Influence of the Crystal Growth Temperature on the Formation of Zr Rich Crystalline Phases in a Nuclear Waste Confinement Glass Ceramic

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Abstract: Many glass ceramics are potential candidates for the confinement of radioactive waste. This is the case of glasses embedding radiation-resistant ceramics as zirconolites, pyrochlores or pyroxenes. This study deals with the influence of the crystal growth temperature on the formation of such phases in a nuclear glass ceramic in the system: $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-CaO-MgO-ZrO}_2\text{-TiO}_2$. The materials with six contents of ZrO_2 , ranging from 1.00 to 6.40 m.%, are synthesized by a discontinuous method, consisting in a double-melting at 1,350 °C, followed by both a nucleation at 564 °C, and a crystal growth treatment at: 900, 100 and 1,100 °C. For the whole of the materials, the morphology reveals a glassy feature, with a opaque aspect. One can also evidence a different crystallization process from the bulk to the surface. The glass ceramics X-ray diffraction analysis (XRD) show that the main identified crystalline skeletons are those of: 2M-zirconolite, $\text{CaZrTi}_2\text{O}_7$ and ZrO_2 , depending on the content of ZrO_2 in materials and the crystal-growth temperature. The material with the middle content in ZrO_2 (4.5 m.%) and crystallized at the middle value of T_c (1,010 °C) show the greatest content in zirconolite (87 %), doped with either lanthanides or alcalin-earth elements, due to the complexity of the mixture of oxides. The temperature of 1,010 °C appears to be more selective with regard to the formation of the 2M-zirconolite.

Key words: Glass ceramic, radioactive waste, crystallization temperature, XRD, crystalline phase.

1. Introduction

The development of specific sequestration matrix designed to confine particular radionuclides is an important research field.

The industrial solution currently adopted for the confinement of the radiotoxic elements belonging to the nuclear waste, consists to incorporate them in a glass of the system: $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-Na}_2\text{O}$. This confinement is not specific, and has the advantage of a good loading ability and an excellent long-term behavior [1].

Various mineral matrices for the specific disposal of many radioisotopes produced from nuclear waste, particularly, for minor actinides (Mac), and fission products “lanthanides” (FP), include ceramics, such as zircon-titanates (zirconolite), zirconates (zirconia, stabilized zirconia, and phosphates (apatite, monazite) [2, 3].

The ceramics elaborating processes are difficult to implement to date, and many glass-ceramics are also under study. They consist of crystals homogeneously distributed in a glass matrix, and exhibit increased performances compared to alumino-borosilicate glasses.

Research on glass-ceramics (noted: GC) matrices for

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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. 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 1,350 °C. This is necessary to ensure a complete homogenization of the oxides mixture, to guarantee isotrope 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 nucleation temperature (T_n) of the parent glass, chosen as the glass transition temperature measured by differential thermal analysis (T_g) plus 30 °C ($T_n = T_g + 30$). $T_n = 564$ °C for 2 h. the crystal growth treatment (T_c) is performed at: 900, 1,010 and 1,100 °C for 3 h, for the whole. The GC materials are cooled to the ambient air.

For the six studied compositions glasses, X-ray diffraction (XRD) analysis was conducted by a Philips X'Pert PRO apparatus, operating at $\text{CuK}\alpha 1$ wavelength ($\lambda_{\text{K}\alpha 1} = 0.15406$ nm). The analytical parameters were as follow: $V = 40$ kV and $I = 40$ mA; a 2θ scanning from 3° to 80°. The XRD data were 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 [7].

3. Results and Discussion

3.1 Characterization of the Materials

The GC phase's identification was performed by XRD analysis, on thin blades from the bulk of the samples to avoid surface effects in the GC [8].

For the three T_c heat treatments and for the GC six chemical compositions studied, the XRD spectra are gathered in Figs. 1-7.

Fig. 1 Diffractogram of the GC with 1 m.% ZrO_2 content. (a) $T_c = 900$ °C, (b) $T_c = 1,010$ °C and (c) $T_c = 1,100$ °C.

Fig. 2 Diffractogram of the GC with 2.49 m.% ZrO_2 content. (a) $T_c = 900$ °C, (b) $T_c = 1,010$ °C and (c) $T_c = 1,100$ °C.

Fig. 3 Diffractogram of the GC with 3.50 m.% ZrO_2 content. (a) $T_c = 900\text{ }^{\circ}C$, (b) $T_c = 1,010\text{ }^{\circ}C$ and (c) $T_c = 1,100\text{ }^{\circ}C$.

Fig. 4 Diffractogram of the GC with 4.50 m.% ZrO_2 content. (a) $T_c = 900\text{ }^{\circ}C$, (b) $T_c = 1,010\text{ }^{\circ}C$ and (c) $T_c = 1,100\text{ }^{\circ}C$.

Fig. 5 Diffractogram of the GC with 5.00 m.% ZrO_2 content. (a) $T_c = 900\text{ }^{\circ}C$, (b) $T_c = 1,010\text{ }^{\circ}C$ and (c) $T_c = 1,100\text{ }^{\circ}C$.

Fig. 6 Diffractogram of the GC with 5.70 m.% ZrO_2 content. (a) $T_c = 900\text{ }^{\circ}C$, (b) $T_c = 1,010\text{ }^{\circ}C$ and (c) $T_c = 1,100\text{ }^{\circ}C$.

Fig. 7 Diffractogram of the GC with 6.40 m.% ZrO_2 content. (a) $T_c = 900\text{ }^\circ\text{C}$, (b) $T_c = 1,010\text{ }^\circ\text{C}$ and (c) $T_c = 1,100\text{ }^\circ\text{C}$.

At the lowest crystal-growth temperature of $900\text{ }^\circ\text{C}$, and for the lowest levels of ZrO_2 in the GCs, there are few Zr-containing phases (especially zirconolite $\text{CaZrTi}_2\text{O}_7$) in the germinated crystals: $\text{CaZrTi}_2\text{O}_7$ (JCPDS: 00-034-0167), ZrO_2 (JCPDS: 01-073-1441), ZrTiO_4 (JCPDS: 01-074-1504), $\text{Nd}_2(\text{Ce}_{0.05}\text{Zr}_{0.95})_2\text{O}_7$ (JCPDS: 01-078-1619), ZrTiO_4 (JCPDS: 01-080-1783), $(\text{Ca}_{0.85}\text{Nd}_{0.075}\text{Zr}_{0.075})(\text{Nd}_{0.075}\text{Zr}_{0.775}\text{Ti}_{0.15})(\text{Ti}_2\text{O}_7)$ (JCPDS: 01-081-1491), $\text{ZrO}_{1.95}$ (JCPDS: 01-081-1544), $\text{Zr}_{0.86}\text{Y}_{0.14}\text{O}_{1.93}$ (JCPDS: 01-082-1243), $\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$ (JCPDS: 01-084-1829).

They reach a significant concentration, when the content of ZrO_2 in the ceramic reaches 3.50 %.

At the intermediate temperature of crystallization ($1,010\text{ }^\circ\text{C}$), the Zr-rich phases are the main crystalline germs in the materials, even for the lowest content in of ZrO_2 (1%).

However, it is only over 2.49 m. % of ZrO_2 in the GC material that the zirconolite skeleton $\text{CaZrTi}_2\text{O}_7$ appears with a significant concentration. The most VC materials contain over 65 m. % of zirconolite jointly with other additive Zr-containing phases.

For $T_c = 1,100\text{ }^\circ\text{C}$, the most crystals formed in the bulk of the GC materials are Zr oxides for the whole of ZrO_2 contents in the materials, with a great content in 2M-zirconolite over 4.5 m.% of ZrO_2 in the GC matrices.

3.2 Discussion

Loiseau and Caurant et al. [9] have synthesized Zr-rich GC materials. They report the co-existence of germs of zirconolite and ZrO_2 fluorine crystals, with a

T_c temperature of $1,000\text{ }^\circ\text{C}$. The fluorine structure shows a very muddled distribution of Ca^{2+} , Zr^{4+} and Ti^{4+} cations in zirconolite. This muddle distribution is attenuated when T_c increases [10].

For the present study, the zirconolite is the main formed phase in the bulk of the GC materials for the T_c temperature of $1,010\text{ }^\circ\text{C}$, which is near this given by Loiseau and Caurant et al. [9] despite the differences in the nature of the GC materials and the synthesis parameters.

The best crystal-growth treatment in term of selectivity toward the 2M-zirconolite formation seems to be that of $1,010\text{ }^\circ\text{C}$.

One can conclude that the lowest crystal-growth temperature $T_c = 900\text{ }^\circ\text{C}$ does not favor the germination of Zr-rich phases, particularly zirconolite. The intermediate T_c temperature of $1,010\text{ }^\circ\text{C}$, leads to the greatest selective formation of zirconolite in the GC materials.

However, 900 and $1,100\text{ }^\circ\text{C}$ also lead to the germination of radiation resistant phases rich in Zr, and thus may ensure a double-confinement of the lanthanides and actinides present in the radioactive waste solution [9].

4. Conclusions

In this study, we performed the synthesis and characterization of Zr-rich GC materials dedicated for the confinement of radioactive waste. The parent glass is an aluminosilicate glass in the system: $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO-ZrO}_2\text{-TiO}_2$.

The synthesis method is based on a double melting at

1,350 °C, followed by a nucleation at 564 °C and a crystal growth at: 900, 1,010 and 1,100 °C. The obtained results allow concluding that the GC materials exhibit typical properties compared to those of the glass matrix, because they contain highly self-irradiation resistant phases, such as zirconolite. Thus, these materials are potential candidates as nuclear waste forms for double-containment of actinides and lanthanides. For the whole of the studied chemical compositions of the materials, and for the three chosen Tc treatments, a Zr-reach crystalline phase, the 2M-zirconolite ($\text{CaZrTi}_2\text{O}_7$), was identified by XRD analysis, with high levels over 60% for the lowest ZrO_2 content in the materials. Minor phases as zirconia (ZrO_2) and zircon (ZrSiO_4) are also observed.

The highest content in zirconolite (87%) is reached for the GC with 4.5 m.% of ZrO_2 . The lowest crystallization temperature (900 °C) does not promote the germination of Zr-rich phases, especially zirconolite. This is intermediate crystal-growth temperature of 1,010 °C, which leads to the greatest selectivity in zirconolite ceramic germination. However, the crystal-growth temperatures of 1,010 and 1,100 °C also result in germination of Zr-reach radiation resistant phases.

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