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# Optical and spectroscopic characterisation of permanently densified GeO<sub>2</sub> glasses

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## Abstract

Optical and spectroscopic characterization was carried out on densified vitreous germania glasses retrieved from pressures in the range 2-6 GPa. The density of the obtained glasses increases with the applied pressure. Ultrasonic and Brillouin measurements show an increase of the longitudinal and shear sound velocity, in agreement with the hardening of the elastic medium. Raman measurements allow us to study the structural modification of the system as a function of its density and to follow the evolution of the Boson Peak, which shifts towards higher frequencies and decreases in intensity.

## 1. Introduction

Vitreous germanium dioxide is the structural analogue to SiO<sub>2</sub>; they represent the prototypes of strong glasses. The structure and the dynamics of vitreous GeO<sub>2</sub> has been investigated widely both with experimental (e.g. Raman [1, 2], X-Ray and neutron spectroscopy [3, 4, 5]) and theoretical methods (e.g. classical molecular dynamics simulations [6, 7], ab-initio calculation [8, 9]). At ambient conditions GeO<sub>2</sub> glass is composed by GeO<sub>4</sub> edge-sharing tetrahedral units. The effect of pressure on tetrahedral structure of germanates and silicates has been the subject of debate in recent years [2, 10-12]. Increasing the pressure two different changes take place in both the intermediate range order and in the short range one. At lower pressures the structural units arrange themselves in the tri-dimensional network decreasing the cage size. A further increase of pressure results in a distortion of angles and a reduction of the bond lengths. Several structural studies on in situ and permanent densification of v-GeO<sub>2</sub> show that the amorphous-amorphous transition from a fourfold coordinated to a sixfold coordination takes place when pressures greater than 7 GPa is applied [11]. In this work we focus our attention to the relation between

the structural and the elastic properties of permanently densified vitreous germania as a function of the applied pressure. The samples were retrieved from various high pressures between 0 and 6 GPa, in order to avoid the amorphous-amorphous transition. We present a detailed optical and spectroscopic characterisation of these samples by means of Brillouin, Raman and ultrasonic measurements performed at room temperature.

## 2. Experimental Details

Vitreous germania was prepared by the conventional melt-quenching method. The obtained glass block was cut into cylindrical pieces of 6 mm diameter and 6 mm length, which were densified using two HT-HP apparatus. In the multi-anvil apparatus the glass cylinders were encapsulated in a platinum foil and then inserted into a graphite heater element. A MgO octahedron was used as a pressure transmitting medium in order to obtain an hydrostatic compression. The samples were compressed at 2, 4 and 6 GPa and then heated at 673 K for 2 minutes under pressure. The pressure was released after cooling.

The densities of the obtained glasses was measured at room temperature by a Micrometrics Accupyc 1300 gas pycnometer under helium gas, having an accuracy of 0.03% and yielded the results reported in Table 1. Raman scattering experiments were performed on a Jobin–Yvon U-1000 spectrometer in vertical–vertical (VV) and horizontal–vertical (HV) polarizations. The incident light was the 514.5 nm line of the argon-ion laser with a power of about 20 mW in order to avoid sample heating and damage. The spectra were collected in the  $-200/+1500\text{ cm}^{-1}$  frequency range with different frequency resolution, in the case of low frequency spectra the resolution was around  $2\text{ cm}^{-1}$ .

10-MHz longitudinal and transverse sound waves were obtained by tuning X-cut and Y-cut quartz crystals at their fundamental frequency by using an apparatus described elsewhere [13], based on the pulse-echo overlap technique and the correct echo overlap was obtained by using the  $\Delta T$  McSkimin criterion [14]. The sample-transducer bonding agent was N-Apiezon grease. Correction which takes into account the bond was not carried out, but a rough evaluation of the corresponding error introduced in the velocity gave less than 0.05%.

Brillouin light scattering spectra were collected both in back-scattering and at a scattering angle of  $90^\circ$  by means of a Sandercock-type 3+3-pass tandem Fabry-Perot interferometer characterized by a finesse of about 100 and a contrast ratio higher than  $10^9$ . A laser of 532.0 nm wavelength was used as light source. The refractive index was measured by prism coupling technique using He–Ne laser operating at 632.8 nm and 543.5 nm.

## 3. Results and discussion

The observed density change as a function of the applied pressure is reported in Table 1 and has a linear increase vs pressure. At the maximum pressure we achieved a densification of 23 %.

The collected Brillouin spectra allow us to study the behaviour of both the longitudinal and the transverse acoustic vibrations. The Brillouin longitudinal Stokes peaks of all the samples are shown in Figure 1, where in the inset we present an example of the longitudinal and the transverse peaks for the 2 GPa sample in the  $90^\circ$  configuration.

Figure 1

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6 Although the use of pressure and temperature in the densification process should ensure the homogeneity  
7 of the glasses, we performed Brillouin measurements in different points of the surfaces of the cylinders,  
8 see figure 2 as an example. The comparison of the Brillouin peaks measured on the lateral surface and on  
9 the plane one confirms the isotropy of the samples. The frequency spread of the longitudinal peak shift is  
10 of the order of 5 % in all the samples. These small differences could be probably ascribed to different  
11 relaxations near the crack present in the samples as a consequence of the densification.  
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14 Figure 2

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17 The longitudinal and shear sound velocities are calculated from the Brillouin frequency shifts and the  
18 refraction indexes (see Table 1) making use of the formula:  
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$$v_s = \frac{v_B \lambda}{2n \sin(\varphi/2)} \quad 1$$

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22 where  $v_s$  is the sound velocity,  $\lambda$  the incident wavelength and  $\varphi$  the scattering angle. The obtained sound  
23 velocities are shown as a function of density and pressure in Table 1. In the same Table we reported the  
24 results obtained from ultrasonic sound velocities measurements.  
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31 Table 1

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34 The dependence of the ultrasonic and visible sound velocity as a function of the density of the systems is  
35 shown in Figure 3. Both sets of measurement show a substantially linear behaviour with the increasing  
36 density. The small differences between them are within the experimental errors, which could be probably  
37 ascribed to the imperfections of the samples due to the densification process.  
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41 Figure 3

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45 In order to study the effects of the densification process from the molecular point of view, Raman  
46 scattering was performed on all the available samples in different frequency ranges and with different  
47 frequency resolutions, allowing us to understand deeper both the structural modifications and the low-  
48 frequency changes in the Boson Peak range.  
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50 Figures 4 and 5 show the Raman spectra of the original and the densified samples retrieved from high  
51 pressure in the VV and HV polarization respectively. The spectrum of the non densified glass is in  
52 agreement with already published results [1,2]. It can be seen how some small modifications in the optical  
53 part of the spectra occur with the increasing density of the system.  
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56 Figure 4

Figure 5

In the VV spectra, the main vibrational band located around  $430\text{ cm}^{-1}$  is assigned to the symmetric stretching mode of the bridging oxygens [1]. This band as a function of pressure moves towards higher frequency with a shift around the 4% (see inset of figure 5) which corresponds to a hardening of the elastic Ge-O constant. Along with the shift, the broadening of this band corresponds to a broadening of the distribution of the Ge-O-Ge inter-tetrahedral angles, which is due to the slightly distortion of the  $\text{GeO}_2$  tetrahedra in the densification process. The high frequency bands observed in the range  $860\text{-}1000\text{ cm}^{-1}$  are the TO and LO split asymmetric stretching bands of the bridging oxygen (Ge-O-Ge) [1]. Their intensities do not change with the densification but their positions slightly shift towards lower frequencies, indicating a softening of the elastic constants (see inset of figure 5). These results are consistent with previous measurements on permanently densified germania [15] and with in situ experiments [2] and show how the densification process does not induce significant structural modification up to 6 GPa applied pressure.

The same considerations can be drawn from the Raman HV polarization spectra reported in Fig.5. Moreover from the comparison of the two polarization spectra, no evident depolarization phenomena are present as a function of density and this is a further confirmation of the sample homogeneity.

On the other hand significant changes take place in the low-frequency part of the Raman spectra. The frequency region of the Boson peak (around  $60\text{ cm}^{-1}$ ) is better shown in Fig.6 where the high resolution Raman measurements are reported for all the glass densities. The Raman intensity has been normalized imposing that the integrated intensity of the high frequency bands in the  $860\text{-}1000\text{ cm}^{-1}$  region, which are not perturbed by the densification process, should be equal. It can be seen that the Boson peak clearly shifts towards higher frequencies as a function of density and its intensity decreases. This change in the shape of the spectra is strong in the peak region while at around  $150\text{ cm}^{-1}$  the curves merge. The detailed study of the Boson peak evolution as a function of density is the subject of another work [16]. Here we just want to emphasize that the Boson Peak shifts and decreases in intensity as a function of density. Moreover, the shift of the peak towards higher frequencies is in agreement with the elastic constant modifications of the medium and is consistent with previous published measurements on different systems [16-19].

Figure 6

#### 4. Conclusions

We have realized a complete set of densified homogeneous GeO<sub>2</sub> samples using an HT/HP method applying pressures in the range from 2 to 6 GPa. We carried out a detailed characterisation of these glasses by means of optical and spectroscopic measurements. From Brillouin and ultrasonic results we derived the sound velocity both in the MHz and in the GHz frequency range. The results show a hardening of the elastic medium of the samples with the increasing density. With Raman measurements we see a continuous change in the structural modification induced by the densification and the high-resolution Raman spectra allow us to follow the evolution of the Boson Peak with increasing density. The Boson Peak shifts towards higher frequencies and decreases in intensity. Our results are in agreement with previous reported measurement on other systems [16-19].

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Fig. 1. Brillouin longitudinal Stokes peak in all the densified samples and in the normal one. In the inset is an example of the longitudinal and the transverse peak in the sample retrieved from 2 GPa pressure.

Fig. 2. Brillouin longitudinal Stokes peaks collected from three different points of the plane surface (continuous lines) and in one point of the lateral surface (dots) of the cylindrical sample at 2 GPa.



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5 Fig. 3: Plot of the longitudinal and shear velocity as a function of increasing density in the ultrasonic (open dots) and visible  
6 range (full dots).

7 Fig. 4: Raman spectra of the original and the densified samples in VV polarization. The inset shows the band centred at  $430 \text{ cm}^{-1}$ .  
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10 Fig. 5: Raman spectra of the original and the densified samples in HV polarization. In the inset is shown the shift of the two  
11 peaks located in the normal  $\text{GeO}_2$  around  $430 \text{ cm}^{-1}$  (open triangle) and  $860 \text{ cm}^{-1}$  (open circle) respectively.  
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14 Fig. 6: Low-frequency Raman spectra of the original and the densified samples in the HV polarization. The figure shows how  
15 the Boson Peak shifts and decreases in intensity with the density.  
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18  
19 Table 1: Main characteristics of the normal vitreous germania and of the densified glasses. Density  $\rho$  as a function of the  
20 applied pressure, the refraction index  $n$ , the longitudinal ( $V_L$ ) and shear ( $V_S$ ) sound velocities measured by Brillouin Light  
21 Scattering (labelled by B) and by ultrasonic measurements (labelled by U).  
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Pressure (GPa)	$\rho$ (Kg/m <sup>3</sup> )	n	$V_L^B$ (m/s)	$V_S^B$ (m/s)	$V_L^U$ (m/s)	$V_S^U$ (m/s)
<b>0</b>	3660	1,61	3650	2150	3729	2265
<b>2</b>	3994	1,68	3943	2357	3882	2428
<b>4</b>	4210	1,71	4314	2575	4207	2524
<b>6</b>	4520	1,74	4631	2759	4383	2626

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Fig.1

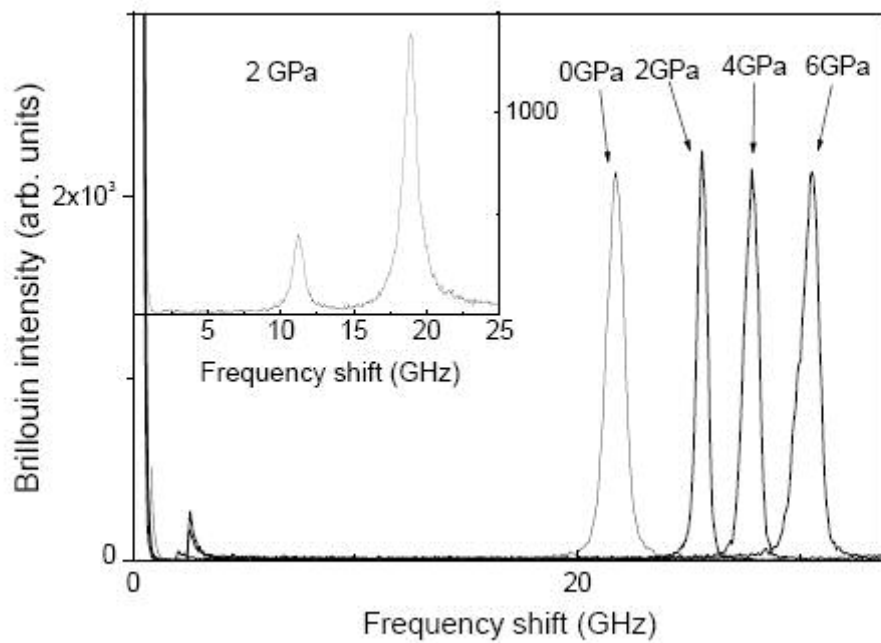


Fig 2

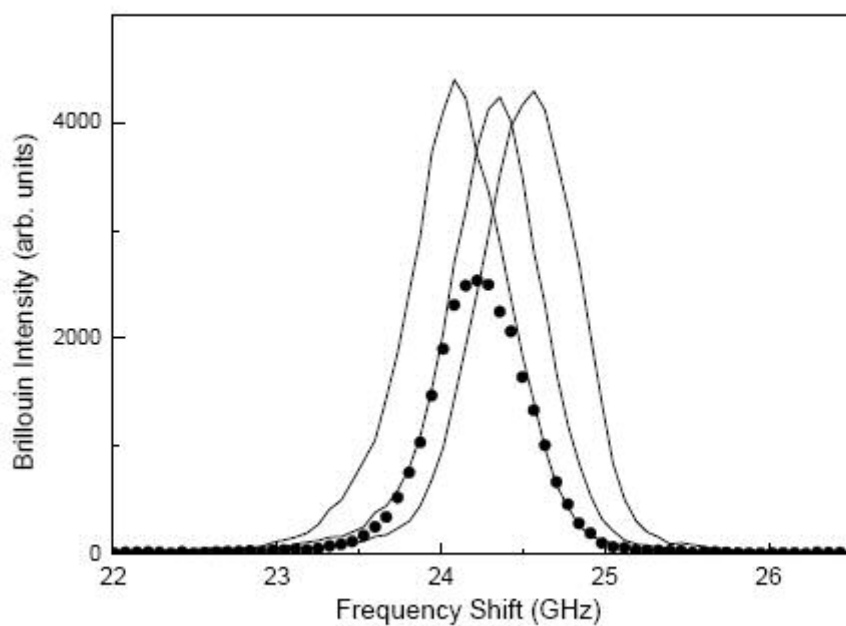


Fig.3

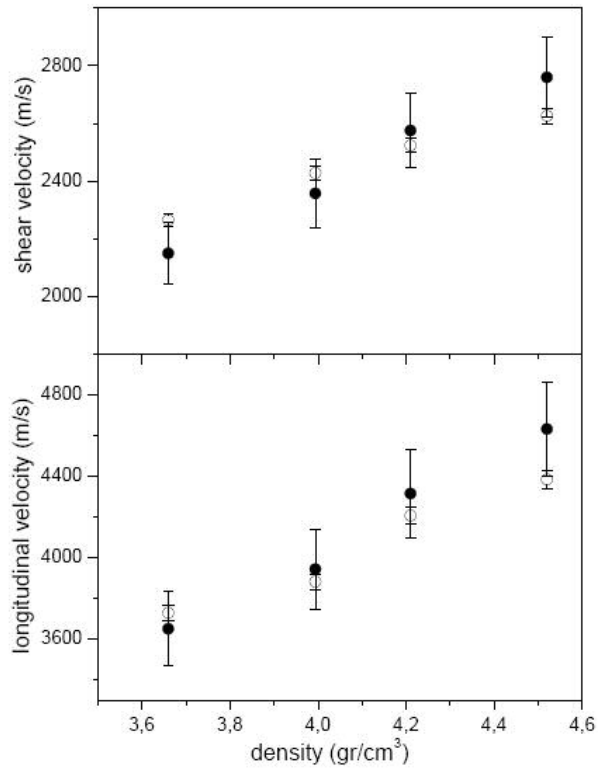


Fig 4

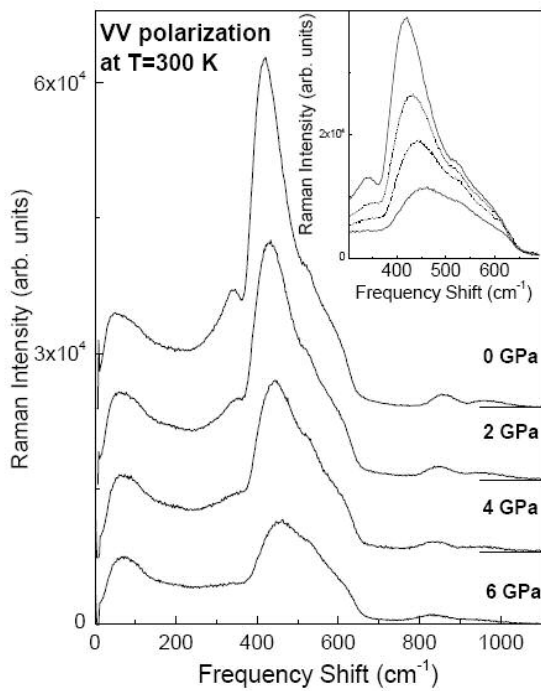


Fig.5

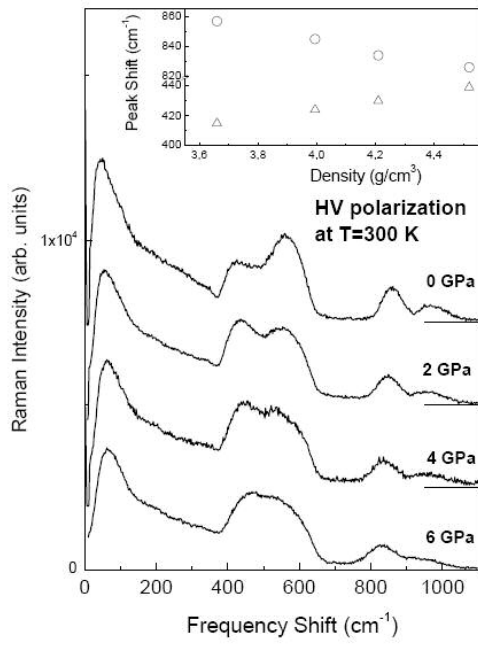


Fig 6

