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The influence of the fictive temperature and the OH content on the dynamical properties of vitreous silica: comparison of Raman, Brillouin, and neutron scattering spectra

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Abstract

We have performed new inelastic light and neutron scattering experiments on different samples of vitreous silica: Puropsil, Spectrosil, Tetrasil, Suprasil and Heralux commercial grade samples have been investigated by means of Raman and Brillouin light scattering and inelastic neutron scattering experiments.

We have found significant changes in the density of states and in the sound velocity, which can be attributed to differences both in the fictive temperature and in the OH bonds present in the different samples.

1. Introduction

An amorphous material may assume different metastable configurations and, from the experimental side, it has been shown that a given glass can change its original arrangement upon heat treatment, also below T_g. In fact, during a long enough annealing time the glass relaxes into a particular equilibrium configuration, which depends only on the temperature of the thermal treatment. This temperature is called the fictive temperature, T_f. When the sample is quenched to room temperature, its structure remains frozen to the T_f equilibrium configuration.

The influence of T_f on the structural and dynamical properties of vitreous systems is a long standing physical problem. Focusing the analysis on vitreous silica, the prototype strong glass former system [1], many experimental and analytical studies can be cited on this argument [2–8].

Not only T_f, but also the presence of impurities has been recognized as a relevant parameter for explaining changes in physical properties both in relaxational and in vibrational modes [3, 4]. In particular, the influence of OH impurities and of T_f has been accurately investigated at the ultrasonic frequency [3], where these two physical parameters strongly affect the acoustic losses.

More recently, this study was extended to the acoustic attenuation measured in the hypersonic frequency range by a Brillouin light scattering experiment [4]; it evidenced the

strong correlation between the OH content and the strength of the secondary relaxation process [4]. The differences in OH content and in T_f also induce changes in the stiffness of the system and as a consequence in the values of the sound velocity [6]. As regards the high frequency vibrations, a detailed study on the Raman scattering spectra is reported in [2], where a strong correlation between T_f and the number of defect rings in the silica structure and the strength of the binding constant is found. Differences in the boson peak (BP) region were also observed but, until now, the low frequency part of the Raman spectra (under 100 cm^{-1}) was not accurately investigated. In fact, a change of the BP shape in the Raman spectrum can be caused by a change of the vibrational density of states, but also by a change of the Raman coupling function, $C(\omega)$.

In this work we present new light and neutron scattering measurements on different silica samples. The data allow us to correlate the variation of the vibrational dynamics in the high and low frequency ranges with the thermal history and the impurity amount of the particular sample.

2. Experimental details

The investigated samples are commercial silica glasses of different origins: Spectrosil and Tetrasil were purchased from Silo, Heralux from Heraeus, and Suprasil from Goodfellow. They were different in impurity content as well as in thermal history. To analyse their vibrational dynamics, Raman scattering experiments were performed using a standard experimental set-up Jobin-Yvon U1000 over a wide frequency range (from 3 to 4000 cm^{-1}). We extended the scans in so wide a frequency range in order to correctly subtract the weak background of luminescence which, especially at low temperature can give a significant contribution [9]. To quantitatively evaluate the OH content of the samples, absorption measurements were performed by using a double-beam spectrophotometer in the range of 2000–3200 nm (with a resolution of 2 nm).

The INS measurements were performed on the IN6 spectrometer of the Institut Laue-Langevin (ILL) (Grenoble, France) at $T = 300$ K. The data were reduced using dedicated programs from the ILL library to subtract the background and the contribution of the empty cell, to correct for the efficiency of the detectors and for the multi-phonon contribution.

The Brillouin light scattering (BLS) spectra were performed in a back-scattering configuration by using a Sandercock-type $(3 + 3)$-pass tandem Fabry–Perot interferometer. The finesse was about 100 and the contrast greater than 5×10^{10} [10]. The excitation source was an Ar$^+$ laser operating at $\lambda = 514.5$ nm. The resolution (as obtained from the elastic peak) varied from about 100 to about 200 MHz, depending on the free spectral ranges adopted.

3. Results and analysis

Figure 1 shows the Raman spectra of Heralux (squares) and Spectrosil (circles). In the reported frequency range, the spectra are dominated by the polarized band centred at $\omega_1 \sim 430$ cm^{-1}, ascribed to the bending of the Si–O–Si linkages [11, 12], and by the defect peaks D1 ~ 480 cm^{-1} and D2 ~ 600 cm^{-1} assigned to the symmetric oxygen breathing vibrations of fourfold rings and threefold rings respectively [12]. The two samples show important differences both in the frequency position and in the width of the ω_1 peak and also in the intensity of the defect lines. According to reference [2], these variations can be related to different thermal treatments. Following the procedure illustrated in that paper, we evaluated the fictive temperature of our samples in two different ways: (i) from the frequency position of the band centred at ~ 1050 cm^{-1} (inset (b) of figure 1) associated with the TO mode of the
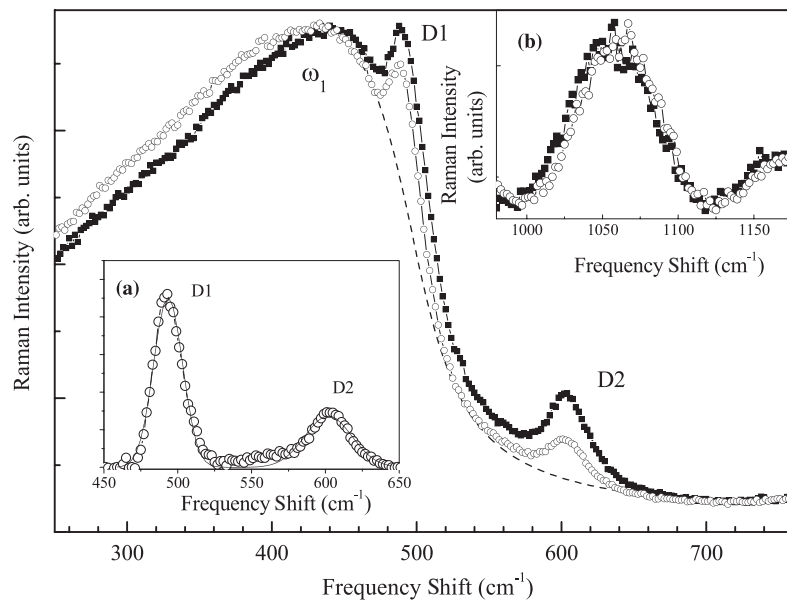
Figure 1. Raman spectra of Heralux (squares) and Spectrosil (circles) at $T = 300$ K. The dashed line is the baseline used for the estimation of the intensity of defect peaks D1 and D2 for the Spectrosil spectrum, reported in the inset (a). In the inset (b) the bands centred at $\sim$1050 cm^{-1} associated with TO mode of the Si–O–Si are reported for the two samples.

Table 1. For the investigated silica samples, the evaluated OH contents are reported together with the estimated values of T_f obtained using two different methods: (i) from the defect line intensity and (ii) from the position of the Raman band centred at $\sim$1050 cm^{-1}. In the last column the mean T_f values are reported. It is interesting to note that, even if the two methods give different T_f values, they indicate the same trend.

Sample	OH content $\pm$10% (ppm)	$T_f \pm 100$ (K) defects	$T_f \pm 100$ (K) frequency position	$\langle T_f \rangle$
Puropsil	20	1250	1400	1320 ± 80
Heralux	200	1320	1550	1430 ± 100
Suprasil	1700	1150	1270	1210 ± 60
Spectrosil	2000	1140	1260	1200 ± 60
Tetrasil	2000	1120	1250	1180 ± 70

Si–O–Si due to asymmetric bond stretching vibration and (ii) from the relative intensity of the defect lines D1 and D2 and the total Raman spectrum intensity. The evaluation of the defect line intensity (see inset (a) of figure 1) was done subtracting the estimated shape of the ω_1 band (broken line of figure 1) from the experimental data. The means of the T_f values obtained with the two methods are reported in table 1, together with the estimated OH content. The latter was evaluated using the Bouguer–Beer–Lambert law [13] from the measurements of the infrared absorption coefficient at 3500 cm^{-1} [14].

Raman and neutron scattering spectra for two different silica samples at room temperature are reported in figures 2(a) and (b) respectively. Both Raman and neutron measurements show different intensities of the boson peak and of the quasielastic scattering evidencing variation in the vibrational density of states.

Figure 3 shows the BLS spectra acquired at room temperature. The frequency shifts of the longitudinal Brillouin peaks differ in the investigated samples. In the insets of the same figure
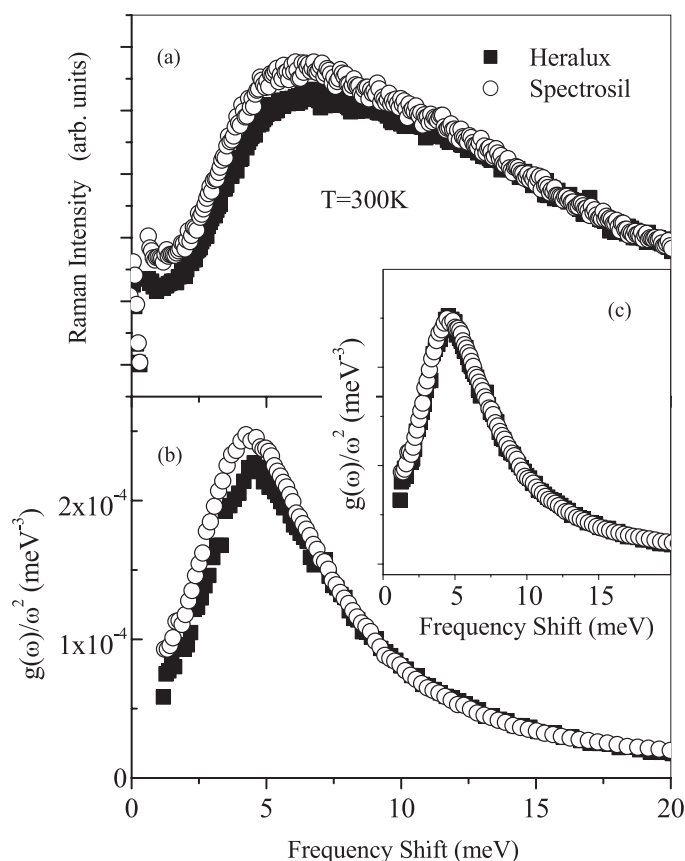
Figure 2. In panel (a) Raman spectra in HV polarization on two different silica samples, named Heralux (squares) and Spectrosil (circles) at $T = 300$ K. In panel (b) neutron scattering measurements on the same samples at the same temperature. In the inset (c) comparison between the neutron scattering spectrum of Heralux and that of the Spectrosil sample reported on a squeezed frequency scale.

the variation of the Brillouin peak as a function of the OH content and the evaluated T_f are reported.

4. Discussion

As briefly mentioned before, the thermal history of the sample and the different OH contents modify the v-SiO$_2$ network. In particular, the fictive temperature indicates the different degree of disorder at which the whole glass structure has been frozen while the OH presence induces local variations in the structural connectivity, breaking the Si–O–Si network. These two effects have an important influence on the vibrational and relaxational dynamics of the system.

The first modification we want to comment is the shift of the Raman band centred at 400 cm^{-1} (ω_1), which is due to relative motion of the tetrahedra SiO$_4$. From the data reported in figure 1 it is possible to note that a lower width and higher frequency of the ω_1 band correspond to higher intensity of the defect lines. In general we found that the higher T_f is, the higher the number of defects is, and the distribution of the intertetrahedral Si–O–Si angles becomes slightly narrower and shifted towards lower angles, indicating a more compact form.
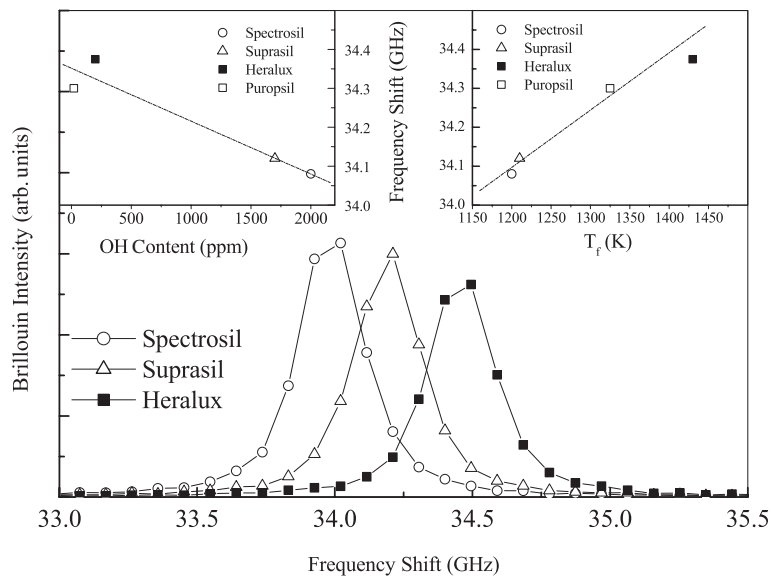
Figure 3. Brillouin peak at room temperature for different silica samples, named Heralux (squares), Spectrosil (circles) and Suprasil (triangles); in the inset the frequency position of the Brillouin peak as a function of the fictive temperature and the OH content.

This scenario is confirmed by Brillouin measurements reported in figure 3. We found that the longitudinal sound velocity, related to the stiffness of the material, increases with increasing fictive temperature (inset of the same figure). Our result confirms the data presented in a preceding paper on other silica samples, where the same dependence was found [6].

Also the position of the boson peak, reported in figure 2 both Raman and neutron scattering spectra, seems to be correlated with the variation in the sound velocity. This result can be interpreted in the framework of the model which attributes the origin of the BP to the flattening, in the high Q limit, of the transverse acoustic branch [15, 16]: changing the sound velocity, the frequency position of the transverse branch changes, and as a consequence the BP position.

Besides the change of the peak position, figure 2 shows also different BP intensities in the Raman and neutron spectra of Heralux and Spectrosil.

The BP intensity in Heralux is less than in Spectrosil indicating a minor excess in the density of states with respect to the Debye model. Let us recall that the excess of modes appears as a broad peak (the BP) in the plot of the Debye-normalized density of states $g(E)/E^2$, so the different intensity of the boson peak could be simply due to its different frequency position. This is confirmed and shown in figure 2(c), where we report the neutron scattering spectra of Spectrosil and Heralux, the last with squeezed abscissa coordinate in order to have the same BP frequency position as Spectrosil. It is worth noting that after this adjustment the spectra are identical.

At first sight it would seem that the influence of T_f would explain the differences in presented experimental data but it is necessary to have further consideration: even the different content of OH bonds can change the excess of density of states [17, 18] and moreover we found a linear correlation between the Brillouin shift and the OH content of our samples (see inset (a) of figure 3). This non-trivial dependence can help us to assess another microscopic origin of different intensities and positions of BP.

In order to have a clear reply to the question of whether the causes of changes in the boson peak are the T_f, the OH content, or both it is necessary to separate the influences of the two

effects. The work is in progress: we are preparing sets of silica samples made with different and known T_f but with the same OH content and vice versa with different OH content and the same T_f. In this way the structural modification of the sample as a function of the fictive temperature and the OH content can be quantitatively investigated.

5. Conclusion

The investigated silica samples show differences in Raman, neutron scattering and Brillouin spectra evidencing differences in the vibrational dynamics. We characterized the samples in terms of OH content and we gave an estimation of T_f through the Raman spectra study. We found a strong correlation between the obtained T_f, the OH content and the sound velocity. This study has allowed us to find that either the T_f or the OH content can explain the changes of the boson peak in vitreous silica. Only a new detailed study with samples with the same content of OH bonds at different fictive temperature will allow us to find the real origin of the differences in the density of states.

Acknowledgments

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