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Mechanical and nuclear properties of soda-lime glasses containing boron and niobia

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1. Introduction

The soda-lime silicates are certainly the most important technological type of oxide glasses with various applications such as flat window glasses, packaging bottles and vessels, and electric devices like light bulbs. [1] Some of their remarking properties include good resistance to crystallization, appropriate viscosity for glass melting and fiberglass extruding, and good compositional control of thermal expansion and refractive index [2]. Glasses belong to the class of ceramic materials and, therefore, present brittle fracture. Their mechanical behavior do not only depend on intrinsic features, as the bonding energy among its atoms and defects, but specially on extrinsic features such as the material surface, the chemical composition of the test medium, the method that is employed and also the glass thermal history[3]. However, other properties such as hardness and fracture toughness are function of the bonding energy, packing density of atoms and defects, and the Young's Modulus is characteristic of each type of material[4].

One of the most challenging uses of soda-lime borosilicate glasses is in the nuclear engineering. They are recognized for their chemical durability against leaching conditions and thermal shock resistance[5]. The structural adaptation of these glasses provide the incorporation of a wide range of long-lived radionuclides (RN) belonging to all groups of the periodic table such as ^{79}Se, ^{36}Cl ^{59}Ni, ^{93}Zr, ^{135}Cs, ^{107}Pd, ^{94}Nb, ^{41}Ca, ^{238}U, ^{93}Mo, ^{239}Pu, ^{241}Am, ^{126}Sn, ^{129}I and ^{237}Np [6]. However, there are still many difficulties concerning the vitrification of HLW. An example is the crystallization of Nepheline ($NaAlSiO_4$) during the pouring of the nuclear waste glasses into stainless steel canisters, as a result of the high concentrations of sodium, nitrates and alumina, especially from the claddings in contact with the glass-forming SiO_2 from the melt [7]. This crystallization reduces drastically the chemical durability of these glasses and therefore, the risks of radionuclide leaching and consequent contamination of the surrounding environment of the nuclear repositories are maximized[8]. There are also problems related to the self-irradiation structural damages, which result in ultra-fast quenching of the damaged sites and consequently impact the chemical durability of the wasteforms[9]. Many are the efforts towards avoiding or minimizing the defects in alumino-borosilicate glasses used for HLW immobilization.

The addition of niobia (Nb_2O_5) to silicate glasses is an interesting task, because the oxide exhibits low cross-section for the capture of thermal neutrons (1,15 barn or $1{,}15 \times 10^{-24}$ cm^2), and the radioactive decay of ^{94}Nb to stable ^{94}Mo presents a half-life time ($t_{1/2}$) of 20.000 years. The niobia integrates the silicate network by connecting itself to the oxygen atoms that have a residual negative charge (NBO, non-bridging oxygen). Therefore, mechanical and nuclear properties of the glasses are expected to change with the niobia additions.

2. Methodology

The glasses belong to the system: xNb_2O_5-(100-x)SiO_2-Na_2O-CaO-B_2O_3-Al_2O_3, for which niobia was added substituting silica (SiO_2)[10]. The Nb_2O_5 contents (mol%) were 2-6%, named Gx (x = mol%) as G0 (reference glass), G2, G4 and G6. A flowchart of the glass production is shown in Figure 1. The powders are individually weighed, mixed and homogenized, transferred to alumina crucibles, and taken to the furnace (1300ºC) during 2h. Then, the melts are poured into molds and taken to the annealing furnace at 430ºC during 4h, cooling after in natural conditions.

Figure 1: Flowchart of the glasses' production.

The Vicker's hardness (H_v) was conducted following the ASTM C 1327-9925 normative, using a diamond sharp point indenter. The Young's Modulus was obtained using a universal testing machine. The Fracture Toughness (K_{ic}) was obtained using calculus from published methodoly[11]. The Biaxial Flexural Strength was conducted using a universal testing machine with the "piston-on-3-ball" technique, following the ISO 6872 normative. The Raman spectroscopy measurements were conducted on a confocal Raman microscope, using monolitic samples.
The Alpha irradiation tests were conducted by using ^{41}Am sources, which emit α particles at 5,5 MeV, resulting in ≈ 165x10^3 atomic bonding ruptures for each α particle, and with unitary medium activity of 1,5x10^7 Bq. For each composition, the tests were conducted during 100h, with the samples in physical contact with the sources, the total estimated number of bonding ruptures was ≈ 3,6x10^{14} and the total absorbed dose was 11 Gy. The beta (β) irradiation tests were conducted on an electron accelerator Electron Beam Accelerator JOB 188 (Dynamitron®), which generates an electron beam of 100 cm width. The samples were exposed to beta irradiation using a beam current of 4,51 mA, DVH (Dose-Volume Hisogram) of 50,95 uA and dose rate of 26,66 kGy/s. The deposited energy in the surface of each sample was 0,771 MeV and the total irradiated dose was 10 kGy.

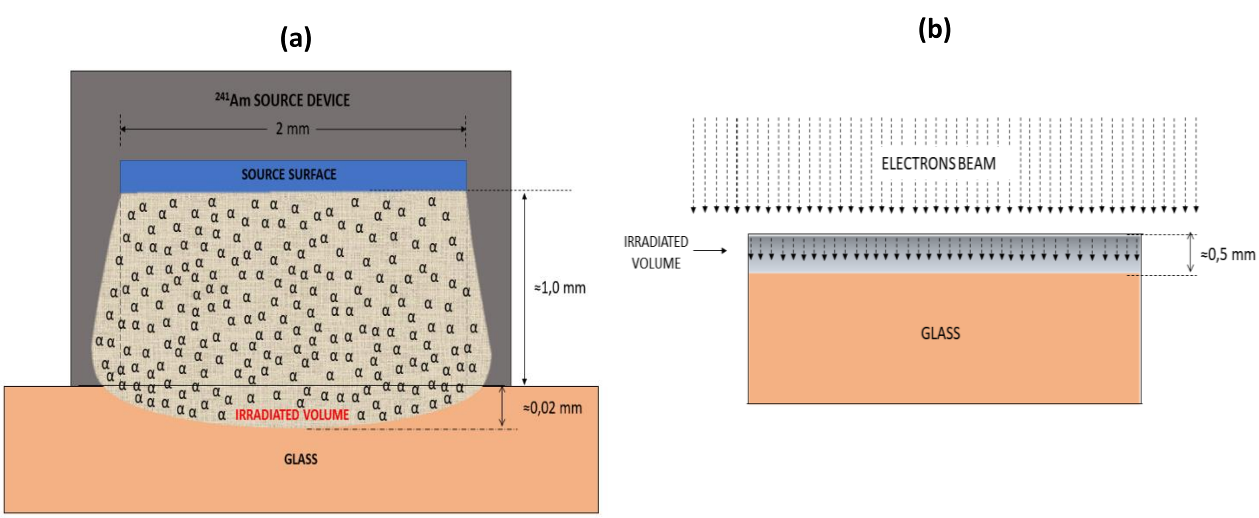

Figure 2: Illustrative schemes of: (a) Alpha irradiation and (b) Beta irradiation.

3. Results and Discussion

The mechanical properties of the glasses are shown in Table 1. Comparing the G0 glass with G2, G4 and G6, it is observed that G4 and G6 presented lower Vickers's Hardness. The hardness of G2 is comparable to G0's, showing that this content of niobia (2 mol%) does not interfere in this property. The glasses exhibit the same trend of Biaxial Flexural Strength compared to the Young's Modulus. Regarding the Fracture Toughness, there are no significant changes with the niobia additions. However, the niobia additions interfered lowering the Young's Modulus of the glasses. The interaction of niobia with the NBO's on the silicate matrix unestablished the overall bonding energy of the glass structure, which resulted in lower hardness and Young's Modulus.

Table 1: Mechanical properties of the glasses with niobia contents varying from 2 – 6 mol%.

Sample	Young's Modulus *E* (GPa)	Biaxial Flexural Strength σf (MPa)	Vickers Hardness H_V (GPa)	Fracture Toughness K_{Ic} (MPa.m$^{1/2}$)
G0	88±3	91±2	4,5±0,1	0,41±0,02
G2	72±5	76±5	4,3±0,3	0,38±0,02
G4	79±3	85±3	4,0±0,1	0,40±0,01
G6	75±4	78±2	3,9±0,2	0,40±0,01

The alpha and beta irradiation results are shown in Figure 3. There are several structural changes after both irradiations, but the most important one is the repolymerization (increase) of Q^2 and Q^3 units area after the beta irradiation, induced by the presence of niobia. Such result attests for the use of niobia in nuclear waste glasses as a polymerizing agent, especially because of its strong need for charge balance of NBO's in the glass structure and its very low interaction with both radiations (alpha and beta).

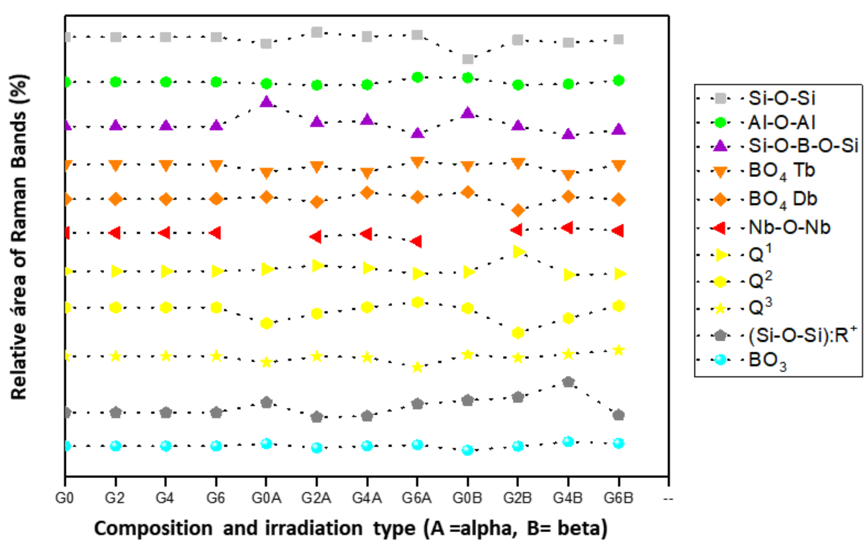

Figure 3: Variation of the relative area of Raman Bands after the alpha and beta irradiation tests on the glass samples.

4. Conclusions

Niobia was successfully added to soda-lime silicate glasses containing boron, and the impact of the oxide on the mechanical and nuclear properties was determined. Due to the mechanism of interaction to the silicate matrix, Nb^{5+} ions must balance their residual negative charge on the oxygens (O^-), and part of the silicate matrix is depolymerized, resulting in lower Vicker's Hardness, Young's Modulus and Fracture Toughness. The very low interaction of niobia with both radiations and its strong need for charge stabilization resulted in a surprising repolymerization of the glass structure after beta irradiation.

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