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Low-frequency Raman scattering under high pressure in diamond anvil cell: Experimental protocol and application to GeO_2 and SiO_2 boson peaks

T. Deschamps [a,b,*], C. Martinet [b], D. de Ligny [b], J.L. Bruneel [c], B. Champagnon [b]

[a] Institut des Nanotechnologie de Lyon, INL-UMR5270, CNRS, Ecole Centrale de Lyon, Université de Lyon, Ecully F-69134, France
[b] Laboratoire de Physico-Chimie des Matériaux Luminescents, Domaine Scientifique de la Doua, Université de Lyon, Université Lyon-1, UMR5620 CNRS, Bât. Kastler, 10 Rue Ada Byron, 69622 Villeurbanne, France
[c] Université de Bordeaux1, CNRS UMR5255, Institut des Sciences Moleculaires, Groupe de Spectroscopie Moleculaire, 351 Cours de la Liberation, F33405 Talence Cedex, France

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A B S T R A C T

Low frequency vibrations, a universal feature of amorphous solids which is responsible for thermodynamical anomalies at low temperature, are complicated to record in high pressure device, notably because of the closeness of the elastic line. We first present an experimental protocol allowing to record the *in situ* low-frequency Raman scattering of samples under high pressure in the diamond anvil cell apparatus with a high quality. This protocol is particularly adapted to study the evolution of the boson peak of glassy materials. The second part is dedicated to the study of the boson peak of a-GeO_2, a typical strong glass. The results, which clearly show the non-Debye behaviour of this material at the beginning of the compression where an anomalous compression takes place, are compared to previous measurements on a-SiO_2. Interpretation in terms of local structural transitions and discussions about the elastic nanoheterogeneities of the amorphous state are addressed.

1. Introduction

A universal feature of amorphous materials like oxide glasses [1–17], chalcogenide glasses [18], polymers [19,20] or a-Si [21,22] is the presence of vibrational modes in the terahertz region. In glassy materials, these modes are responsible for anomalous thermodynamic properties, like a bump of Cp/T^3 at low temperature, and are thus considered as an excess of Vibrational Density Of States (VDOS) compared to the Debye-VDOS [23]. Such low-frequency excitations have been called as the boson peak in the case of vitreous systems. Interpretations of the origin of this boson peak are numerous [24–29], and a way to discriminate between these models is to know its behaviour when changing thermodynamic parameters like temperature or pressure. Several studies concerned the temperature dependence of the boson peak [6,10,11]. Other experiments have linked the change of the boson peak to the permanent densification of glasses after a high pressure/high temperature treatment [5,12,13]. However, systematic results concerning the pressure dependence of this low-frequency Raman band are lacking so far.

In situ spectroscopic studies under high pressure can be carried out with high pressure cells. Of most importance is the diamond anvil cell (DAC) which allows to reach very high pressure [30], but the recording of low-frequency Raman scattering in the DAC is not trivial. In this paper, we display an experimental protocol in order to improve the quality of *in situ* low-frequency Raman spectra under high pressure. This method is applied with success to the elastic compression of a pure GeO_2 glass. The results show the breakdown of the Debye approximation at the beginning of the compression. This behaviour is correlated with the anomalous compression (softening of the elastic moduli under pressure) and interpreted in terms of structural rearrangements of the medium range order. Analogous behaviour between GeO_2 and SiO_2 will be also highlighted.

2. Experimental

The glass chosen for this experiment is a high purity GeO_2 glass (99.99%). The high pressure cell is a DAC equipped with ultra-low fluorescence diamonds, allowing *in situ* Raman scattering acquisition. Experiments are conducted at room temperature. KBr is used as pressure transmitting medium, and the pressure is measured using the well known ruby fluorescence technique [31]. In the DAC, the sample is put into the hole of a metal gasket between the diamond culets. This hole is 100 μm diameter, so the typical size of the sample is 50 μm. This requires the use of a microscope objective. In this study, we work with a ×50 long working distance Olympus objective, and the cell is placed below, in backscattering configuration. High pressures have been applied up to 4 GPa, corresponding to a reversible transformation [32].

To record the low frequency modes, notch filter or edge filter are not suitable, because the Stoke signal is typically recorded above 50 cm^{-1}. We used a XY Dilor Raman spectrometer equipped with a pre-monochromator to eliminate the elastic scattering. The

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[*] Corresponding author at: Institut des Nanotechnologie de Lyon, INL-UMR5270, CNRS, Ecole Centrale de Lyon, Université de Lyon, Ecully F-69134, France.
E-mail address: thierry.deschamps@polytechnique.edu (T. Deschamps).

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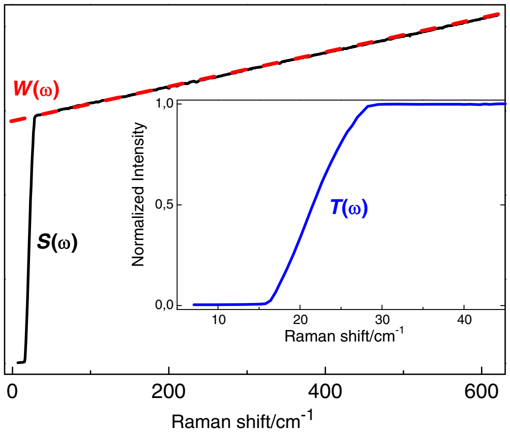

Fig. 1. S(ω) White lamp spectrum recorded after the passage throughout the premonochromator filter, and the actual white lamp spectrum W(ω). Inset: the transfer function T(ω) of the filter calculated using Eq. (1).

pre-monochromator behaves like a band pass filter with tunable cutoff frequency. The signal is recorded with a cooled CCD. The 532 nm line of a Nd^{3+}-YAG crystal, 200 mW power, is chosen as the exciting light source.

3. Experimental problems

Three major drawbacks can be listed in this type of *in situ* Raman experiments at low frequency: signal saturation, signal deformation and air signal superimposition.

3.1. Saturation

Despite the pre-monochromator filter, the reflection of the very intense laser beam at the surface of the top diamond masks the low frequency vibrational modes and saturates rapidly the detector. To avoid saturation, low frequency cutoff can be moved toward higher frequencies. However, a part of the low frequency Raman signal is lost. We propose below a very simple idea to avoid saturation without moving the frequency cutoff.

3.2. Deformation

An ideal band pass filter would have a completely flat pass band and would completely reject frequencies outside the pass band, delimitate by two discrete frequencies. The transfer function of the pre-monochromator filter is not an ideal band pass filter, so the Raman signal can be strongly affected near the low cutoff frequency. A solution to correct this issue is given further.

3.3. Air superimposition

Many rotational lines of N_2 and O_2 caused by scattering from air [33] are superimposed with the Raman signal up to 150 cm^{-1}. These lines are usually subtracted "by hand". However, this way of going on generates additional errors. These lines have to be subtracted properly. This point is also addressed in the Experimental improvements section.

3.4. Experimental improvements

First of all, to avoid saturation near the elastic scattering region, the DAC has to be tilted on the stage. In this way, the reflection of the laser line on the top of the diamond is rejected outside the objective. This allows to considerably decrease the elastic line and to avoid saturation.

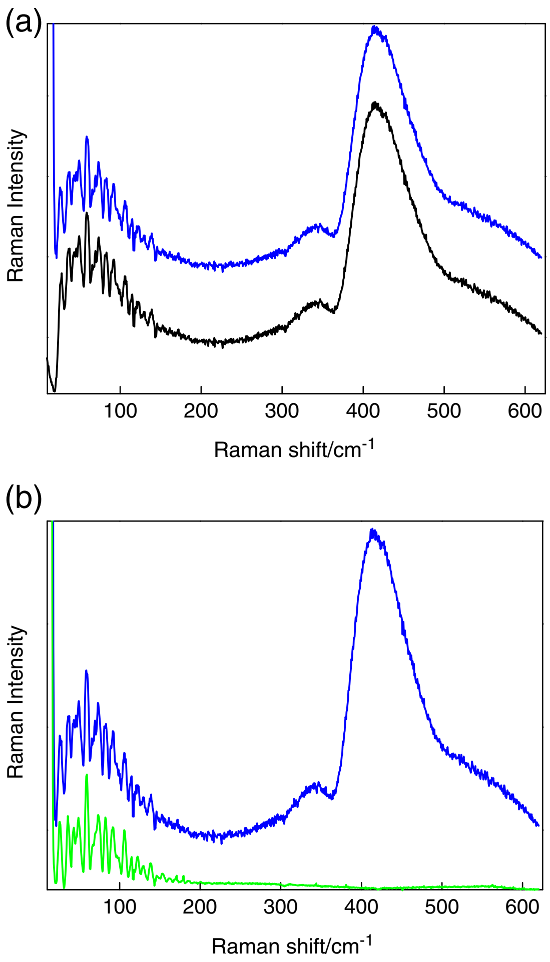

Fig. 2. (a) The raw *in situ* Raman spectrum R(ω) of GeO_2 glass at p = 0.3 GPa (lower black line) and the corrected Raman spectrum taking into account T(ω) (upper blue line). (b) The GeO_2 Raman spectrum at 0.3 GPa after filter correction (upper blue line). The air spectrum $R_{air}(\omega)$ recorded below the objective, corrected by T(ω) and normalized in intensity (lower green line).

Concerning the deformation of the signal induced by the pre-monochromator filter, the Raman spectra have to be corrected taking into account the transfer function of the filter (Fig. 1). This function can be determined experimentally by recording the white lamp spectrum throughout the filter:

$$T(\omega) = \frac{S(\omega)}{W(\omega)} \tag{1}$$

where T(ω) is the transfer function of the filter, S(ω) is the signal of the white lamp recorded throughout the filter and W(ω) the actual white lamp spectrum.

The rotational lines of N_2 and O_2 which are superimposed with the Raman signal of the boson peak can be subtracted after recording the air spectrum. For that, the DAC and the stage sample are removed below the objective. Only the air spectrum is thus recorded (Fig. 2).

$$R_{GeO_2}(\omega) = \frac{R(\omega) - R_{air}(\omega)}{T(\omega)} \tag{2}$$

where R(ω) is the raw Raman spectra of the glass sample, $R_{air}(\omega)$ is the Raman spectra of the air, and $R_{GeO_2}(\omega)$ is the corrected Raman spectra of the sample corresponding to the true signal of the GeO_2 glass (Fig. 3). We note that the intensity of $R_{air}(\omega)$ has to be