

INFORME **DFN/RA-10/SP-26**

REF. EXTERNA

CHARACTERIZATION AND EXAMINATION OF IRRADIATED NUCLEAR FUEL SURROGATE PROPERTIES (IONMAT PROJECT. TASK 3)

DIVISIÓN DE FISIÓN NUCLEAR

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Energéticas, Medioambientales
y Tecnológicas



 DIVISIÓN DE FISIÓN NUCLEAR	INFORME DFN/RA-10/SP-26	HOJA 1 DE 70
	REF. EXTERNA	REVISIÓN 0

TITULO: Characterization and examination of irradiated nuclear fuel surrogate properties (IONMAT PROJECT. TASK 3)

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ABSTRACT:

This document presents and details the main results obtained within task 3 "Characterization and examination of the properties of irradiated nuclear fuel analogs" of the High Level Waste Unit (HLWU) of CIEMAT within the framework of the PID2021-124913OA-I00 project (IONMAT project) funded by the Spanish State Research Agency (Agencia Española de Investigación, AEI).

For comparison, characterization performed on pellets prepared by the same technological process (within tasks 1 and 2), i.e. dry powder method or co-precipitation, will be described, evaluated and discussed. Characterization will be carried out by a broad set of methods/techniques: XRD, Raman spectroscopy, particle size distribution (laser diffraction), density (geometrical, by immersion or pycnometric), BET by physisorption (nitrogen) and surface morphology by SEM. The grain size of the samples will be estimated by means of the linear intercept method.

The aim is to evaluate the effect on the microstructure of the fabrication procedure and assess the changes in the composition and morphology of pellets.

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ACKNOWLEDGMENTS

This research is part of the project of R+D+i PID2021-124913OA-I00, IONMAT project funded by MICIU/AEI/10.13039/501100011033/, Proyectos de Generaci3n de Conocimiento 2021. Authors also want to thank the funding from the European Commission Horizon Europe, EURATOM2027 Research and Training Programme (EURAD-2 project, grant agreement n3 101166718).

The experimental data used in this research were partly generated through access to the ActUsLab/FMR under the Framework of access to the Joint Research Centre Physical Research Infrastructures of the European Commission (OCRAPCI, Research Infrastructure Access Agreement N336922/01). Thanks to J. Boshoven and M. Cologna from JRC-KA for their assistance.

The experimental data used in this research were generated through access to the ActUsLab/HC-KA under the Framework of access to the Joint Research Centre Physical Research Infrastructures of the European Commission (CIATFRAS, Research Infrastructure Access Agreement N336346/01), as well as the collaboration agreement between JRC and CIEMAT (No. 602413). Thanks to L. Emblico and D. Serrano-Purroy from JRC-KA for their assistance.

The experimental data used in this research were generated under the Framework of the collaboration agreement between JRC and CIEMAT (No. 602413), in particular under the initiative THOXAM (THERmal stability and Oxidation of highly Active Materials, collaboration agreement No. 50099). Thanks to L. Emblico and D. Serrano-Purroy from JRC-KA for their assistance.

Authors want to acknowledge R. Wilbraham, J. Parsonage and C. Boxall from The Lloyd's Register Foundation Centre for Nuclear Engineering. Engineering Department, Lancaster University (UK), for facilitating the samples of ZrO₂-CsI.



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1. FABRICATION OF IRRADIATED NUCLEAR FUEL ANALOGUES AS PELLETS. STUDY AND DEVELOPMENT OF ACTINIDE CONVERSION BY WET ROUTE. INFLUENCE OF FABRICATION METHOD ON THE STABILITY OF THE FINAL FUEL PIN (TASK 1).

Within the IONMAT project, a series of irradiated fuel surrogate materials were fabricated to reproduce specific characteristics of spent nuclear fuel while avoiding the constraints associated with highly radioactive materials. The selection of the materials investigated in this task was guided by their relevance to key chemical, structural, and microstructural aspects of spent nuclear fuel behaviour under storage and disposal conditions. Rare-earth-doped UO_2 and CeO_2 -based systems were chosen to reproduce selected features of fission product accumulation and radiation-induced changes in irradiated fuel, while zirconia materials were included to evaluate the procedure to obtain inert matrices. The fabrication and characterization of these materials provide a platform for studying mechanisms that govern spent fuel evolution, dissolution behaviour, and radionuclide release under repository-relevant conditions.

1.1. PRODUCTION AND CHARACTERIZATION OF IRRADIATED NUCLEAR FUEL SURROGATES BY DRY POWDER METHOD (SUBTASK 1.1)

Surrogate nuclear fuel pellets were fabricated using a conventional powder metallurgy route involving powder mixing, grinding, sieving, pellet pressing, and high-temperature sintering under controlled atmosphere conditions. The objective was to investigate the influence of selected fission-products and matrix-forming additives on the microstructure and structural properties of UO_2 -based material.

1.1.1. Effect of Zr content on UO_2 : characterization

The incorporation of zirconium into UO_2 was studied for several compositions, ranging from pure UO_2 to pure ZrO_2 [1]. Density measurements showed a progressive decrease in both immersion and geometric densities as the ZrO_2 content increased, reflecting the lower theoretical density of zirconia compared with uranium dioxide and changes in the sintering behavior of the mixed oxides (Table I).



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Table I. Density values of the as-sintered Zr-doped and undoped UO₂ pellets.

SAMPLE	UO ₂	20 wt% ZrO ₂ - UO ₂	40 wt% ZrO ₂ - UO ₂	80 wt% ZrO ₂ - UO ₂	100 wt% ZrO ₂
Density immersion (g·cm ⁻³)	9.1 ± 0.1	8.6 ± 0.1	8.1 ± 0.1	6.1 ± 0.6	5.5 ± 0.3
Density geom. (g·cm ⁻³)	9.6 ± 0.3	8.5 ± 0.1	8 ± 1	5.7 ± 0.1	5.1 ± 0.1

SEM observations revealed a gradual microstructural evolution with increasing zirconium concentration (Figure 1). Samples containing up to 40 wt% ZrO₂ exhibited relatively homogeneous microstructures, whereas compositions richer in zirconia showed the appearance of smaller grains and secondary microstructural features, suggesting the onset of phase separation and the formation of zirconia-rich regions [2]. Although local variations in grain morphology were observed, the average grain sizes remained within a relatively narrow range (approximately 5-8 μm) for all compositions, with no clear relationship between grain size and zirconia content (Table II). Likewise, BET specific surface areas (SSA) remained low and relatively constant (0.28-0.35 m²·g⁻¹), indicating comparable densification levels and limited accessible porosity across the series.

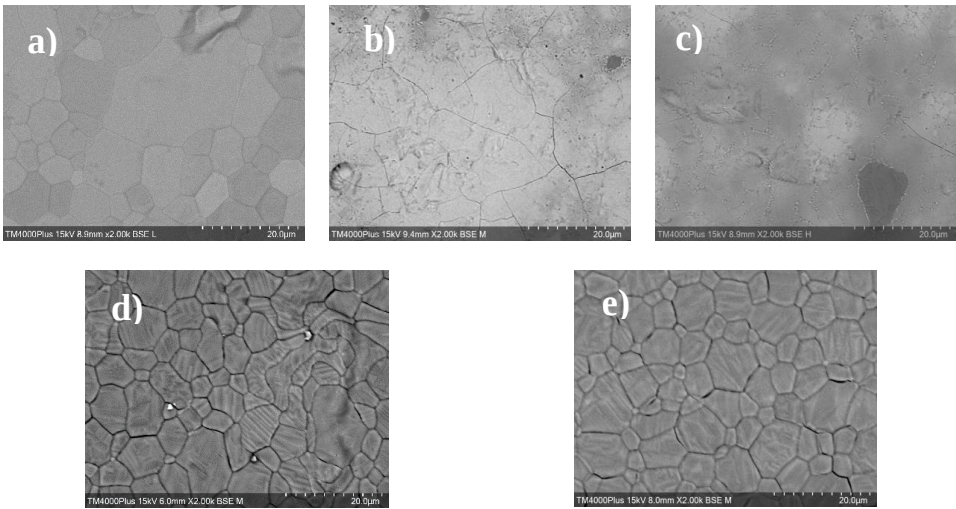


Figure 1. SEM images of the prepared samples: a) 100 wt% UO₂, b) UO₂ - 20 wt% ZrO₂, c) UO₂-40 wt% ZrO₂, d) UO₂-80 wt% ZrO₂ and e) 100 wt% ZrO₂.



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Table II. Average grain size and SSA of the Zr-doped and undoped UO₂ pellets.

SAMPLE	UO ₂	20 wt% ZrO ₂ - UO ₂	40 wt% ZrO ₂ - UO ₂	80 wt% ZrO ₂ - UO ₂	ZrO ₂
Grain size (μm)	7.6 ± 0.6	5 ± 2	5.2 ± 0.4	7.1 ± 0.5	5.8 ± 0.6
SSA (m ² ·g ⁻¹)	0.28 ± 0.01	0.30 ± 0.01	0.32 ± 0.02	0.30 ± 0.01	0.35 ± 0.01

XRD analysis demonstrated a clear evolution of the crystal structure as a function of zirconium content. The diffraction peaks (Figure 2) progressively shifted towards higher diffraction angles up to 40 wt% ZrO₂, indicating lattice contraction due to substitution of U⁴⁺ by the smaller Zr⁴⁺ ions within the fluorite structure (Table III). Mixed compositions contained predominantly cubic fluorite-type (U,Zr)O₂ solid solutions accompanied by increasing fractions of tetragonal zirconia (Table III).

(*) UO₂ ICDD #01-076-1118; (•) t-ZrO₂ ICDD #00-024-1164; (●) m-ZrO₂ ICDD #96-210-8457

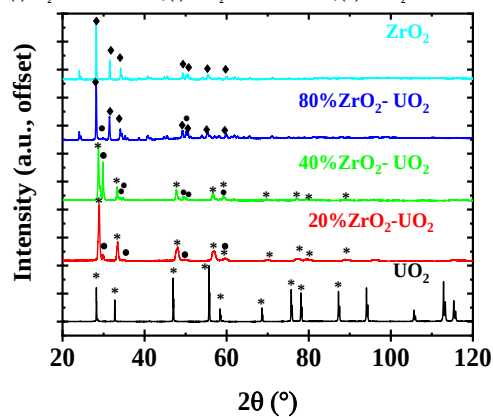


Figure 2. XRD patterns of the sintered pellets: UO₂, UO₂ - 20 wt% ZrO₂, UO₂-40 wt% ZrO₂, UO₂-80 wt% ZrO₂, 100 wt% ZrO₂.

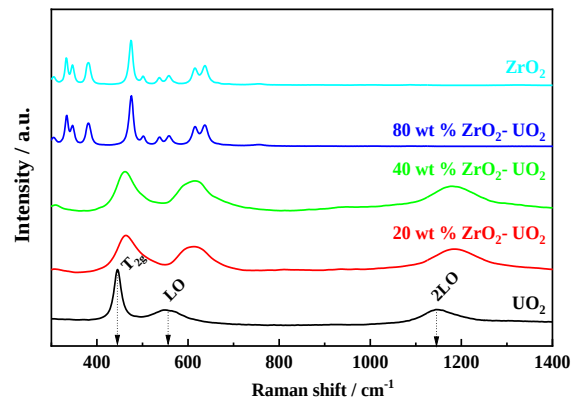


Figure 3. Raman spectra of the sintered pellets: UO₂, UO₂ - 20 wt% ZrO₂, UO₂-40 wt% ZrO₂, UO₂-80 wt% ZrO₂, ZrO₂.

At 80 wt% ZrO₂, a monoclinic phase became dominant, indicating that the solid-solution limit had been exceeded [2]. XRD analyses confirmed the progressive incorporation of zirconium into the fluorite UO₂ structure, accompanied by the formation of secondary zirconia phases as the overall ZrO₂ content increased. For the 20 wt% ZrO₂ composition, the material consisted predominantly of a fluorite-type U_{1-y}Zr_yO₂ phase (92 wt%, y ≈ 0.48, corresponding to approximately 48 mol% Zr on the cation sublattice),



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together with a minor fraction of tetragonal ZrO_2 (<8 wt%). Increasing the zirconia content to 40 wt% resulted in a larger proportion of tetragonal zirconia (33 wt%), while the remaining fluorite phase was consistent with an approximately equimolar U-Zr oxide ($\text{U}_{0.5}\text{Zr}_{0.5}\text{O}_2$). At 80 wt% ZrO_2 , monoclinic zirconia became the dominant phase, indicating extensive phase segregation and a substantial reduction in zirconium incorporation within the fluorite structure. These results demonstrate that significant U-Zr solid-solution formation occurs under the employed processing conditions; however, the persistence and increasing abundance of zirconia secondary phases indicate that complete zirconium incorporation is not achieved, particularly at higher zirconia loadings. Our data suggest that the limit has already been exceeded at 20 wt% ZrO_2 (<35.4 mol% Zr), since <8 wt% tetragonal ZrO_2 was detected.

Table III. Lattice parameters and identified phases of the as-sintered Zr-doped and undoped UO_2 pellets.

SAMPLE	UO_2	20 wt% ZrO_2 - UO_2	40 wt% ZrO_2 - UO_2	80 wt% ZrO_2 - UO_2	100 wt% ZrO_2
Lattice param. (nm)	100% UO_2 Fm-3m a=b=c= 0.5470(2)	92% $\text{U}_{1-y}\text{Zr}_y\text{O}_2$ (y = 0.48) Fm-3m a=b=c= 0.5403(1) < 8% ZrO_2 SG P 42/nmc a=0.3686(2) b=0.3686(2) c= 0.5138(3)	67% $\text{U}_{0.5}\text{Zr}_{0.5}\text{O}_2$ Fm-3m a=b=c= 0.5404(1) 33% t- ZrO_2 SG P 42/nmc a=0.3688(4) b=0.3688(4) c= 0.5150(1)	91% $\text{U}_{1-x}\text{Zr}_x\text{O}_2$ (x = 0.04) P1 21/c1 a=0.5161(2); b=0.5214 (2); c= 0.5324(2) 4% t- ZrO_2 SG P 42/nmc a=0.3660; b=0.3660; c= 0.5206 (8) ~3% $\text{U}_{1-y}\text{Zr}_y\text{O}_2$ (y = 0.5) Fm-3m a=b=c= 0.5461(9) 2% UO_2 Fm-3m a=b=c= 0.5471(2)	100% m- ZrO_2 P1 21/c1 a=0.5156(3) b=0.5211(1) c= 0.5324(7)

The Raman spectra support the conclusions drawn from XRD. Pure UO_2 exhibited the characteristic fluorite fingerprint dominated by the T_{2g} mode (Figure 3). Progressive zirconium addition produced broadening and shifting of the T_{2g} , LO and 2LO bands, indicating increasing structural disorder and distortion of the fluorite lattice. Samples containing up to 40 wt% ZrO_2 retained the main characteristics of the fluorite structure, whereas the 80 wt% ZrO_2 composition displayed multiple Raman bands characteristic of monoclinic zirconia [3]. These observations confirm progressive zirconium incorporation into the UO_2 lattice followed by phase separation at high zirconium contents. Further work involving intermediate compositions (e.g., 50-70 wt% ZrO_2) would be beneficial to better



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define the compositional range over which the fluorite phase remains stable and to establish more accurately the zirconium incorporation limit under the processing conditions employed.

1.1.2. Effect of Eu content on UO₂: characterization

The influence of europium on UO₂ pellets was investigated using Eu₂O₃ concentrations between 0.02 and 2 wt% [1]. Density measurements (Table IV) revealed a slight decrease in bulk density with increasing europium content, although all compositions remained highly densified after sintering.

Table IV. Density values of the as-sintered Eu-doped and undoped UO₂ pellets.

SAMPLE	UO ₂	0.02 wt% Eu ₂ O ₃ -UO ₂	0.2 wt% Eu ₂ O ₃ -UO ₂	2 wt% Eu ₂ O ₃ -UO ₂
Density immersion (g·cm ⁻³)	9.8 ± 0.1	9.6 ± 0.1	9.3 ± 0.2	9.3 ± 0.8
Density geom. (g·cm ⁻³)	9.6 ± 0.3	10.0 ± 0.7	9.7 ± 0.1	9.8 ± 0.3

SEM analysis in Figure 4 showed homogeneous microstructures and only isolated porosity throughout the entire composition range. No evidence of secondary europium-rich phases was observed. Grain size (Table IV) remained comparable to that of undoped UO₂ at low Eu additions and reached a maximum value at 0.2 wt% Eu₂O₃ before decreasing at the highest concentration investigated. BET surface areas remained within the same order of magnitude for all samples (

Table V), ranged between approximately 0.2 and 0.6 m²·g⁻¹.

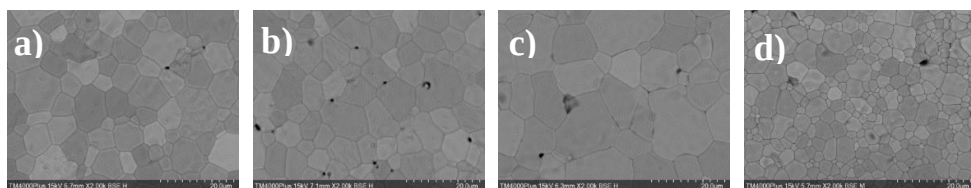


Figure 4. SEM images of the prepared samples: a) UO₂, b) 0.02 wt% Eu₂O₃ - UO₂, c) 0.2 wt% Eu₂O₃ - UO₂, and d) 2 wt% Eu₂O₃ - UO₂.



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Table V. Average grain size and SSA of the Eu-doped and undoped UO₂ pellets.

SAMPLE	UO ₂	0.02 wt% Eu ₂ O ₃ -UO ₂	0.2 wt% Eu ₂ O ₃ -UO ₂	2 wt% Eu ₂ O ₃ -UO ₂
Grain size (µm)	6.9 ± 0.8	6.7 ± 0.5	11.0 ± 1.0	5.0 ± 1.0
SSA (m ² ·g ⁻¹)	0.43 ± 0.01	0.55 ± 0.02	0.26 ± 0.01	0.21 ± 0.01

XRD analysis confirmed the formation of single-phase fluorite-type (U,Eu)O₂ solid solutions for all europium concentrations studied. No secondary phases were detected, indicating complete dissolution of Eu within the investigated compositional range. A progressive shift of diffraction peaks towards higher diffraction angles was observed with increasing Eu content, corresponding to a decrease in lattice parameter. The lattice parameter follows a Vegard-type behavior (Figure 5). A regression analysis was performed on the measured lattice parameters of Eu-doped UO₂ solid solution, which can be expressed as: $a = (0.54713 \pm 2.33 \cdot 10^{-6}) + (-0.01225 \pm 2.4 \cdot 10^{-4}) \cdot x$; where a is the lattice parameter in nm, and x is the Eu content in UO₂. The coefficients of the equation are determined by using a least-squares method, where the relative coefficient is 0.99922. This found linear trend confirms incorporation of Eu into the UO₂ lattice, and indicates that the europium solubility limit is above the maximum concentration considered in this study [4-6].

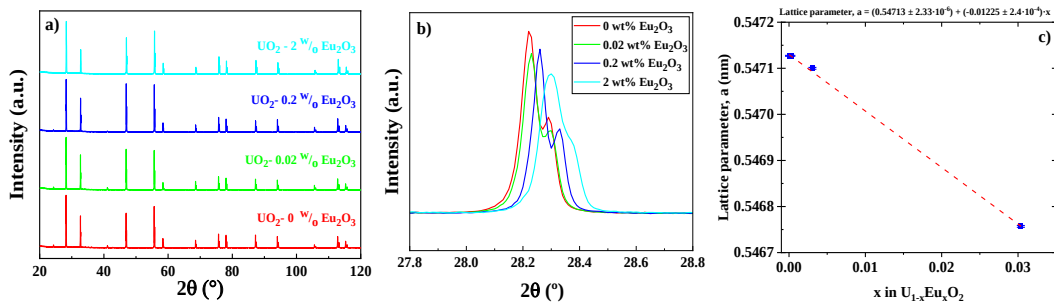


Figure 5. XRD patterns of the UO₂ pellets containing 0 wt%, 0.02 wt%, 0.2 wt% and 2 wt% Eu₂O₃ (a), zoom on the (111) reflection (b), and lattice parameter evolution (c) of the sintered pellets.

Raman spectroscopy further confirmed europium incorporation into the fluorite structure (Figure 6). Increasing Eu concentration resulted in the growth of defect-related bands near 530 and 575 cm⁻¹, which are associated with oxygen-vacancy formation and lattice distortions generated by incorporation of trivalent Eu³⁺ ions. Simultaneously, the intensity of the 2LO band decreased at higher Eu concentrations, indicating increasing structural disorder within the fluorite lattice. However, no other bands associated to other



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crystal structures were found in the spectra. These observations are fully consistent with the XRD results and confirm the generation of charge-compensating defects associated with europium incorporation [7, 8].

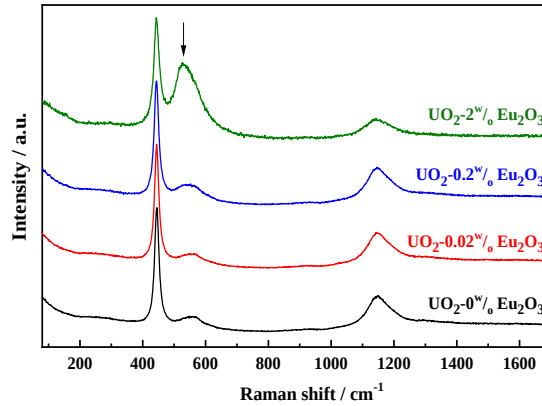


Figure 6. Normalized Raman spectra of UO_2 , UO_2 -0.02 wt% Eu_2O_3 , UO_2 -0.2 wt% Eu_2O_3 , UO_2 -2 wt% Eu_2O_3 .

1.2. POROSITY SIMULATION (SUBTASK 1.2)

The microstructural evolution of irradiated nuclear fuel is strongly influenced by burnup, thermal history, fission product accumulation, and the development of the high burnup structure (HBS) at the pellet rim. These phenomena directly affect fuel performance, radionuclide retention, and long-term disposal behavior. The objective of this subtask was to reproduce, using surrogate materials, two key features of irradiated fuel: (i) the incorporation of fission-products (FPs) analogues (Nd_2O_3) and (ii) the progressive development of porosity associated with the rim structure. To achieve this goal, a series of CeO_2 - (non-radioactive) and UO_2 -based model materials were fabricated and characterized to establish relationships between composition, porosity, and microstructural evolution.

1.2.1. Influence of porosity and fission products on the microstructure of irradiated fuel

CeO_2 - Nd_2O_3 systems were selected as non-radioactive surrogates to simulate the accumulation of rare-earth FPs in irradiated fuel, while ethylene bis-stearamide (EBS) was



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incorporated as a pore-forming agent to reproduce the increase in porosity associated with high burnup microstructures. Nd_2O_3 concentrations between 0 and 25 wt% and EBS contents up to 19 wt% were investigated (Table VI) [9].

Table VI. Masses of CeO_2 and Nd_2O_3 powder precursors used for the preparation of green pellets as a function of Nd_2O_3 wt%. Masses for 10 g mixtures (uncertainty ± 0.0001 g).

Nd_2O_3 (wt %)	Nd_2O_3 (g)	CeO_2 (g)
0	0.0000	10.0003
4	0.4091	9.5983
17	1.7338	8.2664
25	2.5445	7.4553

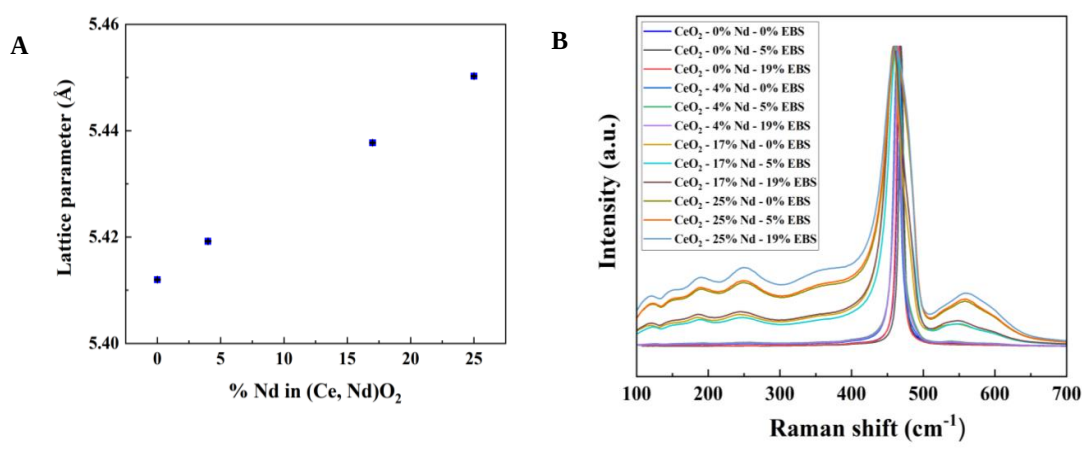


Figure 7. Lattice parameters (A) and Raman spectra obtained from CeO_2 samples doped with 0, 4, 17, and 25 wt% Nd.

XRD and Raman spectroscopy (Figure 7) confirmed the successful incorporation of Nd into the fluorite structure of CeO_2 . Increasing neodymium concentration resulted in a systematic broadening and asymmetry of the characteristic fluorite Raman band (T_{2g} mode), together with the appearance of additional features associated with lattice distortion and oxygen-vacancy formation. These observations indicate that substitution of Ce by Nd^{3+} produces increasing defect concentrations and local structural disorder. The Raman band (Figure 7.B) centered at approximately 540 cm^{-1} became progressively more intense with



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increasing Nd content, providing evidence of oxygen-vacancy formation. This behavior is analogous to that expected for trivalent fission-product incorporation in irradiated fuel and therefore confirms that the surrogate materials successfully reproduce important aspects of spent-fuel defect chemistry.

XRD analyses (Figure 7.A) showed a systematic increase in lattice parameter with increasing Nd concentration, consistent with the larger ionic radius of Nd^{3+} compared with Ce^{4+} . The absence of secondary Nd-containing crystalline phases indicates that neodymium was incorporated into the fluorite lattice rather than segregating into separate phases. In particular, a linear increase of the lattice parameter (following Vegard's law behaviour), a , with increasing Nd content can be observed. The lattice parameter follows the equation below, obtained from the average of the fitted experimental data: $a(x) = 0.00151 \cdot x + 5.41246$ ($R^2 = 0.99904$), where x corresponds to the Nd_2O_3 weight percentage.

SEM-EDS analyses (Figure 8) further demonstrated that Nd was homogeneously distributed throughout the pellets, confirming the effectiveness of the fabrication route and eliminating concerns related to local compositional segregation.

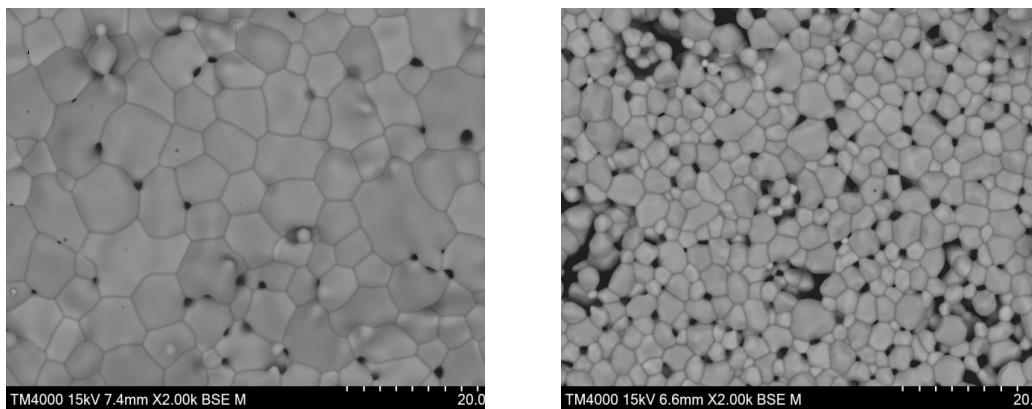


Figure 8. SEM micrographs of pellets containing 0 % Nd-0% EBS (A) and 0 % Nd-19% EBS (B).

Unlike Nd incorporation, EBS had little effect on the crystal structure of the materials. Raman spectra and lattice parameters remained essentially unchanged for a given Nd concentration regardless of EBS content. These results demonstrate that EBS acts solely



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as a pore forming additive and does not participate in the chemistry of the fluorite lattice. SEM observations revealed a progressive increase in porosity and morphological heterogeneity as the EBS concentration increased. Samples containing 19 wt% EBS exhibited extensive pore formation and a more heterogeneous grain structure compared with EBS-free materials. Density measurements showed a nearly linear decrease with increasing EBS content, while BET surface area measurements increased correspondingly.

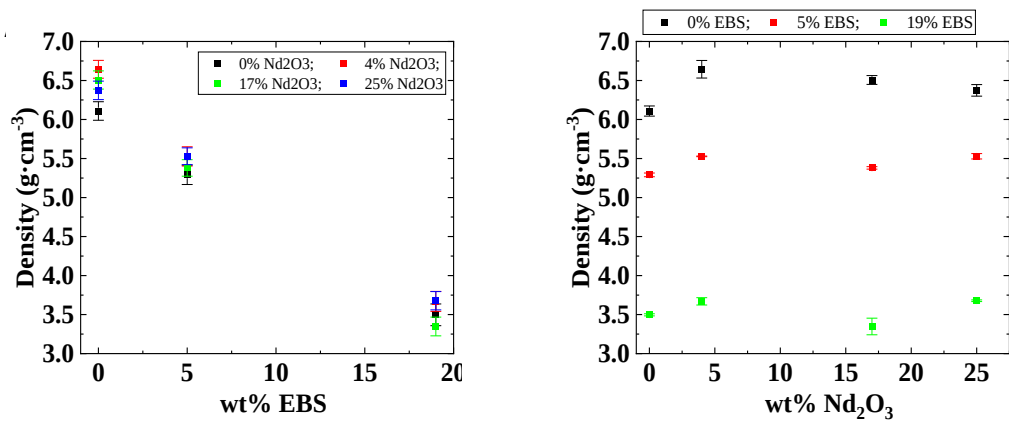


Figure 9. Density as a function of EBS content (A) and % Nd₂O₃ (B).

Importantly, the influence of EBS on porosity was largely independent of neodymium concentration. Samples with the same EBS content exhibited comparable density (Figure 9) and BET surface area values (Figure 10) regardless of Nd loading. The SSA increased almost linearly with increasing EBS content, whereas the influence of Nd concentration was comparatively minor. This confirms that porosity and FP concentration can be controlled independently within this surrogate system.



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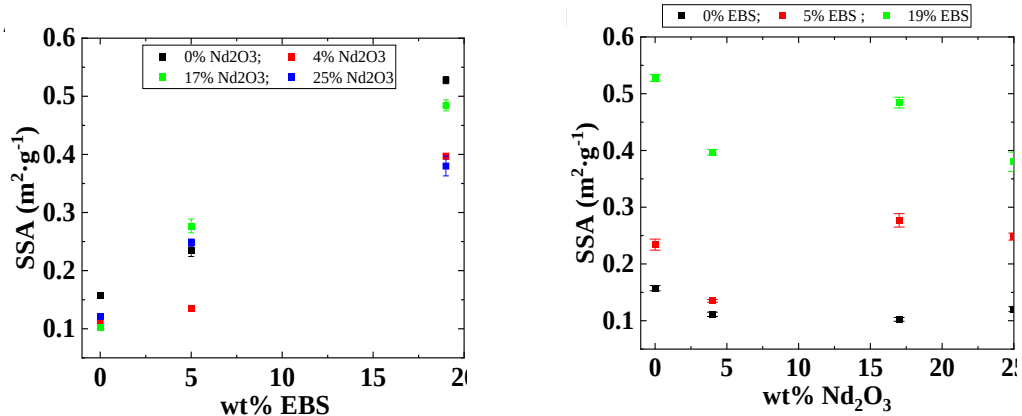


Figure 10. SSA as a function of EBS content (A) and % Nd₂O₃ (B).

The fabricated CeO₂-Nd₂O₃ pellets with EBS materials reproduce two of the most important microstructural features of irradiated fuel; one is the accumulation of representative FPs and the associated defect chemistry, and the other, the development of controlled porosity representative of high-burnup fuel structures. The ability to vary FP content and porosity provides a powerful experimental framework for future studies of spent fuel degradation, radionuclide release, and long-term behavior under storage and disposal conditions. While these materials do not directly reproduce radiation damage, they mimic many of the chemical and microstructural modifications that occur during fuel irradiation and therefore represent valuable irradiated fuel surrogates.

1.2.2. Characterization of spent nuclear fuel surrogates to mimic porosity

A second approach to porosity simulation was based on controlled additions of U₃O₈, as a pore-forming agent, to UO₂ powders prior to sintering [10]. During thermal treatment, U₃O₈ is reduced back to UO₂, generating oxygen release that can influence pore formation and densification. Four compositions containing 0, 5, 12, and 19 wt% U₃O₈ were prepared and sintered under reducing atmosphere (Table VII).



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Table VII. Prepared samples, with different proportions of UO_2 and U_3O_8 .

Reference	UO_2 (wt%)	U_3O_8 (wt%)
UO_2 -0% U_3O_8	100	0
UO_2 -5% U_3O_8	95	5
UO_2 -12% U_3O_8	88	12
UO_2 -19% U_3O_8	81	19

XRD analysis confirmed a complete reduction of U_3O_8 during sintering and only cubic fluorite UO_2 in all samples was identified (Figure 11), with no residual of U_3O_8 . Although slight variations in lattice parameter were observed (Table VIII and Figure 12), these changes were small and cannot be directly interpreted as densification. Nevertheless, they suggest subtle microstructural modifications induced by the initial U_3O_8 additions.

Table VIII. Lattice parameters of the UO_2 pellets sintered with increasing content of U_3O_8 .

Reference	Phase identification	Lattice parameter, a (Å)
UO_2 -0% U_3O_8	UO_2 (Fm-3m)	5.47113(2)
UO_2 -5% U_3O_8	UO_2 (Fm-3m)	5.47143(4)
UO_2 -12% U_3O_8	UO_2 (Fm-3m)	5.47128(2)
UO_2 -19% U_3O_8	UO_2 (Fm-3m)	5.47085(2)

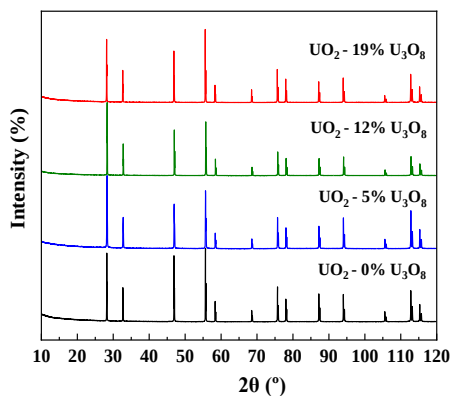


Figure 11. Diffractograms of the UO_2 pellets sintered with increasing content of U_3O_8 .

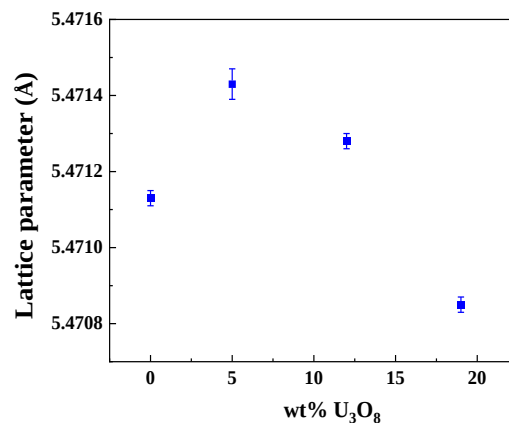


Figure 12. Evolution of the lattice parameter of the UO_2 pellets sintered with increasing content of U_3O_8 .



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Helium pycnometry revealed relative densities between 85.8 and 86.8% of theoretical density (see Table IX). These values are lower than those typically targeted for commercial fuel pellets, but such reduced densification was intentional in order to preserve measurable porosity and evaluate the influence of U_3O_8 additions. The lowest density was obtained for the 5 wt% U_3O_8 sample, while further increases in U_3O_8 concentration resulted in a progressively higher densification.

Table IX. Density values of the UO_2 pellets sintered with increasing content of U_3O_8 .

Reference	Density ($\text{g}\cdot\text{cm}^{-3}$)	Relative Density (%)
$\text{UO}_2 + 0\% \text{U}_3\text{O}_8$	9.474 ± 0.006	86.4
$\text{UO}_2 + 5\% \text{U}_3\text{O}_8$	9.402 ± 0.007	85.8
$\text{UO}_2 + 12\% \text{U}_3\text{O}_8$	9.43 ± 0.01	86.0
$\text{UO}_2 + 19\% \text{U}_3\text{O}_8$	9.51 ± 0.01	86.8

BET measurements showed a similar trend (Figure 13). The SSA remained relatively low for all compositions, ranging from approximately $0.2 \text{ m}^2\cdot\text{g}^{-1}$ for pure UO_2 to $0.35 \text{ m}^2\cdot\text{g}^{-1}$ for the 5 wt% U_3O_8 composition. A slight increase was observed between pure UO_2 and the 5 wt% U_3O_8 , whereas samples containing higher U_3O_8 fractions exhibited lower surface areas, between approximately 0.2 and $0.25 \text{ m}^2\cdot\text{g}^{-1}$. The limited variation in SSA suggests that all materials achieved a relatively high degree of densification, with only minor differences in accessible porosity between compositions.

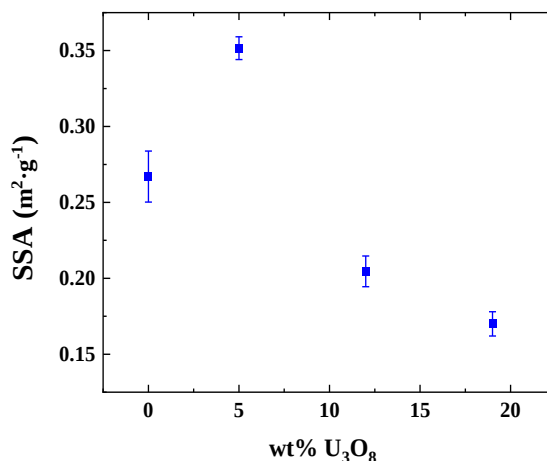


Figure 13. Evolution of the SSA of the UO_2 pellets sintered with increasing content of U_3O_8 .



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Porosity calculations derived from density measurements (Table X) showed maximum porosity for the 5 wt% U_3O_8 composition (14.3%) and minimum porosity for the 19 wt% U_3O_8 sample (13.3%).

Table X. Porosity estimated for the UO_2 pellets sintered with increasing content of U_3O_8 .

Reference	Total Porosity (%)	Porosity estimated from pycnometry/XRD (%)
$\text{UO}_2 + 0\% \text{U}_3\text{O}_8$	13.67	13.50
$\text{UO}_2 + 5\% \text{U}_3\text{O}_8$	14.31	14.14
$\text{UO}_2 + 12\% \text{U}_3\text{O}_8$	14.13	13.94
$\text{UO}_2 + 19\% \text{U}_3\text{O}_8$	13.31	13.17

Morphological characterization of the pellets was also performed by SEM. Figure 14 shows selected images on each of the studied UO_2 pellets (containing 0, 5, 12 and 19 wt. % U_3O_8 before sintering). SEM micrographs revealed negligible differences among the samples. Regarding porosity, the presence of a slightly greater amount of intragranular pores can be deduced from the image corresponding to the addition of 5 wt% U_3O_8 , what is in accordance with the rest of previously mentioned outcomes. Nonetheless, it must be taken into consideration that the variation in porosity values reported in the previous section is so small, that only a subtle distinction would be expected in the SEM images.

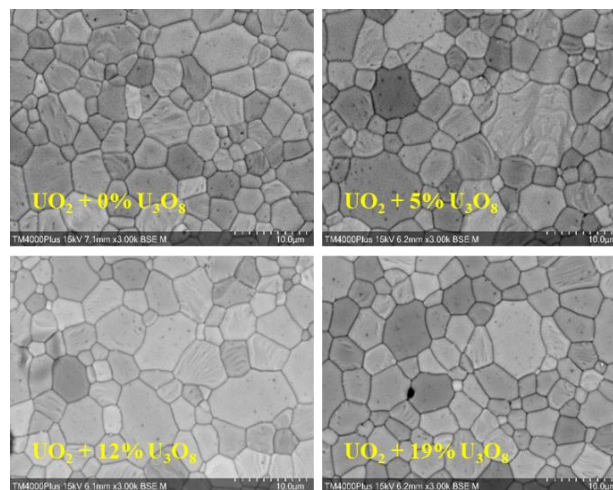


Figure 14. SEM images the UO_2 pellets sintered with increased content of U_3O_8 .



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The observed behavior suggests the existence of a threshold effect. Addition of small amount of U_3O_8 initially promoted pore formation, whereas higher addition may facilitate sintering through enhanced defect generation and atomic mobility associated with the U_3O_8 to UO_2 reduction process. Additional compositions, particularly below 5 wt% U_3O_8 and above 19 wt% U_3O_8 , would be valuable to confirm this hypothesis.

Although the differences are relatively small, the same trend was consistently observed by XRD, pycnometry, BET, and SEM analyses.

1.3. PREPARATION OF MIXED OXIDE FUELS CONTAINING UO_2 (SUBTASK 1.3)

UO_2 - ZrO_2 mixed oxide fuels were synthesized by an aqueous co-precipitation route followed by calcination, reduction, pellet pressing, and sintering [11]. This system was selected because zirconium is a major constituent of Zircaloy cladding materials and therefore represents a relevant component in fuel-cladding interaction scenarios, accident-tolerant fuel concepts, and spent fuel degradation studies. The co-precipitation approach was employed to improve chemical homogeneity compared with conventional powder mixing and to evaluate the influence of zirconium incorporation on phase stability, microstructure, densification, and porosity. The compositions investigated ranged from pure UO_2 to pure ZrO_2 , as summarized in Table XI.

Table XI. Definition of UO_2 - ZrO_2 samples.

Reference	ZrO_2 (wt%)	UO_2 (wt%)
UO_2	0	100
UO_2 - 20% ZrO_2	20	80
UO_2 - 40% ZrO_2	40	60
UO_2 - 60% ZrO_2	60	40
ZrO_2	100	0

The phase evolution of the sintered pellets was investigated by XRD. The results revealed a progressive transition from cubic fluorite UO_2 to monoclinic zirconia as the ZrO_2 content increased (Figure 15 and Table XII). Pure UO_2 retained its characteristic fluorite structure (Fm-3m), whereas pure zirconia crystallized as monoclinic ZrO_2 . Intermediate compositions consisted of mixtures of cubic and tetragonal (U,Zr) O_2 phases.

The fraction of the cubic (U,Zr) O_2 phase (uranium-rich) decreased systematically



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with increasing zirconium content, from 96.4 wt% at 20 wt% ZrO₂ to only 34 wt% at 60 wt% ZrO₂. Simultaneously, the fraction of the tetragonal zirconia-rich phase increased from 3.6 wt% to 66 wt%, indicating progressive destabilization of the fluorite lattice and the formation of zirconia-rich domains with different crystal structure.

Table XII. Quantification of main phases identified by XRD.

Composition	Main phases identified
UO ₂	c-UO ₂ (100 wt%)
UO ₂ - 20%ZrO ₂	3.6 wt% t-U _{0.18} Zr _{0.82} O ₂ + 96.4 wt% c-U _{0.9} Zr _{0.1} O ₂
UO ₂ - 40%ZrO ₂	32.1 wt% t-U _{0.18} Zr _{0.82} O ₂ + 67.9 wt% c-U _{0.9} Zr _{0.1} O ₂
UO ₂ - 60%ZrO ₂	66 wt% t-U _{0.18} Zr _{0.82} O ₂ + 34 wt% c-U _{0.9} Zr _{0.1} O ₂
ZrO ₂	m-ZrO ₂ (100 wt%)

These results demonstrate that zirconium is partially incorporated into the UO₂ structure at low concentrations, while higher zirconium loadings favor phase separation and stabilization of zirconium-rich phases. The coexistence of cubic and tetragonal phases across a broad compositional range (Figure 16) highlights the limited solubility of uranium and zirconium oxides under the investigated sintering conditions and confirms the strong influence of composition on phase stability.

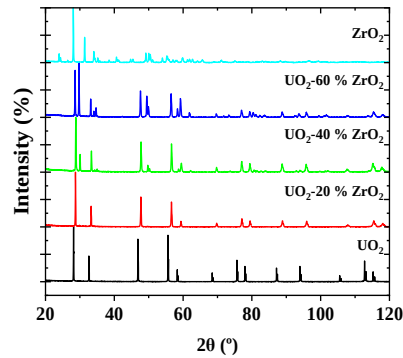


Figure 15. XRD patterns of the sintered pellets: UO₂, UO₂ - 20% ZrO₂, UO₂ - 40% ZrO₂, UO₂ - 60% ZrO₂, ZrO₂.

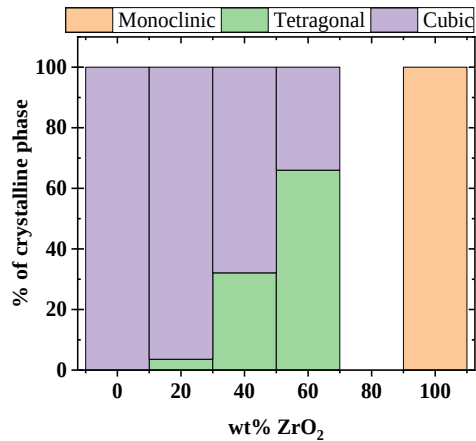


Figure 16. Evolution of crystalline phase composition with increasing ZrO₂ content.



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Raman spectroscopy provided complementary information regarding local structural changes induced by zirconium incorporation (Figure 17). Pure UO_2 exhibited the characteristic fluorite fingerprint dominated by the T_{2g} mode at approximately 445 cm^{-1} together with the LO and 2LO bands [12-14]. As the zirconium content increased, progressive broadening and asymmetry of the fluorite bands were observed, indicating increasing lattice distortion and structural disorder. The UO_2 -20% ZrO_2 sample remained predominantly fluorite-like, although additional Raman features appeared, suggesting the onset of phase separation [15]. For the 40 and 60 wt% ZrO_2 compositions, the spectra became increasingly complex due to the coexistence of cubic and tetragonal environments. Characteristic zirconia-related bands appeared in the low-frequency region and increased in intensity with composition. Pure ZrO_2 exhibited the expected spectrum of monoclinic zirconia, characterized by multiple sharp bands between 150 and 700 cm^{-1} [3, 16]. Overall, the Raman results were fully consistent with the XRD analysis and confirmed the progressive transformation from uranium-rich fluorite structures to zirconia-rich phases.

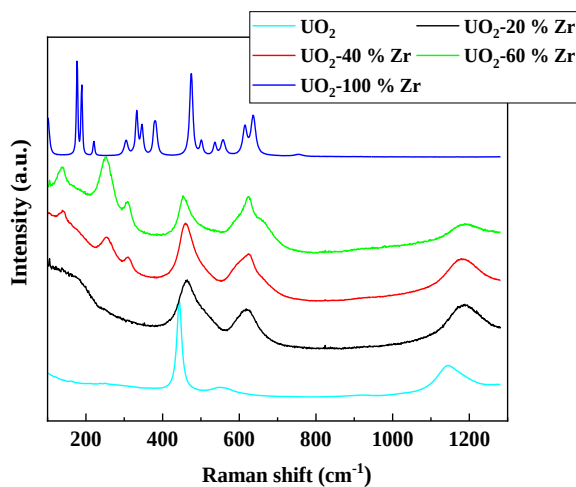


Figure 17. Raman spectra of the sintered pellets obtained from wet route: UO_2 , UO_2 - 20% ZrO_2 , UO_2 - 40% ZrO_2 , UO_2 - 60% ZrO_2 , ZrO_2 .

Pellet densities were determined by helium pycnometry and geometrical measurements. Pycnometric density decreased almost linearly with increasing ZrO_2 content, from approximately $9.7\text{ g}\cdot\text{cm}^{-3}$ for pure UO_2 to $5.5\text{ g}\cdot\text{cm}^{-3}$ for pure zirconia, reflecting the intrinsically lower density of zirconia compared with uranium dioxide (Figure 18).



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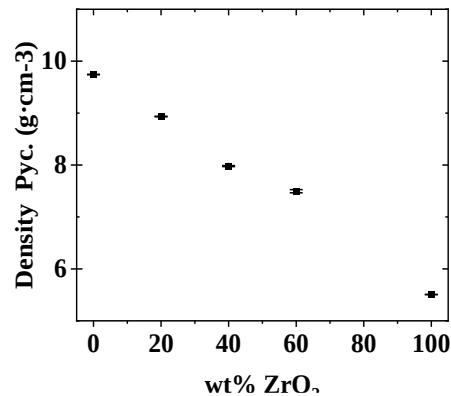


Figure 18. Pycnometer density ($\text{g}\cdot\text{cm}^{-3}$) vs ZrO_2 content (%).

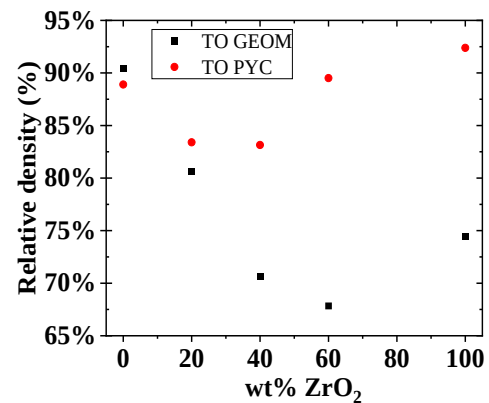


Figure 19. Relative density and total porosity vs ZrO_2 content (%).

Relative density calculations revealed that UO_2 -rich compositions achieved significantly higher densification than zirconia-rich materials. The difference between pycnometric and geometrical densities (Figure 19) was substantially larger in ZrO_2 -rich samples, indicating a greater contribution from open porosity. In contrast, pellets containing 20 wt% ZrO_2 exhibited only about 2.8% open porosity, demonstrating effective pore closure during sintering. The evolution of porosity closely followed the phase and density trends (Table XIII). Total porosity decreased from approximately 25-32% in zirconia-rich compositions to less than 10% in pure UO_2 , confirming the superior sintering behavior of uranium-rich compositions.

Table XIII. Estimated samples porosity.

ZrO_2 (wt %)	Total porosity (%)	Open (%)	Closed (%)	BET SSA ($\text{m}^2\cdot\text{g}^{-1}$)
0	9.6	-	11.1	0.222 ± 0.005
20	19.4	2.8	16.6	0.216 ± 0.005
40	29.4	12.5	16.9	0.24 ± 0.04
60	32.2	21.7	10.5	0.194 ± 0.004
100	25.5	17.9	7.6	0.358 ± 0.003

BET measurements showed relatively low SSAs for all compositions (Table XIII), ranging from 0.19 to $0.36 \text{ m}^2\cdot\text{g}^{-1}$. These values are characteristic of highly sintered ceramic materials and confirm the significant microstructural consolidation achieved during



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sintering. The highest BET value was measured for pure zirconia, whereas UO_2 rich compositions displayed lower surface areas and lower accessible porosity.

SEM analysis (Figure 20) revealed fully consolidated polycrystalline microstructures in all samples. A clear evolution in grain morphology was observed with increasing zirconia content. While pure UO_2 exhibited relatively large grains and limited porosity, zirconia-rich compositions contained smaller grains and a larger volume fraction of pores. Backscattered electron imaging revealed the appearance of darker zirconium-rich regions in the mixed compositions, which became increasingly abundant as the zirconia content increased.

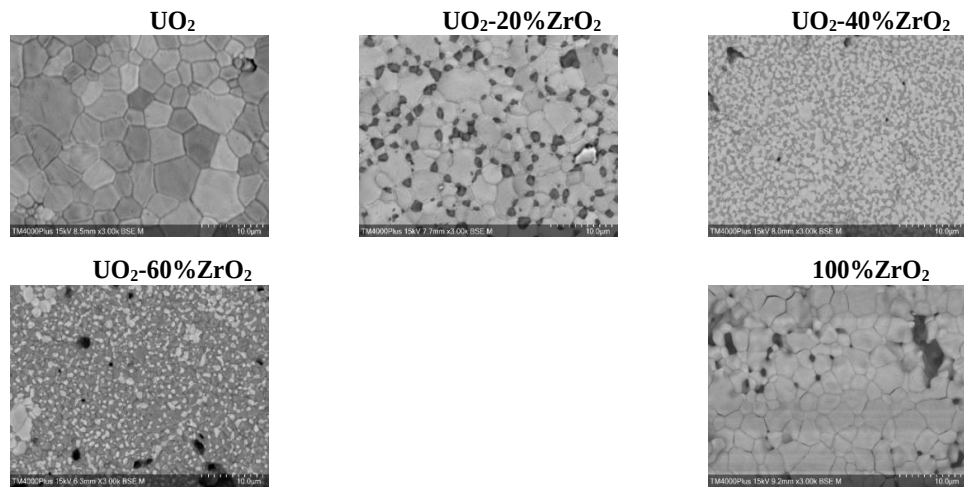


Figure 20. SEM images of UO_2 , UO_2 - 20% ZrO_2 , UO_2 - 40% ZrO_2 , UO_2 - 60% ZrO_2 , ZrO_2 .

EDS mapping confirmed a homogeneous distribution of uranium and zirconium on the micrometer scale, with no evidence of severe macroscopic segregation (Figure 21). The microstructural observations are therefore consistent with the XRD results, which showed the coexistence of U-rich and Zr-rich phases in intermediate compositions.



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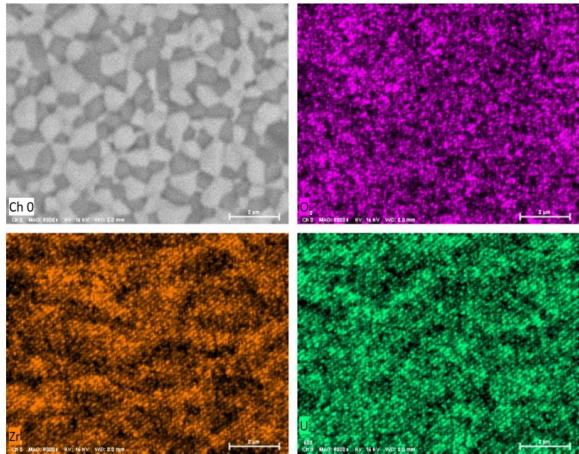


Figure 21. Example of EDS mapping of UO₂-40% ZrO₂ sample.

1.4. INERT MATRICES PREPARATION BY WET ROUTE (SUBTASK 1.4)

The development of homogeneous inert matrix materials is a key step in advanced nuclear fuel cycle strategies and the management of minor actinides (MA). In particular, zirconia-based materials are considered promising candidates for Generation IV reactor applications and high-level waste (HLW) conditioning due to their chemical stability, radiation resistance, and actinide incorporation capability. Within this subtask, an internal gelation (IG) route was developed and optimized to produce homogeneous Zr-based microspheres suitable as precursors for inert matrix fuel fabrication.

Zr-Nd microspheres were prepared from aqueous nitrate solutions containing zirconium and neodymium [17]. Neodymium was selected as a surrogate for trivalent actinides due to its similar chemical behavior and its frequent use in nuclear fuel analog studies. Gelation was achieved through the thermal decomposition of urea and hexamethylenetetramine (HMTA) [17-19], which gradually generates ammonia and promotes homogeneous precipitation of hydrated metal species within each droplet. The influence of several process parameters was investigated, including: metal concentration; nitric acid concentration; urea/HMTA concentration; gelation temperature; needle diameter; washing protocol; and drying and calcination conditions. Figure 22 shows the final experimental configuration corresponding to the optimized process parameters selected after preliminary optimization studies.



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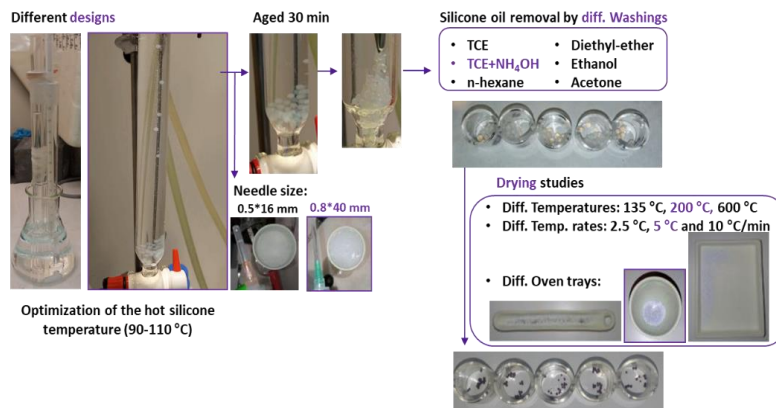


Figure 22. Experimental setup for the IG process to obtain Zr-Nd microspheres.

The optimized compositional range covered materials containing 0, 3, 5, 10 and 30 wt% Nd. Gelation could not be successfully achieved for 50 wt% Nd, indicating practical limitations of the process at high trivalent cation concentrations.

Extensive optimization demonstrated that the gelation temperature strongly influences microsphere quality. Although temperatures between 90 and 100 °C are commonly reported in the literature [19, 20], the best combination of sphericity and mechanical stability was obtained at 110 °C. Under these conditions, highly spherical and mechanically robust microspheres were produced with excellent reproducibility.

The washing procedure was also found to be critical [21-24]. Ethanol, acetone and concentrated NH_4OH produced significant degradation of the microsphere surface, causing erosion and partial dissolution of the gel network. ICP-MS analyses confirmed partial Nd loss when concentrated ammonia solutions were used. In contrast, washing with tetrachloroethane (TCE) followed by dilute NH_4OH generated the cleanest and most stable microspheres and was therefore selected as the optimum treatment.

Thermogravimetric analyses of both precursor reagents and gel-derived materials indicated that the main decomposition processes occur below 600 °C (Figure 23). The decomposition of residual organics took place predominantly between 260 and 300 °C, while no evidence of residual silicone oil contamination was detected after washing. Increasing Nd concentration reduced the overall mass loss, suggesting differences in the composition and thermal stability of the gel network.



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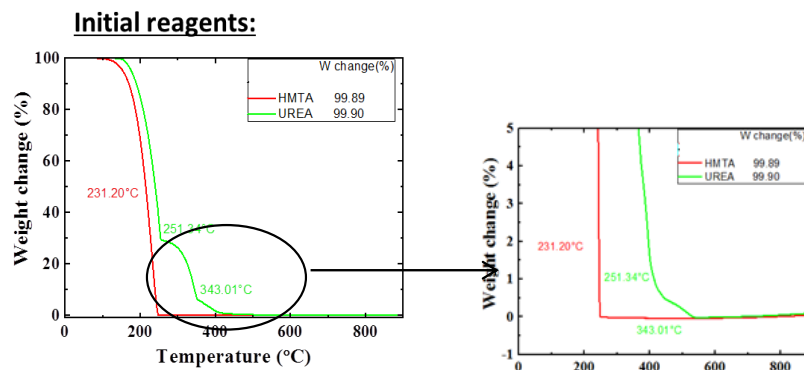


Figure 23. TGA analysis and extension of the temperature range of interest of urea and HMTA, the initial reagents used in IG.

Figure 24 revealed that increasing the proportion of Nd reduced the overall mass loss. The main weight loss occurred between 260 and 300 °C. Previous studies have reported an exothermic event near 405 °C, attributed to the decomposition of residual silicone oil remaining on the microsphere surface [25]. Although DSC measurements were not performed in the present study, the absence of any significant mass-loss event in this temperature range suggests that residual silicone oil, if present, was below detectable levels after washing.

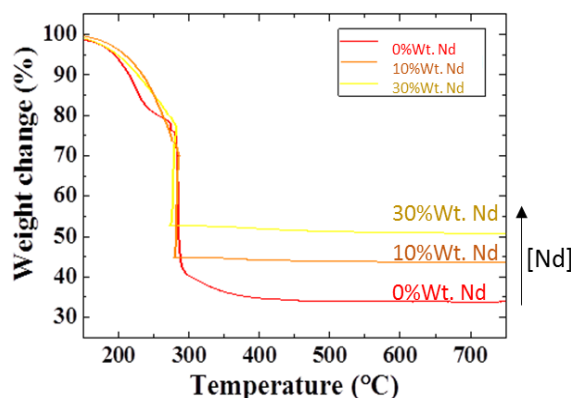


Figure 24. TGA of some representative Zr-Nd samples obtained by IG.

Drying studies revealed that treatment at 135 °C was insufficient to completely remove residual urea and HMTA (Figure 25) [25]. Increasing the drying temperature to 200 °C eliminated these residues and improved the quality of the final calcined



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microspheres. Calcination at 600 °C produced crack-free microspheres with acceptable mechanical integrity and crystallinity.

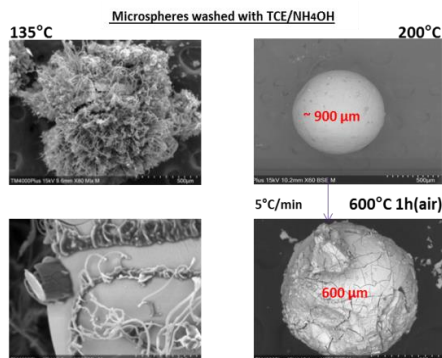


Figure 25. SEM of microspheres obtained by IG dried at 135 °C and 200 °C.

SEM observations (Figure 25 and Figure 26) confirmed the successful production of spherical particles suitable for subsequent pellet fabrication and remote handling operations [19, 26]. The optimized processing conditions produced smooth surfaces and minimized surface defects.

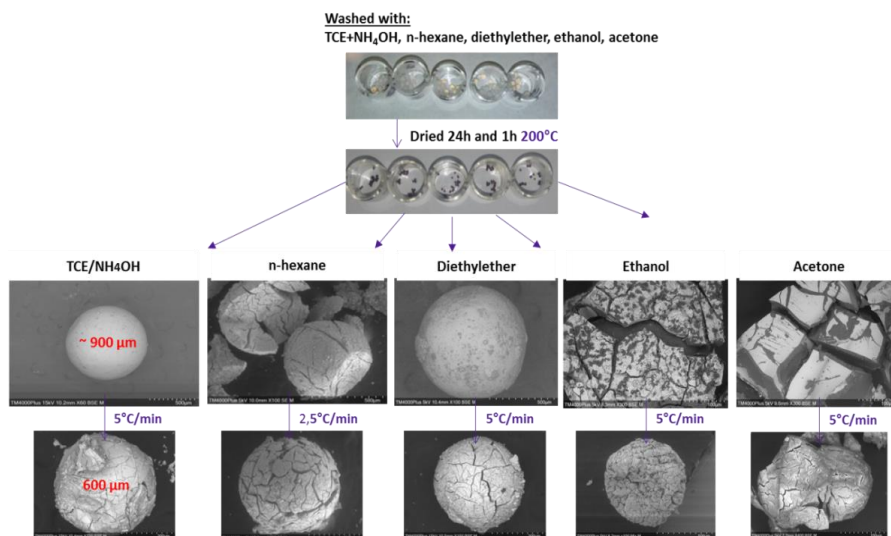


Figure 26. SEM images of Zr-Nd microspheres after different washing procedures.

EDS line scans performed across fractured microspheres demonstrated a homogeneous distribution of neodymium from the core to the surface (Figure 27). No



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evidence of elemental segregation was observed, highlighting one of the major advantages of the IG route compared with conventional powder mixing methods.

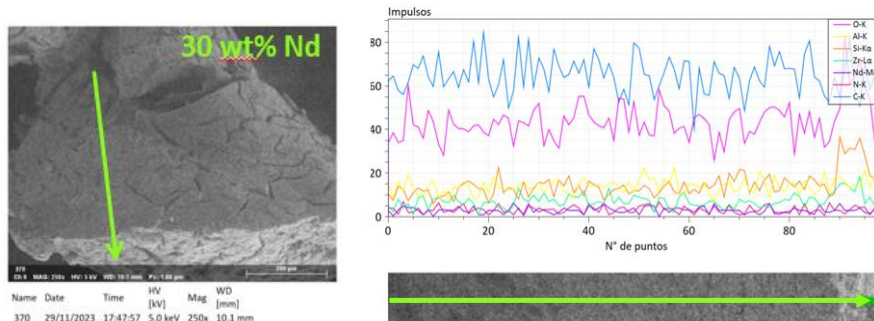


Figure 27. SEM-EDX profile across a 30 wt% Nd microsphere washed with TCE and NH_4OH after calcination.

XRD analyses revealed a progressive increase in crystallinity with increasing thermal treatment temperature (Figure 28). No crystalline Nd_2O_3 phases were detected, indicating that neodymium was incorporated into the zirconia structure rather than precipitating as a segregated secondary phase [27, 28]. Peak broadening analysis also revealed progressive crystallite growth during calcination [26, 28, 29]. The refined lattice parameters differed from those of pure zirconia reported in the literature, which is consistent with Nd incorporation and the nanocrystalline nature of the synthesized materials. Raman spectroscopy could not provide reliable structural information because of the intense fluorescence background characteristic of nanocrystalline zirconia.

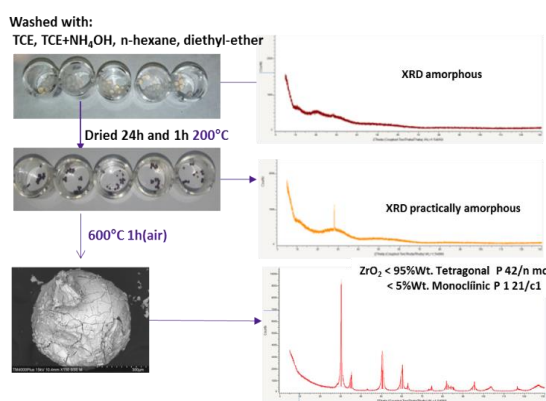


Figure 28. XRD patterns of the Zr-Nd microspheres obtained by IG after thermal treatments.



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The results demonstrate that IG is a robust and reproducible route for the preparation of homogeneous Zr-based microspheres. Compared with conventional powder processing, the method offers superior chemical homogeneity, excellent compositional control and the possibility of producing spherical particles directly from aqueous solutions. The successful incorporation of Nd into the zirconia lattice, together with the absence of detectable segregation, confirms the suitability of the process for the preparation of inert matrix fuel analogs. The optimization studies identified several critical parameters controlling microsphere quality. In particular, gelation temperature, washing conditions and drying treatment were found to significantly influence particle integrity and final material quality. The inability to form stable microspheres at 50 wt% Nd also provides useful information regarding compositional limits of the process.

2. FABRICATION OF ADVANCED TOLERANT FUEL PELLETS AND DEGRADATION STUDIES (TASK 2)

This task focuses on the fabrication and characterization of Cr-doped UO_2 fuels as accident tolerant fuel (ATF) surrogates. Chromium additions are widely used in advanced UO_2 fuels because they promote grain growth during sintering, improve pellet-cladding mechanical interaction, and enhance fission gas retention. These effects are mainly attributed to the development of larger grains and a more stable microstructure compared with conventional UO_2 fuel [30].

The objective of this task involves two pathways. One is to investigate the influence of fabrication parameters and chromium concentration on the microstructure of UO_2 . The second is to evaluate the oxidation behavior of Cr-doped fuels under dry storage conditions, where cladding failure may expose fuel pellets to oxidizing atmospheres. For these reasons, two fabrication routes were studied: 1) Conventional dry powder processing and 2) Aqueous co-precipitation. The resulting pellets were characterized, and oxidation studies were carried out to establish relationships between fabrication route, microstructure, and performance.



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2.1. PRODUCTION AND CHARACTERIZATION OF ATF BY DRY POWDER METHOD (SUBTASK 2.1)

Chromia-doped UO_2 pellets were fabricated through a conventional powder metallurgy route involving powder homogenization, pressing, binder removal by calcination, sintering, and grain-revealing heat treatments. Chromium contents ranging from 200 to 6000 ppm Cr_2O_3 were investigated together with the influence of sintering parameters [31].

For objective 1 (effect of sintering conditions), the UO_2 was obtained via Ammonium Di-Uranate (ADU) following a precipitation process that involves several major steps [28, 29]. The Cr_2O_3 powders were provided by Alfa Aesar. Next, both materials (purified UO_2 and Cr_2O_3) were homogenized together with the binder in a mill-homogenizer at 15 Hz for 15 minutes. Then, a conventional metallurgical procedure was applied following previously tested in our laboratory [32].

For objective 2 (effect of dopant content), UO_2 and Cr_2O_3 powders were provided by ENUSA and Alfa Aesar, respectively. UO_2 was thermally annealed in $\text{H}_2\text{-N}_2$ atmosphere at 1100°C to attain stoichiometric $\text{UO}_{2.00}$. UO_2 was mixed with weighted amounts of Cr_2O_3 , together with 1% of EBS as binder and lubricant [33], using ball mill homogenizer. The batches of mixed powders were then blended, and pelletized following the former procedure, applying a pressure of 700 MPa. As a result, a series of Cr_2O_3 -doped UO_2 solid solutions were obtained. An undoped UO_2 sample was also prepared following the same procedure. Table XIV shows the samples fabricated by this pathway.

Table XIV. Definition of samples for the effect of Cr_2O_3 dopant content on UO_2 pellets.

Reference	Cr_2O_3 added (ppm)
UO_2	0
$\text{UO}_2\text{_{200Cr}_2\text{O}_3}$	200
$\text{UO}_2\text{_{600Cr}_2\text{O}_3}$	600
$\text{UO}_2\text{_{1000Cr}_2\text{O}_3}$	1000
$\text{UO}_2\text{_{6000Cr}_2\text{O}_3}$	6000

2.1.1. Effect of sintering conditions

To evaluate the influence of sintering conditions on the properties of Cr-doped UO_2 pellets, six samples (A-F) containing 600 ppm Cr_2O_3 were fabricated under different



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sintering schedules. Two heating schedules were compared: (i) a two-step profile consisting of heating to 1600 °C at 5 °C·min⁻¹ followed by heating to 1695 °C at 1 °C·min⁻¹, and (ii) direct heating to 1695 °C at 5 °C·min⁻¹. For each heating schedule, sintering dwell times of 4, 6, and 10 h were applied, resulting in six experimental conditions (samples A-F).

- **Samples A, C and E: two-step heating profile**
 - 5 °C·min⁻¹ up to 1600 °C
 - 1 °C·min⁻¹ from 1600 to 1695 °C
 - Dwell times of 4 h (A), 6 h (C), and 10 h (E)
- **Samples B, D and F: direct heating profile**
 - 5 °C·min⁻¹ up to 1695 °C
 - Dwell times of 4 h (B), 6 h (D), and 10 h (F)

XRD (Figure 29) and Raman spectroscopy (Figure 30) confirmed that all samples retained the fluorite UO₂ structure and that chromium was effectively incorporated into the UO₂ matrix. No crystalline Cr₂O₃ secondary phases were detected. The appearance of a Raman band around 540 cm⁻¹ suggested the formation of oxygen-vacancy-related defects associated with incorporation of trivalent chromium into the fluorite structure [14].

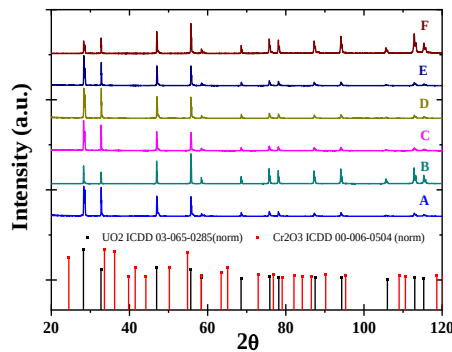


Figure 29. Diffraction patterns of doped UO₂ pellets with 600 ppm of Cr₂O₃ at different sintering conditions.

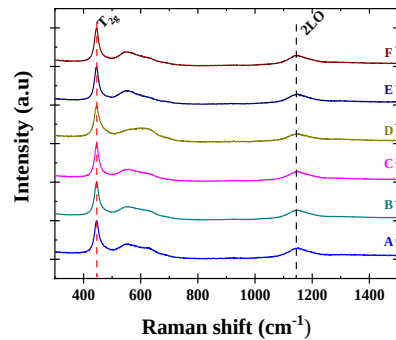


Figure 30. Raman spectra of doped UO₂ pellets with 600 ppm of Cr₂O₃ at different sintering conditions.



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Microstructural characterization revealed very limited influence of the investigated sintering conditions. Grain size, density, surface area and pore structure remained essentially unchanged for sintering durations between 4 and 10 h and heating rates between 1 and 5 °C·min⁻¹ (Figure 31 and Figure 32). BET and Barrett-Joyner-Halenda (BJH) analyses showed that all pellets exhibited mesoporous structures, with no evidence of microporosity (Figure 32). These results indicate that the fabrication process is robust within the range of sintering parameters investigated and that a 4 h sintering treatment is sufficient to obtain fully developed microstructures while minimizing energy consumption.

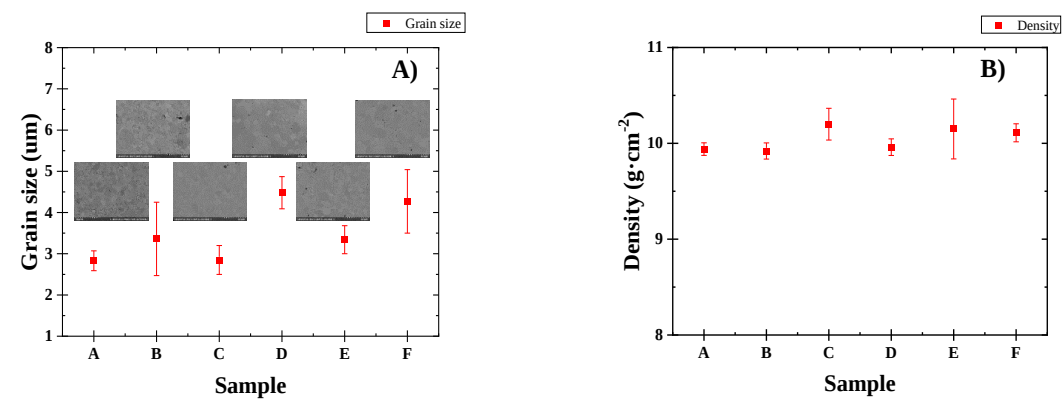


Figure 31. Grain size and SEM images (A) and density values (B).



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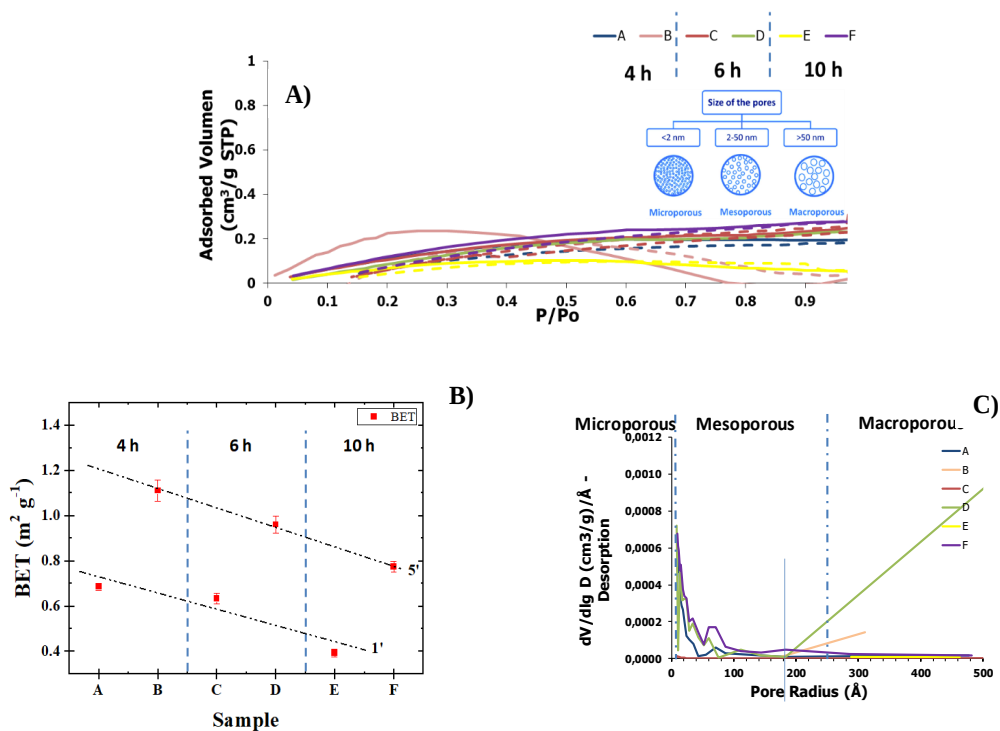


Figure 32. Adsorption isotherms (solid lines) and desorption isotherms (dashed lines) (A), BET surface area (B), and porosity analysis (C).

2.1.2. Effect of chromium content

The influence of chromium concentration was investigated using pellets containing between 0 and 6000 ppm Cr_2O_3 (Table XIV). SEM analysis (Figure 33) showed that chromium strongly influences grain growth. The average grain size increased progressively from approximately 8 μm for undoped UO_2 to values close to 17 μm at the highest chromium concentration investigated (Figure 34). Grain growth was most pronounced around 1000 ppm Cr_2O_3 , after which the effect began to saturate.



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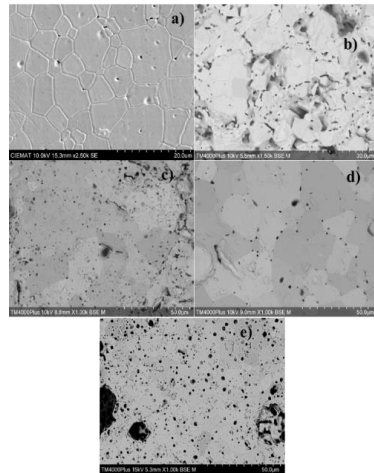


Figure 33. Representative SEM images of the analyzed pellets: a) pure UO_2 , b) $\text{UO}_2_{200}\text{Cr}_2\text{O}_3$, c) $\text{UO}_2_{600}\text{Cr}_2\text{O}_3$, d) $\text{UO}_2_{1000}\text{Cr}_2\text{O}_3$, e) $\text{UO}_2_{6000}\text{Cr}_2\text{O}_3$.

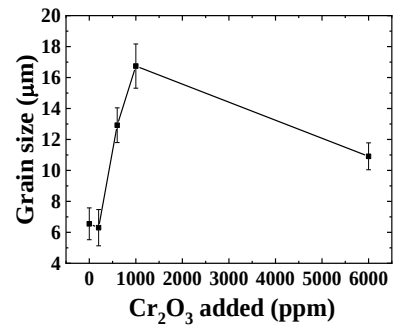


Figure 34. Average grain size of the studied disks vs Cr_2O_3 content. Uncertainty bands correspond to the repeatability of the measurements.

At high chromium concentrations, chromium-rich precipitates were observed preferentially along grain boundaries (Figure 35) [34, 35]. Their abundance increased significantly for the 6000 ppm sample, indicating that the chromium solubility limit had been exceeded. These precipitates inhibit further grain growth and explain why grain size does not continue increasing indefinitely with chromium concentration.

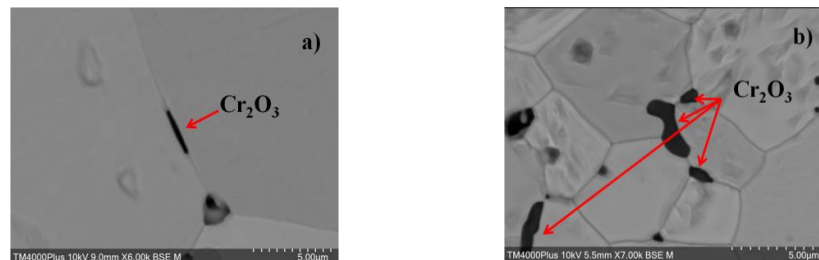


Figure 35. Backscattered SEM images of chromium precipitates in grain boundaries in samples doped with a) 1000 ppm and b) 6000 ppm of Cr_2O_3 , respectively.

XRD analysis (Figure 36) confirmed that all materials retained the fluorite UO_2 structure. No crystalline chromium-containing secondary phases were detected. Increasing



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Cr concentration produced a systematic shift of diffraction peaks towards higher diffraction angles and a corresponding reduction in lattice parameter [36].

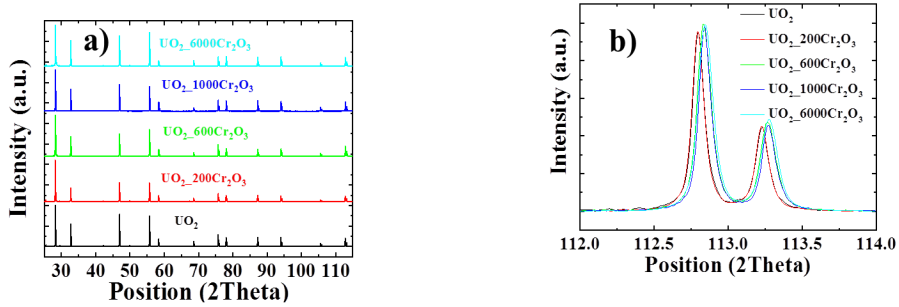


Figure 36. a) Diffraction patterns of the studied samples and b) the (531) $K\alpha_{1,2}$ doublet at 113° of the normalized diffraction patterns.

The lattice parameter followed a Vegard-type behavior up to approximately 1000 ppm Cr_2O_3 (Figure 37), consistent with substitutional incorporation of Cr^{3+} into the uranium dioxide lattice. Beyond this concentration, the lattice parameter became nearly constant, indicating saturation of chromium solubility. Analysis of the lattice parameter evolution allowed estimation of a chromium solubility limit of approximately: (1094 ± 23) ppm Cr_2O_3 or (748 ± 16) ppm Cr^{3+} , which agrees well with previously reported literature values [35-37].

Raman spectroscopy (Figure 38) provided further evidence of chromium incorporation into the UO_2 lattice. Increasing Cr content caused progressive reduction of the T_{2g} and 2LO band intensities, the growth of defect-related bands around 545 and 570 cm^{-1} , an increased oxygen-vacancy concentration, and increased lattice disorder. The 545 cm^{-1} feature is attributed to oxygen-vacancy-related defects generated by substitution of U^{4+} by Cr^{3+} . Its evolution closely follows the lattice parameter changes observed by XRD, confirming that chromium incorporation is accompanied by charge-compensating defect formation. In some spectra, chromium fluorescence bands near 1380 and 1410 cm^{-1} were detected, indicating the presence of small chromium-rich precipitates at the pellet surface [38-41]. Their frequency increased with chromium content, supporting the interpretation derived from SEM observations.



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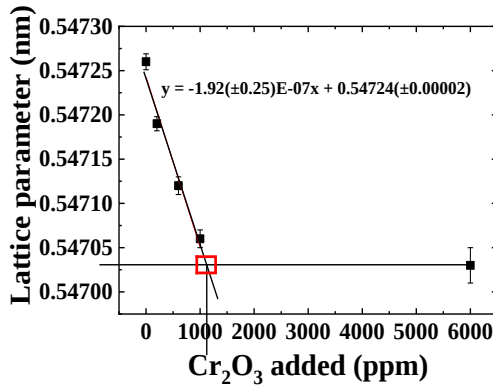


Figure 37. Lattice parameter vs Cr_2O_3 concentration and graphical calculation of solubility limit of Cr_2O_3 in the UO_2 matrix for the samples studied. Uncertainty bands correspond to the repeatability of the measurements.

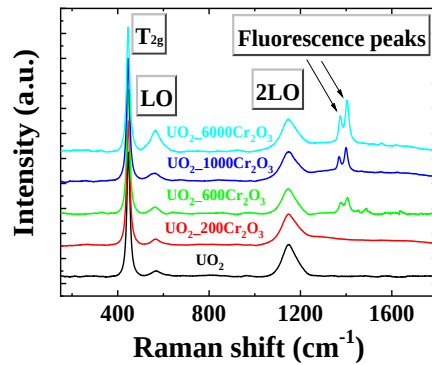


Figure 38. Raman spectra of chromia-doped UO_2 pellets.

In contrast to the strong effect on grain growth, chromium had little influence on densification. Density values remained close to 92%TD for all compositions and BET surface areas remained within the range $0.11\text{-}0.20\text{ m}^2\cdot\text{g}^{-1}$. These results indicate that chromium primarily modifies grain growth mechanisms rather than the final densification of the pellets.

2.2. CO-PRECIPIATION CONCEPT FOR ATF FUELS (SUBTASK 2.2)

To investigate alternative fabrication routes for ATF, Cr-doped UO_2 materials were synthesized using an aqueous co-precipitation method [42]. This route was selected because it enables atomic-scale mixing of uranium and chromium in solution, potentially improving dopant homogeneity compared with conventional powder blending. Uranyl nitrate and chromium nitrate solutions were prepared and mixed in appropriate proportions to obtain precursor solutions corresponding to Cr_2O_3 concentrations ranging from 0 to 3000 ppm. The actual chromium concentrations measured by ICP-MS were in good agreement with the target compositions, confirming accurate preparation of the precursor solutions (Table XV).



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Table XV. Definition of samples, theoretical Cr_2O_3 concentrations used as dopant and experimental concentrations measured by ICP-MS.

Reference	Theoretical Cr_2O_3 concentration (ppm)	Measured Cr_2O_3 concentration (ppm, $\pm 10\%$)
U-Cr 0	0	6
U-Cr 600	600	629
U-Cr 1000	1000	864
U-Cr 1500	1500	1860
U-Cr 2000	2000	1985
U-Cr 3000	3000	2850

Raman spectroscopy of the precursor solutions can be found in Figure 39 and confirmed the progressive incorporation of chromium into the mixed solutions. The intensities of the characteristic uranyl and nitrate bands decreased systematically with increasing chromium concentration, consistent with the replacement of uranium species by chromium-containing species in solution and confirming the suitability of the selected co-precipitation conditions [43].

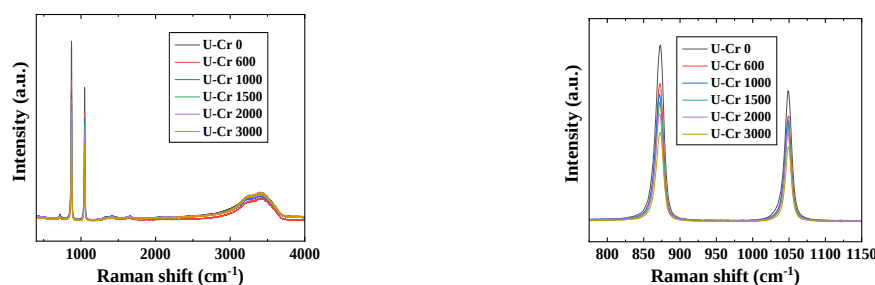


Figure 39. Raman spectra of liquid mixtures of starting U and Cr solutions. Figure on the right represents a zoom in the 800-1150 cm^{-1} region.

Co-precipitation was carried out by slowly adding the mixed U-Cr nitrate solutions into NH_4OH . The resulting precipitates were recovered, washed (with NH_4OH , ultrapure water and ethanol), and thermally treated through successive ADU, U_3O_8 , and UO_2 stages. ICP-MS analyses of the supernatants confirmed essentially complete precipitation of both uranium and chromium. The resulting UO_2 -Cr powders were subsequently pressed (400 MPa) and sintered under reducing atmosphere to produce dense Cr-doped UO_2 pellets (Figure 40).



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Figure 40. Photographs of the Cr-doped UO₂ pellets after sintering.

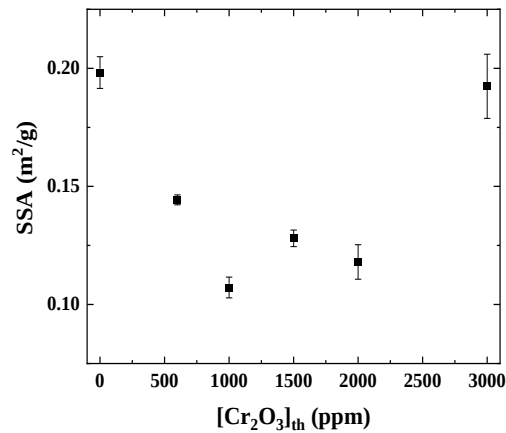


Figure 41. BET surface area (SSA) of the Cr-doped UO₂ pellets, along with their estimated error margins.

BET measurements revealed low SSAs for all sintered pellets, ranging between 0.11 and 0.20 m²·g⁻¹ (Figure 41). No systematic relationship was observed between chromium concentration and residual surface area, indicating that Cr additions have only a minor influence on the accessible porosity of the final pellets.

Similarly, pycnometry showed density values close to 10 g·cm⁻³ for all compositions, corresponding to relative densities above 90 %TD (Table XVI). These results indicate that chromium concentration has little effect on the final densification achieved under the selected sintering conditions.



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Table XVI. Physical properties of the Cr-doped UO_2 sintered pellets, including SSA, density values and mean grain size.

Reference	SSA (m^2/g)	Pycnometer Density (g/cm^3)	Relative Density (%)	Grain size (μm)
$\text{UO}_2\text{-Cr 0}$	0.20 ± 0.01	10.050 ± 0.004	91.70	8.1 ± 0.7
$\text{UO}_2\text{-Cr 600}$	0.14 ± 0.01	9.969 ± 0.005	91.02	11 ± 2
$\text{UO}_2\text{-Cr 1000}$	0.11 ± 0.01	10.021 ± 0.004	91.54	12 ± 2
$\text{UO}_2\text{-Cr 1500}$	0.13 ± 0.01	10.073 ± 0.008	92.06	14.5 ± 0.9
$\text{UO}_2\text{-Cr 2000}$	0.12 ± 0.01	10.070 ± 0.007	92.08	14 ± 2
$\text{UO}_2\text{-Cr 3000}$	0.19 ± 0.01	10.069 ± 0.005	92.18	17 ± 2

In contrast, chromium had a pronounced effect on grain growth. SEM observations (Figure 42) revealed a continuous increase in grain size with increasing Cr concentration, from approximately 8 μm in undoped UO_2 to 17 μm in the sample containing 3000 ppm Cr_2O_3 (Table XVI).

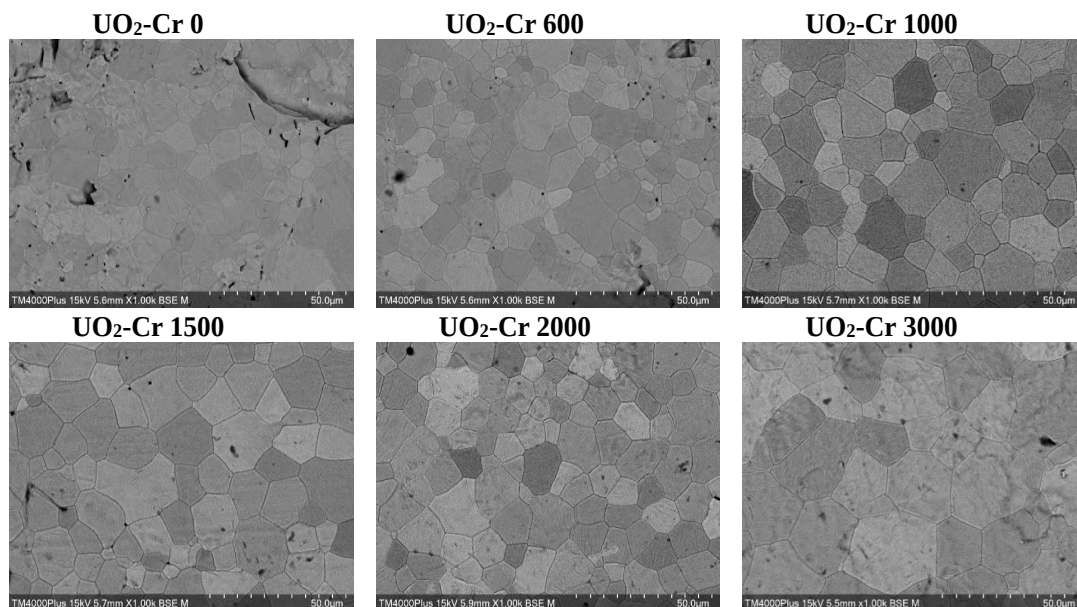


Figure 42. SEM images of the Cr-doped UO_2 pellets after sintering, showing the different grain sizes achieved.

The grain size of the highest-doped pellet was therefore approximately twice that of the undoped material. This behavior confirms that chromium acts as an effective grain-growth promoter during sintering. In addition, no secondary phases attributable to segregated chromium were identified in the SEM micrographs. These results demonstrate that Cr_2O_3 1) is embedded (at least in an extensive manner) within the UO_2 microstructure and 2) acts as a grain growth promoter during the sintering of UO_2 [30, 44].



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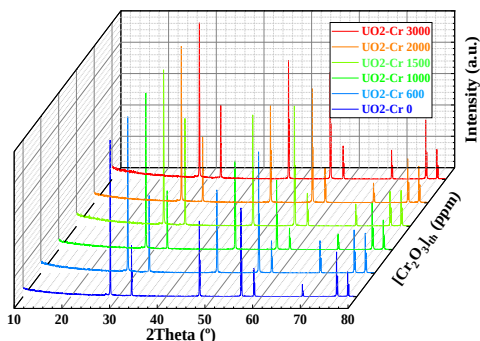


Figure 43. XRD patterns of the Cr-doped UO_2 pellets after sintering.

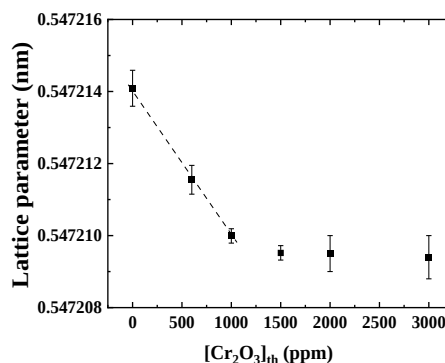


Figure 44. Refined lattice parameters plotted as a function of Cr_2O_3 content of Cr-doped UO_2 sintered pellets.

XRD analysis (Figure 43) confirmed that all samples retained the fluorite UO_2 crystal structure after sintering. No secondary chromium-containing phases were detected, indicating that chromium is incorporated into the lattice or remains below the diffraction detection limit. The lattice parameter (Figure 44) decreased progressively with increasing chromium concentration up to approximately 1000-1500 ppm Cr_2O_3 , consistent with the incorporation of Cr^{3+} ions into the UO_2 fluorite lattice. Beyond this concentration, the lattice parameter tended to stabilize, suggesting that chromium solubility had been largely reached. This behavior is consistent with the existence of a chromium solubility limit close to that previously estimated for dry route materials. The observed lattice contraction can be explained by substitution of U^{4+} by the smaller Cr^{3+} ion and the formation of charge-compensating defects such as oxygen vacancies or U^{5+} species. These defect mechanisms produce a measurable contraction of the fluorite unit cell and are consistent with previous studies on Cr-doped UO_2 .

Compared with the conventional dry route, co-precipitation provides significantly improved chemical homogeneity because uranium and chromium are mixed at the molecular scale before precipitation [45]. This improved homogeneity promotes a more uniform chromium distribution throughout the microstructure and facilitates grain growth during sintering. While chromium additions had little influence on density or BET surface



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area, they produced a substantial increase in grain size, confirming that their primary effect is on grain-boundary mobility rather than densification. The results indicates that co-precipitation for Cr-doped ATFs enable homogeneous dopant incorporation while maintaining high density and promoting significant grain growth. These characteristics are desirable for improving fission gas retention and fuel performance during operation.

2.3. OXIDATION BEHAVIOR OF ATFs UNDER DRY STORAGE CONDITIONS (SUBTASK 2.3)

The oxidation behavior of Cr-doped UO_2 fuels fabricated by both dry powder processing [31] and aqueous co-precipitation [42] was investigated to assess their performance under potential dry storage conditions [31, 42, 44, 46]. Such scenarios are particularly relevant in the event of cladding failure, where exposure to oxidizing atmospheres may accelerate fuel degradation. Since chromium additions are known to modify grain size and microstructure, this study sought to determine whether they also influence oxidation resistance and oxidation kinetics.

Representative pellets containing 600, 1000, and 6000 ppm Cr_2O_3 (dry route, section 2.1.2) and 600, 1000, and 3000 ppm Cr_2O_3 (co-precipitation route, section 2.2) were exposed to synthetic air and analyzed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) [47]. A series of kinetic parameters, including oxidation onset temperatures, maximum oxidation rates, oxidation peak temperatures, and final O/M ratios, were extracted from the experimental curves. The nominal sample composition $\text{U}_{1-x}\text{Cr}_x\text{O}_2$ was first obtained from the Cr_2O_3 theoretical content (see Table XVII).

Table XVII. Calculated stoichiometry of Cr-doped UO_2 .

ppm Cr_2O_3	wt% Cr_2O_3	x in $\text{U}_{1-x}\text{Cr}_x\text{O}_2$	Molar mass in $\text{U}_{1-x}\text{Cr}_x\text{O}_2$ ($\text{g}\cdot\text{mol}^{-1}$)
0	0	0.0000	270.03
600	0.06	0.0002	269.99
1000	0.1	0.0004	269.96
3000	0.3	0.0011	269.83
6000	0.6	0.0021	269.63



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On one hand, all dry route samples exhibited a progressive mass increase associated with oxygen uptake and oxidation of UO_2 (Figure 45.A). Derivative analysis indicated that oxidation occurred essentially through a single dominant reaction step. The final O/M ratios were very similar for all compositions (2.66-2.68), indicating that chromium additions do not significantly alter the final oxidation state reached after heating to 700 °C (Figure 46.A). The main influence of chromium was observed in the oxidation kinetics. Increasing Cr concentration reduced the maximum oxidation rate and produced a slight delay in the oxidation peak temperature. The sample containing 6000 ppm Cr_2O_3 exhibited the highest oxidation resistance, as demonstrated by its lower oxidation rate and higher oxidation onset temperature. These results suggest that chromium additions slow the oxidation process, although they do not modify the final oxidation products.

On the other hand, the oxidation behavior of co-precipitated materials differed significantly from that observed for dry route fuels (Figure 45.B). Instead of a single dominant oxidation event, the co-precipitated samples exhibited two distinguishable oxidation stages. The first stage is associated with initial oxygen incorporation into UO_2 , whereas the second corresponds to transformation into higher uranium oxides such as $\text{U}_4\text{O}_9/\text{U}_3\text{O}_7$ and U_3O_8 . Chromium additions delayed the first oxidation stage. The temperature of the first oxidation peak increased from approximately 302 °C for undoped UO_2 to around 334 °C for the sample containing 3000 ppm Cr_2O_3 . Similar increases were observed in oxidation onset temperatures. In contrast, the second oxidation stage remained largely unaffected by chromium content. All compositions ultimately reached similar O/M values (Figure 46.B), indicating that chromium primarily affects oxidation kinetics rather than the final degree of oxidation. The more gradual oxidation behavior observed in co-precipitated samples is consistent with their more homogeneous microstructure and more uniform chromium distribution. The atomic-scale mixing achieved during co-precipitation appears to modify the oxidation pathway and delay initial oxygen incorporation into the fluorite lattice.



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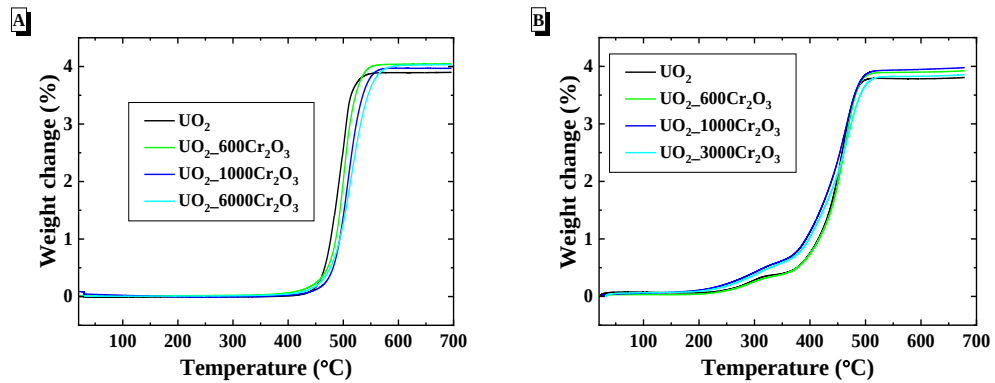


Figure 45. Oxidation curves of the ATFs studied from RT to 700 °C in air (21% O₂). A) Undoped and Cr-doped UO₂ obtained by dry route; B) undoped and Cr-doped UO₂ obtained by co-precipitation route.

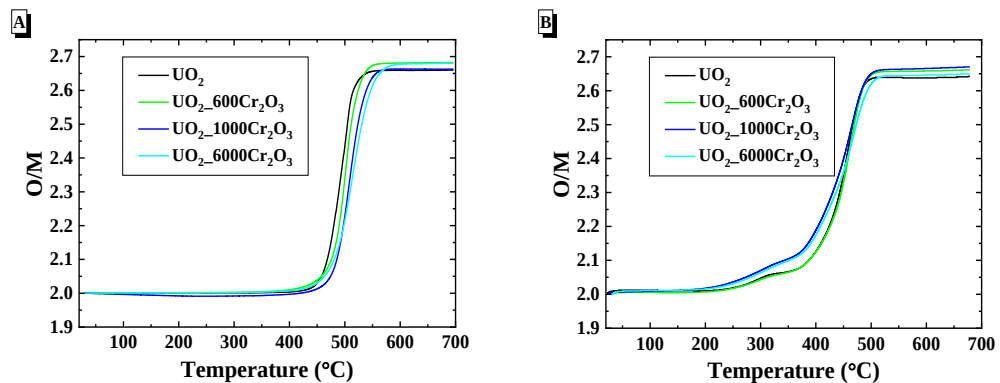


Figure 46. O/M curves of the ATFs studied from RT to 700 °C in air (21% O₂). A) Undoped and Cr-doped UO₂ obtained by dry route; B) undoped and Cr-doped UO₂ obtained by co-precipitation route.

DSC measurements supported the conclusions drawn from TGA. Multiple exothermic contributions were observed in co-precipitated materials (Figure 47), confirming the existence of a multistep oxidation mechanism. The strongest effect of chromium was observed for the first oxidation stage, where increasing Cr content reduced the associated reaction enthalpy and shifted the thermal peak towards higher temperatures.



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These changes are consistent with enhanced oxidation resistance during the early stages of oxidation. Although the DSC results clearly indicate differences in oxidation kinetics, no systematic relationship was observed between chromium concentration and the total oxidation enthalpy. Therefore, the interpretation of individual heat contributions should be considered preliminary and requires additional investigation.

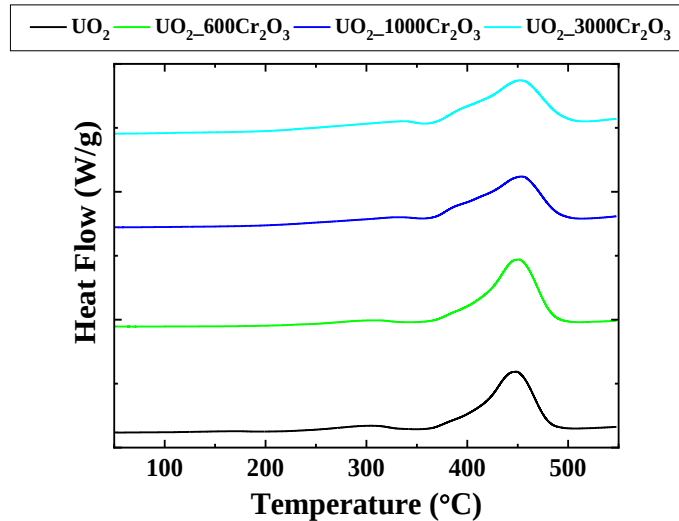


Figure 47. DSC curves of the ATFs studied from RT to 550 °C in air (21% O₂) for undoped and Cr-doped UO₂ obtained by co-precipitation route.

The results demonstrate that fabrication route has a greater influence on oxidation behavior than chromium concentration itself. While chromium additions improve oxidation resistance in both fabrication routes, the effect is considerably more pronounced in co-precipitated materials. The final oxidation state reached after heating is essentially independent of chromium content. However, the oxidation pathway and oxidation kinetics are strongly influenced by the pellet microstructure. Dry route materials exhibit a rapid, single-step oxidation process, whereas co-precipitated materials display delayed gradual oxidation occurring through multiple stages. These differences are attributed to variations in grain structure, defect distribution, porosity, and chromium homogeneity generated by the respective fabrication methods. The results therefore suggest that oxidation resistance in Cr-doped UO₂ fuels is controlled primarily by microstructural characteristics rather than by chromium concentration alone. Optimizing the fabrication route may consequently be as important as optimizing the dopant concentration for improving fuel performance during



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dry storage.

3. OTHER SAMPLES CHARACTERIZATION

3.1. SAMPLES FROM JRC COLLABORATION

A series of $\text{UO}_2\text{-ZrO}_2$ pellets fabricated at the Joint Research Centre (JRC) Karlsruhe were received for further characterization and comparison with CIEMAT-developed materials. The samples cover a broad compositional range from pure UO_2 to 60 mol% ZrO_2 and were prepared by a sol-gel route followed by hydraulic pressing and sintering. Initial characterization was performed by Raman spectroscopy and XRD. This section summarizes the fabrication conditions, density measurements, Raman spectroscopy results, and XRD observations available for the received materials. The discussion focuses on identifying compositional trends and microstructural evolution with increasing zirconium content.

The precursor powders were produced by a sol-gel process previously reported in the literature [15]. Pellets were fabricated by uniaxial pressing under the following conditions: pressing pressure of 400 MPa and dwell time of 5 s. Sintering was carried out under reducing atmosphere at 1690 °C for 6 h under Ar/H_2 atmosphere using a heating rate of 200 °C h^{-1} . The investigated compositions are shown in Table XVIII:

Table XVIII. JRC samples reference and composition.

Reference	Nominal Composition mol%	Zr Content (mol%)	ZrO ₂ wt %
24KB0045	UO_2	0	0
24KB0046	$(\text{U}_{0.95}\text{Zr}_{0.05})\text{O}_2$	5	5
24KB0047	$(\text{U}_{0.90}\text{Zr}_{0.10})\text{O}_2$	10	9.96
24KB0048	$(\text{U}_{0.80}\text{Zr}_{0.20})\text{O}_2$	20	20
24KB0049	$(\text{U}_{0.60}\text{Zr}_{0.40})\text{O}_2$	40	40.1
24KB0050	$(\text{U}_{0.50}\text{Zr}_{0.50})\text{O}_2$	50	49.9
24KB0051	$(\text{U}_{0.40}\text{Zr}_{0.60})\text{O}_2$	60	59.9

One of the most remarkable features of the JRC materials is their exceptionally high densification (Table XIX). All compositions achieved relative densities above 95%TD and, in some cases, approached full densification. The highest density was measured for the composition containing 60 mol% Zr, reaching approximately 99.6 %TD. These values are



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significantly higher than those obtained for the dry route and co-precipitated $\text{UO}_2\text{-ZrO}_2$ materials investigated in Tasks 1.1 and 1.3, highlighting the effectiveness of the sol-gel route for producing highly dense mixed oxides. BET measurements (Table XIX) confirmed the excellent densification behavior. All samples exhibited extremely low SSAs ($<0.3 \text{ m}^2\cdot\text{g}^{-1}$), indicating negligible open porosity after sintering. Although the total porosity remained low throughout the series, the morphology of the residual pores evolved with composition. Larger BJH pore diameters were observed in zirconium-rich compositions, suggesting that zirconium addition affects pore morphology more strongly than total pore volume.

Table XIX. $\text{UO}_2\text{-ZrO}_2$ (JRC) samples characterization.

Zr Content (mol%)	Average relative density (%TD)	BET surface area ($\text{m}^2\cdot\text{g}^{-1}$)	BJH average pore diameter (Adsorption, Å)
0	96.3	0.201 ± 0.007	35.8
5	95.8	0.143 ± 0.005	42.4
10	95.0	0.083 ± 0.003	-
20	96.7	0.145 ± 0.004	23.9
40	97.7	0.223 ± 0.008	478.1
50	95.1	0.154 ± 0.004	83.5
60	99.6	0.265 ± 0.007	120.6

Raman spectroscopy measurements revealed a progressive structural evolution with increasing zirconium content (Figure 48). Up to 10 mol% Zr, the spectra remain characteristic of a fluorite-type solid solution, although progressive broadening of the T_{2g} band (see dashed line in Figure 48) indicates increasing lattice disorder caused by zirconium incorporation within the UO_2 lattice. A major change occurs at approximately 20 mol% Zr. At this composition, new Raman bands appear and two spectral populations can be identified: one corresponding to a highly distorted uranium-rich fluorite structure and a second one that might associated with a zirconium-rich structure with tetragonal symmetry. Above this concentration, the contribution of zirconia-rich structural domains becomes increasingly important and the fluorite signature progressively weakens. The Raman results therefore indicate that approximately 20 mol% Zr represents a critical composition where the structure begins to evolve from a single fluorite solid solution towards a multiphase system.



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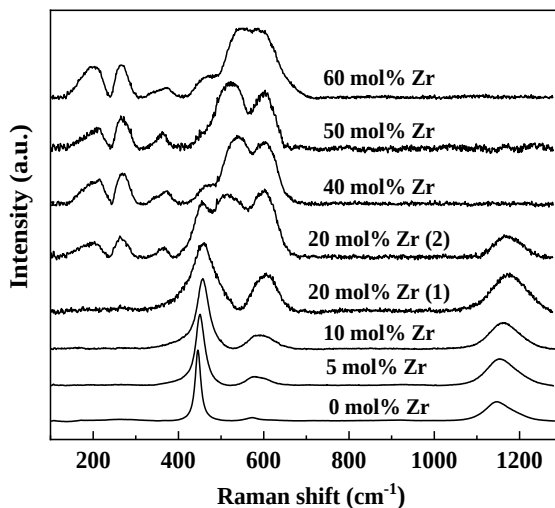


Figure 48. Raman spectra taken on the $\text{UO}_2\text{-ZrO}_2$ (JRC) samples.

XRD results fairly support the Raman observations (Figure 49 and (Table XX)). Samples containing 0, 5 and 10 mol % Zr were adequately described by a single fluorite phase. At 20 mol% Zr, however, diffraction peak asymmetry and peak splitting became evident, indicating the appearance of a second crystallographic contribution. The preliminarily proposed interpretation is the coexistence of two fluorite-type solid solutions with different Zr contents. At higher contents (40-60 mol% Zr), multiphase behavior becomes increasingly pronounced, with evidence of zirconia-rich cubic $(\text{U,Zr})\text{O}_2$ phases and minor secondary contributions. However, the Raman results, suggesting that a tetragonal zirconia-rich phase is also formed, provide a more realistic explanation. Consequently, future Rietveld refinements should consider the possible presence of tetragonal zirconia phases when analyzing these compositions.



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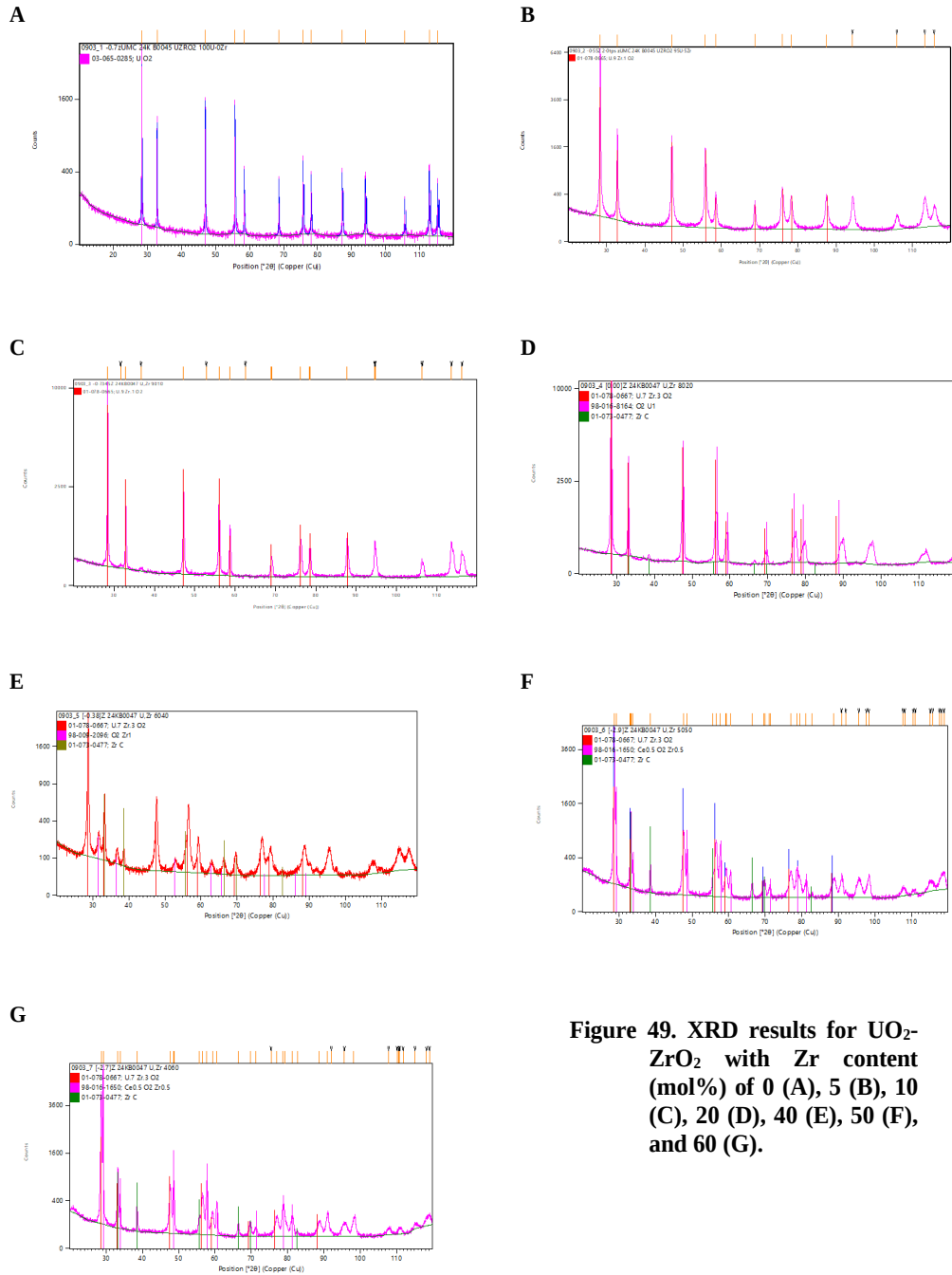


Figure 49. XRD results for $\text{UO}_2\text{-ZrO}_2$ with Zr content (mol%) of 0 (A), 5 (B), 10 (C), 20 (D), 40 (E), 50 (F), and 60 (G).

Nevertheless, the dominant observation remains the progressive transformation from a uranium-rich fluorite structure towards different zirconia-rich structures.



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Table XX. Analysis of crystalline phases observed in the $\text{UO}_2\text{-ZrO}_2$ (JRC) samples.

Zr Content (mol%)	Composition	Main Phase	Lattice parameter / Å
0	UO_2	100 wt% cubic UO_2	$a = 5.47216(3)$
5	$(\text{U}_{0.95}\text{Zr}_{0.05})\text{O}_2$	100 wt% cubic $(\text{U,Zr})\text{O}_2$	$a = 5.45949(12)$
10	$(\text{U}_{0.90}\text{Zr}_{0.10})\text{O}_2$	100 wt% cubic $(\text{U,Zr})\text{O}_2$	$a = 5.44538(6)$
20	$(\text{U}_{0.80}\text{Zr}_{0.20})\text{O}_2$	Predominantly cubic $(\text{U,Zr})\text{O}_2$ (54 wt%) with cubic UO_2 (46 wt%)	$a = 5.43277(16)$ $a = 5.39896(18)$
40	$(\text{U}_{0.60}\text{Zr}_{0.40})\text{O}_2$	Predominantly cubic $(\text{U,Zr})\text{O}_2$ (64 wt%) with nano- ZrO_2 (29 wt%)	$a = 5.4073(3)$ $a = 4.9009(10)$
50	$(\text{U}_{0.50}\text{Zr}_{0.50})\text{O}_2$	One major fluorite-related contribution (86 wt%) with minor secondary phases (14 wt%)	$a = 5.3962(5)$ $a = 4.6682(7)$

The JRC series provides independent confirmation of the phase evolution observed in the $\text{UO}_2\text{-ZrO}_2$ materials fabricated at CIEMAT. Both Raman spectroscopy and XRD identify a critical composition around 20 mol% Zr, where phase coexistence begins to develop and structural complexity increases markedly. However, a significant difference is observed in densification behavior. While the IONMAT materials obtained by dry route and co-precipitation exhibited relative densities between approximately 75 and 90%TD depending on composition, the JRC sol-gel materials consistently exceeded 95%TD.

Helium pycnometry measurements revealed a progressive decrease in skeletal density with increasing zirconium content (Table XXI), from $10.31 \text{ g}\cdot\text{cm}^{-3}$ for pure UO_2 to approximately $7.79 \text{ g}\cdot\text{cm}^{-3}$ for the compositions containing 50-60 mol% Zr (31 – 41 wt% ZrO_2).

Table XXI Helium pycnometry results for JRC sol-gel $\text{UO}_2\text{-ZrO}_2$.

Zr Content (mol%)	Density ($\text{g}\cdot\text{cm}^{-3}$)
0	10.31 ± 0.05
5	9.85 ± 0.01
10	9.559 ± 0.006
20	9.035 ± 0.006
40	8.280 ± 0.003
50	7.790 ± 0.004
60	7.782 ± 0.004

The density evolution was gradual up to 20 mol% Zr (~10 wt% ZrO_2), suggesting zirconium incorporation into the fluorite structure without major interference of the crystal lattice. At higher zirconium contents, a more pronounced density decrease was observed, consistent with the phase coexistence and structural modifications identified by Raman spectroscopy and XRD. The nearly identical densities measured for the 50 and 60 mol%



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Zr samples further suggest that the system approaches a compositional regime dominated by zirconium-rich phases. These results provide additional support for the structural evolution inferred from the spectroscopic and diffraction analyses.

3.2. SAMPLES FROM LANCASTER UNIVERSITY COLLABORATION

A second collaborative activity involved SPS-sintered ZrO_2 -CsI materials supplied by Lancaster University. These materials were designed as simplified surrogates for investigating the retention of volatile FPs, particularly Cs and I, in zirconia-based matrices; and are foreseen to be used to investigate the influence of FPs on corrosion and radionuclide release under storage and disposal conditions. The interest of these materials extends beyond simple CsI retention. Volatile FPs such as cesium and iodine contribute significantly to the radiological inventory of spent fuel and play an important role in fuel degradation scenarios. The ZrO_2 -CsI materials therefore represent simplified surrogate systems for investigating retention mechanisms and developing methodologies that may later be applied to more complex SIMFUEL and spent fuel surrogate materials.

The samples were prepared by mixing ZrO_2 powder with predetermined amounts of CsI (1-5 wt%). A slurry was produced using water as processing medium, followed by drying and powder recovery. The resulting mixtures were consolidated by Spark Plasma Sintering (SPS), a field-assisted sintering technique capable of producing highly dense materials while minimizing processing times. A pure ZrO_2 pellet fabricated under identical conditions was used as the reference material. The fabricated materials were subsequently characterized by X-ray fluorescence (XRF) and XRD in order to determine elemental retention and identify possible crystalline phases.

XRF results reveal different behaviors for Cs and I (Table XXII). All concentrations are reported in wt% and the instrument detection limits for Cs and I range between 50 and 150 ppm. Cesium concentration increases systematically with increasing nominal CsI loading, indicating measurable retention within the zirconia matrix during SPS processing. In contrast, iodine concentrations remain low and do not proportionally scale with initial CsI content, suggesting either partial volatilization during SPS processing (*e.g.*, I_2), as the measured values show substantial scatter and remain relatively close to the concentration



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observed in the blank sample.

Table XXII. XRF results and physical properties from ZrO₂-CsI samples (Lancaster).

Sample	Cs (wt %)	I (wt %)	Density (g·cm ⁻³)	BET surface area (m ² ·g ⁻¹)	BJH average pore diameter (Adsorption, Å)
ZrO₂ reference	0.038	0.037	5.467 ± 0.004	0.451 ± 0.005	145.89
1% CsI	0.132	0.085	5.564 ± 0.003	0.587 ± 0.003	128.58
2% CsI	0.154	0.063	5.583 ± 0.004	n.d.	n.d.
3% CsI	0.197	0.056	5.573 ± 0.003	n.d.	n.d.
4% CsI	0.223	0.064	5.568 ± 0.003	n.d.	n.d.
5% CsI (large)	0.204	0.051	5.521 ± 0.005	0.699 ± 0.008	129.65
5% CsI (small)	0.257	0.027			

Helium pycnometry, BET surface area and BJH pore structure analyses (Table XXII) indicate that CsI incorporation produces only small changes in the physical properties of the sintered zirconia materials. Densities remained within a relatively narrow range of 5.47-5.97 g·cm⁻³, while BET specific surface areas increased from 0.45 m²·g⁻¹ for pure ZrO₂ to 0.59 and 0.70 m²·g⁻¹ for the materials containing 1 and 5 wt% CsI, respectively. The BJH adsorption average pore diameter decreased from approximately 146 Å for pure ZrO₂ to about 129 Å for the CsI-containing materials. In contrast, both BET surface area slightly increased with CsI content. This behaviour suggests that CsI incorporation maintain a relatively similar mesoporous structure, as evidenced by the nearly identical average pore diameters measured for the 1 and 5 wt% CsI samples. It should be noted that BET measurements could only be performed on the pure ZrO₂, 1 wt% CsI and 5 wt% CsI samples. The remaining specimens were not analysed because several pellets exceeded the dimensions of the available sample holder, while others fractured during handling and preparation. Therefore, the available BET and BJH data should be regarded as representative but not fully comprehensive of the entire compositional series.

XRD analyses (Figure 50) identified monoclinic zirconia (P21/c) as the only crystalline phase present in all samples. No diffraction peaks corresponding to CsI or secondary Cs- and I-bearing compounds were detected. This indicates that retained Cs and I concentrations remain below the XRD detection limit or are present either as highly dispersed species or in amorphous phases.



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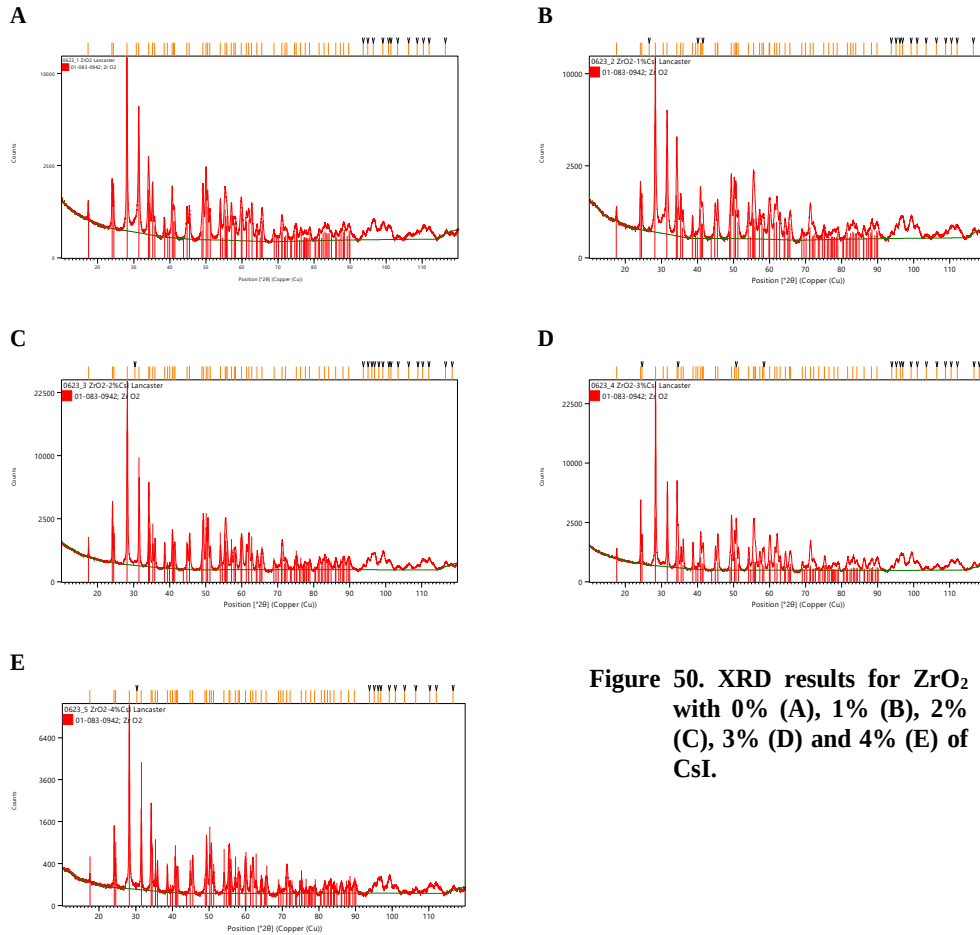


Figure 50. XRD results for ZrO_2 with 0% (A), 1% (B), 2% (C), 3% (D) and 4% (E) of CsI.

The discrepancy between cesium and iodine behavior is likely related to the volatility of iodine-bearing species under SPS conditions [48]. Elevated temperatures combined with vacuum or reduced pressure conditions may volatile iodine compounds, leading to preferential iodine depletion relative to cesium. Although additional analyses would be required for confirmation, the results demonstrate that zirconia is capable of retaining measurable quantities of cesium after SPS processing and therefore represents an interesting candidate matrix for future studies on volatile fission-product immobilization.

4. DISCUSSION

The investigated systems cover complementary aspects of advanced nuclear fuel cycles (see Table XXIII). Eu- and Nd-containing materials provide representative surrogates for FPs incorporation and irradiated fuel evolution, U_3O_8 containing materials



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allow porosity generation, $\text{UO}_2\text{-ZrO}_2$ systems contribute to the understanding of PCI, inert matrix and transmutation fuel concepts, Cr-doped UO_2 supports the development of ATFs, and the Lancaster $\text{ZrO}_2\text{-CsI}$ materials address volatile FPs retention. Together, these studies provide a framework connecting fuel fabrication, microstructural evolution, and advanced nuclear fuel cycle development.

Table XXIII. Global comparison of fabrication routes investigated in IONMAT.

Material System	Fabrication Route	Objective	Advantage	Limitation
$\text{UO}_2\text{-Eu}$	Dry powder	Simulation of trivalent FP incorporation	Complete solid solution and clear defect chemistry evolution	Limited to low surrogate concentrations investigated
$\text{UO}_2\text{-ZrO}_2$	Dry powder	Simulation of fuel-cladding interaction	Simple and industrially representative route	Lower densification and phase homogeneity
	Co-precipitation	Simulation of fuel-cladding interaction and inert matrix development	Improved phase homogeneity and distribution of Zr	More complex fabrication route
	Sol-gel (JRC)	Highly homogeneous simulation of fuel-cladding interaction and inert matrix development	Highest densification (>95%TD)	External fabrication route not developed within IONMAT
$\text{CeO}_2\text{-Nd}_2\text{O}_3\text{-EBS}$	Dry powder	Irradiated fuel analogue with controlled FP content and porosity	Independent control of porosity and fission-product concentration	Does not reproduce radiation damage directly
$\text{UO}_2\text{-U}_3\text{O}_8$	Dry powder	Porosity simulation in spent fuel analogues	Direct control of pore generation within U-based materials	Limited porosity range achieved
$\text{UO}_2\text{-Cr}$	Dry powder	ATFs	Industrially relevant route and identification of Cr solubility limit	Less homogeneous Cr distribution
	Co-precipitation	Homogeneous ATF fabrication	Excellent Cr distribution and strong grain growth	More processing stages required
Zr-Nd	Internal gelation	Inert matrix fuel precursor development	Excellent compositional homogeneity and microsphere production	Process optimization required at high Nd contents
$\text{ZrO}_2\text{-CsI}$	Wet (+ SPS)	Volatile FP retention studies	Useful model for Cs-I immobilization studies	Partial iodine loss and retention uncertainties

4.1. INFLUENCE OF FABRICATION ROUTE ON MICROSTRUCTURE

One of the most important outcomes of the present work is the demonstration that fabrication route has a strong influence on the final properties of nuclear fuel analogues, in some cases comparable to or even greater than the effect of composition itself. Three different fabrication strategies were investigated for UO_2 -based materials: conventional dry powder processing, aqueous co-precipitation, and, through the JRC collaboration, sol-gel



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fabrication. The comparison between these approaches reveals significant differences in densification, phase homogeneity, porosity evolution, and microstructural development.

The dry powder route (conventional procedure used in nuclear industry) produced acceptable but relatively heterogeneous microstructures when UO_2 matrix is doped. In these materials, phase formation relies on solid-state diffusion during sintering, making the final product strongly dependent on powder mixing efficiency, particle size distribution, and local compositional variations [44, 49, 50]. As a consequence, lower densification levels and greater microstructural variability were observed, particularly in multiphase systems such as $\text{UO}_2\text{-ZrO}_2$ (section 1.1.1).

In contrast, co-precipitation significantly improved chemical homogeneity by mixing the constituent elements at the molecular scale before calcination and sintering [45]. This enhanced homogeneity was reflected in a more uniform phase distribution, improved reproducibility of structural properties, and more controlled microstructural evolution [30]. This effect was particularly evident in the Cr-doped UO_2 fuels (see section 2), where co-precipitated samples exhibited more uniform grain growth and oxidation behavior than dry route materials.

The JRC sol-gel materials the highest densification levels among the systems investigated in this work (section 3.1). Relative densities exceeded 95%TD throughout the entire compositional range and approached full densification for the highest zirconium concentrations. These values are significantly higher than those obtained through either dry powder processing or co-precipitation. The low BET surface areas obtained for these materials further confirm their high densification. The larger densification is likely related to the close mixing achieved during the sol-gel synthesis route, which promotes enhanced mass transport during sintering and results in a more uniform final microstructure.

These findings have direct implications for future fabrication of advanced nuclear fuels and inert matrix materials, where strict control of composition and microstructure is essential.



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4.2. STRUCTURAL EVOLUTION OF THE $\text{UO}_2\text{-ZrO}_2$ SYSTEM

All results from the dry route, co-precipitation route and JRC (sol-gel route) samples indicate a common structural evolution pathway. At low zirconium concentrations, zirconium is incorporated into the fluorite UO_2 structure, producing lattice contraction and increasing disorder. Both Raman and XRD results indicate that a critical transition occurs near 20 mol% Zr, where additional Raman bands appear simultaneously with changes in diffraction peak shape. The JRC series provides evidence of this transition, as both techniques indicate the appearance of a second crystallographic contribution around this composition. Although the original interpretation was considered as two fluorite phases, the Raman results suggest that a tetragonal zirconia-rich phase represents a more physically realistic explanation. Future Rietveld refinements including tetragonal structural models will be essential for obtaining a rigorous description of phase evolution within this compositional range.

At low zirconium concentrations, zirconium is incorporated into the fluorite UO_2 lattice, producing a progressive contraction of the unit cell and increasing local lattice disorder. This behavior is evidenced by the reduction of the lattice parameter, broadening of Raman bands, and preservation of the fluorite diffraction, where the sample behaves as a single phase solid solution.

The situation changes at approximately 20 wt% Zr. In the investigated systems, this composition corresponds to the appearance of new Raman bands, increased broadening and asymmetry of the fluorite T_{2g} mode, diffraction peak asymmetry and peak splitting, and evidences of additional crystallographic contributions. The fact that the same behavior is observed independently in dry route materials, co-precipitated samples, and JRC pellets strongly suggests that this transition is intrinsic to the $\text{UO}_2\text{-ZrO}_2$ system rather than an artefact of a particular fabrication method. Beyond 20 wt% Zr, increasing zirconium concentration promotes the progressive destabilization of the fluorite structure and the development of zirconia-rich domains.

4.3. EFFECT OF TRIVALENT FISSION PRODUCT ANALOGUES

Eu-doped UO_2 pellets provide valuable information regarding the effect of trivalent



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FPs on the fluorite lattice. The observed Vegard-type behavior, the generation of vacancy-related Raman bands and the absence of secondary phases indicate complete incorporation of Eu^{3+} within the investigated composition range. Raman and XRD results demonstrate that trivalent FPs modify lattice parameters and defect chemistry without destabilizing the fluorite structure. These observations are consistent with the behaviour observed in the Nd-containing analogue systems discussed in Section 1.2.1, where rare-earth incorporation also occurred without evidence of phase separation. Together, these results indicate that trivalent FPs can be accommodated within the UO_2 fluorite lattice through charge-compensation mechanisms involving oxygen vacancies while preserving the fundamental crystal structure. Although the fluorite phase remains stable, the incorporation of trivalent species may influence densification behaviour and microstructural development, affecting pellet porosity and sintering efficiency. These findings are directly relevant for understanding the structural evolution of irradiated nuclear fuels containing rare-earth FPs.

4.4. POROSITY SIMULATION AND IRRADIATED FUEL ANALOGUES

A major objective of Task 1 was to reproduce some of the characteristic microstructural features of irradiated nuclear fuel, particularly fission-products accumulation and increased porosity in high-burnup structures. The $\text{CeO}_2\text{-Nd}_2\text{O}_3$ with EBS system proved highly effective for this purpose. Nd incorporation successfully reproduced the structural effects associated with trivalent FPs, while EBS provided independent control of porosity. Observations demonstrated that FPs simulation and porosity generation can be controlled. This is particularly valuable for future studies seeking to isolate the effect of specific variables on fuel behavior.

The $\text{UO}_2\text{-U}_3\text{O}_8$ approach provided a second strategy for generating porosity. The results suggest the existence of a threshold effect around 5 wt% U_3O_8 , where maximum porosity was achieved. Further additions did not increase porosity but instead promoted partial densification. This behavior may be related to enhanced defect generation and mobility associated with the reduction of U_3O_8 during sintering, which generates a high concentration of defects and locally modifies the oxygen potential within the pellet. The increased defect mobility and temporary oxygen availability may enhance diffusion processes, promoting grain growth and densification and thereby partially compensating



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for the pore formation expected from the U_3O_8 to UO_2 reduction. Although additional experiments, particularly at lower initial U_3O_8 contents, would be required to confirm this interpretation, the observed trend indicates that porosity development is not simply proportional to additive concentration.

Together, both approaches demonstrate the feasibility of producing realistic surrogate materials that reproduce key aspects of irradiated fuel microstructure while maintaining full control over composition and porosity.

4.5. INTERNAL GELATION VERSUS PELLET ROUTES

IG represents a fundamentally different fabrication strategy compared with conventional pellet routes. In powder-based methods, homogeneity must be achieved through mixing of individual particles. In contrast, IG establishes homogeneity during droplet formation itself, producing chemically uniform microspheres from the outset. The homogeneous Nd distributions demonstrate that segregation can be minimized using this approach. In addition, IG directly generates spherical particles suitable for pellet fabrication and remote handling. This reduces the number of intermediate processing steps and may simplify future fabrication of minor-actinide-bearing fuels. The successful incorporation of neodymium into the zirconia lattice, together with the absence of “noticeable” segregated phases, confirms the potential of IG as a route for preparing advanced inert matrices and transmutation targets. Extension of this methodology to uranium-bearing systems therefore represents a logical next step in future developments.

4.6. EFFECT OF CHROMIUM ON UO_2 -BASED ATF MATERIALS

The results obtained for Cr-doped UO_2 pellets demonstrate that chromium acts primarily as a grain growth promoter rather than a densification aid. In both processing routes, increasing chromium concentration produces grain enlargement and lattice contraction, indicating chromium incorporation into the fluorite matrix. The estimated chromium solubility limit remains close to 1000 ppm under the investigated sintering conditions. Beyond this concentration, secondary chromium-rich precipitates become increasingly important.



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The results obtained for Cr-doped UO_2 demonstrate that chromium acts primarily as a microstructural modifier. Both dry route (section 2.1) and co-precipitated (section 2.2) materials show evidence of chromium incorporation into the fluorite lattice. XRD detected progressive lattice contraction, while Raman spectroscopy revealed the development of oxygen vacancy related bands. These observations are consistent with substitution of U^{4+} by Cr^{3+} and the associated formation of charge compensating defects. The presence of these defects influences grain-boundary mobility and contributes to the enhanced grain growth observed after sintering. In addition, modifications of the local oxygen potential during sintering may further increase diffusion rates and grain-boundary migration, thereby promoting microstructural coarsening. The maximum grain size was obtained near the estimated chromium solubility limit, approximately 1000 ppm Cr_2O_3 . Above this concentration, chromium-rich precipitates develop along grain boundaries and progressively inhibit further grain growth. The existence of a defined optimum chromium concentration is therefore experimentally confirmed.

4.7. OXIDATION BEHAVIOUR OF ATF_s AND THE ROLE OF FABRICATION ROUTE

The oxidation results further reveal that fabrication route has a stronger influence on oxidation behaviour than chromium concentration itself. Homogeneous Cr distribution obtained by co-precipitation leads to more complex and delayed oxidation pathways than those observed for dry route materials.

The oxidation experiments performed on UO_2 -Cr ATF fuels reveal that microstructure plays a major role in oxidation resistance. All investigated materials reached very similar oxidation states, demonstrating that chromium does not change the final oxidation products. However, oxidation kinetics varied depending on the fabrication route. Dry route materials exhibited a rapid single step oxidation process, whereas co-precipitated materials displayed a delayed and multistep oxidation pathway. The better oxidation resistance of the co-precipitated samples is most likely associated with their improved microstructural homogeneity. Atomic scale mixing of uranium and chromium during co-precipitation produces a uniform dopant distribution, and a more homogeneous grain structure. These features appear to delay the initial oxygen incorporation stage and increase



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oxidation onset temperatures.

The results therefore suggest that fabrication route optimization may be as important as dopant optimization for improving fuel performance during interim storage and long-term disposal scenarios.

4.8. EXTERNAL VALIDATION THROUGH INTERNATIONAL COLLABORATIONS

The incorporation of materials developed externally at JRC Karlsruhe and Lancaster University provides independent validation of the methodologies developed within IONMAT. The JRC $\text{UO}_2\text{-ZrO}_2$ pellets (fabricated by sol-gel route) confirmed the phase evolution identified in the project and, most importantly, verified the existence of a critical transition near 20 mol% Zr. In addition, they demonstrated a superior densification. Meanwhile, the Lancaster $\text{ZrO}_2\text{-CsI}$ materials extended the scope of the project towards volatile fission-products retention. The results illustrate the challenges associated with volatile FPs retention, and suggest that cesium is retained more effectively than iodine during SPS processing. These findings provide useful information for future studies on FPs stabilization and waste form development.

The external collaborations strengthen the conclusions of the project and demonstrate the robustness of the characterization methodologies developed within IONMAT.

5. CONCLUSIONS

- Dry powder processing successfully produced UO_2 -based surrogate materials containing Eu, Zr and Cr over a broad compositional range. Structural characterization confirmed the formation of solid solutions in all investigated systems below their respective solubility limits.
- Eu incorporation into UO_2 produced a systematic contraction of the fluorite lattice and followed Vegard-type behavior throughout the investigated compositional range, confirming complete solid solution formation and homogeneous dopant incorporation.



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- Zirconium additions progressively destabilize the fluorite structure of UO_2 . Raman and XRD analyses indicate that a significant structural transition occurs near 20 mol% Zr, where additional Raman bands appear simultaneously with the development of secondary crystallographic contributions in diffraction patterns.
- Controlled porosity was successfully introduced by adding U_3O_8 to UO_2 precursor powders. The highest porosity was observed for the 5 wt% U_3O_8 composition, while larger additions promoted partial recovery of densification. Similar microstructural effects were observed in Nd-containing analog systems, where the incorporation of trivalent rare-earth species influenced densification behaviour and pore development without destabilizing the fluorite structure.
- Internal gelation proved to be a robust route for the production of homogeneous Zr-Nd microspheres. Homogeneous elemental distributions, acceptable mechanical integrity and good crystallinity were achieved after calcination.
- Chromium incorporation promoted grain growth in UO_2 without significantly modifying density. The chromium solubility limit was estimated to be close to 1000 ppm under the sintering conditions investigated. Above this limit, segregated chromium-rich phases increasingly influence the final microstructure.
- Oxidation experiments on UO_2 -Cr ATFs demonstrated that fabrication route exerts a greater influence on oxidation behavior than chromium concentration. Co-precipitated materials displayed delayed and multi-step oxidation mechanisms compared with dry route samples, suggesting a strong effect of dopant distribution and microstructural homogeneity.
- Co-precipitation generally produced more homogeneous microstructures than conventional dry powder processing, leading to improved phase uniformity and more controlled microstructural evolution. Internal gelation and co-precipitation routes demonstrated superior chemical homogeneity compared with conventional powder metallurgy, highlighting the importance of precursor design for advanced nuclear fuel fabrication. JRC sol-gel materials exhibited outstanding densification, with relative



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densities generally higher than 95%TD throughout the full compositional range. Their Raman and XRD behavior independently confirmed the structural transition occurring near 20 mol% Zr identified within the IONMAT materials.

- Lancaster SPS sintered ZrO₂-CsI samples demonstrated measurable cesium retention after processing. XRF results indicate that cesium provides a more reliable indicator of CsI retention than iodine. The low iodine concentrations observed may reflect either quantification limitations or partial iodine loss during SPS processing.
- Independent characterization of materials supplied by JRC and Lancaster University validated the robustness of the characterization methodology developed within IONMAT and extended its applicability to externally fabricated materials.
- Overall, the work demonstrates that composition, fabrication route and sintering conditions collectively determine the final microstructure of advanced nuclear fuel analogues. The characterization methodologies developed within IONMAT provide a robust framework for future studies involving irradiated-fuel surrogates, accident-tolerant fuels and inert-matrix systems.

6. SCIENTIFIC AND SOCIETAL IMPACT OF IONMAT

The results obtained within IONMAT demonstrate the feasibility of several fabrication strategies relevant to future nuclear fuel cycles. Beyond the specific characterization outcomes, the project provides a systematic assessment of fabrication routes that may contribute to advanced fuel development, waste minimization strategies, and future partitioning and transmutation concepts. The work performed on surrogate fuels, inert matrices and ATFs establishes a comprehensive experimental framework for evaluating the relationship between fabrication route, composition, microstructure and performance. Such information is essential for the future implementation of innovative fuel concepts, particularly those requiring high chemical homogeneity, controlled porosity or incorporation of minor actinides and FPs. The different material systems investigated throughout the project address complementary aspects of advanced nuclear fuel cycles. The UO₂-ZrO₂ materials contribute to the understanding of PCI, inert matrix and transmutation



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fuel concepts, whereas Cr-doped UO_2 supports the development of accident-tolerant fuels for current and future reactors. The $\text{UO}_2\text{-Eu}_2\text{O}_3$ and $\text{CeO}_2\text{-Nd}_2\text{O}_3$ systems provide representative analogues of irradiated fuels, allowing the investigation of degradation phenomena without the constraints associated with highly radioactive materials. These developments support future strategies aiming at improved fuel utilization, reduction of long-term radiotoxic inventories and optimization of high-level waste management.

Additionally, the knowledge acquired regarding fuel fabrication routes, microstructural control, surrogate fuel development, and advanced characterization methodologies has directly contributed to the preparation of a new European research proposal (MOXAIC, *MOX fuel: Accelerated and Integrated fuel-Cycle qualification for liquid-metal fast-reactor concepts in Europe*, call HORIZON-EURATOM-LS-2026-01, coordinated by CEA). Within this initiative, CIEMAT will participate in the fabrication of $\text{UO}_2\text{-ThO}_2$ model materials designed to simulate MOX type fuels using both conventional dry powder processing and aqueous co-precipitation routes. The objective will be to investigate how fabrication methodology affects microstructural evolution, phase homogeneity, and the dissolution behavior of MOX analogue materials during storage and disposal scenarios. The use of low-radiotoxicity surrogate systems will allow the study of key degradation phenomena while avoiding many of the experimental constraints associated with highly radioactive materials. These developments illustrate how the knowledge generated by IONMAT is already contributing to the design of future European research activities in advanced nuclear fuels and radioactive waste management.

Finally, although the present work is primarily focused on material science and nuclear fuel technology, its long-term implications extend beyond the technical domain. Improvements in fuel fabrication, fuel performance and waste minimization contribute directly to safer management of radioactive waste and to the sustainability of nuclear energy as a low-carbon energy source. The production of representative non-radioactive analogues also facilitates research activities while reducing radiological risks, expanding the possibility of developing new methodologies and improving public confidence in scientific studies related to radioactive waste management. In this context, the project contributes to the broader objectives of reducing environmental impact, improving resource utilization and supporting long-term strategies for responsible radioactive waste



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 DIVISIÓN DE FISIÓN NUCLEAR	INFORME DFN/RA-10/SP-26	HOJA 70 DE 70
	REF. EXTERNA	REVISIÓN 0 FECHA 10/05/2026

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<u>FIRMANTE</u>	<u>NOMBRE</u>	<u>FECHA</u>	<u>NOTAS</u>
FIRMANTE[1]	MARIA NIEVES RODRIGUEZ VILLAGRA	24/09/2026 11:38 Sin acción específica	
FIRMANTE[2]	JONE MIREN ELORRIETA BAIGORRI	24/09/2026 12:38 Sin acción específica	
FIRMANTE[3]	M.SOLEDADE FERNANDEZ FERNANDEZ	24/09/2026 12:55 Sin acción específica	
FIRMANTE[4]	ENRIQUE MIGUEL GONZALEZ ROMERO	24/09/2026 13:50	

