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Analysis of molecular oxygen formation in irradiated glasses: a Raman depth profile study

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Abstract

Depth profiles experiments have been performed by Raman spectroscopy on three alkali (Na, Li, K) borosilicate glasses irradiated with 1.8 MeV electrons at 1 and 3 GGy. These experiments show that molecular oxygen produced under β irradiation is concentrated near the glass surface according to a depth depending on the irradiation dose. Moreover, we observed that the polymerisation increase is the same in the entire volume sample. The average Si–O–Si angle decrease under irradiation is also homogeneous in the whole irradiated glass volume. From all results, we demonstrate that oxygen migrates up to the glass surface during irradiation without strong interaction with the glass network. Migration of oxygen and probably alkalis takes place through percolation channels with a possible departure of oxygen in some cases.

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1. Introduction

Numerous studies have been conducted on irradiation effects on glasses especially in links with high-level nuclear waste glasses. Under alpha, beta and gamma radiations, macroscopic changes occur like positive or negative volume changes; mechanical properties such as hardness and fracture toughness are also affected [1,2]. Concerning microscopic changes, two damages have been observed under the electronic beam of a transmission electron microscope (TEM): formation of gas bubbles [3,4] and phase separation [4,5]. Under sufficient irradiation dose (1 GGy) obtained with high energy electrons, Boizot et al. [6] demonstrated, on borosilicate glasses, that most of the structural modifications (polymerization increase and molecular oxygen formation) were associated with alkali migration. However, our recent studies extended to other glass compositions reveal that molecular oxygen is not systematically detectable in irradiated borosilicate glass samples [7], implying complex mechanisms. It has to be mentioned that the detailed mechanisms of molecular oxygen formation are still discussed in irradiated silica, despite the important number of studies [8–11]. In general, spectroscopic methods used for characterizing the glass structure

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(NMR, EXAFS, or luminescence) probe the glass volume. On the other hand, methods allowing to establish profiles like SIMS or RBS give mainly informations on the glass composition. To our knowledge, we did not find in the literature studies analyzing multicomponent irradiated glasses structure in depth. Only results on defects production by VUV absorption and EPR studies have been reported on 10 MeV protons implanted wet SiO_2 glass by Hosono et al. [8]. These authors showed that Si–Si bonds concentration as well as E' centers and PORs (peroxy radicals) concentration follows the energy loss profile into the sample depth.

The purpose of the present work is to better understand the formation of molecular oxygen in multicomponent irradiated glasses (Na, K and Li borosilicate glasses) by performing Raman experiments at different depths. We proceed either by polishing progressively the irradiated glass or by analyzing the sample edge. These methods allow us to probe the irradiated glass from the surface to 300 μm in depth (glass thickness is about 500 μm).

2. Experimental

Three aluminoborosilicate glasses were synthesized, each one containing a different alkali ion: Na, Li and K. All glasses were prepared by mixing stoichiometric amounts of SiO_2, H_3BO_3, Al_2O_3, ZrO_2 (Na_2CO_3 or K_2CO_3 or Li_2CO_3). For Na and K glasses, the dried mixed powders were first heated at 750 °C in a Pt crucible during 10 h for decarbonation. Then, it was melted at 1500 °C for 1 h and quenched in air. The glass was annealed at 500 °C during 1 h to evacuate strains. For the Li glass, powders were melted at 1400 °C in a Pt crucible and annealed at 520 °C in a graphite crucible during 1 h. Each glass was analyzed by X-ray diffraction which confirms the amorphous character of glass. Nominal glasses compositions are displayed in Table 1 in oxide weight percentage.

All glasses were irradiated with 1.8 MeV electrons provided by a Van de Graaff accelerator. 1×10^9 and 3×10^9 Gy irradiation doses were reached with a 20 μA beam, the sample temperature was maintained at 30 °C. Glasses were cut in squares of 0.5 mm side, the thickness is less than 600 μm, which allows a homogeneous irradiation in the glass volume.

Table 1
Nominal glasses composition given in weight percent

	Na	K	Li
SiO_2	59.13	55.44	63.34
Al_2O_3	6.38	5.98	6.83
B_2O_3	18.24	17.10	19.54
Na_2O	12.82		
ZrO_2	3.43	3.22	3.67
K_2O		18.26	
Li_2O			6.62

Raman spectra were recorded on a Labram HR micro-spectrometer using the 514.5 nm line of an Ar^+ laser. Experiments were carried out through a ×100 Olympus objective with a laser power of 20 mW on the sample. Spatial resolution obtained with the confocal configuration is about 10 μm^3. Between each Raman analysis, the glass was polished mechanically in order to remove a thin layer, the sample thickness was measured with a precision of 1 μm.

3. Results

3.1. Molecular oxygen

Fig. 1 presents a comparison between the pristine Li glass and the β-irradiated glass at 3 GGy (polished and unpolished) Raman spectra. It shows that an intense and narrow peak appears at about 1550 cm^{-1} on the spectrum of irradiated Li glass surface. This peak corresponds to the stretching vibration mode of the O–O bond in molecular oxygen O_2 [12]. Molecular oxygen was detected on both the front and rear surfaces of the irradiated glass. On one face, the O_2 signature disappears after a slight polish removing of 4 μm (see Fig. 1). On the other face, dissolved molecular oxygen is detected up to 40 μm of depth (see Fig. 2). The O_2 concentration is however lower in depth than in surface. This result implies that molecular oxygen is mainly localized on the first microns of the irradiated glass surfaces; the O_2 thickness layer being not identical on both faces.

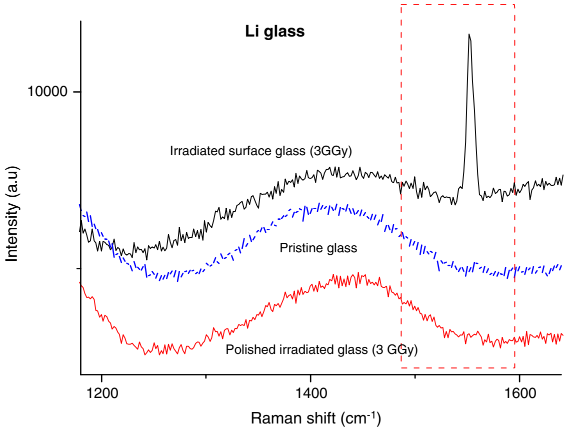

Fig. 1. Raman spectra in the 1200–1600 cm^{-1} range of the pristine Li glass, the irradiated surface glass (3 GGy) and the irradiated polished glass (removing 4 μm s).

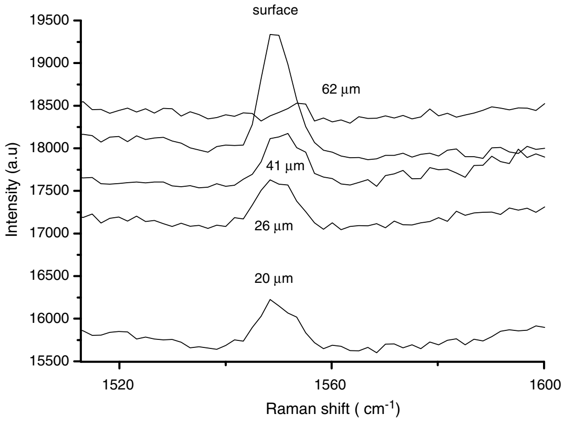

Fig. 2. Raman spectra in the 1520–1600 cm^{-1} range of the Li irradiated glass at 3 GGy. Measurements are made on the glass surface and at different depths (20, 26, 41 and 62 µm s).

The O_2 peak is also observed for the lower 1 GGy irradiation dose with a weaker intensity (not shown).

The Na glass irradiated at 3 and 1 GGy displays a 1550 cm^{-1} Raman peak weaker than in the Li glass. As a consequence, the molecular oxygen thickness layer is lower (less than 15 µm for 3 GGy).

Concerning the K glass, no molecular oxygen was detected either at the glass surface or in the volume whatever the irradiation dose.

3.2. *Q^n species*

Fig. 3 shows the Raman spectra of the Na glass irradiated at 1 and 3×10^9 Gy in the 900–1200 cm^{-1} range. Concerning the 3 GGy dose, several points have been recorded, one on the irradiated glass surface and 6 all along the 500 µm glass edge.

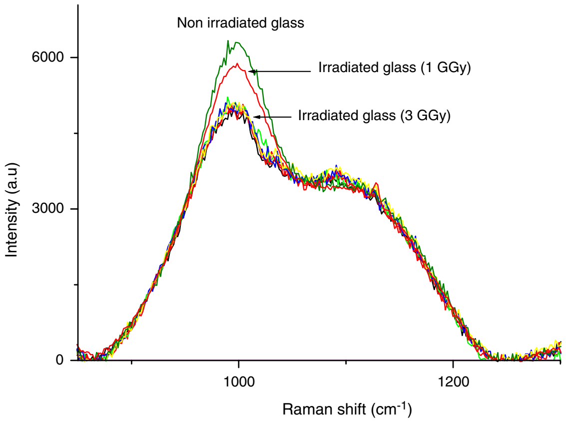

Fig. 3. Raman spectra in the Q^n species region (850–1250 cm^{-1}) comparing the pristine Na glass with the irradiated glass at 1 GGy (surface) and several points recorded along the 3 GGy irradiated glass edge.

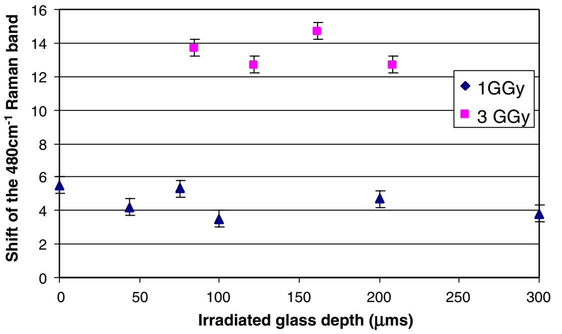

Fig. 4. Shift of the 480 cm^{-1} Raman band between the pristine Na glass and irradiated sample as a function of the irradiated glass depth (µm s) calculated at 1 GGy (triangle symbols) and 3 GGy (square symbols).

This 900–1200 cm^{-1} region corresponds to the Q^n species (i.e. SiO_4 tetrahedra with *n* bridging oxygen) vibration modes and more precisely Q^2 and Q^3 bands can be found in Fig. 2 at respectively 980 cm^{-1} and 1100 cm^{-1} [13]. Raman spectra have been normalized on the Q^3 band for an easier comparison of the Q^2/Q^3 ratio. This result can be interpreted as a polymerization increase linked to the Na migration under irradiation [14,15]. First, the polymerization increase appears to be sensitive to the irradiation dose implying a much more efficient alkaline migration for a higher dose. Secondly, we can notice that the Q^2/Q^3 ratio is the same whatever the probed depth, indicating a homogeneous polymerization increase in the irradiated glass volume.

3.3. *Si–O–Si angle*

The borosilicate glass Raman band peaking at 480 cm^{-1} corresponds to the bending vibration mode of the Si–O–Si bond. A shift towards the much higher frequency operates under irradiation, indicates an average Si–O–Si angle decrease with irradiation [14]. We can observe in Fig. 4 that the average variation angle is much higher for 3 GGy than for 1 GGy dose. Moreover, the shift can be considered as constant on the whole irradiated glass volume.

4. Discussion

The formation of dissolved molecular oxygen under β irradiation in a Na borosilicate glass was already observed by Raman spectroscopy by Boizot et al. [14]. According to the authors, molecular oxygen is formed from the alkali migration which leads to a glass polymerization increase as well as the conversion of BO_4 into BO_3 species [6]. Recent results obtained on Mixed Alkali composition [7,15] show that molecular oxygen production in irradiated glasses is due to two different processes. The first one is correlated to alkaline migration in a network modifier and in charge compensator of boron positions. The second process is correlated to defect conversion like the peroxy radical from EPR measurements [10,11]. In simple silica glasses, Skuja and Guttler [9] succeed in measuring the concentration of O_2 using the infrared luminescence band at 1272 nm corresponding to a forbidden transition. This technique is much more sensitive than Raman spectroscopy and a molecular oxygen content down to $10^{-15}/cm^3$ can be detected. Molecular oxygen production in that case is only due to the destruction of peroxy bridges. Raman experiments performed in β-irradiated silica glasses (5×10^9 Gy) clearly shows the lack of molecular oxygen dissolved [16]. We can therefore conclude that the molecular oxygen in multicomponent glasses detected by Raman spectroscopy is correlated only to alkaline migration under irradiation.

Results obtained on the successive polished glasses as well as along the edge clearly demonstrate that molecular oxygen is mainly localized on the first 50 μm s under the glass surface, the O_2 layer thickness depending on the irradiation dose and on the glass composition. A higher oxygen content is observed in Li glass which is consistent with the higher cationic mobility of Li compared to Na [7]. However, this result cannot be explained by a preferential alkali migration from the surface to the glass bulk. As a matter of fact, we show that the polymerization increase takes place in the whole irradiated glass volume. Alkali migration is thus suspected to occur in the whole glass volume, indeed, the high energy of electrons allow them to cross over the sample without considerable loss energy and almost no surface effects are expected (there is no major electric field caused by charges implantation). Such a result can be interpreted as follows: the oxygen migrates to the surface without any possibility to recombine with Q^n species because no lower glass polymerization is observed close to the sample surface. The oxygen motion is probably associated to those of alkaline ion, we thus suggest that oxygen could migrate through the same percolation channels as alkalis. As it was previously pointed out, molecular oxygen is not detected for all compositions, one surprising case corresponds to the K borosilicate irradiated glass not showing any 1550 cm^{-1} Raman peak whereas a polymerization increase was attested by Raman spectroscopy [7,15] as well as a boron conversion from ^{11}B MAS NMR measurements [15]. Some channels have been clearly observed on etched cross section of potassium irradiated glasses with scanning electronic microscope by Jurek et al. [17,18]. The departure of oxygen could be explained from a big size percolation channel not allowing the trapping of molecular oxygen near the glass surface.

The measured shift of the 480 cm^{-1} Raman band on the irradiated glass surface is the same than in successive analysis points in depth (see Fig. 4) at 1 and 3 GGy. This result indicates that Si–O–Si average angle decrease occurs in the whole glass volume. Average angle behavior is consistent with a network densification process that appears under irradiation, often associated in silicate glasses with an increase of the low-size rings (three or four membered SiO_4 rings) [7,14,16]. The bulk behaviour is consistent with the scheme that has been proposed above, i.e. the migration of oxygen and alkalis operating through percolation channels are independent from the network densification.

5. Conclusion

This non-usual Raman study allows analyzing the structure of β-irradiated glasses in depth. This type of measurement was particularly instructive and reveals that molecular oxygen is concentrated into the first microns of the irradiated glass less than 10 μm s for 1 GGy and 50 μm s for 3 GGy in the case of Li glass. As the polymerization increase and the average Si–O–Si decrease were revealed as homogeneous in the irradiated glass volume, we concluded to an oxygen and alkalis migration independent from the network changes, operating through percolation channels. For high channels size (K case), the oxygen near the glass surface leads to a possible oxygen departure.

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