



**HAL**  
open science

# The Raman coupling function in permanently densified GeO<sub>2</sub> glasses

Aldo Fontana, Laura Orsingher, Giacomo Baldi, F. Rossi

► **To cite this version:**

Aldo Fontana, Laura Orsingher, Giacomo Baldi, F. Rossi. The Raman coupling function in permanently densified GeO<sub>2</sub> glasses. *Philosophical Magazine*, 2010, pp.1. 10.1080/14786435.2010.527865 . hal-00642938

**HAL Id: hal-00642938**

**<https://hal.science/hal-00642938>**

Submitted on 20 Nov 2011

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



## The Raman coupling function in permanently densified GeO<sub>2</sub> glasses

Journal:	<i>Philosophical Magazine &amp; Philosophical Magazine Letters</i>
Manuscript ID:	TPHM-10-Jun-0278.R1
Journal Selection:	Philosophical Magazine
Date Submitted by the Author:	09-Sep-2010
Complete List of Authors:	Fontana, Aldo; university of trento, physics Orsingher, Laura; Università di Trento, Fisica Baldi, Giacomo; University of Trento, Physics Rossi, F.; Università di Trento, Fisica
Keywords:	Raman spectroscopy, neutron scattering, glass
Keywords (user supplied):	permanently densified glass, vitreous germania



## RESEARCH ARTICLE

**The Raman coupling function in permanently densified GeO<sub>2</sub> glasses**L. Orsingher<sup>a</sup>, G. Baldi<sup>b,c</sup>, A. Fontana<sup>a,b\*</sup>, and F. Rossi<sup>a</sup><sup>a</sup>*Dipartimento di Fisica, Università di Trento, I-38050 Povo, Trento, Italy;* <sup>b</sup>*IPCF-CNR, UOS Roma, c/o Università di Roma "La Sapienza", I-00185 Roma, Italy;* <sup>c</sup>*European Synchrotron Radiation Facility, BP 220, 38043 Grenoble, France;*

(September 27, 2010)

We report on a Raman and inelastic neutron scattering investigation of the vibrational dynamics of permanently densified v-GeO<sub>2</sub> glasses. The comparison between the two techniques allows us to derive the Raman coupling function  $C(\omega)$ . This quantity shows a linear frequency dependence in the boson peak range and is not affected by the sample densification. We thus show that Raman spectroscopy can be used as a complementary technique to neutron scattering as a probe of the density of vibrational states in glasses. The evolution of the Raman spectra with the density of the studied samples compares well with the neutron results, confirming the existence of a master curve associated to a single scaling parameter.

**Keywords:** vitreous germania, permanently densified glass, Raman light scattering, neutron inelastic scattering

**1. Introduction**

The vitreous state is a state of matter intermediate between crystals and liquids. The structure is characteristic of the instantaneous structure of a liquid but the atoms are constrained to vibrate, more or less harmonically, around their disordered quasi-equilibrium sites so that the dynamics is characteristic of a solid. Therefore, it is still possible to define a vibrational density of states  $g(\omega)$ , which describes the vibrational characteristics of a disordered system and determines its thermal properties, as in the case of the crystal. An excess of modes over the Debye law in the low frequency regime, called Boson Peak (BP), has been ubiquitously observed in a wide range of materials both in experiments [1–4] and in numeric simulations [5–7]. Modifications of the Boson Peak take place when a hardening of the elastic medium, due to different varying thermodynamic parameters, occurs. For example, the temperature [8, 9], the applied pressure [5, 10, 11] or the permanent densification [12] lead to an increase of the BP position and a decrease of its intensity.

Therefore, in the case of disordered solids the evaluation of the vibrational density of states  $g(\omega)$  becomes crucial for the study of the vibrational properties and their connection with thermal anomalies. In general one can experimentally deduce the density of states, DoS, from Raman, neutron and specific heat measurements [13], but all these techniques have nevertheless some drawbacks.

---

\*Corresponding author. E-mail: afontana@science.unitn.it

In the case of inelastic neutron scattering (INS), the incoherent double scattering cross section is directly related to the DoS. In a one-component systems the one-phonon incoherent cross section reads [14]:

$$\frac{d^2\sigma_{incoh}}{d\Omega dE'} = \frac{k'}{k} \frac{N\sigma_i}{8\pi m} \frac{g(\omega)}{\omega} Q^2 e^{-2W(Q)} [n(\omega) + 1] \quad (1)$$

where  $n(\omega, T)$  is the Bose-Einstein population factor. For a coherent scatterer like germania, we are obliged to calculate the density of states in the framework of the incoherent approximation. The incoherent approximation assumes that the interference term in the coherent scattering function averages to zero at relatively high  $Q$ , so that the dynamic structure factor can be described in terms of an average atom, which scatters only incoherently. This works astonishingly well for the two coherently scattering glasses silica and germania [15]. Moreover, it should be noted that in the case of a glass consisting of two or more elements, this density is called the *generalized vibrational density of states*, to emphasize that it is not the *true* density of states, but its reflection in the scattering, weighted by the cross sections and masses of the atoms in the sample.

On the other hand, in the case of Raman scattering, the direct evaluation of the vibrational density of states from the experimental spectra is not straightforward because of the presence of a coupling spectral function, i.e. the Raman coupling function  $C(\omega)$ , which measures the efficiency of the coupling between the incident photon and the vibrations of the system.

The first order Stokes Raman scattering intensity,  $I_{exp}$ , for harmonic excitations at a given temperature  $T$ , is connected to the vibrational density of states [16] by:

$$I_{exp}(\omega) \propto \frac{n(\omega, T) + 1}{\omega} g(\omega) C(\omega). \quad (2)$$

The reduced Raman intensity,  $I^{red}$ , is obtained by dividing the experimental spectrum for  $n(\omega, T) + 1$  and  $\omega$ :

$$I^{red}(\omega, T) = \frac{C(\omega)g(\omega)}{\omega^2}. \quad (3)$$

Different theoretical models have been so far proposed for the frequency dependence of  $C(\omega)$  under different approximations. It should be noted however, that even if all the proposed models predict a power-law frequency behavior for  $C(\omega)$ , a complete understanding of the value of the exponents is still lacking. On the experimental side, the direct comparison between Raman scattering and inelastic neutron scattering measurements is the most faithful procedure to evaluate  $C(\omega)$ . It is, however, worth noting that this experimental determination of the coupling function  $C(\omega)$  is based on the assumption that the generalized vibrational density of states measured with INS closely resembles the true DoS. During the last decade, it has been shown for several glasses that  $C(\omega)$  seems to follow a linear dependence in the BP frequency range. The aim of the present work is to determine the spectral shape of  $C(\omega)$  by combined Raman and neutron scattering experiments in permanently densified  $\text{GeO}_2$ .

## 2. Experimental procedure

Vitreous germania was prepared by the conventional melt-quenching method. The obtained glass block was cut into cylindrical pieces which were densified using an HT-HP multi-anvil apparatus following a procedure described elsewhere [17]. The samples were compressed at 2, 4 and 6 GPa and then heated at 673 K for 2 minutes under pressure. The densities,  $\rho$ , were measured at room temperature by a Micrometrics Accupyc 1300 gas pycnometer under helium gas, yielding the values of 3.99 g/cm<sup>3</sup>, 4.21 g/cm<sup>3</sup> and 4.52 g/cm<sup>3</sup> (23% of densification with respect to the normal density of 3.66 g/cm<sup>3</sup>) respectively. In the following, we will refer to the samples using the pressure at which they were densified.

Raman scattering experiments were performed on a Jobin-Yvon U-1000 spectrometer in vertical-vertical (VV) and horizontal-vertical (HV) polarizations with an incident light of 514.5 nm. The spectra were collected in a wide frequency range (-200/+1500 cm<sup>-1</sup>) with varying frequency resolution, around 2 cm<sup>-1</sup> for the low frequency spectra. Such wide range spectra were necessary to have a proper self-consistent normalization of the spectra corresponding to different samples. The relative Raman intensity has been adjusted imposing the same integrated intensity in the 860-1000 cm<sup>-1</sup> region, i.e. where the high frequency bands are not significantly perturbed by the densification process. In order to study the effects of the densification process from the molecular point of view, high frequency Raman scattering was performed on all the available samples [17]. No strong structural modification has been detected with the densification process. This is in agreement with x-ray-absorption near-edge structure (XANES) measurement of in-situ densified GeO<sub>2</sub> glass, which shows that the amorphous-amorphous transition from a fourfold to a sixfold structure takes place at pressure above 7 GPa [18].

INS experiments were performed at the time of flight spectrometer TOF-TOF at FRM II München using a wavelength of 3 Å, which gives a resolution of 0.3 meV and a Q range of 0.4-4 Å<sup>-1</sup> [12]. To exactly match the instrument geometry, the samples were piled in an Al cylindrical container, with a wall thickness of 0.1 mm in order to reduce the empty cell signal. The sample mass was about 2 gr for each density. The inelastic neutron data were analyzed following a standard procedure: subtraction of empty cell, correction for the absorption coefficient, normalization to a reference scatterer. Moreover, with an iterative self-consistent procedure, we accounted for the entire inelastic scattering including the multi-phonon terms and the Debye-Waller factor. The convergence function is the one-phonon density of states.

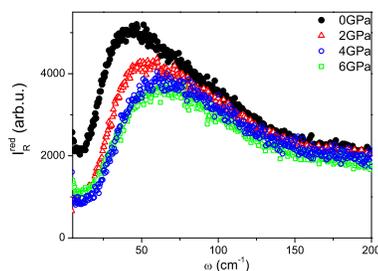


Figure 1. Room temperature low frequency HV reduced Raman intensity at different densities as indicated in the legend. The peak intensity reduces as the density is increased.

4

### 3. Results and Discussion

Figure 1 shows the reduced Raman intensity (see Eq.(3)) for all the samples. The neutron scattering data, published in [12], show that the boson peak undergoes a strong decrease in its amplitude and an increase in its frequency as a function of density. This is confirmed by the present Raman data. This assures the validity of our normalization of the Raman intensity previously described. Moreover, for all the samples, Raman and neutron spectra have a qualitatively similar shape.

We now report the ratio between the Raman and neutron scattering for all the samples in order to both evaluate the shape of the coupling function and to confirm the close relation between the two experimental quantities. The  $C(\omega)$  results to be a

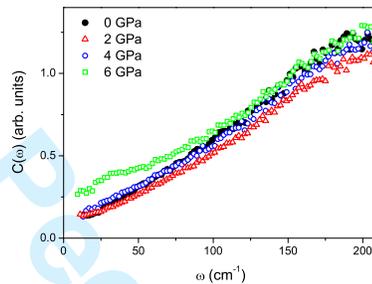


Figure 2. The Raman coupling function  $C(\omega)$ , calculated as the ratio between Raman and Neutron intensities at the same densities of figure 1.

linear function of the frequency in the BP region, thus explaining the shift towards high frequencies observed in the BP maximum in Raman scattering with respect to the neutron one. The  $C(\omega)$  relative to the 6 GPa sample is slightly different, at low frequency, with respect to those of 2 and 4 GPa. This difference could be due to a stronger depolarization of light due to the presence of defects in the sample. The experimental data show that  $C(\omega)$  extrapolates to a non-vanishing value for  $\omega \rightarrow 0$ , confirming previous results reported in the literature [19–21].

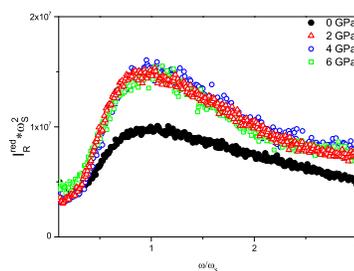


Figure 3. Reduced Raman intensity rescaled according to the scaling parameter  $\omega_s$ , at the indicated sample densities.

Taking this result into account we can now turn to a quantitative comparison of the BP evolution as a function of density as measured by the two different experimental techniques. In particular, we rescale the x-axis of the Raman spectra using  $\nu = \omega/\omega_s$ , where  $\omega_s$  is the squeezing frequency obtained imposing the conservation of the total number of vibrational states,  $g(\nu)d\nu = g(\omega)d\omega$ . The intensity has been

then rescaled as [22]

$$I(\nu) = I^{red}(\omega) \times \omega_s^2. \quad (4)$$

where we took into account the linear dependence of  $C(\omega)$  in the BP frequency range. The so-squeezed spectra are shown in Figure 3: the spectra rescale one on top of the other using the one scaling parameter  $\omega_s$ . A master curve is obtained. The existence of this master curve demonstrates that the  $g(\omega)$  is unchanged at all investigated densities, the number of low-frequency modes remains the same and hence the decrease of the BP intensity is only an apparent effect. This confirms the results obtained on the rescaling of the BP in the case of neutron data [12].

The same results is reached if the scaling is performed using  $g(\omega)/\omega^2$ , as shown in Figure 4. As before, imposing the conservation of the total number of vibrational states, the rescaled intensity is:

$$g(\nu)/\nu^2 = [g(\omega)/\omega^2] \times \omega_s^3. \quad (5)$$

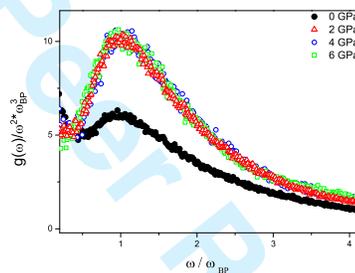


Figure 4. Reduced density of vibrational states rescaled according to the scaling parameter  $\omega_s$ , at the indicated sample densities.

In both Figure 3 and Figure 4 the curve of the 0 GPa  $\text{GeO}_2$  doesn't collapse on the master curve. The reason of this discrepancy has been already discussed in [12].

#### 4. Conclusions

In conclusion, in the present work, we have reported Raman and inelastic neutron scattering data on permanently densified  $\text{GeO}_2$  glasses. This study has demonstrated that: i) Raman and neutron spectroscopies give similar information on the dynamics in glasses, in the boson peak frequency range; ii) the densification process does not significantly affect the coupling between the probe and the target; iii) the blue shift of the boson peak with density appears also in vitreous  $\text{GeO}_2$ , confirming the results found in  $\nu\text{-SiO}_2$  [20, 24].

#### References

- [1] U. Buchenau, H. M. Zhou, N. Nücker, K. S. Gilroy and W. A. Phillips, Phys. Rev. Lett. **60**, 1318 (1988).
- [2] A. P. Sokolov, U. Buchenau, W. Steffen, B. Frick and A. Wischnewski, Phys. Rev. B **52**, R9815 (1995).
- [3] A. Fontana, F. Rossi, G. Carini, G. D'Angelo, G. Tripodo and A. Bartolotta, Phys. Rev. Lett. **78**, 1078 (1997).

- 1 [4] K. Lipinska-kalita, A. Fontana, A. Leonardi, G. Carini, G. D'Angelo, G. Tripodo, G. Saunders, Phil.  
2 Mag. B **71**, 571-581 (1995).
- 3 [5] O. Pilla, L. Angelani, A. Fontana, J. R. Gonsalves, and G. Rocco, Journal of Physics: Condensed  
4 Matter **15**, S995 (2003).
- 5 [6] O. Pilla, S. Caponi, A. Fontana, J. R. Goncalves, M. Montagna, F. Rossi, G. Viliiani, L. Angelani, G.  
6 Ruocco, G. Monaco and F. Sette, J. Phys.: Condens. Matter **16**, 8519 (2004).
- 7 [7] T. S. Grigera, V. Martin-Mayor, G. Parisi and P. Verrocchio, Nature **422**, 289 (2003).
- 8 [8] S. Caponi, A. Fontana, F. Rossi, G. Baldi, and E. Fabiani Phys. Rev. B **76**, 092201 (2007).
- 9 [9] G. Baldi, A. Fontana, G. Monaco, L. Orsingher, S. Rols, F. Rossi, B. Ruta, Phys. Rev. Lett. **102**,  
10 195502 (2009).
- 11 [10] A. Monaco, A. I. Chumakov, G. Monaco, W. A. Crichton, A. Meyer, L. Comez, D. Fioretto, J. Korecki,  
12 and R. Rüffer, Phys. Rev. Lett. **97**, 135501 (2006).
- 13 [11] K. Niss, B. Begen, B. Frick, J. Ollivier, A. Beraud, A. Sokolov, V. N. Novikov, and C. Alba-Simionesco  
14 Phys. Rev. Lett. **99**, 055502 (2007).
- 15 [12] L. Orsingher, A. Fontana, E. Gilioli, G. Carini, Jr., G. Carini, G. Tripodo, T. Unruh, and U. Buchenau,  
16 J. Chem. Phys. **132**, 124508 (2010).
- 17 [13] A.P. Sokolov, A. Kislink, D. Quitmann and E. Duval, Phys. Rev. B **48**, 7692 (1993).
- 18 [14] S. W. Lovesey, *Theory of Neutron Scattering from Condensed Matter*, Clarendon Press, Oxford (1984).
- 19 [15] E. Fabiani, A. Fontana, U. Buchenau, J. Chem. Phys. **128**, 244507 (2008) and references therein.
- 20 [16] R. Shuker and R. W. Gammon, Phys. Rev. Lett. **25**, 222 (1970); F. L. Galeener and P. N. Sen, Phys.  
21 Rev. B **17**, 1928 (1978).
- 22 [17] L. Orsingher, M. Cavicchio, G. Carini Jr., R. Dal Maschio, D. Fioretto, A. Fontana, P. Fumagalli, E.  
23 Gilioli, M. Matterelli, E. Moser, and F. Rossi, Phil. Mag. **88**, 3907 (2008)
- 24 [18] J. P. Itie, A. Polian, G. Calas, J. Petiau, A. Fontaine, and H. Tolentino, Rev. Lett. **63**, 398 (1989).
- 25 [19] A.P. Sokolov, U. Buchenau, W. Steffen, B. Frick, and A. Wischnewski, Phys. Rev. B **52**, R9815 (1995).
- 26 [20] A. Fontana, R. Dell'Anna, M. Montagna, F. Rossi, G. Viliiani, G. Ruocco, M. Sampoli, U. Buchenau,  
27 A. Wischnewski, Europhys. Letters **47**, 56 (1999).
- 28 [21] A. Fontana, F. Rossi, G. Viliiani, S. Caponi, E. Fabiani, G. Baldi, G. Ruocco, and R. Dal Maschio,  
29 Journal of Physics: Condensed Matter **16**, 8519 (2004).
- 30 [22] S. Caponi et al., Phys. Rev. B **76**, 092201 (2007).
- 31 [23] A. Fontana, E. Moser, F. Rossi, R. Campostrini, G. Carturan, J. Non-Cryst. Solids **212**, 292 (1997)
- 32 [24] A. Fontana, F. Rossi, and E. Fabiani, J. Non-Cryst. Solids **352**, 4601 (2006).
- 33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60