Low-frequency dynamics in silica xerogels

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Abstract. Brillouin and Raman experiments have been performed in hydrogenated silica sol–gel and vitreous silica samples made by sol–gel processes (xerogels) and by the melting powder method. The aim of this work has been the study of the low-frequency dynamics of sol–gel systems in comparison with that of amorphous silica. By thermal treatment of the gel a progressive densification of the system was obtained: at 500 °C we obtained densification (temperature well below the usual temperatures); at higher temperature ($\approx$700–800 °C) the pores were eliminated and the dynamics (Brillouin shifts, quasielastic scattering, and Boson peaks) became equivalent to that of fused silica.

1. Introduction

In the present work, we present measurements of Brillouin and Raman scattering experiments in order to investigate the nature of low-frequency dynamics of a family of sol–gel systems, in comparison with the results obtained in amorphous silica obtained by the quenching method. Sol–gel and xerogel (sol–gel after heat treatment) systems represent a fascinating class of amorphous solids [1, 2] because it is possible to study the frequency dependence of low-frequency vibrations for solids of different connectivity (apart obviously from a lot of properties which are not the object of the present investigation). In particular we have studied a family of hydrogenated silica sol–gels, at different concentrations of hydrogen, and the corresponding xerogels heated at various temperatures. The sol–gel samples [3] were obtained by diluting two alkoxides (TREOS and TEOS) in ethanol and hydrolysing the mixtures with acid water (pH = 4 by HCl). Gelation usually occurred in 7 days forming monolithic samples. By thermal treatment of the gel a progressive densification of the system was obtained and at high temperatures ($\approx$ 800 °C) the pores were eliminated and the density became nearly equivalent to fused silica. The nominal stoichiometric formulae of samples are: $Si_2O_3H_2$ (pure TREOS, called in the following sample A), $Si_8O_{13}H_6$ (75% TREOS, called in the following sample B), $Si_4O_7H_2$ (50% TREOS, called in the following sample C), and $Si_8O_{15}H_2$ (25% TREOS, called in the following sample D).The sample characterization as well as the experimental techniques are described elsewhere [4]; here we want only to emphasize that the measures of density show that on decreasing the hydrogen content the sol–gel matrix becomes more compact and at the same time the superficial area decreases significantly.

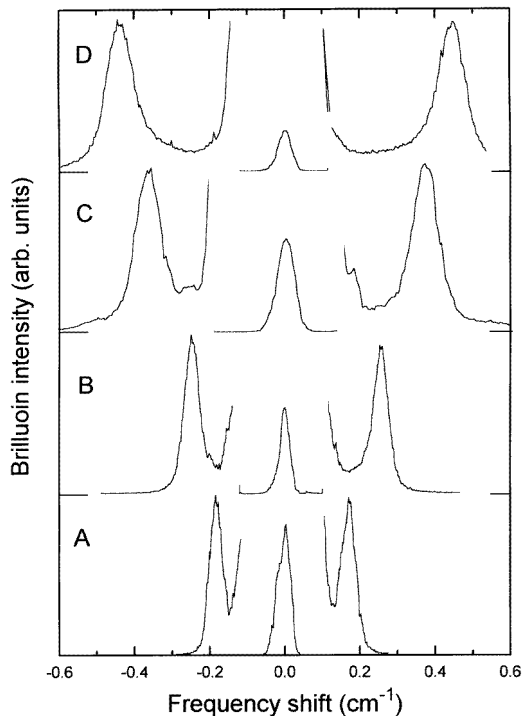§ Coresponding author. E-mail: afontana@alpha.science.unitn.it

Figure 1. Brillouin measurements in hydrogenated A,B,C, and D sol–gel systems. The instrumental resolution was different in each spectrum.

2. Results and discussion

2.1. Brillouin scattering

Brillouin scattering from an amorphous system consists of a pair of doublets due to longitudinal (L) and transverse (T) phonons in the material. In figure 1 we present (as an example) the Brillouin spectra of the untreated A, B, C, and D samples. The resolution was 0.06 cm^{-1} and the position of the Brillouin peak was determined by fitting experimental features with a Lorentzian function. Due to the low-frequency shifts in these systems we was not able to resolve the transverse modes, while in the xerogel samples it has been possible. Brillouin shifts on sol–gel systems linearly decrease on increasing the hydrogen content reflecting a decreasing of system connectivity. Brillouin shifts in the sample A heated at $800\,^{\circ}$C are quite similar to those measured in melt quenched amorphous silica [5] (in the following called AS) showing that sound velocities (and elastic constants) become indistinguishible. The Brillouin shifts, in A, B, C, and D samples, start from different values depending on hydrogen content and all tend to the value of AS at about $700\,^{\circ}$C indicating a full densification.

2.2. Raman scattering

In figure 2 we present experimental Raman scattering on xerogel D heated at $500\,^{\circ}$C, on xerogel A heated at $800\,^{\circ}$C, and on melt quenched AS at room temperature; the probed
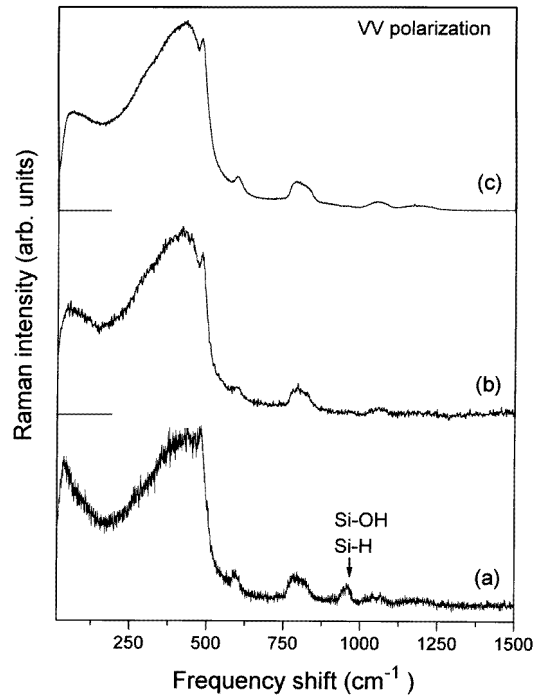
Figure 2. Raman spectra of xerogel D (heated at 500 °C) (a), of xerogel A (heated at 800 °C) (b), and of amorphous silica (c), recorded at room temperature in VV geometry.

frequency shifts run from 5–10 cm^{-1} up to 1500 cm^{-1}. The spectrum of the xerogel D sample is the typical spectrum which is given by a glass made from the melting process indicating that the densification occurs well below the usual temperatures in similar systems. At first sight such a spectrum has a very similar shape in comparison to that of AS indicating that the presence of hydrogen inside the glassy matrix (identified in significant amounts by infrared measurements) does not modify the vibrational dynamics. Anyway a band centred at about 960 cm^{-1} indicating the presence of Si–H and Si–OH bonds and a slightly different low-frequency shape are evident. In the low-frequency region the Raman spectrum consists of a broad band, the Boson peak (BP) associated with the acoustical density of states [6], and, at lower frequency and elevated temperatures, in the quasielastic scattering (QS) of which the intensity increases faster than the Bose population factor [7]. The frequency shapes of QS and BP are very similar in the two samples, even if the frequency of the BP maximum is slightly different being 35 ± 2 cm^{-1} in xerogel D and 46 ± 2 cm^{-1} in AS. It could be interesting to connect this difference with the acoustic properties measured by Brillouin scattering [5]. In fact the sound velocities in xerogels are smaller than those of AS showing a similar behaviour.

The depolarization ratio $R(\omega) = I_{dep}/I_{pol} = I_{hv}/I_{vv}$, where h and v indicate the direction of the polarization of light perpendicular and parallel to the scattering plane, is an important parameter for the understanding of the origin of the light scattering spectrum and was studied for many glassy systems [8]. It was found, in the 5–50 cm^{-1} frequency range, to have values varying from 0.4 for SiO_2 to 0.75 for some organic systems. However in all investigated systems it was found to be frequency independent indicating that the QS
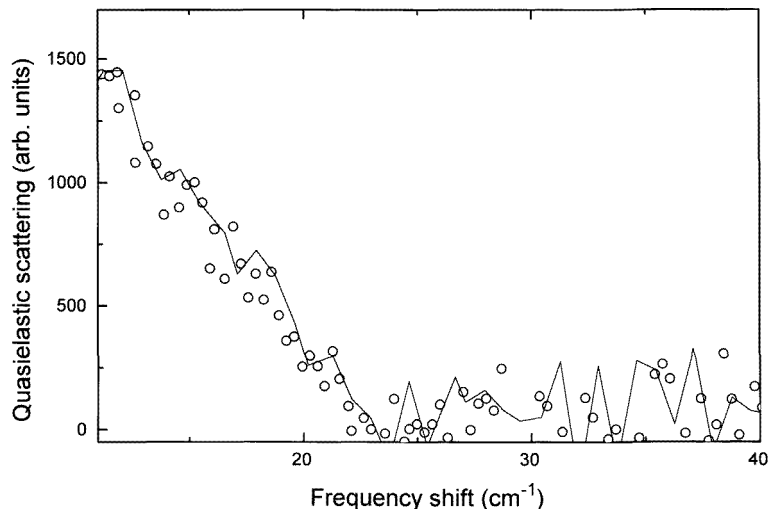
Figure 3. Quasielastic scattering in xerogel D (heated at 500 °C) (circles) and amorphous silica (solid line).

and BP have some microscopic connection. The depolarization ratio in our xerogels has the same behaviour in frequency.

QS can be separated from BP measuring the Raman spectrum at different temperatures. In fact the Raman intensity above 50 cm^{-1} exhibits a temperature dependence proportional to the population factor $n(\omega, T) + 1$; so it is straighforward to normalize the reduced spectra, obtained at different temperatures, above 50 cm^{-1}. The normalized spectrum obtained at the lowest temperature (10 K) has been subtracted from those at higher temperatures and the result multiplied by $n(\omega, T) + 1$ [7]. The major feature is that the QS shape in these samples have (within the limits of experimental error) the same shape, although the intensities may differ (see figure 3). The origin of QS is a very intriguing problem: it was observed that in all glasses it has a Lorentzian spectral shape centred at zero frequency and its intensity increases on increasing the temperature faster than the Bose population factor without changing the width [7]. Nevertheless, in the literature it has been assigned to some relaxation process due to the large number of degrees of freedom in glasses [9]. So it could be expected that in xerogel systems with different connectivity the widths of QS would be different: our results seem to indicate that the physical origin of QS in these samples is the same.

3. Conclusion

We have analysed the low-frequency dynamics of a new family of hydrogenated silica sol–gels and of corresponding xerogels as a function of heating temperature by means of Brillouin and Raman spectroscopies. We have compared the results with those obtained on melt quenched amorphous silica. The major results are mainly three:

(i) The hydrogenated silica sol–gel densified at a temperature well below the usual temperatures found in similar systems.

(ii) In the densified systems the dynamics is very similar to that of melt-quenched

amorphous silica.

(iii) In the limit of experimental error, the quasielastic scattering in xerogels has the same spectral shape of that of melt-quenched amorphous silica, indicating that the different connectivity of these amorphous systems does not modify the microscopic origin of quasielastic scattering.

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