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**Preparation and characterization of $\text{UO}_2\text{-ZrO}_2$ model materials as analogues of spent nuclear fuel produced by co-precipitation.
(IONMAT PROJECT. SUBTASK 1.3)**

DIVISIÓN DE FISIÓN NUCLEAR

Ciemat Centro de Investigaciones
Energéticas, Medioambientales
y Tecnológicas



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TITULO: preparation and characterization of $\text{UO}_2\text{-ZrO}_2$ model materials as analogues of spent nuclear fuel produced by co-precipitation. (IONMAT PROJECT. SUBTASK 1.3)

AUTORES: N. Rodríguez-Villagra, A. Núñez, J.M. Elorrieta, A. Milena-Pérez, S. Fernández-Carretero, L. Gutiérrez, P. Joseph, H. Galán

ABSTRACT:

$\text{UO}_2\text{-ZrO}_2$ mixed oxide materials are representative analogues of the interaction products formed at the fuel-cladding interface of spent nuclear fuel during reactor operation. The characterization of these phases is of considerable interest for understanding fuel performance and long-term behaviour during storage and disposal. In this work, a series of $\text{UO}_2\text{-ZrO}_2$ model materials covering the full compositional range from pure UO_2 to pure ZrO_2 (0, 20, 40, 60 and 100 wt.% ZrO_2) were synthesized by an aqueous co-precipitation route within the framework of the IONMAT project. Following precipitation, the powders were subjected to calcination-reduction treatments under H_2/Ar atmosphere, pressed into pellets and sintered at 1675 °C under reducing conditions.

The obtained materials were characterized by XRD, Raman spectroscopy, helium pycnometry, BET surface area measurements and SEM-EDS. XRD analysis revealed a progressive structural evolution from cubic fluorite UO_2 to monoclinic ZrO_2 with increasing zirconia content. Intermediate compositions exhibited mixtures of cubic and tetragonal (U,Zr) O_2 solid-solution phases, demonstrating partial mutual incorporation of uranium and zirconium within the oxide lattice. Raman spectroscopy confirmed this phase evolution and provided evidence of increasing local structural disorder and zirconia-rich phase formation as the zirconium content increased.

Density measurements showed improved sintering behaviour for UO_2 -rich compositions, with pycnometric density increasing from approximately 5.5 $\text{g}\cdot\text{cm}^{-3}$ for pure ZrO_2 to 9.7 $\text{g}\cdot\text{cm}^{-3}$ for pure UO_2 . Correspondingly, relative density increased and total porosity decreased significantly with increasing uranium content. BET measurements revealed low specific surface areas after sintering (0.19-0.36 $\text{m}^2\cdot\text{g}^{-1}$), consistent with extensive densification. SEM-EDS observations confirmed the formation of consolidated polycrystalline microstructures, homogeneous uranium and zirconium distributions, and the progressive development of zirconia-rich regions in compositions with higher zirconium contents.

Overall, the results demonstrate that aqueous co-precipitation is an effective route for producing homogeneous and well-characterized $\text{UO}_2\text{-ZrO}_2$ model materials. Compared with previously investigated dry powder processing, the wet route provides improved homogeneity and densification, making these materials suitable surrogates for the study of fuel-cladding interaction products and their long-term behaviour under nuclear waste management conditions.

	NOMBRE	FIRMA	FECHA	
Preparado por:	N. Rodríguez-Villagra			FECHA DE EMISIÓN
Revisado por:	J. M. Elorrieta			
Conf por A. C.:	S. Fernández			
Aprobado por:	E. González Romero			



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1. INTRODUCTION

Uranium dioxide (UO_2) is the reference nuclear fuel material used in most commercial light water reactors (LWRs), while zirconium-based alloys are employed as fuel cladding materials because of their low neutron absorption cross-section, good corrosion resistance and satisfactory mechanical performance under reactor operating conditions [1]. During irradiation, the fuel pellet experiences thermal expansion, fission gas production, fuel swelling and cladding creep progressively reduce the pellet–cladding gap, promoting direct contact between the UO_2 fuel and the zirconium alloy cladding [2, 3]. This phenomenon, commonly referred to as Pellet–Cladding Interaction (PCI), results in the formation of complex chemical and mechanical interaction layers at the fuel–cladding interface [3].

Post-irradiation examinations have shown that the PCI interaction zone is generally composed of zirconia-rich regions next to the cladding and mixed uranium–zirconium oxide phases, typically described as $(\text{U,Zr})\text{O}_2$ solid solutions, located closer to the fuel pellet [4, 5]. Depending on composition, these mixed oxides may exhibit cubic fluorite-type or tetragonal crystal structures. The formation and evolution of these interfacial phases are of particular interest because they can influence the mechanical stability, chemical reactivity and long-term behaviour of spent nuclear fuel during storage and disposal [4, 5].

Despite their critical importance to fuel performance and safety assessments, the physical and chemical properties of UO_2 – ZrO_2 interaction products remain insufficiently characterized. The complexity of irradiated fuel and the radiological constraints associated with handling and examination of spent nuclear fuel, makes fundamental investigations challenging. As a result, model materials are required to isolate specific phenomena and improve the understanding of phase formation, structural evolution and microstructure in the UO_2 – ZrO_2 system.

Under the IONMAT project, UO_2 – ZrO_2 model materials were previously synthesized by a dry powder method within subtask 1.1 [6]. In the current study, they were produced through an aqueous co-precipitation process to obtain more homogeneous mixtures over a broad compositional range. The objective is to investigate the effect of zirconium incorporation on phase stability, densification and microstructure, and to provide well-characterized surrogate materials representative of fuel–cladding interaction products



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formed in spent nuclear fuel. These model materials will provide a valuable experimental stage for investigating fuel-cladding interaction and support future studies by addressing fuel performance, degradation mechanisms, and long-term behaviour under interim storage and final disposal conditions.

2. MATERIALS AND METHODS

2.1. REAGENTS

UO₂-ZrO₂ powders were synthesized by an aqueous co-precipitation route using zirconyl nitrate hydrate, ZrO(NO₃)₂·nH₂O (99.5%, Acros Organics), and U₃O₈ were obtained by oxidation of UO₂ powder, as zirconium and uranium precursors, respectively.

Nitric acid (HNO₃, 4 M) was employed for uranium dissolution and preparation of the uranium-bearing precursor solution. Ammonium hydroxide solution (NH₄OH, 25% analytical grade, Merck) was used as the precipitating agent. Deionized water was utilized throughout the synthesis procedure, while isopropyl alcohol (iPrOH) was used during the final washing stage to facilitate powder recovery and minimize dissolution losses. Table I summarizes the UO₂-ZrO₂ compositions investigated in this work.

Table I Definition of UO₂-ZrO₂ 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

2.2. CO-PRECIPIATION AND PELLET FABRICATION

U₃O₈ was dissolved in 4 M HNO₃ and maintained under stirring for 24-48 h to ensure complete dissolution. In parallel, zirconyl nitrate was dissolved in deionized water with the help of ultrasonic treatment for at least 4 h. Both solutions were then mixed in stoichiometric proportions according to the target UO₂-ZrO₂ composition (Figure 1, Table I).



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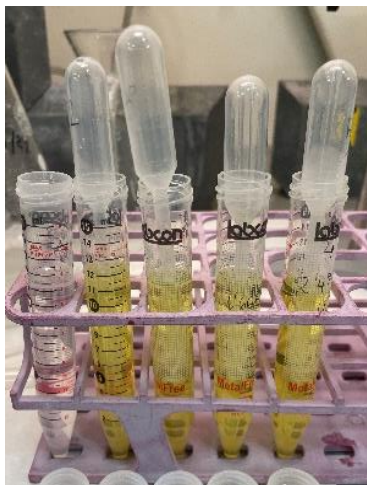


Figure 1 Photographs of a co-precipitation process step.

Co-precipitation was induced by the slow addition of 5 M NH_4OH under continuous stirring until the pH reached values between 9 and 12, depending on the target composition. The resulting precipitate was allowed to age for at least 1 h to promote complete precipitation of uranium and zirconium species. The precipitate was subsequently filtered and washed twice with 5 M NH_4OH solution and once with deionized water. Previous semi-quantitative ICP-MS analyses indicated partial dissolution of the co-precipitated solids during NH_4OH and water washing, particularly for zirconium-containing samples[7]. Therefore, all washing steps were performed rapidly and using cooled solutions whenever possible. A final wash with isopropanol (iPrOH) was applied to minimize solid loss and improve powder handling during drying and filtration.

No intermediate thermal treatment was applied after precipitation. Following washing with iPrOH, the powders were directly subjected to a calcination-reduction treatment under a reducing atmosphere of 4.7 % $\text{H}_2\text{-Ar}$. Figure 2 shows photographs of the co-precipitated powders after drying and the corresponding sintered pellets obtained for the different $\text{UO}_2\text{-ZrO}_2$ compositions. The thermal treatment consisted of heating at 3°C min^{-1} up to 200°C with a 1 h dwell time, followed by heating at 5°C min^{-1} up to 600°C and a 5 h isothermal step at this temperature. This treatment enabled dehydration, decomposition of residual nitrate species and reduction of uranium oxides towards the desired oxidation state. A second identical reduction treatment was performed before pellet fabrication to ensure



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complete reduction of residual oxidized uranium phases. Green pellets were then fabricated by uniaxial pressing at 400 MPa for 5 s, and sintered under flowing H_2/Ar atmosphere with a heating rate of $200\text{ }^{\circ}\text{C h}^{-1}$ up to $1675\text{ }^{\circ}\text{C}$, followed by a 6 h isothermal dwell [8]. These reducing conditions were selected to prevent oxidation of uranium dioxide during high-temperature densification.

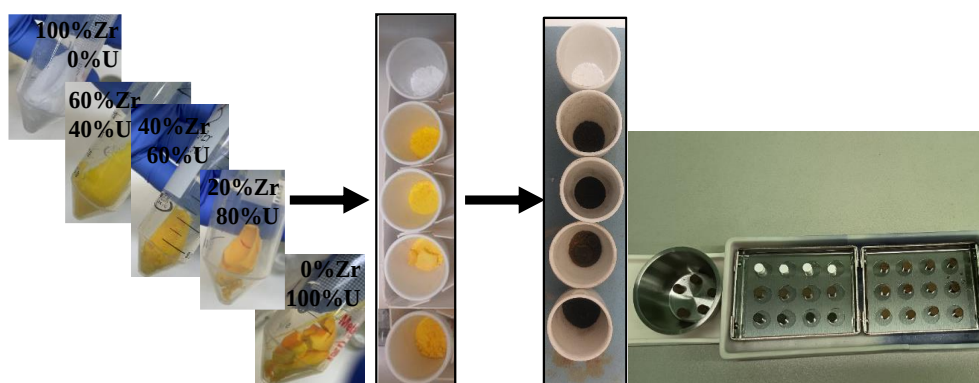


Figure 2 Photographs of the dried co-precipitated powders obtained for different UO_2 - ZrO_2 compositions (UO_2 , UO_2 - 20% ZrO_2 , UO_2 - 40% ZrO_2 , UO_2 - 60% ZrO_2 , ZrO_2), together with the corresponding powders after calcination-reduction and the pellets after sintering.

2.3.CHARACTERIZATION TECHNIQUES

After sintering, the samples were comprehensively characterized using the techniques summarized in Table II.

Table II Methods and techniques used in this study.

Technique	Parameter	Equipment
BET	N_2 -BET Surface Area	ASAP 2020 (Micromeritics) ISO 12800E [6, 9]
XRD	Microstructure/crystalline identification (quantification)/chemical composition	D8 ADVANCE Eco (Bruker) – ICDD Cu $K\alpha 1$ radiation ($\lambda=1.54056\text{ \AA}$), 40 kV and 25 mA Bragg-Brentano configuration geometry software TOPAS (Bruker Analytical X-Ray Systems)
Raman spectroscopy	Microstructure/speciation/chemical composition	LabRam HR Evolution (HORIBA) He-Ne laser with wavelength=632.8 nm.



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Technique	Parameter	Equipment
SEM-EDS	Surface morphology/grain size/elemental identification (quantification)	TM4000 Plus 15 kV (HITACHI) ASTM E 112-96; UNE-EN ISO 643:2012
Pycnometer	Density	AccuPyc II 1350 (Micromeritics)
Furnace	Max. 1700 °C, atmosphere	Termolab
Mixer Mill	Max. frequency of 30 Hz	MM 400 (Retsch)
Uniaxial Press	25 T	WEBER P-O PW 10 (0 – 130 kN)

3. RESULTS: EFFECT OF ZR LOADING ON UO₂-ZrO₂ PELLETS. CHARACTERIZATION

Here are the main results obtained in this study.

3.1. PHASE ANALYSIS (XRD)

The crystal structure of the pellets was studied by XRD at 40 kV and 25 mA using Cu K α 1 radiation ($\lambda = 1.54056 \text{ \AA}$), with a Bragg-Brentano configuration over the 2θ range of 20 - 120° and at a step size of 0.01°. Calibration was carried out by using an alumina standard. The lattice parameter of each sample was calculated by a Rietveld refinement Quantitative Phase Analysis (RQPA). XRD analysis revealed a progressive phase evolution from a UO₂ cubic fluorite-type structure to monoclinic zirconia as the ZrO₂ content increased (Figure 3 and Table III).

Pure UO₂ exhibited the fluorite-type cubic structure. As the ZrO₂ content increased, the stability of this cubic phase progressively decreased, and intermediate compositions consisted of mixtures of cubic and tetragonal (U,Zr)O₂ solid-solution phases. With further increases in Zr content, the fraction of the tetragonal phase increased at the expense of the cubic phase, reflecting the destabilization of the fluorite structure and the growing influence of zirconia-rich phases. Finally, pure ZrO₂ consisted entirely of monoclinic zirconia. These results confirm the formation of mixed U-Zr oxide phases and highlighted the strong influence of composition on phase stability across the UO₂-ZrO₂ system.



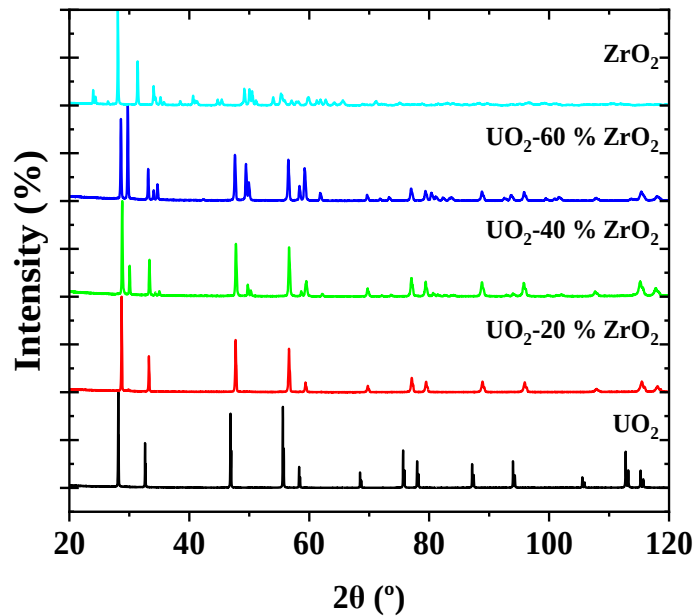


Figure 3 XRD patterns of the sintered pellets: UO_2 , UO_2 - 20% ZrO_2 , UO_2 - 40% ZrO_2 , UO_2 - 60% ZrO_2 , ZrO_2 .

Pure UO_2 displays a fully cubic fluorite structure. The addition of ZrO_2 progressively reduces the fraction of the cubic phase, which decreases from 96.4 wt.% at 20 wt.% ZrO_2 to 34 wt.% at 60 wt.% ZrO_2 . This trend reflects the increasing influence of Zr on the UO_2 lattice and the corresponding reduction in the stability of the cubic fluorite phase.

Table III Quantification of main phases identified by XRD.

Composition	Main phases identified
UO_2	c- UO_2 (100 %)
UO_2 - 20% ZrO_2	3.6% t- $\text{U}_{0.18}\text{Zr}_{0.82}\text{O}_2$ + 96.4% c- $\text{U}_{0.9}\text{Zr}_{0.1}\text{O}_2$
UO_2 - 40% ZrO_2	32.1% t- $\text{U}_{0.18}\text{Zr}_{0.82}\text{O}_2$ + 67.9% c- $\text{U}_{0.9}\text{Zr}_{0.1}\text{O}_2$
UO_2 - 60% ZrO_2	66% t- $\text{U}_{0.18}\text{Zr}_{0.82}\text{O}_2$ + 34% c- $\text{U}_{0.9}\text{Zr}_{0.1}\text{O}_2$
ZrO_2	m- ZrO_2 (100 wt.%)



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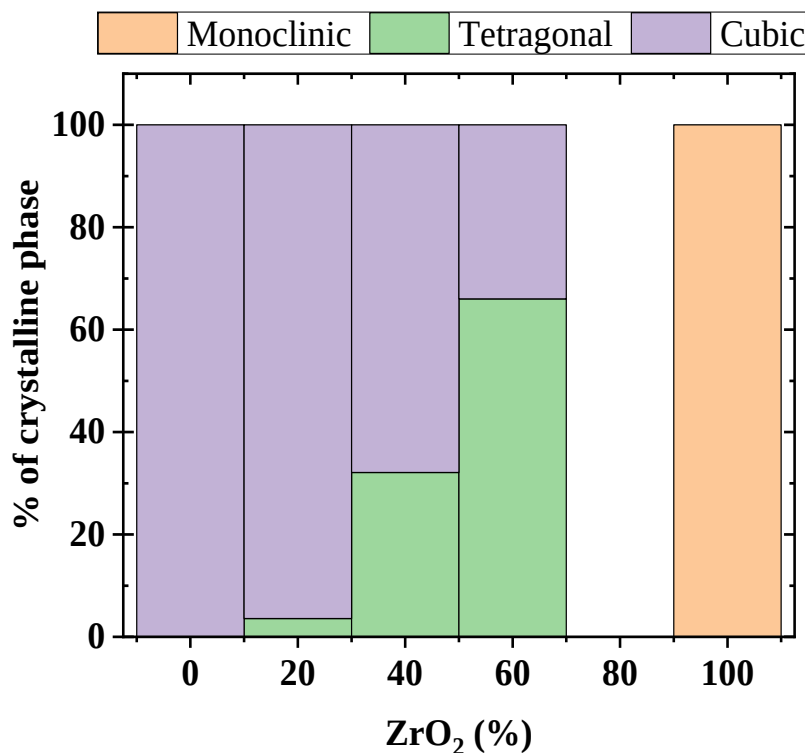


Figure 4 Evolution of crystalline phase composition with increasing ZrO₂ content.

The XRD results indicate that zirconium is partially incorporated into the fluorite lattice of uranium dioxide, leading to the formation of solid-solution phases over a broad compositional range. The coexistence of tetragonal and cubic phases in intermediate compositions indicates incomplete stabilization of a single phase after sintering (Figure 4). Increasing zirconia content leads to stabilization of zirconia-rich tetragonal and monoclinic polymorphs. The complete monoclinic structure observed for pure zirconia and the full cubic structure obtained for pure UO₂ represent the two end members of the investigated compositional series.

3.2. RAMAN SPECTROSCOPY ANALYSES

Raman spectroscopy analyses were carried out using a He-Ne 633 nm laser, which was focused on the sample surface using an Olympus BX41 microscope. Scattered Raman light emitted by the sample was collected with a spectral resolution $< 1 \text{ cm}^{-1}$. For each



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spectrum, an acquisition time of 120 s and 3 accumulations was considered. Before analysis, the apparatus was calibrated with a silicon wafer, using the first-order Si line at 520.5 cm^{-1} . Five spectra were acquired at different locations for each homogeneous sample, in order to obtain the resulting Raman spectra by summing the individual ones.

Raman spectra of the sintered $\text{UO}_2\text{-ZrO}_2$ pellets revealed significant structural changes as a function of zirconium content (Figure 5). The spectrum of pure UO_2 features the intense first-order fluorite T_{2g} vibrational mode centred at approximately 445 cm^{-1} , together with broader second-order bands observed at about 575 and 1150 cm^{-1} , all of which conform the characteristic Raman signature of cubic UO_2 [10-12].

The incorporation of zirconium into UO_2 progressively modifies the Raman profile. For the $\text{UO}_2\text{-20\% ZrO}_2$ composition, the fluorite T_{2g} band remains clearly visible, indicating that the cubic uranium dioxide structure is still dominant. However, the shift and asymmetric broadening observed for this band, as well as the detection of new contributions in the spectrum (two of which especially intense at around 640 and 1200 cm^{-1}), suggest the growth of lattice distortions and the formation of mixed U-Zr oxide solid solutions.

For intermediate compositions (40 and 60% ZrO_2), the presence of the latter additional Raman bands confirms the coexistence of different crystallographic environments. In particular, the appearance of bands in the $100\text{-}350\text{ cm}^{-1}$ region and at $\sim 640\text{ cm}^{-1}$, and their increasing intensity with ZrO_2 content, is consistent with the presence of zirconia-rich phases detected by XRD [13]. These spectra become progressively more complex, reflecting increased structural disorder and the coexistence of tetragonal and cubic phases. The spectrum of pure ZrO_2 exhibits numerous sharp bands distributed throughout the $150\text{--}700\text{ cm}^{-1}$ range, typical of monoclinic zirconia [14, 15].

Overall, the Raman results are in good agreement with the XRD phase analysis. The progressive evolution of the Raman spectrum therefore confirms the structural transition from a uranium-rich fluorite lattice towards zirconia-rich tetragonal phases as the ZrO_2 concentration increases.



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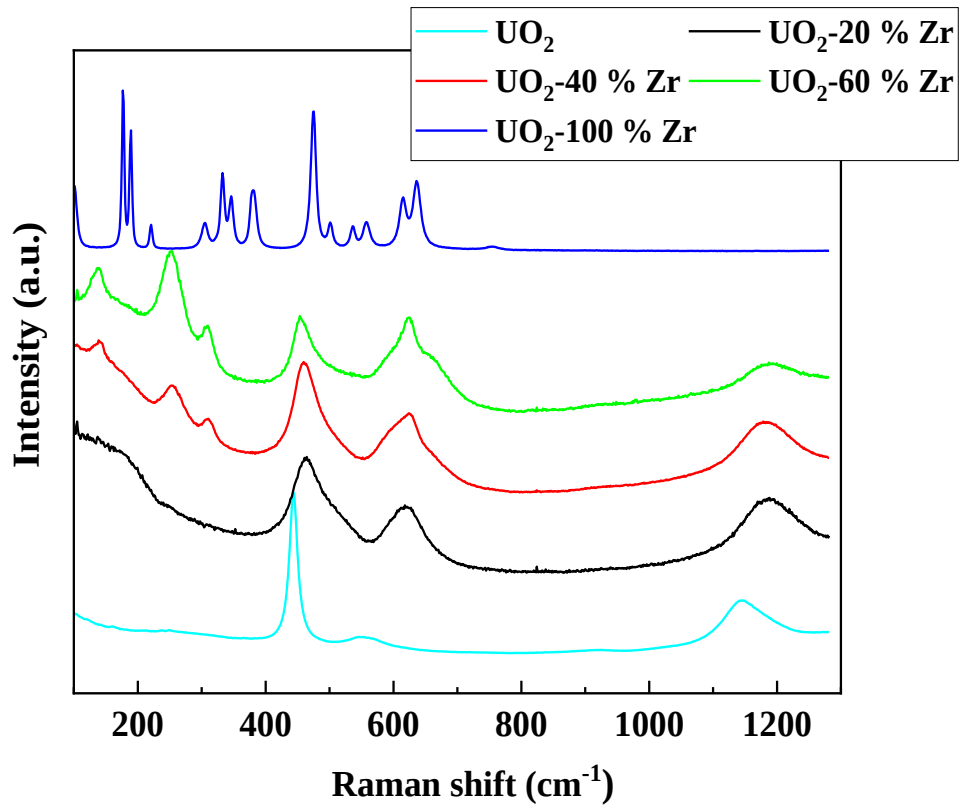


Figure 5 Raman spectra of the sintered pellets obtained from wet route: UO₂, UO₂ - 20% ZrO₂, UO₂ - 40% ZrO₂, UO₂ - 60% ZrO₂, ZrO₂.

3.3.DENSITY EVOLUTION

The density of the sintered pellets was determined by geometrical measurements and helium pycnometry. The geometric measurements (height and diameter) were obtained using a caliper (± 0.05 mm). Assuming cylindrical pellet geometry, the apparent density of the sample, ρ_{geom} ($\text{g}\cdot\text{cm}^{-3}$) was calculated (associated error of ± 0.2 $\text{g}\cdot\text{cm}^{-3}$) and compared to the theoretical density ρ_{theo} ($\text{g}\cdot\text{cm}^{-3}$) (from crystallographic parameters) in order to determine the associated total porosity P_{tot} (expressed in %) considering the following equations [16]:

$$\rho_{geom} = \frac{Mass}{Volume} = \frac{m}{\pi * \left(\frac{d}{2}\right)^2 * h}$$



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$$\rho_{theo} = \frac{M * Z}{N_a * V}$$

Where m (g) is the measured mass of the $\text{UO}_2\text{-ZrO}_2$ pellet, d (cm) is the diameter of pellet, h (cm) is the thickness of the pellet, M ($\text{g}\cdot\text{mol}^{-1}$) is the molar weight of the mixed oxide, Z is the number of formula units per unit cell, N_a is the Avogadro constant and V (cm^3) is the volume of the unit cell obtained from lattice parameters of the sintered pellets and XRD patterns refinement.

Helium pycnometry was used to measure the density of the pellets ρ_{pyc} ($\text{g}\cdot\text{cm}^{-3}$) and then to evaluate the total porosity P_{tot} as the sum of closed and open porosity, P_{closed} and P_{open} (expressed in %), respectively, as shown in the following equations:

$$P_{closed} = \left(1 - \frac{\rho_{pyc}}{\rho_{calc}}\right) \cdot 100$$

$$P_{open} = \left(\frac{\rho_{pyc} - \rho_{geom}}{\rho_{calc}}\right) \cdot 100$$

The measured pycnometer density increases almost linearly with UO_2 concentration, from $5.51 \text{ g}\cdot\text{cm}^{-3}$ for pure zirconia to $9.74 \text{ g}\cdot\text{cm}^{-3}$ for pure uranium dioxide. This trend reflects the intrinsically higher density of UO_2 compared with ZrO_2 (Figure 6).



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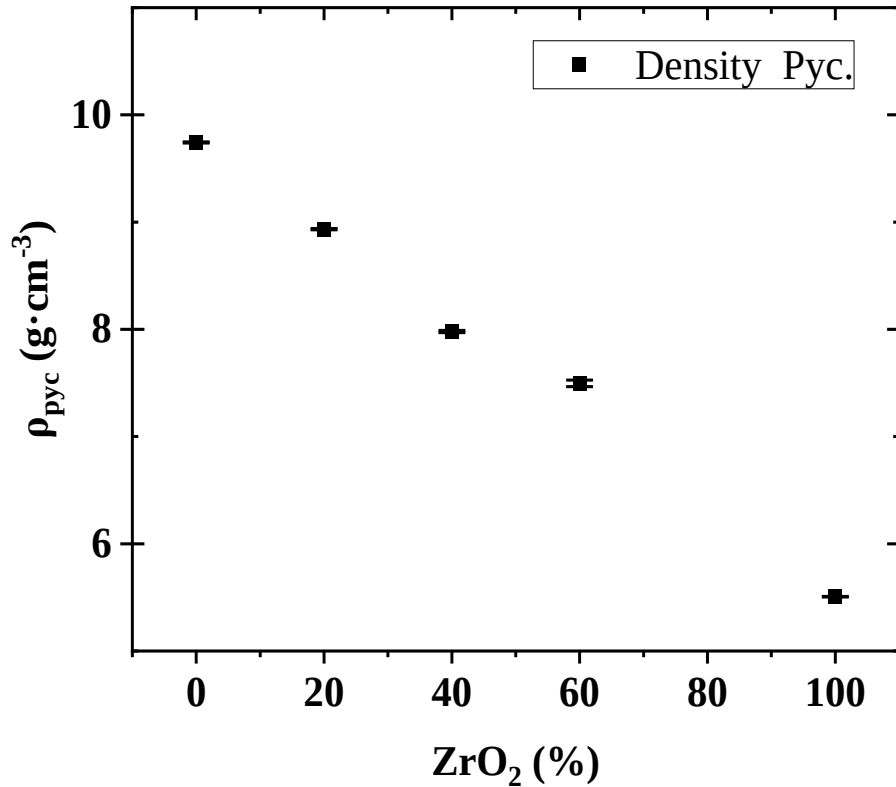


Figure 6 Pycnometer density (g·cm⁻³) vs ZrO₂ content (%).

Figure 7 shows the relative density values calculated from both the geometric density and the pycnometric density, normalized to the theoretical density of each composition. In all cases, the relative densities obtained by pycnometry are higher than those derived from the geometric measurements, reflecting the influence of open and interconnected porosity on the bulk density determination. Both methods show the same overall trend, with relative density increasing as the UO₂ content increases. The difference between the two measurements is more pronounced for ZrO₂-rich compositions, indicating a higher contribution of porosity, whereas UO₂-rich pellets exhibit higher densification and a smaller discrepancy between the two density estimates.



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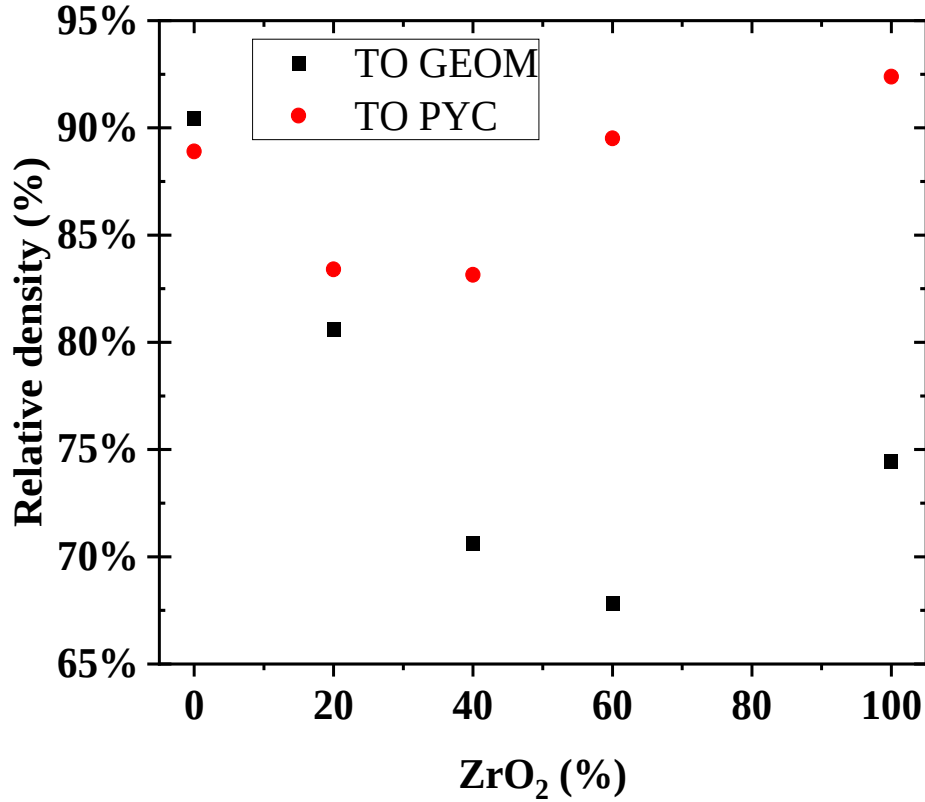


Figure 7 Relative density and total porosity vs ZrO₂ content (%).

Increasing ZrO₂ content results in a marked increase in both total and open porosity. As shown in Table IV, the total porosity for pure UO₂ exhibits the lowest total porosity (10%) and no measurable open porosity, indicating a highly consolidated microstructure. As the ZrO₂ fraction increases, the total porosity rises, reaching a maximum of 32% for the 60 wt.% ZrO₂ composition. A similar trend is observed for the open porosity, which increases from negligible values in pure UO₂ to 22% at 60 wt.% ZrO₂ and remains high (18%) for pure ZrO₂. These results suggest that increasing the ZrO₂ content hinders densification and pore closure during sintering, leading to a larger fraction of interconnected pores. In contrast, the closed porosity varies within a narrower range (8-17%) and does not show a clear dependence on composition, indicating that the increase in total porosity is primarily associated with the development of open porosity.



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Table IV Estimated samples porosity.

ZrO ₂ (wt. %)	Total porosity (%)	Open (%)	Closed (%)
100	26	18	8
60	32	22	10
40	29	13	17
20	19	3	17
0	10	-	10

3.4. BET SURFACE AREA

The specific surface areas of the pellets were determined by N₂ adsorption and desorption isotherms at 77 K (BET method). The BET model was applied over the relative pressure range (P/P_0) exhibiting linear adsorption behavior. The specific surface area obtained after sintering remained relatively low for all compositions (Table V), ranging from 0.19 to 0.36 m²·g⁻¹, which is consistent with the significant densification achieved during high-temperature sintering.

The highest BET surface area was measured for pure ZrO₂ (0.358 m²·g⁻¹), whereas mixed UO₂-ZrO₂ compositions exhibited values between 0.194 and 0.236 m²·g⁻¹. The lower surface areas observed in UO₂-rich compositions are consistent with enhanced particle coarsening and neck growth during sintering. The BET results correlate well with the density measurements and porosity evolution. Samples exhibiting higher relative densities generally presented lower accessible surface areas, indicating that pore removal and grain growth occurred during thermal treatment. Consequently, the BET measurements confirm the progressive microstructural consolidation of the UO₂-based materials.

Table V Specific surface area of the samples measured by BET (N₂).

ZrO ₂ (%)	BET area (m ² ·g ⁻¹)
0	0.222 ± 0.005
20	0.216 ± 0.005
40	0.24 ± 0.04
60	0.194 ± 0.004
100	0.358 ± 0.003

3.5. SEM-EDS

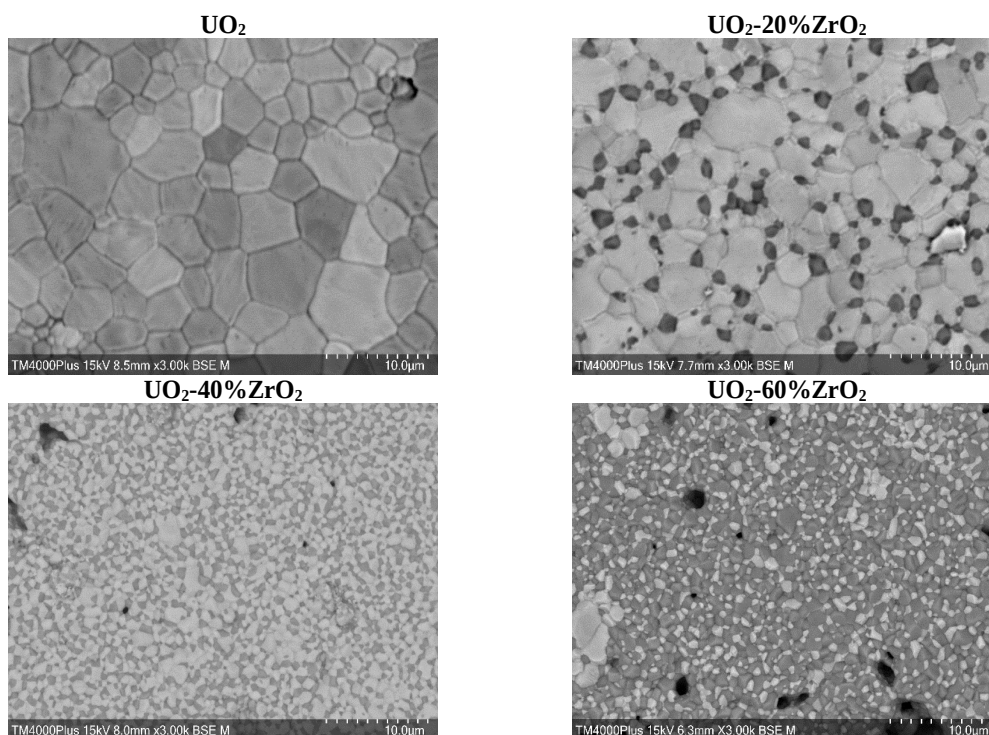
The morphological characterization of the pellets was performed by Scanning



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Electron Microscopy (SEM) using back-scattered electrons. The samples were observed under vacuum conditions with an acceleration voltage of 15 kV at various magnifications without any metallization step. Several images recorded at a magnification of x3000 were selected at the surface of each sample.

SEM observations revealed the formation of consolidated polycrystalline microstructures in all sintered pellets (Figure 8). An evolution in the microstructure was observed with increasing ZrO_2 content. While pure UO_2 exhibited relatively large grains, the average grain size decreased markedly in compositions containing 40-60 % ZrO_2 . In the mixed compositions, BSE imaging revealed the presence of darker Zr-rich grains, which were absent in pure UO_2 . These grains became increasingly abundant as the ZrO_2 content increased, representing a significant fraction of the microstructure in the 60 % ZrO_2 sample. In addition, zirconia-rich compositions displayed a higher amount of residual porosity, in agreement with the lower relative densities measured for these materials. These observations confirm the progressive development of Zr-rich regions and the strong influence of composition on microstructural evolution within the UO_2 - ZrO_2 system.



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100%ZrO₂

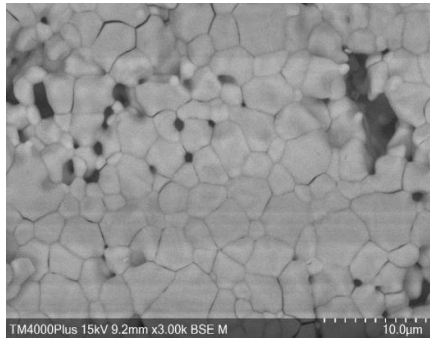


Figure 8 SEM images of UO₂, UO₂ - 20% ZrO₂, UO₂ - 40% ZrO₂, UO₂ - 60% ZrO₂, ZrO₂.

No evidence of severe cracking or macroscopic phase segregation was observed at the magnification employed. The homogeneity observed in most regions suggests a good distribution of uranium and zirconium throughout the pellets. An example of EDS mapping is shown in Figure 9 for UO₂-40% ZrO₂, where homogeneous distribution of Zr and U can be observed.

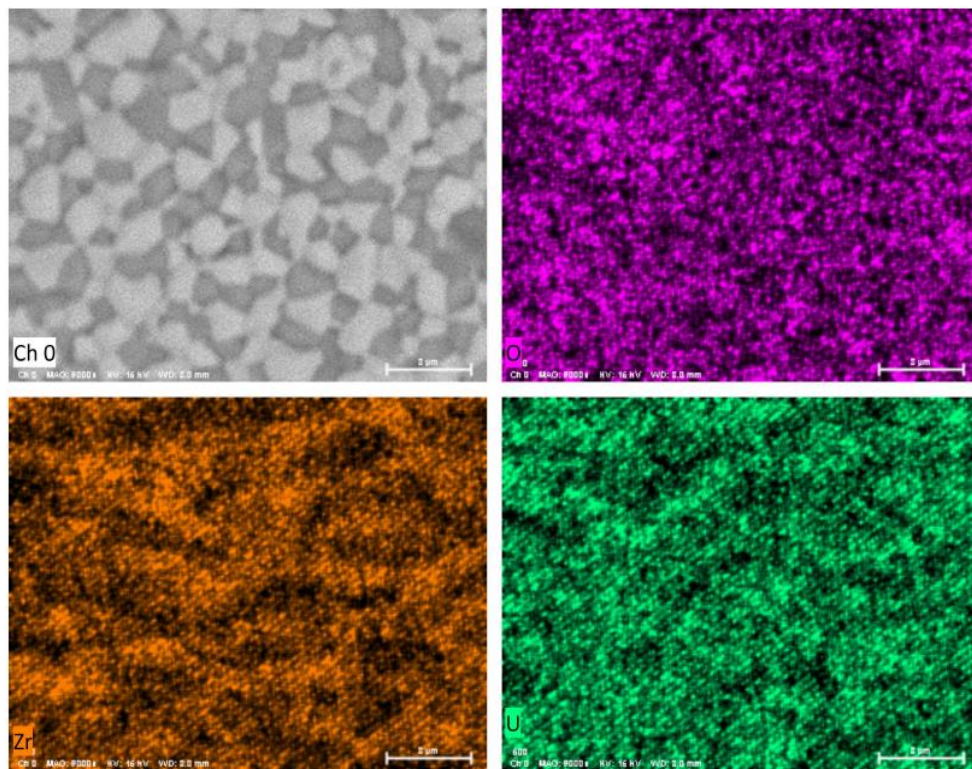


Figure 9 Example of EDS mapping of UO₂-40% ZrO₂ sample.

SEM observations are therefore in good agreement with pycnometry and porosity



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measurements, confirming improved densification and pore closure with increasing UO_2 content. Furthermore, the microstructural contrast observed in the BSE images is consistent with the XRD results, which revealed the coexistence of U-rich and Zr-rich phases in the intermediate compositions. The appearance of the Zr-rich grains with increasing ZrO_2 content support the formation of ZrO_2 -rich regions, in agreement with the phases identified by diffraction.

4. SUMMARY OF RESULTS

A series of UO_2 - ZrO_2 model materials covering the entire compositional range between pure UO_2 and pure ZrO_2 were successfully synthesized by an aqueous coprecipitation route, followed by calcination-reduction, pellet pressing and high-temperature sintering.

XRD analysis demonstrated a gradual phase evolution from fluorite-type cubic uranium dioxide to monoclinic zirconia as the Zr content increased. Intermediate compositions consisted of mixtures of tetragonal and cubic phases, indicating partial solid solution formation between both oxides.

Raman analyses also indicate that zirconium incorporation destabilizes the pure fluorite UO_2 structure and promotes phase separation into cubic and tetragonal zirconium-containing oxide phases. At low zirconium concentrations, Zr^{4+} ions can be accommodated within the UO_2 fluorite lattice, producing only moderate spectral changes. At higher zirconium contents, the formation of zirconia-rich phases becomes increasingly evident, leading to the appearance of additional Raman-active modes and a more complex spectral fingerprint.

These results confirm that Raman spectroscopy is a sensitive complementary technique to XRD for monitoring phase evolution in the UO_2 - ZrO_2 system. While XRD provides quantitative phase information, Raman spectroscopy reveals local structural disorder and lattice distortions, particularly in the intermediate compositions where mixed phases are present.

Pycnometric density increased from approximately $5.5 \text{ g}\cdot\text{cm}^{-3}$ for pure zirconia to $9.7 \text{ g}\cdot\text{cm}^{-3}$ for pure uranium dioxide, while relative density increased from 74.5% to more than 90%. Simultaneously, total porosity decreased markedly, demonstrating improved sintering behaviour in UO_2 rich pellets.



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BET and SEM analyses further confirmed the progressive consolidation of the microstructure after sintering. The combination of density, porosity and surface area analyses indicates that uranium-rich compositions achieved more effective densification and pore closure under the selected sintering conditions.

Moreover, it should be noted that the co-precipitation route has produced pellets with improved phase homogeneity and densification compared with materials prepared by the previously studied dry powder route for $\text{UO}_2\text{-ZrO}_2$ pellets [6].

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<u>FIRMANTE</u>	<u>NOMBRE</u>	<u>FECHA</u>	<u>NOTAS</u>
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FIRMANTE[2]	JONE MIREN ELORRIETA BAIGORRI	24/09/2026 12:39 Sin acción específica	
FIRMANTE[3]	M.SOLEDADE FERNANDEZ FERNANDEZ	24/09/2026 12:56 Sin acción específica	
FIRMANTE[4]	ENRIQUE MIGUEL GONZALEZ ROMERO	24/09/2026 13:50 Sin acción específica	

