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ATOMIC PACKING AND LOW ENERGY VIBRATIONS IN B_2O_3 GLASSES, COMPACTED UNDER GPA PRESSURES

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ABSTRACT. Vibrational properties of crystals are well described by Debye's theory. This doesn't hold for vitreous systems, where an excess density of low frequency vibrational states, called Boson peak, appears. In this work we study glassy boron trioxide (B_2O_3), a prototype system widely used as basic element of multi-component glasses. Our aim is to get some insight into the dependence of mechanical and vibrational properties on the structure of glasses, *i.e.*, on the atomic packing. For this reason, samples were compacted by using a multi anvil press up to pressures of 10 GPa. A comparative analysis of light Raman scattering and mechanical characteristics have been performed on densified samples. The results show that either Raman spectra and elastic constants are affected by the densification process owing to the hardening of the elastic continuum.

1. Introduction

Solids are divided in two categories: crystalline and amorphous. The latter include glasses which are characterised by two main features: i) the glass transition, implying the lack of a well defined melting point and ii) an excess volume, reflecting a density which is lower than that of the corresponding crystal. For this reason, the present work is focused on studying how mechanical and vibrational properties depend on the atomic packing, which has been changed by increasing density. Glasses were compacted by using a multi anvil apparatus, which allows to perform two different kinds of densification. Samples can be densified either below the glass transition temperature T_g (Carini Jr. *et al.* 2008; Orsingher *et al.* 2008; Carini Jr. *et al.* 2011a) or by increasing temperature up to the melting point and then pressure quenched (Carini Jr. *et al.* 2012, 2013, 2014).This method allows to tune the structure of the solid by modifying the content of the structural units building up the network, leading to a progressive increase of the density from that of the "normal" glass, obtained by quenching at ambient pressure, towards that of the crystal. The structure can be changed with or without chemical bond modifications.

The studied system is glassy B_2O_3. Crystalline boron oxide has two polymorphs (Mackenzie and Claussen 1961): (B_2O_3-I) made up by infinite chains of BO_3 planar triangles (Gurr *et al.* 1970) with an average density of 2560 kg/m^3 and (B_2O_3-II) made up

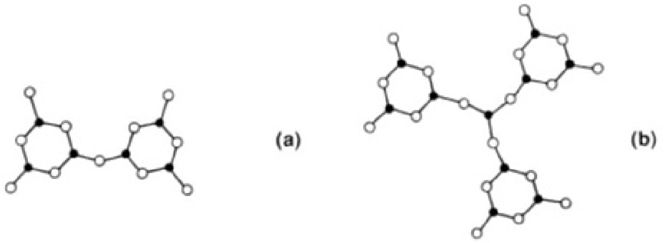

FIGURE 1. Typical structure of glassy B_2O_3: a) two boroxol rings connected via a single bridging oxygen atom; b) three boroxol rings linked via a triangle BO_3.

by corner-linked BO_4 tetrahedra with an average density of 3110 kg/m^3. In the latter, each tetrahedron has three long B-O distances (about 1.5 Å) with oxygen atoms coordinated by three borons and one B-O short distance (1.373 Å) with the oxygen coordinated by only two borons. The above distortions ensure the local charge neutrality in the crystal (Shannon and Prewitt 1969).

The structure of glassy boron oxide (v-B_2O_3) consists of BO_3 planar triangles and plane boroxol rings (B_3O_6), with an average density of 1826 kg/m^3 (Wright *et al.* 2010). These building blocks can form different molecular arrangements as sketched in figure 1.

B_2O_3 glasses, which have been pressure compacted up to 9 GPa at temperatures below T_g, reveal substantial modification of the structure characterizing the normal glass, evidencing the progressive collapse of boroxol rings with increasing pressure (Wright *et al.* 2000). After pressure release, however, glasses relax to their final compacted form over few days, restoring the original ring fraction. Quite differently, B_2O_3 glasses quenched from melt under increasing pressures in the GPa range preserve permanently the compacted structure, also exhibiting stable polyamorphism (Brazhkin *et al.* 2010) based on the transition from low- to high-density amorphous phases due to a coordination increase from 3 to 4 of network forming ions (boron atoms). In particular, NMR measurements reveal that the fraction of tri-coordinated boron atoms involved in boroxol rings decreases gradually from about 0.78 in the normal glass to about 0.3 in the glass compacted up to 5.8 GPa, also disclosing the formation of tetra-coordinated borons for pressures above 4 GPa. These findings appear to be in agreement with previous in situ measurements of inelastic X-ray scattering in vitreous B_2O_3 at pressures up to 22.5 GPa, which showed a continuous and progressive transformation from tri-coordinated to tetra-coordinated boron above 4 GPa (Lee *et al.* 2005). After decompression from high pressure, the original situation of tri-coordinated boron is recovered in the network, but preserving some permanent densification.

The present study reveals that compaction under GPa pressures of B_2O_3 glasses, at room temperature, doesn't modify the morphology of the network but it only results in a progressive hardening of the elastic continuum.

2. Experimental setup

Glasses of B_2O_3 were prepared by melt quenching, using the same procedure already described (Carini Jr. *et al.* 2011b). Samples were densified by loading B_2O_3 glasses in a

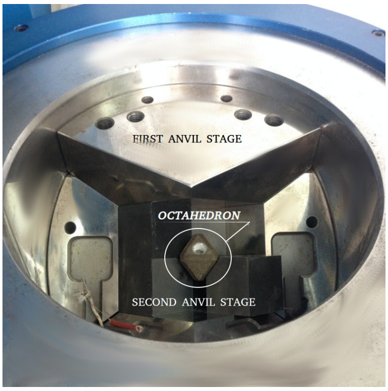

FIGURE 2. Internal configuration of the high pressure module.

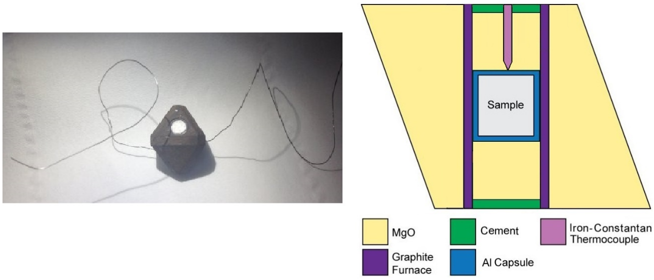

FIGURE 3. Octahedron mounting set-up, wires are the thermocouple terminals.

multi-anvil apparatus, under pressures ranging from 1 to 10 GPa for about 2-4 hours. A multi-anvil apparatus is one class of devices used to generate high pressures. Pressure is achieved by compressing the sample volume with a number (typically 4 or 6) of hard anvils. Rockland research press has 6/8 geometry that uses anvils driven together by a hydraulic press. The exact geometry depends on the type of multi-anvil and in our case a Kawai-type apparatus is used. Figure 2 shows the internal configuration of the module. It consists of two different pressurization levels: the first-stage is driven by 6 anvils that compress 8 second-stage anvils wrapping an octahedral cell assembly. For pressure experiments performed at room temperature, the cell assembly is simply composed of a pressure medium (a sintered magnesium chromite octahedron), the sample and a sample jacket (Al, Pt, Ag and Au are the materials mainly used). For higher temperatures, the system requires a graphite furnace and a thermocouple sensor. A through hole, having a length of 17 mm and a diameter of 6 mm, is made between two opposite faces of the octahedron. The sample and its capsule are put inside the hole and fixed at half height by using a MgO cement. Figure 3 shows the octahedron and a schematic illustration of the whole sample chamber. B_2O_3 cylindrical samples (height and diameter of about 6 mm) were loaded in the octahedron and pressurised. Samples were prepared by applying pressures up to 10 GPa and there dwelling for about 3 hours. Densified glasses were characterized by x-ray diffraction which

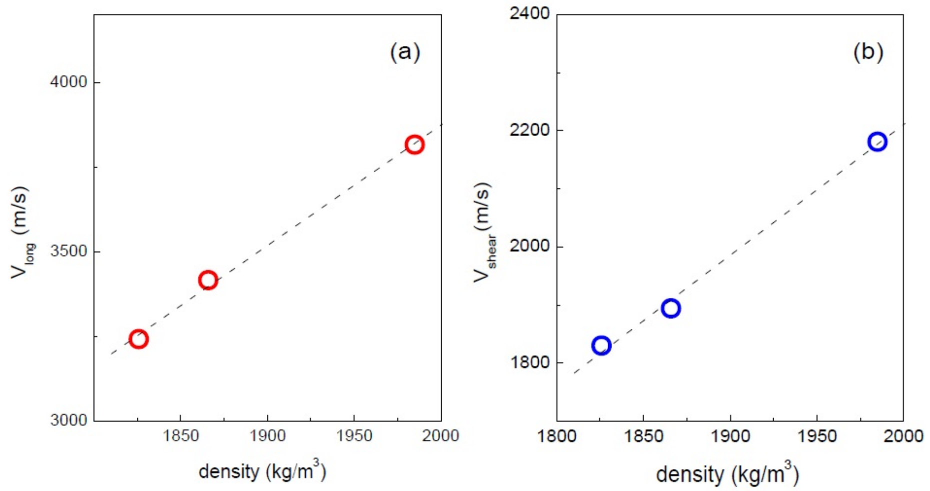

FIGURE 4. Density behaviours of longitudinal (a) and shear (b) sound velocities, measured at an ultrasonic frequency of 10 MHz.

revealed no sign of crystallization. Afterwards we determine specific physical quantities that do not depend on the observer (Carini *et al.* 2007). Mass density was determined by using a Micromeritics Accupyc 1330 gas pycnometer under helium gas having a nominal accuracy of 0.03%. The densities of normal and densified B_2O_3 glasses are: 1826 kg/m^3 (v-B_2O_3), 1866 kg/m^3 (5-GPa glass) and 1985 kg/m^3 (10-GPa glass). Mechanical and vibrational properties were measured by means of ultrasonic echo-pulse technique and Raman spectroscopy.

Longitudinal and shear sound waves were obtained by tuning X- and Y-cut quartz crystals at their fundamental frequency. The velocity of longitudinal (v_l) and shear (v_s) waves were performed at 10 MHz via a echo-pulse technique as described previously (Caponi *et al.* 2004; Carini Jr. *et al.* 2005). The correct echo overlap for sound velocity measurements was obtained by using the Δt McSkimin criterion (Papadakis 1976). The sample-transducer bonding agent was N-Apiezon grease. A correction to account for the bonding was not carried out, but a rough evaluation of the corresponding error introduced in the velocity gave a value less than 0.1%.

Raman light scattering spectra were measured in VV backscattering geometry (incident and scattered light is polarized vertical to the scattering plane) using a Horiba LabRam HR spectrometer with a laser power of 100 mW at a wavelength $\lambda_0 = 532.0$ nm.

3. Results and discussion

3.1. Mechanical properties. Figure 4 reports the density behaviour of both longitudinal (v_l) and shear (v_s) sound velocities, which increase with increasing density. The Debye

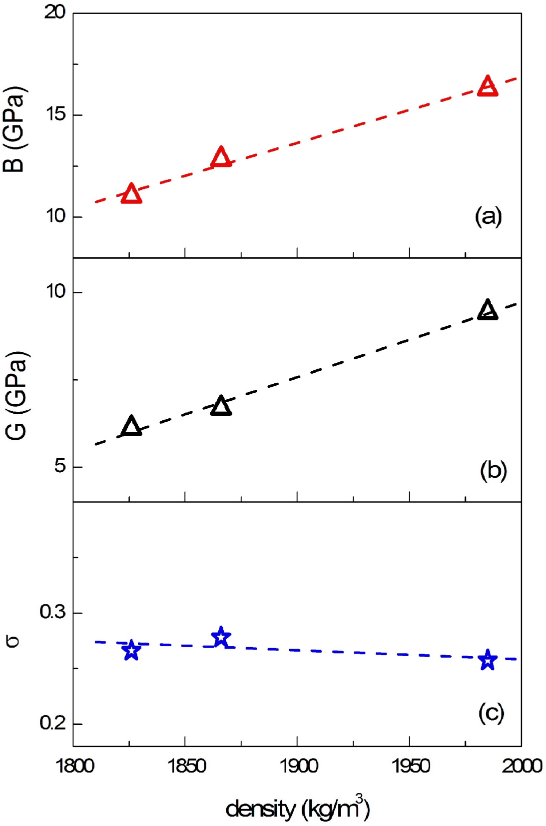

FIGURE 5. Density behaviours of (a) bulk modulus (B), (b) shear modulus (G) and (c) Poisson's ratio (σ).

sound velocity v_D and the elastic Debye temperature Θ_D, defined as follows

$$\frac{3}{v_D^3} = \frac{1}{v_l^3} + \frac{2}{v_s^3} \qquad ; \qquad \Theta_D = \frac{\hbar}{k_B} v_D \left(\frac{6\pi^2 N_A}{V_{molar}} \right)^{\frac{1}{3}}$$

have been determined by the values of v_l and v_s measured at room temperature: $v_D = 2035$ m/s, $\Theta_D = 260.6\ K$ (v-B_2O_3); $v_D = 2110$ m/s, $\Theta_D = 271.3\ K$ (5-GPa glass); $v_D = 2423$ m/s, $\Theta_D = 318.6\ K$ (10-GPa glass). The elastic moduli were calculated by using the following relations

$$G = \rho v_s^2 \quad ; \quad B = \rho v_l^2 - \frac{4}{3} G \quad ; \quad \sigma = \frac{v_l^2 - 2v_s^2}{2(v_l^2 - v_s^2)}$$

where G and B are the rigidity and bulk moduli, respectively, and σ the Poisson's ratio. Figure 5 shows their behaviour with increasing density, revealing a definite linear increase of both G and B. It is worth noting that increasing densification leads the system towards a structure having a progressively most efficient packing of the structural units, which

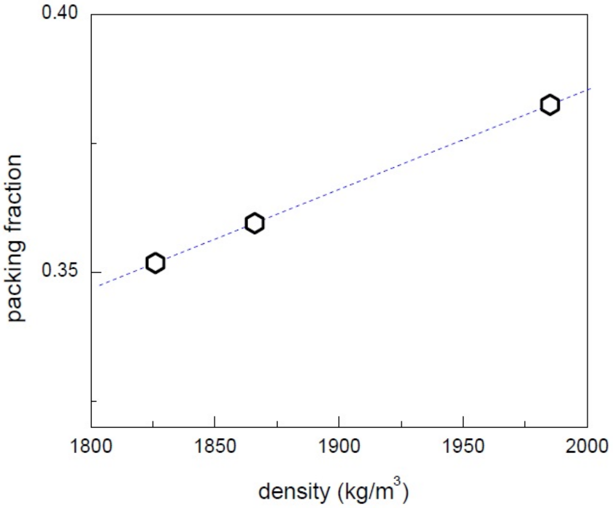

FIGURE 6. Density behaviour of the packing fraction ϕ.

build up the glassy network. Figure 6 shows an increasing monotonic trend of the packing fraction ϕ with increasing density of B_2O_3 glasses. The packing fraction is defined as $\phi = (N_A V_{atomic}) V_{molar}^{-1}$, being V_{atomic} the ionic volume and V_{molar} the molar volume. The theoretical ionic volume is given by:

$$V_{atomic} = \sum \frac{4}{3} \pi r_i^3 X_i$$

where X_i are the atomic fraction and r_i the ionic radii, which are taken from Shannon (1976), accounting for the coordination of the network forming ions (NFI). It results that both bulk (B) and rigidity (G) moduli increase linearly with growing atomic packing fraction ϕ (from 0.35, in normal glass, up to 0.382 in 10 GPa glass) pointing to a hardening of the elastic continuum. Quite differently, the Poisson's ratio remains nearly constant despite a density variation of about 9%. As well known the Poisson's ratio is defined as the negative of the ratio of shear to longitudinal strain, produced when a tensile loading is applied. It is expected that σ is strongly correlated to the connectivity of a glassy network, defined by the number of bridging bonds per NFI. This means that the larger the connectivity is the smaller σ becomes, because an increase of the connectivity causes an increasing resistance to the shear deformation. The present observations (figure 5(c)) prove that the variation of the elastic continuum, obtained by compaction, does not change the resistance to the shear deformation of glassy B_2O_3, as expected from a system whose connectivity is unchanged.

3.2. Low and high frequency Raman spectra. Figure 7 shows the normalized Raman spectra of studied samples, measured at room temperature between 8 and 1800 cm^{-1} in VV polarization. After subtraction of a background value observed above 1600 cm^{-1} where contributions from molecular vibrations are fully missing, the experimental Raman intensities have been normalized by the total integrated intensity of the bands between 8

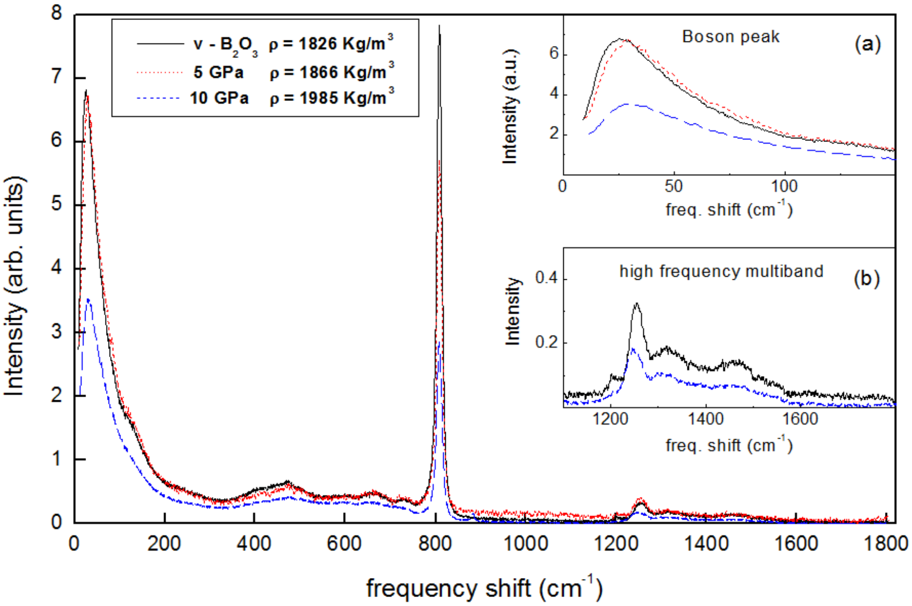

FIGURE 7. Normalized Raman intensity of densified B_2O_3 glasses for VV polarization: $v-B_2O_3$, black solid line; 5-GPa glass, red dotted line; 10-GPa glass, blue dashed line.

and 1600 cm^{-1}, which reflect the vibrations of all the units forming the glassy network. To perform a roughly quantitative comparison between the spectra in normal and densified glasses, the same procedure previously proposed (Carini Jr. *et al.* 2011b) has been used. In particular, the Raman intensity obtained for densified glasses has been reduced by the ratio between the densities of compacted and normal glasses (about 1.02 and 1.08 for 5 and 10 GPa glasses, respectively) in order to account for a larger average number of particles characterizing the scattering volume. The spectra can be regarded in terms of the contributions from two different regions: low (below 100 cm^{-1}) and high (above 100 cm^{-1}) frequency regions. The former is characterised by vibrational features arising from acoustic-like modes, while the latter reflects contributions from optical modes. It is well known that, in crystals, light Raman scattering usually don't exhibit any contribution below 100 cm^{-1}. In amorphous materials, however, the breakdown of wave-vector selection rules leads to a continuous low frequency vibrational spectrum characterised by a broad band, the so called Boson peak (inset (a)) (Jäckle 1981). The Boson peak is related to the number of vibrational excitations via the photon-phonon coupling coefficient $C(\nu)$, as stated by Shuker and Gammon (1970):

$$I(\nu) = g(\nu)C(\nu)\frac{n(\nu)+1}{\nu}$$

Low energy vibrational dynamics is given by the overlap of Debye-like modes and low frequency optic-like vibrations of coupled boroxol rings (soft librations) (Carini Jr. *et al.* 2013). The hardening of the elastic continuum, by glass densification, leads to the observed small increase of ν_{BP}, the Boson peak frequency position, from 26 cm^{-1} in v-B_2O_3, to about 31 cm^{-1} in 10-GPa glass.

At higher frequencies, there are the main band at 808 cm^{-1} due to localized breathing-type vibrations of oxygen atoms inside the boroxol rings and a multi-band above 1000 cm^{-1} (inset (b)), reflecting the vibrations of all the structural groups forming the whole glassy network (Carini Jr. *et al.* 2011b). Both the bands strictly preserve their frequencies with densification. It is observed that glass densification leads to a parallel and progressive decrease of the intensity of all the bands characterizing the vibrational spectrum either at low and high frequencies. This behaviour can be ascribed to the decrease of the average molecular polarizability α of the system. In fact, Raman intensity I_{VV} is proportional to α^2 (Bernath 2005):

$$I_{VV} = \frac{\pi^2}{\varepsilon_0 \lambda^4} \alpha^2 N_0 V_0 I_0$$

where ε_0 is the permettivity of vacuum, I_0 is the intensity of the incident laser beam with wavelength λ, N_0 the number of molecules per m^3 in the initial state, V_0 the scattering volume. It is expected that the polarizability α decreases with increasing compaction of the system (Zha *et al.* 1994) giving rise to the uniform decrease of the intensity over the whole spectrum.

4. Conclusions

Boron oxide glasses were densified at room temperature and analysed by light Raman scattering and ultrasound propagation. Raman spectra show a reduction of the intensity of the whole patterns with increasing density of glasses compacted under growing GPa pressures. This observation has been ascribed to a decrease of the average molecular polarizability. Both bulk (B) and rigidity (G) moduli and the Poisson's ratio (s) have been determined by longitudinal and shear ultrasound velocities measurements. While the Poisson's ratio remains essentially constant, quite differently B and G increase linearly with increasing density, disclosing a well-defined hardening of the elastic continuum of these compacted glasses.

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