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## Transient grating experiments on $\text{CCl}_4$ -filled porous glasses

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We performed heterodyne detected transient grating experiments on porous glasses, characterized by different pore sizes, filled with liquid carbon tetrachloride. The measured signal shows an articulated profile characterized by different dynamic phenomena. In the faster time scale ( $t < 0.1 \mu\text{s}$ ) the acoustic processes take place. In the slower time scale ( $t > 0.1 \mu\text{s}$ ) unexpected relaxation/thermal diffusion phenomena show up. In order to measure and address these dynamic features, we studied the effect of sample preparation on the experimental signal. Furthermore, we measured the sound velocity and attenuation as a function of sample treatment and temperature. The reported data shows clearly how the unremoved water contained in the pores can play a relevant role in the measurement of physical parameters of liquid filled-glass systems.

### 1. Introduction

The study of dynamical and transport processes in materials characterized by nanoheterogeneity is a basic issue for contemporary physics. Its understanding pertains to the technological applications and to fundamental issues.

Porous silica glasses have proven to be excellent media for this research. A porous glass is a silicate glass presenting a random network of empty pores with a diameter of a few nanometres. Porous glasses with pores of different diameter, from a few to a hundred nanometres, are commercially available. Furthermore, the pores can be easily filled with liquids of different nature. Indeed, liquid-filled porous glass represents an interesting material with a partially controllable nanoheterogeneity.

Transient grating experiments [1–8] are particularly suitable to measure the dynamics of complex liquids in a very broad time window, typically from  $10^{-9}$  to  $10^{-3}$  s. This time-resolved spectroscopic tool is able to probe, covering with a single experiment, a dynamic range hardly explored by other methods. With this technique

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it is possible to gain relevant information on the low-frequency range of acoustic propagation and on slow thermal relaxation phenomena.

We report in this paper the results of a heterodyne detected transient grating (HD-TG) experiment on two porous glasses filled with carbon tetrachloride. The two matrices are characterized by different pore dimensions: the Vycor 7930 [9] having a mean pore size of 4 nm and another porous glass with a mean pore size of 200 nm. We measured the acoustic properties of these nanoheterogeneous materials, focusing our attention on the role played by the water contained in the pores on the acoustic dynamics.

## 2. Experiment and results

In a TG experiment [5, 10–12] two infrared laser pulses interfere in the sample to produce a spatial modulation of the dielectric constant. The relaxation of the induced transient modulation can be probed by means of the Bragg scattering of a third laser beam, generally a continuous-wave laser at a different wavelength. There are two main excitation processes inducing the grating in the sample [1]. The first one is the electrostrictive effect that produces a pressure grating. The second is a weak absorption of the pump radiation that generates a temperature grating. Both the excitation processes give rise to a density grating. The first one creates only a stationary acoustic wave, whereas the second one also produces a constant density grating relaxing by thermal diffusion phenomena. So, the relaxation dynamics of the induced grating gives us information about the acoustic and thermal properties of the sample. In particular by this experiment we are able to measure the sound velocity, the damping time of the acoustic waves and the thermal diffusion time.

The experimental details concerning the laser and the optical set-up used here are extensively reported in [1]; here we recall only the main features. The excitation is produced by two infrared pulses at 1064 nm wavelength, 100 ps duration and with a repetition rate of 100 Hz. The pulses are generated by an amplified laser system: a mode-locked Nd-YAG laser (Antares-Coherent) followed by a regenerative Nd-YAG cavity (R3800-Spectra Physics). The probe beam, at 532 nm wavelength, is produced by a diode-pumped intracavity-doubled Nd-YVO (Verdi-Coherent). The HD-TG signals are detected by a DC-800 MHz amplified photodiode and recorded by a Tektronix oscilloscope with a bandwidth of 7 GHz at a sampling rate of 20 Gs/s. Each datum is an average of 5000 waveform acquisitions, and this is enough to produce an excellent signal-to-noise ratio, thanks also to the heterodyne detection, which substantially increases the quality of the data.

The samples were the Vycor 7930 and another porous glass which hereafter will be named PM200. The Vycor 7930 is composed of 96% fused silica, it has a mean pore size of 4 nm and a porosity of 28%; the PM200 is composed of 99% fused silica, it has a mean pore size of 200 nm and a porosity of 36%. These porous glasses are produced by sol-gel techniques and have been purchased from Advanced Glass and Ceramics [9] in a cylindrical form, with a diameter of 8 mm and 4 mm thickness.

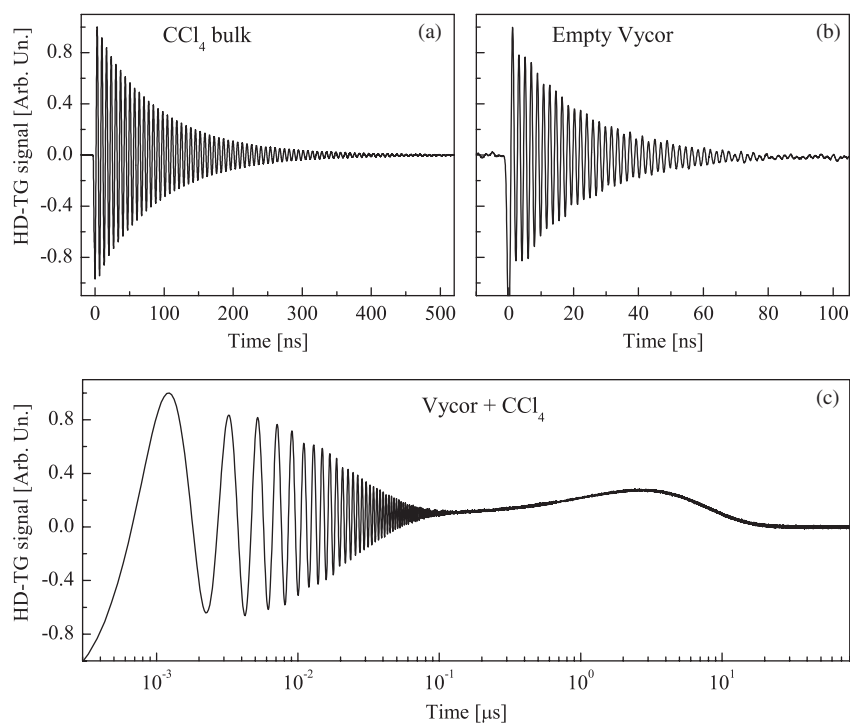


Figure 1. Typical HD-TG data obtained on bulk  $\text{CCl}_4$  (a), empty Vycor (b) and on the system Vycor- $\text{CCl}_4$  (c). The signals on the pure liquid and on the empty Vycor show only the damped acoustic oscillations due to the electrostrictive effect while the data on the filled Vycor shows a thermal contribution.

We chose carbon tetrachloride as filler liquid for several reasons. One reason is that the molecule of  $\text{CCl}_4$  is a simple spherical molecule which cannot make strong bonds with the inner pore surfaces of the matrices (silanol groups). Another reason is that the liquid does not absorb the pump radiation at 1064 nm, thus we expect to have only acoustic oscillation due to the electrostrictive effect without any thermal grating. But the most important reason is that the refractive index of this liquid matches the refractive index of the fused silica and this allows us to perform an optical experiment in the visible range also in the sample with the pore size of 200 nm.

The treatment and cleaning of porous glasses is not an easy task. As a first cleaning process we followed the procedure suggested by the company. This is a full immersion in a solution of hydrogen-peroxide at 90°C followed by washing in distilled water. To remove the water we kept the porous glasses for a few days under vacuum at 250°C. This procedure removes most of the organic contamination and for the Vycor sample produces a fully transparent sample. After this procedure, the samples were kept in pure  $\text{CCl}_4$  until used. In figure 1a we report a typical HD-TG signal on pure carbon tetrachloride. As stated above, the pump radiation is not absorbed by the liquid and only damped acoustic oscillations due to the

electrostrictive effect appear. A similar signal is obtained on the empty Vycor as reported in figure 1b. Surprisingly, the HD-TG signal on the  $\text{CCl}_4$ -filled Vycor sample shows an unexpected slower signal contribution ( $t > 0.1 \mu\text{s}$ ), see figure 1c. A very similar signal is present on the PM200- $\text{CCl}_4$  system too. So two main issues must be addressed: why do the filled samples present such a contribution and what is the origin of its articulate pattern (rising signal in the intermediate scale,  $0.1 < t < 3 \mu\text{s}$ , followed by a slow exponential decay,  $t > 3 \mu\text{s}$ ).

In our opinion, the presence of the slower signal is due to a thermal grating contribution to the HD-TG signal. This is produced by a weak absorption of the pump radiation from the unremoved water in the pores. Indeed, these samples are strongly hygroscopic and the complete elimination of water is rather difficult. The inner water absorbs the laser radiation producing a temperature grating in the sample, this grating modifies the  $\text{CCl}_4$  density by the thermal expansion phenomena generating the slower signal. Since water must be present also in the empty Vycor we would expect a similar thermal contribution also in this sample. However, our signal does not report it, see figure 1b. The reason why this thermal contribution is not observed has to be ascribed to the very low thermal expansion coefficient of the Vycor ( $\alpha = 7.5 \times 10^{-7} \text{K}^{-1}$ ) which is almost four orders of magnitude lower than the thermal expansion coefficient of  $\text{CCl}_4$  ( $\alpha = 1.2 \times 10^{-3} \text{K}^{-1}$ ). Thus a temperature grating is produced in both the empty and the filled Vycor but this produces a density grating only in the filled system, thanks to the thermal expansion of the liquid.

The slow exponential decay, present in the thermal grating signal, represents heat diffusion phenomena. The thermal diffusivity rate obtained by this decay should be compared with a theoretical model for heat diffusion in heterogenous matter. The intermediate rising pattern recalls the structural relaxation effect present in HD-TG data on supercooled liquids [1]. However, it cannot be ascribed to the structural relaxation of the silica matrix or  $\text{CCl}_4$  molecular liquid because their relaxation times are very fast, far below the time resolution of this experiment. We suggest these signal features to be connected with the expansion and flow of liquid  $\text{CCl}_4$  in the glass pores. As stated above, thanks to the large difference between the thermal expansion coefficients of the silica matrix and  $\text{CCl}_4$ , the matrix can be considered not expandable by the temperature. So the thermal grating, induced by the excitation laser, builds up, in the long time scale, a density grating only through the expansion of the confined liquid. In order to expand, the liquid is forced to flow in the pores. This phenomenon prevents the fast shaping of the density, typical of the bulk liquid, yielding the slow rising time in the HD-TG signal. This time should depend on the viscosity of the liquid, on the geometry of the tubules and on the dimension of the pores.

Since we would like to focus on the acoustic phenomena we tried to remove the water from the porous glass. Water in porous glasses can be divided into *chemical water*, that is strongly bound to the silanol groups present on the pore surface, and *physical water* that is simply absorbed inside the pores. While the chemical water can be removed only by chemical processes, the presence of the physical water can be strongly reduced by heating up the sample over  $800^\circ\text{C}$  [13, 14]. Hence, we heated the matrices up to  $800^\circ\text{C}$  for several hours in order to remove as much as possible of the physical water. Figure 2 shows the comparison between the HD-TG signals obtained from the sample treated with a low temperature ( $250^\circ\text{C}$ ) or high temperature ( $800^\circ\text{C}$ )

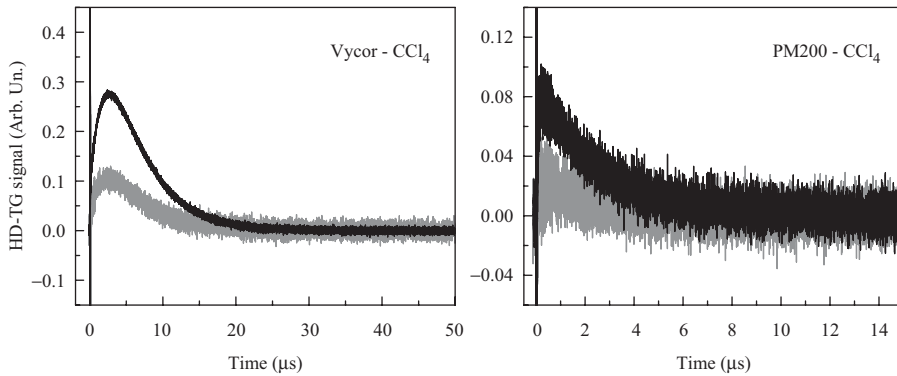


Figure 2. Comparison between the HD-TG signals on the two porous systems treated with low (black line) and high (grey line) temperature heating process. The small thermal contribution measured after the heating process suggests that most of the physical water has been removed.

drying process, on both the studied systems. The small thermal contribution measured in the samples, which have been subjected to the high-temperature process, suggests that most of the physical water has been removed.

As we shall report in the next section, the presence of water not only gives a thermal contribution in the signal but can also strongly affect the propagation of the acoustic waves.

### 3. Data analysis

We performed HD-TG measurements on the Vycor- $\text{CCl}_4$  system in the temperature range 245–343 K and on the PM200- $\text{CCl}_4$  system in the temperature range 268–338 K at the  $q$ -vector  $q = 1 \mu\text{m}^{-1}$ . For this latter sample we used a narrower temperature range because outside this range the refractive indices of the liquid and the fused silica no longer match, and the transmitted intensity of the probe falls considerably. To extract the interesting parameters from the data we made a least-squares fitting procedure with the following phenomenological analytical function:

$$S(q, t) = A \exp(-t/\tau_s) \cos(c_s q t) + B \exp(-t/\tau_s) \sin(c_s q t) + C \exp(-t/\tau_r) + D \exp(-t/\tau_l) \tag{1}$$

where the first two terms account for the damped acoustic oscillations induced by the temperature grating and the electrostrictive effect, respectively, the third one accounts for the rise of the signal connected to the liquid flow phenomena and finally the last term accounts for the decay of the temperature grating due to heat diffusion. The free fitting parameters are the sound velocity  $c_s$ , the acoustic damping time  $\tau_s$ , the thermal diffusion time  $\tau_l$ , the rise time  $\tau_r$  and the amplitudes  $A$ ,  $B$ ,  $C$  and  $D$ .

Now we want to focus on the effect of sample treatment on the acoustic processes. In figure 3 we compare the temperature dependence of the sound velocities

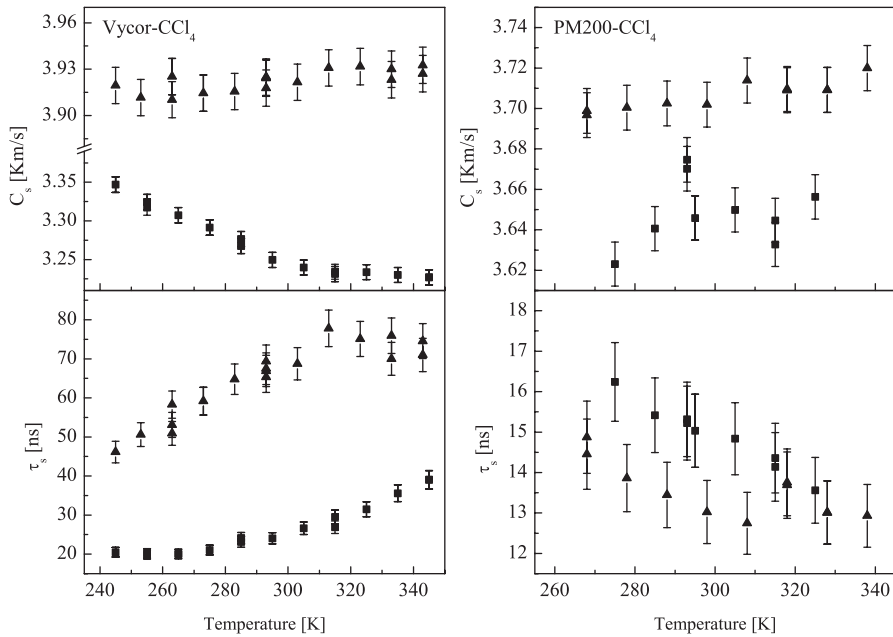


Figure 3. Temperature behaviour of the sound velocity (upper graphs) and acoustic damping time (lower graphs) in the two studied porous systems treated with low (squares) or high (triangles) temperature drying process.

and the acoustic damping times measured on the two porous glasses treated with the low or high temperature drying process. Our data clearly show that water is able to modify both the values and the temperature dependence of the sound velocity and of the acoustic damping time, especially in the Vycor case. In the PM200 this effect seems to be less relevant.

In the samples dried at high temperature, we measured the temperature dependence of the sound velocity similar to bulk silica. This result is in agreement with the results in empty dried porous glasses (areogels and xerogels), where the sound velocity has been measured to be proportional to the sound velocity of the bulk silica, with a proportionality factor dependent on the porosity of the matrix [15].

It is known that the trapped water reduces the pore diameter and the porosity of the system. We could hence think that the changes in the sound velocity, measured in the samples subjected to the low and high temperature drying processes, could be explained by these geometrical considerations. On the contrary, the theoretical predictions, obtained from the Biot theory (nowadays the most complete theory of acoustic propagation in porous materials [16–19]), show how the induced modifications on the sound propagation cannot be explained in these simple ways. In fact, the Biot theory predicts, in our frequency range, a sound velocity that does not depend on the pore dimension and an increasing sound velocity with decreasing porosity, contrary to our experimental results. Thus a more complete theoretical model should be considered in order to explain the water effect on acoustic

propagation. Probably, the inner water produces a relevant modification of the friction phenomena at the silica/liquid surface inside the pores. Our data suggest these effects to be more relevant in porous glasses characterized by smaller pore diameter, such as the Vycor 7930.

#### 4. Conclusions

We proved that HD-TG experiments can be performed on nanoheterogenous materials and in particular we investigated two porous glasses (with 4 and 200 nm pore sizes) filled with liquid carbon tetrachloride. The measured data lead to interesting results on the dynamical processes taking place in this matter.

The HD-TG signal shows an articulated pattern characterized by acoustic and relaxation phenomena. Performing measurements on samples prepared with different drying processes, we addressed the slower signal contributions to an induced thermal grating effect, supported by the presence of unremoved water in the pores. We suggest a possible physic interpretation of the dynamic processes measured by HD-TG experiments in the intermediate/slow time scale. On the contrary, the HD-TG signal in the faster time scale can be safely assigned to the acoustic processes. Hence, we studied the propagation of the acoustic waves at frequencies around 600 MHz as a function of temperature. Again, the experimental results show clearly that the presence of unremoved water can strongly affect the propagation of the acoustic waves in these samples.

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