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Comparison of radiation and quenching rate effects on the structure of a sodium borosilicate glass

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ABSTRACT

The effects of quenching rate and irradiation on the structure of a sodium borosilicate glass were compared using ^{29}Si, ^{11}B, and ^{23}Na nuclear magnetic resonance and Raman spectroscopy. Quenching rate ranging from 0.1 to 3×10^4 K min^{-1} was studied. Various irradiation conditions were performed, i.e. gold-ion irradiation in a multi-energy mode (from 1 to 6.75 MeV), and Kr and Xe ion irradiations with energy of 74 and 92 MeV, respectively. In pile irradiation with thermal neutron flux was performed as well, to study the effect of alpha radiation from the nuclear reaction $^{10}B(n,\alpha)^7Li$.

Both irradiation and high quenching rate induce similar local order modification of the glass structure, mainly a decrease of the mean boron coordination and an increase of Q^3 units. Nevertheless, the variations observed under irradiation are more pronounced than the ones induced by the quenching rate. Moreover, some important modifications of the glass medium range order, i.e. the emergence of the D2 band associated to three members silica rings and a modification of the Si–O–Si angle distribution were only noticed after irradiation. These results suggest that the irradiated structure is certainly not exactly the one obtained by a rapidly quenched equilibrated melt, but rather a more disordered structure that was weakly relaxed during the very rapid quenching phase following the energy deposition step.

Raman spectroscopy showed a similar irradiated structure whereas the glass evolutions were controlled by the electronic energy loss in the ion track formation regime for Kr-ion irradiation or by the nuclear energy loss for Au and OSIRIS irradiation. The similar irradiated structure despite different irradiation routes, suggests that the final structural state of this sodium borosilicate glass is mainly controlled by the glass reconstruction after the energy deposition step.

1. Introduction

The ultimate waste forms produced by the French nuclear industry are immobilized in a borosilicate glass matrix. The effects on the glass behavior of radiation arising from the immobilized radioactive elements must be assessed to ensure the containment performance of this type of glass over time. After a few centuries of storage, the largest part of the residual radioactivity will be due to the α decaying actinides [1]. Therefore, it is important to investigate the consequences of the accumulation of α-radiation damage on the glass structure.

Several studies have been performed to better understand the effects of α radiation build-up on different macroscopic properties of French nuclear glass, see e.g. [2–4]. Recent works investigated the structural evolution of borosilicate glasses induced by irradiation, analyzing data obtained from external irradiated samples [5] and molecular dynamics simulations [6,7]. According to these studies, the nuclear interactions of the recoil nuclei of the α decay events, induce some reorganization of the borosilicate network, namely: a decrease of the mean boron coordination, a slight decrease of the glass polymerization and an increase of the global glass disorder (broadening of ring size distributions [6]). Recently an increase of the fictive temperature of the nuclear glass was observed with the accumulation of alpha decay damage [4]. These structural and macroscopic evolutions suggest that the modification induced by alpha decay irradiation on the glass structure is similar to the one induced by a very fast quenching of a molten glass.

This phenomenological description suggests the formation of ion tracks in the thermal spike model [8] during irradiation by swift heavy ions (SHI). In this model, the passage of a swift heavy ion produces a localized high energy deposit by electronic interaction, resulting in local melting along the ion track followed by very rapid thermal quenching. Mendoza recently observed some evolutions of borosilicate glass structure under SHI irradiation that are very similar to the ones induced by a very fast quenching rate of a molten glass [9].

Toulemonde [10] developed a unified thermal spike (u-TS) model to explain the structural evolution observed by IR spectroscopy in

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Table 1
CJ1 glass composition.

	SiO_2	Na_2O	B_2O_3
Oxide molar percentage	67.73	14.23	18.04

silica glass irradiated with Au ions in the intermediary regime, where both electronic and nuclear stopping powers are significant. This u-TS model suggests that the modification of the silica structure is linked to the total amount of energy deposition, and that an additive synergetic effect exists between electronic and nuclear interactions. In this respect Mendoza recently observed some similar modifications of the Raman spectra of a borosilicate glass submitted to three different irradiation conditions, i.e. alpha decay damage, Au-ion irradiation in the intermediary regime and SHI irradiation [11], which suggest that the structure of the irradiated borosilicate glass is not controlled by the energy deposition step but could be linked to the "thermal history" of the glass following the energy deposition step.

In this paper we compare the effects of different quenching rates and of various irradiation conditions on the structure of a sodium borosilicate glass by using Raman and Nuclear Magnetic Resonance (NMR) spectroscopies. Quenching rates ranging from 0.1 to 3×10^4 K min^{-1} were studied. Various irradiation conditions were used, i.e. gold-ion irradiation in a multi-energy mode (from 1 to 6.75 MeV), in pile irradiation with thermal neutron flux to try to simulate the effects induced by alpha decays, and SHI irradiation by Kr or Xe ions with energy of 74 and 92 MeV, respectively, to create ion tracks in the glass.

2. Materials

Table 1 lists the composition of the borosilicate glass used in this work, here called CJ1. It corresponds to the simplest glass model of the French nuclear glass.

The reference sample was prepared by melting a mixture of SiO_2, H_3BO_3 and Na_2CO_3 in a platinum–rhodium crucible at 1763 K for 3 h. The glass was then poured into a graphite crucible and annealed in a furnace for 1 h at 863 K. The furnace was switched off after annealing, and the glass was cooled slowly to room temperature. The glass homogeneity has been determined by Rayleigh–Brillouin light scattering in a previous paper [12]. No crystallization or phase separation exceeding about 50 Å was observed; the glass was considered therefore homogeneous at this scale.

In order to study the effects of different thermal treatments on the borosilicate structure, glasses were prepared following various procedures, described in the following sections.

Two reference samples were melted and then cooled at two different rates, 0.1 and 1 K min^{-1}, in a high temperature furnace heated by tubular SiC heating elements. The samples were placed in a platinum crucible. At the bottom of the crucible was mounted a thermocouple, allowing a continuous measurement of the temperature. A third sample was melt in a tubular furnace and then fast quenched by dropping the melt on a copper bulk cooled with liquid nitrogen. The quenching rate of this sample was calculated in a previous work [4] to be 1000 K min^{-1}.

The components of the borosilicate glass listed in Section 2.1 were mixed in a platinum crucible and heated up to 1763 K for 2 h. The temperature was then decreased to 1473 K. Part of the melt was then collected by dipping a platinum stick ending with a ring (like a bubble wand used for making soap bubbles) and quickly withdrawing it. The obtained very thin film of the melt was then rapidly blown with compressed air gun. The obtained glass lamella was collected at the end of a cylinder placed in front of the gun. This technique allows obtaining glass with a cooling rate of about 3×10^4 K min^{-1}[13].

In order to study the effects of electronic and nuclear stopping powers on the glass, some reference samples were irradiated with various irradiation conditions.

Four reference samples, called CJ1 OSIRIS, were irradiated into the research nuclear reactor of the CEA Nuclear Energy Division located in the Research Centre of Saclay. In particular, the ^{10}B present in the glass has a high cross-section for thermal neutron capture (about 3837 barn), therefore, when the borosilicate glass is irradiated with thermal neutron, the ^{10}B gives rise to the nuclear reaction $^{10}B(n, \alpha)^7Li$, that produces highly energetic α particles and recoiling ^7Li ions with an energy of 1.47 and 0.84 MeV, respectively. A specific aluminium sample holder was used to ensure important cooling of the glass sample in the pool of the reactor. Metallic temperature controllers were placed near the glass sample that proved that the glass temperature was maintained below70 °C during the irradiation.

The number of nuclear reactions is a direct function of the neutron fluence. Table 2 lists the external neutron irradiation conditions with corresponding number of reactions, nuclear and electronic stopping power, deposited nuclear and electronic energies and displacements per atom (dpa) calculated with the SRIM 2008 code [14].

Two reference samples, called CJ1-Au, were polished and irradiated with Au ions at the ARAMIS accelerator at IN2P3/CSNSM (Orsay, France). The samples were irradiated at room temperature with multi-energy Au ions with energy ranging from 1 to 7 MeV. The glass temperature in the irradiated zone should not overpass 100 °C. The ion energy is dispersed mainly by electronic interaction (75%) and the rest in the form of nuclear interaction. Table 3 lists the external irradiation conditions with corresponding fluence, nuclear and electronic stopping power, deposited nuclear and electronic energies and displacements per atom (dpa) calculated with the SRIM 2008 code [14]. The depth of damaged area was calculated to be about 1.8 μm, allowing confocal Raman microspectrometry characterization of the irradiated zone [5].

Swift Heavy Ion (SHI) irradiations were carried out at room temperature at the IRRSUD line of the GANIL facility located at the CIMAP laboratory (Caen, France). A polished massive reference sample, called CJ1-Kr, was irradiated with high energy Kr 74 (see Table 3) to study the damage induced by very high electronic stopping power on CJ1 glass. The ion fluence was 3×10^{13} ions cm^{-2}. Moreover another reference sample was crushed into powder and grain sizes smaller than 8 μm were selected for irradiation by settling. The granulometry of the obtained powder was estimated by laser diffraction measurement to

Table 2
In pile irradiation conditions for the CJ1 OSIRIS samples.

Irradiation fluence	D1	D2	D3	D4
E (MeV)		He (1.47) + Li (0.84)		
Fluence (neutron cm^{-2})	5.9×10^{18}	1.2×10^{19}	3.5×10^{19}	5.2×10^{19}
Number of events (ion cm^{-3})	3.5×10^{19}	7.0×10^{19}	2.1×10^{20}	3.1×10^{20}
dE/dx_{nucl} (keV nm^{-1})		dE/dx(He) < 0.03 dE/dx(Li) < 0.06		
dE/dx_{elec} (keV nm^{-1})		dE/dx(He) < 0.33 dE/dx(Li) < 0.56		
E_{nucl} (keV cm^{-3})	9.8×10^{20}	2.0×10^{21}	5.9×10^{21}	8.7×10^{21}
E_{elec} (keV cm^{-3})	7.9×10^{22}	1.6×10^{23}	4.7×10^{23}	7.0×10^{23}
dpa	0.27	0.54	1.6	2.38