \phi)$ smaller than 2.2 g/cm³ and open meso and macro pores occupy the remaining volume fraction $\phi |10|$.

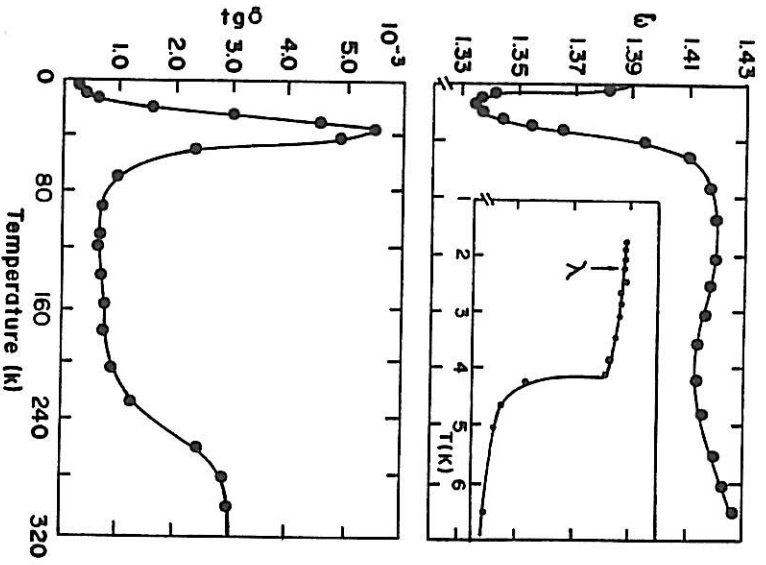


Fig.1 : Dielectric response ϵ' and $\text{tg } \delta$ of a silica aerogel prepared under neutral conditions measured at 10 KHz .

As foreseen the dielectric constant ϵ' measured for $T > 120$ K is lower than that of amorphous fused silica ($\epsilon' \sim 3.8$) while the $\text{tg } \delta$ 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 $\epsilon_2 = 1$. Figure 2 gives the results of the mean values of ϵ' taken for $T > 120$ K for four aerogels as a function of the porosity P defined as $P = (1 - \rho_a / \rho)$ where ρ is the density of fused silica. The theoretical curves (a) and (b) of the figure refer to the Looyenga's equation $|\epsilon'| = \epsilon_1^{1/3} + (1-P) (\epsilon_1^{1/3} - \epsilon_2^{1/3})$]

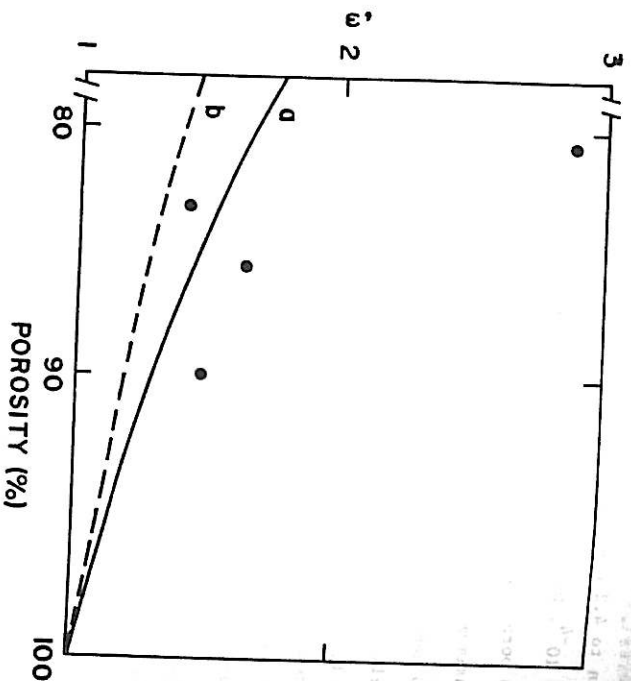


Fig. 2: Measured dielectric constant ϵ' of aerogels as a function of the porosity (●). The curves are theoretical models (see text).

calculated using the values $\epsilon_1 = 7.0$ (SiO_2), $\epsilon_2 = 1.0$ and $\epsilon_1 = 3.8$ and $\epsilon_2 = 1.0$ respectively. Except for one measurement curve a) gives a good fit and confirms that elemental carbon or the remaining organic compounds probably alter the dielectric constant of the SiO_2 matrix.

At lower temperature a decrease of the dielectric constant ϵ' 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 also follow an Arrhenius type behavior $\tau = \tau_0 \exp(U/KT)$ with $U = 20.2$ meV and $\tau_0 = 2.3 \cdot 10^{-8}$ s.

As the temperature is lowered, ϵ' passes through a minimum and then increases

smoothly down to 4.2 K while the dielectric loss continues to decrease to value smaller than 10^{-4} . We believe that He atoms start to condense at $T \sim 13$ K on the aerogels pores superfluids due to Van der Waals interaction. At $T=4.2$ K, ϵ' reaches a maximum when liquid helium fills 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 with $\epsilon_2 = 1.049$ (dielectric constant of liquid He). The variation observed at $T < 4.2$ K can be accounted for by the temperature variation $|\lambda|$ of the dielectric constant of ^4He . No increase of ϵ' is detected at the lambda transition (onset of He superfluidity), confirming that the micropores are either closed or have a size smaller than the atomic dimension of He atoms.

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