

**PRODUCTION AND CHARACTERIZATION OF Cr-DOPED UO_2 AS AN ATF
BY WET ROUTE (IONMAT PROJECT. SUBTASK 2.2)**

DIVISIÓN DE FISIÓN NUCLEAR

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TITULO: Production and characterization of Cr-doped UO_2 as an ATF by wet route (IONMAT project. Subtask 2.2)

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ABSTRACT:

Among the current variety of materials comprising Accident-Tolerant Fuels (ATFs), Cr-doped UO_2 is one of the shortest-term concepts, due to its improved properties with respect to standard UO_2 . Here, a set of Cr-doped UO_2 pellets were prepared. Solid precursors were obtained by following a wet method based on co-precipitation of U and Cr in basic media. The quality of the co-precipitated solid (ADU-Cr) and the subsequent products (U_3O_8 -Cr, UO_2 -Cr) was evaluated by Raman spectroscopy, XRD, SEM and BET. Then, sintered pellets were obtained as final fuel surrogates. They were also characterised in terms of grain size, density, morphology and Cr incorporation into the UO_2 lattice, which turned out to be successful.

	NOMBRE	FIRMA	FECHA	
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1. INTRODUCTION

The most commonly used nuclear fuel in light-water reactors consists of a ceramic matrix of uranium oxide (UO_2). The addition of various elements can help improve the fuel's properties both in the reactor and during the subsequent storage phase. These advanced fuels, which are being developed as alternatives to traditional UO_2 fuel, are called Accident-Tolerant Fuels (ATF).

According to the Nuclear Energy Agency (NEA), ATFs encompass a wide range of materials that can be used in light-water reactor (LWR) cores, directly in existing second and third-generation reactors [1]. Although the concept of ATFs includes everything related to the materials used in the nuclear fuel assembly—such as the fuel itself, the cladding surrounding it, control rods, etc.—in this work we will focus on the study and analysis of advanced UO_2 -based fuels. Additives introduced into traditional UO_2 fuels help improve the fuel's mechanical properties and prevent the release of certain radioactive products formed in the reactor, thereby making the fuel safer. Furthermore, according to recent studies, the introduction of modern nuclear fuels, such as those doped with Cr, Al, and Si, has been shown to result in a significant improvement in the performance of conventional light-water reactors compared to traditional undoped fuels [2, 3].

In this study, we will examine candidates for chromium-doped UO_2 ATFs at different doping levels. The improved properties of Cr-doped fuels stem from the induced coarse-grained microstructure, which leads to greater retention of fission products within the fuel itself, thereby preventing their release [4]. However, to achieve these improved properties, it is first necessary to ensure efficient incorporation of the elements, understand how they chemically interact with uranium, and thus producing homogeneous materials. To this end, it is necessary to study the microstructural and chemical characteristics of the doped UO_2 fuels.

A novel method for producing homogeneous materials from different precursors is the co-precipitation of ammonium diuranate (ADU), which is doped with chromium in this work. ADU is a precursor to uranium oxides, and the influence of precipitation conditions on its properties is highly significant [5].

The properties of the fuels depend on the amount of the dopant in the fuel matrix, which, in turn, depends on the sintering conditions [6, 7]. Regarding the solubility of



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chromium(III) oxide in the UO_2 matrix, it was found that the solubility limit is around 1000 ppm of Cr_2O_3 , depending on the specific sintering conditions used [6-8]. This parameter is important when analyzing the results of the different Cr_2O_3 concentrations chosen to dope UO_2 , as it will be reflected in the final properties of the $\text{UO}_2\text{-Cr}$ in terms of its performance and efficiency. The Cr_2O_3 concentrations were selected based on the described solubility limit to study all possible scenarios resulting from doped UO_2 , whether below, around, or above the limit. Specifically, the range of Cr_2O_3 concentrations in this study has been 0, 600, 1000, 1500, 2000, and 3000 ppm.

Within the framework of the IONMAT project, Cr-doped UO_2 model materials were previously prepared by a dry powder route [9]. Here, they were produced through an aqueous co-precipitation process aimed at obtaining more homogeneous mixtures, with the objective of investigating the effect of Cr as a grain size enlarger and densifier, as well as to provide well-characterised ATF surrogates.



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2. MATERIALS AND METHODS

2.1. REAGENTS

Cr-doped UO_2 samples were synthesised by following an aqueous co-precipitation method, starting from aqueous solutions of uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2$, and chromium (III) nitrate, $\text{Cr}(\text{NO}_3)_3$. To prepare the Cr solution, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Thermo Scientific) was used. In the case of U, commercially grade UO_2 pellets were dissolved in HNO_3 65% using a FlexiWAVE microwave digester (Milestone), using 800 W at 200 °C. The resulting solution was then heated to evaporate the solvent. The solid residue was then washed with alcohol and confirmed to be $\text{UO}_2(\text{NO}_3)_2$ by XRD (data not shown). An schematic view of the preparation process is shown in Figure 1.

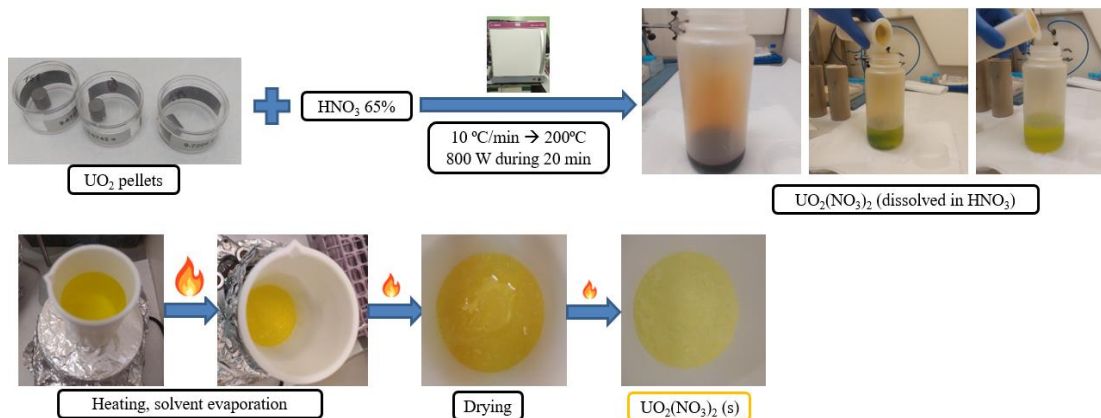


Figure 1 Schematic view of the carried-out process to obtain the starting $\text{UO}_2(\text{NO}_3)_2$.

Both solid phases were dissolved in water to obtain the corresponding aqueous solutions. The targetted concentrations were decided based on the best conditions for the ulterior co-precipitation phase [4]:

- 2 M $\text{UO}_2(\text{NO}_3)_2$ (aq).
- 0.02 M $\text{Cr}(\text{NO}_3)_3$ (aq).

Then, stoichiometric amounts of each solution were mixed in order to obtain the desired amounts of Cr, acting as a dopant in the UO_2 matrix. Table I shows such concentrations, expressed as ppm of Cr_2O_3 , in order to compare the dopant values with Cr-doped UO_2 samples obtained by dry routes and found in the literature [6-8]. Same table also



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includes the measured Cr concentrations of the liquid mixtures by ICP-MS, expressed in ppm of Cr₂O₃ too.

Table I Definition of samples, theoretical Cr₂O₃ concentrations used as dopant and experimental concentrations measured by ICP-MS.

Reference	Theoretical Cr ₂ O ₃ concentration (ppm)	Measured Cr ₂ O ₃ concentration (ppm, ±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

Besides ICP-MS, liquid mixtures were also analyzed by Raman spectroscopy. Such results can be found in Figure 2. As can be seen, the spectra are characterised by two main bands around 1000 cm⁻¹. At higher Raman shifts, the bands corresponding to O-H bond stretching in water appear for all the samples [10]. The zoom in the main region of interest, Figure 2 at right, shows two main bands for each solution: the one corresponding to the stretching vibration of UO₂²⁺ ion at around 875 cm⁻¹, and the one corresponding to the N-O stretching of the NO₃⁻ ion, at around 1050 cm⁻¹. Interestingly, for the same acquisition conditions, the intensity of both bands decreases with increasing Cr concentration, as seen in the corresponding figure. Since doping with Cr means replacing U by Cr in the molecule, both the concentration of UO₂²⁺ and NO₃⁻ (the Cr(NO₃)₃ solution is less concentrated) should decrease with increasing doping level. Therefore, the behaviour observed by Raman for both bands confirms that Cr has entered into the lattice and the doping process, at least in this initial liquid stage, is satisfactory.



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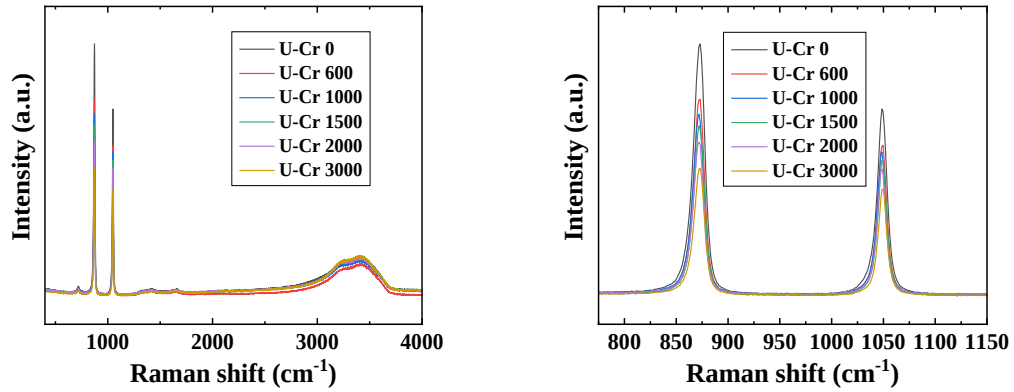


Figure 2 Raman spectra of liquid mixtures of starting U and Cr solutions. Figure on the right represents a zoom in the 800-1150 cm^{-1} region.

2.2. CO-PRECIIPITATION METHOD

For co-precipitation, each liquid solution containing U and Cr in the proportions stated before was added drop by drop to a solution of NH_4OH 25%. Dripping was made by using a peristaltic pump, rotating at 5 rpm. Once all the solution was added, the formed solid was stirred for two hours. Representative pictures of the process are presented in Figure 3.



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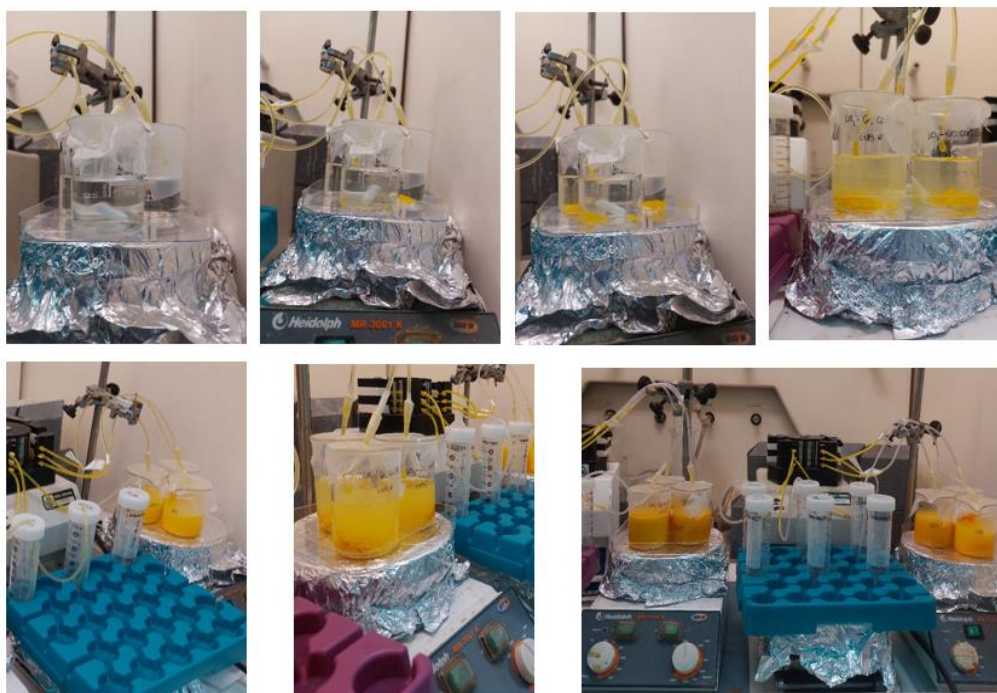


Figure 3 Photographs at different steps of the co-precipitation process.

After precipitation, the solid and the liquid were separated by centrifugation (6500 rpm, 10 minutes). Three different washing steps were carried out: (1) NH_4OH , (2) H_2O , and (3) H_2O . After each wash, samples were centrifuged in the same conditions. Supernatants were analyzed by ICP-MS (not shown), confirming total precipitation. A final washing step was done to the solid, recovering the final, yellow product, identified as ammonium diuranate (ADU).

After characterization of the samples of ADU with varying Cr amounts (named as ADU-Cr, see section 3.1.1), the compounds were calcined at 650 °C in air, holding that temperature for 5 hours. During calcination, dehydration, decomposition of nitrogen species and oxidation of uranium took place, obtaining black powders identified as U_3O_8 (labelled $\text{U}_3\text{O}_8\text{-Cr}$, see section 3.1.2). Finally, the $\text{U}_3\text{O}_8\text{-Cr}$ samples were reduced under a 4.7% H_2/Ar atmosphere at 650 °C during 5 hours, obtaining the corresponding UO_2 samples ($\text{UO}_2\text{-Cr}$, see section 3.1.3). Figure 4 presents a representative picture of each of the powders obtained at every step.



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Figure 4 Photographs of the solid obtained along the co-precipitation method: a) ADU-Cr, b) U_3O_8 -Cr, and c) UO_2 -Cr. For every set of samples, Cr concentration increases from left to right.

2.3. PELLET SINTERING

UO_2 -Cr precursors were used for obtaining the final, sintered pellets. For doing so, they were uniaxially pressed at 400 MPa for 5 seconds. Ethylene-bis-stearamide (EBS) was used as lubricant before pressing each batch of samples. These green pellets were then sintered in a tubular furnace under flowing 4.7% H_2 /Ar atmosphere with a heating rate of 200 $^{\circ}C\ h^{-1}$ up to 1675 $^{\circ}C$, followed by a 8 h isothermal dwell.

2.4. CHARACTERIZATION TECHNIQUES

For the accomplishment of the objectives, the methods/techniques listed in Table II were used.



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Table II Methods and techniques used in this project.

Technique	Parameter	Equipment
BET	N ₂ -BET Surface Area V abs (N ₂ , cm ³ ·g ⁻¹) vs P/P ₀	ASAP 2020 (Micromeritics) ISO 12800E
XRD	Microstructure/crystalline identification (quantification)/chemical composition	D8 ADVANCE Eco (Bruker) – ICDD Cu K α 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.
SEM	Surface morphology/grain size	TM4000 Plus 15 kV (HITACHI) ASTM E 112-96 ;UNE-EN ISO 643:2012
ICP-MS	Elemental concentration	Thermo Fischer Sci ICAP-Qc
Pycnometer	Density	AccuPyc II 1350 (Micromeritics)
Furnace	Max. 1700 °C, atmosphere	Termolab
Uniaxial Press	0-130 kN	Manual 2-column lab press WEBER P-O PW 10



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3. RESULTS

3.1. POWDERED MATERIALS OBTAINED BY CO-PRECIPITATION.
CHARACTERIZATION OF INTERMEDIATE PRODUCTS

In the next subsections, a detailed characterization of the different steps of the co-precipitation method applied will be presented. This can be considered as a quality control of the process.

3.1.1. ADU-Cr

Figure 5 shows the Raman spectra and the XRD patterns obtained from the ADU-Cr samples. Both the Raman spectroscopy and the XRD results confirm that each resulting compound is as expected. On the one hand, all the Raman spectra show the main bands of ADU, particularly the intense doublet around 860 cm⁻¹, corresponding to the uranyl ion (UO₂²⁺) [10]. Meanwhile, the Rietveld analysis performed on the XRD diffractograms (data not shown) indicates that the composition of all samples is 100% ADU, confirming that the co-precipitation reaction has been completed. Based on the results obtained, no incorporation or segregation of Cr is discerned in these compounds, as the concentrations are very low.

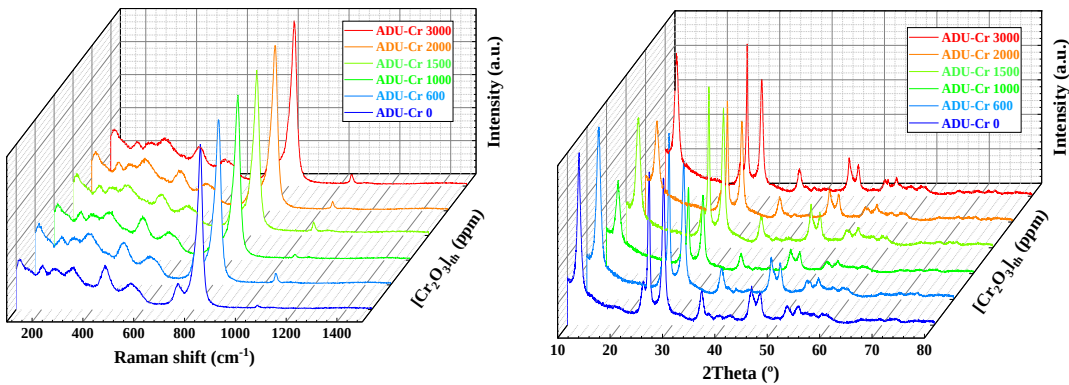


Figure 5 Raman spectra (left) and XRD patterns (right) of co-precipitated ADU samples with varying Cr concentration.



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3.1.2. U_3O_8 -Cr

After calcination of the ADU-Cr samples, the set of U_3O_8 -Cr powders was obtained. In a similar way to ADU-Cr, Figure 6 presents the Raman and XRD results of U_3O_8 -Cr. Raman spectroscopy showed that, in general, the ADU-Cr samples were properly calcined, resulting in bands corresponding to U_3O_8 , notably its characteristic triplet in the 350–480 cm^{-1} region [11].

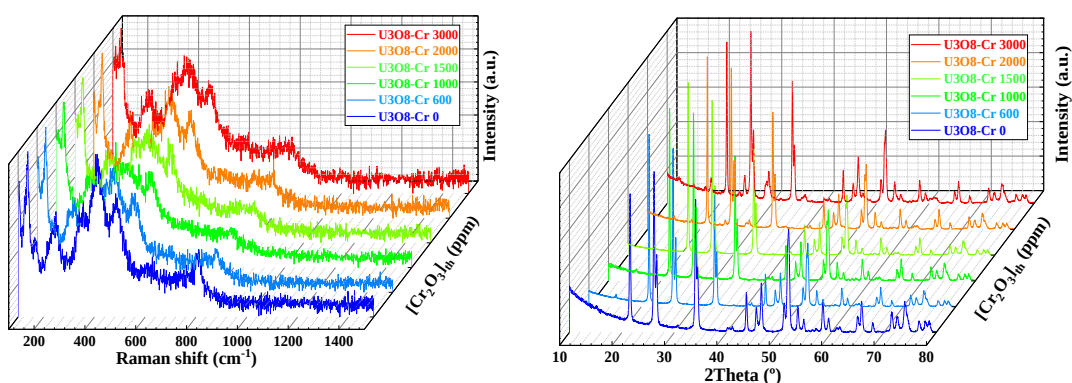


Figure 6 Raman spectra (left) and XRD patterns (right) of co-precipitated U_3O_8 samples with varying Cr concentration.

On the other hand, by analyzing the samples via XRD (Figure 6 at right) and applying the Rietveld refinement method to these diffractograms (results displayed in Table III), it was found that, although the first four samples —corresponding to Cr_2O_3 concentrations ranging from 0 to 1500 ppm— were confirmed to consist of 100% U_3O_8 , the last two samples —corresponding to 2000 and 3000 ppm of Cr_2O_3 — were not completely calcined. Indeed, non-negligible amounts of UO_3 were found: 10% and 29% in the samples doped with 2000 and 3000 ppm of Cr_2O_3 , respectively. It is known that UO_3 is an intermediate product formed during ADU calcination [5]. Obtaining it here would probably mean that selected temperature was not high enough for attaining full conversion to U_3O_8 . On top of that, the fact that UO_3 is only seen in those samples with the highest Cr-doping amounts would suggest that Cr might be hindering the process, in a similar way as it slows down oxidation from UO_2 to U_3O_8 [12].



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Table III Rietveld analysis results of the U_3O_8 -Cr samples measured by XRD.

Reference	Phase	Weight percent (%)
U_3O_8 -Cr 0	U_3O_8	100
U_3O_8 -Cr 600	U_3O_8	100
U_3O_8 -Cr 1000	U_3O_8	100
U_3O_8 -Cr 1500	U_3O_8	100
U_3O_8 -Cr 2000	U_3O_8 UO_3	90(1) 10(1)
U_3O_8 -Cr 3000	U_3O_8 UO_3	71(2) 29(2)

Confirmation of the presence of UO_3 was made by Raman spectroscopy, as seen in Figure 7. A doublet of peaks similar to that characteristic of ADU at around 800 cm^{-1} is found, but in this case the rest of the bands match with the Raman signal of UO_3 , previously reported [13]. It is interesting to highlight that UO_3 was also visually identified, since in the last sample there were some reddish inclusions in the generally black powder. This color is shown in the inset in Figure 7, where the Raman spectrum was acquired.

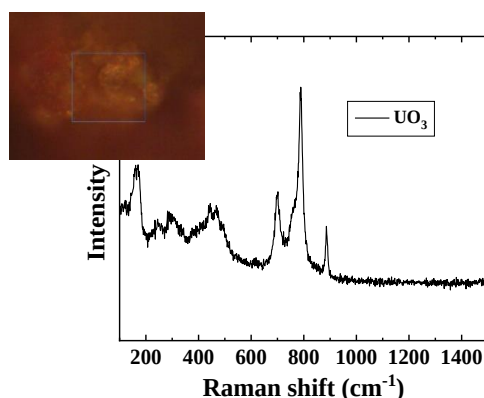


Figure 7 Raman spectrum of the identified UO_3 phase, retrieved from the U_3O_8 -Cr_3000 sample.

Inset shows the reddish area where the spectrum was acquired.

3.1.3. UO_2 -Cr

Finally, and as explained before, U_3O_8 -Cr samples were reduced to obtain the final precursors in the form of UO_2 -Cr. In this case, samples could not be characterized using Raman spectroscopy because excessive fluorescence was observed when attempting to measure them. The XRD diffractograms obtained for these samples are shown in Figure 8.



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Upon applying Rietveld analysis (data not shown), it was found that all samples consisted of 100% of the UO_2 phase. In addition, unit cell refinement was also applied to these diffractograms, which allowed us to determine the lattice parameters of the different phases. These parameters are plotted against Cr_2O_3 concentration in Figure 8. As can be seen, for the Cr_2O_3 -doped samples, the lattice parameter decreases linearly as the dopant concentration increases, indicating that Cr_2O_3 is incorporated into the cubic lattice of UO_2 , and therefore that the incorporation process was successful. This trend is known as Vegard's law-like behaviour and has been previously observed for this kind of samples [8].

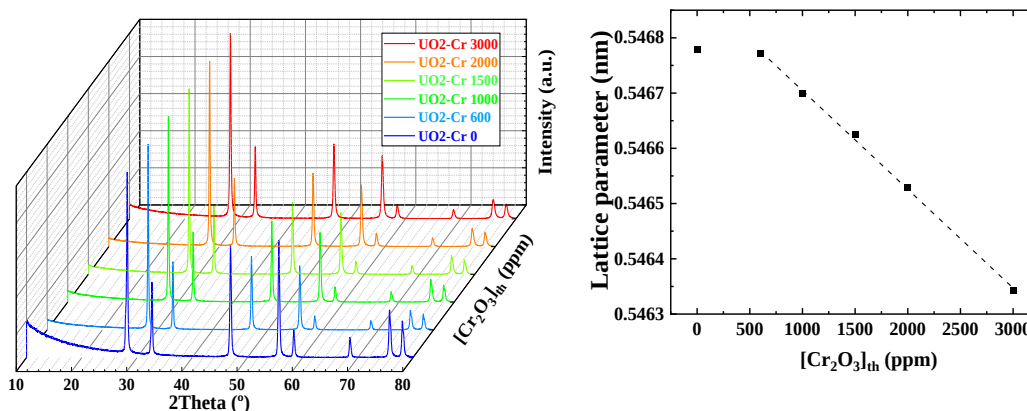


Figure 8 XRD patterns (left) and refined lattice parameters plotted as a function of Cr_2O_3 content (right) of co-precipitated UO_2 samples with varying Cr concentration.

3.1.4. Additional characterization (SEM and BET)

Besides Raman spectroscopy and XRD, the three set of powders (ADU-Cr , $\text{U}_3\text{O}_8\text{-Cr}$ and $\text{UO}_2\text{-Cr}$) were also characterised by SEM and BET surface area. Figure 9 shows, for comparison, surface SEM images taken of the powdered samples at different stages of the process, at the two extremes of Cr_2O_3 concentration (0 and 3000 ppm), to more clearly observe whether there are significant differences between the total absence and the maximum amount of the dopant in the powders. In general, the morphology of the samples is pretty similar in most cases, not showing relevant surface differences.



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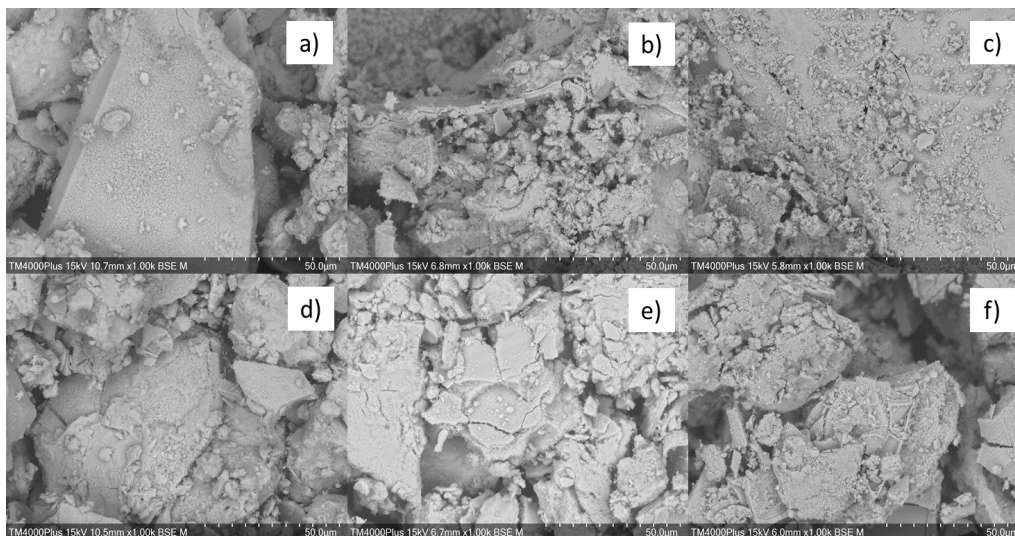


Figure 9 SEM images at 1000X magnification. The top row of images shows 0 ppm of Cr_2O_3 , and the bottom row corresponds to a concentration of 3000 ppm of Cr_2O_3 . a) and d): ADU-Cr samples. b) and e): U_3O_8 -Cr samples. c) and f): UO_2 -Cr samples.

In addition, the specific surface area (SSA) of the sample set for each of the three stages was measured using the BET method. The SSA values obtained are shown in Figure 10. As can be seen, for each sample type, the SSA follows a general growth trend with increasing Cr_2O_3 concentrations. The set of samples that deviates most from this trend is the ADU-Cr sample, because at Cr_2O_3 concentrations of 1000 and 1500 ppm, the values slightly decrease compared to that of 600 ppm, and both measurements reflect a virtually constant SSA. When the dopant is increased to 2000 ppm, there is an increase that once again follows the trend alongside the amount of Cr_2O_3 . In the case of the U_3O_8 -Cr sample set, it can be seen that between 0 and 1000 ppm of Cr_2O_3 , the SSA remains practically constant; however, upon reaching 1500 ppm, it begins to decrease again, and—as in the case of ADU-Cr—it begins to increase once more starting at 2000 ppm of Cr_2O_3 . Finally, the UO_2 -Cr sample set exhibits linear behaviour, indicating that as the Cr_2O_3 content in the powders increases, the specific surface area also does.

It is important to emphasize that there is a significant difference in the SSA of the ADU-Cr set compared to the subsequent sample sets. It can be seen that, in the case of U_3O_8 -Cr and UO_2 -Cr, the SSA of both decreases dramatically from the preceding ADU process. The marked decrease in SSA during calcination is consistent with particle coarsening and



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structural rearrangements associated with the decomposition of ADU and the formation of oxide phases. In contrast, the reduction from U_3O_8 to UO_2 produces somewhat small changes in SSA, indicating that most of the microstructural evolution occurs during the calcination stage.

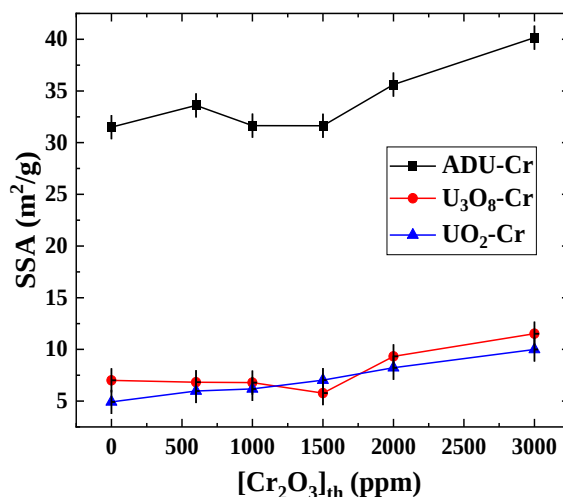


Figure 10 BET surface area (SSA) of the three sets of samples obtained, ADU-Cr, U_3O_8 -Cr, and UO_2 -Cr, as a function of the amount of Cr_2O_3 added to each (ppm), along with their estimated error margins.

3.2. SINTERED PELLETS

By using the final powdered Cr-doped UO_2 precursors, a series of UO_2 pellets doped with different Cr_2O_3 concentrations (0-3000 ppm) were fabricated. The obtained sintered pellets (Figure 11) were characterized in terms of SSA, density, and microstructure in order to evaluate the influence of chromium additions on the final properties of the material.



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Figure 11 Photographs of the Cr-doped UO₂ pellets after sintering.

The SSA of the sintered pellets was determined by the BET method (Figure 12). The measured values ranged from 0.11 to 0.20 m²/g for all compositions investigated. The undoped sample exhibited a SSA of 0.20 m²/g, the highest value obtained. Although slight variations were observed among the different chromium concentrations, all measurements remained within the same order of magnitude. Therefore, no clear relationship between Cr₂O₃ content and SSA can be established. The differences observed are comparable to the expected variability of the measurement technique, suggesting that chromium addition does not significantly affect the residual surface area of the pellets after sintering.

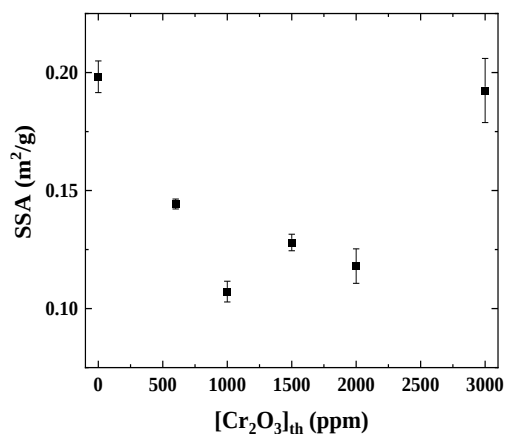


Figure 12 BET surface area (SSA) of the Cr-doped UO₂ pellets, along with their estimated error margins.

Density measurements were carried out using helium pycnometry. The pycnometric density values remained close to 10.0 g/cm³ for all compositions (Table IV). These results



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indicate that the addition of chromium oxide has a negligible effect on the densification behaviour under the selected fabrication conditions. Furthermore, the relative density values (calculated using the theoretical density of 10.97 g/cm³ proposed by Physical Measurement Laboratory of National Institute of Standards and Technology (NIST-PML)) reported for all compositions were above 90% (see Table IV and Figure 13), confirming that the sintering process was effective and that highly densified pellets were obtained regardless of the chromium concentration.

Table IV Physical properties of the Cr-doped UO₂ 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)
UO ₂ -Cr 0	0.20 ± 0.01	10.050 ± 0.004	91.70	8.1 ± 0.7
UO ₂ -Cr 600	0.14 ± 0.01	9.969 ± 0.005	91.02	11 ± 2
UO ₂ -Cr 1000	0.11 ± 0.01	10.021 ± 0.004	91.54	12 ± 2
UO ₂ -Cr 1500	0.13 ± 0.01	10.073 ± 0.008	92.06	14.5 ± 0.9
UO ₂ -Cr 2000	0.12 ± 0.01	10.070 ± 0.007	92.08	14 ± 2
UO ₂ -Cr 3000	0.19 ± 0.01	10.069 ± 0.005	92.18	17 ± 2



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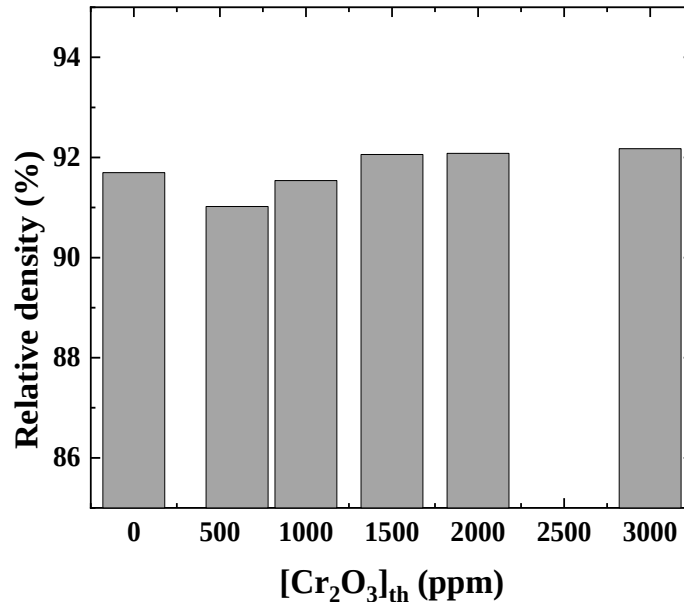


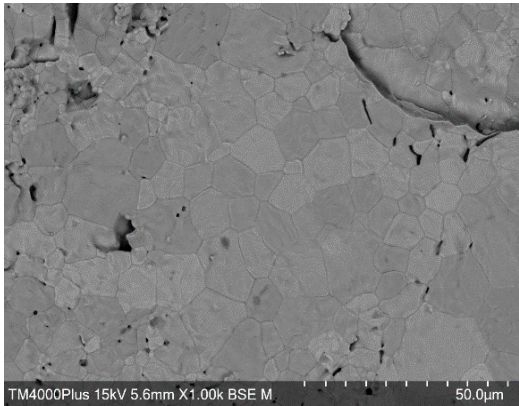
Figure 13 Relative density (expressed in %) of the Cr-doped UO₂ pellets, as a function of the amount of Cr₂O₃ present (ppm). Values calculated from the pycnometer densities given in Table IV.

The most significant effect of chromium addition was observed in the pellet microstructure. Grain size analysis (outcomes shown in Table IV) performed using SEM images (Figure 14) showed a continuous increase in mean grain size with increasing Cr₂O₃ concentration. The undoped UO₂ pellets exhibited an average grain size of 8.1 μm , while the values increased to 11 μm and 12 μm for the samples containing 600 and 1000 ppm Cr₂O₃, respectively. A more pronounced grain growth was observed at higher dopant concentrations, reaching a value of around 14 μm for the 1500 and 2000 ppm samples and 17 μm for the 3000 ppm sample. Overall, the highest chromium concentration resulted in a grain size approximately twice as large as that of the undoped material.

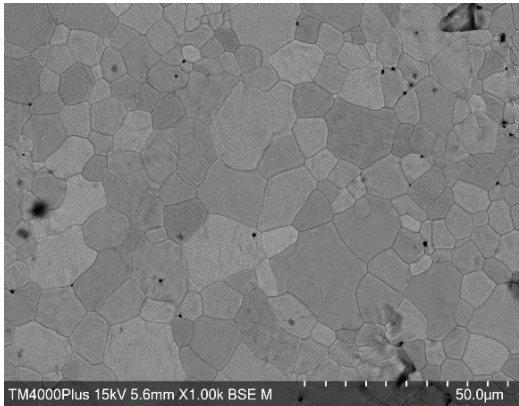


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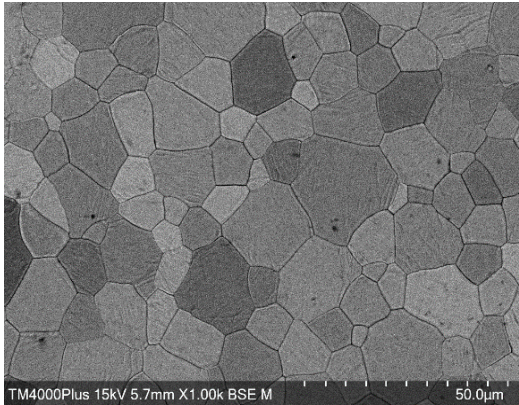
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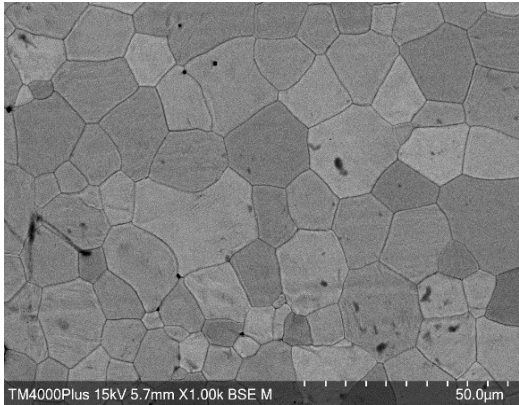
UO₂-Cr 600



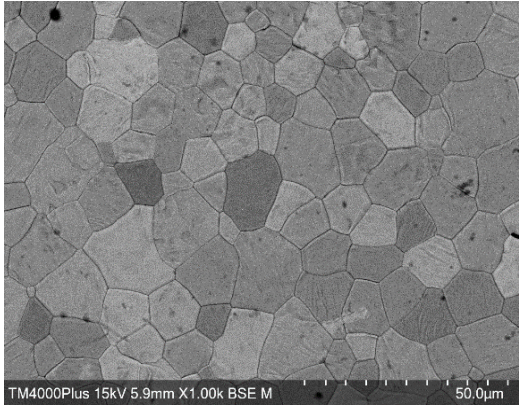
UO₂-Cr 1000



UO₂-Cr 1500



UO₂-Cr 2000



UO₂-Cr 3000

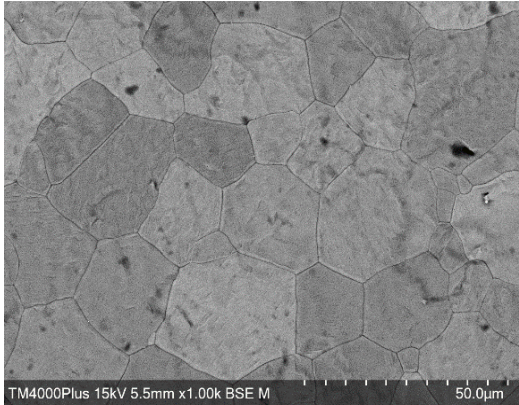


Figure 14 SEM images of the Cr-doped UO₂ pellets after sintering, showing the different grain sizes achieved.

In addition, no secondary phases attributable to segregated chromium were identified in the SEM micrographs. These results demonstrate that Cr₂O₃ 1) is embedded (at least in an extensive manner) within the UO₂ microstructure and 2) acts



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as a grain growth promoter during the sintering of UO_2 . The observed behaviour is consistent with the role of chromium as a sintering additive that enhances grain boundary mobility and promotes microstructural coarsening [8, 15]. The progressive increase in grain size with dopant concentration indicates that the effect becomes increasingly important above approximately 1000 ppm Cr_2O_3 . Despite this considerable grain growth, the density remained largely unchanged, indicating that chromium primarily influences microstructural evolution rather than final densification.

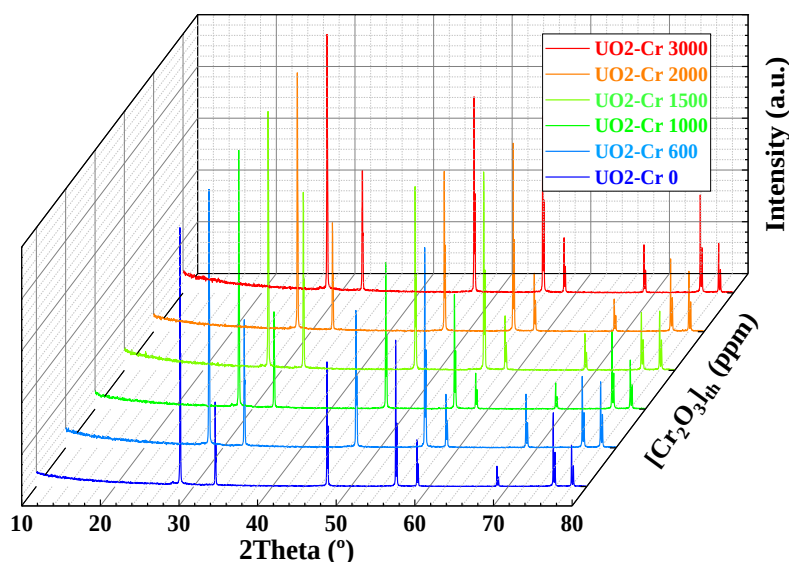


Figure 15 XRD patterns of the Cr-doped UO_2 pellets after sintering.

The XRD patterns of pure UO_2 and Cr-doped UO_2 pellets show a very similar set of diffraction peaks over the entire composition range (Figure 15), which correspond to the typical diffraction of cubic UO_2 . This indicates that all samples retained the fluorite-type cubic crystal structure characteristic of UO_2 . No additional diffraction peaks attributable to secondary chromium-containing phases can be distinguished in the diffractograms, particularly those associated with pure Cr_2O_3 .

From the XRD results, in a similar way to the powdered UO_2 -Cr samples (Figure 8), lattice parameters of the cubic lattices were also obtained from the unit cell refinement. They



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are plotted as a function of initial Cr_2O_3 concentration in Figure 16. In this case, the Vegard's law-like behaviour is only observed for the first three samples (those doped with 0, 600 and 1000 ppm Cr_2O_3), linearly decreasing with increasing Cr concentration. This trend is consistent with the incorporation of chromium into the UO_2 lattice. From that value, lattice parameters seem to slightly decrease and even stabilize with higher Cr doping levels. This behaviour contrasts with that observed in the powdered UO_2 -Cr samples, where the decrease in lattice parameter persisted over a wider concentration range (see Figure 8). In the pelletized materials, the lattice parameter reaches a nearly constant value above approximately 1000-1500 ppm Cr_2O_3 , suggesting a saturation of the structural effect induced by chromium incorporation. Although no secondary phases or chromium-rich segregations were detected by SEM or XRD within the experimental detection limits, the observed plateau may indicate that the solubility limit of chromium in the UO_2 matrix is being approached. Alternatively, further chromium addition may not result in a measurable contraction of the lattice parameter, either because the incorporation mechanism changes or because the sensitivity of the technique is insufficient to detect additional local structural modifications.

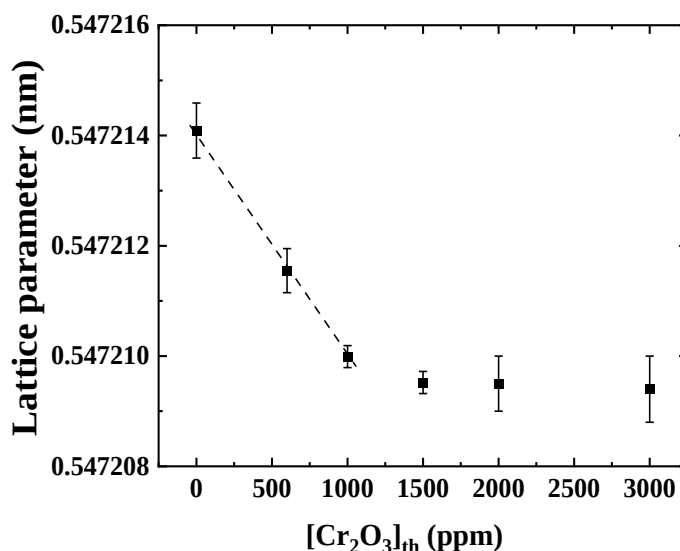


Figure 16 Refined lattice parameters plotted as a function of Cr_2O_3 content of Cr-doped UO_2 sintered pellets.



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4. SUMMARY OF RESULTS

A set of Cr-doped UO_2 pellets, with Cr_2O_3 theoretical concentrations ranging from 600 to 3000 ppm, were produced by a wet, co-precipitation method. An undoped UO_2 pellet was also prepared, as a reference.

Starting dissolutions prepared from the solid reagents were characterized by ICP-MS and Raman spectroscopy, confirming the mixture between U and the added Cr. The co-precipitation method led to a set of yellow powders, identified as ADU by both Raman and XRD. Calcination of those samples allowed obtaining U_3O_8 powders. In this case, Rietveld analysis revealed that, for the two samples containing the highest amount of Cr (*i.e.*, 2000 and 3000 ppm Cr_2O_3), the calcination process was not complete, obtaining some UO_3 in both samples. Isolation of a reddish powder by visual inspection confirmed the formation of UO_3 by Raman spectroscopy too. Finally, the U_3O_8 -Cr powders were reduced to obtain the corresponding UO_2 -Cr final precursors. Unit cell refinement from the XRD patterns showed that the lattice parameters followed a linear trend with Cr concentration, confirming the incorporation of Cr as a dopant in the cubic UO_2 lattice.

This set of UO_2 -Cr powders were pressed and sintered following a conventional, high-temperature reducing treatment. The produced pellets were characterized by SEM, pycnometry, BET and XRD. SEM images were used to calculate the mean grain sizes of the pellets, finding a steady growth with increasing Cr concentration, as expected. Pycnometric density measurements suggested that the addition of chromium oxide has a negligible effect on the densification behaviour under the selected fabrication conditions. Finally, the BET values showed no particular trend, probably indicating insensibility of the technique with the amounts of Cr used. Analogously to the powders, lattice parameters obtained from the XRD patterns revealed a linear decrease with Cr content; however, in this case, such trend was observed to be followed only up to 1000 ppm Cr_2O_3 . After that, the lattice parameter stabilized, likely indicating that the solubility limit was reached at that dopant concentration.



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5. ACKNOWLEDGEMENTS

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 Generación de Conocimiento 2021.



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<u>FIRMANTE</u>	<u>NOMBRE</u>	<u>FECHA</u>	<u>NOTAS</u>
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FIRMANTE[2]	MARIA NIEVES RODRIGUEZ VILLAGRA	23/09/2026 10:36 Sin acción específica	
FIRMANTE[3]	M.SOLEDADE FERNANDEZ FERNANDEZ	23/09/2026 11:01	
FIRMANTE[4]	ENRIQUE MIGUEL GONZALEZ ROMERO	23/09/2026 13:35 Sin acción específica	

