Research Article

Synthesis and characterization of a Mo-rich aluminoborosilicate glass by a double melt process

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ABSTRACT

A Mo-rich aluminoborosilicate glass dedicated for nuclear waste confinement, containing 0.3 to 0.6 wt.% of Cs, is synthesized by a double melting at 1380°C during 3 h, followed by a 2 h annealing step at 600°C. The glasses density varied randomly with the Cs content from 1.43 to 2.73. The X-ray diffraction phase identification reveals similar features for the glasses with 0.3 and 0.6wt.%, with a minor crystalline phase identified as powellite. For 0.4 wt.% Cs, traces of crystalline phases of monoclinic coesite SiO_2, iron silicate ($Fe_3Al_2(SiO_4)_3$), and Sr-Nd-Fe oxide $SrNdFeO_4$ appear in that sample. Scanning electron microscopy micrographs show the glasses morphology. The nucleation temperature, measured by differential scanning calorimetry is in the interval 501-509°C, and the crystal growth temperature between 649 and 689°C. The glasses melt between 770 and 812°C. Fourier Transform Infrared spectroscopy shows that the Cs addition in the glass composition increases the polymerization rate in the glass network. The MCC2 standard leach test gave high amounts of dissolved Mo, indicating that Mo should be embedded in a glass-ceramic to ensure a good chemical stability against water alteration.

Key words: Radioactive waste, alkali-earth elements confinement, allotropic transformations, spectroscopic characterization
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1. INTRODUCTION

The choice of a particular nuclear glass, suitable for the radioactive waste (RW) confinement, results from a compromise between several glasses properties. Currently, alumino-borosilicate glasses are used on an industrial scale to contain high-level waste.

Alumino-borosilicate glass has interesting properties, which make it applicable for RW confinement, namely: high mechanical and chemical durability, thermal stability and ion exchange capacity [1-2].

Nowadays, with the goal of reducing the stocks of RW to be disposal, many researches, to obtain nuclear glasses capable of confining diversified, large amounts of waste, in their bulk are in progress [3-5].

To this end, the problem of containment of transition metal-rich wastes such as molybdenum (Mo), platinoids (Rh, Ru, etc.) and some volatile elements, such as cesium, remains.

The amounts of waste containing these last elements are important. However, their addition in glassy phases, as borosilicates and aluminosilicates, cause problems, compromising both coherence and uniformity of such materials.

In this context, higher concentrations of Mo, rare earths elements (REE), and platinoid elements (Ru, Rh, Pd) that are abundant in the wastes would be present in glasses [6]. As all these elements are sparingly soluble in borosilicate glasses [7] because of the high field strength of REE^{3+}, Mo^{6+}, and Ru^{4+} ions [8,9], the increase of waste loading might induce the formation of vitreous or crystalline heterogeneities in the glasses which could lower their long-term performances, such as their thermal stability, resistance to self-irradiation, and water alteration, in comparison with current nuclear waste glasses [10].

Studies published throughout literature, discuss the heterogeneity and phase separation tendency of Mo-rich glasses, which can lead to corrosion problems in the melting tanks [3, 11-14].

Bardes et al. [5] have synthesized a REE-rich borosilicate glass for the immobilization of high-level waste, and have riched 2.3 wt% MoO_3 without crystallization of molybdates.

Henry et al. [15] obtain a glass ceramic with a legacy solution derived from the reprocessing of spent Mo–Sn–Al fuels, which led to a new glass formulation, a Ca-Zr-enriched alumino-boro-silicate matrix, able to incorporate 12 wt% of MoO_3.

Moreover, studies dealing with soda-lime borosilicate glass or more simplified silicate glasses have shown that increasing MoO_3 amount induced an increase of the silicate network reticulation. The presence of less than 1 mol.% MoO_3 is sufficient to cause a 3% drop in the number of non-bridging oxygen (NBO) atoms and clearly shows the influence of MoO_3 glass structure based on the increase of the polymerization [6, 7]. In this study, the amount of Mo incorporated into the glass was voluntarily high (10%).

On the other hand, the amounts of Cs that can be added to an aluminosilicate network are often limited due to the volatility of this element and its ability to change the nature of the glasses structural units.

For this purpose, Cs is a radioisotope originated from the production of electricity by the nuclear way, which is the second source of ^{137}Cs. The core of a 1300 MWe reactor contains at the end of cycle approximately 3.10^{17} Bq of ^{137}Cs, confined within the fuel. In normal operation, a small fraction of this cesium passes in the effluents, released into the environment. A nuclear reactor releases ^{137}Cs almost entirely in the liquid effluents.

When reprocessing spent fuel, ^{137}Cs is extracted with other fission products [16].

The platinoids are known to form phase separations on the glasses surface, and to induce the corrosion of industrial melting tanks. Their effect, in the presently studied glasses, has not been investigated, for materials reasons [17, 18]. Their concentration in the RW arises from both the reprocessing of higher burn-up spent nuclear fuel and Mo-rich waste solutions [6, 7, 19-22].

This study is part of a global framework of investigations on the attempt to improve the chemical resistance of Mo-rich borosilicate glasses, and glass-ceramics in the same network, starting from a new glass chemical composition, so to study the influence of different REE elements as well as cesium, on the material performance. The goal of all of our research is first, to obtain an aluminosilicate glass, and then crystallize this glass, to see how the crystal growth parameters can improve the performance of this material.

This publication deals only with the first part of the work, which consists of the synthesis and characterization of Mo-rich aluminosilicate glass, with the chemical formula Al_2O_3-Na_2O-B_2O_3-SiO_2-MoO_3, and different cesium (Cs) contents between 0.3- 0.6 w.%. These amounts are low because a large amount of the alkali element, Cs, will substitutes Ca or Na, in the molybdate phase, during the separation phase of Mo excess during the synthesis; resulting in a decrease of chemical durability of the glass [8, 23].

In order to avoid scheelite formation by potential crystallization, large amounts of B_2O_3 and CaO were added to the glass composition [7]. The amount of MoO_3 incorporated into the present glasses was of 10 wt.%.

The material is synthesized by a double melting at 1380°C followed by annealing at 600°C. The density of the glass is measured. The synthesized glasses are characterized by different methods: X-ray diffraction (XRD), scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). The glass units' functional groups are identified by Fourier transform infrared spectroscopy (FTIR). To get an idea about the stability and containment capacity of the synthesized glass, a standard leaching test (Material Characterization Center: MCC2) is performed on one of the samples at 90°C in a dark, closed medium, in nitric acid.

2. MATERIAL AND METHODS

2.1. Glass synthesis:

The following commercial reagents are used for the glass synthesis: Al_2O_3 (Fluka), B_2O_3 (Labosi, $\geq$ 99%), CaO (Merck, $\geq$ 97%), Fe_2O_3 (Merck, $\geq$ 99%), Li_2O (Labosi $\geq$ 99%), MoO_3 (Merck, $\geq$ 99.5%), Nd_2O_3 (Fluka, $\geq$ 99.9%), P_2O_5 (Merck, $\geq$ 98%), SiO_2 (Supelcoanalytica), ZrO_2 (Aldrich, 99%), Na_2O (Merck, > 99%), ZnO (Labosi), Cs_2CO_3 (Fluka), $Sr(NO_3)_2$ (BDH Chemicals, 99%), Co_3CO_4 (Fluka, > 98%). Cobalt carbonate, Co_3CO_4 is calcined during 5 h at 500°C. The oxides are milled before weighing. The synthesis process is performed according to Vance et al [24] method. A batch of $60\ 10^{-3}$ kg, for each Cs content, is prepared, and homogenized during 5 h. In order to ensure good glass homogeneity and isotropic properties in the bulk of the material, a double stage melting is conducted in Pt crucibles in a BLF 1800 Carbolite furnace, at 1380°C during 3 h, with a heating step of 6°C min^{-1}. After the second melting, the glasses are annealed at 600°C during 2 h. The glasses chemical composition according to the Mo content is given in table 1. The glasses geometrical (d_g) densities are measured.

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Table -1 Glasses chemical composition as a function of the glasses Cs content

Cs content (wt.%)	0.30	0.40	0.60
Oxide	Content (wt. %)		
Na_2O	09.00	09.00	09.00
B_2O_3	13.00	13.00	13.00
Li_2O	03.00	03.00	03.00
Al_2O_3	07.00	07.00	07.00
MoO_3	10.00	10.00	10.00
P_2O_5	03.10	03.10	03.10
ZnO	05.00	05.00	05.00
ZrO_2	03.00	03.00	03.00
CaO	06.10	06.10	06.10
Cs_2O	00.30	00.40	00.60
SrO	00.70	00.70	00.70
Nd_2O_3	01.50	01.50	01.50
SiO_2	37.50	37.40	37.20
Fe_2O_3	00.60	00.60	00.60
Co_3O_4	00.20	00.20	00.20
Total	100.00	100.00	100.00

2.2. Phase identification and SEM observation:

Phases identification is conducted by XRD analysis using a Philips X'Pert PRO diffractometer, employing Cu-Kα radiation (λ=0.15406 nm), with X'Pert High Score Plus software as identification tool.XRD patterns were recorded for 2θ ranging from 10° to 80° with a step of 0.02°. Microstructure observation is performed by a ESSEM FEG PAN'Alytical SEM microscope in BSE (back scattered electron) mode.

2.3. DSC and FTIR analyses:

The glass transition (Tg), crystallization (Tc) and melting (Tm) temperatures are assessed using DSC analysis, with a Netzsch Setaram 409. The FTIR spectroscopy is performed with a Thermo NICOLET 380. The grinded samples are mixed with small amounts of dried KBr powder, and pelletized in very fine films. For each Cs content, aglass FTIR spectrum is recorded. The results are analyzed using OMNIC software [25].

2.4. MCC2 leach test:

A preliminary chemical durability assessment test, consisting in MCC2 standard leach test, is performed at 90°C, in a closed, dark and HNO_3 acid medium, for 3 days [26].

3. RESULTS

3.1. Materials density:

The glasses have similar morphological aspects whatever the Cs content. They are opaque and blue colored (fig.1). Their densities are given in table 2. The geometrical density is comprised between 1.43 and 2.76.

Fig. 1 Morphological aspect of the glasses

Table -2 Glasses densities as a function of Cs content in the glasses

Cs content (wt.%)	0.30	0.40	0.60
d_g	1.96	1.43	2.76

3.2. XRD phases identification:

For the three studied glasses, XRD diagrams are gathered on fig. 2. For 0.3 and 0.6 wt.% Cs content, the glass shows an amorphous feature with a minor crystalline phase, identified to $CaMoO_4$ tetragonal powellite crystal, corresponding to the JCPDS (Joint Committee for Power Diffraction Data Standard) data 01-085-0585 [27], of the space group I41/a number

88. For 0.4 wt.% Cs, traces of crystalline phases of SiO_2 monoclinic coesite (JCPDS N° 01-083-1831), having a C2/c space group and 15 number; $Fe_3Al_2(SiO_4)_3$ iron silicate (JCPDS: 01-085-2498) and $SrNdFeO_4$ oxide (JCDPS :01-076-1876) seams to appear in that sample [27]. However, further investigations are required to confirm this result.

3.3. Scanning electron microscopy:

The scanning electron microscope provides images with information on microstructural characterization: morphology, compounds distribution in mixtures or composites, crystallographic information, dimensional measurements, etc.

The glasses micrographs were obtained in BSE mode, with magnifications of the order of one micrometer. They are represented in Fig. 3. The ob-long forms of the monoclinic coesite crystals, and the deformed faces of some powellite crystals faces, can be observed. These results remain to be confirmed by further analytical investigations.

3.4. Differential scanning calorimetry:

The DSC spectra allow to rich the Tg, Tc and Tm temperatures (table 3).Tg is comprised in the interval 507-522°C, Tc between 609 and 651°C. These values seem to grow according to the Cs content. However, SiO_2, which compensates the Cs content in the glass, has refractory properties, and is expected to lower Tg and Tc, when its content decreases.

3.5. FTIR Analysis:

The FTIR spectrum for the three glasses compositions are given in Fig.4. They show the main chemical bonds vibrations in the glasses. The 457.8 cm^{-1} band can be attributed to the vibration of the Si-O-Si and O-Si-O bonds of the glass. It is at 464.2 cm^{-1} for the intermediate composition glass of 0.4% Cs [28]. The very weak band at 680-690 cm^{-1}, can be attributed to the vibration of BO_3 [8].

3.6. Leaching test:

A preliminary static leaching of the glass containing 0.6 wt.% Cs was carried out. Thus, a glass pellet was immersed in 1N HNO_3 acid for three days at 90°C. in a dark and closed glass bottles. (MCC2 test). The leachate analysis is carried out by optical emission spectroscopy (ICP: inductively coupled plasma spectroscopy) using a Jobin Yvon 32 spectrometer. After calibration of the equipment, the main element of the glass was analyzed: Si, as well as Mo. We find: $255 \cdot 10^{-3}$ kg m^{-3} of Si (255 ppm) and 8.483 kg m^{-3} of Mo (8483 ppm).The glass did not release much Si inside the acid solution. It is stable in its overall structure.
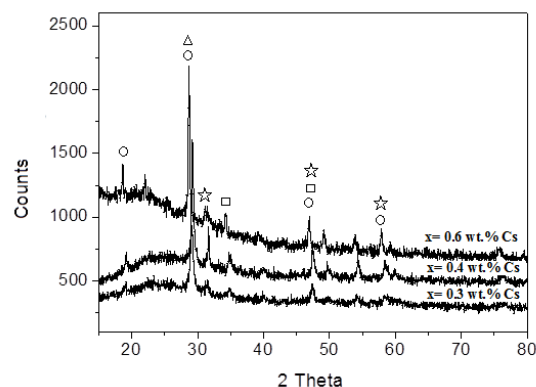

Fig. 2 XRD spectra of the synthesized glasses with different Cs contents

○ : Tetragonal Powellite, △ : Monoclinic Coesite, ☆: $Fe_3Al_2(SiO_4)_3$ iron silicate,
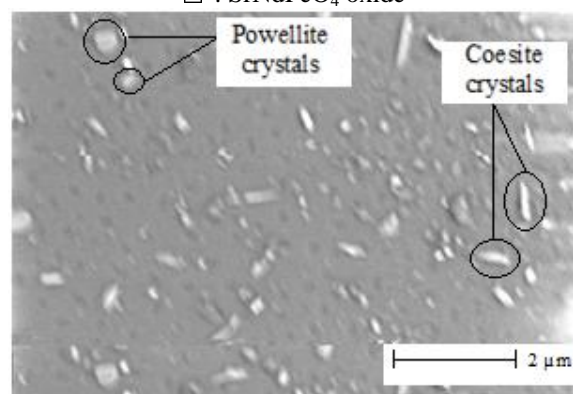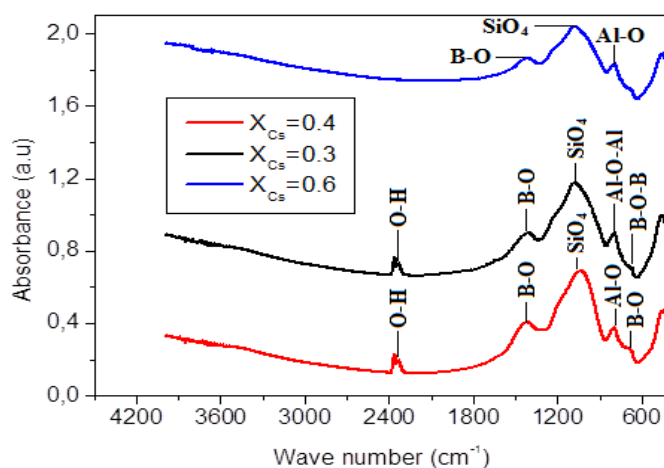
□ : $SrNdFeO_4$ oxide

Fig. 3 A typical MEB micrograph of the synthesized glasses

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Table -3 Glass transition T_g crystallization T_c, and melting T_m temperatures of the glasses with various Cs contents

Cs content (wt. %)	0.3	0.4	0.6
Tg (°C)	507.16	509.12	522.00
Tc (°C)	609.07	648.60	650.77
Tm (°C)	770.00	---	812.25

Fig. 4 Glasses FTIR spectra for different Cs content in the glasses

4. Discussion

4.1. Materials density:

The glasses geometrical density, between 1.43 et 2.76, is in accordance with that of Gautam et al. [27] which is in the interval:2.55-2.84. Quintas [29] found a glass density of 2.72, for an alumino-borosilicate synthesized by double melting at 1300°C. E.R. Vance et al. [24] synthesized a Mo-rich glass-ceramic material, with a similar composition to that of the present study. They found a density of 2.71. These results are comparable to that of the present study.

4.2. XRD phases identification:

For the whole of samples, the High-Score analysis shows that no Na_2MoO_4 crystals are identified. Globally, the powellite phase is identified for the Mo-rich glasses presently studied.

The annihilation step is the first parameter incriminated in the formation of the germs of such crystals.

Many authors report the crystallization of $CaMoO_4$ phases and Na_2CaMoO_4 phases and their REE doped forms in the bulk of Mo-rich glasses. These crystallizations occur during cooling/poring phases and may form during the glass heating; enhancing the importance of optimizing the glass fabrication process [4, 7, 13, 19, 30, 31].

The increase of Ca concentration enables to stabilize Mo in the form of the more durable $CaMoO_4$ (powellite) crystalline phase during cooling of the melt rather than in the poorly durable Na_2MoO_4 phase.

Chouard et al. [3] synthesized an alumino-borosilicate glass at the melting temperature of 1300°C for a composition containing 1.61 % Mo oxide and 3.59 % Nd-La oxides. These authors observed the formation of the $CaMoO_4$ powellite phase, both in the glass and after crystallization. It has been demonstrated that the relative contents in REE elements (such as Nd) versus Mo will drive the formation of molybdate / apatite phase formation. High amounts of Nd oxide (3.54 to 16.83 wt%) in the glass composition will inhibit the crystallization of molybdate phases, with a total disappearance of this phase from 8 wt.% Nd_2O_3. This shows the tendency of Mo to crystallize in Mo-rich aluminosilicate glasses [30].

The molybdate phases formation is directly linked to the poor solubility in the glass network of Mo oxoanions, such as molybdate tetrahedral anion $[MoO_4]^{2-}$, containing Mo^{+VI} cation. This +VI oxidation state is present in oxidizing synthesis conditions, as in the present study where the cooling process is performed in air atmosphere.

$[MoO_4]^{2-}$ anions are often abundant in depolymerized regions of the glassy network, where there is a lack in NBO atoms. These oxoanions charges are compensated by alkaline and alkaline-earth cations charges in the molybdate precipitated phases. $[MoO_4]^{2-}$ anions are weakly linked to the glass network.

Contrary to the present study, where the ratio $Nd_2O_3/MoO_3=1.5/10$ favors the molybdate formation; MoO_3 relative content being high in the glasses composition (10 wt.%).

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As a positive result, the molybdate is in the form of powellite and not in the form of scheelite crystal; the Cs content being very small, and B_2O_3 and CaO contents are sufficient enough to avoid scheelite formation.

4.3. Differential scanning calorimetry:

For the whole of glasses, DSC analysis gave transition temperatures, Tg, comprised between 507 and 522°C, and Tc between 609 and 651°C. The growth in Tc and Tg should be attributed to the secondary phases, identified by XRD in the material such as: $CaMoO_4$. These phases create a decrease of alkali elements (Ca, Sr, etc.) in the amorphous phase. These alkali elements migrate to powellite phase. The glasses become more refractory and consequently, Tg and Tc temperatures growth.

Banerjee et al. [32] found: Tg = 515 ° C and Tc = 550 ° C for a series of Cs-borosilicate glasses of general formula (mol%): $17.5Na_2O-2.5Cs_2O-45SiO_2$- (35-x) B_2O_3-xCaO, where x varies from 0 to 10.The values of Tg are close to those of the currently studied glass. However, Tc is smaller than that of our glasses, probably because of the chemical composition of the glass, which consists of lighter atoms.

Chouard [33] demonstrated that when the glass undergoes a heat treatment of nucleation and growth, the mechanism that controls the microstructure of the final material at low temperature (between 650 and 950°C) is the crystallization of molybdate phases, in particularly calcium molybdate, $CaMoO_4$. While the mechanism that controls the microstructure of the final material at high temperature (> 950°C) is phase separation.

Indeed, for temperatures below 950°C, the powellite crystallizes uniformly in the bulk of the samples, due to the micro-separation of the phases initially present in the glass, and which serve as a heterogeneous nucleation site for the crystallization of $CaMoO_4$.

Chouard et al [3] studied a Mo-rich glass in SiO_2-Al_2O_3-B_2O_3-Na_2O-CaO system. The effect of adding Nd_2O_3, MoO_3, and RuO_2 separately or concurrently, on the crystallization of a soda-lime aluminoborosilicate glass during cooling from the melt or glass heating was studied by DTA. Tg increases from 556 to 580°C by addition of Nd and/or Ru. The same trend is observed for Tc, which varies from 748 to 940°C. Nd_2O_3 addition strongly reduces liquid-liquid phase separation and crystallization of Ca and Na molybdates ($CaMoO_4$ (powellite) and Na_2MoO_4 in Mo-rich compositions as long as Nd^{3+} ions remain solubilized in the glassy network.

Gong et al. [34] studied an alumino-borosilicate glass of chemical composition: 56.2% SiO_2, 17.3% B_2O_3, 12.2% Na_2O, $6.1Al_2O_3$, 5.0% CaO and 2.8% ZrO_2. They find by ATD analysis a Tg temperature of 570-572°C and Tc = 705°C.

Lopes et al. [35] studied the phase transition temperatures of a single borosilicate glass of chemical formula $60BaO$-$30B_2O_3$-$10SiO_2$.They find transformation temperatures varying with the heating step of the glass. Tg ranging from 720 to 750°C; the first crystallization temperature ranging from Tg=798 to 805°C. This glass appears more refractory than the glass currently studied. This is contradictory, since the abundance of alkaline elements in this glass, expected to make it less refractory.

4.4. FTIR Analysis:

The presently studied glasses show many particularities that highlights their microstructural properties, namely for B-O-B bonds and SiO_4 units.

For borate glasses, the BO_3 is located at 700 cm^{-1} [8]. For the studied glasses, it appears as a very weak band at 680-690 cm^{-1}. Ojhar [28] report the B-O-B elongation vibration at 683 cm^{-1}.

Between 798-805 cm^{-1}, the vibration absorption band of Al-O-Al appears, due to the binding of the AlO_4 tetrahedra [36].

For 0.3% Cs in the glass, the absorption band at about 1042 cm^{-1} can be attributed to the vibration of the SiO_4 unit in a partially depolymerized network. This band is reported between 1030 and 1020 cm^{-1} by Kashchieva [8]. When the Cs content increases to 0.4 and 0.6% in the glass, this band shifts to 1081.4-1087.8 cm^{-1}, indicating the polymerization of the network which increases with the Cs content, and hence the decrease in NBO oxygen, in favor of bridged (BO) oxygen.

The vibration at 1422.1 cm^{-1} for glasses with Cs content of 0.3 and 0.4% shifts to 1428.6 cm^{-1} for the glass with 0.6% Cs. This can be attributed to the asymmetric elongation relaxation of the B-O bond of trigonal BO_3 units. The appearance of this band may vary within a very wide range of 1200-1635 cm^{-1}, depending on the composition of the glass [37]. And the adjacent intense bands at 2350 and 2360.7 cm^{-1} reflect -OH bonds on the glasses surfaces, which proves the ability of the glasses to hydrate on the surface, and thus to corrode [35].

One can conclude that the addition of Cs increases the degree of polymerization of the glassy network, and therefore affects the number of O-Si-O bonds.

4.5. Leaching test:

The preliminary MCC2 static leaching of the glass containing 0.6 wt.% Cs in HNO_3 acid for three days at 90°C gave 255 10^{-3} kg $m^{-3}$of Si and 8.483 kg $m^{-3}$of Mo.

Vance et al. [24] conducted a normalized PCT test, during 7 days at 90°C on a UMo glass–ceramic with the chemical composition (in wt.%) of :9.3Na$_2$O-14.2B$_2$O$_3$-7.0Al$_2$O$_3$-9.9MoO$_3$-3.0P$_2$O$_5$-5.9ZnO-3.3ZrO$_2$-6.1CaO-0.3Cs$_2$O-0.4SrO-1.7Nd$_2$O$_3$-38.9SiO$_2$. They found leached amounts of Mo between 0.7 and 1.2 kgm^{-3}, depending on the employed cooling rate of the glass–ceramic melt.

These results are better to our findings.

The purpose of the leaching test is to check the durability of the synthesized vitreous matrix, which contains cesium. The lixiviation test shows that the glassy matrix is less solubilized. It still releases a lot of Mo (8.483 kgm^{-3}-Mo) compared to Si (255 10^{-3} kgm^{-3}-Si). Mois a transition metal belonging to the fission products. So, this result reinforces the idea that it will be necessary to crystallize this glass before using it to confine radioactive Mo.

5. CONCLUSIONS

The objective of this study is to study and understand the structural and microstructural changes in a Mo-rich alumino-borosilicate glass intended to confine both Mo-rich RW containing some elements, difficult to embed in glass, as Cs.

For this, we realized the synthesis and the characterization of a Mo-rich aluminosilicate glass (Mo), containing variable contents of Cs oxides ranging from 0.3 to 0.6%.

The synthesis is carried out by the conventional method of double melting at 1380°C, followed by annihilation at 600°C for 2 hours, in order to obtain a glass with good physicochemical properties. Neodymium (Nd), a chemical analogue of actinides, is a simulator of the radioisotopes of actinides and even lanthanides.

The obtained glass matrices were characterized by their physical and microstructural properties. The geometric density of the samples is between 1.960 and 2.757. It increases slightly with the increase of the Cs rate. The densest glass contains the most Cs content (0.6 wt%).

The XRD analysis showed that the appearance of the whole of synthesized glasses is amorphous with traces of phase seeds identified with the crystalline residues formed during cooling, and which are mainly associated with the Ca-molybdate phase, CaMoO$_4$ powellite and SiO$_2$ coesite. As a positive result, Mo is in the form of powellite and not scheelite crystal, the Cs content being very small, and B$_2$O$_3$ and CaO contents are sufficient enough to avoid scheelite formation.

SEM microscopy revealed the microstructure of cross-sections of glass with different Cs contents. In particular, one can observe the ob-long forms of monoclinic coesite crystals and the deformed faces of some powellite crystals faces.

DSC analysis gives Tg values in the range of 507-522°C, and Tc between 609 and 651°C. These values seem to grow according to the Cs content. The growth in Tc and Tg should be attributed to the secondary phases, identified by XRD in the material.

The FTIR analysis confirms the similarity of composition between the studied glasses, for all the Cs contents. The main chemical bonds identified in the glasses are: Si-O-Si and O-Si-O of SiO$_4$, B-O-B of BO$_3$, Al-O-Al of AlO$_4$. The addition of Cs increases the polymerization degree of the glassy network, and therefore decreases the NBO oxygen in favor of BO oxygen.

A three-day leaching by the MCC2 method at 90°C shows that silica, the main element of the glass, is less solubilized. Mo that shows a high solubility in the acid solution, at high temperature, which can compromise the chemical durability of such a glass. The synthesized material must undergo further physicochemical analysis to better identify, and illustrate the formation of bonds in the glass network, as well as its long-term durability.

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