Study of The Effect of TiO₂ Addition On The Crystalline Phases, Structure and Chemical Durability of a Nuclear Glass Ceramic

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Study of the effect of TiO₂ addition on the crystalline phases, structure and chemical durability of a nuclear glass ceramic

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Abstract

This study focused on the effect of TiO₂ addition on the crystalline phases' formation, structure and chemical durability of a nuclear glass ceramic constituted by an aluminosilicate glass in the system: SiO₂-Al₂O₃-CaO-MgO-ZrO₂-TiO₂. The materials with four contents of TiO₂, ranging from 4.11 to 7.11 wt.%, are synthesized by a discontinuous method,. For the whole of materials, X-ray diffraction analysis allow identifying an aluminosilicate belonging to pyroxenes silicates family as a main phase, powellite and calzirtite. Both SEM and DTA analyses confirmed these results. The materials FTIR analysis reveals the glass ceramics complex chemical composition. MCC1 and MCC2 tests, performed on selected glass ceramic materials, indicate that the materials with 4.11 and 5.11 wt.% TiO₂ are the most durable against Si, Al, Mg and Ce elements release, in MCC2 test; The results make conclusions valuable on the selection of such glass ceramics as candidate for the disposal of high-level waste.

Keywords: Nuclear glass ceramics; TiO₂; XRD; SEM; Chemical durability

1. Introduction

The storage and disposal of radioactive waste (RW) is a difficult task. It necessitates meticulous control. One of the RW disposal principles is to follow the waste through all stages of its life: packaging, storage, disposal, and monitoring until its radioactivity is comparable to natural background radiation [1]. A multitude of sequestration materials have been studied, among glasses, minerals, and glass-ceramic matrices.

The main works dealing with this last kind of materials concern the sequestration of the whole of radionuclides present in a liquid waste solution [2,3].

Nevertheless, because of both their high chemical durability and high ability to incorporate specific radionuclides, several ceramic matrices such as zirconates, titanates and phosphates have been proposed for the immobilization of long-lived radionuclides such as minor actinides [4-6].

The ceramics elaboration processes are difficult to implement, and many glass-ceramics are also under study. They consist of crystals homogeneously distributed in a glass matrix, and exhibit increased performances. Both glass technology and the interesting confinement properties of crystalline ceramic phases will support research on glass-ceramics (noted: GC) matrices for RW sequestration. It have been demonstrated that different nucleating agents added to a chosen parent glass has an important role on the crystallization processes and on the physico-mechanical properties of a given GC [7, 8]. The effect of many nucleating agents such as ZrO_2 and TiO_2 on the crystallization, microstructure and durability properties of the prepared GC was reported in the literature [9-11].

Despite the significance of TiO_2 's role in the structure of silicate glasses, few studies have been conducted to date [12]. TiO_2 is known to be quite soluble in silicate melts. It decreases the melt glass viscosity [7]. TiO_2 addition influences the crystalline phase nature and the microstructure formed in the GC materials, and their physico-mechanical properties [13, 14]. Zhou et al. [15] noted that TiO_2 is often used to facilitate nucleation in silicate glass-ceramics systems. The effect of TiO_2 content on the crystalline phases, structure, and aqueous dissolution rate of iron phosphate based glass ceramic waste forms was studied in depth by Fu Wang et al. [16].

In this study, we have synthesized a TiO_2 -rich GC by a discontinuous method, consisting in a double melting at 1350 °C, followed by both a crystallization and crystal-growth, treatments at 564 and 1010 °C, respectively. In order to study the influence of the effect of TiO_2 addition

on the crystalline phases, structure and chemical durability of a nuclear GC, constituted by an aluminosilicate glass in the system: $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO-ZrO}_2\text{-TiO}_2$, the materials with four contents of TiO_2 , ranging from 4.11 to 7.11 wt.%, are synthesized. The materials densities are measured. The materials are characterized by many spectroscopic techniques (X-ray diffraction (XRD), scanning electronic microscopy (SEM), differential thermal analysis (DTA) and Fourier Transform Infrared Spectroscopy (FTIR)). In addition, chemical durability testing was carried out using the standard MCC-1 and MCC-2 static leach test methods at 25 °C and 90 °C, respectively.

2. Experimental

The GC chemical compositions are inspired from previous research studies [17, 18]. The samples are prepared with the following TiO_2 contents: 4.11, 5.11, 6.11 and 7.11 wt. % (Table 1). The corresponding glass ceramics are noted: GC1, GC2, GC3, GC4, respectively.

The employed commercial reagents are: Al_2O_3 (Fluka), B_2O_3 (Purity $\geq 99\%$), CaO (Merck, $\geq 97\%$), CeO_2 (Aldrich, 99.999 %), CrO_3 (Merck, $\geq 99\%$), Fe_2O_3 (Merck, $\geq 99\%$), K_2CO_3 (Merck, $\geq 99\%$), Li_2O (Merck, $\geq 99\%$), MgO (Fluka, $\geq 97\%$), MnO_2 (Merck), MoO_3 (Merck, $\geq 99.5\%$), Nd_2O_3 (Fluka, $\geq 99.9\%$), P_2O_5 (Merck, $\geq 98\%$), Pr_6O_{11} (Merck, $\geq 99\%$), SiO_2 (Prolabo), Ta_2O_5 (Merck, $\geq 99\%$), TiO_2 (Merck, $\geq 99\%$), V_2O_5 (Labosi), WO_3 (Merck), Y_2O_3 (Merck, $\geq 99\%$), Yb_2O_3 (Aldrich, 99.9 %), ZrO_2 (Aldrich, 99 %). REE elements' oxides are dried over night at 1000 °C, and the other oxides at 400 °C, for the same time. BaO , Er_2O_3 , La_2O_3 and NiO are prepared by calcination at 450 °C of BaNO_3 (Fluka, 99.6 %), $\text{ErN}_3\text{O}_9 \cdot 5 \text{H}_2\text{O}$ (Acros Organics, 99.9 %), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Fluka, 99.99 %), and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Fluka, 99.6 %), respectively.

The GC synthesis is carried out by a double melting at 1350 °C. This is necessary to ensure a complete homogenization of the oxides mixture, and thus isotropic properties of the final products. The melts are poured in a graphite cylindrical mold to obtain pellets. The nucleation step is carried out at a T_n temperature during 2h, such that: $T_n = T_g + 30^\circ\text{C}$, with T_g is the glass transition temperature. The crystal growth treatment (T_c) is performed at 1010 °C for 3 h, for the whole of materials. They are finally cooled to ambient air. Both T_g and T_c are deducted from the DTA (differential thermal analysis) diagram of the parent glass. The details of DTA diagrams are given in a previous study [17].

Table 1. Chemical composition of the synthesized GC materials

Oxides (wt. %)	Content (%)			
	GC1	GC2	GC3	GC4
TiO ₂	4.110	5.110	6.110	7.110
Al ₂ O ₃	13.040	13.040	13.040	13.040
B ₂ O ₂	0.800	0.800	0.800	0.800
BaO	1.600	1.600	1.600	1.600
CaO	9.000	9.000	9.000	9.000
CeO ₂	3.010	3.010	3.010	3.010
CrO ₃	0.400	0.400	0.400	0.400
Er ₂ O ₃	1.310	1.310	1.310	1.310
Fe ₂ O ₃	1.310	1.310	1.310	1.310
K ₂ O	0.670	0.670	0.670	0.670
La ₂ O ₃	0.500	0.500	0.500	0.500
Li ₂ O	4.220	4.220	4.220	4.220
MgO	3.500	3.500	3.500	3.500
MnO ₂	0.200	0.200	0.200	0.200
MoO ₃	2.810	2.810	2.810	2.810
Nd ₂ O ₃	1.200	1.200	1.200	1.200
NiO	0.600	0.600	0.600	0.600
P ₂ O ₅	0.400	0.400	0.400	0.400
Pr ₆ O ₁₁	0.100	0.100	0.100	0.100
SiO ₂	49.02	48.020	47.02	46.02
Ta ₂ O ₅	0.200	0.200	0.200	0.200
V ₂ O ₅	0.100	0.100	0.100	0.100
WO ₃	0.800	0.800	0.800	0.800
Y ₂ O ₃	0.500	0.500	0.500	0.500
Yb ₂ O ₃	0.100	0.100	0.100	0.100
ZrO ₂	0.500	0.500	0.500	0.500
Total	100.000	100.000	100.000	100.000

The materials Archimedes density is measured by pycnometer with water as a wetting liquid. The XRD analysis is carried out using a PANALytical X'Pert Pro diffractometer equipped with a copper anticathode, with $K\alpha_1 = 1.5418\text{\AA}$. The analyses are performed with a voltage of

40 kV and a current intensity of 40 mA, for 2θ ranging between 3 and 80 °. The ceramics phase identification is performed using a Philips X'Pert High Score Plus software, version 4.1 [19]. The materials microstructure is revealed by SEM microscopy observations, conducted on a Philips XL30 microscope.

The DTA analysis of GCs with different TiO₂ contents is performed using a NETZSCH STA 409 PC device on powders, for which 11 to 25 mg of powder in an alumina crucible, is heated in a 20% N₂–80% O₂ atmosphere at 15 °C/min up to 1050°C. The analyzes are carried out in the temperature range from 20 to 1450 °C.

The FTIR spectra of the samples are recorded from 4000 to 400 cm⁻¹ (wave numbers) by a standard KBr pellet method using a NICOLET 380 spectrometer. The pellets are prepared by mixing about 1–2 mg of glass powder with 100–200 mg of anhydrous KBr. The resolution of the device is 4 cm⁻¹. The spectra data processing is performed by the OMNIC software [20].

Two normalized IAEA static leach tests, MCC1 and MCC2, are performed on selected GC materials among the different TiO₂ contents [21]. The Surface/Volume ratio must be constant throughout the test and equal to 1/10. The GC materials cylindrical pellets are immersed in bi-distilled water, in dark glass bottles. MCC1 leach test is performed at ambient temperature (25 ± 1) °C in opened bottles, and MCC2 leach test in closed bottles, left in an oven heated at (90 ± 1) °C. For both tests, water samplings are performed at: 1, 3, 7, 14, 21, 36, 42 and 96 days. The materials kinetic of dissolution was performed following: Si, Al, Mg and Ce (actinide surrogate), elements dissolution in the leachates. The speed of dissolution is assessed by a PANALytical Magi-xPro wavelength dispersive X-ray fluorescence (WDXRF) spectrometer. The calibration curves of Si, Al, Mg and Ce elements are made from ICP/DCP standards of 1000 ± 4 mg/L for each element. The concentrations are all between 20 and 500 mg/L. All XRF analyses are performed on Myllar films of spectroscopic grade, on which 30 µL of each elemental standard solution is dropped.

The leachates concentrations C_i (g/cm³) for each i element (Si, Al, Mg or Ce) were deduced from WDXRF spectrometric calibration curves. The i element mass loss, N_{Li} (g/cm²), for each range of time, taken from the starting time of test, was calculated using the formula:

$$N_{Li} = C_i \cdot V_o / S_o \cdot F_i \quad (1)$$

where V : is the leaching mixture total volume (cm³), S is the initial sample surface effectively in contact with the leachate (cm²), and F_i is the i element weight fraction of the GC materials

pellet. $S(\text{cm}^2)$ is assumed to be constant during the tests, and C_i , the initial elemental concentrations in the leachate negligible.

Each i element mean normalized dissolution rate RL_i ($\text{g}/\text{cm}^2\text{d}^{-1}$) was deduced from the mathematical relation number (2). The Origin 8.5 Graph software was used for mathematical calculations.

$$RL_i = (C_i * V) / (f_i * S * \Delta t) \quad (2)$$

where: Δt : is the test duration in days (d).

3. Results and Discussion

3.1 Materials morphologies and densities

The 7.11wt.% TiO_2 content GC synthesis was not successful, this GC exhibits a very strong crystallization in the mass during melting.

For the other TiO_2 contents in the GC, after the crystallization step, the transparent glassy samples color turns into an opaque dark gray color with brown reflections (Fig. 1). On the cross-sections of the glass-ceramics, one can observe with the naked eye a relatively clear difference in appearance between the surface and the bulk of the samples, which has a darker gray color in the materials bulk compared to the surface color.

Fig. 1. General appearance of synthetic GC materials, (a) Parent glass after fusion and (b) Parent glass after crystallization

The density of the obtained GCs with different contents of TiO_2 is measured by the Archimedes method. The results are given in Table 2.

The GC density varies randomly with the TiO_2 content. In general, it is between 2.8913 and 2.9618 g/cm^3 , for GC' TiO_2 contents ranging from 4.11 to 6.11 %. Overall, the results are close to other nuclear GC materials densities reported in the literature. GC with diopside (PNC 62) and diopside (PNC 718) mineral phases, synthesized in a TiO_2 –rich borosilicate

glass melted at $T_f = 1185^\circ\text{C}$ and 1120°C , have densities of 3.01 and 2.94 g/cm^3 , respectively. Other GC materials with sphenes minerals formed in their structure have a density between 2.78 and 2.95 g/cm^3 [22]. A. Quintas et al. [23] have synthesized a GC from a Lu-aluminoborosilicate glass, for high-level waste (HLW) sequestration, at a melting temperature of 1350°C and a crystallization step at $T_c = 934^\circ\text{C}$. They report a density of 2.946 g/cm^3 . This value is close to our experimental values.

Table 2. The GC Archimedes density (ρ_A) as a function of TiO_2 content

GCs	GC1	GC2	GC3	GC4
TiO_2 (%)	4.11	5.11	6.11	7.11
ρ_A (g/cm^3)	2.9618	2.8913	2.9192	-----

T. Wakiyara et al. [24] studied the effect of TiO_2 content in a glass in the system Y-Si-Al-O-N melted at 1700°C , and concluded of a random variation of density with the TiO_2 content. All the reported values are over 3.5 g/cm^3 , and are higher than the GC densities of the present GC materials. Yttrium (Y) of atomic mass 88.90 amu being the preponderant dopant in the studied glass contributed to increase the material density.

3.2 Microstructural characterization

The diffractograms of the studied GCs are gathered in fig. 2. The phases' identification of the GC at different TiO_2 contents is given in table 3.

Fig. 2. XRD diffractograms of glass-ceramics with different contents of TiO_2

Except for GC7, for the whole of materials, the main formed crystalline phase is an aluminosilicate, of the pyroxene family (Si_2O_6), which is known to be a containment barrier against radionuclide dissipation. Its crystal structure is orthorhombic or monoclinic. Its content in the GC is more than 70%. For 4.11 and 5.11 wt.% TiO_2 GCs, the XRD semi-quantitative analysis gave: 77 % of $\text{Mg}_{0.6}\text{Al}_{1.2}\text{Si}_{1.8}\text{O}_6$ pyroxene phase (JCPDS N°01-075-1568), 10 % of CaMoO_4 (JCPDS N° 01-085-0585) and 13 % of $\text{Ca}_2\text{Zr}_5\text{Ti}_2\text{O}_{16}$ calzirtite phase (JCPDS N° 01-077-1131). The presence of these phases means that ions in the glass matrix are moving and reacting [25]. The formation of calzirtite, is favored by the increase in TiO_2 content in the GC materials. It increases to 25 % for the 6.11 wt.% TiO_2 content GC. One can conclude that for the whole of TiO_2 contents in the materials, (4.11 to 6.11 wt.%), the GC microstructure contains self-irradiation highly resistant crystals, which are able to confine radioactive waste elements [26].

One can note that calzirtite was identified by HJ Rossell [27] in a similar glass system, $\text{CaO-ZrO}_2\text{-TiO}_2$ system, melted at temperatures below 1370 °C. Yu-Han and Wu Taiwan [28] have also investigated a comparable GC material: a Ti-Zr-rich Li-aluminosilicate, and identify calzirtite minerals. These last authors observed the formation of β -quartz phase at a low crystallization temperature $T_c = 750$ °C, which transforms in a pyroxene-type β -spodumene at 880 °C. L.S. Bozadzhiev et al. [29] also observe an isomorph $(\text{Ca,Na})(\text{Mg,Fe,Al})(\text{Si,Al})_2\text{O}_6$ pyroxene phase which forms a solid solution with radioactive waste elements as : Sr, Ba, Zr, Y, Ga, Ce, Pr, Nd, Gd, etc. These phases are obtained from a basanite GC containing radionuclides surrogates from I-VIII group (5-15 wt.%). The materials were melted at 1450 °C, and crystallized at 950 °C. M. Chavoutier et al.[30] have synthesized Ti-rich GC materials in the system SiO_2 , Li_2CO_3 , Al_2O_3 , ZrO_2 and TiO_2 , with a double-melting at 1450 °C. They observe the spodumene phase (Si_2O_6) germination for a T_c temperature above 1105 °C. From all these results, it appears that a crystallization heat treatment at a temperature higher than 950 °C, in systems comparable to the one we used, promotes the formation of an aluminosilicate, of the pyroxene family. This is the case for the GCs currently studied, which crystallize at 1010 °C.

Table 3. The GCs' phase identification for different contents of TiO₂

GC	TiO ₂ (wt.%)	Semi-quantitative composition (%)	JCPDS data [18]
GC1	4.1	77 % Mg _{0.6} Al _{1.2} Si _{1.8} O ₆	01-075-1568
		11 % CaMoO ₄	01-085-0585
		10 % Li ₂ Fe ₅ Cr ₅ O ₁₆	01-073-0213
		1% KFeO ₂	01-083-2153
GC2	5.1	77 % Mg _{0.6} Al _{1.2} Si _{1.8} O ₆	01-075-1568
		9 % CaMoO ₄	01-085-0585
		11% Ca ₂ Zr ₅ Ti ₂ O ₁₆	01-077-1131
		3% Pr ₁₅ Ni ₇ Si ₁₀	01-077-1647
GC3	6.1	70 % Mg _{0.6} Al _{1.2} Si _{1.8} O ₆	01-073-2338
		15% CaMoO ₄	01-085-0585
		12% Ca ₂ Zr ₅ Ti ₂ O ₁₆	01-077-1131
		3 % Ba _{0.905} Ca _{0.08} (TiO ₃)	01-082-2234
GC4	7.1	---	---

The SEM observations of the GC specimen microstructure were carried out on the samples cross sections. The SEM micrographs are depicted on Fig. 3. Such micrographs allowed us to observe both types of phases: crystalline and glassy ones, and confirm the nature of the crystalline phases identified by XRD analysis. The samples are fully ceramized. The dark prisms are characteristics features of pyroxene phase's germination in most samples. This form often appears in the monoclinic structure. Some authors describe these prisms as "stocky" forms [28, 31]. The crystals of calziritite are dipyramidal but light in color. They appear as small piles on the micrographs contrast [26]. The phases appearing in clear platelets are tetragonal powellite crystals [32].

Fig. 3. SEM micrographs of the GC materials with different TiO_2 contents. a) 4.11wt.% TiO_2 -GC, b) 5.11wt.% TiO_2 -GC. c) 6.11wt.% TiO_2 -GC

Fig. 4 shows the DTA curve of the GCs with different TiO_2 contents. For the GC with 5.11wt.% TiO_2 , the parent glass crystallization temperature appears around 563 °C. An allotropic transformation of the calzirtite ($\text{Ca}_2\text{Zr}_5\text{Ti}_2\text{O}_{16}$) crystal from monoclinic to tetragonal is revealed around 990 °C for the three GC at different TiO_2 contents. It should be noted that the calzirtite crystal, $\text{Ca}_2\text{Zr}_5\text{Ti}_2\text{O}_{16}$, is often associated with that of zirconolite in magma-type rocks, and shows slight variations in their composition, especially the substitution type with respect to lanthanides and actinides, found in trace amounts in these rocks [33]. An allotropic transformation around 1090 °C and 1150 °C, attributable to the pyroxene and wollastonite crystal (of the pyroxenoids family) respectively, is observed for the three GCs at different TiO_2 contents. M. Chavoutier et al [30] report the phase transformation of spodumene, a compound of the same family as pyroxene, around 1050 °C, in a GC made from a Li_2O - Al_2O_3 - SiO_2 type glass. Indeed, H. Khedim et al [10] show a transformation, attributed to the formation of pseudo wollastonite at 1170 °C. The ternary phase diagram of: SiO_2 - Al_2O_3 - CaO shows well the range of existence of these phases. We note that the allotropic transformations of CaMoO_4 (630 and 690, 810 and 880 °C) are undetectable on the DTA diagrams, because the content of this molybdate is very low and therefore the transformations are not apparent on the spectra. Finally, no melting phenomenon is observed up to 1450°C.

Fig. 4. DTA curve of GC materials with different TiO_2 contents

The Allotropic transformation of the different crystalline phases observed for the GC materials with different TiO₂ contents is given in table 4.

Table 4. Allotropic transformation of the different crystalline phases identified in the GCs of different TiO₂ contents

Crystalline phases	Allotropic transformation (°C)			
	GC1	GC2	GC3	GC4
Calzirtite (Ca₂Zr₅Ti₂O₁₆)	999.1	986.1	997.4	-----
Pyroxene (Mg_{0.6}Al_{1.2}Si_{1.8}O₆)	1096.3	1085.2	1083.8	-----
Wollastonite (CaSiO₃)	1142.1	1142.7	1143.1	-----

The FTIR analysis of the different GCs with different TiO₂ contents gave the spectra gathered on Fig. 5. FTIR spectra of GCs with different TiO₂ contents highlight an absorption band at 1427.1 cm⁻¹ corresponding to the Ba-O vibration [34]. In the region of the spectrum from 1100 to 1200 cm⁻¹, the band corresponding to the presence of [SiO₄] tetrahedra is almost non-existent. Si-O-Si and amorphous SiO₂ bond vibrations at 1083.0, 1081.4, and 1081.7 cm⁻¹ for GCs: GC1, GC2, and GC3, respectively. This absorption band is reported at 1080 cm⁻¹ in pure glass [35]. The observed shift is due to compositional differences in the synthesized GCs. The characteristic band of the ring structure of [SiO₄] tetrahedra is observed at 775.2, 774.8, 776.7 cm⁻¹, for GCs: GC1, GC2 and GC3, respectively. The latter is quoted at 775 cm⁻¹ in the literature. This band is very weak indicating the strong ceramization of the parent glass. It also confirms the presence of Si-O-Me bonds, in a Si-Al-Me (Al, Mg) base glass system [34, 36]. The Ti-O elongation vibration appears at 440, 436 and 455 cm⁻¹, for the glass ceramics: GC1, GC2 and GC3, respectively. This band appears at 455.7 cm⁻¹ in the literature. The elongations of the Ti-O bonds characteristic of the formation of the Ti-O-Ti bridge appear in the range 493-456 cm⁻¹ [37]. The absorption band around 405 cm⁻¹ for GCs: GC1, GC2 and GC3, correspond to the vibration of Zr-O. This band is known to occur at 400 cm⁻¹ [38]. It indicates the presence of calzirtite with a Ca₂Zr₅Ti₂O₁₆ skeleton in greater proportion in GC3

(12%) than in the other GCs. Overall, we can conclude that these spectra are representative of the complex chemical composition of the studied GCs.

Fig. 5. FTIR spectra of the GCs with different contents of TiO_2

3.3 Chemical durability

The variation of the elemental mass loss of Si, Al, Mg and Ce (actinide surrogate) elements (NL) and the elemental leaching rate of Si, Al, Mg and Ce elements (RLi) are calculated using the formulas (1) and (2) of section 1, respectively.

For Si and Mg, the MCC2 test leads to a leaching equilibrium, but for different GCs at values of: $3.4593 \cdot 10^{-5} \text{ kg/m}^2$ of Si for GC1, $11.9431 \cdot 10^{-5} \text{ kg/m}^2$ and $14.4076 \cdot 10^{-5} \text{ kg/m}^2$ of Mg for GC2 and GC3 respectively. For Ce, the whole of tests lead to a steady state, except for GC2 leached in MCC1. The GC that leaches the least Ce is GC1 leached in MCC2, with 4.5837 kg/m^2 of Ce. For Al, NL is increasing for all TiO_2 contents in GCs, whatever the employed leaching test. Therefore, Al is not redeposited on the GCs as a passivation layer under the present operating conditions. The best result is for GC2, leached in MCC2. We can conclude that MCC2 test is favorable for leaching unlike the MCC1 test; the high temperature is therefore a limiting factor for the release of GC elements, except for Al, for which the concentration doesn't stabilize in the leachates at the end of test. T. Geisler et Al. [39] studied the leaching of a borosilicate glass with a composition similar to that of a German nuclear glass (54.0 SiO_2 , 14.8 B_2O_3 , 2.4 Al_2O_3 , 1.1 TiO_2 , 1.8 MgO , 4.8 CaO , 2.9 Li_2O , 7.2 Na_2O , 10.0 CeO_2) in an acidic medium (1M HCl, at 150 °C). This high temperature test, compared to our results for GC1 (4.11wt.%), leached in MCC2 shows that these values are of the same order

of magnitude as those of the present study. They are lower than our values for Al: $8.847 \cdot 10^{-5} \text{ Kg/m}^2$ ($12.4783 \cdot 10^{-5} \text{ kg/m}^2$), and higher than our values for Mg: $9.579 \cdot 10^{-5} \text{ Kg/m}^2$ ($8.8626 \cdot 10^{-5} \text{ Kg/m}^2$) and Ce $9.10 \cdot 10^{-5} \text{ Kg/m}^2$ ($4.5837 \cdot 10^{-5} \text{ Kg/m}^2$) and Si: $0.44 \cdot 10^{-5} \text{ Kg/m}^2$ ($26.0148 \cdot 10^{-5} \text{ kg/m}^2$).

The leaching rate (RL) of Si, Al, Mg and Ce as a function of time, for each material doped with different contents of TiO_2 are gathered on Fig. 6, for all the tests (MCC1 and MCC2). For Si, leaching equilibrium is achieved for all GCs and for both leaching tests. The leaching rate in Si is also negligible. The best leaching rate is $61.47 \cdot 10^{-9} \text{ Kg/m}^2\text{d}$ in Si for GC1 leached in MCC2. This represents a GC1 mass percentage present in the leachate of 0.015%. All the GCs show a stabilization of the Mg leaching rate, at the end of MCC2 test. The best Mg leaching rate is $191.94 \cdot 10^{-9} \text{ Kg/m}^2\text{d}$ for GC2 leached in MCC2, which represents a GC1 Mg mass percentage present in the leachate of 0.047%. This rate is negligible after 14 days of leaching. The sole GC that shows a decrease in Al leaching rate is GC1 leached in MCC2 test, which reaches $48.9 \cdot 10^{-9} \text{ kg/m}^2\text{d}$, representing a mass content present in the leachate relative to the total amount in GC1 of 0.25%. These results are predicted by the presence of sphene: $\text{Mg}_{0.6}\text{Al}_{1.2}\text{Si}_{1.8}\text{O}_6$ with a content of 77% in both GC1 and GC2), which constitutes a double barrier. S.Gavarini [40] reports much higher Si leaching rate values ($23 \cdot 10^{-3} \text{ Kg/m}^2\text{d}$ and $50 \cdot 10^{-3} \text{ Kg/m}^2\text{d}$) for the leaching of Ce-rich glasses of chemical formula CeYSiAlO when leached in static mode at 90°C in a closed system. For Ce, the steady state is reached for all GCs in both leaching tests, except for GC3 leached in MCC1 test. The leaching rate in Ce is also negligible. The best leaching rate is $193.71 \cdot 10^{-9} \text{ Kg/m}^2\text{d}$ in Ce for GC2 leached in MCC2; this represents a GC2 Ce mass percentage released in the leachate of 0.032%, this value complies with nuclear industry requirements ($<10^{-3} \text{ Kg m}^{-2} \text{ d}^{-1}$) [41,42]. The best results are for GC with 4.11 and 5.11 % TiO_2 for the MCC2 test.

Fig. 6. Elemental leaching rates (RL_i) of Si, Al, Mg and Ce as a function of time for the GCs with different TiO₂ contents, leached in both MCC1 and MCC2 tests

4. Conclusion

In this study, we performed the synthesis and characterization of glass-ceramic matrices, based on an aluminosilicate glass, in the system SiO₂-Al₂O₃-CaO-MgO-ZrO₂-TiO₂, with four contents of TiO₂, ranging from 4.11 to 7.11 wt.%. These GC confinement matrices are intended to confine in their structure both fission products and lanthanides elements, from radioactive waste. The GC synthesis is carried out in several stages: a double fusion of the oxides mixture at 1350 °C, a nucleation at 564 °C, and a crystal growth at 1010 °C. The GC synthesis of the material with 7.11wt.% TiO₂ content, was not successful. For the others materials, the obtained GC have Archimedes densities in the range of 2.891 - 2.962 g/cm³. Except for the GC with 7.11 wt.% TiO₂, the XRD phase identification show that the main formed phases in the materials are pyroxene, powelite and calzirtite phases, which are known as self-irradiation resistant phases. The SEM confirmed the morphological aspect of these phases in the microstructures. The DTA analysis reveals the allotropic transformations of such

phases. The FTIR analysis spectra are representative of the complex chemical composition of the studied glass-ceramics. MCC1 and MCC2 tests, performed on selected glass ceramic materials among the different TiO₂ contents GCs, indicate that the materials with 4.11 and 5.11 wt.% TiO₂ have the best leaching behavior, for MCC2 test (90°C), for the four analyzed elements (Si, Al, Mg and Ce). The leaching rate in Ce (actinide surrogate) is negligible. The best leaching rate is 193.7×10^{-9} Kg/m²d after 28 leaching days in Ce for 5.11 wt.% leached in MCC2. The studied GCs with different TiO₂ contents may potentially be candidate matrix for the disposal of high-level waste.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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