Journal of Materials Science and Engineering A 3 (4) (2013) 209-223

Effect of the Ce Content on a Nuclear Waste Glassy Matrix in the System SiO_2-Al_2O_3-CaO-MgO-ZrO_2-TiO_2, Synthesized at a Low Melting Temperature

Nour-el-Hayet Kamel[1], Dalila Moudir[1], Ziane Kamel[1], Abdelmoumene Djerridi[2], Samy Mouhamou[2], Abdelbaki Benmounah[2], Rafika Souag[2], Mustapha Taouinet[3] and Hamid Ait-Amar[4]

1. Department of Spectrometry, Algiers Nuclear Research Centre, Algiers, Algeria

2. Faculty of Sciences, M'hamed Bougara University, Boumerdes 35000, Algeria

3. Metallurgy Department, Draria Nuclear Research Centre, Sebala, Draria, Algeria

4. Faculty of Mechanical and Process Engineering El-Alia, Houari Boumediene University of Science and Technology, Bab-Ezzouar, Algiers, Algeria

Received: December 24, 2012 / Accepted: January 08, 2013 / Published: April 10, 2013.

Abstract: Aluminosilicated glasses containing Zr and Ti metals have satisfactory properties, and may be suitable as nuclear glasses, dedicated for storage of radioactive waste solutions. This study summarizes the synthesis of a glassy matrix in the system: SiO_2-Al_2O_3-CaO-MgO-ZrO_2-TiO_2. Ce element was added as an actinide surrogate. The effect of Ce addition on the glass structure is investigated, for Ce contents ranging between 0 and 15 wt.%. For the whole of glasses, a double melting at 1,350°C during 5 h gave monophasic homogeneous glasses. Both X-ray diffraction and scanning electron microscopy analyses reveal a pure amorphous structure. Most of the basic properties increase with the glass Ce content, the Archimedes density from 2.827 to 3.049 g/cm^3, and Vickers indentations from 680 to 862 HV. Oxygen molar volumes are not affected by the glasses Ce contents. The differential thermal analysis show that the glass transformation temperature decreases with the Ce content, and with the heavy elements content. The optical absorption spectroscopy study shows that the Nd cations environment is not altered by the glasses Ce concentration. A preliminary corrosion test leads to low dissolutions of Si, Ca and Zr, estimated by ICP analyses to few ppms. Out coming investigations are in course for further glasses network characterizations.

Key words: Nuclear glass, aluminosilicate, XRD, SEM, DTA, corrosion, optical absorption.

1. Introduction

Glass matrices are currently used as non-specific nuclear waste confinement matrix, because of their good mechanical and chemical durability, and their ability to incorporate simultaneously in their structure large amounts of most elements exiting in high level waste and fission products solutions. Thus, nuclear glasses are employed in nuclear industry for waste confinement, and are forecasted suitable for long-term storage of these wastes [1-3].

Contrary to monophasic crystalline matrices which are radioelements selective host matrices, glassy matrix have a tolerant nature, which may confine radionuclides with many chemical characteristics (natures). Furthermore, glasses have a flexible microstructure which permits waste liquids compositions fluctuations. Indeed, several oxides belong to fission products solutions (over 30 oxides). Only platinoids (Pd, Ru, Rh) and chalcogenide glasses (Se and Te) are immiscible in the glass matrice, and remain dispersed as oxide or metallic fine particles with micrometric sizes.

Nuclear glasses must be durable against both

Corresponding author: Nour-el-Hayet Kamel, senior of research, research fields: materials science and nuclear waste confinment matrix. E-mail: kamel.nour_el_hayet@hotmail.fr.

self-irradiation and water corrosion [4-6]. This point is important in deep geological disposal conditions since the nuclear glass is the first barrier for the radionuclide release toward biosphere. The study of very old natural glasses (obsidian and basaltic glasses) allowed validating experimental models of long term behavior [4]. Similarly, glass water corrosion in presence of corrosion products coming from containers and clay materials from nearest geological formations has been the aim of many studies [5]. Experience in glasses surveys gained today over than 40 years of knowledge, covering both laboratory and industrial scale experiments [7].

At an operational (industrial) scale, many glass systems are employed in nuclear industries, mainly alkali borosilicates, aluminoborosilicates [8] and phosphates glasses. Furthermore, fission products wastes are rich of rare-earth elements (REE), rending of great interest glass compositions of lanthanoids family, namely: LnSiAlO [9-13].

With regard to their physic-chemical properties, it has been demonstrated that these kind of glasses may be suitable candidates for minor actinides confinement (Np, Am, Cm, etc., and/or REE elements, and fission products) [8]. However, their formulation is a major task regarding to melting and melting/nucleation processes. In fact, each kind of glass will exhibit a complex behavior depending on its basic structure (borosilicate, aluminoborosilicate, etc.) and the dopents it contents [14-16].

As a result, the selection of a kind of a glass matrice dedicated to a particular kind of waste will result in jeopardy between all these properties.

Currently in the nuclear industry, borosilicated glasses are the most used at an industrial scale in several countries: in France (R7T7 glass), in USA (PNL76-68), in UK (Magnox GB), in Russia Republic, in Belgium, in Germany (GP 98/12) and in Japan (JAERI vitrification facility) [17-32]. However, future improvement of the existing melting technologies will lead to the development of corrosion-resistant glass contact materials (e.g., electrodes, bubblers, refractories and thermowells) which may allow for higher temperature operation (reducing the need for alkali for low melt temperature) and allow varying the glass compositions. These advances will help to increase the loading of waste in glass and enhance technological parameters [33].

Programs to investigate the application of other glass families (e.g., phosphates) are conducted to improve loading and properties of waste glasses [33].

Borosilicated glasses are mainly amorphous, but often contain few crystalline phases, occurring during cooling, because nevertheless the glasses are over equilibrium solids. During cooling in steel containers crystalline phases may form within the glassy matrice [34]. This devitrification phenomenon is compromising for many reasons: these crystalline phases may become amorphous under the effect of auto-irradiation, provoking their swelling and thus cracks formation in the waste package. In another way, crystalline phases could sediment during the melting process creating a sludge in the bottom of the melters [35]. This dense sludge, which conduct electricity is visqueous, and negatively affect the casting [36]. A competitive corrosion at materials interfaces will occur as a consequence [2].

Crystallization phenomena occurring in borosilicate glasses make them composite materials, called: composite glasses (GCM: glass composite materials) [37].

A glass composition change often accompanies crystalline phase’s formation, altering the glass basic properties, as the chemical durability. However, the crystallization phenomena may be favorable by providing a waste double-containment (ceramic in glass) [38, 39].

The precipitation of crystalline phases in nuclear glasses is extensively studied, either with the aim of inducing crystallizations or with that to avoid them [8]. For example, alkali-iron-phosphate glasses are used to avoid certain precipitations. The solubility of P, S, Cr, Fe, Mo, Cl, F and many other components are generally higher in alkali-iron phosphate waste glasses than in silicate glasses [33, 40].

However, for every kind of glass matrice, the disposal material must remains durable in its chemical environment, and under self-irradiation, during the forecasted disposal time period. It should also be resistant against cracks formation. This last characteristic will determines the cracking area, which directly affects the exchange ability between the glass and its nearest environment, and thus influences the dissolution speed in water.

Under the present state of knowledge, glasses and ceramics are considered suitable for final disposal. So, the vitrification is currently employed at a full-scall for the disposal of the most part of high level waste (fission products and actinides), since large pilot scale operations of vitrification processes have been successfully demonstrated [41]. Although a specific conditioning of long-lived radionuclides in highly durable ceramics (hollandite, apatite, etc.) is an interesting solution. However, glasses remain the most adopted industrial process for high-level wastes, due to both technical and economical considerations.

Aluminosilicated glasses when added with specific metals, like: Zr or Ti has satisfactory physico-chemical durability properties, which make them suitable for disposal of transuranic elements. These glasses can have either a single-phase structure or doubled by a secondary ceramic phase. The melting processes of aluminosilicated glasses are not factory-made yet, mainly because of the high melting point of the glass, which is less profitable.

REE elements rich aluminosilicated glass matrix is scarcely studied in the field of nuclear waste confinement. This paper summarizes the optimization of a glass synthesis process, applied to the glass matrix SiO_2-Al_2O_3-CaO-MgO-ZrO_2-TiO_2. The highlights of the present study covers mainly the basic features of the process that is being developed to illustrate the possibility of use of this parent glass for the nucleation of several glass ceramics, containing Zr-based, and Ti-based minerals, like zirconolites, hollandites, powellite structured, molybdates, etc.; and there derivate chemical formulas [42, 43]. Also, it is aimed that further improvements of the process arising from the current research and development, will allow decreasing the process temperatures, and improving the product characteristics and thus give useful data for the economic aspects of a full-scale glass fabrication.

That is why the goal of this survey is to produce a homogeneous nuclear glass in the system: SiO_2-Al_2O_3-CaO-MgO-ZrO_2-TiO_2, with a melting temperature as low as possible, to facilitate casting, in the chosen experimental conditions. Cerium (Ce) was employed as a lanthanide/actinide surrogate. The effect of the Ce content on the glass microstructure was studied for Ce concentrations ranging between 0 to 15 wt.%; the effect of lanthanides/actinides contents giving useful results regarding to the behavior of a nuclear glass, filled with these elements.

The selected glass composition was fixed based on tested nuclear glasses compositions [37], to reproduce the glass principal characteristics inferred by its different constituents. However, an aluminosilicated major structure was deliberately selected, since aluminosilicated nuclear glasses are not envisaged yet for the nuclear waste confinement.

The glassy products are characterized by their physical, mechanical and microstructural properties. The glasses densities and Vickers microhardenesses are measured. The amorphous structure was confirmed by X-ray diffraction (XRD), scanning electron microscopy (SEM), and differential thermal analysis (DTA). This last allows reaching the glasses phase transition temperatures: glass transition (T_g), crystallization (T_c) and melting (T_m) temperatures. Finally, a preliminary static corrosion test in an acidic medium, at 90 °C, was performed for the glasses chemical durability.

2. Experiments

The glasses were prepared using the method described by Quintas, et al. [8] and Chouar, et al. [15], which consisted in a two melting/casting steps.

The following commercial reagents were employed: Al_2O_3 (Fluka), B_2O_3 (Purity ≥ 99%), CaO (Merck, ≥ 97%), CeO_2 (Aldrich, 99.999%), CrO_3 (Merck, ≥ 99%), Fe_2O_3 (Merck, ≥ 99%), K_2CO_3 (Merck, ≥ 99%), Li_2O (Merck, ≥ 99%), MgO (Flucka, ≥ 97%), MnO_2 (Merck), MoO_3 (Merck, ≥ 99.5%), Nd_2O_3 (Fluka, ≥ 99.9%), P_2O_5 (Merck, ≥ 98%), Pr_6O_{11} (Merck, ≥ 99%), SiO_2 (Prolabo), Ta_2O_5 (Merck, ≥ 99%), TiO_2 (Merck, ≥ 99%),V_2O_5 (Labosi), WO_3 (Merck), Y_2O_3 (Merck, ≥ 99%), Yb_2O_3 (Aldrich, 99.9%), ZrO_2 (Aldrich, 99%). REE elements' oxides are dried over night at 1,000 °C, and the other oxides at 400 °C, for the same time. This step ensures a good homogeneity of the products, and confers them isotropic properties. BaO, Er_2O_3, La_2O_3 and NiO are prepared by calcination at 450 °C of $BaNO_3$ (Fluka, 99.6%), $ErN_3O_9 \cdot 5H_2O$ (Acros Organics, 99.9%), $La(NO_3)_3 \cdot 6H_2O$ (Fluka, 99.99%), and $Ni(NO_3)_2 \cdot 6H_2O$ (Fluka, 99.6 %), respectively.

The whole of reagents are then milled in a Retsch Gmbh 5657 automatic agath mortar, until the particles granulometry becomes lower than 20 µm. Six powder mixtures were prepared with Ce contents ranging between 0 and 15 wt.%. The glasses are named glass 1 to 6, for a Ce content of 0, 3, 6, 9, 12 and 15 wt.%, respectively. A batch of 30 g was prepared for each glass, having the chemical compositions gathered in Table 1. The mixtures are homogenized in an Automatic Sieve Shaker D403 during 6 h, to achieve a good particles' dispersion.

Table 1 Chemical composition of the studied glasses.

Glass	1	2	3	4	5	6
Ce content(wt.%)	0	3	6	9	12	15
Al_2O_3	13.0005	13.004	14.04	12.04	11.74	11.54
B_2O_3	0.80	0.80	0.40	0.40	0.40	0.30
BaO	0.60	0.60	0.50	0.50	0.50	0.60
CaO	8.74	8.33	7.02	7.02	6.42	6.22
CeO_2	0.00	3.01	6.02	9.03	12.04	15.05
CrO_3	0.10	0.40	0.10	0.10	0.10	0.10
Er_2O_3	1.51	1.31	1.21	1.10	1.00	1.00
Fe_2O_3	1.41	1.31	0.95	0.95	0.95	0.95
K_2O	0.82	0.67	0.61	0.61	0.61	0.61
La_2O_3	0.50	0.50	0.40	0.40	0.40	0.40
Li_2O	4.52	4.22	3.51	3.51	3.41	3.31
MgO	5.52	5.72	4.52	4.52	4.31	4.11
MnO_2	0.40	0.20	0.30	0.30	0.30	0.30
MoO_3	2.71	2.81	2.51	2.51	2.41	2.21
Nd_2O_3	1.51	1.20	0.80	0.80	0.80	0.80
NiO	0.70	0.60	0.15	0.15	0.15	0.15
P_2O_5	0.60	0.40	0.30	0.30	0.30	0.30
Pr_6O_{11}	0.70	0.10	0.40	0.40	0.40	0.40
SiO_2	47.18	47.16	48.14	48.14	47.14	45.13
Ta_2O_5	0.40	0.20	0.20	0.20	0.20	0.20
TiO_2	3.52	4.11	3.31	3.01	2.81	2.71
V_2O_5	0.70	0.10	0.30	0.30	0.20	0.20
WO_3	1.00	0.80	1.00	0.80	0.80	0.80
Y_2O_3	1.00	0.50	1.00	0.80	0.80	0.80
Yb_2O_3	0.20	0.10	0.30	0.30	0.30	0.30
ZrO_2	1.81	1.81	2.01	1.81	1.51	1.51
Total (wt.%)	100	100	100	100	100	100

For each composition, the powders mixtures are melted and refined at 1,350 °C in air, for 5 h, in a platinum crucible using a Carbolite RHF 1600 furnace. The heating step was of 5°/min. The melted glasses are poured in water, grinded with a heavy alloy pestle; throw a cotton fiber tissue, to avoid glasses contamination. There are then milled in a Retsch Gmbh 5657 automatic agath mortar. The grinded glasses are re-melted in platinum crucibles, with the same heating cycle, at 1,350 °C for 5 h, in order to obtain much homogeneous glasses after a second melting. The melts are heated at 1,380 °C for 15 min, to decrease the melts viscosities and facilitate casting; and then casted in steel cylindrical moulds, heated at 350 °C, in order to relieve internal stresses (Fig. 1). The cylindrical materials final sizes are of 1 cm diameter with various heights, ranging between 0.8 and 1.5 cm.

3. Results and Discussion

3.1 Optimization of the Synthesis Parameters

The aim of this study is to obtain a nuclear glass at a melting temperature as low as possible. Thus, several operating parameters have been optimized, namely: the starting amount of the reagents mixture batch, the milling/melting step, and the melting temperature.

3.1.1 Optimization of the Starting Amount of the Reagents Mixture Batch

The Several melting experiences were performed in a 20 mL platinum crucible, with initial reagent mixtures ranging between 10 and 25 g, at a relatively high melting temperature of 1,420 °C. One can remark that at least 25 g of the starting mixture were required to perform a satisfactory pouring, without an early solidification of the melt.

3.1.2 Introduction of a Supplementary Step of Milling/Melting

Several preliminary melting tests at 1,350, 1,380, 1,400 and 1,420 °C evidenced the agitation difficulty during the melting stage.

Thus, and as recommended in the literature [8], we introduce a second melting step on the first casted melt, finely grinded, in order to get homogeneous synthesized glasses; nuclear glasses requiring isotropic properties, which confer them the chemical, thermal and nuclear durability, needed for their safe disposal.

3.1.3 Optimization of the Melting Temperature

The isothermal melting stage of the glasses fabrication process has been optimized for several glasses chemical compositions, as follow:

For the glass 1, which is a Ce-free glass, many melting tests at 1,200 °C during 2, 3 and 5 h show that the product is not pourable and solidifies quickly when it is in contact with air.

The glasses with 0 wt.%, 3 wt.% and 6 wt.% of Ce (glasses 0, 1 and 2, respectively) have entirely melted at 1,300 °C after 5 h of an isothermal heat. The melted produced were viscous, and difficult to pour. The melting temperature was then increased to 1,350 and 1,380 °C, and the melted mixtures were poured easily in cylindrical final shapes.


(a) (b)

Fig. 1 Pictures of (a) the fabricated nuclear glasses and (b) the casting mould.

Finally, we choose a melting temperature of 1,350 °C with 5 h isothermal step, for the whole of glass compositions.

3.2 Glasses Characterizations

The synthesized glasses have been characterized by their physical, mechanical, microstructural and chemical properties.

3.2.1 Physical and Mechanical Characterization

3.2.1.1 Densities Measurements

The glasses density was measured by both Archimedes and the geometrical methods.

(1) Archimedes density

Archimedes densitiy (ρ_A) gives the specific gravity of the several glasses. It was performed at "Unité de Recherche Matériaux, Procédés et Environnement (UR-MPE) of Boumerdes University" using a hydrostatic balance, with water as immersion liquid. For each sample, three consecutive measures were made. The results are mean values and are given in Table 2.

Table 2 Archimedes densities of the studied glasses.

Glass No.	Ce content (wt.%)	ρ_A (g/cm^3)
1	0	2.8268
2	3	2.8523
3	6	2.8637
4	9	2.9525
5	12	2.9648
6	15	3.0489

One can remark that the obtained densities are high values. The glasses density often increases with the heavy elements content. Then, the substitution of Ca^{2+} by La^{3+} or Y^{3+} leads to this rise [44].

Our results are similar to those of Lassalle et al. [45], which are comprised between 2.8 and 3.0 g/cm^3. Quentas, et al. [14] also report the increase of the glass density with the atomic weight of the rare earth dopent cation. They report densities ranging from 2.710 to 2.946 g/cm^3, for Y-doped to Lu-doped glasses, respectively.

(2) Geometrical densities

The glasses geometrical density (ρ_g) gives the macroscopic density of the glass bulk, the samples shape being cylindrical. The results are summarized in Table 3.

Table 3 The geometrical density of the glasses.

Glass No.	Ce content (wt.%)	ρ_g (g/cm^3)
1	0	2.2795
2	3	2.4167
3	6	2.3445
4	9	-
5	12	2.2661
6	15	2.7104

The samples densities are comprised between 2.2661-2.7104 g/cm^3, and rises slightly with the Ce content. For the first three glasses, the density seems to be constant. The geometrical density was not measured for the glass number 3, which has no accurate shape.

3.2.1.2 Vickers Microhardeness

Vickers microhardeness (*H*) was measured using a MHT-10 apparatus, equipped with a Carl Zeiss Hall 100 microscope. For an applied force of 10 N, the glasses Vickers microhardenesses are given in Table 4.

The synthesized glasses have satisfactory hardenesses. The glasses microhardenesses rise with the Ce content from 5,971 MPa to 8,211 MPa. These values are consistent with those given by Bonfils, et al. for R7T7 glass which is about 5,924 MPa [46]. The authors demonstrate that the glasses hardeness is not influenced by the glass composition; because under irradiation several studied glasses decrease in hardeness until 30% to 35% of their initial value and then stabilize at constant indentations.

3.2.2 Microstructural Characterization

3.2.2.1 Molar Volumes

The volume filled by one mole of glass, V_m, is calculated using the mathematical relation:

$$V_m = \Sigma xi \cdot Mi/\rho_A$$

where *Mi* are the molar weight and *xi* the molar fraction of I oxide, in percentage. ρ_A is the glass density.

The glass oxygen molar volume, V^0_m is the volume

Table 4 Vickers microhardenesses of the glasses.

Glass N°	1	2	3	4	5	6
Ce content (wt.%)	0	3	6	9	12	15
H (HV)	608.9	745.3	749.75	806.01	862.27	837.23
H (MPa)	5,971	7,309	7,353	7,905	8,456	8,211

Table 5 The molar volumes of the synthesized glasses.

Glass No.	Ce content (wt.%)	V_m ($cm^3 \cdot mol^{-1}$)	V^0_m ($cm^3 \cdot mol^{-1}$)
1	0	23.38	12.73
2	3	23.22	12.67
3	6	24.03	12.75
4	9	23.47	12.55
5	12	23.83	12.70
6	15	23.72	12.63

filled by one mole of oxygen. It is calculated from the following relation:

$$V^0_m = \Sigma x_i \cdot M_i / \rho_A \cdot \Sigma ni \cdot x_i$$

where Mi are the molar weight and xi the molar fraction of i oxide, in percentage. ρ_A is the glass density, and n_i is the number of oxygen belonging to the basic formula unit of the considered i oxide [15, 31, 47].

The glasses molar volumes and oxygen molar volumes calculated results are given in Table 5.

The glasses oxygen molar volumes are representative values. There are all ranging in the interval between 12.55 and 12.75 cm^3/mol, and thus are quite independent of the Ce content in the glasses. This indicates that there is no significant volatilization of the glasses compounds, as alkali elements (Na, Ba, etc.) during the melting process.

Indeed, a decrease of V^0_m indicate the shrinkage of the oxygen network provoked by the remove of Na^+ monovalent cations from the glassy network, and the replacement of Na^+ by Ca^{2+} cations, which have higher linkage forces compared to Na^+ cations, but are less numerous in the glass network [48].

3.2.2.2 X-Ray Diffraction

For the six studied compositions glasses, X-ray diffraction (XRD) analysis was conducted by a Philips X'Pert PRO apparatus, operating at CuKα1 wavelength ($\lambda_{K\alpha 1}$ = 0.15406 nm). The analytical parameters were as follow: V = 40 kV and I = 40 mA; a 2θ scanning from 3° to 80°, with a scanning speed of 0.0701°/s. The XRD data are collected at room temperature on milled and sieved glass samples, with a mean size of 80 µm. For this, a 5657 Gmbh Retsch automatic agath mortar was used. The crystalline phase (s) identification was done using the Philips X'Pert plus 2004 software [49]. The obtained diffractograms are gathered on Figs. 2a-2f.

The spectra analyses confirm the amorphous structure of the glasses, with no residual crystalline phase.

3.2.2.3 Differential Thermal Analysis (DTA)

In order to determine the glass transformation, T_g, cristallization, T_c, and melting, T_m, temperatures; and to study the glass crystallization behavior we performed the differential thermal analyses (DTA) of the several studied glasses.

Measurements were performed under air on parent glasses with the help of a NETZSCH STA 409 thermal analysis apparatus at the laboratory of "Unité de Recherche Matériaux, Procédés et Environnement (UR-MPE)", following the tangent method, using the row data for a maximum of accuracy.

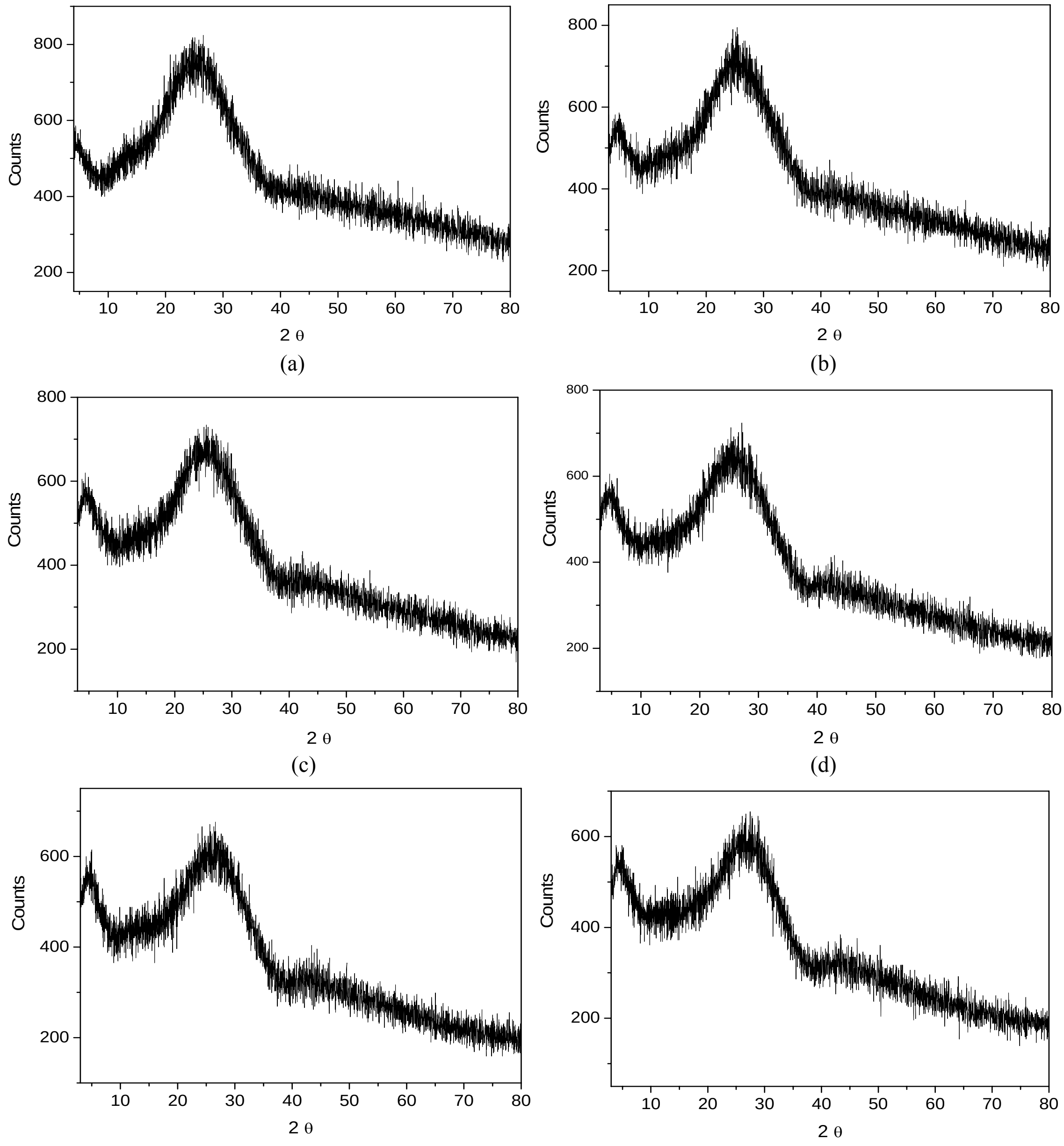
The operating conditions are gathered in Table 6.

T_g was determined using the onset of the corresponding DTA endothermic effect. The same reasoning was followed for both the crystallization (T_c) and the melt beginning (T_m) temperatures of the samples.

The DTA data are reported in Table 7. They are extracted from the row data of the DTA diagrams (Figs. 3a-3f).

Table 6 DTA measurements analytical conditions.

Atmosphere	Air
Crucible	Alumina
Weight samples (mg)	11 à 25
Granulometry (μm)	80-125
Reference compound	Alumina (α-Al_2O_3)
Heating steps	15 °C/min until 1,000 °C 5 °C/min until 1,450 °C Stage of 600 s at 1,450 °C
Cooling step	15 °C/min until 20 °C
Type of thermocouple	Type S



(a) (b) (c) (d) (e) (f)

Fig. 2 XRD diagrams of the studied glasses. (a) Ce-free glass; (b) 3 wt.% Ce glass; (c) 6 wt.% Ce glass; (d) 9 wt.% Ce glass; (e) 12 wt.% Ce glass and (f) 15 wt.% Ce glass.

The DTA data are reported in Table 7. They are extracted from the row data of the DTA diagrams (Figs. 3a-3f).

One can note that the glass transition temperature diminishes slightly from 913 to 658 °C, when the glass Ce concentration rises, and the high melting point elements, such as Al, Zr and Ti, decrease, except for the glass 4, which contains 12 wt.% of CeO_2.

However, as required for a waste package, these temperatures are below the waste package temperatures (400 °C for R7T7, which have a glass temperature about 515 °C after the melt casting [34]).

3.2.2.4. Scanning Electron Microscopy (SEM) Analysis

The glasses microstructure was revealed by both the bulk and surface SEM observations. The SEM analysis was conducted on a Philips XL30 microscope. A typical micrograph of the glasses is depicted on Fig. 4.

The micrography confirms the homogeneity of the glasses for the different Ce contents.

The SEM results confirm the XRD data, and thus the amorphous nature of the products. No crystalline micro-grains can be visualized, in the bounds of accuracy of these spectroscopic methods.

Transition metals and lanthanides are generally highly soluble in silicate glasses and do not tend to limit the loadings of typical HLWs in glass. However, with advanced separations technologies, in the future, high-concentration of transition metals or lanthanides streams may be generated for immobilization in glass. In these cases the loadings are likely to be limited by transition metals and lanthanides, but are still expected to be high relative to current loading levels [33]. Crum et al. [51] describe the issues and summarize the loadings for these wastes.

3.2.2.5. Optical Absorption Analysis

In order to observe the optical transitions to excited states from the lowest and from higher Stark doublets of $^4I_{9/2}$ ground state of Nd, optical absorption spectra of Nd^{3+} ions were recorded with a Uv-vis-NIR Varian Cary 500 double beam spectrometer at T = 300 K on transparent polished thin glass samples. The glasses thicknesses do not exceed 1 cm. The optical absorption spectra are given in Figs. 5a-5f.

The optical absorption spectra show that the glasses do not absorb in the UV area. In the visible spectrum, the transitions from the $^4I_{9/2}$ ground state of Nd^{3+} ions to the excited levels appears in the low Ce content glasses. For the 12 wt.% and 15 wt.% glasses, these transitions are less significant, indicating that the Ce cations replaces progressively the Nd cations in the glass network. For the whole of glasses, the absorption bands are at the same positions (about 584, 750, 800 and 892 nm), indicating that the Nd-O bond covalency is the same whatever the Ce contents in the glasses.

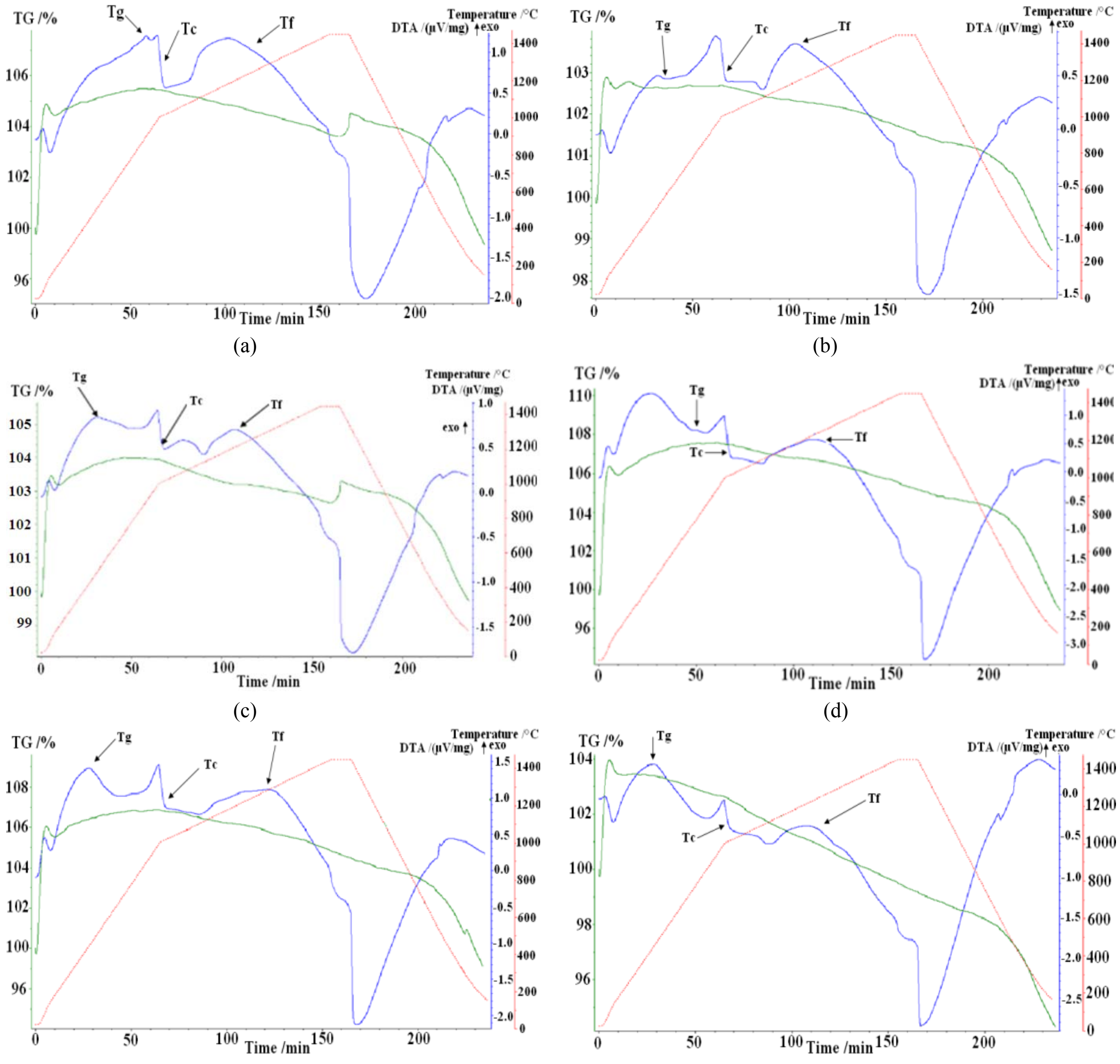
In a chemical point of view (charges and bonds), the chemical environment of Nd seems to be not affected because the $^4I_{9/2}\rightarrow{}^2G_{7/2}$, $^4G_{5/2}$ transition is unchanged for all the glasses with different Ce concentrations.

3.2.3 Chemical Characterization

A batch static leach test was performed on the whole of aluminosilicated glasses. The glasses cylindrical pellets are weighed in order to reach a constant solid/liquid ratio equal to 1/50. The leaching

Table 7 Variations of the temperatures of glass transformation (T_g) cristallisation (T_c) and melting (T_m) as a function of the Ce content in the glasses.

Glass No.	Ce content (wt.%)	T_g (°C)	T_c (°C)	T_m (°C)
1	0	913.15	1,010.43	1,188.80
2	3	802.93	1,006.59	1,181.03
3	6	740.13	1,010.45	1,203.80
4	9	733.64	1,017.56	1,217.30
5	12	658.42	1,019.79	1,289.69
6	15	801.20	1,015.04	1,223.98



(a)
(b)
(c)
(d)
(e)
(f)

Fig. 3 DTA diagrams of the studied glasses, (a) Ce-free glass; (b) 3 wt.% Ce glass; (c) 6 wt.% Ce glass; (d) 9 wt.% Ce glass; (e) 12 wt.% Ce glass and (f) 15 wt.% Ce glass.

is performed at 90 °C, in HCl-1N (MERCK) aqueous solution, at the atmosphere pressure. Each test is conducted in dark glass closed bottles during 5 days. The leachates are then analyzed by a Jobin Yvon 32 ICP spectrometer. The ICP outcomes are summarized in Table 8. The leachates concentrations are in ppm.

One can remark the presence of Ca, Si, and Zr, in very weak concentrations, estimated to few ppms, and traces of Li, Mn, Mg, Mo, Ba and Al, in all the samples. A deeper identification of the leachates was not

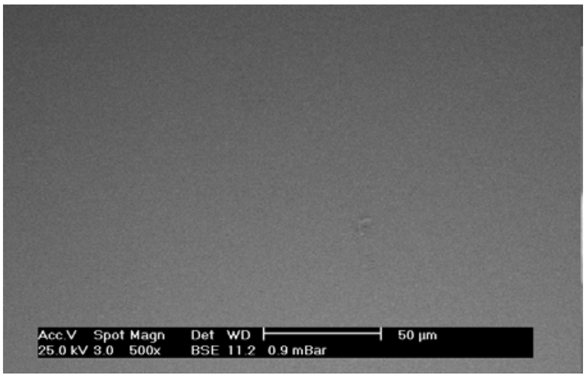
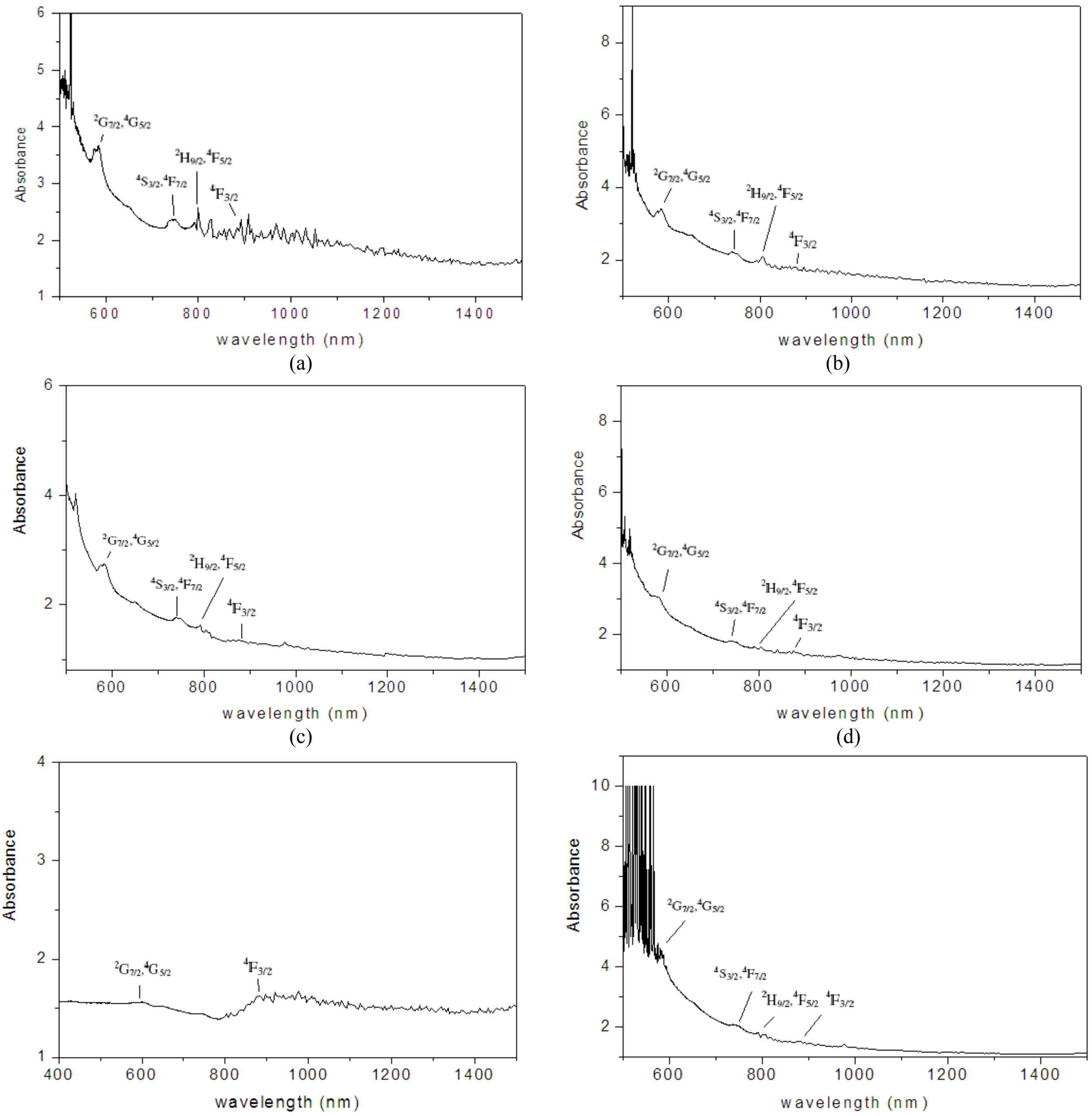


Fig. 4 A typical SEM micrograph of the studied glasses.



(a) (b) (c) (d) (e) (f)

Fig. 5 Optical absorption spectra of the studied glasses (a) the Ce-free glass; (b) the 3 wt.% Ce glass; (c) the 6 wt.% Ce glass; (d) the 9 wt.% Ce glass; (e) the 12 wt.% Ce glas and (f) the 15 wt.% Ce glass.

possible. However, these preliminary results reveal a suitable chemical stability of the studied glasses, because these last release few amounts of their components.

4. Conclusions

The aim of this study is the synthesis and characterization of an aluminosilicated glass, in the system: SiO_2-Al_2O_3-CaO-MgO-ZrO_2-TiO_2, at a melting temperature as low as possible. The glass matrix should be able to incorporate high-level waste in its amorphous network.

The effect of Ce content (actinide surrogate) on the structure of the glass was studied for Ce concentrations

Table 8 ICP analyses of the glass leachates.

Glass N°	1	2	3	4	5	6
Ce content (wt.%)	0	3	6	9	12	15
Al	Tr*	-	-	Tr	-	Tr
Ca	12	-	-	4	-	
Mg	Tr	-	-	Tr	-	Tr
Mn	Tr	-	-	Tr	-	Tr
Li	Tr	-	-	Tr	-	Tr
Si	11.5	-	-	11	-	-
Zr	12	-	-	Tr	-	16.5
Mo	Tr	-	-	Tr	-	Tr
Ba	Tr	-	-	Tr	-	Tr

*: Tr: traces: < 4 ppm.

in the glass ranging between 0% and 15%. Thus, in order to reach a melting temperature as low as possible, the following synthesis parameters were optimized: the initial amount of reagents, the melting/milling step, and the melting temperature. Several melting tests have been conducted. Many initial amounts of oxides mixtures have been melt at a high melting temperature. It has been demonstrated that at least 20 g of the batch mixture oxide are required to pour the melt without an early solidification. Also, many preliminary melting experiments at 1,350, 1,380 and 1,400 °C, show the difficult stirring of the mixture during the melting step, leading to perform a second melting stage in the glass fabrication process, after pouring and milling the first poured glass, in order to ensure a good homogeneity in the bulk glass.

The melting temperature was optimized for different glass compositions; the temperatures of 1,350 and 1,380 °C permit a good pouring of the glasses. Consequently, the temperature of melting was fixed to 1,350 °C, during 5 h.

By this synthesis method, we obtained a nuclear glass with good physico-chimical properties: XRD analysis show an amorphous structure without residual crystalline phases, for the whole of glasses, whatever the Ce concentration in the glasses. This result was confirmed by SEM analyses; the synthesized glasses have an homogeneous microscopic structure. The geometrical density of the glasses is similar to that of known nuclear glasses, as R7T7 glass density. It increases with the Ce content in the glasses.

The glasses Archimedes densities often increase with the heavy elements content. Then, the substitution of Ca^{2+} by La^{3+} or Y^{3+}, leads to this increase, because we introduce heavy elements in the structure.

The synthesized glasses have satisfactory hardenesses. The glasses microhardenesses rise with the Ce content from 5,971 MPa to 8,211 MPa.

The differential thermal analyses gave the temperatures characterizing the phase's changes in the glasses: the glass transition, the crystallization and the melt starting temperatures. The glass transition temperature diminishes from 913 to 658 °C, when the glass Ce concentration rises, and the high melting point elements, such as Al, Zr and Ti, decrease, except for the glass 4, which contains 12 wt.% of CeO_2; these temperatures being below the waste package temperatures (≈ 400-450 °C). The crystallization temperature is independent of the glasses Ce content and the melt starting temperatures are close each other for the whole of glasses. The optical absorption spectroscopy structural study shows that the Nd cations environment is not altered by the Ce concentration in the glasses.

A static corrosion test in an acidic medium, at 90 °C, was performed for a first assessment of the glasses chemical durability. It leads to low dissolutions of Si, Ca and Zr, estimated to few ppms (< 20 ppm), and traces of Li, Mn, Mg, Mo, Ba and Al. This preliminary survey allows concluding on the possible utilization of this glass formula for the nuclear waste confinement. Out coming investigations are in course for further glasses network characterizations, jointly with Zr and Ti based ceramic-glasses germinations.

Acknowledgments

The authors acknowledge Daniel Caurant from ENSCP of Paris (UMR-CNRS 7574), for the usefull documentation he provided us.

References

[1] M.I. Ojovan, W.E. Lee, An Introduction to Nuclear Waste Immobilization, Elsevier Ltd., Oxford, 2005, p. 214.

[2] R.J. Short, Incorporation of molybdenum in nuclear waste glasses, Ph.D. Thesis, University of Sheffield, 2004.

[3] D. Caurant, O. Majerus, P. Loiseau, I. Bardez, N. Baffier, J.L. Dussossoy, Crystallization of neodymium-rich phases in silicate glasses developed for nuclear waste immobilization, Journal of Nuclear Materials 354 (1-3) (2006) 143-162.

[4] B. Grambow, Nuclear waste glasses: How durable?, Elements 2 (6) (2006) 357-364.

[5] G. De Combarieu, Altération du verre de confinement de déchets type R7T7 en condition de stockage géologique, Ph.D. Thesis, University of Paris XI, 2007.

[6] A. Zaoui, Academy of sciences. materials for the nuclear, RST report No. 5, Tec. and Doc. (eds.) Lavoisier, Paris, 2000.

[7] M.I. Ojova, O.G. Batyukhnova, Glasses for nuclear waste immobilization, in: WM'07 Conference, 2007, p. 15.

[8] N. Chouard, D. Caurant, O. Majérus, J.L. Dussossoy, A. Ledieu, S. Peuget, et al., Effect of neodymium oxide on the solubility of MoO_3 in an aluminoborosilicate glass, Journal of Non-Crystalline Solids 357 (14) (2011) 2752-2762.

[9] S. Gavarini, M.J. Guittet, P. Trocellier, M.G. Soyer, F. Carrot, G. Matzen, Cerium oxidation during leaching of CeYSiAlO glass, Journal of Nuclear Materials 322 (2-3) (2003) 111-118.

[10] S. Gavarini, Chemical durability and radiation damage of quaternary glasses LnYSiAlO (Ln = La or Ce), candidate matrix for the immobilization of minor trivalent actinides, Ph.D. Thesis, Orleans University, 1992.

[11] S. Gavarini, B. Boizot, F. Carrot, P. Trocellier, G. Matzen, Dissolution of LnYSiAlO glass (Ln = La or Ce) in aqueous media: 3. Influence of beta irradiation on structure and hydrolysis mechanisms, Journal of Non-Crystalline Solids 332 (1-3) (2003) 141-152.

[12] S. Gavarini, F. Carrot, G. Matzen, P. Trocellier, Dissolution of LnYSiAlO glass (Ln = La or Ce) in aqueous media: 1. Influence of the pH on hydrolysis mechanisms and kinetics, Journal of Non-Crystalline Solids 332 (1-3) (2003) 115-127.

[13] S. Gavarini, F. Carrot, P. Trocellier, G. Matzen, Dissolution of LnYSiAlO glass (Ln = La or Ce) in aqueous media: 2. Influence of heavy ion irradiation on mechanisms and rate of hydrolysis, Journal of Non-Crystalline Solids 332 (1-3) (2003) 128-140.

[14] A. Quintas, D. Caurant, O. Majérus, J.L. Dussossoy, T. Charpentier, Effect of changing the rare earth cation type on the structure and crystallisation behaviour of an aluminoborosilicate glass**,** European Journal of Glass Science Technology B 49 (4) (2008) 192-197.

[15] A. Quintas, O. Majérus, D. Caurant, J.L. Dussossoy, P. Vermaut, Crystallization of a rare earth-rich aluminoborosilicate glass with varying CaO/Na_2O ratio, Journal of the American Ceramic Society 90 (3) (2007) 712-719.

[16] A. Quintas, T. Charpentier, O. Majérus, D. Caurant, J.L. Dussossoy, P. Vermaut, NMR study of a rare-earth aluminoborosilicate glass with varying CaO-to-Na_2O ratio, Applied Magnetic Resonance 32 (4) (2007) 613-634.

[17] E. Schmieman, W.E. Johns, Vitrification publication bibliography, PNNL report-10967, Richland, US Department of Energy, Home page, http://www.iaea.org/inis/collection/nclcollectionstore/_public/30/024/30024547.pdf (accessed Sep. 20, 2012).

[18] A. Abdalkrim, Contribution to the study of the effects of alpha-irradiation on the nuclear glasses, Ph.D. Thesis, University of Paris 07, 2001.

[19] J.J. Mazer, Temperature effects on waste glass performance, ANL report ANL-91/17, Feb. 1991, US DO, Argonne, Illinois.

[20] G.V. Hutson, The Nuclear Fuel Cycle: From Ore to Waste, P.D. Wilson, ed., Oxford University Press, Oxford, 1996, pp. 161-183.

[21] C.M. Jantzen, Advances in Ceramics, Nuclear Waste Management 2, D.E. Clark, W.B. White and A.J. Machiels, ed., American Ceramic Society, Westerville OH, 1986, pp. 157-165.

[22] I.W. Donald, B.L. Metcalfe, R.N. Taylor, Review the immobilization of high level radioactive wastes using

ceramics and glasses, Journal of Materials Science 32 (22) (1997) 5851-5887.

[23] N.C. Hyatt, W.E. Lee, R.J. Hand, M.I. Ojovan, P.K. Abraitis, C.R. Scales, Vapour phase hydration of magnox waste glasses, in: 2002 MRS Fall Meeting, Symposium 2, 2003, pp. 183-188.

[24] S. Morgan, R.J. Hand, N.C. Hyatt, W.E. Lee, Interactions of simulated high level waste (HLW) calcine with alkali borosilicate glass, in: 2003 MRS Fall Meeting, Symposium 2, 2004, pp. 151-156.

[25] N.C. Hyatt, W.E. Lee, R.J. Hand, P.K. Abraitis, C.R. Scales, Vapour phase hydration of blended oxide-magnox waste glasses, in: 2003 MRS Fall Meeting, Symposium 2. 2004, pp. 181-186.

[26] N.C. Hyatt, K.J. Taylor, F.G. Gibb, W.E. Lee, R.J. Hand, P.K. Abraitis, et al., A study of Magnox waste glass under conditions of high temperature, very deep, geological disposal, in: 2003 MRS Fall Meeting, Symposium 2, 2004, pp. 199-204.

[27] B. Luckscheiter, M. Nesovic, Development of glasses for the vitrification of high level liquid waste (HLLW) in a joule heated ceramic melter, Waste Management 16 (7) (1997) 571-578.

[28] A. Ghezal, Elaboration and experimental study of the borosilicate glass GP 98/12 for the vitrification of the radioactive wastes of Kfkarlsruhe centre (R.F.A.), Ph.D. Thesis, Commissariat aux Energies Nouvelles of Algiers, 1987.

[29] Hj. Matzke, L. Kahl, JL. Routbort, J. Saidl, The effect of composition and radiation on the hertzian indentation behavior of nuclear waste glasses, http://www.osti.gov/bridge/servlets/purl/6002196-vxmkvg/6002196.pdf (accessed Oct. 15, 2012).

[30] H. Kamizono, T. Sagawa, S. Tashiro, Continouos-flow leach tests of simulated high-level wasteglass in synthetic basalt groundwater, Waste Management 9 (3) (1989) 189-194.

[31] A. Quintas, Study of the structure and the behavior under crystallization of a rare-earth-aluminosilicate nuclear glass, Ph.D. Thesis, University of Pierre et Marie Curie, Paris 6, 2007. (in French)

[32] A. Abbas, Contribution to the study of alpha radiations effects on nuclear glasses, Ph.D. Thesis, University of Paris, 2001. (in French)

[33] J.D. Vienna, Nuclear waste vitrification in the united states: Recent developments and future options, International Journal of Applied Glass Science 1 (3) (2010) 309-321.

[34] X. Orlhac, Study of the nuclear glass thermal stability. Modeling of its long term evolution, Ph.D. Thesis, Montpellier II University, 1999. (in French)

[35] W. Grünewald, G. Roth, W. Tobie, K. Weiβ, S. Weisenburger, The role of the platinum group elements ruthenium, rhodium and palladium in the vitrification of radioactive high level liquid waste using joule heated ceramic lined waste glass melters, Glass Technology: European Journal of Glass Science and Technology A 49 (6) (2008) 266-278.

[36] P. Hrma, J. Matyas, D.S. Kim, Evaluation of crystallinity constraint for HLW glass processing, in: 104th Annual Meeting of the American Ceramic Society, 2002, pp. 133-141.

[37] P.B. Rose, D.I. Woodward, M.I. Ojovan, N.C. Hyatt, W.E. Lee, Crystallization of a simulated borosilicate high-level waste glass produced on a full-scale vitrification line, Journal of Non-Crystalline Solids 357 (15) (2011) 2989-3001.

[38] P. Loiseau, D. Caurant, I. Bardez, O. Maje´rus, N. Baffier, C. Fillet, Zirconolite-based glass-ceramics for actinides immobilization: Effects of glass composition and of actinides stimulant nature, in: 2002 MRS Fall Meeting, 2003, pp. 281-287.

[39] P. Loiseau, D. Caurant, N. Baffier, L. Mazerolles, C. Fillet, Glass-ceramic nuclear wasteforms obtained from SiO_2-Al_2O_3-CaO-ZrO_2-TiO_2 glasses containing lanthanides (Ce, Nd, Eu, Gd, Yb) and actinides (Th): Study of internal crystallization, Journal of Nuclear Materials 335 (1) (2004) 14-32.

[40] C.W. Kim, C.S. Ray, D. Zhu, D.E. Day, D. Gombert, A. Aloy, et al., Chemically durable iron phosphate glasses for vitrifying sodium bearing waste (SBW) using conventional and cold crucible induction melting (CCIM) techniques, Journal of Nuclear Materials 322 (2-3) (2003) 152-164.

[41] J.R. Grover, The solidification of high-level radioactive wastes, IAEA Bulletin 20 (4) (1977) 23-29.

[42] S. Komarneni, R. Roy, D.M. Roy, Evaluation of SrMoO/sub 4/in repository simulating tests, Nuclear Technology 62 (1) (1983) 71-74.

[43] E. Schiewer, H. Rabe, S. Weisenburger, The material balance-scientific fundamentals for the quality assurance of vitrified waste, in: 1981 MRS Fall Meeting, 1982, pp. 289-297.

[44] J. Hiet, Structural patterns in model glasses for actinides disposal, Ph.D. Thesis, University of Orléans, 2009. (in French)

[45] O.L. Herraud, M. Matecki, B. Glorieux, V. Montoullout, N. Sadiki, J.L. Dussossoy, Effect of the addition of Na_2O on the thermal stability of rare-earth reach aluminosilicated glasses, in: Materials International Congres, 2006, p. 10. (in French)

[46] J. de Bonfils, Radiations effects on the structure of borosilicated glasses: Long-term behavior of nuclear waste disposal, Ph.D. Thesis, University of Lyon 1, 2007,

(in French)

[47] J. Barton, C. Guillemet, The Glass: Science and Technology, EDP Sciences, Les Ulis Cedex 2005. (in French)

[48] A. Quintas, O. Majerus, D. Caurant, J.L. Dussossoy, P. Vermaut, Crystallization of a rare earth-rich aluminoborosilicate glass with varying CaO/Na_2O ratio, Journal of the American Ceramic Society 90 (3) (2007) 712-719.

[49] JCPDS data Philips X'Pert High Score Package, Diffraction data CD-ROM, International Center for Diffraction Data, Newtown Square PA, 2004.

[50] J.V. Crum, A. L. Billings, J. Lang, J.C. Marra, C. Rodriguez, J.V. Ryan, et al., Baseline glass development for combined fission products waste streams, Advanced fuel cycle initiative, PNNL-18524 technical report, U.S. Department of Energy, Washington, DC, 2009.

[51] Home Page, http://www.pnnl.gov/main/publications/external/technical_reports/PNNL-18524.pdf (accessed Dec. 23, 2012).