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NIOBIUM MODIFIED GLASS FOR NUCLEAR WASTE IMMOBILIZATION

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ABSTRACT

The impact of Nb_2O_5 addition to glasses belonging to the system SiO_2-Na_2O-CaO-B_2O_5-Al_2O_3 were investigated for nuclear waste immobilization applications. The glass samples, produced by the traditional melting method, were characterized by XRD, Differential Thermal Analysis (DTA) and Fourier-Transform Infrared Spectroscopy (FT-IR). The XRD results confirmed the amorphous state of the glasses and the thermal and FT-IR analyses revealed that Nb_2O_5 was dispersedly incorporated to the glass structure and that higher contents of the oxide result in a niobate network growth. The glasses showed good resistance to devitrification and are applicable for nuclear waste vitrification processes. These results show that the process is a promising alternative to produce a new family of glasses with optimized thermal resistance for the immobilization of nuclear wastes.
Keywords: vitrification, nuclear glasses, nuclear waste, niobium oxide.

1. INTRODUCTION

The immobilization of High-Level Nuclear Wastes (HLW) in borosilicate glasses or ceramic hosts has been conducted worldwide over the past 40 years, due to the reprocessing of spent fuel from nuclear power plants [1]. Considering the amorphous state of these glasses and their structural adaptability with open networks capable of retaining well many cations, they are able to incorporate an extensive range of long-lived radionuclides (RN) such as ^{41}Ca, ^{135}Cs, ^{238}U, ^{93}Mo, ^{239}Pu, ^{36}Cl, ^{59}Ni, ^{241}Am, ^{93}Zr, ^{107}Pd, ^{79}Se, ^{94}Nb,^{126}Sn, ^{129}I, ^{237}Np, etc. However, the incorporation of RN in these glasses is dependent on their chemical identity. The cationic specimens present in the RN have a good solubility in glass and are readily integrated in the glass structure [2]. Even though the vitrification of nuclear waste is extensively used, it shows several problems related to the integrity of the wasteforms, which are subjected to radiation and thermal aging conditions [3]. The chemical and mechanical resistances are some of the most important properties of the wasteforms and are related to the atomic alterations resultant from internal/external irradiation processes [4]. The chemical resistance of nuclear glasses does not only depend intrinsically on the material but also on the environmental conditions to which the glass is submitted. In France in the geological repository of radioactive waste the sereve dissolution of the glass matrix was detected [5]. Although the nuclear glasses are the best choice for immobilizing HLW, there are still many problems related to the vitrification processes and to the long time storage of the wasteforms. In this work, the use of Nb_2O_5 was explored, due to its stability under radiation and glass former chacterisitcs, for improving the properties of glass matrixes used for immobilization of radioactive wastes, searching for a possible element to be added to the glass composition to improve its chemical resistance.

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9 788599 141083

2. EXPERIMENTAL PROCEDURE

The glasses were based on compositions previously studied by our group [7-12] using SiO_2 (mineral quartz 99% pure), NaOH (CAAL P.A. 99% pure), Al_2O_3 (Almatis P.A. 99% pure), H_3BO_3 (CAAL P.A. 99% pure), CaO (Vetec P.A. 99% pure), powder metallic Nb (99,9% pure, mesh -325) and K_2CO_3 (CAAL P.A. 99% pure) as precursors. The compositions were formulated with the substitution of B_2O_3 by Nb_2O_5 in 4.0 mol% in the glass BNb4, in 8.0 mol% in the glass BNb8, and with the substitution of SiO_2 by Nb_2O_5 in 4.0 mol% in the glass SiNb4 and 8.0 mol% in the glass SiNb8. The formulated composition of the glasses is shown in Table 1.

Table 1 – Nominal composition (wt.%) of the glasses RG (reference glass), BNb_x and $SiNb_x$.

Oxide	RG	BNb4	BNb8	SiNb4	SiNb8
SiO_2	43.5	43.5	43.5	41.4	39.2
Na_2O	25.6	25.6	25.6	25.6	25.6
CaO	19.9	19.9	19.9	19.9	19.9
Al_2O_3	2.0	2.0	2.0	2.0	2.0
K_2O	1.0	1.0	1.0	1.0	1.0
B_2O_3	8.0	7.7	7.4	8.0	8.0
Nb_2O_5	0.0	0.3	0.6	2.1	4.3

The glasses were produced by the method, using alumina crucibles. The melting was conducted in a Lindberg/Blue M vertical furnace, at 1300°C, in air, for 2h. The melts were poured in a steel mold (prismatic with a cross-sectional area of 10mm), and annealed at 430°C during 2h. The X-ray Diffractometry (XRD) analyses were conducted in a Rigaku II diffractometer with a 0.05° step during 5 seconds. The Fourier-Transform Infrared Spectroscopy (FT-IR) was carried out using a Thermo Nicolet Nexus 670 spectrometer and the samples were pulverized and mixed with KBr. The Differential Thermal Analyses (DTA) were conducted using a Netzsch STA 402-E equipment, with synthetic air, heating rate of 10°C/min until the temperature reached 1300°C.

3. RESULTS AND DISCUSSION

All the prepared samples present typical XRD patterns of glasses, as shown in Figure 1.

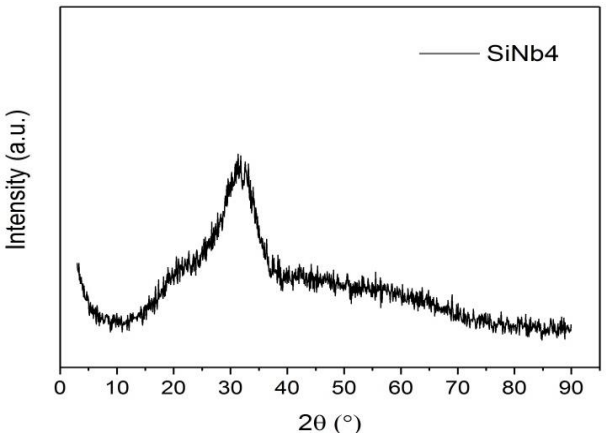

Figure 1 – XRD pattern of SiNb4 glass.

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The FT-IR results are shown in Figure 2 for the reference glass, samples BNb4 and BNb8 (0.3-0.6 wt.% of Nb_2O_5) and for SiNb4 and SiNb8 (2.1-4.3 wt.% of Nb_2O_5). All compositions present the typical bands related to silicate glasses modified with B_2O_3. The band at ~460 cm^{-1} is related to the stretching vibrations of Si-O-Si in the SiO_4 tetrahera and the bands ranging from 611 cm^{-1} to 780 cm^{-1} are related to Si-O-B vibrations and to metal silicates like Si-O-M (M=Al, Nb). The spectra also exibit bands ranging from 860 cm^{-1} to 1100 cm^{-1}, related to stretching vibrations of Si-O-R (R= Ca, Na, B), the band at ~1410 cm^{-1}, related to the vibrations of B-O in BO_3 units and a band at 1200 cm^{-1} related to stretching vibrations of Si-O in the SiO_4 tetrahedra. However, due to the presence of Nb_2O_5 in the network structure, changes in the metallic silicates bands (~720 cm^{-1}) can be observed, and become more pronounced as the Nb_2O_5 content increases from BNb4 – SiNb4, when compared to the reference glass, indicating the connectivity of NbO_6 octahedra to the silicate structure and the increase in the concentrations of segregated boron BO_3 units. For SiNb8, the metallic silicates band (~720 cm^{-1}) decreases, showing that less Nb is connected to the silicate network for this composition and this might indicate the segregation of a niobate network. Similar results were observed relating sub-network formation for Nb_2O_5 additions to other glass systems like, i.e. bioactive glasses, and can be explained as follows: due to the expected immiscibility of the Nb_2O_5 in the silicate system, low contents of the oxide are dispersedly interacting with the network structure, but as higher amounts are introduced, the connectivity between NbO_6 octahedra is preferentially increased, possibly forming a niobate network structure. The increase of the structure connectivity with Nb_2O_5 might also result in higher chemical resistance and decrease of the radiation damages caused by α and β^- particles, which analysis is in progress and will be completed soon.

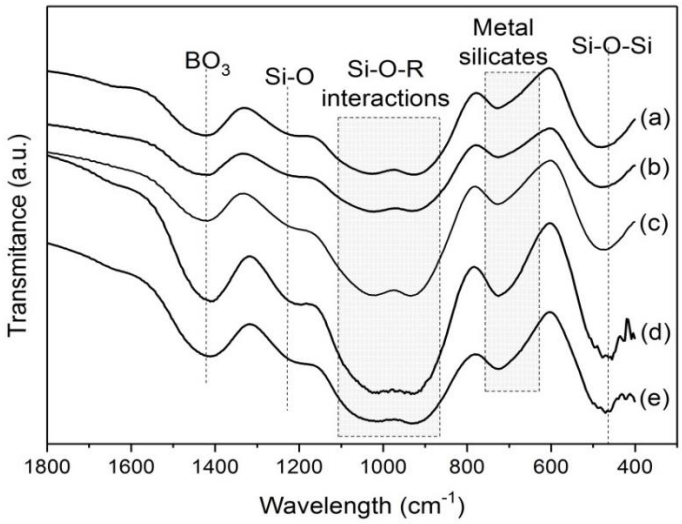

Figure 2 – FT-IR spectra of the glasses: (a) Reference glass, (b) BNb4, (c) BNb8, (d) SiNb4 and (e) SiNb8.

The DTA curves related to the glasses are shown in Figure 3, with the following temperatures (°C): (1) the glass transition temperature *Tg*, (2) T_c^i is the onset crystallization temperature and is indicated by the initial exothermic slope, which culminates at the (3) *Tc*, the crystallization temperature. Lastly, there is an endothermic event related to the melting of the glasses where (4) *Tf* is the flow temperature. These

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9 788599 141083

temperatures are listed in Table 2. Comparing the *Tg* of the reference glass with the BNbx and SiNbx glasses, it can be seen that the Nb_2O_5 additions increased the *Tg* of BNb8, SiNb4 and SiNb8 indicating that, for these compositions, the oxide is connected to the silicate structure and it might impact positively in the mechanical resistance of the glass matrix. A shoulder is observed in the curves right after the *Tf* and this is an indication of structural adaptations and phase separations that usually occur in the range of the initial crystallization until the flow of the material, during the heating. In Figure 3-b, for SiNb8, the exothermic peak (950°C - 1030°C) evidences a second structural reordering and possibly the growth of crystalline compounds involving the highly immiscible SiO_2 and Nb_2O_5. This shows once more that for higher Nb_2O_5 contents (SiNb8 glass) a possible niobate network might be present in the glasses. The occurrence of different glass networks in the immobilized wasteforms is rather common, due to the complexity of the RN that are immobilized, and the strong bondings of the niobate network might be an ally for the optimized retention of radionuclides in the glassy state.

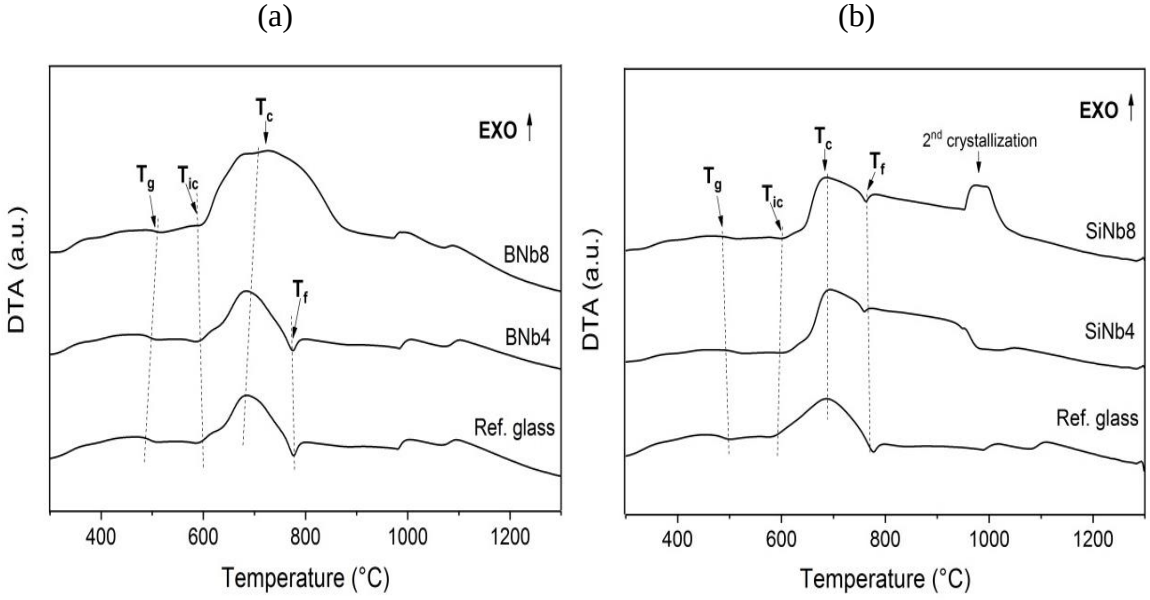

Figure 3 – DTA curves of the glass samples: (a) BNb4 and BNb8, and (b) SiNb4 and SiNb8.

The stability against devitrification was evaluated using the specific temperatures determined in the DTA curves (Table 2) for the Hrubÿ parameter in the equation:

$$K_{gl} = \frac{(T_c^i - T_g)}{(T_f - T_c^i)} \quad (1)$$

where K_{gl} is the glass stability (Hrubÿ parameter) for the glasses. According to the literature, K_{gl}: 0.1 indicates low stability, K_{gl}: ≥ 0.5 good stability and K_{gl} > 1.0 excellent stability, and the higher the value of K_{gl}, the greater is the thermal stability against devitrification. The K_{gl} values calculated for the compositions and the specific DTA temperatures are shown in Table 2, in which is observed that except for BNb8, all K_{gl} values indicate good stability against devitrification, especially for the SiNb4 that

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presented the highest K_{gl}. The stability of glasses used for nuclear waste immobilization is reported to be K_{gl} = 0.35 and this shows that all glasses in this study have good thermal stability applicable for nuclear waste immobilization. Therefore, this is an evidence that Nb_2O_5 might help the glasses become more resistant to devitrification/crystallization, and be an ally against the undesired crystallization that usually occurs in nuclear glasses.

Table 2 – Temperatures determined in the DTA analyses and calculated Hrubÿ parameters.

Sample	T_g (°)	T_{ic} (°)	T_c (°)	T_f (°)	K_{gl}
RG	481	592	686	775	0.6
BNb4	481	592	686	775	0.6
BNb8	495	600	727	N.D.	N.D.
SiNb4	495	611	690	760	0.8
SiNb8	485	604	685	762	0.7

4. CONCLUSIONS

The Nb_2O_5 was successfully incorporated to the glass network structure (FTIR). The oxide is able to act as dispersed niobate units for low contents and also forming of a niobate sub-network for higher contents, proving to be an excellent and stable component to be added to the glasses. The Nb_2O_5 also improved the resistance of the glasses to devitrification (Hrubÿ parameter), and therefore all glasses are thermally stable for nuclear applications, which is an excellent result and might help suppress the undesired crystallization during the processes of the nuclear waste vitrification. The direct response to thermal stability after the Nb_2O_5 addition to the glass matrix is promising for the development of a new family of glasses adequate to nuclear waste immobilization, as the Nb does not interact with the thermal neutrons radiation emitted by the nuclear waste, and might be an ally for the maintenance of the integrity of the wasteforms during the long time of radiation decay.

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