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Study of the Effect of Ca/Mg Alkali-Oxides Ratio on the Structure of a Glass-Ceramic Based on an Aluminosilicated Glass Containing 2wt.% of Zirconolite Crystalline Phase

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Abstract:

New nuclear glass-ceramics are extensively studied for the radioactive waste confinement, due to the double confinement conferred by the glass-ceramics. In this study, a glass-ceramic constituted by an aluminosilicate glass in the system: SiO_2-Al_2O_3-CaO-MgO-ZrO2-TiO2, containing 2wt.% of $Ca_{0.83}Ce_{0.17}ZrTi_{1.66}Al_{0.34}O_7$ zirconolite, has been synthesized by the discontinuous method. Cerium, an actinide surrogate is introduced both in the glass and ceramic phases. The synthesis is performed by a double melting at 1350 °C, followed by a nucleation at 564°C, during 2 h, and a crystal growth at 1010°C during 3 h. Then effect of Ca / Mg ratio on the distribution of the crystalline network in the material was studied for Ca / Mg ratios ranging from 0.4 to 5.5. For the whole of the materials, Archimedes density is about 2.80 g/cm^3. X-ray diffraction (XRD) analysis shows that the increase of Ca/Mg ratio leads to the increase of aluminosilicated crystalline phases with high Ca contents; the materials molar volumes remaining constant. The zirconolite phase is not affected by these additive aluminosilicated phases. The scanning electron microscopy analysis (SEM) coupled with energy dispersive X-ray (EDX) analysis confirmed these results; and shows the uniformity of distribution of the ceramics in the bulk of the materials.

Keywords: *Radioactive waste, Nuclear glass-ceramics, Zirconolite, XRD, SEM.*

1. Introduction

The storage and disposal of radioactive waste (RW) is a hard operation in the point of view of management. It requires precision in monitoring of radioisotopes. One of the principles of RW disposal is to accompany the waste in the wholes stages of its life: packaging, storage, disposal, and monitoring, until its radioactivity becomes comparable to natural background radiation [1]. A multitude of storage materials are being studied, among which glasses, minerals, and glass-ceramic matrices. The main works dealing with this last kind of materials concern the containment of the whole of radionuclides present in the waste [2].

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Nevertheless, because of both the higher chemical durability and the higher capacity of several single-phase ceramic matrices such as zirconates, titanates and phosphates to incorporate specific nuclear wastes (corresponding either to a specific element or to a family of elements with similar chemical properties), ceramic waste forms have been proposed for the immobilization of long-lived radionuclides such as and minor actinides [3-6]. Zirconolite was the most durable phase designed for the incorporation of actinides and lanthanides in Synroc phase assemblages developed in Australia in 1980s for immobilization of unpartitioned Purex-type HLW produced by the reprocessing of spent fuel. The use of glass and Synroc materials is limited due to the high prices of the base raw materials and to the relatively complex technological scheme [7].

Glass-ceramic containing highly durable crystalline particles such as zirconolite (nominally CaZrTi2O7) homogeneously dispersed in the bulk of a glassy matrix and able to incorporate high quantities of actinides (such as minor actinides or Pu) or actinide surrogates (such as lanthanides) in their structure have been proposed as host candidates for the immobilization of these long-lived radionuclides [8-10].

Zirconolite based glass ceramics have also been developed as potential waste forms for the immobilization of some compositionally diverse actinide-rich waste streams, e.g. separated minor actinides. They combine the process and chemical flexibility of glasses with the excellent chemical durability of ceramics. This can be achieved by capitalizing on the glass forming components properties present in the waste, along with appropriate additives, to form in the same time a durable glass, to accommodate processing chemicals, and desired high-resistant crystalline phases to host actinides. The developed glass-ceramics have been proven to be chemically durable [11].

This study deals with the synthesis of a glass-ceramic based on an aluminosilicate glass, doped with 2 % of 2M-zirconolite RW confinement mineral. The zirconolite chemical formula is: $Ca_{0.83}$ $Ce_{0.17}ZrTi_{1.66}Al_{0.34}O_7$. Cerium is employed as an actinide surrogate. The influence of the Ca/Mg ratio on the nature of the crystalline phases formed in the bulk of the material is studied for Ca/Mg ratios ranging from 0.4 to 5.5. This interval is maintained consistent with the basic structure of the homogeneous glass used for the synthesis of the studied material.

2. Experimental

The following reagents are used: Al_2O_3, B_2O_3, Nd_2O_3, MgO, Li_2O (FLUKA), CaO, CrO_3 Fe_2O_3, K_2CO_3, MnO_2, MoO_3, P_2O_5, Ta_2O_5, TiO_2, Pr_6O_{11}, WO_3, Y_2O_3 (MERCK), CeO_2, Yb_2O_3, ZrO_2 (ALDRICH), SiO_2 (PROLABO), V_2O_5 (LABOSI). The rare-earth oxides (REE) are dried at 1000 °C, and the other oxides at 400 °C, overnight. The oxides BaO, Er_2O_3, La_2O_3 and NiO were prepared by calcination at 450 °C of $BaNO_3$, $La(NO_3)_3.6H_2O$, $Ni(NO_3)_2.6H_2O$ (Fluka) $ErN_3O_9.5H_2O$ (ACROS ORGANICS). They are manually grounded in an agath mortar, till a fine granulometry (<20 μm). Each reagent is weighed in order to meet the final product chemical formula. A batch of 30 g is prepared in each case. The mixture was homogenized using an automatic shaker during 5 h.

The glass-ceramics are produced from a homogeneous aluminosilicate glass with the chemical composition given in Table I, and the glass ceramics with different Ca/Mg ratios are prepared according to the compositions shown in the same table. The parent glass is synthesized according A. Quintas et al. method [12], which consists of a double melting at 1350 °C during 5 h. Then, the glass is poured in a cylindrical mold to obtain pellets.

The materials nucleation is performed during 2 h, at a temperature Tn (Tn = Tg + 30), where Tg, the glass transition temperature is of 564 °C. The grains growth step is performed during 3 h at the crystallization temperature, Tc, of the pure glass, which is 1010 °C. This method is the one used in previous studies [12]. The glass-ceramic is naturally cooled to room

temperature. Both Tg and Tc are deducted from the DTA (differential thermal analysis) diagram of the parent glass. The details of DTA diagrams are given in a previous study [13]. The nucleation temperature was kept constant for all glass samples because Tg did not significantly change between the different compositions studied. Indeed, the temperature range where zirconolite nucleation remains significant was shown slightly higher than Tg [14].

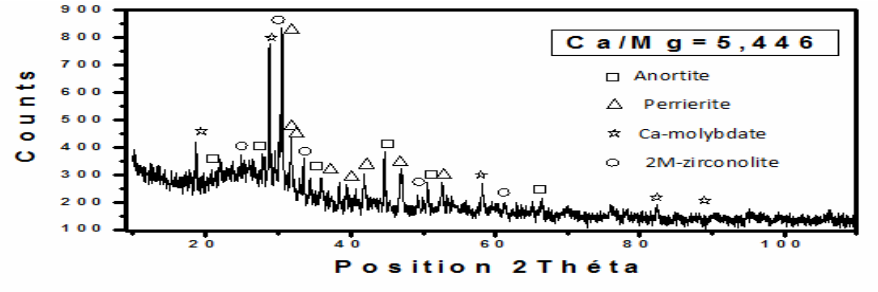
Tab. I Chemical compositions (m.%) of the parent glass and the glass-ceramics with different Ca/Mg ratios.

Oxide		Glass-ceramics			
	Parent glass	Ca/Mg			
		0.472	1.789	2.959	5.446
Al_2O_3	12.948	12.948	12.948	12.948	12.948
B_2O_2	0.782	0.782	0.782	0.782	0.782
BaO	0.586	0.586	0.586	0.586	0.586
CaO	8.415	3.987	8.415	9.987	11.487
CeO_2	3.113	3.113	3.113	3.113	3.113
CrO_3	0.391	0.391	0.391	0.391	0.391
Er_2O_3	1.281	1.281	1.281	1.281	1.281
Fe_2O_3	1.281	1.281	1.281	1.281	1.281
K2O	0.978	0.978	0.978	0.978	0.978
La_2O_3	0.489	0.489	0.489	0.489	0.489
Li_2O	4.105	4.105	4.105	4.105	4.105
MgO	5.572	10.000	5.572	4.000	2.500
MnO_2	0.195	0.195	0.195	0.195	0.195
MoO_3	2.737	2.737	2.737	2.737	2.737
Nd_2O_3	1.173	1.173	1.173	1.173	1.173
NiO	0.586	0.586	0.586	0.586	0.586
P_2O_5	0.391	0.391	0.391	0.391	0.391
Pr_6O_{11}	0.098	0.098	0.098	0.098	0.098
SiO_2	45.940	45.940	45.940	45.940	45.940
Ta_2O_5	0.195	0.195	0.195	0.195	0.195
TiO_2	4.790	4.790	4.790	4.790	4.790
V_2O_5	0.098	0.098	0.098	0.098	0.098
WO_3	0.782	0.782	0.782	0.782	0.782
Y_2O_3	0.489	0.489	0.489	0.489	0.489
Yb_2O_3	0.098	0.098	0.098	0.098	0.098
ZrO_2	2.487	2.487	2.487	2.487	2.487
Total	100	100	100	100	100

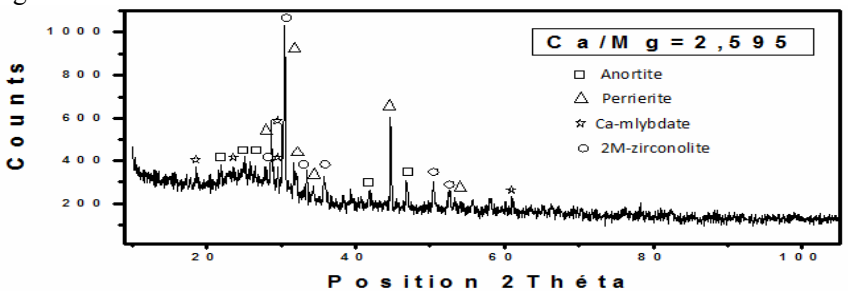
The materials Archimedes density is measured by picnometry in water. The X-ray diffraction (XRD) analysis is carried out using a PanAnalytical X'Pert Pro diffractometer equipped with a copper anticathode, with a wavelength λ (Kα) of 1.5418 Å, at a voltage of 40 kV and a current intensity of 40 mA, for 2θ ranging between 3 and 80 °C. The ceramics phase identification is performed using a Philips X'Pert High Score Plus software, version 4.1 [15]. The micrographic observation is made by a scanning electron microscope (SEM), Philips XL'30 equiped with an ESEM-FEG EDX probe.

3. Results and Discussion

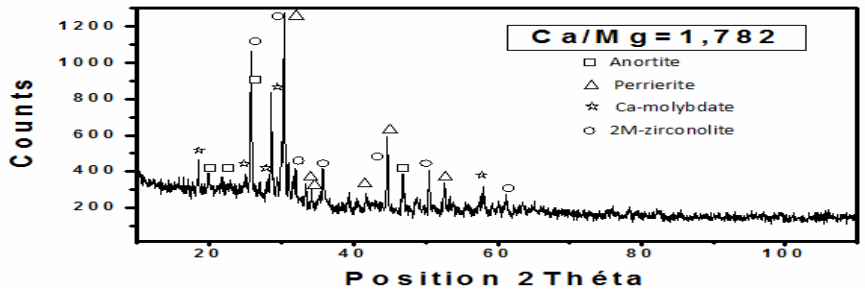
The materials Archimedes density approximates 2.80 g/cm^3, for the whole of the materials. Seokju J. and al. report densities values close to our results (≈ 2.8 g/cm^3) for cordierite glass-ceramics synthesized by a melting at 1450°C and a crystallization and crystal growth treatments, at 750 and 1020°C, respectively [16].



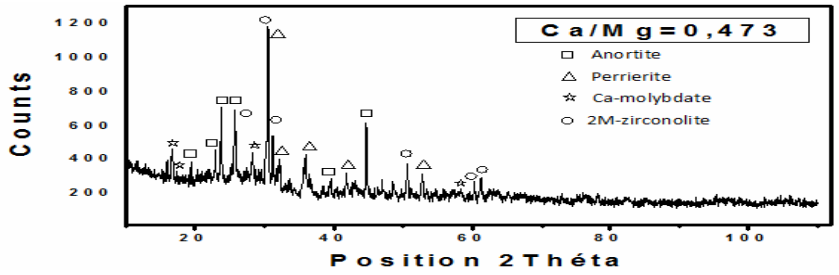
1.a. Ca/Mg= 5.44



1.b. Ca/Mg = 2.95



1.c. Ca/Mg= 1.78



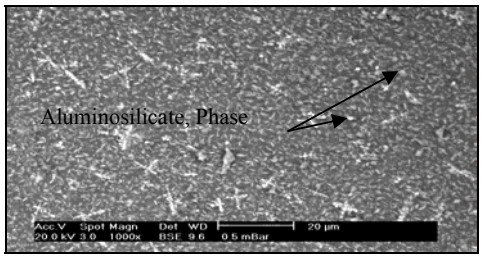
1.d. Ca/Mg = 0.47

Fig. 1. XRD diffractograms of glass-ceramics with different Ca/Mg ratios.

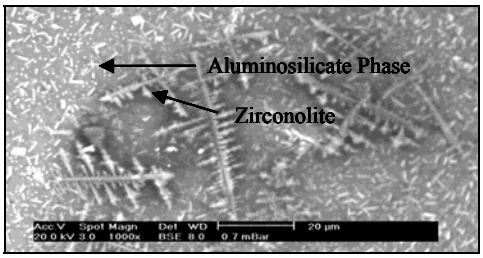
The glass-ceramics XRD analysis gave the diffractograms shown in Fig. 1. For the maximum Ca/Mg ratio value (5.44), the main crystalline phase is a Ca-aluminosilicate, identified to a $CaAl_2Si_2O_8$ anortite of JCPDS number 00-041-1486, of orthorhombic structure [17]. The main piks of this phase are those of d= 3.18, 3.6, 4.04 and 1.94. For the other values of Ca/Mg, the major crystalline phase is a (CeCa)Fe(AlTi)TiSiO perrierite of JCPDS 00-020-0260, which is an aluminosilicate phase, rich in Ti, Ca and Ce; the excess elements in the glass phase. The main piks of this phase are those of d= 2.92, 2.81, 2.95 and 3.52. The minor phases are a Ca-molybdate $CaMO_4$ (JCPDS 01-085-0585). The main piks of this phase are those of d= 3.103, 1.92, 1.587 and 4.752; and a 2M-zirconolite $CaZrTi_2O_7$ (JCPDS 00-034-0167). The main piks of this phase are those of d= 2.931, 2.824, 2.507 and 1.797. Traces of ZrO_2 and $ZrSiO_4$ phases are also observed. These results prove the successful synthesis of a glass-ceramic containing high-level waste sequestration ceramics, as zirconolite, in the bulk of the materials; this kind of phases ensuring the double confinement of actinides, and thus a higher durability of the disposal material under materials self-irradiation [9].

Therefore, one can conclude that the excess Ca in the glass-ceramic leads to the preferential nucleation of anortite aluminosilicate phase, which is rich in Ca.

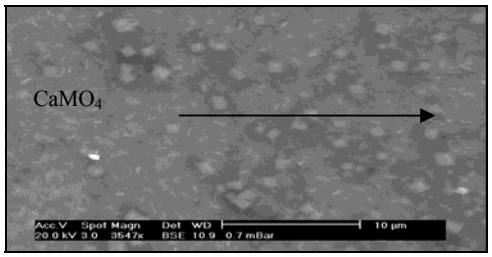
The SEM observations of the glass-ceramics specimen microstructure was carried out on the cross section of the samples, in order to avoid the surface effect during ceramization, which leads to the formation of border phases that are different from those in the bulk of the samples [10]. The SEM micrographs are depicted on Fig. 2.



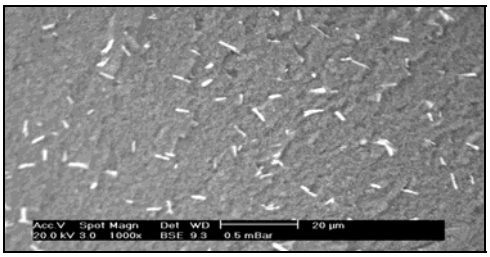
2.a.Ca/Mg=5.44



2.b. Ca/Mg = 2.95



2.c. Ca/Mg =1. 789



2.d. Ca/Mg = 0.472

Fig. 2. SEM micrographs of glass-ceramics with different Ca/Mg ratios.

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. Zirconolite crystals are long light gray and have a needle-square form. Titanite appears as grey crystals whereas anortite crystals are darker than the residual glass. These characteristically crystal shapes are reported by many authors in this area of research [10, 18, 19].

One can remark that the increase of Ca/Mg ratios favors the formation of anorthic crystals. The main phase of anortite identified by XRD analysis was confirmed by EDX analysis, as a Ca rich aluminosilicate. A typical EDX diagram is shown in Fig. 3. [19].

EDX analysis of these crystals confirms the typical forms of the crystalline structure

of the minerals.

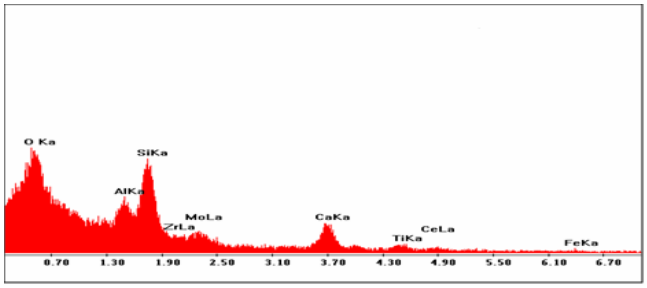


Fig. 3. EDX spectrum of the aluminosilicate mineral present in the glass-ceramic.

4. Conclusion

In this study, we performed the synthesis and characterization of glass-ceramic matrices based on an aluminosilicate glass, in the system SiO_2-Al_2O_3-CaO-MgO-ZrO_2-TiO_2, able to incorporate elements of radioactive waste (fission products and lanthanides) in their structure. The employed synthesis method is the devitrification of a parent glass. It 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 Archimedes density was calculated for all materials, and approximates 2.80 g/cm^3. Both XRD and SEM analyses allow identifying the main crystalline phases, which germinates in the glass-ceramic. The main results show that the formation of Ca-rich aluminosilicate phases is favored to the detriment of zirconolites and other Zr-rich phases, when the Ca/Mg ratio increases. The studied glass-ceramics have satisfactory mineralogical compositions, because they contain suitable crystalline phases for the double confinement of actinides, such as aluminosilicates, Zr-bases phases, and powellites.

5. References

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Садржај: *Нове нуклеарне стакло-керамике су проучаване ради складиштења нуклеарног отпада. У овом раду, стакло-керамика је састављена из: SiO_2-Al_2O_3-CaO-MgO-ZrO_2-TiO_2, са 2wt.% $Ca_{0.83}Ce_{0.17}ZrTi_{1.66}Al_{0.34}O_7$ цирконилита, и синтетисана је дисконтинуалном методом. Церијум, заменик актинида, убачен је и у стакло и у керамику. Синтеза је урађена двоструким топљењем на 1350 °C, праћена нуклеацијом на 564°C, током 2 сата, и кристалним растом на 1010°C током 3 сата. Онда је утицај односа Ca/Mg на расподелу кристалне мреже проучаван и износио је од 0,4 до 5,5. Густина израчуната Архимедесовом методом је око 2,80 g/cm^3. Рендгеноструктурна анализа је показала да са порастом односа Ca/Mg расте алуминосиликатна кристална фаза са високим садржајем Ca; моларна запремина материјала остаје константна. Цирконолитна фаза није промењена додавањем адитива алуминосиликатној фази. Ове резултате је потврдила и скенирајућа електронска микрографија заједно са рендгенско енергетско дисперзивном методом; и указују на униформност дистрибуције керамике у материјалу.*

Кључне речи: *радиоактивни отпад, нуклеарна стакло-керамика, цирконилит, рендгенска дифракција, скенирајућа електронска микроскопија.*