Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Bimodal distribution of Si–O–Si angles in sodo-silicate glasses

B. Hehlen[a,*], D.R. Neuville[b], D. Kilymis[a], S. Ispas[a]

[a] Université Montpellier and CNRS, Laboratoire Charles Coulomb UMR 5221, F-34095 Montpellier, France
[b] IPGP-CNRS, Géomatériaux, Sorbonne Paris Cité, 1 rue Jussieu, Paris 75005, France

ARTICLE INFO

Keywords:
Glass
Sodo-silicates
Vibrations
Raman
Structure

JEL classification:
77.80.-e
63.20.-e
78.30.-j

ABSTRACT

Polarized Raman scattering is performed in a series of sodo-silicate glasses. The Si–O–Si inter-tetrahedral angle and its distribution are extracted using a model developed previously for densified silica, and the result are compared to *ab initio* atomistic calculations. The two techniques reveal a reduction of the most probable angle of about 0.30°/mol% of Na_2O, but the shape of the angular distributions are different. The results suggest that Raman scattering enhances a specific angular distribution of Si–O–Si bridges, likely those close to sodium atoms, highlighting local angular heterogeneities.

1. Introduction

Sodo-silicate glasses have been widely investigated experimentally and numerically, so far. This interest is partly motivated by the fact that sodium is the main substitution element (with calcium) in the composition of the float glass. Furthermore, this binary system can be synthesized over a wide concentration range of alkali and constitutes a very interesting model for investigating the structural changes of the silica network due to a network-modifier oxide. When introduced in vitreous silica (v-SiO_2), sodium (Na) atoms are expected to form rather weak bonds with oxygens, leading to the depolymerization of the silica network by breaking the Si–O–Si bridges. This creates non-bridging oxygens (NBO) where the O-atoms are connected to only one Si atom and have nearby at least one Na^+ cation, in opposition to the bridging oxygens (BO) connecting two Si atoms (or two different network-formers for more complex glasses). The presence of Na and NBOs atoms produces the so-called Q_n species which are tetrahedral environments with $n = 4,3,2,1,0$ BOs. In sodo-silicates, the cations potentially form channels which serve as preferential pathway for ionic conduction [1–3]. The structural modifications with Na_2O content have been followed by X-ray and neutron diffraction [4,5], NMR [6,7], and inelastic light spectroscopies (Raman and infrared absorption) [8–11], as well as by atomistic simulations [12–18]. The Raman spectra of sodo-silicates show spectacular modifications [19,20] with sodium content, notably due to the reduction of the Si–O–Si angle, the formation of Q_n species with $n < 4$, and changes in the Si–O–Si ring distribution.

Among all the structural information that can be gained using Raman scattering in binary or more complex oxide glasses, very few investigations have focused on a *quantitative* analysis of the broad *R*-band associated to bending motions of Si–O–Si bridges. For silica glasses, the frequency of these vibrations is intimately related to the Si–O–Si angle [21–23]. The latter is accessible using neutron diffraction [24] and NMR [25,26] but a quantitative analysis using Raman would also be worthwhile since the spectra are easy to collect and it is part of the characterization tools of many laboratories and industries. This paper will therefore concentrate on the evolution of this Raman response in a series of sodo-silicate glasses. After introducing the experimental and computational details (Section 2) as well as the Raman spectra (Section 3), it will be described how to extract the angular distribution of the inter-tetrahedra Si–O–Si bridges from the Raman data, and what are the structural implications of its peculiar shape as well as its frequency shift with sodium content (Sections 4 and 5). Finally, the outcomes of this cross experimental and numerical analysis are summarized in Section 6.

2. Experimental and computational details

2.1. Experimental details

This work follows that recently reported in Ref. [20] where the depolarized Raman spectra (VH) of the same glasses were investigated. In the present case, the polarized spectra (VV) are exploited rather than

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[*] Corresponding author.
E-mail address: bernard.hehlen@umontpellier.fr (B. Hehlen).

http://dx.doi.org/10.1016/j.jnoncrysol.2017.04.009
Received 6 February 2017; Received in revised form 31 March 2017; Accepted 16 April 2017

Please cite this article as: Hehlen, b., Journal of Non-Crystalline Solids (2017), http://dx.doi.org/10.1016/j.jnoncrysol.2017.04.009

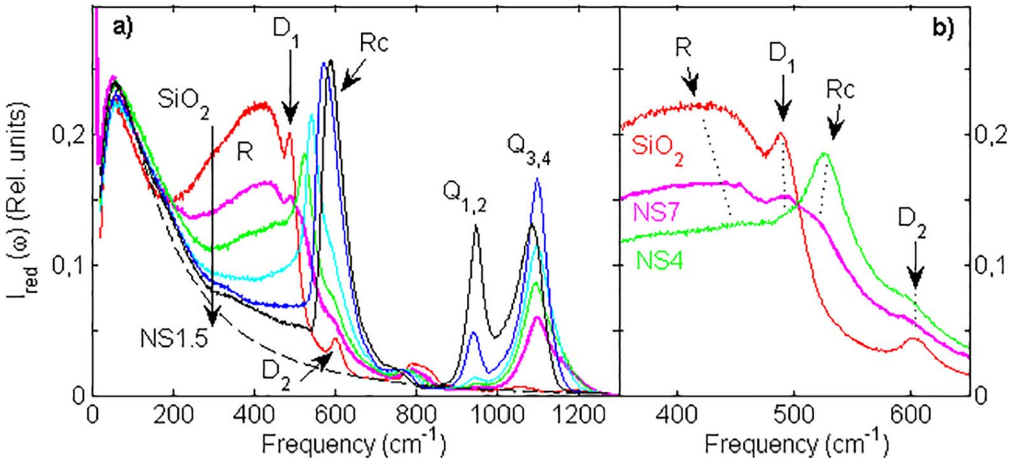

Fig. 1. Polarized (VV) reduced Raman spectra of sodo-silicate glasses in relative units. a) Full spectra for SiO_2, NS7, NS4, NS3, NS2, and NS1.5 glasses, with increasing Na content following the arrow. The dashed line is a fit of the boson peak in NS1.5 with a log-normal function. b) Detailed view of the spectra for the SiO_2, NS7 and NS4 glasses for the intermediate frequency domain, emphasizing the growth of R_c peak between D_1 and D_2.

the unpolarized ones (V + H) as often done in literature. The reason is to reduce at most the contribution of the cation band, mostly active in VH [20], and whose scattering occurs in the same frequency region as the *R*-band. Six glasses of general formula $(1-x)SiO_2 : xNa_2O$ with $x = 0,0.125,0.2,0.25,0.33,0.4$ have been investigated, and they are hereafter labeled NS*y* with $y = (1-x)/x$ (SiO_2, NS7, NS4, NS3, NS2, NS1.5). Raman data have been collected in the same conditions as in [20]. Similarly to the preceding experiments, much care has been taken to collect reliable relative intensities: the samples have been polished to get flat surfaces of the same optical quality, the optical microscope was focused at the same depth for all glasses, and the optical settings (laser power, polarization devices on the incident and scattered beam, …) were identical throughout the experimental campaign. We also checked that the Raman intensities were not changing significantly from place to place into the samples.

2.2. Computational details

We have generated structural models for two sodium silicate glasses within a combined classical and *ab initio* molecular dynamics (MD) framework which previously was successfully applied for simple silicate glasses [16,27-32]. Their molar compositions correspond to $x = 0.2$ and $x = 0.33$ in the general formula $(1-x)SiO_2$-xNa_2O, labeled hereafter NS4 and NS2, respectively, as for the experimental glasses. The size of the NS4 model is equal to 180 atoms (48 silicon atoms, 108 oxygen atoms, and 24 sodium atoms), while that of the NS2 model is equal to 144 atoms (32 silicon atoms, 80 oxygen atoms, and 32 sodium atoms). For both models, we have confined the atoms in cubic boxes of edge length equal to 13.62 Å for NS4, and 12.48 Å for NS2. These sizes correspond to the experimental mass densities of at 300 K for the two glasses, namely 2.383 g/cm^3 for NS4 and 2.48 g/cm^3 for NS2 measured with Archimede's method using toluene as the immersion liquid [33].

The classical MD simulations have performed using the same computational procedure as the one previously used to study a sodium tetrasilicate glass [27]. Within the classical approach, we have performed long equilibration runs in the liquid state at 3500 K, and then we have quenched at room temperature using a quenching rate of 10^{13} K/s. At 300 K, we have firstly performed runs in the canonical ensemble and then propagated in the microcanonical ensemble which assumes constant number of particles, constant volume, and constant energy (NVE). The length of these runs were of the order of 1 ns. The classical glass models were then used as starting configurations (*i.e.* coordinates and velocities of the atomic nuclei) for the Car-Parrinello (CP) *ab initio* simulation. Shortly after the switching on the CP dynamics, we observed for both models a temperature increase of ≈100–150 K with respect to average temperature during their classical NVE simulation. Similar behaviors were reported in studies done following the same approach for glasses like silica, sodium tetrasilicate or a calcium aluminosilicate [27,29,31].

The *ab initio* simulations were performed using the CPMD software [34]. The electronic structure was treated *via* the Kohn-Sham (KS) formulation of density functional theory [35] within the generalized gradient approximation (GGA) employing the B-LYP functional [36,37]. The KS orbitals were expanded in a plane wave basis at the Γ-point of the supercell up to an energy cutoff of 90 Ry. The choices of the pseudopotentials, exchange and correlation functionals and plane-wave cutoffs are justified by previous studies carried out on the NS4 glass [16,25,27]. Finally we note that the CP simulations were performed in the microcanonical ensemble NVE, with a time step of 4 a.u. (0.097 fs) and a fictitious electronic mass of 800 a.u. used for the integration of the equations of motion. The lengths of the CP trajectories were equal to 6 ps and 4 ps for the NS4 and NS2 glass, respectively. We have neglected the first ps of these runs and used the remaining trajectory to extract the structural data.

3. Raman spectra of sodo-silicates

For a population of mode σ, the imaginary part of the electric susceptibility $\chi''_\sigma(\omega)$, the Raman intensity $I_\sigma^{RS}(\omega)$ (Stokes side), and the density of vibrational states (VDOS) $g_\sigma(\omega)$, are related as follows [38,39]

$$\chi''_\sigma(\omega) = \frac{1}{\omega_s^3}\frac{I_\sigma^{RS}(\omega)}{n(\omega)+1} \propto C_\sigma(\omega)\frac{g_\sigma(\omega)}{\omega}, \qquad (1)$$

where ω_s is the frequency of the scattered light, $n(\omega)$ the Bose factor. $C_\sigma(\omega)$ is the coupling-to-light coefficient of the vibrations of type σ and relates to its scattering cross-section. It is the quantity which in glasses replaces the particular square product of the polarizability tensor $\overline{\overline{\alpha}}_\sigma$ in the calculation of the Raman scattering efficiency of the modes of symmetry σ in crystals and liquids [39].

The polarized (VV) Raman spectra of our series of sodosilicate glasses are shown in Fig. 1a. To anticipate the discussion below, we have plotted the reduced intensities, *i.e.*

$$I_{red} = \chi''(\omega)/\omega. \qquad (2)$$

At low frequency, below 200 cm^{-1} one observes the boson peak whose spectral shape and maximum frequency show a very small change over the full concentration range, in contrast with all other spectral responses.

At intermediate frequencies, between 250 and 700 cm^{-1}, the oxygen bending vibrations dominate the Raman signal. The broad *R*-