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Structural transformations, elastic moduli and thermal expansion of permanently compacted B_2O_3 glasses

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ABSTRACT

We have measured the elastic moduli and the thermal expansion in permanently compacted B_2O_3 glasses whose structural transformations have been determined by Raman spectroscopy. Growing glass densification, obtained by melt-quenching under pressures in the GPa range, is mainly associated to the decrease of the population of boroxol rings (B_3O_6), the glassy molecular units formed by connected BO_3 planar triangles. Increasing density gives rise to a substantial hardening of the elastic continuum, while reducing the thermal expansion of these glasses. Evaluation of the average thermal Grüneisen parameter γ_{th} evidences an increase which has been explained in terms of bending vibrations gradually depressed in glassy networks having a growing packing fraction.

1. Introduction

Glasses quenched under GPa pressures may potentially represent a new class of materials because their structure can be tuned in order to get enhanced mechanical [1] and optical characteristics [2,3] useful for specific technological applications. Since their density may be progressively increased up to values involving also changes of the chemical bonding without altering the stoichiometry, they also permit to explore the mechanism of polyamorphism in disordered systems [4–7], that is the transition from low- to high-density amorphous phases characterized by a coordination increase of network forming ions. In addition to this, they are a powerful tool to investigate the relation between disordered topology and low-energy excitations which cause anomalies in the low temperature properties of amorphous solids, usually quite insensitive to changes of the composition [8–10]. Pressure-quenching a glass-forming liquid in the GPa range, in fact, permits to increase gradually the density of the glassy system changing its structure with modifications of the short- and medium-range orders. Growing densification of a prototypical glass-forming system, such as vitreous B_2O_3 (v-B_2O_3), leads to (i) the decrease of the fraction of boroxol rings (B_3O_6), the molecular groups formed by connected BO_3 planar triangles which are the basic units building up the network of v-B_2O_3 quenched at ambient pressure, (ii) the formation of tetra-coordinated boron atoms, and (iii) a reduction of the population of locally mobile structural defects [1,6,11]. In this work, we have investigated the structural modifications of compacted B_2O_3 glasses having increasing density and also measured their elastic characteristics and thermal expansion with the aim of exploring the structural mechanisms governing these properties. The results prove that the decrease of boroxol ring population with increasing density lead to a substantial and progressive increase of the rigidity, also affecting the anharmonicity of these glasses.

2. Experimental details

B_2O_3 glasses were prepared by melt-quenching using, as starting material, laboratory reagent 99.999% purity grades of boron oxide isotopically enriched in ^{11}B (99%), because the same samples considered for the present analysis will be used for future experiments of elastic and inelastic neutron scattering. Densification was obtained by loading $^{11}B_2O_3$ glasses in a high temperature/high pressure multi-anvil apparatus for the synthesis up to 4 GPa. In the pressure device, six anvil wedges press on 8 cubes which in turn press on MgO octahedrons press medium. The pressure is determined by a calibration curve obtained by reporting the ram force vs the pressure of fixed phase transitions of different sample assemblies. The glasses were fused under pressure at 1150 °C for about 10 min (2-GPa glass), at 1060 °C for about 20 min (4-GPa/B3 glass) and at 1200 °C for about 30 min (4-GPa/B4 glass) and then quenched at those pressures.

A typical raw sample had a diameter and a length of about 4.5 mm. Both the normal and compacted samples were clear, transparent, and did not show any traces of internal cracks. The samples were stored in a desiccator with dry nitrogen atmosphere to prevent hydration. After the synthesis and also one year later, densified B_2O_3 glasses were characterized by X-ray diffraction which revealed no signs of crystallization.

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The density was measured at room temperature by a Micromeritics Accupyc 1330 gas pycnometer under helium gas having an accuracy of 0.03%. The densities of normal and densified B_2O_3 glasses are reported in Table 1.

Raman spectra were measured at room temperature on a double monocromator Jobin–Yvon U-1000 and were recorded in 90° scattering geometry in both VV (incident and scattered light is polarized vertical to the scattering plane) and VH geometry (perpendicular polarizations). A 514.5 nm excitation was used with a laser power kept below 300 mW, along with a polarization scrambler between the sample and the entrance slit of the spectrometer. The accuracy of all stated measurements is within 1 cm^{-1}. To minimize the effect of surface depolarization, the sample surfaces have been polished before each run of measurement.

The velocity of longitudinal (V_l) and shear (V_t) waves was measured at 10 MHz via a pulse-echo technique, as described previously [1]. The short lengths of 4-GPa glasses led to partial overlap of adjacent echoes from the specimen following the application of a pulse of longitudinal ultrasonic waves, preventing a reliable measurement of the very high sound velocity. In this case, V_l was determined by measuring the velocity of shear waves and using the values (1.75 for 4-GPa/B3 and 1.77 for 4-GPa/B4) of the ratio $\frac{\nu_{B,l}}{\nu_{B,t}}\left(=\frac{V_l}{V_t}\right)$ between the Brillouin frequency shifts $\nu_{B,i}$ of transverse (TA) and longitudinal (LA) acoustic modes observed in Brillouin light scattering (BLS) spectra. BLS spectra were measured at room temperature using a Sandercock tandem Fabri–Perot interferometer [12]. The spectra were measured at 90° scattering, this geometry providing the frequency shifts $\nu_{B,i}$ determined by light scattering from an acoustic wave of velocity V_i in a isotropic medium: $\nu_{B,i} = \frac{2nV_i}{\lambda_L}\sin\left(\frac{\theta}{2}\right)$ ($\lambda_L = 532.0$ nm is the laser wavelength, the index i corresponds to TA or LA modes, $\theta = 90°$ is the scattering angle).

Thermal expansion measurements were made from 100 K up to 300 K using a Netzsch Industries silica pushrod LVDT horizontal dilatometer with a heating rate of 2 K/min.

The specific heat capacities of normal and densified samples were determined using a Perkin Elmer Differential Scanning Calorimeter (DSC-Pyris) over the temperature interval between 200 K and 840 K with a heating rate of 10 K/min. Calibrations of the DSC output were performed using a standard sapphire sample. The measured specific heat capacities C_p of normal and densified B_2O_3 glasses are coincident over the interval between 200 K and 500 K. We will use the room temperature values of C_p, just to determine the thermal Grüneisen parameters. The specific heat capacity data of normal v-B_2O_3 are in very good agreement with those of Richet et al. [13], measured by adiabatic calorimetry from about 5 K up to 350 K.

3. Results and discussion

3.1. Raman scattering

The room temperature Raman spectra of v-B_2O_3, 4-GPa/B3 and 4-GPa/B4 glasses between 6 and 1100 cm^{-1} are compared in Fig. 1. The main features are the Boson peak (BP), the broad band observed below 100 cm^{-1} and the intense and highly polarized line at 808 cm^{-1} arising from a localized breathing-type vibration of oxygen atoms inside the boroxol rings. At even higher frequencies, inset of Fig. 1, there is the multi-component band between 1200 and 1600 cm^{-1} which is determined by the vibrations of all the units forming the whole glassy network [11]. Densification decreases the intensity of BP while increasing its frequency from about 26 cm^{-1} in normal glass, through 52 cm^{-1} in 4-GPa/B3 glass, up to 68 cm^{-1} in 4-GPa/B4 glass. Also the intensity I_{808} of the band at 808 cm^{-1} is substantially reduced, but preserving its frequency. In 4-GPa/B4 glass, there is a further band at 775 cm^{-1} due to vibrations of structural units containing tetrahedral BO_4 groups, a feature which implies changes in the chemical bonding characterizing the network [11]. The charge neutrality of BO_4 groups formed in the glass compacted at 4 GPa is maintained because the tetrahedra must be very distorted, these distortions reflecting those revealed in β-B_2O_3 (or B_2O_3 II) crystal, the high-pressure tetrahedral phase of boron oxide. In fact, X-ray diffraction of B_2O_3 II disclosed a structure made up of corner-linked BO_4 tetrahedra, each tetrahedron having three long B–O distances (about 1.5 Å) and one B–O short distance (1.373 Å) [14]. The oxygen associated with the short distance is coordinated by only two boron atoms, while the others by three boron atoms. The above distortions permit to ensure the local charge neutrality in the crystal.

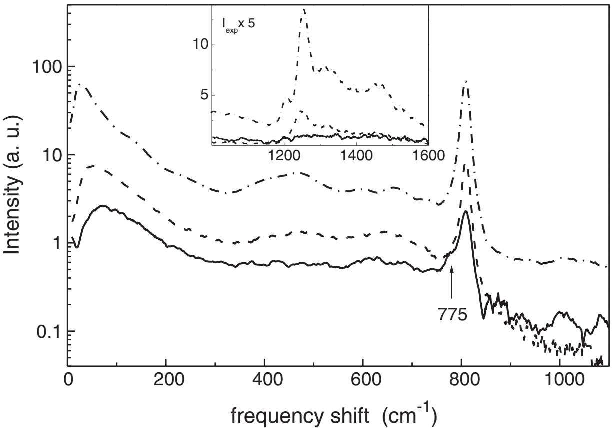

Fig. 1. Room temperature Raman spectra of v-B_2O_3 (dashed-dotted line), 4-GPa/B3 glass (dashed line) and 4-GPa/B4 glass (solid line) in VV configuration; the region above 1000 cm^{-1} is reported in the inset with an y scale expanded by a factor 5.

Table 1
Parameters of normal and densified B_2O_3 glasses. Room temperature values of the density ρ, longitudinal (V_l) and shear (V_t) sound velocities, the Debye sound velocity (V_D), bulk (B) and rigidity (G) moduli and the average thermal Grüneisen parameter γ_{th}.

B_2O_3 glasses	ρ (kg m^{-3})	V_l (m s^{-1})	V_t (m s^{-1})	V_D (m s^{-1})	B (GPa)	G (GPa)	γ_{th}
v-B_2O_3	1826	3242	1830	2036	11.04	6.12	0.33
2-GPa	2082	3737	2141	2379	16.35	9.54	0.39
4-GPa/B3	2174	5287[a]	3021	3357	34.31	19.84	0.47
4-GPa/B4	2373	6462[a]	3651	4061	56.91	31.63	0.49

[a] These values of V_l have been obtained by considering $\frac{V_l}{V_t} = 1.77$ (4-GPa/B4) and $\frac{V_l}{V_t} = 1.75$ (4-GPa/B3), that are the values obtained by the ratio between the Brillouin frequency shifts of longitudinal and transverse acoustic modes observed in Brillouin light scattering spectra.

Quite differently, 4-GPa/B3 glass preserves the shape of the band at 808 cm^{-1} implying no variation of boron coordination. These observations indicate that the same short-range order characterizes the networks of v-B_2O_3 and 4-GPa/B3 glass, the only modifications due to densification arising from changes of the medium-range order which give rise to the reduction of I_{808} and I_{BP} and to the frequency shift of BP. A decreasing I_{808}, in fact, is associated with a decreasing fraction of boroxol rings, as already proved by nuclear magnetic resonance (NMR) [6] and Raman [11] spectroscopy studies. Pressure quenching of boron oxide melts gives rise to the progressive reduction of the ring population, because the compacted glass is forced towards a structure having a more efficient packing of molecular units and experiencing a substantial hardening which leads to the observed increase of the BP frequency.

3.2. Elastic moduli

As discussed above, the medium- and short-range orders of B_2O_3 glasses critically depend on densification: the population of boroxol rings progressively decreases with increasing pressure of synthesis and the formation of tetra-coordinated boron atoms also results at 4 GPa under suitable thermodynamic conditions. The latter leads to an increase of the connectivity (defined as the number of bridging bonds