Journal of Non-Crystalline Solids 13 (2017) 5–13

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Raman spectra of indented pristine and irradiated sodium borosilicate glasses

Dimitrios Kilymis[a,*], Annelise Faivre[a], Thierry Michel[a], Sylvain Peuget[b], Jean-Marc Delaye[b], Julien Delrieu[b], Michel Ramonda[c], Simona Ispas[a]

[a] Laboratoire Charles Coulomb (L2C), UMR 5221 CNRS-Université de Montpellier, Place Eugène Bataillon - CC069, Montpellier Cedex 5 34095 - France
[b] CEA, DEN, DTCD, SECM, Bagnols-sur-Cèze F-30207, France
[c] DRED Services Communs de la Recherche/Centre Technologique de Montpellier, Université de Montpellier, Montpellier Cedex 5 34095, France

ARTICLE INFO

Article history:
Received 22 December 2016
Received in revised form 14 February 2017
Accepted 5 March 2017
Available online xxxx

Keywords:
Borosilicate glass
Indentation
Raman spectroscopy
Irradiation effects

ABSTRACT

In this work we have carried out variable-load indentation testing on three sodium borosilicate glasses and characterized the indentation imprints using Raman spectroscopy. The resulting analysis of the spectra helps towards the description of the relative amount of densification and shear flow appearing in each glass, as well as the different microstructural mechanisms that take place during deformation. Additionally, we show that the two glasses that are relatively poor in sodium exhibit enhanced mixing of the silicate and borate subnetworks after indentation. For the indentations performed using the highest load, we have also acquired spectra by focusing at various depths below the imprint, in order to characterize the deformed region of the glasses and estimate its size. Similar experiments have been also carried out for one of the three glasses after neutron irradiation, in order to study the effects of mechanical deformation on its depolymerized and swollen structure.

1. Introduction

The mechanical properties of alkali borosilicate glasses are an important field of research in different disciplines, such as the design of stronger glasses for optical devices or in the nuclear industry, where they are used as a confinement matrix for the immobilization of waste. In every case, a good knowledge of the microstructure and the atomic-scale mechanisms that appear under deformation of these materials is crucial in order to understand and predict their response under mechanical stress.

In sodium borosilicate glasses the glass matrix is made up of two glass formers, silicon and boron, which are interlinked by oxygen bridgings (bridging oxygens, BOs). Silicon is always tetra-coordinated in ambient conditions, while boron can exist either in a three- or tetra-coordinated state. On the other hand, sodium atoms are expected to fulfill two different roles: charge compensator or network modifier. In the former case it is situated close to a BO_4 tetrahedron in order to balance its negative charge, while in the latter case it depolymerizes the glass-former network by forming a non-bridging oxygen (NBO), which is linked to only one glass former. The structure of sodium borosilicate glasses is usually described through the Yun-Dell-Bray model [1–3] and its recent refinement by Manara et al. [4], which use the ratios $R = [Na_2O]/[B_2O_3]$ and $K = [SiO_2]/[B_2O_3]$ to describe the evolution of boron coordination and the role of the alkali atoms. For high-SiO_2 glasses, it is predicted that the initial addition of sodium will convert boron atoms from a threefold to a fourfold coordination, up to a maximal point. Further addition reverses this effect with boron atoms gradually changing their coordination back to three and the excess alkali atoms reverting to a network modifier role by depolymerizing the glass network.

Raman spectroscopy is a prominent tool for the characterization of silicate glasses, due to its simple application and the wealth of information it can deliver on the structure. Various structural properties can be probed, such as the amount of polymerization of the matrix or the mixing level between silicate and borate entities. Moreover, the presence of medium-order structures, such as rings, can be identified and its use is frequently extended to the investigation of the response of glasses under mechanical stress [5–7]. For pure silica, early experiments by Walrafen and Krishnan have indicated that the main peak of the Raman spectra shifts to higher frequencies as the glass is densified [8]. Subsequent experiments have linked the shift of the main band with the change in the average Si-O-Si angle [9,10], while recent diamond anvil cell compression

* Corresponding author at: Institut Pprime - CNRS UPR3346, Université de Poitiers - CNRS - ISAE-ENSMA, F86962 Chasseneuil Futuroscope Cedex, France.
E-mail addresses: dimitrios.kilymis@umontpellier.fr (D. Kilymis), annelise.faivre@umontpellier.fr (A. Faivre).

http://dx.doi.org/10.1016/j.jnoncrysol.2017.03.012
0022-3093/

experiments have provided a calibration curve linking the densification ratio with the integral of the main band [11]. These correlations have been used in order to probe the densified region of indented silica [12].

In the case of more complex alkali-silicate and borosilicate glasses, Raman spectroscopy has been also used to investigate the structural changes due to deformation, many times in conjunction with indentation testing [6,13-19]. In these works an upshift of the broad band around 500–600 cm^{-1}, related to the average Si-O-Si angle, is also observed for densified glasses, while changes in the amount of polymerization can be probed by analyzing the changes in the band situated between 850 and 1250 cm^{-1}. Such information can be used in order to study the interplay between the two possible deformation mechanisms under indentation, densification and shear flow, such as in the work of Zhao et al. for a series of sodosilicates, where it was shown that shear flow is favoured for glasses with a high alkali content [17]. However, further experimental results are required in order to arrive to a thorough understanding of the processes that take place during the mechanical deformation of silicate glasses.

In this work, we have performed indentation testing using variable loads on three sodium borosilicate glasses. The Raman spectra acquired at the bottom of the imprint marks have been compared to the ones of the glasses prior to indentation. Additionally, we have also acquired spectra by focusing below the imprint mark, in order to investigate the structural changes in the deformed zone. Similar experiments have also been performed for one of the glasses after neutron irradiation in order to test if the mechanism of glass deformation is affected by irradiation. To our knowledge, this is the first Raman study on indented pristine borosilicates, or neutron irradiated glasses in general, where this particular technique has been applied. The paper is organized as follows: in Section 2 we describe the sample preparation and the experimental conditions. In Section 3, we initially provide results on the hardness, as well as the AFM mapping of the smallest indentations (3.1) and proceed with the analysis of the Raman spectra acquired at the bottom of the indentations made with variable loads (3.2.1), the ones beneath the 2000 g imprints (3.2.2) and finally those for the irradiated SBN14 glass (3.2.3). We then proceed to the Discussion and Conclusions.

2. Materials and methods

2.1. Samples

Bulk samples for each one of the three non-irradiated glasses were prepared by PrimeVerre (France). The precursors, silica (SiO_2), boron oxide (B_2O_3) and sodium carbonate monohydrate (Na_2CO_3) were mixed in a platinum crucible and slowly heated in an electrical oven up to a temperature of 350° C, where they were kept for two hours. They were then slowly heated to the elaboration temperature and left for one hour before being quenched. The latter stage was repeated after the quenched glasses were crushed and the melts were afterwards transferred to a carbon crucible, where they were cooled from the glass transition temperature at a rate of 10° C/h. The homogeneity and compositions of the resulting glasses were verified by means of energy dispersive X-ray spectroscopy (SEM-EDX). Their molar content and elaboration temperatures are given in Table 1.

Table 1
Molar compositions, *K* and *R* ratios, as well as elaboration temperature of the non-irradiated glasses under study.

Name	% SiO_2	% B_2O_3	% Na_2O	K	R	T (°C)
SBN12	58.5	28.7	12.8	2.04	0.45	1250
SBN14	67.7	18.2	14.1	3.72	0.77	1250
SBN55	57.2	13.2	29.6	4.33	2.24	1150

The irradiated SBN14 sample was not issued from the same synthesis as the non-irradiated one, but has an almost identical composition (within 0.1%). It was irradiated in the OSIRIS reactor of CEA Saclay, France, at a fluence of $3.5 \times 10^{19} n/cm^2$. By using the (n, α) reaction on ^{10}B, an important glass damage was generated in order to simulate the ageing of a nuclear glass during around 100,000 years of disposal. More information about the preparation and irradiation of this sample can be found in Ref. [20].

2.2. Indentation, AFM mapping and Raman spectra of the non-irradiated glasses

The three non-irradiated glasses were indented in a Shimadzu HMV-G indenter, using a Vickers tip with variable loads of 10 g, 100 g, 500 g, 1000 g and 2000 g, and a holding time equal to 10 s. The hardness of each sample was calculated using the formula:

$$H_v = \frac{1.854P}{d^2} \quad (1)$$

where *P* is the charge in Newtons and *d* is the diagonal length of the imprint measured using an optical microscope. The hardness values presented in the Results Section were derived by averaging over five indentations for each load.

The apparatus used to obtain the atomic force microscopy (AFM) profiles was a Bruker Instruments D3100 guided by a 3A Quadrex electronic nanoscope. The images were acquired in tapping mode using a Nanosensors NCH PointProbePlus cantilever with a radius of 5–10 nm, a force constant of 50 N/m and a resonance frequency of 270 kHz. Profiles were acquired on ten indentations of 10 g for each glass, over the two directions perpendicular to the imprint sides. Measurements obtained from asymmetric or contaminated indentations were discarded, leaving at least ten profiles for each glass. These profiles were then divided into their two symmetric halves, which were subsequently averaged. Similar measurements have been attempted for higher indentation loads but cracking and inhomogeneities in the indentations do not guarantee statistically sound results. Post-processing of the profiles has been performed using Gwyddion (http://gwyddion.net) [21].

The Raman characterization of the samples was carried by focusing the beam on the surface of the glasses prior to indentation, as well as at the bottom of the imprint after the indentation. In the latter case, we chose to analyze indentations that exhibited well-formed and symmetrical cracks. The acquisition of the spectra was performed on a Renishaw Invia spectrometer in confocal mode. The 532 nm laser beam was focused on the sample via a 100x lens with a numerical aperture equal to 0.85 and delivered 20 mW of power. Spectra collected as a function of depth below the imprint mark were acquired on fresh indentations using a load of 2000 g, with the sample being mechanically displaced using a step of 1 μm. The size of the probed volume of the sample was estimated at approximately 1 μm^3. The analysis of the spectra has been performed using Fityk (http://http://fityk.nieto.pl) [22]. When comparing spectra obtained from different measurements, we subtracted a polynomial baseline with a node at approximately 200 cm^{-1}, and two more before and after the band at 850–1250 cm^{-1}. The integral of the spectra was then normalized to unity.

2.3. Indentation and Raman spectra of the irradiated SBN14 glass

The same protocol was applied on the irradiated sample, which has been analyzed in a hot-cell, in the Atalante facility of CEA Marcoule, France, since it was strongly activated by the irradiation. In this case the Raman spectrometer used was a Labram HR800 from HORIBA coupled to an optical microscope designed by Optique Peter, France, placed in the hot cell and linked through optical fibres. The