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Low frequency light scattering in silica xerogels

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Abstract. New Brillouin and Raman scattering measurements on silica xerogels in a wide range of densities ($0.5\text{--}2.2\text{ g cm}^{-3}$) are compared among each other and with data in melt quenched vitreous silica, in the $10\text{--}750\text{ K}$ temperature region. In the low frequency part of the Raman spectra, the boson peak characteristic of glasses is observed for all studied densities at low and high temperature when the quasielastic contribution is negligible. The results provide strong evidence of the presence of water in the pores of the silica skeleton.

The vibrational dynamics of amorphous solids have a close relationship to their atomic-scale structure and to their mechanical and thermal properties [1, 2]. In this regard, the silica xerogel systems are particularly interesting since they can be produced with density in an exceptionally broad range [3]. Moreover, the density can be increased by heat treatment and it is possible to obtain a fully densified glass and hence deduce physical information by comparing the properties of the xerogels with those of the well known melt quenched glasses [1, 2, 4]. Xerogels have large surface area, the surface being covered by dangling Si–OH bonds. The porous structure easily absorbs H_2O molecules, which can be bonded to the surface (chemical water) or can fill the pores (physical water) [5].

In this paper we studied the effect of the absorbed water on Brillouin and low frequency Raman scattering.

Alcogel samples were prepared by hydrolysis and polycondensation reactions of tetraethoxysilane dissolved in methanol [3]. The alcogel is aged at $200\text{ }^\circ\text{C}$ temperature in an autoclave for 12 hours at 4 MPa. The ageing favours the gel syneresis dissolution redeposition of the silica. As a function of the network stiffening, the drying shrinkage can be controlled and this allows us to synthesize sol–gel with a bulk density in the range $0.5\text{--}1.7\text{ g cm}^{-3}$. The samples were heat treated at $600\text{ }^\circ\text{C}$ for 24 hours to eliminate the adsorbed impurities.

Raman and Brillouin scattering experiments were performed on these systems spanning a wide range of density and temperature (from 10 to 750 K) with a standard experimental set-up. Brillouin spectra were taken using a six multipass interferometer in backscattering configuration; the free spectra range was 15 GHz and the finesse was 70.

The first order Raman scattering in a disordered system is conventionally expressed by the vibrational density of states $g(\omega)$ modulated by a smoothly varying coupling function $C(\omega)$ [6]:

$$I^{expt} = C(\omega)g(\omega)[n(\omega, T) + 1]/\omega$$

where $n(\omega, T)$ is the Bose population factor for a harmonic oscillation.

A broad band observed in glasses in the 20–100 cm^{-1} range, the boson peak, is then identified with the corresponding bump in the $g(\omega)/\omega^2$ frequency dependence [7]. At lower frequencies ($<20 \text{ cm}^{-1}$), Raman spectra of glasses show another characteristic feature: the quasielastic scattering (QES) which seems centred at zero frequency and increases in intensity with temperature at a higher rate than the Bose factor [8, 9]. In glasses obtained by the melt-quenched method, like vitreous silica, rare-earth metaphosphate glasses and borate glasses, the temperature variation of the quasielastic intensity may be approximated by a power law T^β . The exponents are found to be material dependent and vary from 1.4 to 2.4 [8]. Another characteristic feature is that the spectral shape does not change with changing temperature [9].

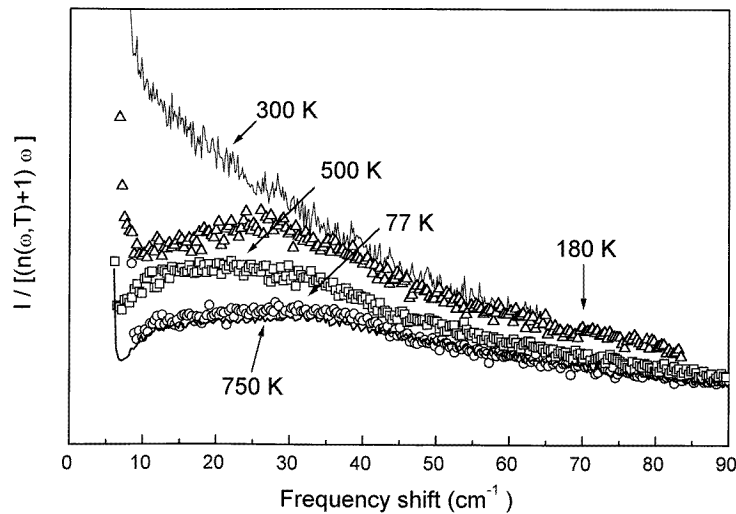


Figure 1. Reduced Raman intensity at different temperatures for the xerogel with $\rho = 1.73 \text{ g cm}^{-3}$.

Silica xerogels present quite strong low frequency Raman scattering [4, 10]. However, the nature of this scattering seems to be different from that of QES in melt quenched glasses, having a different temperature behaviour, as shown in figure 1. Here we present the Raman spectra at some significant temperatures for a sample with a density $\rho = 1.73 \text{ g cm}^{-3}$. The spectra are presented in the spectral function form:

$$I^{expt} / \omega [n(\omega, T) + 1] = C(\omega)g(\omega) / \omega^2.$$

In the room temperature spectrum the QES is quite strong. At low temperature as well as at high temperature the intensity of QES is relatively lower and the boson peak becomes evident. The frequency of the maximum is more or less the same either at low temperature or at high temperature in all the studied samples (and decreases with decreasing sample density). The low energy light scattering seems due to the superposition of two kinds of scattering: an intense quasielastic scattering and the usual Raman scattering, i.e. the boson peak. The presence of the boson peak suggests the idea that the vibrational dynamics of these systems is very similar to

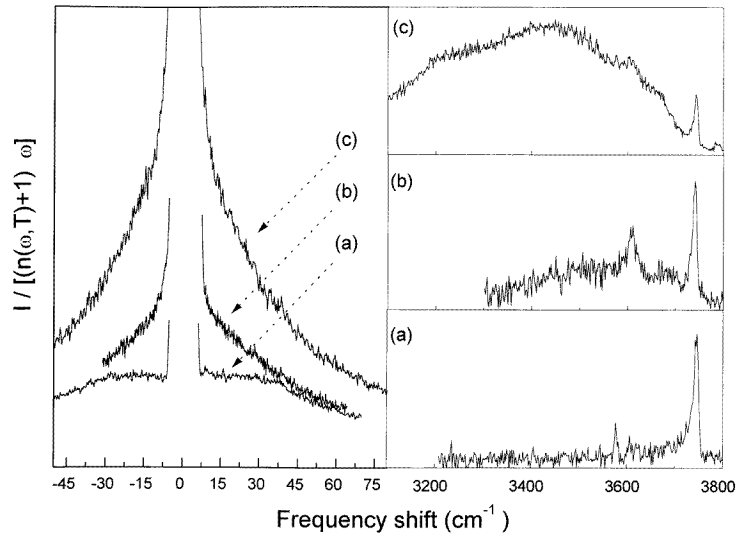


Figure 2. Reduced Raman intensity at room temperature for the xerogel with $\rho = 1.73 \text{ g cm}^{-3}$; after annealing at 750 K (a), after ageing in air for 4 hours (b), after ageing in air for 48 hours (c).

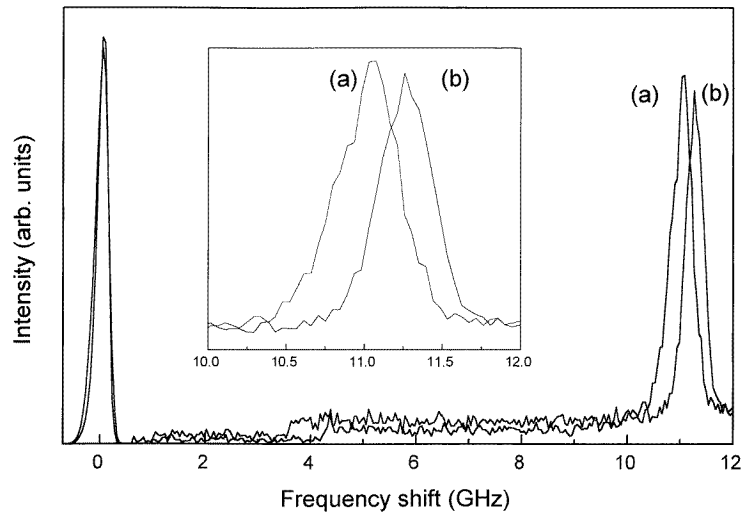


Figure 3. Brillouin scattering spectra at room temperature in the xerogel with $\rho = 0.81 \text{ g cm}^{-3}$ before (a) and after (b) heat treatment at 600 °C. The elastic lines have been divided by a factor of 70.

that of the melt-quenched glasses. The differences in the boson peak position can be attributed to a softening of the structure.

The origin of the QES is well shown by the Raman results of figure 2, taken at room temperature at different steps of thermal history. The broad band centred at about 3500 cm^{-1} is due to the O–H stretching vibration of water. After annealing at high temperature it disappears and the sharp peak at 3740 cm^{-1} of the O–H stretching of the free silanol groups at the pore surface dominates the spectrum [5]. At the same time the intensity of the QES is strongly

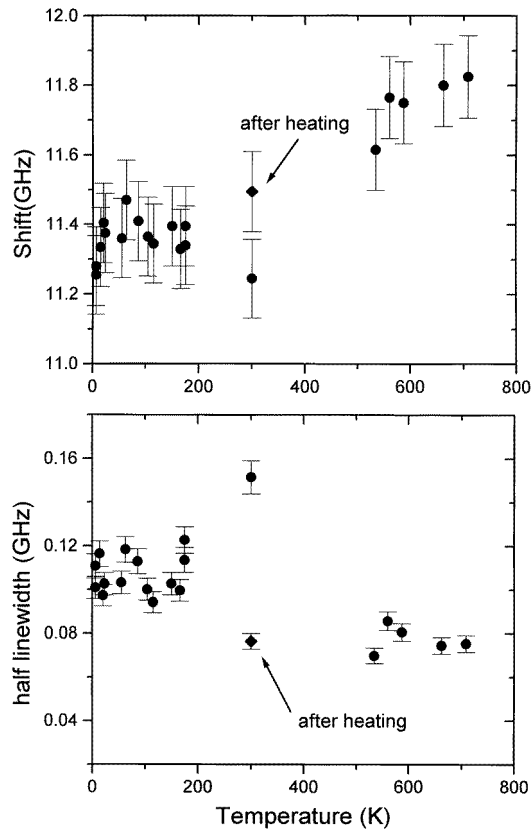


Figure 4. Brillouin shift and Brillouin linewidth for $\rho = 1.81 \text{ g cm}^{-3}$ as a function of the temperature.

reduced (figure 2(a)). Ageing in air at room temperature restores the broad band of water and the intensity of QES increases (figures 2(b), (c)). It is evident from these results that QES can be attributed to the presence of water inside the pores. We can now understand the temperature behaviour of the QES of figure 1. At room temperature the QES is strong because the sample absorbed water. At low temperature, the intensity of QES decreases because the water is frozen; at high temperature the intensity also decreases because the water is expelled.

This interpretation is confirmed by an accurate analysis of the Brillouin scattering data in the same samples. The Brillouin frequency is in the $0.1\text{--}1 \text{ cm}^{-1}$ range ($1 \text{ cm}^{-1} = 30 \text{ GHz}$) and is proportional to the sound velocity (and to the index of refraction), while the linewidth is related to the attenuation of hypersonic waves [11]. In the backscattering configuration, the frequency and the linewidth of the longitudinal waves are investigated with a good accuracy. Figure 3 gives an example of Brillouin spectra of a xerogel with density $\rho = 0.81 \text{ g cm}^{-3}$, at room temperature before and after high temperature heat treatment. The comparison shows clearly differences both for the position and for the linewidth of Brillouin lines. The sound velocity increases after heat treatment while the sound attenuation decreases. This effect has been observed systematically for all densities. As for Raman data the influence of heat treatment appears to be reversible: ageing at room temperature in air after heat treatment decreases the sound velocity and increases attenuation.

In figure 4, the Brillouin shift and linewidth have been reported versus temperature. Above room temperature, the sound velocity increases with temperature, as already found in fused silica [12]. In contrast to observations in dense glasses [12], both the sound velocity and acoustical attenuation appear constant at low temperature in the limit of the experimental resolution. These experimental observations mean that a different process originating from the absorbed water could be responsible for this behaviour.

In conclusion, we have shown that the inelastic light scattering is very sensitive to the presence of absorbed water confined in the porous silica network. Before comparing the experimental results and deducing the physical interpretation of the structure and the dynamics of porous material it is necessary to carefully verify the sample thermal history and preparation conditions. In this way, spurious effects due to the presence of absorbed compound could be avoided.

Acknowledgment

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