Monitoring of alpha-decay radiation damage in a ^{241}Am-doped glass-ceramic material [1]

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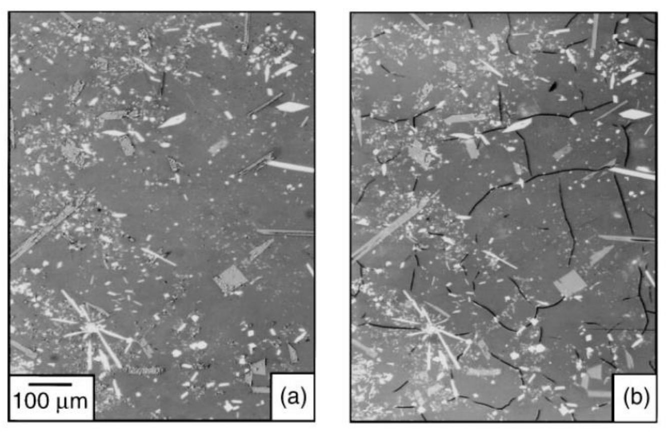
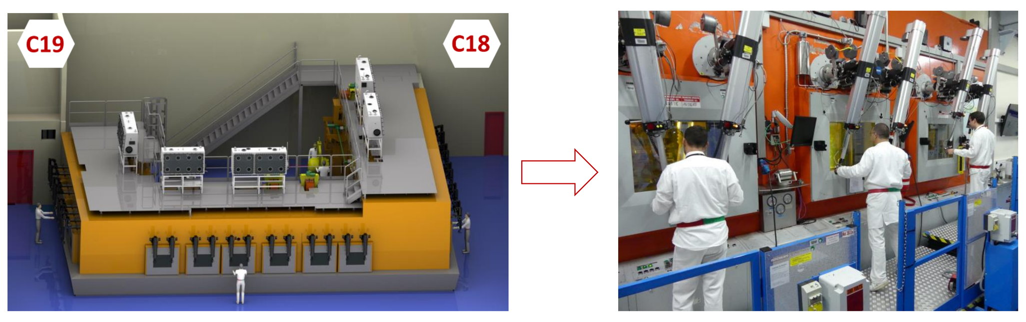
Context

Glass-ceramics could be an alternative to R7T7 glass for immobilizing larger quantities of waste (> 18.5 wt.% of fission products and minor actinides oxides [2]). However, ceramic phases included in glass-ceramics, such as silicate apatite, could amorphise and swell under self-irradiation, which could lead to cracking of the glass matrix [3]. The development of these conditioning materials requires the study of their response to self-irradiation.

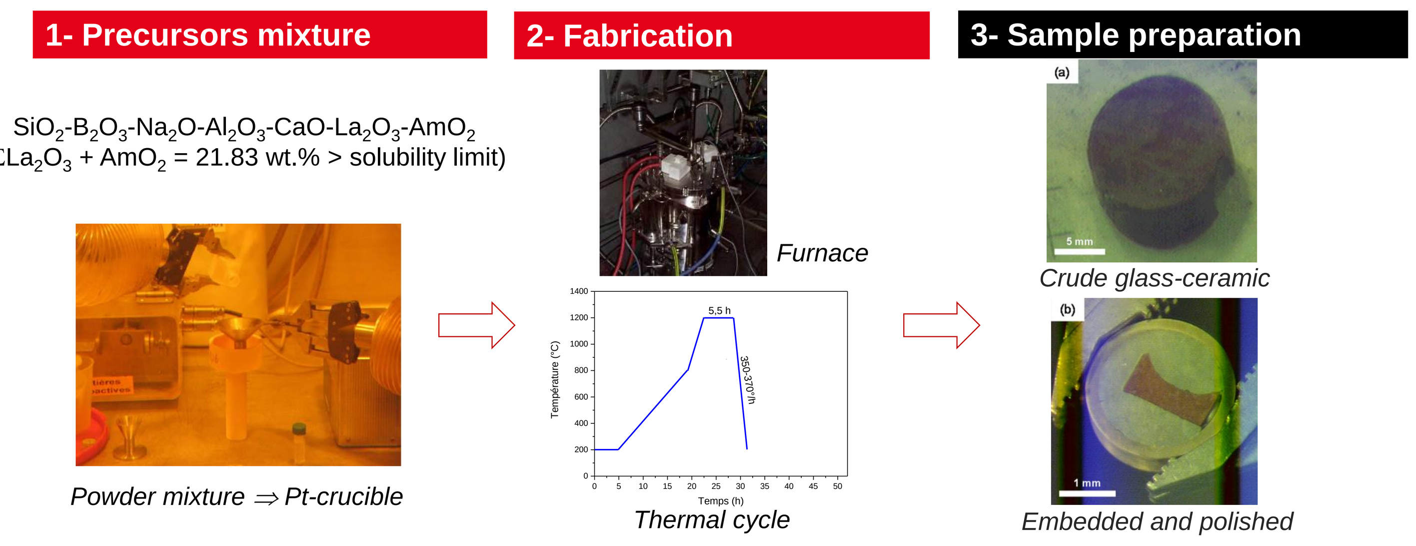


Effect of α-decay in crystalline phases in a partially devitrified glass:
a) $6x10^{15}$ α-decays/g and
b) $2.4x10^{17}$ α-decays/g

Fabrication of a ^{241}Am glass-ceramic in hot cells (DHA-ATALANTE)



DHA-Atalante facility.

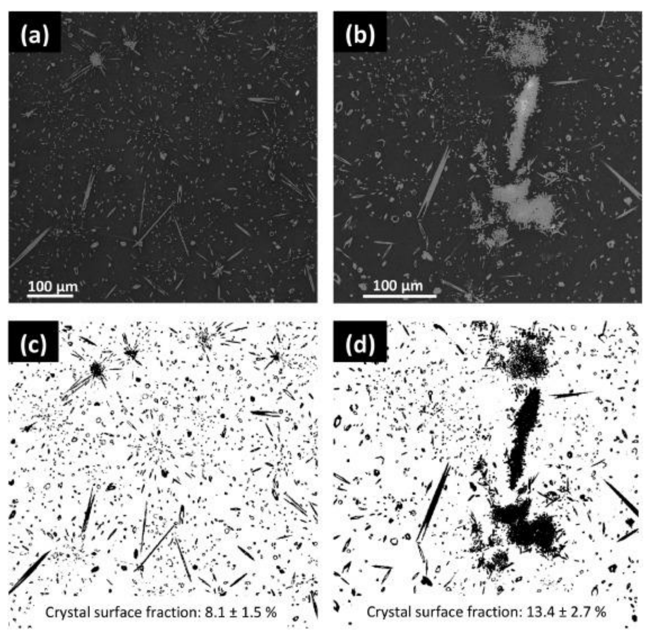


Initial characterizations in hot cells

SEM

Crystals are either isolated or grouped as aggregates with a hexagonal-shaped morphology, characteristic of apatite crystals.

- *Surface crystal fraction: 10 ± 3.9 %*
- *Max length of needle: 120 µm ± 50 µm*
- *Width of needle: 8 µm ± 3 µm*

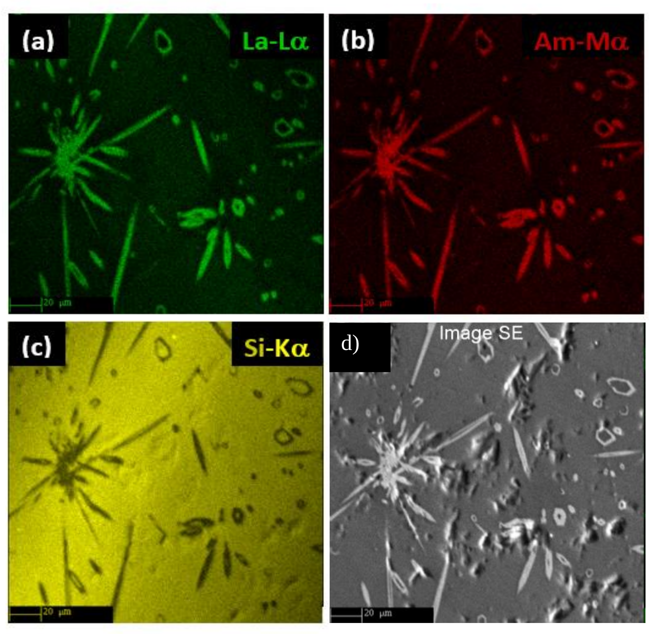


(a, b) SEM micrographs and (c, d) the corresponding binarized images obtained with the ImageJ freeware.

EPMA

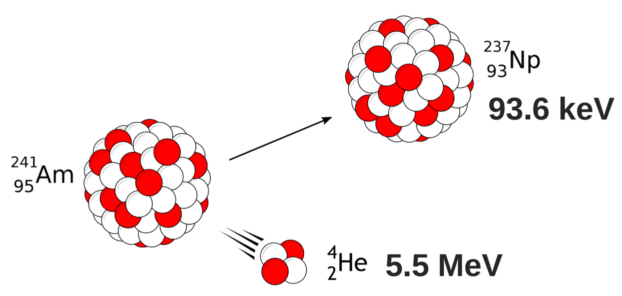
- *Enrichment in La and Am within the crystals.*
- *Average composition of apatite crystals:*

$Ca_{2.02}La_{3.96}Am_{4.07}(SiO_4)_6O_{1.99}$



EPMA elemental mapping of the glass-ceramic: (a) La-Lα, (b) Am-Mα and (c) Si-Kα X-ray maps and d) SE image.

Cumulative doses



Cumulative dose $D_{\alpha d}$ (alpha-decays/g) for both apatite and glass matrix:

$$D_{\alpha d} = N_0 [1-\exp(-\lambda t)],$$

N_0: number of ^{241}Am atoms per g incorporated in each phase,
λ: decay constant of ^{241}Am (λ= day^{-1}),
t: time (days).

Phase		Apatite		Glassy matrix	
Particle		α Particle	Recoil nucleus	α Particle	Recoil nucleus
Energy (keV)		5500	93.6	5500	93.6
R_p (µm)		16 µm	23 nm	22 µm	39 nm
$(dE/dx)_e$ (keV/nm)		<0.54	<0.6	<0.4	<0.5
$(dE/dx)_n$ (keV/nm)		<0.023	<4.7	<0.024	<3.4
Atomic displacements induced by each particle		200	1350	250	1600
1400 days after synthesis	$D_{\alpha d}$ (α decay/g)	$6.68x10^{18}$		$1.69x10^{18}$	
	Total number of dpa	0.890		0.095	

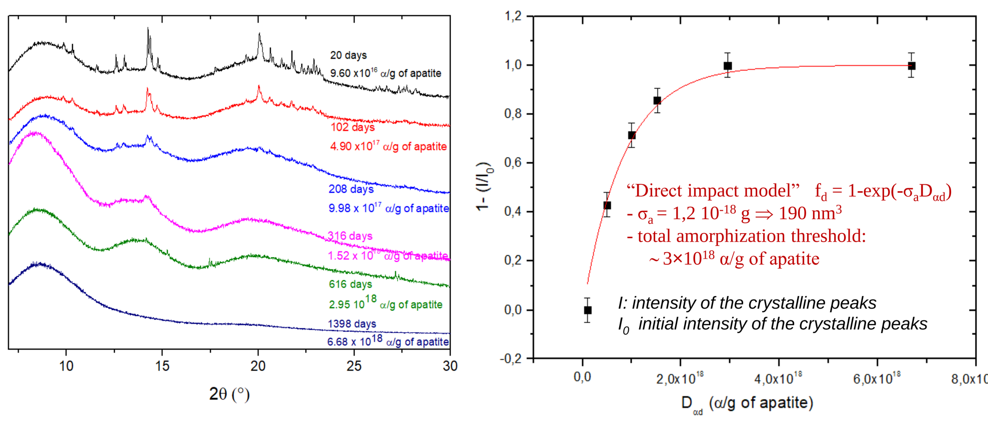
α-decay self-irradiation parameters calculated with SRIM-2013 software

Evolution under self-α irradiation

Structural and microstructural evolutions under self-irradiation were followed for 8 years.

Crystalline-to-amorphous tranformation

The combinaison of XRD and Raman spectroscopy data suggest a drastic transformation of the apatite structure with the α-decay dose.

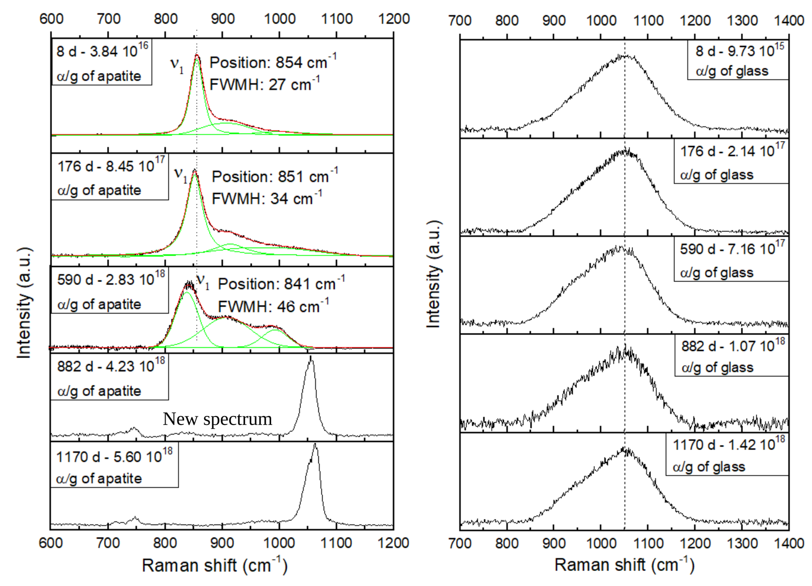


- *The evolution of the XRD patterns is the result of a progressive radiation-induced amorphization in apatite crystals.*
- *The fully amorphous state is reached at an α-decay dose of around 3 × 10^{18} α/g.*

a) X-ray diffraction pattern of the glass-ceramic at different cumulative dose
b) 1-I/I_0 versus dose with the least-squares fit with the direct impact model.

- *Shift of ν_1 (stretching mode) due to SiO_4 tetrahedral distorsions.*
- *Broadening of ν_1 up to 46 cm^{-1} due to amorphous state.*
- *After the amorphization threshold, new spectrum with a band ~ 1050 cm^{-1}.*

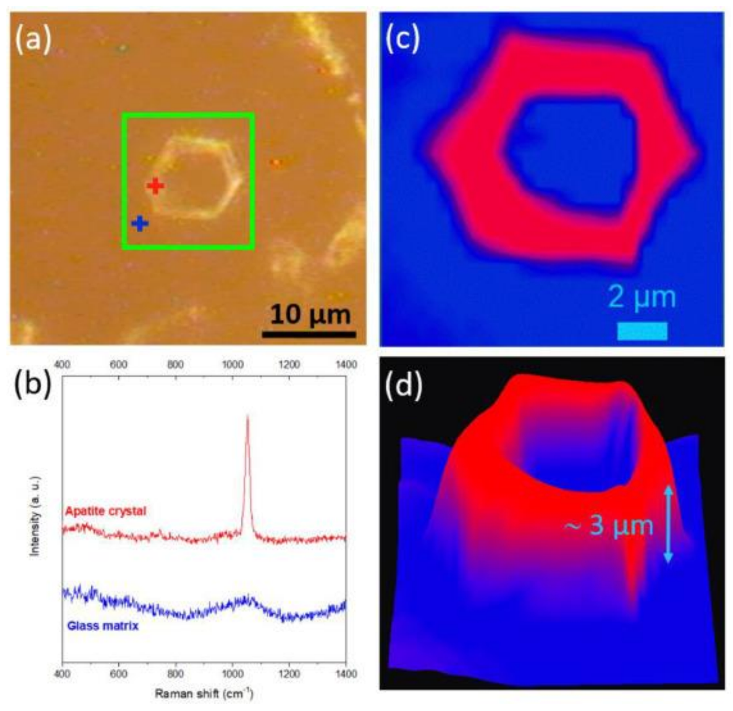
⇒ transition from isolated SiO_4 to connected SiO_4 units in the metamict state.



Raman spectra versus dose on (a) apatite crystals and (b) glass matrix.

Macroscopic dimensional change of apatite crystals

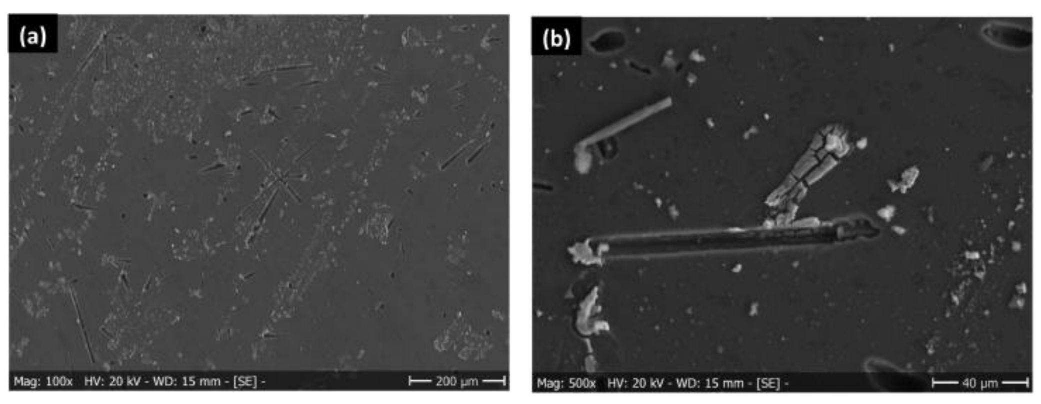
The crystalline-to-amorphous transformation is accompanied by a macroscopic dimensional change.



- *The crystalline-to-amorphous transformation in silicate apatite is accompanied by an increase in their macroscopic volume (swelling).*
- *The out-of-plane expansion is due to differential swelling behavior between the crystals and the glass.*

(a) Optical picture (100x), (b) Raman spectra, (c) 2D Raman image and (d) 3D Raman image.

- SEM reveal the appearance of holes caused by the grain pull-out of some crystals. The macroscopic dimensional change is associated to a decohesion of the crystals from the glassy matrix.
- However, any significant cracks in the residual glass by self-irradiation are observed contrary to Weber's study [3].



SEM micrographs (a) magnification x100 and (b) x500, 3010 days after synthesis.

Conclusion and outlooks

This study shows that the microcracking of glass-ceramic due to differential swelling under self-irradiation ageing can be avoided and is certainly strongly depending on the material microstructure. Some future work is needed to improve our understanding of the conditions that control the microcracking under irradiation and therefore to develop some mechanical resistant glass-ceramics with respect to their radiation aging.

References
1 S. Miro et al., JNM 580 (2023) 154397.
2 S. Gin et al., Radiochim. Acta 105 (11) (2017) 927-959.
3 W. J. Weber et al., J. Mater. Res., Vol. 13, No. 6, Jun (1998) 1434-1484.

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