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Effect of chemical composition on borosilicate glass behavior under irradiation

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ABSTRACT

Assessing the behavior under irradiation of oxide glasses used for nuclear waste immobilization is essential for qualifying the long-term behavior of the wasteform. This study focuses on a series of borosilicate glasses of increasing chemical complexity. The effects of irradiation in these materials were investigated through multi-energy external irradiation by gold ions to obtain a constant nuclear damage level to a depth of about 2 μm. The macroscopic behavior of the glass was estimated from Vickers hardness measurement. The mechanical properties of all the borosilicate glasses studied were observed to improve, their hardness decreasing with the dose down by 30–35%. This evolution is also associated to an increase of the fracture toughness of the glass under irradiation. Analysis of the structural changes in the sodium borosilicate glass common to all the compositions studied with respect to dose revealed a progressive shift to higher wavenumbers in the vibration Raman band near 495 cm^{-1} indicating a drop in the mean Si–O–Si angle. At the same time, modifications in the Q_n band between 850 and 1200 cm^{-1} are observed and characterize increasing depolymerization of the silicate network.

1. Introduction

The ultimate wasteforms 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 estimated to ensure the containment performance of this type of glass over time. Numerous published studies carried out to assess the impact of radiation arising from beta and alpha decay [1–3] has revealed variations in the macroscopic properties due to the accumulation of alpha decay within the glass matrix. Depending on their chemical composition, nuclear glasses may be subject to volume expansion or densification; variations are also observed in their mechanical properties for alpha decay doses up to about 2×10^{18} α/g, followed by a stabilization state that has been many time demonstrated up to 6×10^{18} α/g. Although recent studies suggest that nuclear interactions with alpha decay recoil nuclei are most likely responsible for these changes in the behavior of R7T7-type French nuclear glass [4,5], the structural origin of these modifications and their stabilization have not been clearly established. The chemical complexity of these systems (almost 30 oxides [6]) and the radioactivity of the principal materials used to investigate the effect of alpha decay (actinide-doped glass specimens) make it difficult to carry out and interpret structural studies.

We examined a glass system with simplified chemical compositions to understand the irradiation impact on the mechanical behavior and structure of this type of glass. All the glass compositions were based on silicon, boron and sodium oxides, the three major component of the non-active R7T7-type glass [6,7]. The increasing complexity of the studied glass series was obtained by adding other oxides to approach the composition of the industrial containment glass. Damage caused by the accumulation of alpha disintegrations was simulated using external irradiation by heavy ions. This approach was found to be highly representative of the effects arising from alpha decay on the hardness of R7T7-type glass [5] and also allowing easier samples comparison to the real radioactive materials.

2. Materials

The purpose of this study was to assess the influence of the major chemical elements of R7T7-type glass on its behavior under irradiation. We therefore examined a family of simplified glasses [8]. Defining a simplified glass structurally related to R7T7-type glass implies that it must include silicon, boron and sodium oxides, the three main components of the industrial containment glass. The glass complexity is then progressively increased by incorporating the other oxides (Al_2O_3, CaO, ZrO_2, etc.) while maintaining the same molar ratios among the main oxides as in R7T7-type glass.

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Table 1
Theoretical CJ glass chemical compositions (oxide mol%).

	SiO_2	Na_2O	B_2O_3	Al_2O_3	CaO	ZrO_2	Ce_2O_3	Li_2O
CJ1	67.73	14.23	18.04					
CJ2	64.93	13.64	17.30	4.13				
CJ3	61.16	12.85	16.29	3.89	5.81			
CJ4	60.12	12.63	16.01	3.82	5.71	1.71		
CJ5	59.99	12.60	15.97	3.81	5.69	1.71	0.23	
CJ6	56.61	11.89	15.07	3.60	5.37	1.61	0.90	4.95
CJ7	63.77	13.39	16.98	4.05		1.81		
CJ8	63.65	13.36	16.95		6.04			
CJ9	62.51	13.13	16.65	5.93	1.78			

For the CJ6 glass, whose composition is the closest to the industrial glass, all the rare earth elements (La, Ce, Pr, and Nd) were simulated by cerium. The theoretical chemical compositions of the test glasses are shown in Table 1.

3. Fabrication conditions

The glass samples for this study were prepared in a platinum crucible by melting a mixture of oxides and carbonates at different temperatures depending on the chemical composition to ensure pourability. The samples were refined for three hours at the process temperature and then poured into preheated graphite molds and annealed at suitable temperatures ($T_g + 20$ °C) to relieve the stresses accumulated during cooling after pouring. The fabrication conditions are indicated in Table 2.

Table 2
CJ glass fabrication conditions.

	Preparation temperature (°C)	Refining time (h)	Annealing temperature (°C)	Annealing time (h)
CJ1	1500	3	590	1
CJ2	1450	3	530	1
CJ3	1400	3	530	1
CJ4	1400	3	530	1
CJ5	1400	3	530	1
CJ6	1450	3	530	1
CJ7	1400	3	530	1
CJ8	1400	3	530	1
CJ9	1350	3	570	1

Table 3
Conditions of glass irradiation by Au ions.

	Dose (ions cm^{-2})	E (MeV)	E_{nucl} (keV cm^{-3})	E_{elec} (keV cm^{-3})
F1	1.9×10^{11}	1	1.6×10^{19}	5.5×10^{19}
	5.8×10^{11}	3.5		
	1.4×10^{12}	7		
F2	6.1×10^{11}	1	5.0×10^{19}	1.7×10^{20}
	1.8×10^{12}	3.5		
	4.2×10^{12}	7		
F3	1.1×10^{12}	1	9.0×10^{19}	3.1×10^{20}
	3.3×10^{12}	3.5		
	7.6×10^{12}	7		
F4	2.4×10^{12}	1	2.0×10^{20}	6.8×10^{20}
	7.3×10^{12}	3.5		
	1.7×10^{13}	7		
F5	6.1×10^{12}	1	5.0×10^{20}	1.7×10^{21}
	1.8×10^{13}	3.5		
	4.2×10^{13}	7		
F6	4.6×10^{13}	1	3.8×10^{21}	1.3×10^{22}
	1.4×10^{14}	3.5		
	3.2×10^{14}	7		

4. Irradiation conditions

The glass specimens were polished and subjected to multi-energy gold ion bombardment at the ARAMIS accelerator at IN2P3/CSNSM[1] (Orsay, France). The ion energies and fluence ratios were defined to obtain a constant deposited nuclear energy over an irradiation depth of about 2 μm allowing Vickers micro-indentation and confocal Raman microspectrometry characterization of the irradiated zones.

The initial ion bombardment energy was dispersed by electronic interaction (75%) and the remainder in the form of nuclear interaction. The nuclear and electronic energy loss profiles, due to Au ions with energies of 1, 3.5 and 7 MeV, have been determined with SRIM-2003 software [9] in a previous work [5]; the fluence values are shown in Table 3. Contrary to nuclear damage, the electronic energy losses varied with depth; the surface was damaged to a greater degree by incidents ions interactions. The irradiation fluence was selected in each case to simulate deposited nuclear energies representative of those resulting from alpha decay doses between 8×10^{16} and 1.9×10^{19} α/g [5].

5. Characterization methods

5.1. Micro-indentation

The glass hardness was measured in air by Vickers micro-indentation (pyramidal indent) on polished specimens, with indenter loads ranging from 5 to 500 g maintained for 20 s (Fig. 1). The Vickers hardness was determined from the length of the indentation diagonals according to Eq. (1).

$$H_V = \frac{2F \sin\left(\frac{136}{2}\right)}{d^2} \quad (1)$$

where H_V is the Vickers hardness, F the applied force, and d the mean length of the indentation diagonal. For each characterization, the hardness was determined from the mean value of 10 indentations, hence the errors on the measured values correspond to the standard deviation and is of 2%.

5.2. Raman spectroscopy

Unpolarized Raman spectra were recorded at room temperature using a Labram Raman microspectrometer from Jobin–Yvon with an excitation wavelength of 532 nm from a 200 mW COHERENT DPSS 532 laser (supplying 70 mW to the sample). The laser beam hits the sample at a perpendicular angle with respect to the irradiated surface. The experiments were carried out with a confocal ×100 objective. The Raman signal is collected through the same objective and sent in direction of the CCD without the reflected laser beam which is stopped by edge filters. Each Raman spectrum was obtained with a total acquisition time of 900 s (60 s per spectrum and 15 successive acquisitions to reduce spurious noise) and a 1800 grooves per mm grating. Slit and confocal hole were both settled to 200 μm. The resolution of the system is less than 1 cm^{-1}. This technique not only illuminates a spot on the sample but also spatially filters the signal received from the sample, making it particularly suitable for examining multilayer materials – in particular the irradiated glass samples used in this study, as the irradiated layer is no more than 2 μm deep. The suitability of the Raman characterization conditions was confirmed by acquiring Ra-

[1] ARAMIS: Accélérateur pour la Recherche en Astrophysique, Microanalyse et Implantation dans les Solides. IN2P3: Institute National de Physique Nucléaire et de Physique des Particules. CSNSM: Center de Spectroscopie Nucléaire et Spectroscopie de Masse.