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## RESEARCH ARTICLE

**The vibrational dynamics of GeO<sub>2</sub> at the glass transition: a Raman and Brillouin scattering study**

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(September 23, 2010)

New temperature-dependent Brillouin and Raman scattering experiments were performed on vitreous GeO<sub>2</sub> in the 10 K - 1200 K temperature range. We found that, while the sound velocity above room temperature slightly increases (2-3%), the frequency of the Boson Peak maximum shows an unexpected behavior, decreasing of more than 15% when the temperature is increased. The results are interpreted in the framework of a phenomenological model.

**Keywords:** glasses, vitreous germania, boson peak, Brillouin light scattering, Raman light scattering

**1. Introduction**

The growing interest in the study of the dynamics in vitreous materials has been stimulated by recent experiments on vibrational properties which have revealed some remarkable and in some extent unexpected results [1–5]. As a matter of fact an excess of modes in the density of states over the Debye prediction is observed in glasses: the so-called Boson Peak (BP). Although the BP has been observed in all vitreous systems, both in experiments and in simulations, no agreement exists about the nature of the modes responsible for this excess [2, 6–8]. Recent experiments show that, whenever a hardening of the elastic medium occurs [9–11], there is an increase of the frequency of the maximum of the BP and a decrease of its intensity. These effects have been observed as a function of temperature [12, 13] or applied pressure [14], during densification due to chemical reaction [15] and in permanently densified samples [16–18]. Despite the large number of investigations, the connection between the frequency of the maximum of the BP and the sound velocity at temperatures in the glass transition range, is still unsettled. In the specific case of GeO<sub>2</sub>, one of the archetype of strong glasses, up to now this connection has not been investigated. In this work we present a Raman and Brillouin scattering study of the dynamics of  $\nu$ -GeO<sub>2</sub> in the temperature range between 10 K and 1200 K, crossing the glass transition temperature ( $T_g \sim 800$

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K). We found that the BP does not scale with the Debye-law, i.e. it does not scale with the elastic constants which are at the origin of the measured sound velocity. Moreover the shape of the BP does not change in the whole temperature range, indicating the conservation of the modes responsible of the BP.

## 2. Experimental and Results

Appropriate amounts of GeO<sub>2</sub> powder (Aldrich 99.99%) were melt in a crucible for 6 hours at about 1600°C. The homogeneous and bubble free melt was subsequently quenched in air. The samples were annealed at 500°C and polished in order to obtain good optical surface. The vitreous nature of our samples was verified by X-ray diffraction measurements. Raman scattering experiments were performed using a double monochromator Jobin Yvon U1000 in the 90° HV configuration with resolution of 2 cm<sup>-1</sup>. Brillouin light scattering spectra were obtained using a Sopra double monochromator, in the 90° VU configurations (U is to indicate no analyzing polarizer) with resolution of 0.02 cm<sup>-1</sup>. The first order Raman scattering intensity in a glass ( $I_R$ ), for a Stokes process, [19], can be written as:

$$I_R(\omega, T) = C(\omega)g(\omega) \frac{[n(\omega, T) + 1]}{\omega}; \quad (1)$$

where  $n(\omega, T)$  is the Bose-Einstein population factor,  $g(\omega)$  is the density of states and  $C(\omega)$  is the light-vibration coupling function. The reduced Raman intensity,  $I^{red}$ , is obtained by dividing the experimental spectrum for for  $n(\omega, T) + 1$  and  $\omega$ :

$$I^{red}(\omega, T) = \frac{C(\omega)g(\omega)}{\omega^2}. \quad (2)$$

In order to compare spectra taken at different temperatures, we normalized the reduced spectra to the area of the molecular peak centered at 840 cm<sup>-1</sup> that does not significantly change in the entire investigated temperature range.  $I^{red}$  scattering spectra (equation 2) at some temperatures are reported in figure 1 in the BP frequency range. In the inset A we report the spectra in the normalization region. The BP do not show any significant changes either in the shape or in the intensity up to 550 K, even if they show an increase of quasi-elastic scattering (QES) at frequency below 20 cm<sup>-1</sup> [20]. In figure 1, in the inset B, we report an example of the fitting procedure of the QES and the BP at T = 896 K in order to show that the temperature variation of QES does not modify the position of the BP. The QES temperature behavior is not the object of the present work and we do not discuss it further. At higher temperature, in the glass transition temperature range, significant changes of the BP shape and intensity occur: we observe a BP shift to lower frequency and an increase of its intensity. These evidences are clearly appreciable in figure 1.

Similar measurements have been recently reported on SiO<sub>2</sub> [21] showing an opposite behaviour, i.e. at increasing the temperature the BP shifts to higher frequency, although SiO<sub>2</sub> and GeO<sub>2</sub> are very similar systems. At present we are not able to explain the microscopic origin of this different behaviour. In the framework of the possible connection between the BP and the elastic properties of the system, we have evaluated the longitudinal and transverse sound velocities taking properly into account the temperature variation of the refractive index. The results are reported in figure 2 together with the available literature data [22, 23]. The comparison of the data shows a good agreement both in the temperature behavior and

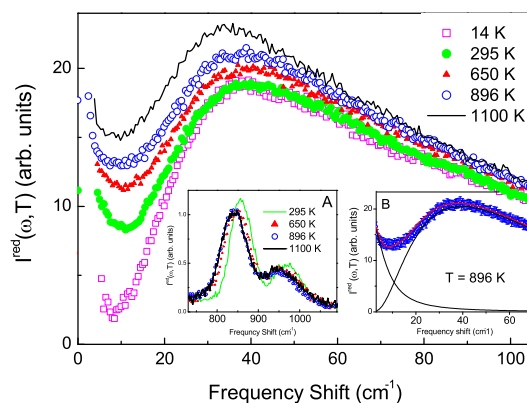


Figure 1. Low frequency reduced Raman spectra for selected temperatures. Increasing the temperature the BP clearly shifts towards lower frequency spectra and increases its intensity. Inset A: some spectra reported in the normalization region. Inset B: an example at  $T = 896$  K of the fitting curves (continuous lines) used in order to evaluate the BP position

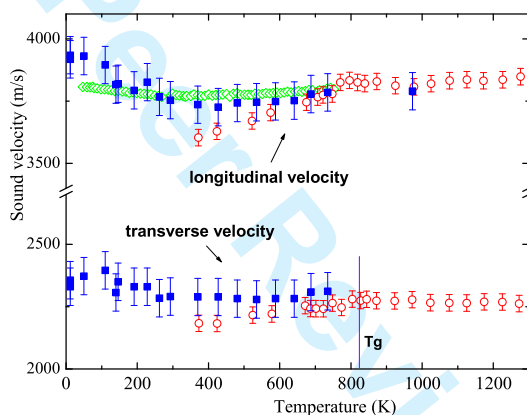


Figure 2. Temperature evolution of the longitudinal and transverse sound velocity; full squares represent the data obtained in the present work; literature data are also reported, open diamonds from [22] and open circles from [23].

in the absolute values at high  $T$  ( $> 400$  K), while some differences are observed in the low temperature range. These differences are probably related to different heat treatment when the glass is produced. At temperatures near the glass transition the sound velocities are almost constant, varying less than 3%.

### 3. Discussion

In order to understand the microscopic origin of the boson peak variation, taking in account the empirical relation  $C(\omega, T) \sim \omega$  in the frequency region near the BP, as already found in several glassy systems [24, 25]. The  $I^{red}$  spectra, taken at different temperature, could be evaluated in terms of a rescaled frequency  $\Omega = \omega/\omega_s$  where  $\omega_s(T)$  is the squeezing frequency, i.e. the frequency which normalized the intensity of the maximum of the BP at all the measured temperatures accordingly to equation 3:

$$I(\Omega, T) = I^{red}(\omega, T)\omega_s^2(T). \quad (3)$$

The squared factor of  $\omega_s$  is related to the conservation of the total number of vibrational states, i.e.  $g(\Omega)d\Omega = g(\omega)d\omega$ . When applying equation 3, the spectra taken at different temperatures collapse on a master curve, as reported in figure 3 (the temperatures are those of figure 1), indicating that the intensity increase is only apparent and related only to the BP shift.

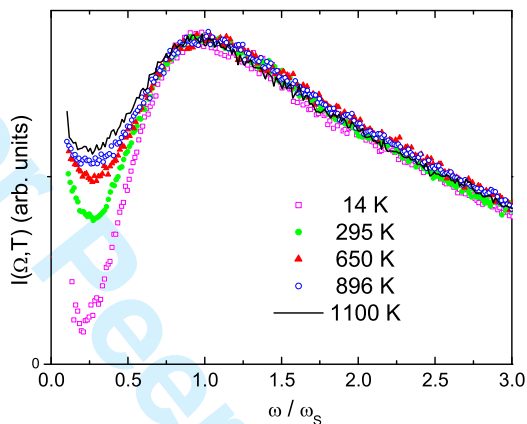


Figure 3. Boson Peak at some temperatures reported as a function of the rescaled frequency  $\Omega$  (see equation 3).

In figure 4 we report the temperature behavior of  $\omega_s$ : it shows a nearly constant value up to 500 K, then a decay in the  $T_g$  range. In the high temperature region (supercooled liquid)  $\omega_s$  tends again to a constant value. In the same figure the frequency  $\omega_{BP}$ , obtained by fitting the data of figure 1 with a log-normal curve, are reported. The behavior of  $\omega_s$  and  $\omega_{BP}$  are very similar and in our opinion the differences are substantially ascribed to  $\omega_s$  because it is quite difficult to measure absolute Raman intensities when changing the experimental conditions.

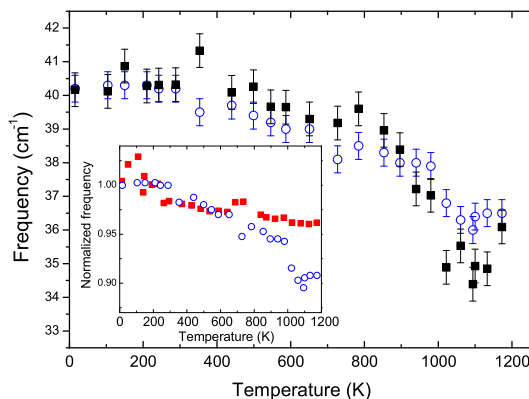


Figure 4. comparison between BP position, full squares, and the squeezing frequency  $\omega_s$ , open circles; in the inset is also reported a comparison between  $\omega_{BP}$ , open circles and  $\omega_D$ , full squares.

1 Now we want to compare  $\omega_{BP}$  with the corresponding variations of the Debye  
2 frequency, expressed as:

$$\omega_D = \left[ 6\pi^2 \times \rho \times N_A \times \frac{N_f}{M_w} \times 3 \left( \frac{1}{v_l^3} + \frac{2}{v_t^3} \right)^{-1} \right]^{-1/3}; (4)$$

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8 where  $\rho$  is the density,  $N_A$  is the Avogadro number,  $N_f$  is the formula number,  
9  $M_w$  is the molecular weight and  $v_l$  and  $v_t$  are the longitudinal and transverse sound  
10 velocity respectively. The density  $\rho$  was measured at room temperature and in the  
11 liquid phase [26, 27] and changes of less than 6%. We have extrapolated these  
12 data in order to evaluate  $\omega_D$  for all our measured temperatures. The comparison is  
13 reported in the inset of figure 4: it is evident that the elastic medium modification  
14 cannot explain the BP behavior. A possible phenomenological explanation is that  
15 during the phase transition, two phenomena are present: a change of the elastic  
16 constants and a change in the microscopic structure. In fact vitreous germania is  
17 a strong glass and its structure, made by rings of distorted tetrahedra, is surely  
18 more anisotropic than the super-cooled liquid phase. In this last situation, because  
19 of the greater mobility of the system, the tetrahedra should rearrange in a more  
20 homogeneous and isotropic configuration. This leads to an increase of the vibrations  
21 disorder and this could induce a BP shift to lower frequency, as proposed in a recent  
22 model [28, 29].  
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#### 26 4. Conclusions

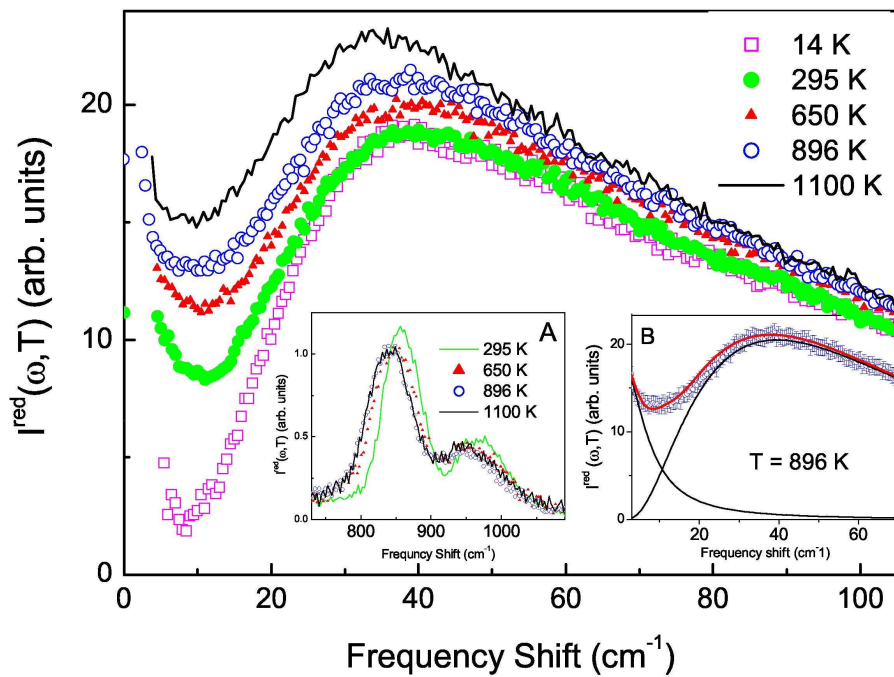
27  
28 In conclusion we studied the variation of the BP from glass to super-cooled liquid  
29 and we found that the distribution of the low frequency states in the BP range is  
30 conserved under temperature variation. Moreover, from the comparison between  
31 Raman and Brillouin measurements, the difference observed in the behaviour of  
32  $\omega_{BP}$  and  $\omega_D$ , suggests that the elastic medium modification do not fully explain  
33 the BP shift. A possible explanation of these results comes from considering that  
34 at high temperature the tetrahedra forming the network could gradually rotate  
35 settling in a more isotropic configuration.  
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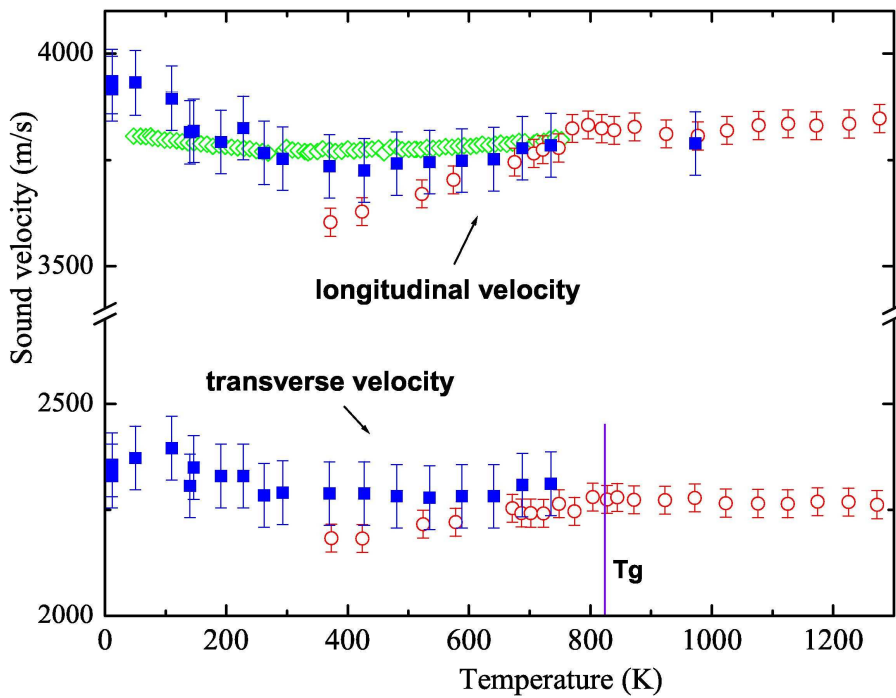
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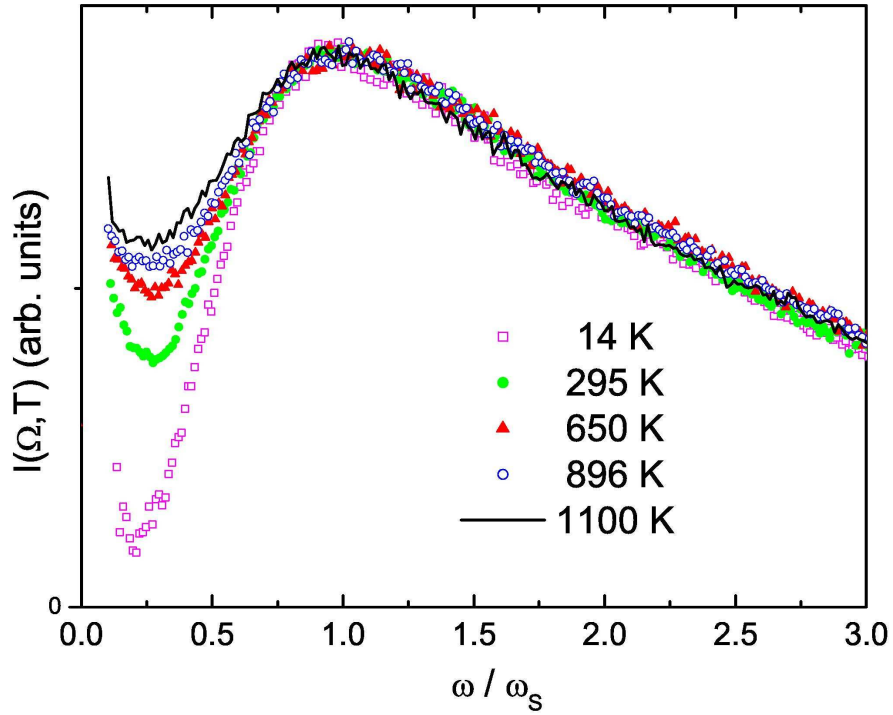


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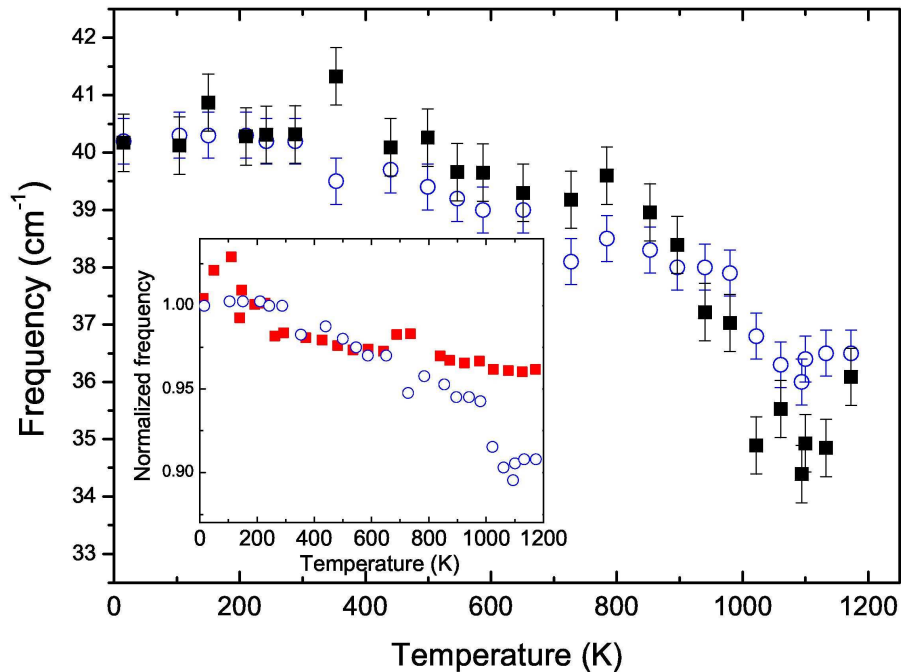
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